Supplementary Information

Iridium-Catalyzed Enantioselective Alkynylation and Kinetic Resolution of Alkyl Allylic Alcohols

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General Methods

Unless otherwise noted, reagents and solvents were purchased from commercial sources and used without further purification. 1,16-Dihydroxytetraphenylene (**DHTP**) and **DHTP**-derived ligands [(*S*)-**L1**, (*R*)-**L1**, (*S*)-**L2**, (*S*)-**L3** and (*S*)-**L4** and (*S,S,S*)-**L5**] were synthesized according to literature procedure (*Synthesis* **2017**, *49*, 181-187; *Chem. Sci.* **2022**, *13*, 4608-4615). Potassium alkynyltrifluoroborates were prepared according to literature (*Org. Lett.* **2020**, *22*, 7427-7432; *J. Am. Chem. Soc.* **2018**, 140, 16387-16391; *Org. Lett.* **2013**, *15*, 5052-5055). (±)-Allylic alcohols were prepared according to literature (*ACS Catal.* **2021**, *11*, 7060-7069; *Angew. Chem. Int. Ed.* **2017**, *56*, 6558-6562; *Angew. Chem. Int. Ed.* **2012**, *51*, 3470-3473). The iridium-catalyzed allylic alkynylations were performed in Schlenk tubes under an atmosphere of argon. Thin layer chromatography was performed on precoated silica gel 60 F^{254} plates. Flash column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Ascend™ 400 and Ascend™ 600 spectrometers. Chemical shifts (ppm) were referenced to TMS or deuterated solvents, and coupling constants were given in Hz. Data for ^{1}H NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; brs, broad singlet; d, doublet; dd, double doublet; ddd, double-double doublet; t, triplet; td, triple doublet; tt, triple triplet; q, quartet; qd, quadruple doublet, m, multiplet), coupling constants (Hz), integration. Data for ^{13}C NMR are reported in chemical shift (δ, ppm). Data for ^{19}F NMR and ^{31}P NMR were reported in chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained on Thermo Scientific Q Exactive (ESI), or Waters Xevo G2-XS QTof spectrometers (ESI and APCI). X-ray crystallographic data were recorded on Bruker CMOS area detector diffractometer. High pressure liquid chromatography (HPLC) analyses were performed on Agilent 1260 Infinity II equipped with chiral column from Daicel®. Melting points (mp) were determined on an SGW X-4A microscopic melting point apparatus. Optical rotations were recorded on a Rudolph Automatic Polarimeter. IR spectra were collected on Bruker VERTEX 70v and Bruker VERTEX 80v spectrometers. Selectivity factors (*s*) and conversion (C) of kinetic resolution were calculated using the method reported by Kagan (*Top. Stereochem.* **1988**, *18*, 249-330; *Angew. Chem. Int. Ed.* **2005**, *44*, 3974-4001): $s = \ln[(1-C)(1-ee_s)]/\ln[(1-C)(1+ee_s)]$, $C = ee_s/(ee_s+ee_p)$. Known compounds were characterized by comparison of their previously reported ^{1}H and ^{13}C NMR spectra.

List of allylic alcohols (±)-1

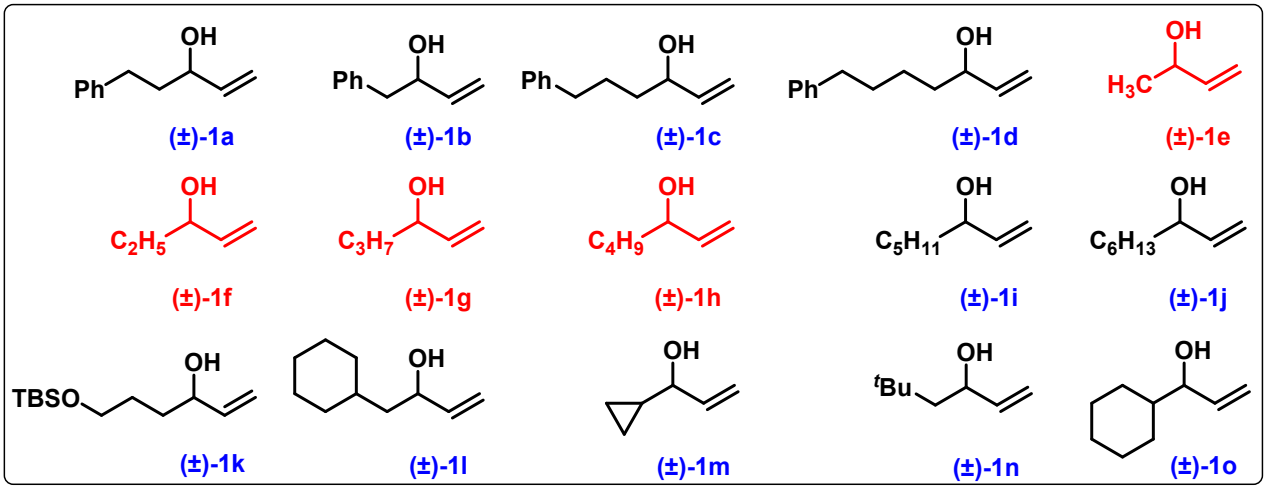
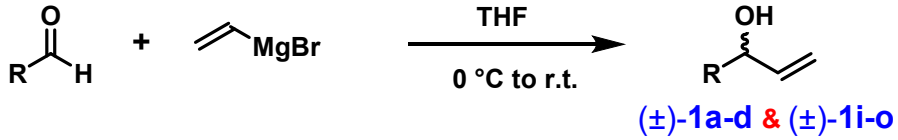


Figure S1 List of allylic alcohols (±)-**1**

Allylic alcohols (±)-**1e-h** were purchased from commercial sources, (±)-**1a-d** and (±)-**1i-o** were synthesized according to the literature. [1]

Genneral procedure:

Vinyl magnesium bromide (1.0 M in THF, 1.0 eq.) was added to a solution of the corresponding aldehyde (1.0 eq.) in THF at 0 °C. After being stirred for 15 min, the reaction was allowed to warm to room temperature (25 °C) and stirred for 1-3 h. The reaction mixture was quenched by the addition of saturated aqueous NH_4Cl and extracted with Et_2O. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum. The residue was purified by column chromatography to provide the corresponding allylic alcohol **1** as a colorless oil.



Scheme S1

List of potassium alkynyltrifluoroborates 2

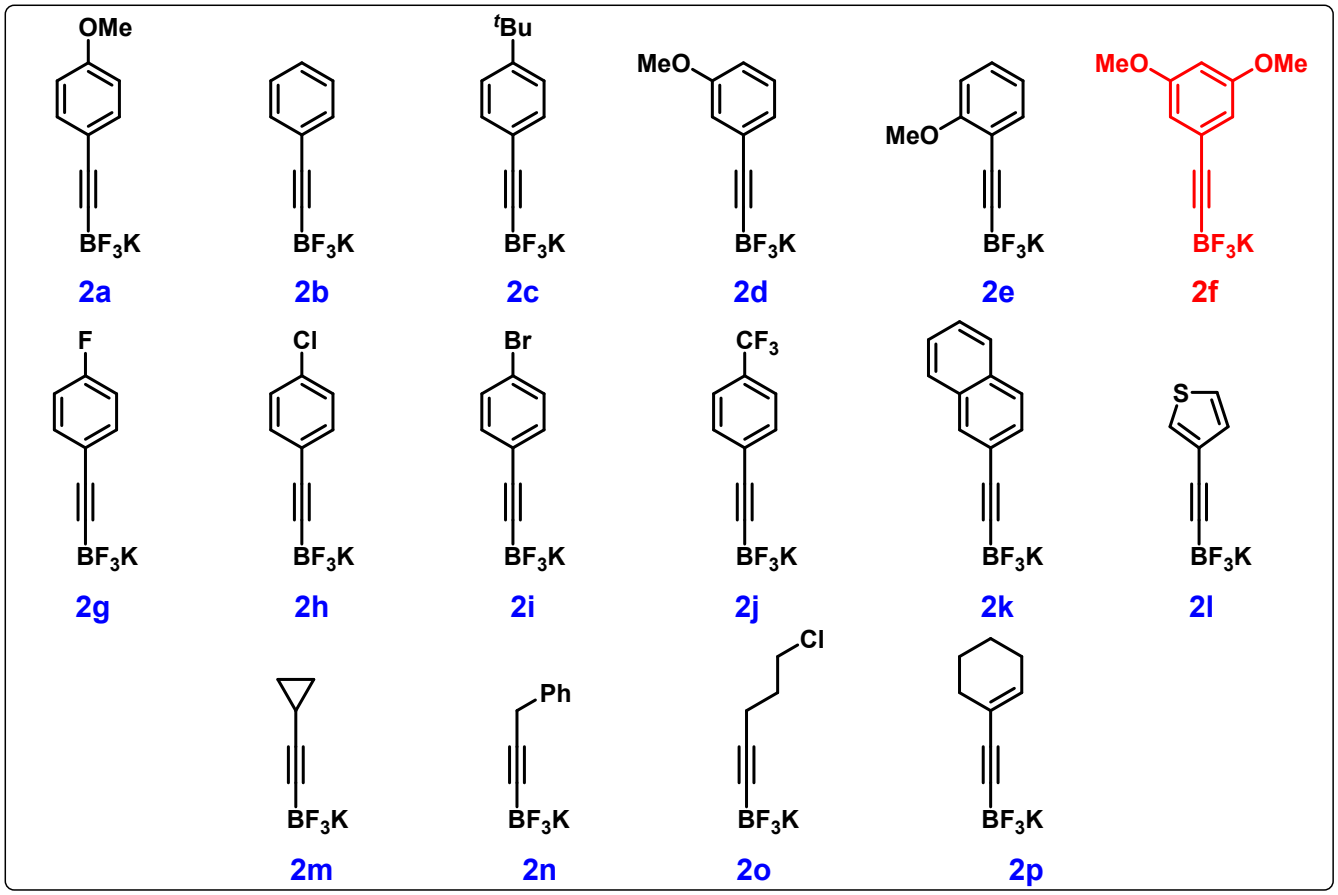


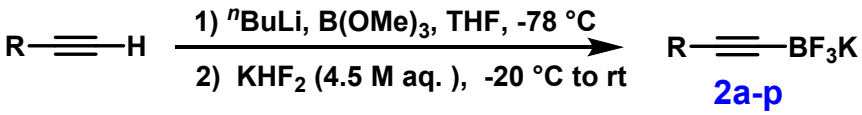
Figure S2 List of potassium alkynyltrifluoroborates **2**

All potassium alkynyltrifluoroborates **2a-p** were synthesized according to the literature. [2]

Genneral procedure:

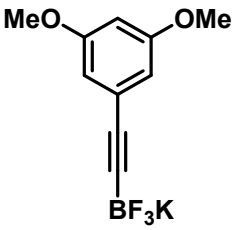
To a solution of terminal alkyne (1.0 eq.) in dry THF (0.4 M) at -78 °C was added ^{n}BuLi (1.6 M in hexane, 1.0 eq.) dropwise. The resulting solution was stirred for 0.5 h at -78 °C. Trimethylborate (1.5 eq.) was then added dropwise at -78 °C. After being stirred for 0.5 h at -78 °C, the reaction mixture was warmed to -20 °C and stirred for 0.5 h. A solution of potassium hydrogen difluoride (6.0 eq.) in H_2O (4.5 M) was then added. The resulting mixture was vigorously stirred for 1 h at room temperature (25 °C). The solvent was removed under reduced pressure. The resulting solid was dried under vacuum to remove water and then dissolved in hot acetone. The solution was filtered, and the filtrate was concentrated under vacuum to ~10 mL. Then, Et_2O (10 mL) was added to precipitate the potassium trifluoroborate. The

mixture was cooled to 0 °C to complete the precipitation. The white solid was collected by filtration to give the corresponding potassium alkynyltrifluoroborate **2**.



Scheme S2

Potassium alkynyltrifluoroborates **2a-e** and **2g-p** are known compounds and their NMR data are consistent with reported data. While **2f** is a new compound, the characterizations of **2f** are shown below.



2f

White solid. 53% yield. mp 214.2 – 215.4 °C.

^{1}H NMR (400 MHz, Acetone-d_6): δ = 6.48 (d, J = 2.3 Hz, 2H), 6.35 (t, J = 2.1 Hz, 1H), 3.75 (s, 6H).

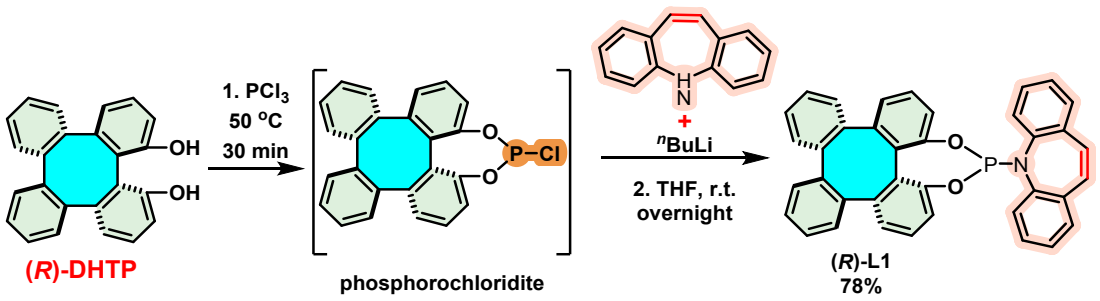
^{13}C NMR (100 MHz, DMSO-d_6) δ 160.56, 127.43, 109.16, 100.38, 89.79 (relaxation time d1 = 3 seconds, no clear signal for the second acetylenic carbon atom), 55.59.

^{19}F NMR (376 MHz; DMSO-d_6) δ = -131.88 (s).

HRMS (ESI): $[M-K]^-$ Calcd. for $[C_{10}H_9BF_3O_2]^-$ 229.0653, found 229.0643.

IR (neat): 3300, 2943, 2843, 2195, 1584, 1456, 1421, 1211, 1159, 983, 918, 833, 814, 671 cm^{-1}.

Synthesis of ligand (*R*)-L1



Scheme S3

A flame-dried Schlenk flask under argon was charged with the (*R*)-**DHTP** (1 mmol, 1.0 eq.) and PCl_3 (15.0 eq.). The mixture was heated at 50°C for 30 min. The initially heterogeneous mixture turned into a brownish homogenous solution. After cooling to room temperature (25°C), the excess PCl_3 was thoroughly evaporated in vacuo to remove the remaining PCl_3. The resulting phosphorochloridite was redissolved in anhydrous THF (5 mL). In a separate Schlenk flask under argon, the corresponding amine (1.2 eq.) dissolved in anhydrous THF (10 mL) was deprotonated at -78°C by the slow addition of ^{n}BuLi (1.6 M solution in hexanes, 1.1 eq.). After being stirred at -78 °C for 1 hour, the aforementioned phosphorochloridite solution was slowly transferred into the resulting solution via syringe. The resulting mixture was stirred at -78°C, then warmed to 25°C and continued to stir overnight. The solvent was evaporated in vacuo and purification by flash chromatography on silica gel using hexanes/toluene as the eluents to give (*R*)-**L1** as a white solid in 78% yield (434.9 mg). **$[\alpha]^{20}_D$:** +287.20 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.39 – 7.16 (m, 15H), 7.08 – 6.95 (m, 6H), 6.91 – 6.82 (m, 2H), 6.75 (d, *J* = 7.5 Hz, 1H).

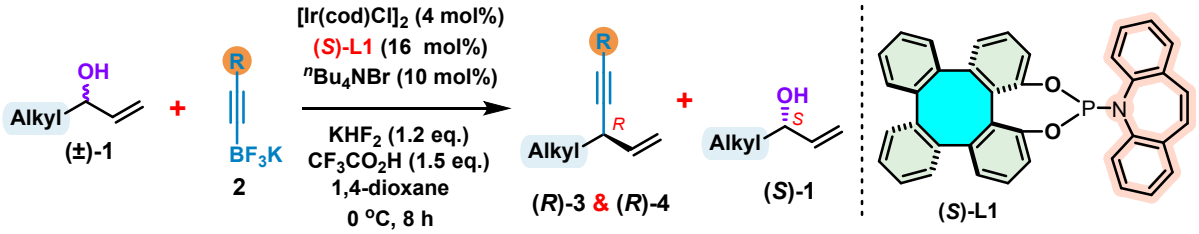
^{13}C NMR (100 MHz, Acetone-d_6) δ 149.45, 149.05 (d, *J* = 6.5 Hz), 144.06 (d, *J* = 1.6 Hz), 142.99 (d, *J* = 1.4 Hz), 142.94, 142.75, 142.28 (d, *J* = 4.4 Hz), 141.25, 141.15, 141.01, 140.58, 136.43 (d, *J* = 3.2 Hz), 135.98 (d, *J* = 1.1 Hz), 131.59, 131.59, 131.19, 130.41 (d, *J* = 4.5 Hz), 129.51, 129.40, 129.22, 129.07 (d, *J* = 5.0 Hz), 129.06, 128.98, 128.61, 128.59 (d, *J* = 1.1 Hz), 128.43 (d, *J* = 8.4 Hz), 128.26, 128.16, 127.81, 127.70, 127.30, 127.27, 126.91 (d, *J* = 1.1 Hz), 126.66, 126.65, 125.12, 120.66 (d, *J* = 2.3 Hz), 120.36.

DEPT 135 ^{13}C NMR (100 MHz, Acetone-d_6) δ 131.59, 131.19, 129.51, 129.40, 129.22, 129.21, 129.07 (d, *J* = 5.0 Hz), 129.06, 128.98, 128.62, 128.59 (d, *J* = 1.4 Hz), 128.44 (d, *J* = 8.3 Hz), 128.26, 128.16, 127.82, 127.70, 127.30, 127.27, 126.91 (d, *J* = 1.4 Hz), 126.67, 126.65, 125.13 (d, *J* = 1.2 Hz), 120.66 (d, *J* = 2.3 Hz), 120.37.

^{31}P NMR (162 MHz, Acetone-d_6) δ = 135.09.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{38}H_{25}NO_2P]^+$ 558.1617, found 558.1614.

General procedure for the Ir-catalyzed allylic alkynylation/kinetic resolution

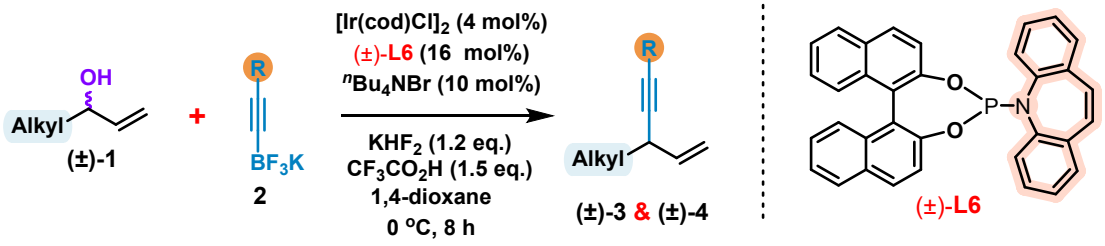


Scheme S4

$[Ir(cod)Cl]_2$ (10.8 mg, 16.0 μmol, 4 mol%) and (*S*)-**L1** (35.6 mg, 64.0 μmol, 16 mol%) were dissolved in 1,4-dioxane (0.4 mL) in a Schlenk tube and stirred for 30 min. To the resulting brownish red solution, alkyl allylic alcohol (±)-**1** (0.4 mmol, 1.0 eq.), potassium alkynyltrifluoroborate **2** (0.48 mmol, 1.2 eq.), $^{n}Bu_4NBr$ (13.0 mg, 40 μmol, 10 mol%), KHF_2 (37.5 mg, 0.48 mmol, 1.2 eq.), and CF_3CO_2H (68.4 mg, 0.6 mmol, 1.5 eq.) were sequentially added. The resulting heterogeneous yellow mixture was stirred at 0 °C for 8 h. The reaction mixture was diluted with hexane (1.0 mL), treated with triethylamine (0.1 mL), and directly subjected to silica gel flash chromatography to afford the corresponding 1,4-enyne and unreacted allylic alcohol.

The stereoconfigurations of obtained 1,4-enynes and unreacted allylic alcohols were determined by comparison of optical rotations of (*R*)-**3a** and (*S*)-**1a** previously reported in literature. [3] For (*S*)-**1a**, the absolute configuration (*S*) was further confirmed by an X-ray crystallographic analysis of its derivative (*S*)-**1a'**.

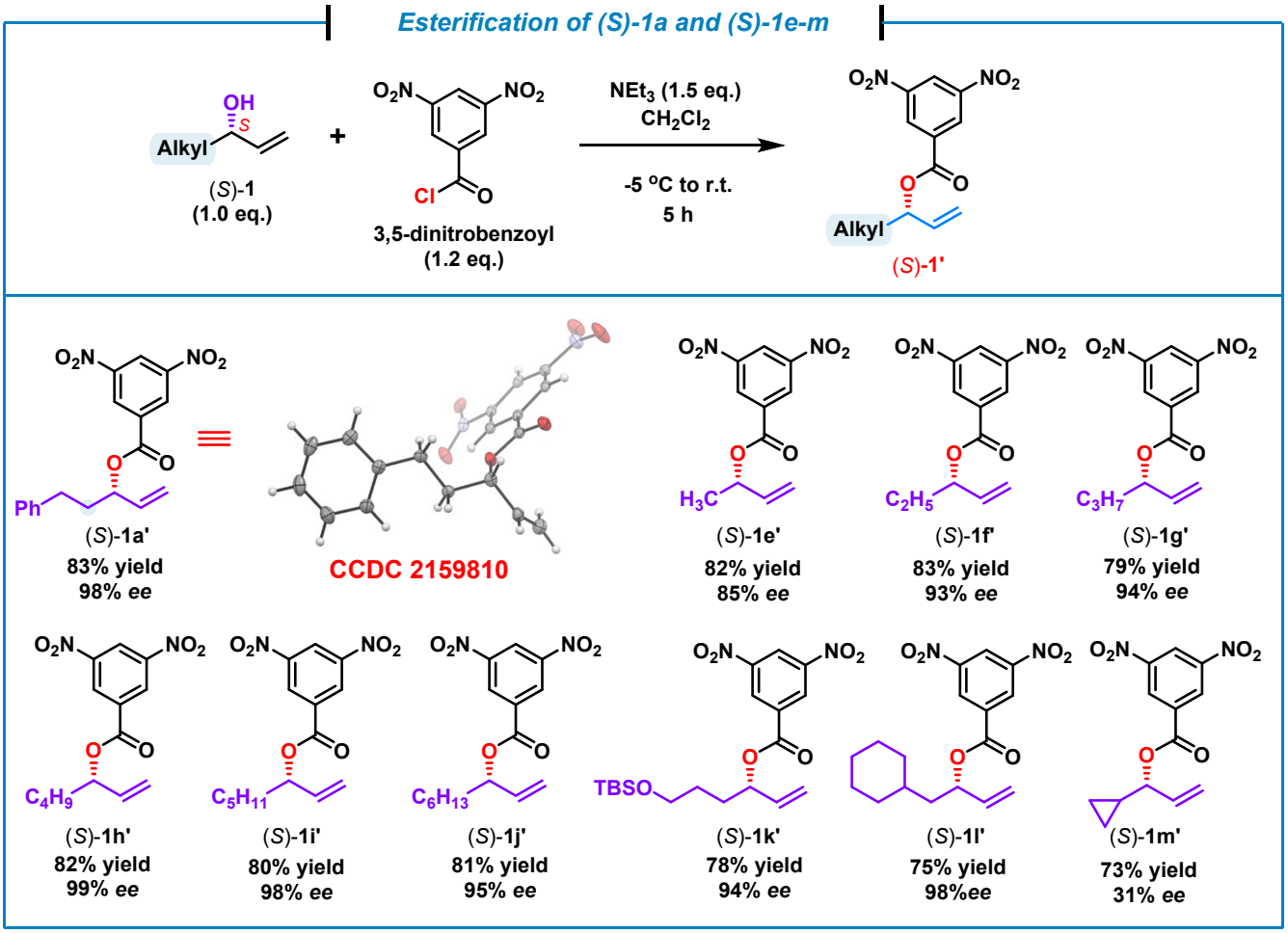
*The 1,4-enynes (±)-**3a-p** and (±)-**4a-m** for HPLC determination were prepared by using racemic **BINOL**-based (±)-**L6** as a ligand under the above standard conditions.*



Scheme S5

General procedure for the esterification of (*S*)-1a and (*S*)-1e-m

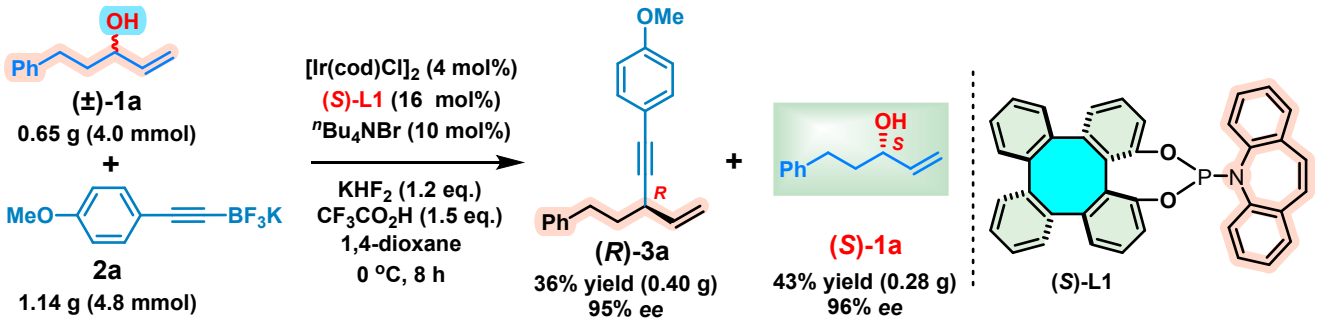
Table S1 Esterification of allylic alcohols (*S*)-**1a** and (*S*)-**1e-m**



To a solution of the obtained allylic alcohol (1.0 eq.) in CH_2Cl_2 was added triethylamine (1.5 eq.) and 3,5-dinitrobenzoyl chloride (1.2 eq.) at -5 °C. The mixture was stirred for 5 h at room temperature before water (2.0 mL) was poured into the mixture at 0 °C. The aqueous phase was extracted with Et_2O, and combined organic phases were washed with saturated brine solution, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography to give the corresponding esterification products (*S*)-**1a'** and (*S*)-**1e'-m'**.

The absolute configuration of (*S*)-**1a** was further confirmed by an X-ray crystallographic analysis of its esterification product (*S*)-**1a'**. The enantiomeric excesses of (*S*)-**1e-m** were determined by HPLC analysis of their corresponding esterification products (*S*)-**1e'-m'**.

Scale-up preparation of (*S*)-1a

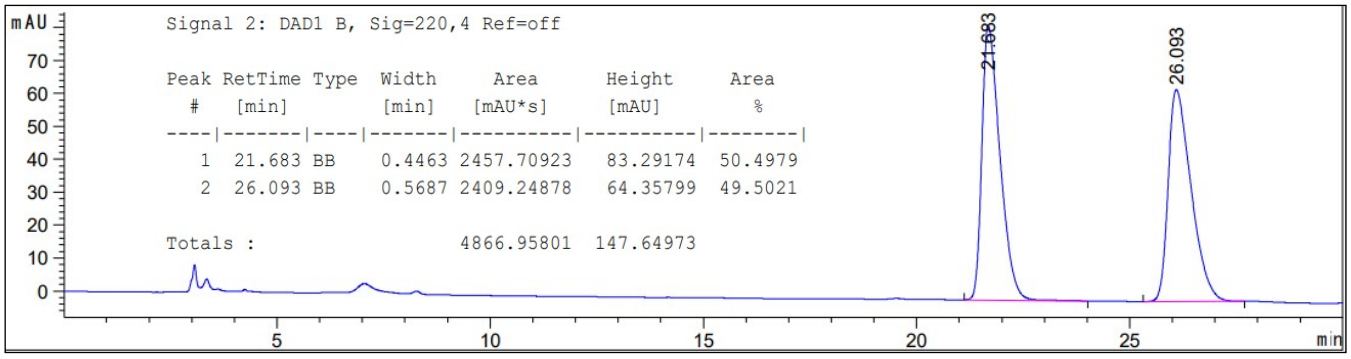


Scheme S6

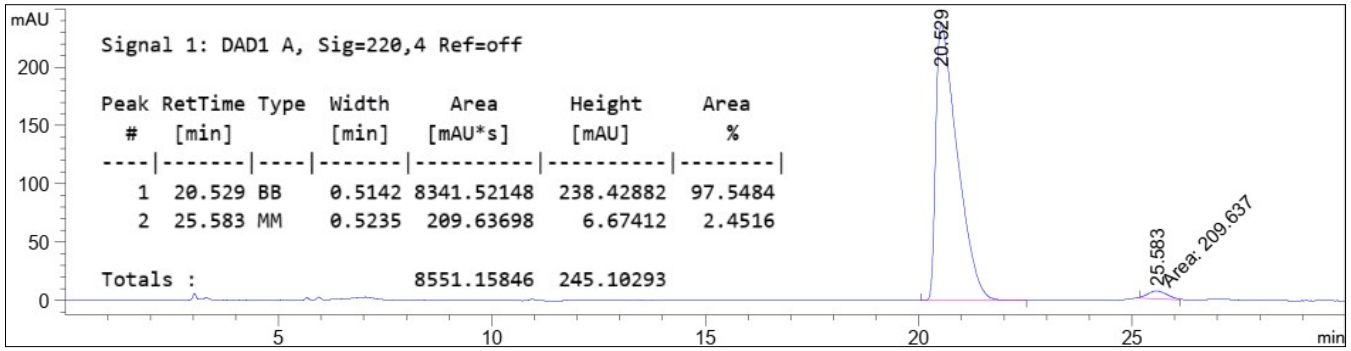
[Ir(cod)Cl]$_2$ (107.5 mg, 0.16 mmol) and (*S*)-**L1** (356.9 mg, 0.64 mmol) were dissolved in 1,4-dioxane (4.0 mL) in a Schlenk tube and stirred for 30 min. To the resulting brownish red solution, alkyl allylic alcohol (±)-**1a** (0.65 g, 4.0 mmol), potassium alkynyltrifluoroborate **2a** (1.14 g, 4.8 mmol), ^{n}Bu$_4$NBr (0.13 g, 0.4 mmol), KHF_2 (0.37 g, 4.8 mmol), and CF_3CO_2H (0.68 g, 6.0 mmol) were sequentially added. The resulting heterogeneous yellow mixture was stirred at 0 °C for 8 h. The reaction mixture was diluted with hexanes (10.0 mL) and treated with triethylamine (1.0 mL). After being stirred for 10 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give (*R*)-**3a** (0.40 g, 36% yield, 95% *ee*) and (*S*)-**1a** (0.28 g, 43% yield, 96% *ee*).

HPLC for the obtained (*R*)-**3a**: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 95% *ee* (t_R (major) = 20.53 min, t_R(minor) = 25.58 min).

Racemic



Enantioenriched



HPLC for the obtained (*S*)-**1a**: Daicel Chiralcel® OD-H, 12 % ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 96% *ee* (t_R (major) = 6.03 min, t_R(minor) = 7.38 min).

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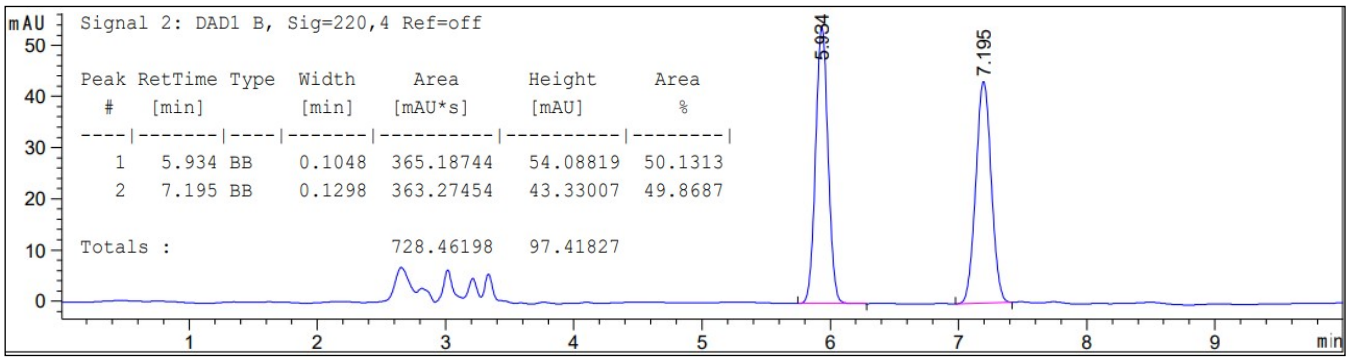

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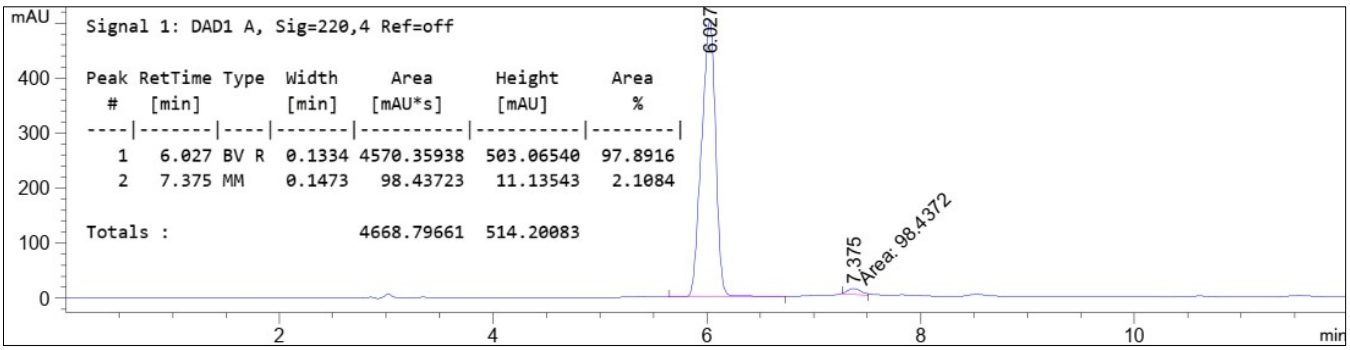
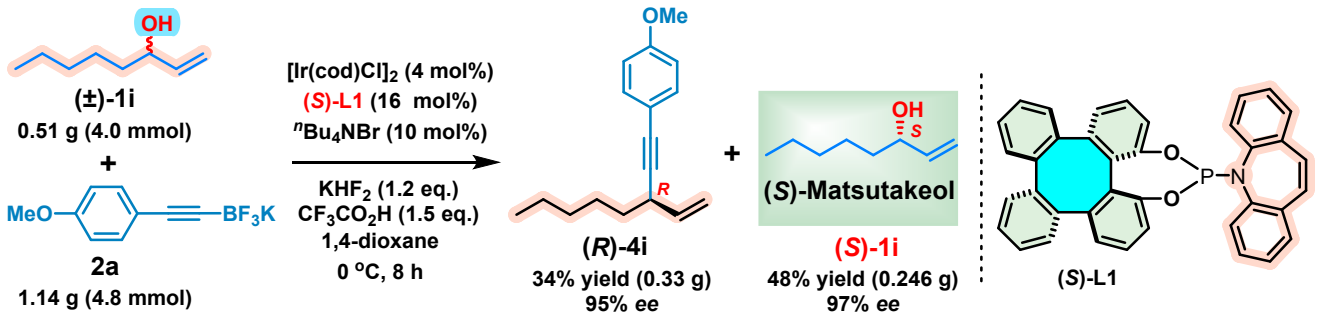


Scale-up preparation of (*S*)-matsutakeol

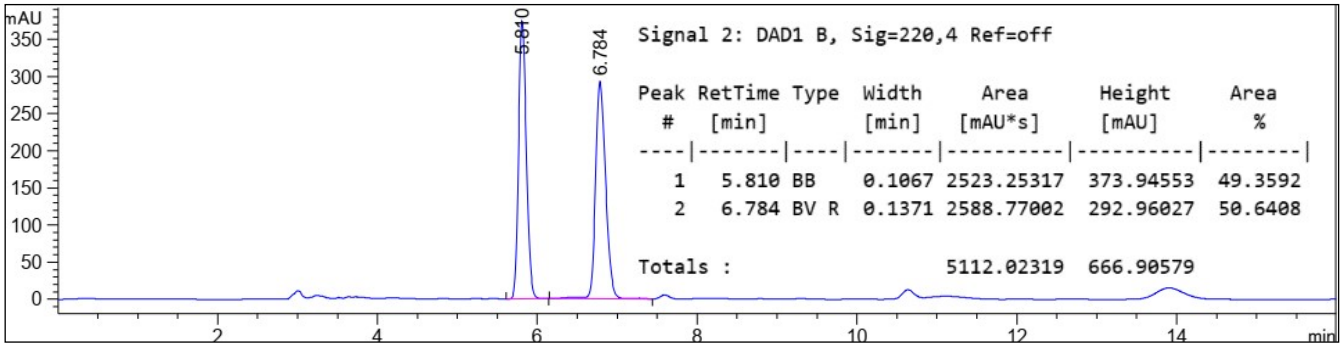


Scheme S7

[Ir(cod)Cl]$_2$ (107.5 mg, 0.16 mmol) and (*S*)-**L1** (356.9 mg, 0.64 mmol) were dissolved in 1,4-dioxane (4.0 mL) in a Schlenk tube and stirred for 30 min. To the resulting brownish red solution, alkyl allylic alcohol **1i** (0.51 g, 4.0 mmol), potassium alkynyltrifluoroborate **2a** (1.14 g, 4.8 mmol), ^{n}Bu$_4$NBr (0.13 g, 0.4 mmol), KHF_2 (0.37 g, 4.8 mmol), and CF_3CO_2H (0.68 g, 6.0 mmol) were sequentially added. The resulting heterogeneous yellow mixture was stirred at 0 °C for 8 h. The reaction mixture was diluted with hexanes (10.0 mL) and treated with triethylamine (1.0 mL). After being stirred for 10 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give (*R*)-**4i** (0.33 g, 34% yield, 95% *ee*) and (*S*)-**1i** (0.246 g, 48% yield, 97% *ee*).

HPLC for the obtained (*R*)-4i: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 95% *ee* (t_R (major) = 5.66 min, t_R(minor) = 6.48 min).

Racemic



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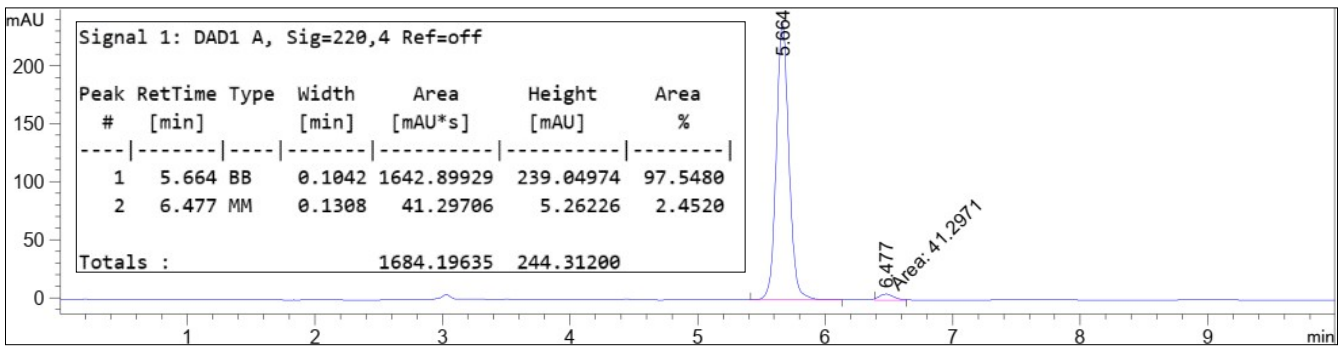
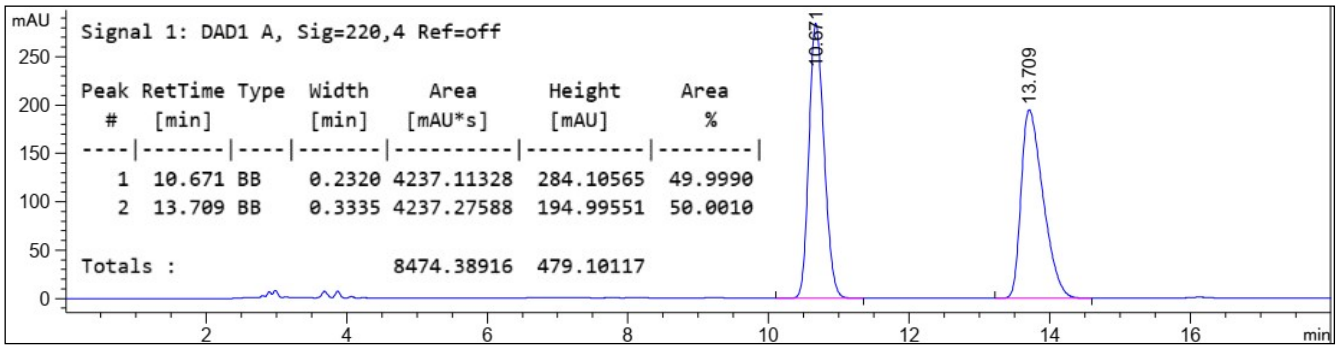


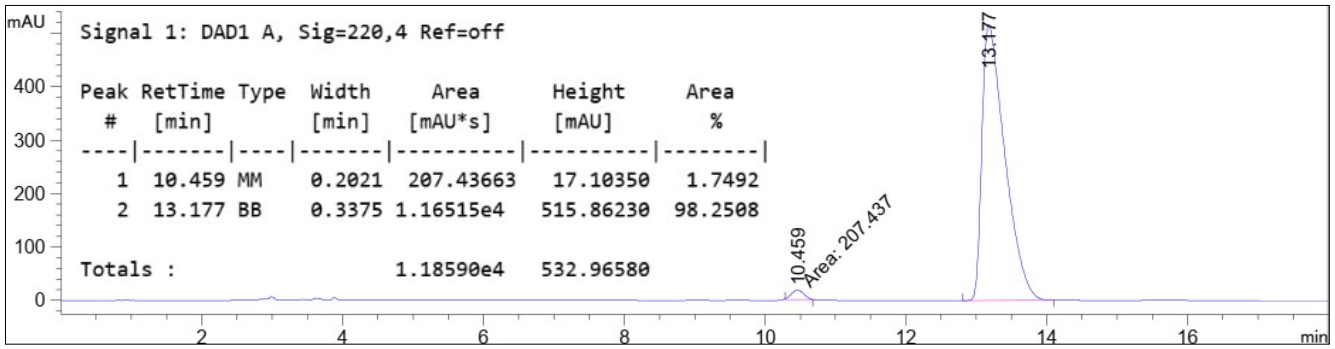
(*S*)-**1i** was converted to (*S*)-**1i'** for the HPLC analysis.

HPLC for the obtained (*S*)-1i' : Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 97% hexane, 1.0 mL/min, 35 °C, 220 nm; 97% *ee* (t_R (major) = 13.18 min, t_R(minor) = 10.46 min).

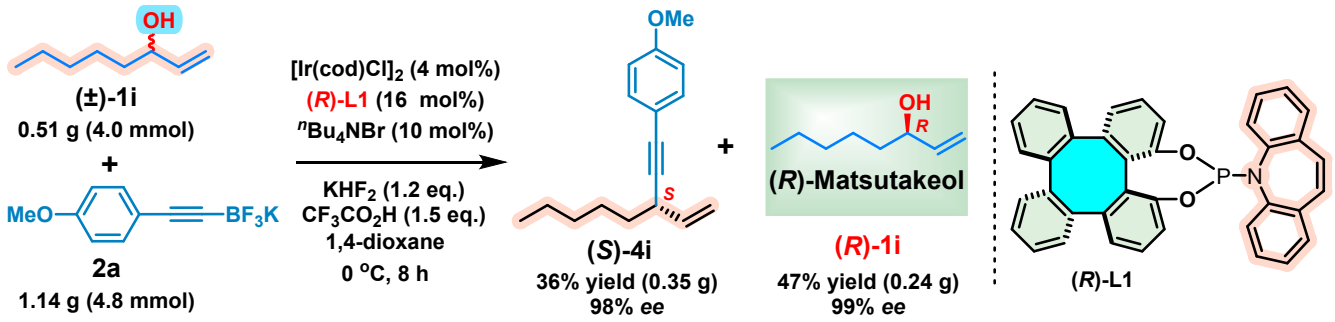
Racemic



Enantioenriched



Scale-up preparation of (*R*)-matsutakeol



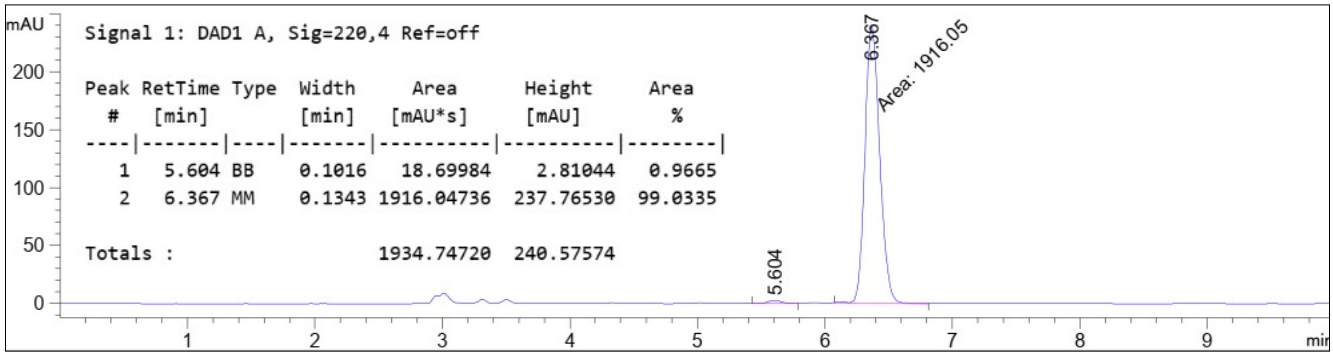
Scheme S8

$[Ir(cod)Cl]_2$ (107.5 mg, 0.16 mmol) and (*R*)-**L1** (356.9 mg, 0.64 mmol) were dissolved in 1,4-dioxane (4.0 mL) in a Schlenk tube and stirred for 30 min. To the resulting brownish red solution, alkyl allylic alcohol **1i** (0.51 g, 4.0 mmol), potassium alkynyltrifluoroborate **2a** (1.14 g, 4.8 mmol), $^{n}Bu_4NBr$ (0.13 g, 0.4 mmol), KHF_2 (0.37 g, 4.8 mmol), and CF_3CO_2H (0.68 g, 6.0 mmol) were sequentially added. The resulting heterogeneous yellow mixture was stirred at 0 °C for 8 h. The reaction mixture was diluted with hexanes (10.0 mL) and treated with triethylamine (1.0 mL). After being stirred for 10 min, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to give (*S*)-**4i** (0.35 g, 36% yield, 98% *ee*) and (*R*)-**1i** (0.24 g, 47% yield, 99% *ee*).

HPLC for the obtained (*S*)-4i: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 98% *ee* (t_R (major) = 6.37 min, t_R(minor) = 5.60 min).

Racemic

Enantioenriched

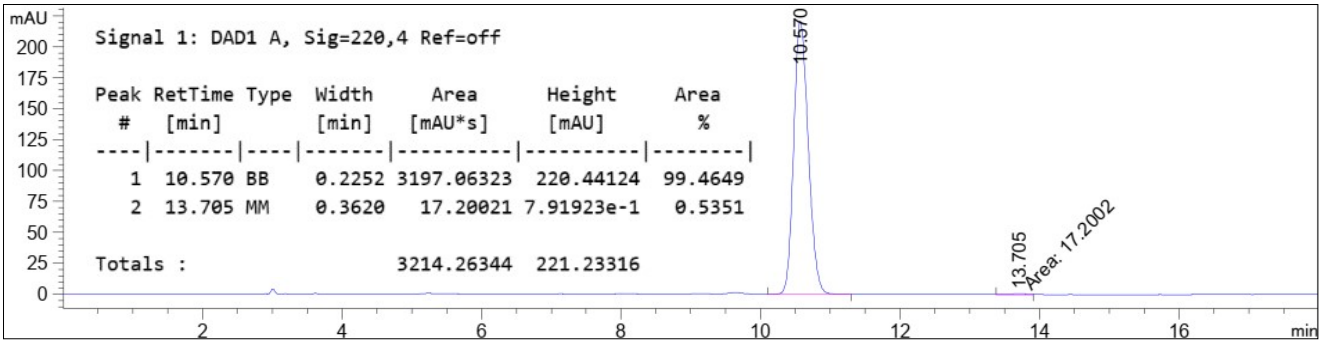


(*R*)-**1i** was converted to (*R*)-**1i'** for the HPLC analysis.

HPLC for the obtained (*R*)-1i' : Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 99% *ee* (t_R (major) = 10.57 min, t_R(minor) = 13.71 min).

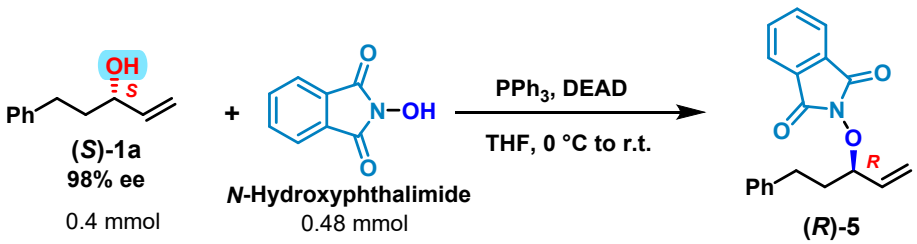
Racemic

Enantioenriched



The synthetic transformations of (*S*)-1a

A) The Mitsunobu reaction of (*S*)-1a with *N*-hydroxyphthalimide

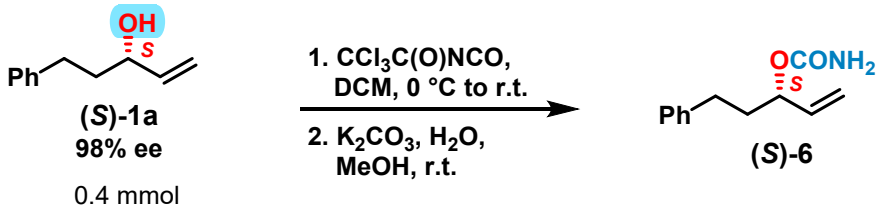


Scheme S9

To a solution of (*S*)-**1a** (64.9 mg, 0.4 mmol, 98% *ee*) in THF (1.5 mL) was added PPh_3 (125.9 mg, 0.48 mmol,) and *N*-Hydroxyphthalimide (78.3 mg, 0.48 mmol). The resulting mixture was cooled to 0 °C before diethyl azodicarboxylate (**DEAD**, 83.6 mg, 0.48 mmol) was added dropwise. After being stirred 0.5 h at 0 °C, the reaction was allowed to warm to room temperature (25 °C) and stirred until the reaction completed by TLC analysis. The solvent was evaporated in vacuo and the residue was purified by column chromatography to provide 103.3 mg (*R*)-**5** as a colorless oil in 84% yield (103.3 mg) with 99% *ee*.

The stereoconfiguration of (*R*)-**5** was determined by comparison of optical rotation of its enantiomer previously reported in literature. [4]

B) The esterification of (*S*)-1a

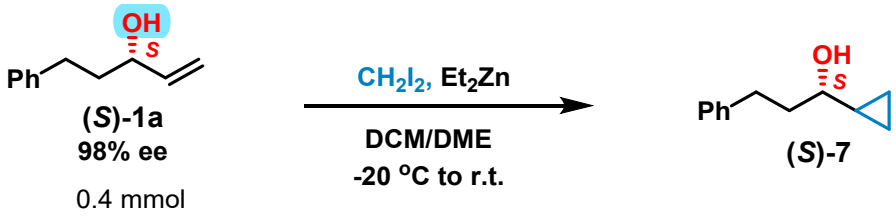


Scheme S10

To a solution of (*S*)-**1a** (64.9 mg, 0.4 mmol, 98% *ee*) in CH_2Cl_2 (1.0 mL) was added Trichloroacetyl isocyanate (90.4 mg, 0.48 mmol) dropwise at 0 °C. The reaction was allowed to warm to room temperature (25 °C) and stirred until the reaction completed by TLC analysis. The excess solvent was evaporated in vacuo. The residue was cooled to 0 °C and dissolved in MeOH-water (4:1, 2.0 ml). K_2CO_3 (221.2 mg, 1.6 mmol) was added in one portion to the mixture. The resulting mixture was warmed to room temperature (25 °C) and continued to stir overnight. The solvent was removed under vacuum, and the residue was purified by column chromatography to provide 69.6 mg (*S*)-**6** as a white solid in 85% yield with >99% *ee*.

The stereoconfiguration of (*S*)-**6** was determined by comparison of optical rotation of its analogue previously reported in literature. [5]

C) The cyclopropanation of (*S*)-1a

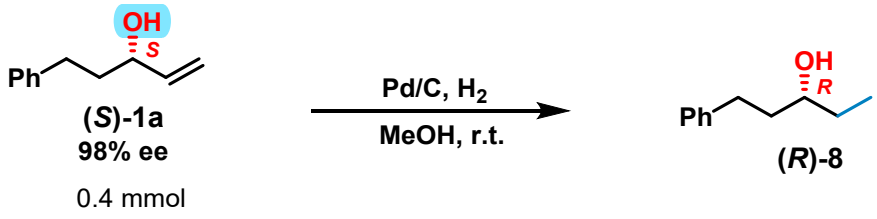


Scheme S11

To a solution of Dimethoxyethane (**DME**, 144.2 mg, 1.6 mmol) in CH_2Cl_2 (10.0 mL) was added Et_2Zn (1.0 M in hexane, 1.6 mL, 1.6 mmol) and CH_2I_2 (857.1 mg, 3.2 mmol) dropwise at -20 °C under argon. Then a solution of (*S*)-**1a** (64.9 mg, 0.4 mmol, 98% *ee*) in CH_2Cl_2 (2.0 mL) was added at -20 °C. The reaction was allowed to warm to room temperature (25 °C) and stirred until the reaction completed by TLC analysis. The reaction was quenched by saturated solution of NH_4Cl and the resulting mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography to provide 60.1 mg (*S*)-**7** as a colorless oil in 85% yield with 99% *ee*.

The stereoconfiguration of (*S*)-**7** was determined by comparison of optical rotation of its analogue[4] and its enantiomer[6] previously reported in literature.

D) The hydrogenation of (*S*)-1a



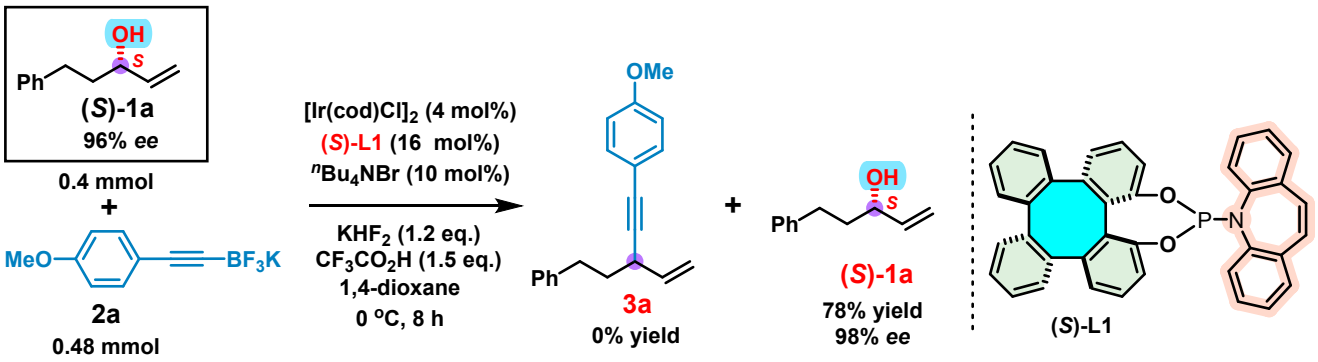
Scheme S12

To a solution of (*S*)-**1a** (64.9 mg, 0.4 mmol, 98% *ee*) in MeOH (2.0 mL) was added 10 wt% Pd/C (100.6 mg, 0.1 equiv). The reaction was stirred at room temperature under H_2 (1 atm balloon) overnight. The reaction was filtered through a celite plug. Then the solvent was removed under vacuum and the residue was purified by column chromatography to provide 63.6 mg (*R*)-**8** as a white solid in 98% yield with 98% *ee*.

The stereoconfiguration of (*R*)-**8** was determined by comparison of its optical rotation previously reported in literature. [7]

Control experiments using enantiopure allylic alcohol (*S*)-1a as substrate

A) Using (*S*)-L1 as ligand:

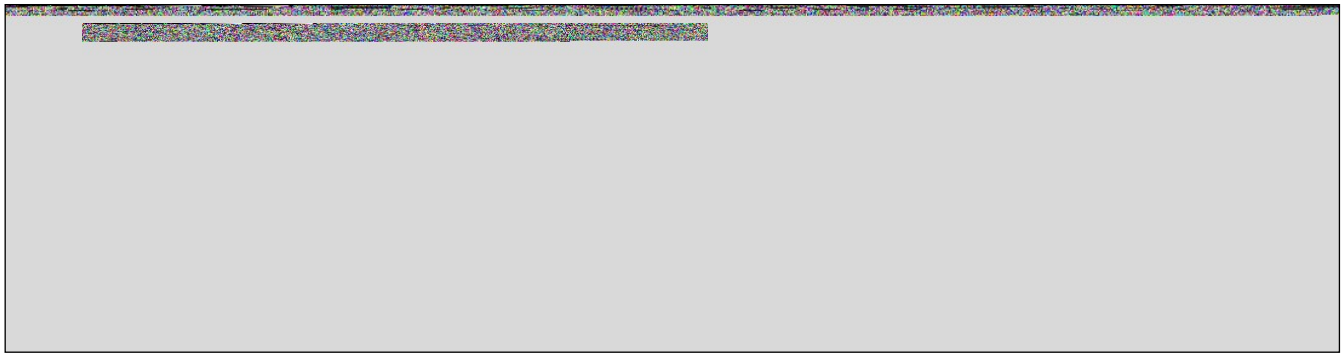


Scheme S13

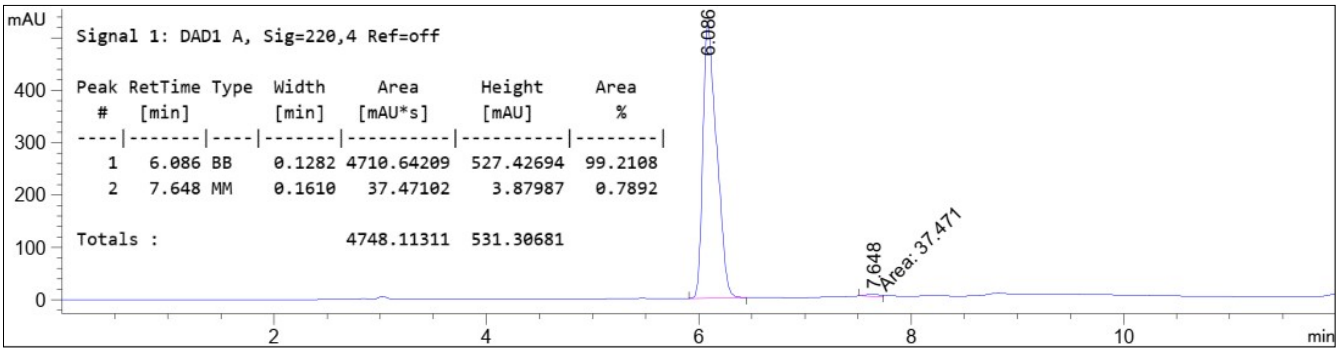
[Ir(cod)Cl]$_2$ (10.8 mg, 16.0 μmol) and (*S*)-**L1** (35.6 mg, 0.64 μmol) were dissolved in 1,4-dioxane (0.4 mL) in a Schlenk tube and stirred for 30 min. To the resulting brownish red solution, alkyl allylic alcohol (*S*)-**1a** (64.9 mg, 0.4 mmol, 96% *ee*), potassium alkynyltrifluoroborate **2a** (114.3 mg, 0.48 mmol), ^{n}Bu$_4$NBr (13.0 mg, 40 μmmol), KHF_2 (37.5 mg, 0.48 mmol), and CF_3CO_2H (68.4 mg, 0.6 mmol) were sequentially added. The resulting heterogeneous yellow mixture was stirred at 0 °C for 8 h. The reaction mixture was diluted with hexanes (1.0 mL) and treated with triethylamine (0.1 mL). The resulting mixture was purified by flash chromatography on silica gel to only give (*S*)-**1a** in 78% yield with 98% *ee*, while no **3a** was afforded.

HPLC for (*S*)-1a: Daicel Chiralcel® OD-H, 12 % ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 6.09 min, t_R(minor) = 7.65 min).

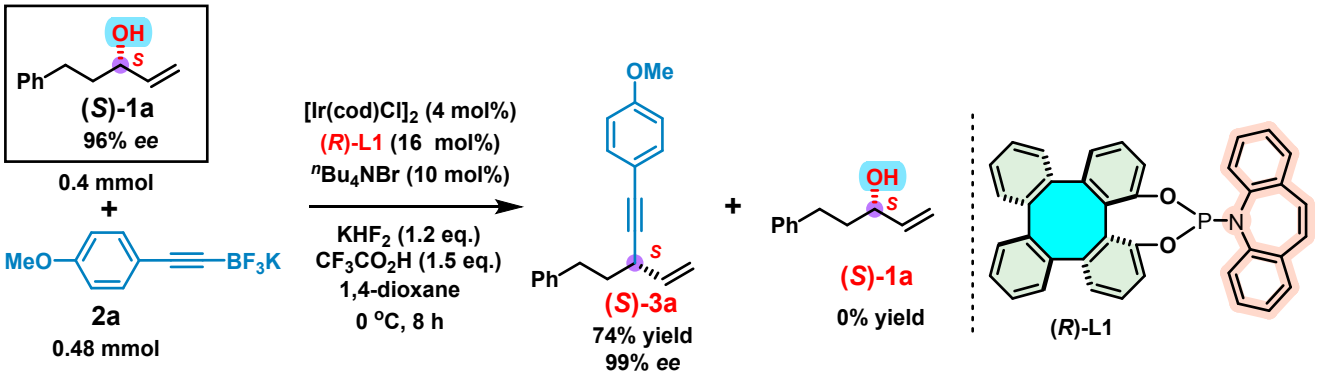
Racemic



Enantioenriched



B) Using (*R*)-L1 as ligand:

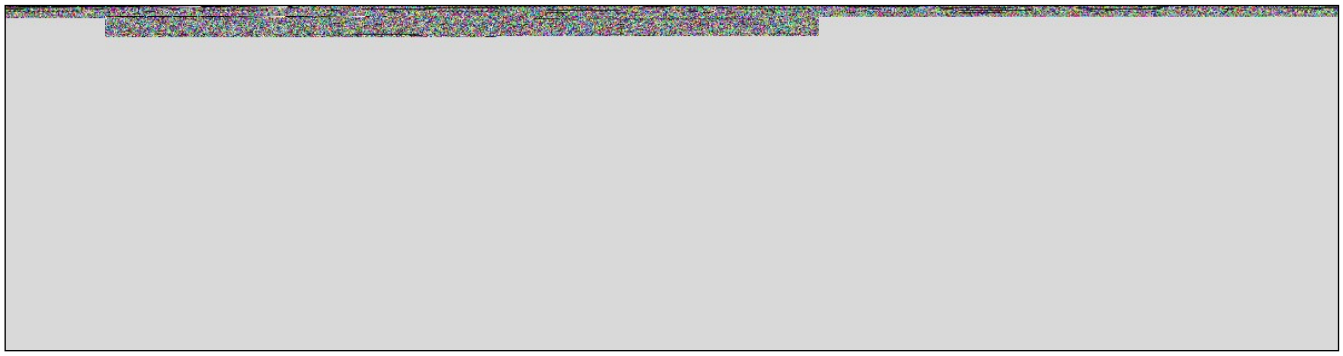


Scheme S14

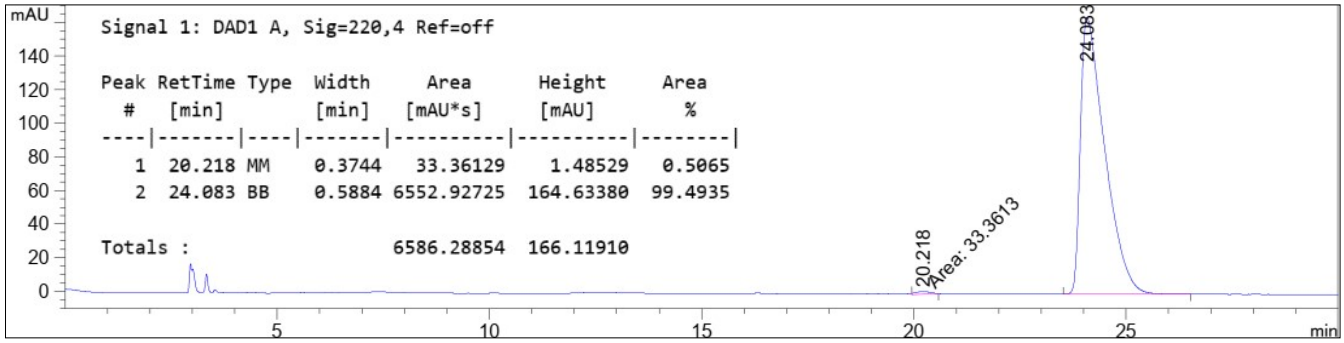
[Ir(cod)Cl]$_2$ (10.8 mg, 16.0 μmol) and (*R*)-**L1** (35.6 mg, 0.64 μmol) were dissolved in 1,4-dioxane (0.4 mL) in a Schlenk tube and stirred for 30 min. To the resulting brownish red solution, alkyl allylic alcohol (*S*)-**1a** (64.9 mg, 0.4 mmol, 96% *ee*), potassium alkynyltrifluoroborate **2a** (114.3 mg, 0.48 mmol), ^{n}Bu$_4$NBr (13.0 mg, 40 μmmol), KHF_2 (37.5 mg, 0.48 mmol), and CF_3CO_2H (68.4 mg, 0.6 mmol) were sequentially added. The resulting heterogeneous yellow mixture was stirred at 0 °C for 8 h. The reaction mixture was diluted with hexanes (1.0 mL) and treated with triethylamine (0.1 mL). The resulting mixture was purified by flash chromatography on silica gel to give (*S*)-**3a** in 74% yield with 99% *ee*, and no (*S*)-**1a** was recovered.

HPLC for the obtained (*S*)-3a: Daicel Chiralcel® OJ-H, 1% *i*PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 99% *ee* (t_R (major) = 24.08 min, t_R(minor) = 20.22 min).

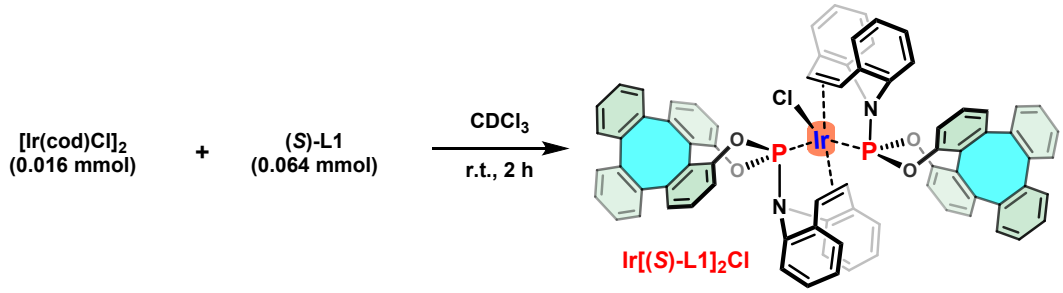
Racemic



Enantioenriched



^{31}P NMR experiment of (*S*)-L1 and [Ir(cod)Cl]$_2$ in a ratio of 4: 1



Scheme S15

In a glove box, to a bottle was added [Ir(cod)Cl]$_2$ (10.7 mg, 0.016 mmol, 1.0 equiv.), (*S*)-**L1** (35.7 mg, 0.064 mmol, 4.0 equiv.) and $CDCl_3$ (0.8 mL). The resulting solution was stirred at room temperature for 2 hours. The reaction solution was transferred into an NMR tube and analyzed by ^{31}P NMR and HRMS spectroscopies.

^{31}P NMR (162 MHz, $CDCl_3$) δ = 135.6 (s).

HRMS (ESI): $[M\text{-}Cl]^+$ Calcd. for $[C_{76}H_{48}IrN_2O_4P_2]^+$ 1307.2713, found 1307.2744.

According to the ^{31}P NMR and HRMS analyses, the structure of the generated product was proposed as **Ir[(*S*)-L1]$_2$Cl**.

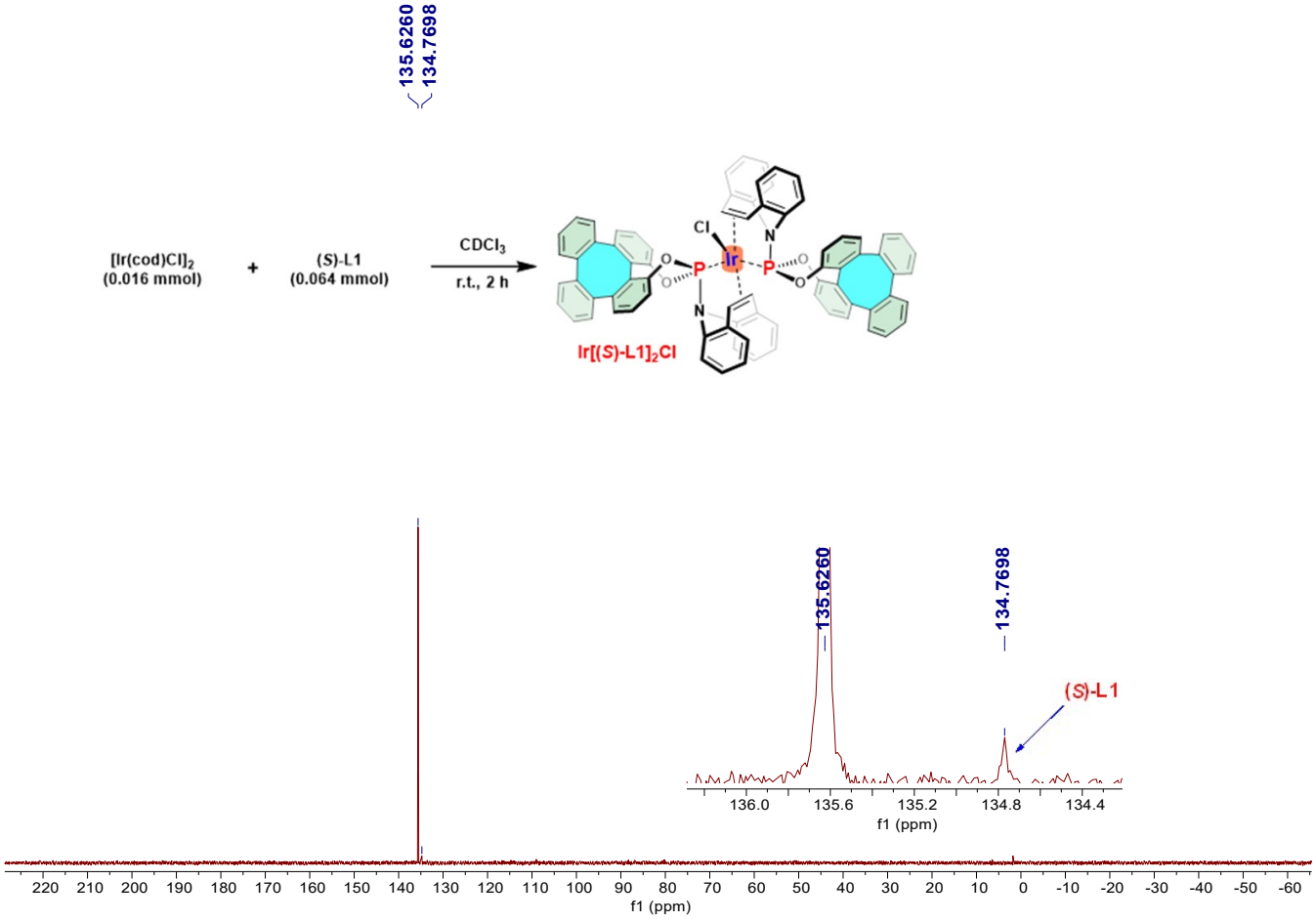


Figure S3 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of the *in situ* generated **Ir[(*S*)-L1]$_2$Cl**

HRMS anylysis of the *in situ* generated Ir[(*S*)-L1]$_2$Cl

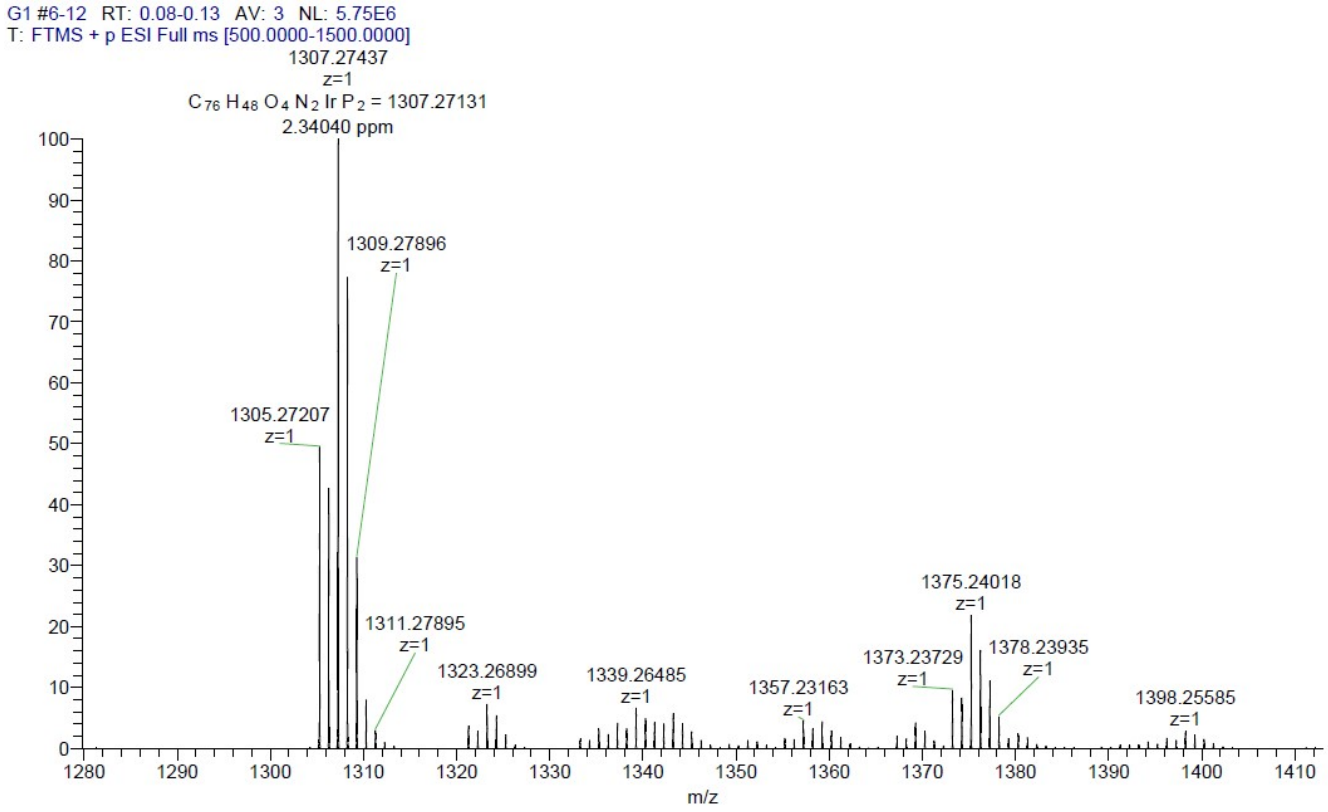
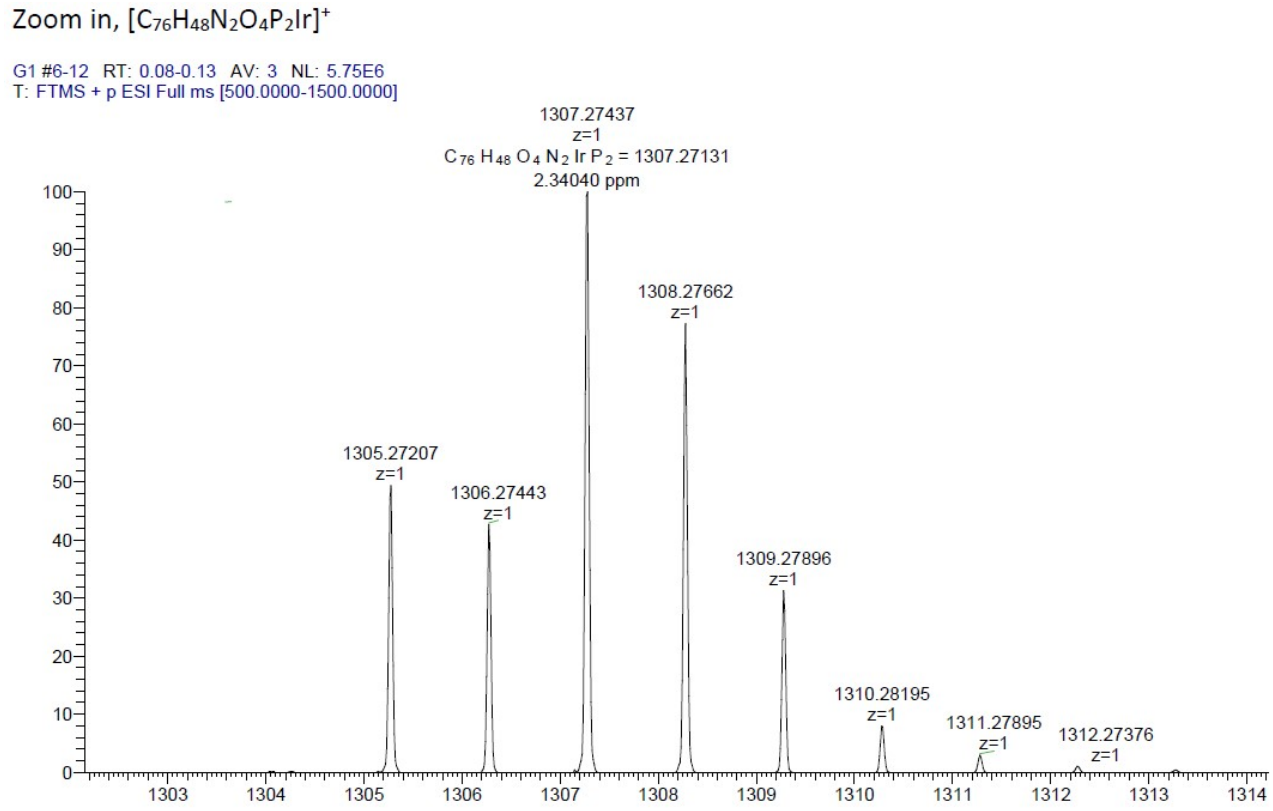


Figure S4 ESI-MS spectrum of the spectrum of the *in situ* generated **Ir[(*S*)-L1]$_2$Cl**

a)



b)

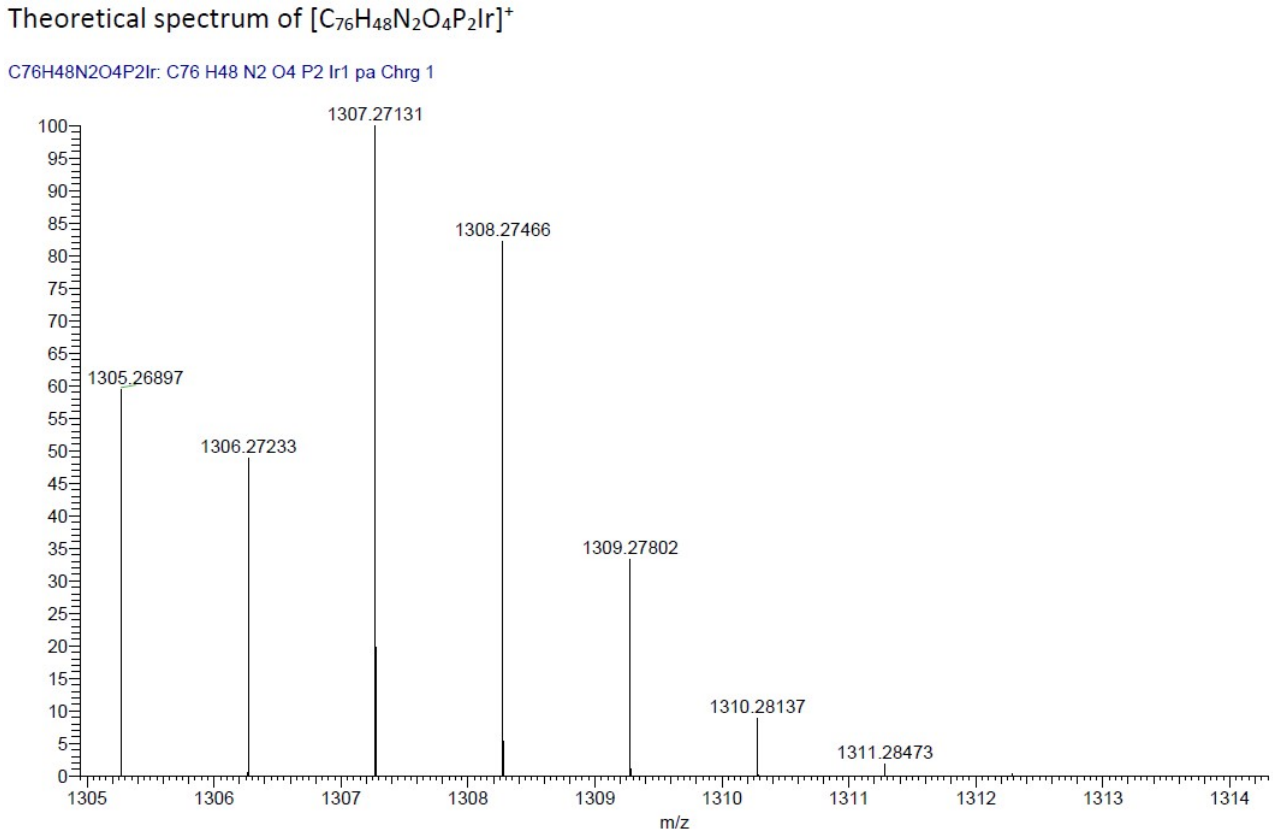
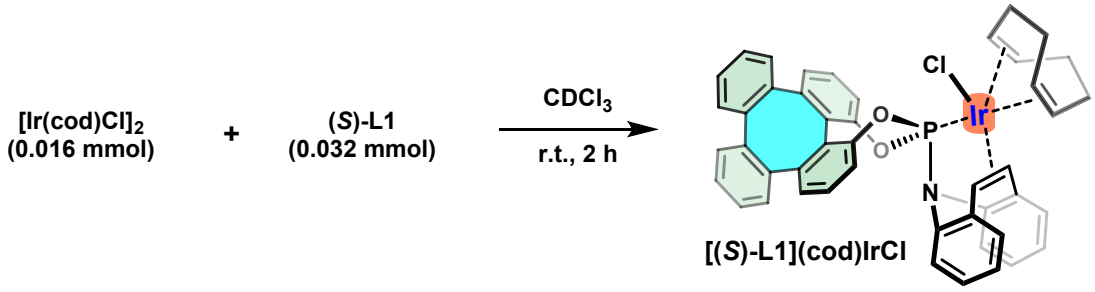


Figure S5 a) Experimental and b) simulated isotopic distribution of {**Ir[(*S*)-L1]$_2$**}$^+$

^{31}P NMR experiment of (*S*)-L1 and [Ir(cod)Cl]$_2$ in a ratio of 2: 1



Scheme S16

In a glove box, to a bottle was added [Ir(cod)Cl]$_2$ (10.7 mg, 0.016 mmol, 1.0 equiv.), (*S*)-**L1** (17.9 mg, 0.032 mmol, 2.0 equiv.) and $CDCl_3$ (0.8 mL). The resulting solution was stirred at room temperature for 2 hours. The reaction solution was transferred into an NMR tube and analyzed by ^{31}P NMR and HRMS spectroscopies.

^{31}P NMR (162 MHz, $CDCl_3$) δ = 109.0 (s).

HRMS (ESI): $[M\text{-}Cl]^+$ Calcd. for $[C_{46}H_{36}IrNO_2P]^+$ 858.2118, found 858.2114.

According to the ^{31}P NMR and HRMS analyses, the structure of the generated product was proposed as **[(*S*)-L1](cod)IrCl**.

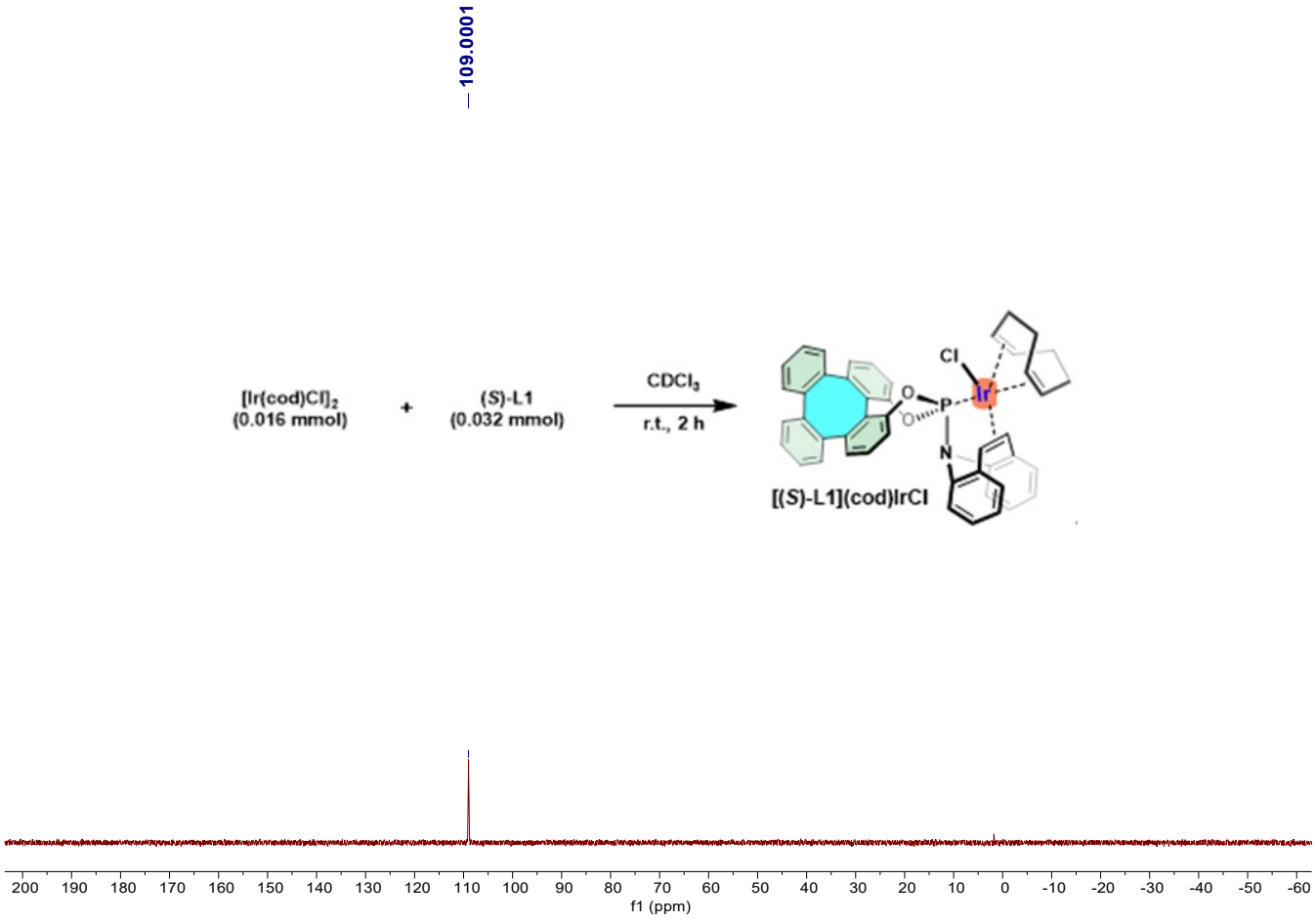


Figure S6 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of the *in situ* generated **[(*S*)-L1](cod)IrCl**

HRMS anylysis of the *in situ* generated [(*S*)-L1](cod)IrCl

Positive mode:

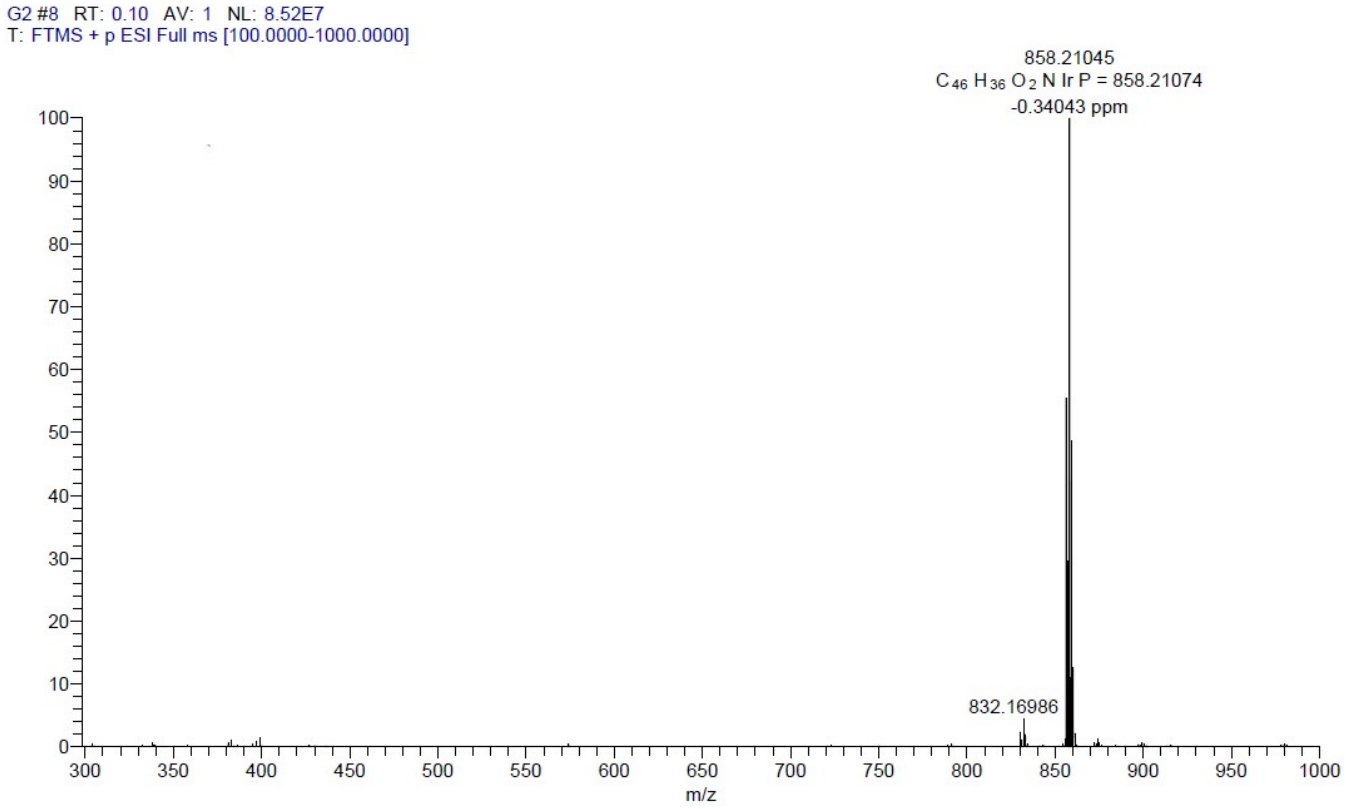
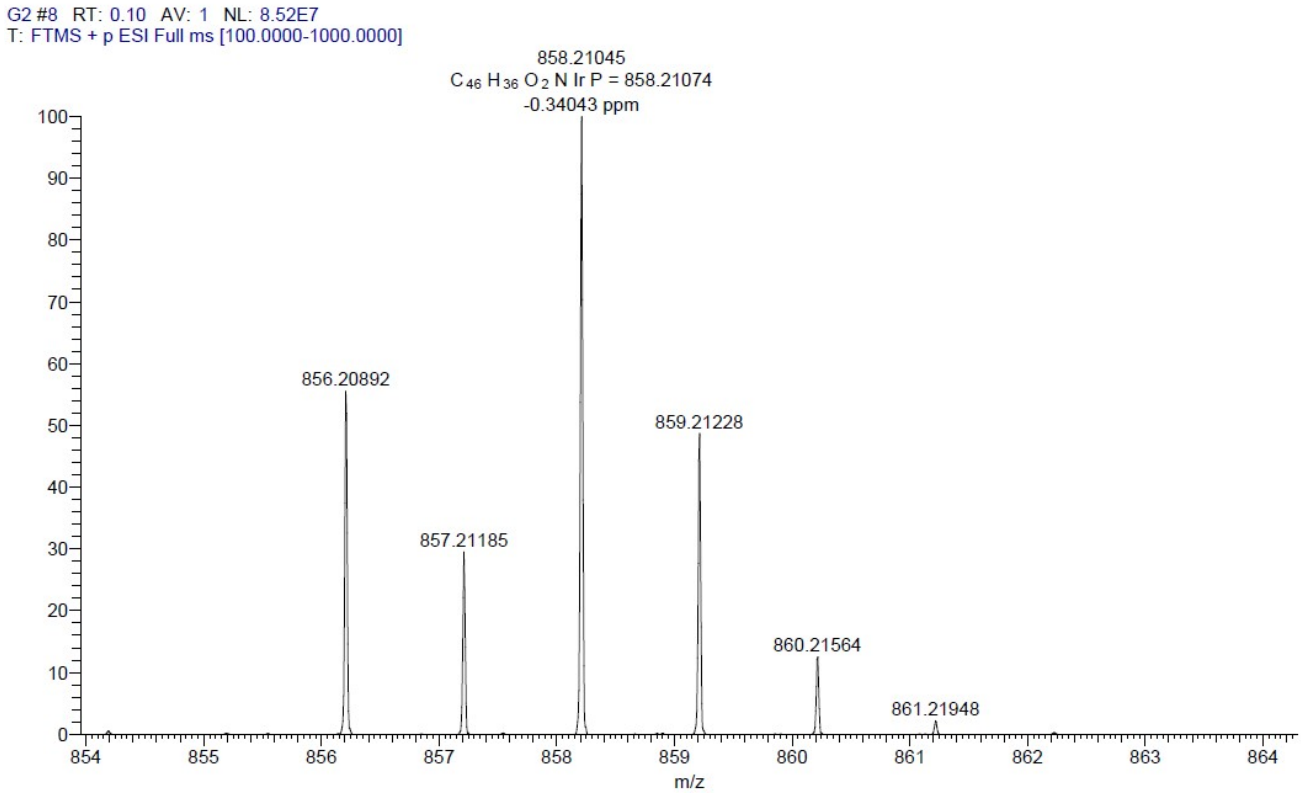


Figure S7 ESI-MS spectrum of the spectrum of the *in situ* generated **[(*S*)-L1](cod)IrCl**

a)

Zoom in, $[C_{46}H_{36}NO_2PIr]^+$



b)

Theoretical spectrum of $[C_{46}H_{36}NO_2PIr]^+$

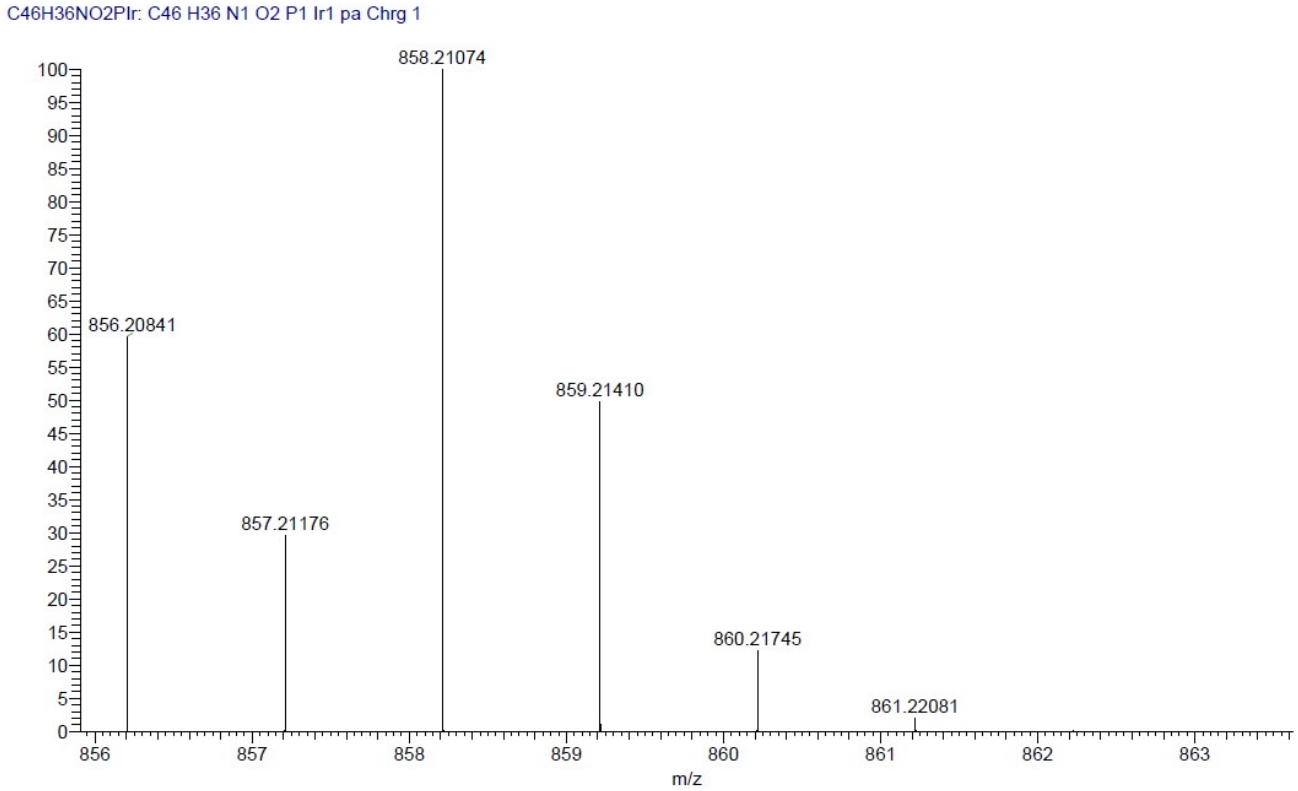


Figure S8 a) Experimental and b) simulated isotopic distribution of {**[(*S*)-L1](cod)Ir**}$^+$

The comparison of ^{31}P NMR spectra of (*S*)-L1, [(*S*)-L1](cod)IrCl and Ir[(*S*)-L1]$_2$Cl

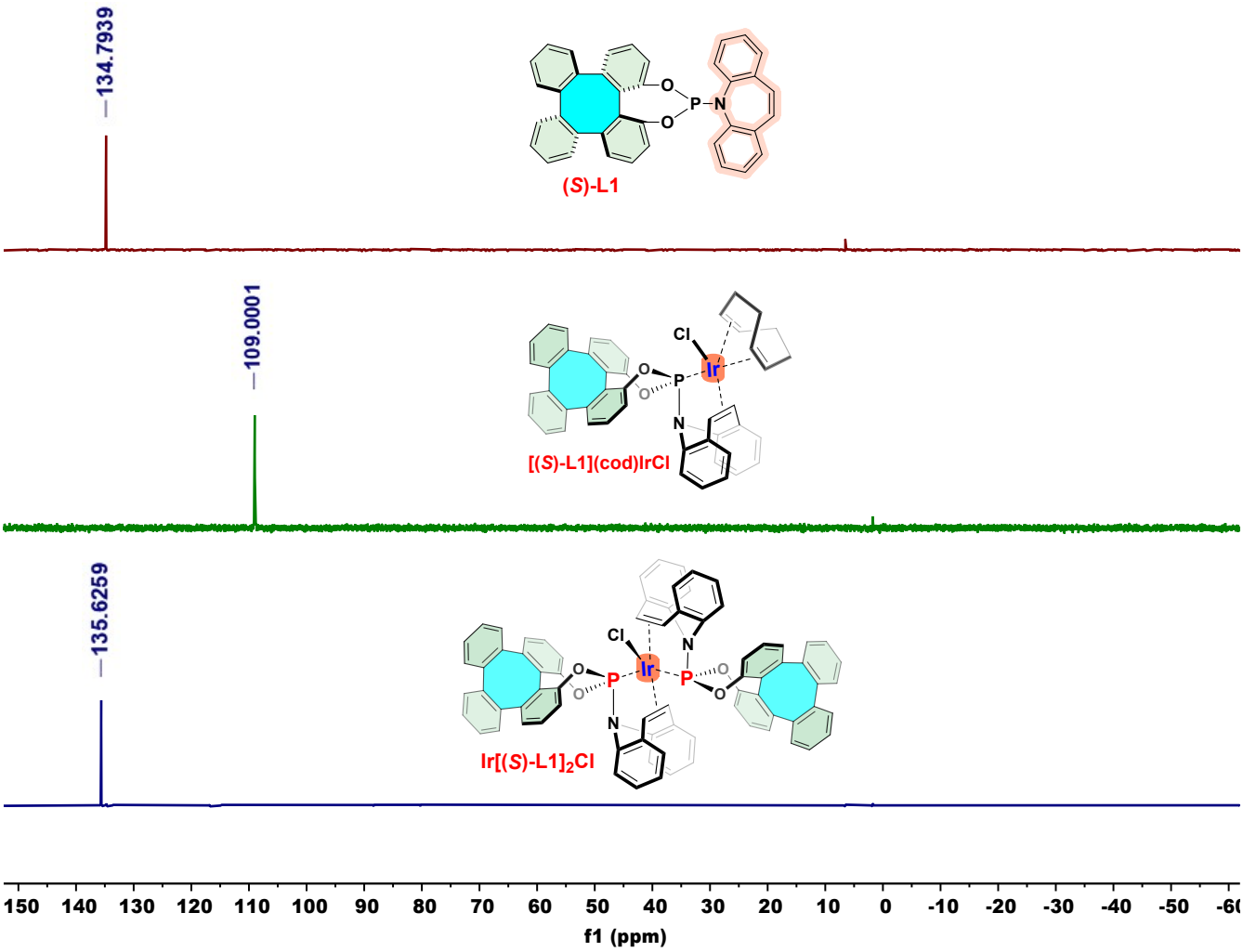


Figure S9 ^{31}P NMR spectra of **(*S*)-L1, [(*S*)-L1](cod)IrCl** and **Ir[(*S*)-L1]$_2$Cl**

^{31}P NMR experiment of (*R*)-1a combined with [Ir(cod)Cl]$_2$ and (*S*)-L1

In a glove box, to a bottle was added [Ir(cod)Cl]$_2$ (10.7 mg, 0.016 mmol, 1.0 equiv.), (*S*)-**L1** (35.7 mg, 0.064 mmol, 4.0 equiv.), (*R*)-**1a** (15.6 mg, 0.096 mmol, 6.0 equiv.) and $CDCl_3$ (0.8 mL). The resulting solution was stirred at room temperature for 2 hours. The reaction solution was transferred into an NMR tube under Ar and analyzed by ^{31}P NMR spectroscopy.

^{31}P NMR (162 MHz, $CDCl_3$) δ = 108.6 (d, *J* = 30.2 Hz), 103.1 (d, *J* = 29.9 Hz).

According to the ^{31}P NMR anylysis, the structure of the generated intermediate was proposed as **(*S*,*S*,*R*)-A**.

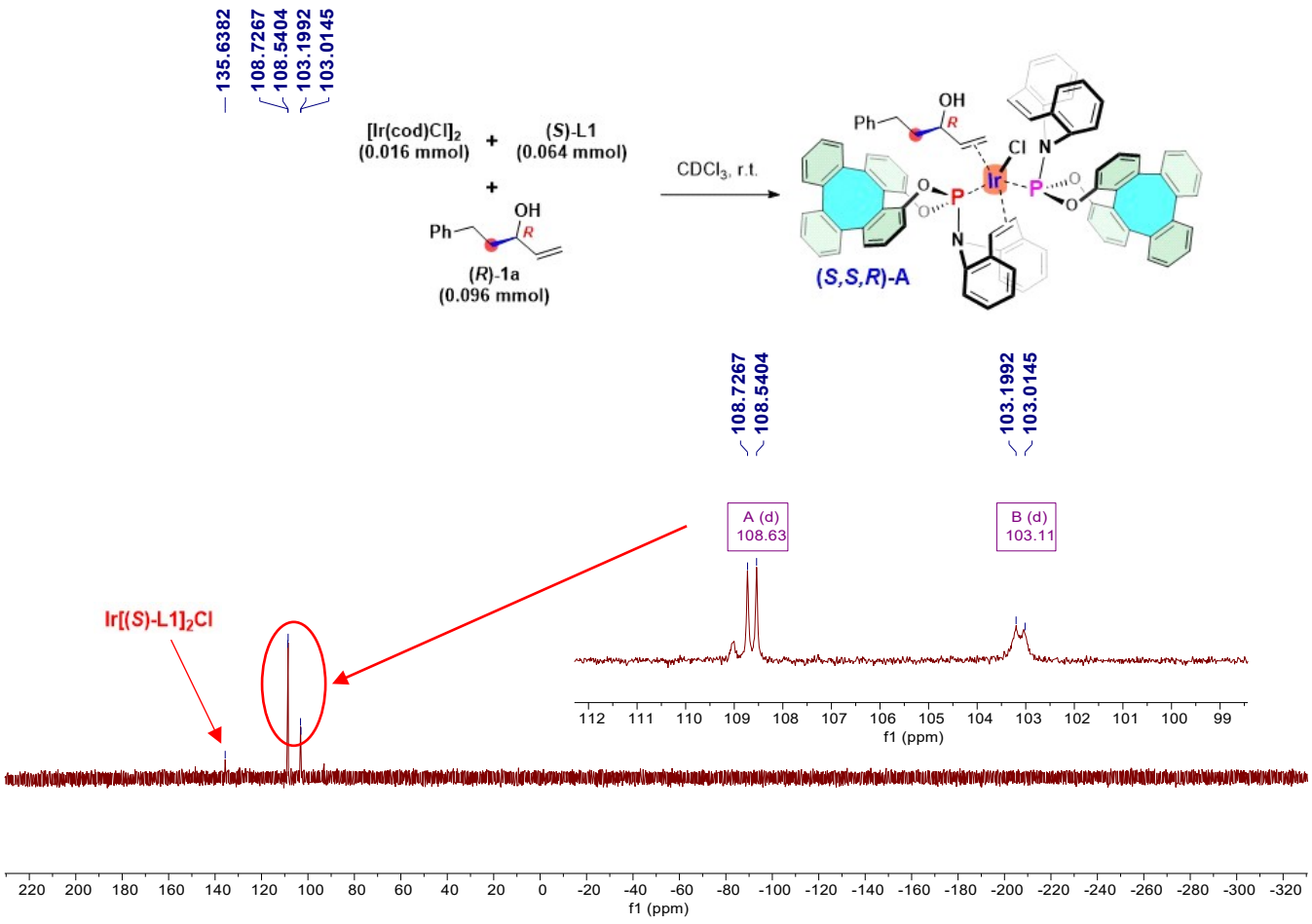


Figure S10 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of the *in situ* generated **(*S*,*S*,*R*)-A**

^{31}P NMR experiment of (*S*)-1a combined with [Ir(cod)Cl]$_2$ and (*S*)-L1

In a glove box, to a bottle was added [Ir(cod)Cl]$_2$ (10.7 mg, 0.016 mmol, 1.0 equiv.), (*S*)-**L1** (35.7 mg, 0.064 mmol, 4.0 equiv.), (*S*)-**1a** (15.8 mg, 0.096 mmol, 6.0 equiv.) and $CDCl_3$ (0.8 mL). The resulting solution was stirred at room temperature for 2 hours. The reaction solution was transferred into an NMR tube under Ar and analyzed by ^{31}P NMR spectroscopy.

^{31}P NMR (162 MHz, $CDCl_3$) δ = 135.7 (s).

According to the ^{31}P NMR anylysis, the structure of the mainly generated intermediate was **Ir[(*S*)-L1]$_2$Cl**, while no propoesd **(*S*,*S*,*S*)-A** was generated.

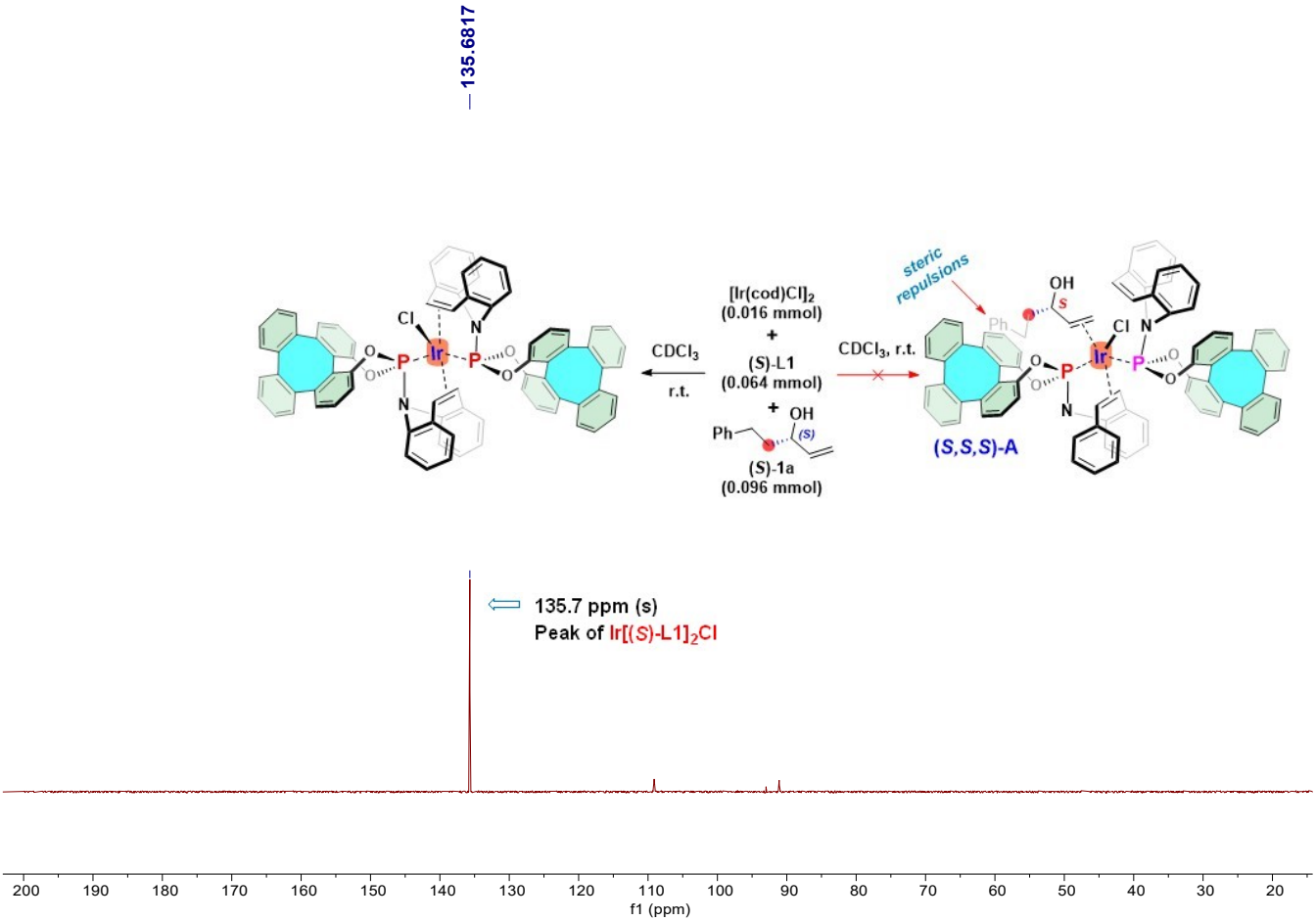
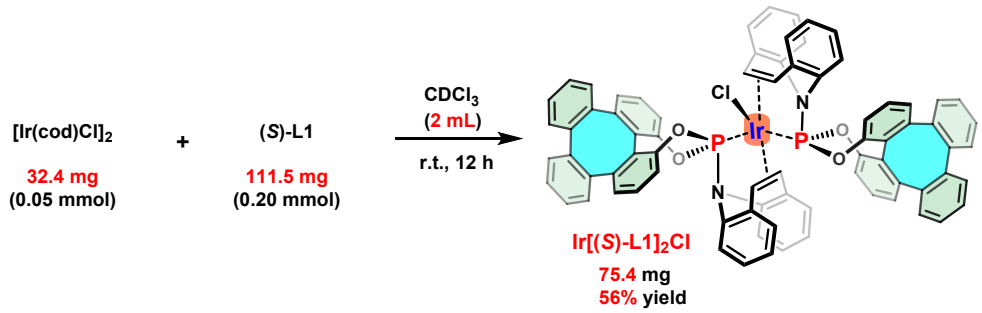


Figure S11 ^{31}P NMR (162 MHz, $CDCl_3$) spectrum of **(*S*)-1a** combined with **[Ir(cod)Cl]$_2$** and **(*S*)-L1**

Synthesis and isolation of Ir[(*S*)-L1]$_2$Cl



Scheme S17

In a glove box, a solution of [Ir(cod)Cl]$_2$ (32.4 mg, 0.05 mmol) and (*S*)-**L1** (111.5 mg, 0.20 mmol) in $CHCl_3$ (2 mL) was stirred for 12 hours. The reaction mixture was concentrated to about 2/3 of the initial volume, then *n*-pentane (5 mL) was added. The resulting precipitate was isolated by filtration. The filter cake was washed with *n*-pentane (3 x 5 mL) and dried under vacuum to give **Ir[(*S*)-L1]$_2$Cl** (75.4 mg) in 56% yield as a yellow solid.

^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.20 (m, 6H), 7.19 – 7.10 (m, 7H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.00 (dd, *J* = 13.2, 7.5 Hz, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.49 (d, *J* = 8.1 Hz, 1H), 4.85 – 4.74 (m, 1H), 3.68 – 3.61 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 147.74, 147.52, 144.05, 143.48, 141.91, 141.14, 141.12, 140.80, 140.74, 140.39, 139.42, 139.33, 131.42, 130.84, 129.89, 129.81, 129.43, 128.76, 128.19, 128.15, 128.00, 127.98, 127.92, 127.77, 127.73, 127.53, 127.23, 127.18, 127.09, 126.38, 126.11, 125.39, 121.11, 46.95, 42.85.

^{31}P NMR (162 MHz, $CDCl_3$) δ 135.6.

HRMS (ESI): $[M\text{-}Cl]^+$ Calcd. for $[C_{76}H_{48}IrN_2O_4P_2]^+$ 1307.2713, found 1307.2716.

Crystallographic Data

X-ray diffraction of (*S*)-1a' (CCDC 2159810)

Single-crystal X-ray diffraction data for (*S*)-**1a'** as recorded on a Bruker CMOS area detector diffractometer. The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation. Basic information pertaining to crystal parameters and structure refinement is summarized in follow (Table S2). **CCDC 2159810** contains the supplementary crystallographic data of (*S*)-**1a'** for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

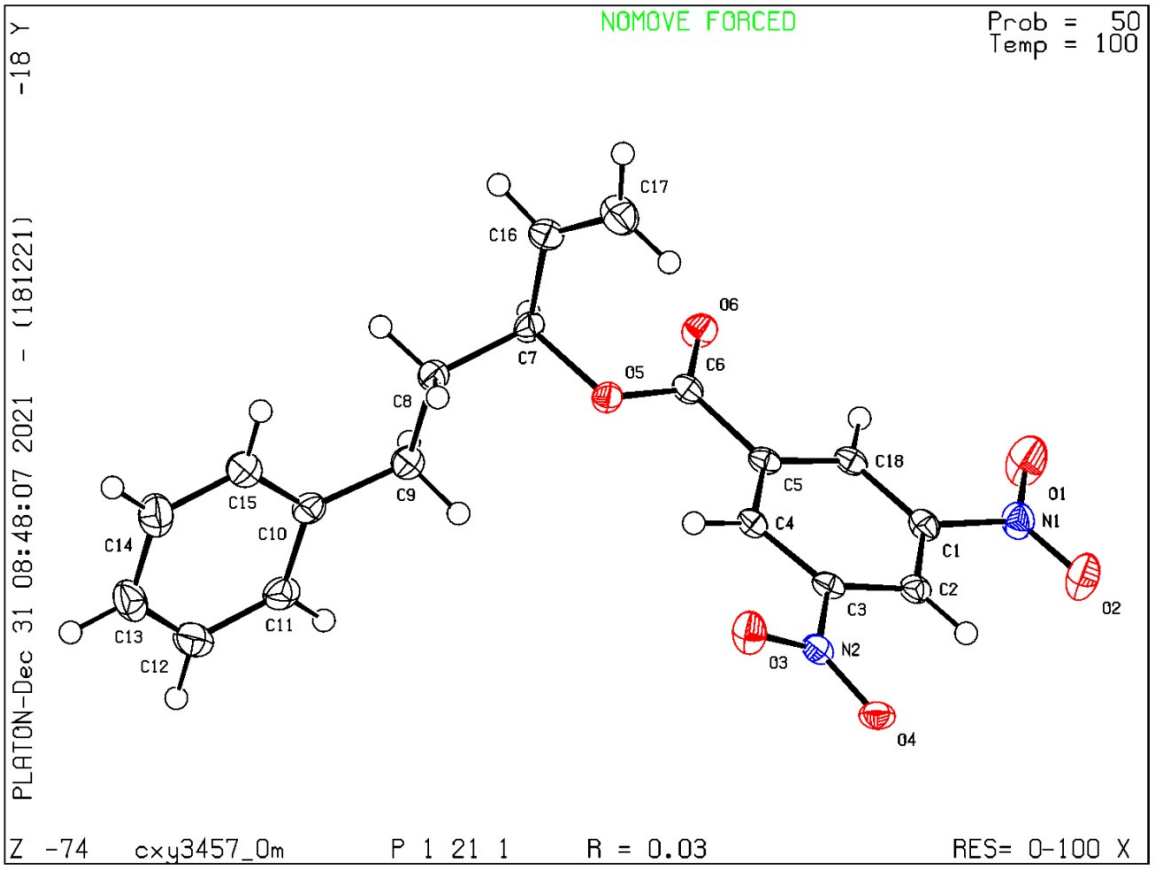
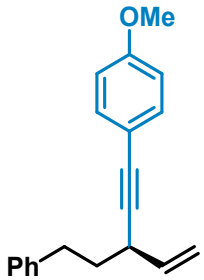


Figure S12 X-ray structure of of (*S*)-**1a'**

Table S2 Crystal data and structure refinement for (*S*)-1a'

Identification code	cxy3457_0m
Empirical formula	$C_{18}H_{16}N_2O_6$
Formula weight	356.33
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.6781(3)
b/Å	9.7730(6)
c/Å	15.2351(9)
α/°	90
β/°	92.831(3)
γ/°	90
Volume/Å^3	844.40(8)
Z	2
ρ_{calc}g/cm^3	1.401
μ/mm^{-1}	0.900
F(000)	372.0
Crystal size/mm^3	0.32 × 0.32 × 0.29
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.808 to 136.53
Index ranges	-6 ≤ h ≤ 6, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	14263
Independent reflections	3048 [R_{int} = 0.0493, R_{sigma} = 0.0351]
Data/restraints/parameters	3048/1/236
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0293, wR_2 = 0.0745
Final R indexes [all data]	R_1 = 0.0297, wR_2 = 0.0747
Largest diff. peak/hole /e Å^{-3}	0.22/-0.22
Flack parameter	0.00(5)

Characterization data



(*R*)-**3a**

Colorless oil. 43.1 mg, 39% yield. **[α]$^{20}_{D}$**: +7.4 (*c* = 1.0, $CHCl_3$) (lit[3b]: **[α]$^{25}_{D}$:** +2.4 (*c* = 1.0, $CHCl_3$)).

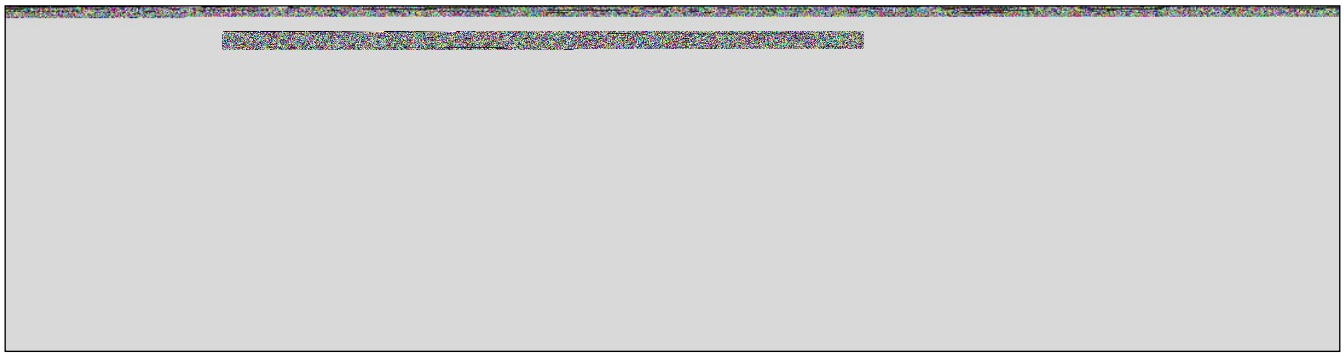
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.17 (m, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.86 (ddd, *J* = 16.5, 10.0, 6.1 Hz, 1H), 5.38 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.14 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.81 (s, 3H), 3.28 (q, *J* = 6.4 Hz, 1H), 2.90 – 2.77 (m, 2H), 1.98 – 1.88 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.21, 141.85, 137.95, 132.99, 128.58, 128.38, 125.88, 115.88, 115.32, 113.84, 88.42, 83.89, 55.30, 37.09, 35.57, 33.30.

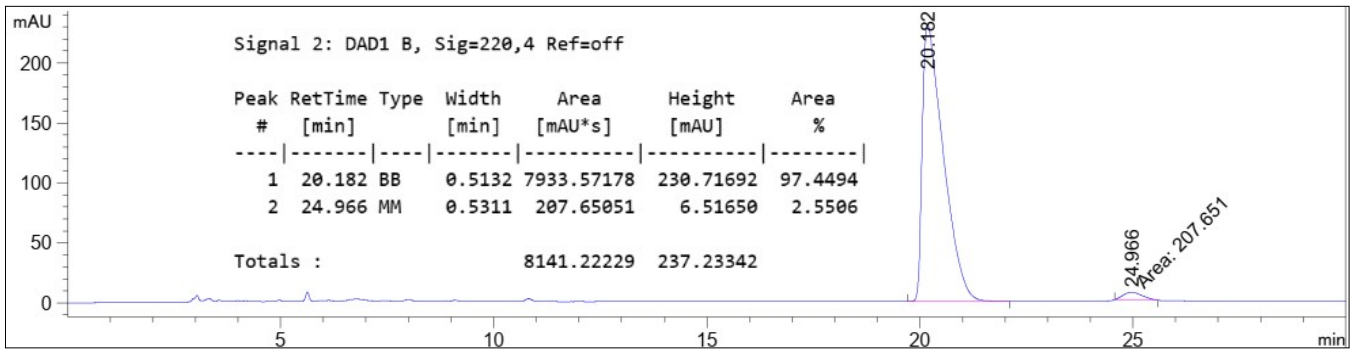
HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{20}H_{21}O]^+$ 277.1587, found 277.1585.

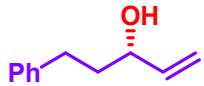
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 95% *ee* (t_R (major) = 20.18 min, t_R(minor) = 24.97 min).

Racemic



Enantioenriched





(*S*)-**1a** Obtained from the preparation of (*R*)-**3a**.

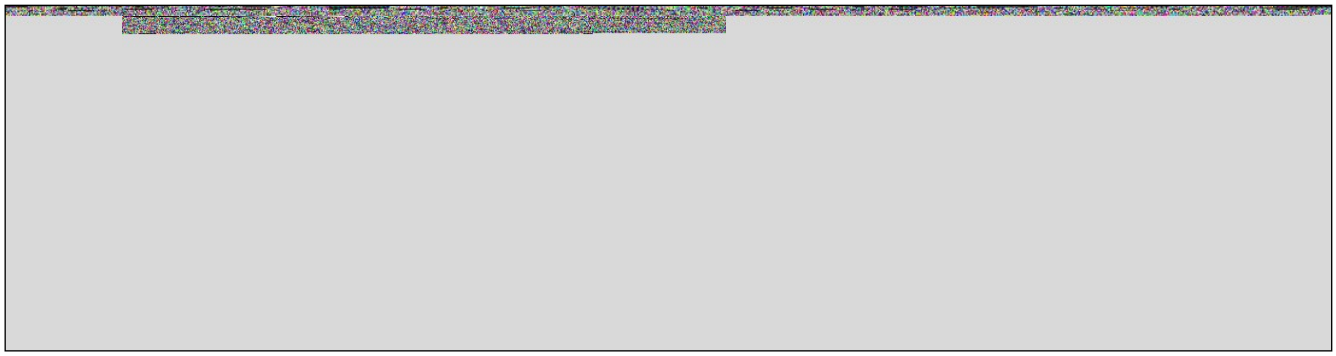
Colorless oil. 27.9 mg, 43% yield. **[α]$^{20}_{D}$:** -3.5 (*c* = 1.0, $CHCl_3$) (lit[8]: **[α]$^{25}_{D}$:** -3.6 (*c* = 0.4, $CHCl_3$)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.25 – 7.16 (m, 3H), 5.99 – 5.85 (m, 1H), 5.26 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.15 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.14 (q, *J* = 6.4 Hz, 1H), 2.82 – 2.64 (m, 2H), 1.93 – 1.82 (m, 2H).

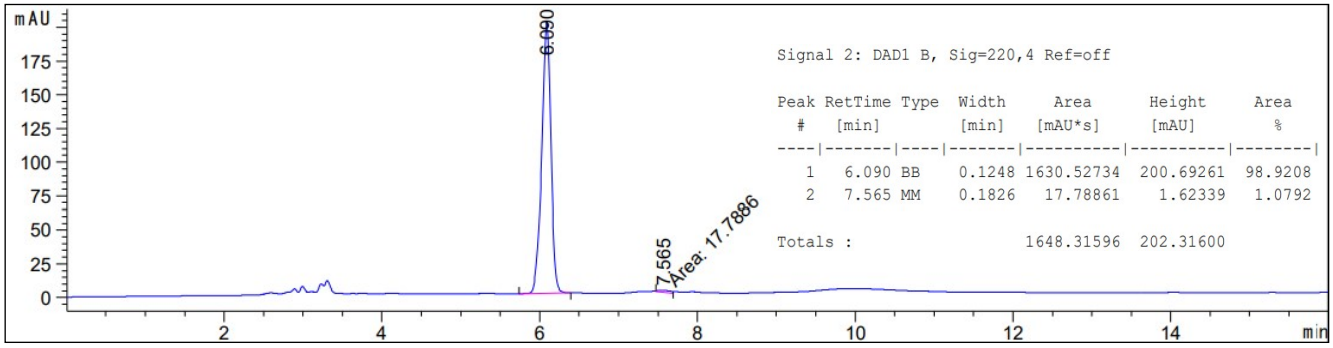
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.89, 141.02, 128.48, 128.42, 125.87, 114.96, 72.49, 38.53, 31.65.

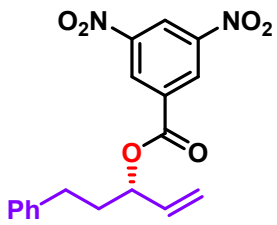
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 6.09 min, t_R(minor) = 7.57 min).

Racemic



Enantioenriched





(*S*)-**1a'**

White solid. 50.9 mg, 83% yield. mp: 60.3 – 60.8 °C. **[α]$^{20}_{D}$**: -19.7 (*c* = 1.0, $CHCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 9.08 (d, *J* = 2.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 1H), 5.97 (ddd, *J* = 17.2, 10.5, 6.8 Hz, 1H), 5.63 (q, *J* = 6.6 Hz, 1H), 5.43

(d, J = 17.2 Hz, 1H), 5.36 (d, J = 10.5 Hz, 1H), 2.88 – 2.70 (m, 2H), 2.27 (dt, J = 15.3, 7.4 Hz, 1H), 2.17 (dq, J = 14.3, 6.3 Hz, 1H).

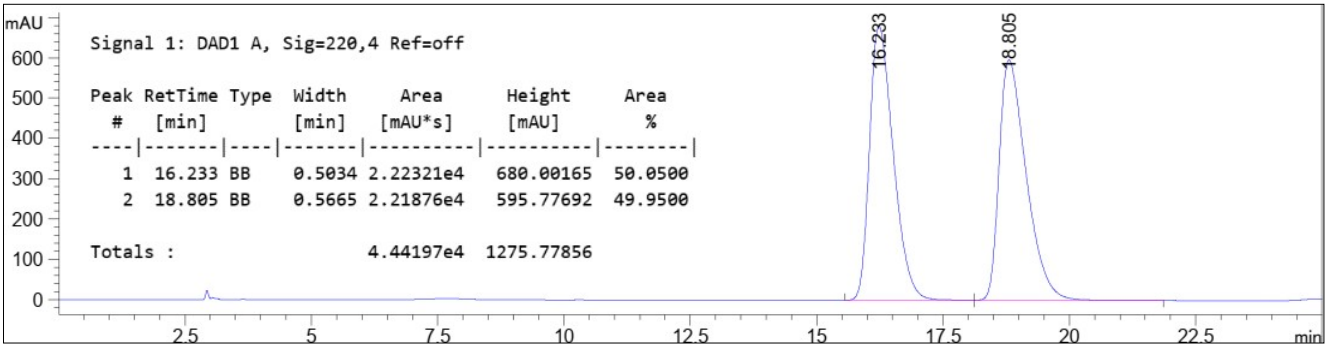
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.70, 148.60, 140.75, 135.06, 134.05, 129.35, 128.56, 128.29, 126.08, 122.31, 118.83, 77.65, 35.34, 31.65.

HRMS (ESI): $[M-H]^-$ Calcd. for $[C_{18}H_{15}N_2O_6]^-$ 355.0936, found 355.0921.

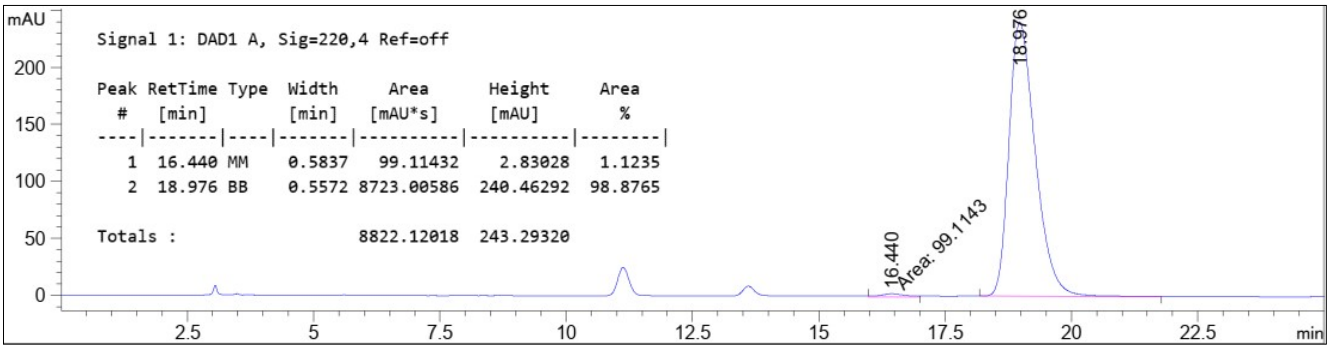
IR (neat): 3112, 2988, 2922, 1719, 1630, 1539, 1452, 1342, 1280, 1171, 1072, 923, 866, 719 cm^{-1}.

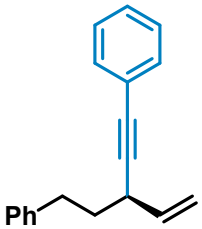
HPLC: Daicel Chiralcel® OJ-H, 30% ^{i}PrOH, 70% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 18.98 min, t_R(minor) = 16.44 min).

Racemic



Enantioenriched





(*R*)-**3b**

Colorless oil. 27.6 mg, 28% yield. **[α]$^{20}_D$**: +7.8 (c = 1.0, $CHCl_3$) (lit[3b]: **[α]$^{25}_D$**: +7.28 (c = 0.98, $CHCl_3$)).

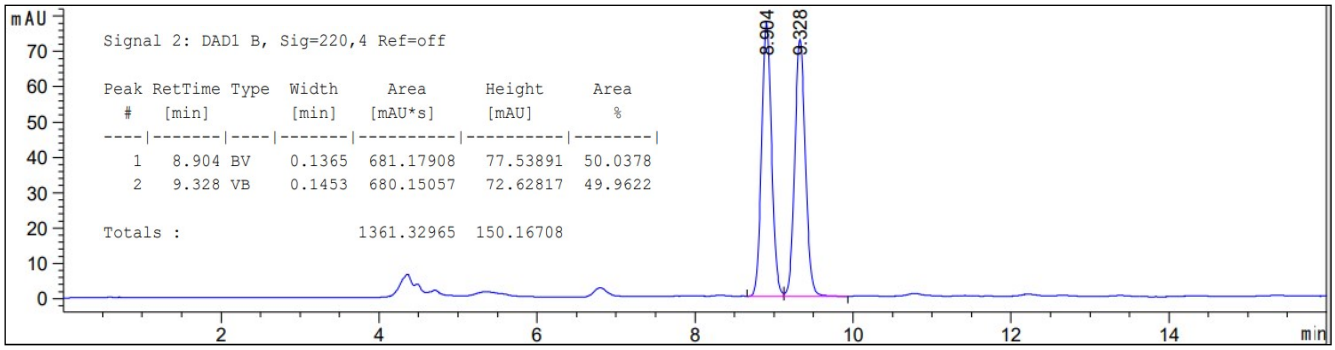
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.36 – 7.26 (m, 5H), 7.26 – 7.17 (m, 3H), 5.87 (ddd, J = 16.3, 10.0, 6.1 Hz, 1H), 5.40 (dt, J = 16.9, 1.5 Hz, 1H), 5.16 (dt, J = 10.1, 1.4 Hz, 1H), 3.30 (q, J = 6.4 Hz, 1H), 2.94 – 2.76 (m, 2H), 2.01 – 1.87 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.77, 137.72, 131.65, 128.57, 128.40, 128.23, 127.78, 125.90, 123.72, 115.44, 90.02, 84.15, 37.02, 35.53, 33.28.

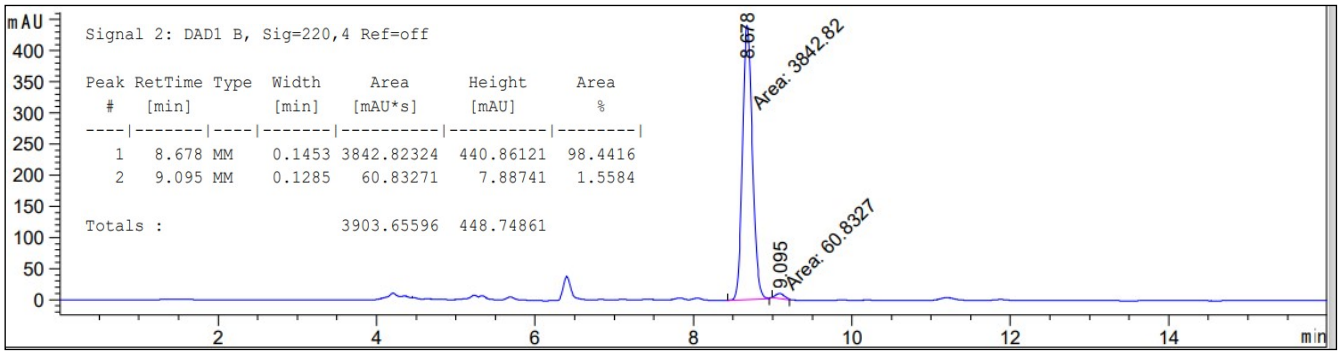
HRMS (APCI): $[M]^+$ Calcd. for $[C_{19}H_{18}]^+$ 246.1403, found 246.1406.

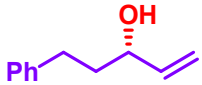
HPLC: Daicel Chiralcel® OJ-H, 5 % ^{i}PrOH, 95% hexane, 0.7 mL/min, 40 °C, 220 nm; 97% *ee* (t_R (major) = 8.68 min, t_R(minor) = 9.10 min).

Racemic



Enantioenriched





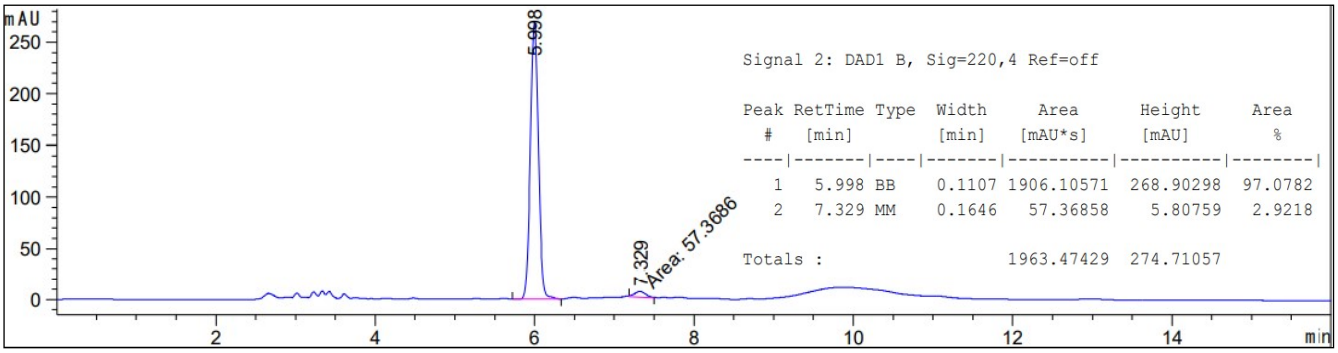
(*S*)-**1a** Obtained from the preparation of (*R*)-**3b**.

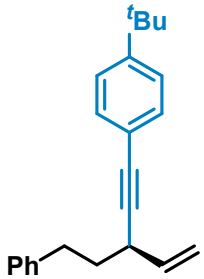
Colorless oil. 30.4 mg, 47% yield.

HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 94% *ee* (t_R (major) = 6.00 min, t_R(minor) = 7.33 min).

Racemic

Enantioenriched





(*R*)-**3c**

Colorless oil. 42.3 mg, 35% yield. $[\alpha]^{20}_{D}$: +1.6 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.29 (m, 4H), 7.29 – 7.19 (m, 3H), 5.89 (ddd, *J* = 16.9, 10.0, 6.0 Hz, 1H), 5.42 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.0, 1.3 Hz, 1H), 3.32 (q, *J* = 7.2, 6.7 Hz, 1H), 2.88 (tt, *J* = 14.4, 6.4 Hz, 2H), 2.03 – 1.89 (m, 2H), 1.34 (s, 9H).

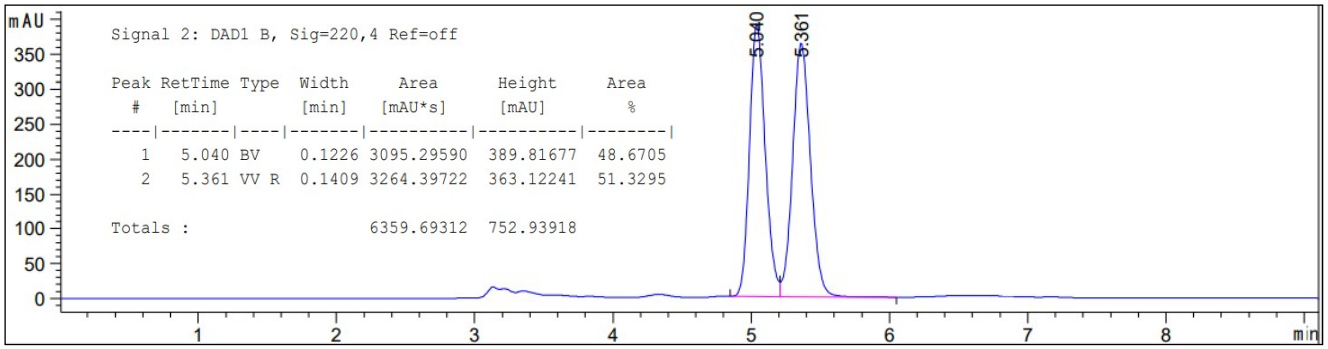
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.98, 141.85, 137.86, 131.35, 128.58, 128.38, 125.87, 125.22, 120.72, 115.33, 89.24, 84.21, 37.10, 35.54, 34.72, 33.29, 31.21.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{23}H_{26}]^+$ 302.2029, found 302.2035.

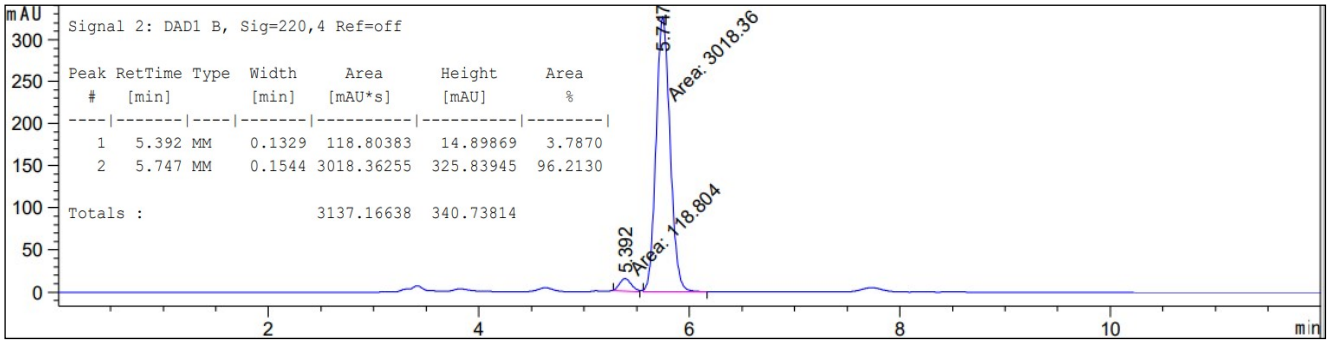
IR (neat): 3022, 2966, 2203, 1703, 1605, 1499, 1456, 1263, 1215, 1090, 1022, 750, 700, 667 cm^{-1}.

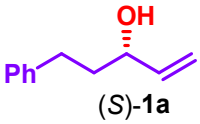
HPLC: Daicel Chiralcel® OJ-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 92% *ee* (t_R (major) = 5.75 min, t_R(minor) = 5.39 min).

Racemic



Enantioenriched



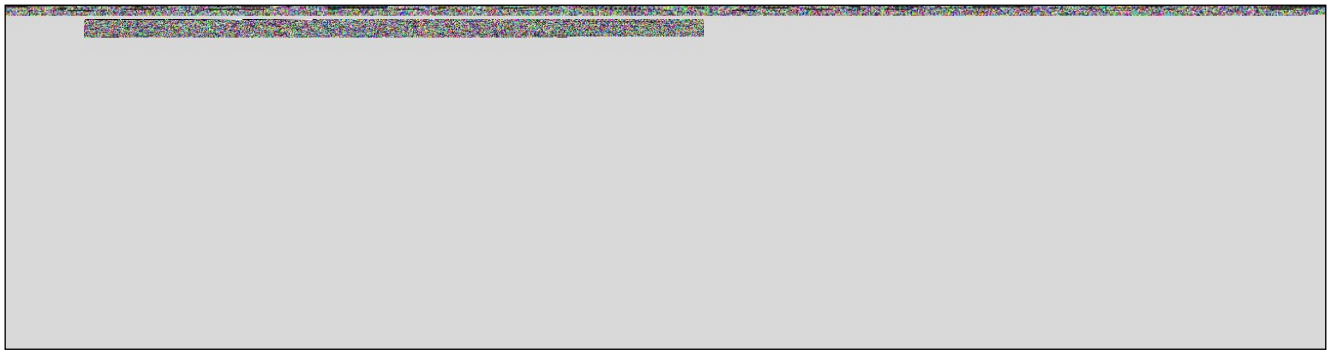


(*S*)-**1a** Obtained from the preparation of (*R*)-**3c**.

Colorless oil. 28.6 mg, 44% yield.

HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 93% *ee* (t_R (major) = 6.50 min, t_R(minor) = 8.12 min).

Racemic



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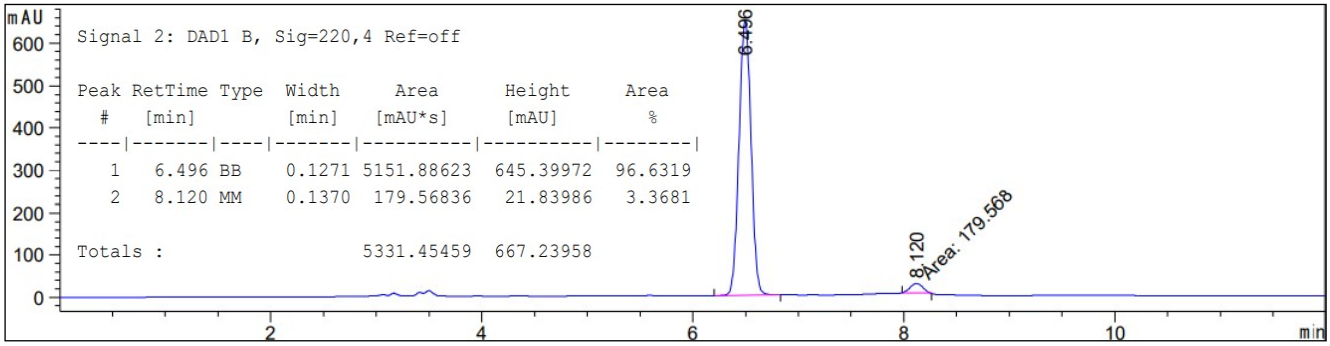
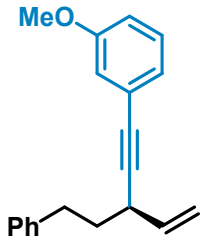




(*R*)-**3d**

Colorless oil. 34.3 mg, 31% yield. **[α]$^{20}_{D}$**: +8.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.07 (m, 4H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 6.78 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.78 (ddd, *J* = 16.3, 10.0, 6.1 Hz, 1H), 5.31 (d, *J* = 17.0 Hz, 1H), 5.08 (d, *J* = 10.0 Hz, 1H), 3.72 (s, 3H), 3.21 (q, *J* = 6.2 Hz, 1H), 2.85 – 2.67 (m, 2H), 1.95 – 1.78 (m, 2H).

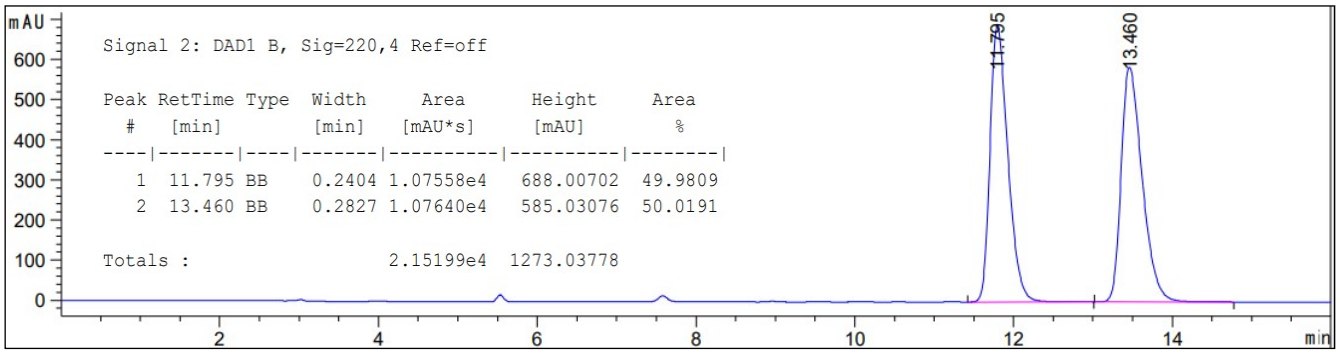
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.31, 141.75, 137.68, 129.29, 128.57, 128.41, 125.92, 124.74, 124.24, 116.54, 115.50, 114.38, 89.92, 84.07, 55.29, 37.00, 35.53, 33.29.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{20}H_{20}O]^+$ 276.1509, found 276.1518.

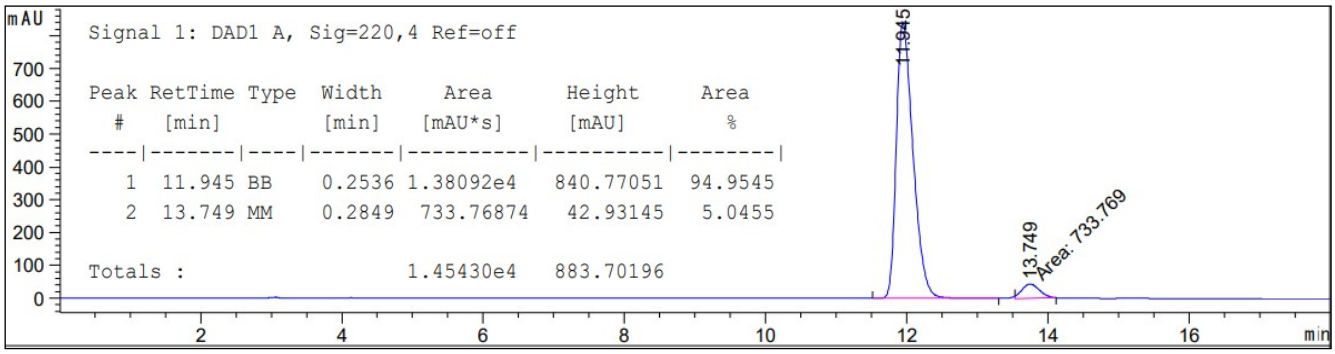
IR (neat): 3078, 3028, 2924, 2856, 2191, 1639, 1599, 1574, 1491, 1456, 1285, 1205, 1165, 1045, 991, 922, 854, 748, 700, 687 cm^{-1}.

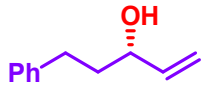
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 90% *ee* (t_R (major) = 11.95 min, t_R(minor) = 13.75 min).

Racemic



Enantioenriched



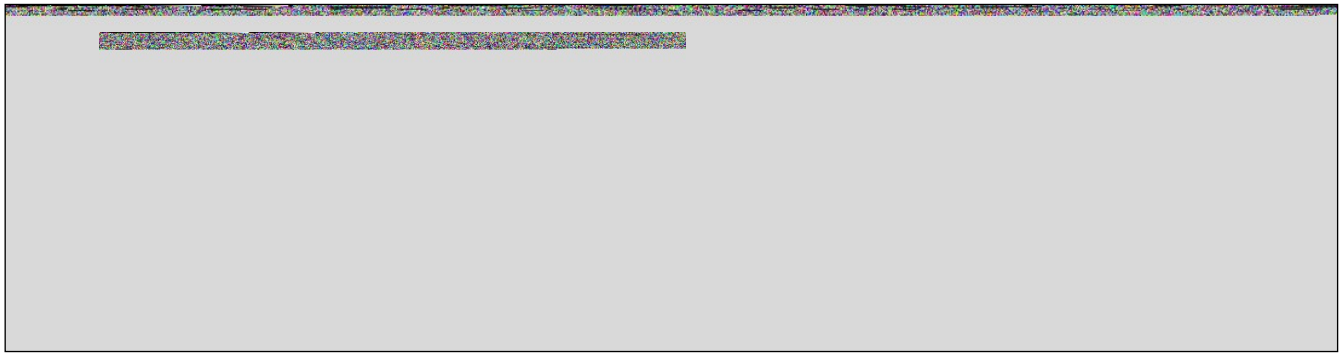


(*S*)-**1a** Obtained from the preparation of (*R*)-**3d**.

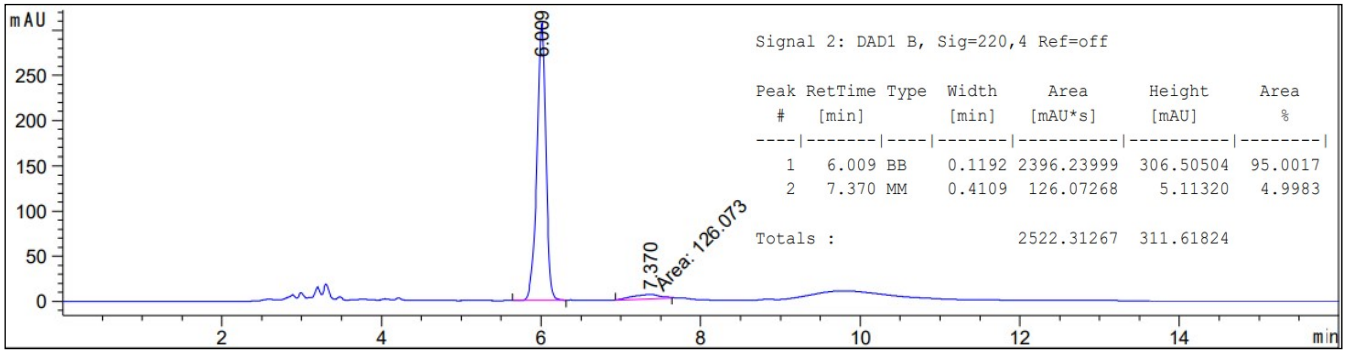
Colorless oil. 31.8 mg, 49% yield.

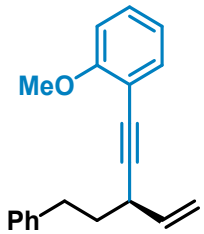
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 90% *ee* (t_R (major) = 6.01 min, t_R(minor) = 7.37 min).

Racemic



Enantioenriched





(*R*)-**3e**

Colorless oil. 30.9 mg, 28% yield. $[\alpha]^{20}_{D}$: +6.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.18 – 7.16 (m, 1H), 7.15 – 7.09 (m, 1H), 6.87 – 6.76 (m, 2H), 5.80 (ddd, *J* = 17.0, 10.0, 5.9 Hz, 1H), 5.39 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.08 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.82 (s, 3H), 3.28 (q, *J* = 6.2 Hz, 1H), 2.88 – 2.74 (m, 2H), 1.93 – 1.81 (m, 2H).

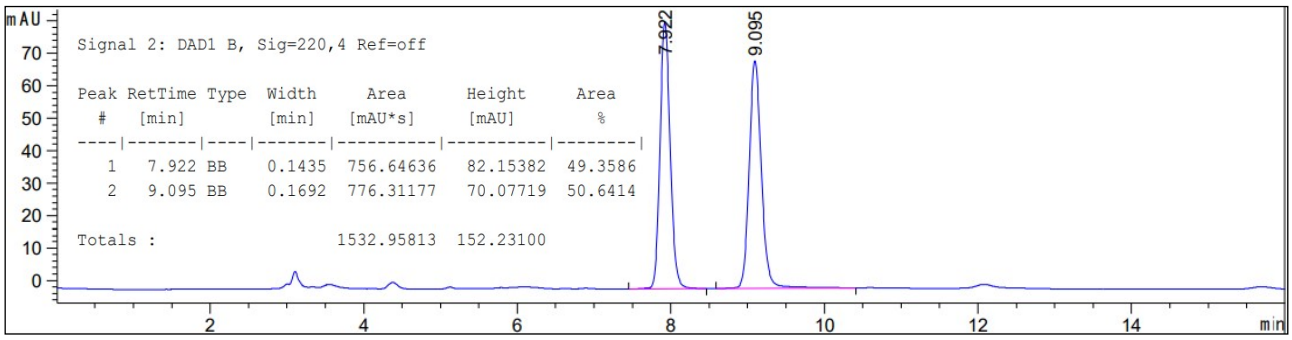
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.06, 142.01, 137.73, 133.49, 129.14, 128.63, 128.36, 125.82, 120.34, 115.44, 112.91, 110.59, 94.17, 80.42, 55.77, 37.16, 35.80, 33.22.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{20}H_{20}O]^+$ 276.1509, found 276.1519.

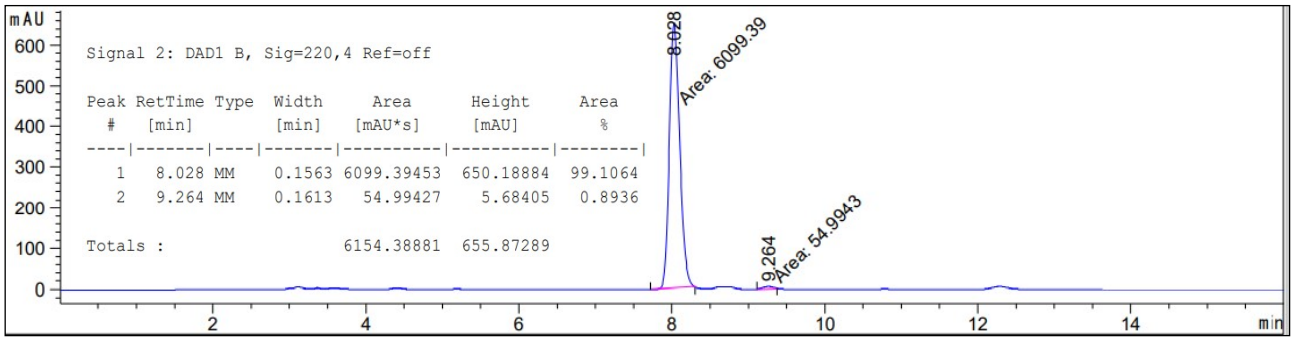
IR (neat): 2991, 2930, 2192, 1668, 1601, 1494, 1456, 1217, 1155, 1049, 1026, 752, 665 cm^{-1}.

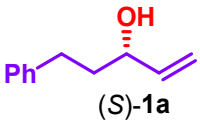
HPLC: Daicel Chiralcel® OJ-H, 5% iPrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 98% *ee* (t_R (major) = 8.03 min, t_R(minor) = 9.26 min).

Racemic



Enantioenriched



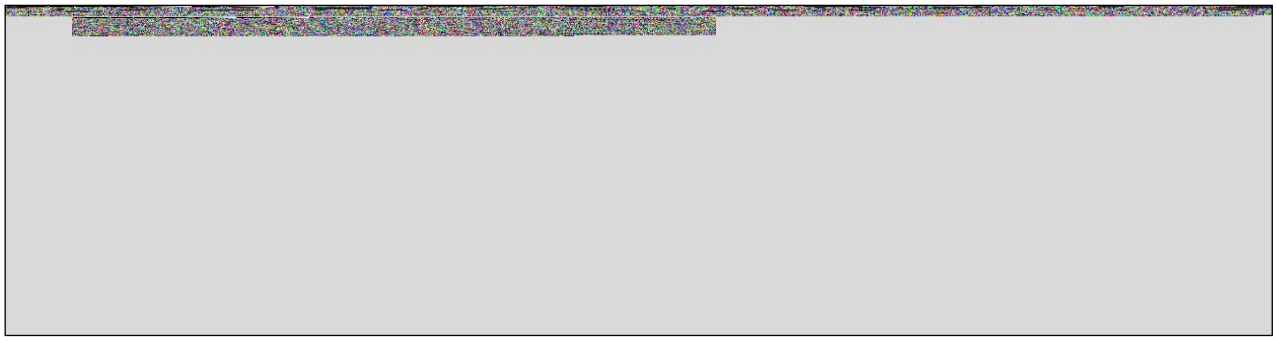


(*S*)-**1a** Obtained from the preparation of (*R*)-**3e**.

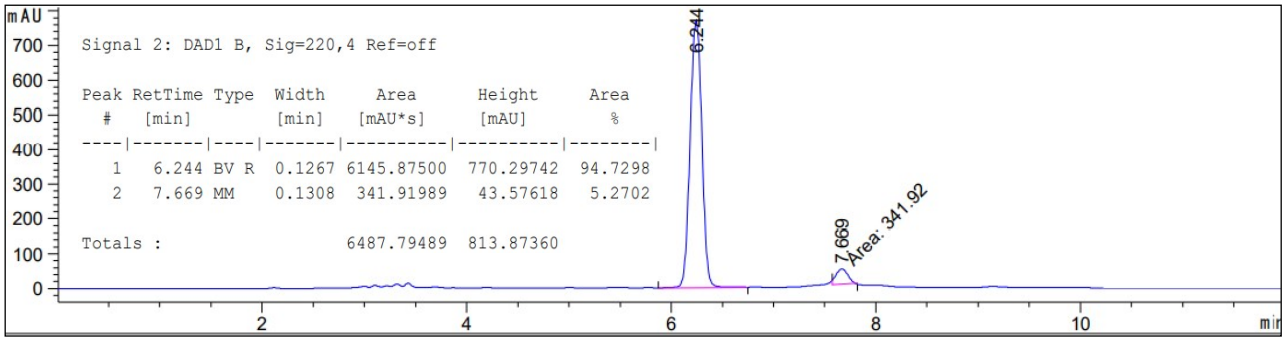
Colorless oil. 30.5 mg, 47% yield.

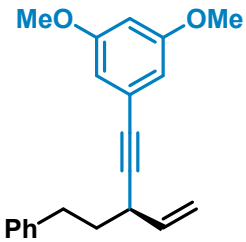
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 89% *ee* (t_R (major) = 6.24 min, t_R(minor) = 7.67 min).

Racemic



Enantioenriched





(*R*)-**3f**

Colorless oil. 55.2 mg, 45% yield. $[\alpha]^{20}_{D}$: +3.5 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.16 (m, 3H), 6.61 (dt, *J* = 4.7, 2.0 Hz, 2H), 6.43 (d, *J* = 2.1 Hz, 1H), 5.92 – 5.80 (m, 1H), 5.42 – 5.35 (m, 1H), 5.18 – 5.13 (m, 1H), 3.78 (s, 6H), 3.33 – 3.24 (m, 1H), 2.90 – 2.76 (m, 2H), 1.94 (q, *J* = 7.9, 7.1 Hz, 2H).

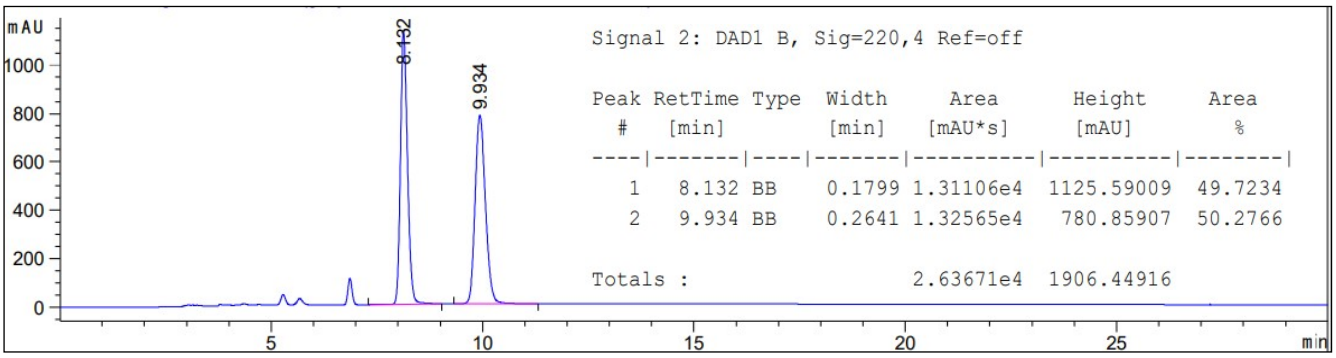
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.51, 141.73, 137.64, 128.58, 128.42, 125.94, 125.03, 115.55, 109.50, 101.30, 89.71, 84.12, 55.42, 36.97, 35.52, 33.30.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{21}H_{23}O_2]^+$ 307.1693, found 307.1693.

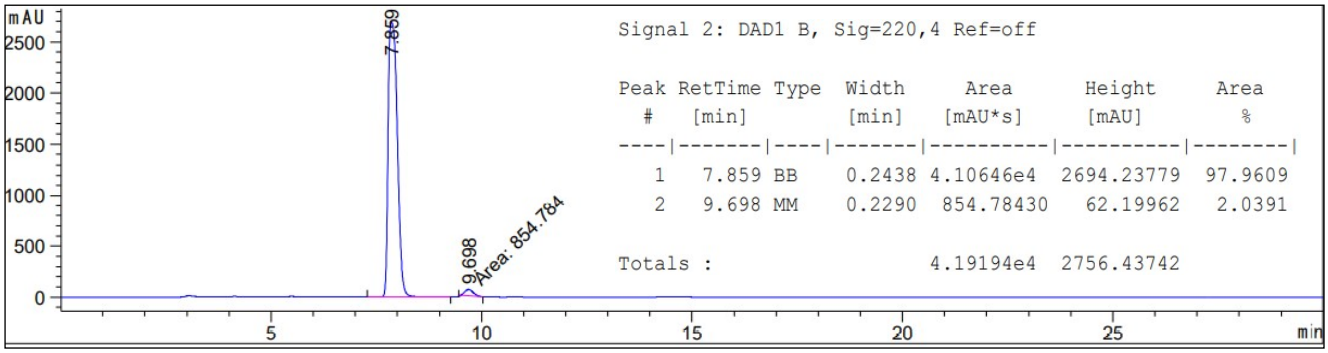
IR (neat): 3003, 2937, 2841, 2208, 1591, 1456, 1420, 1205, 1155, 1065, 926, 839, 771, 700 cm^{-1}.

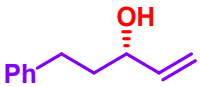
HPLC: Daicel Chiralcel® OJ-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 96% *ee* (t_R (major) = 7.86 min, t_R(minor) = 9.70 min).

Racemic



Enantioenriched



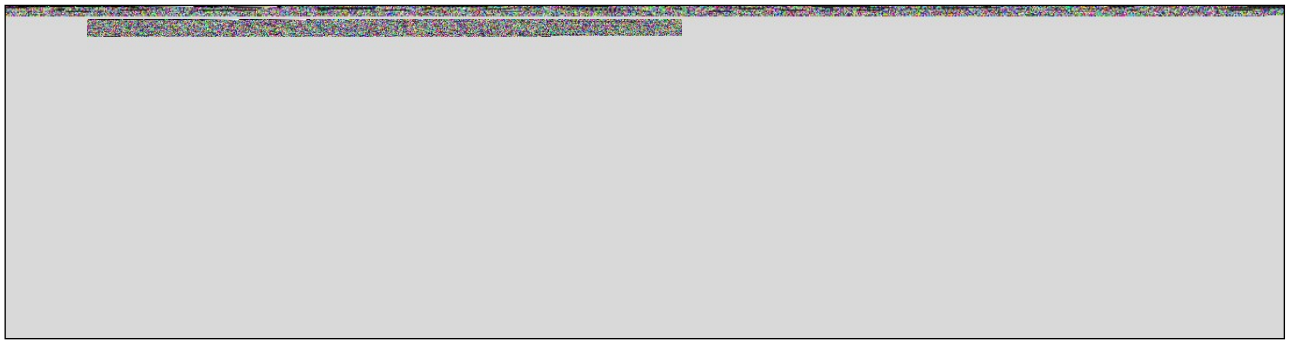


(*S*)-**1a** Obtained from the preparation of (*R*)-**3f**.

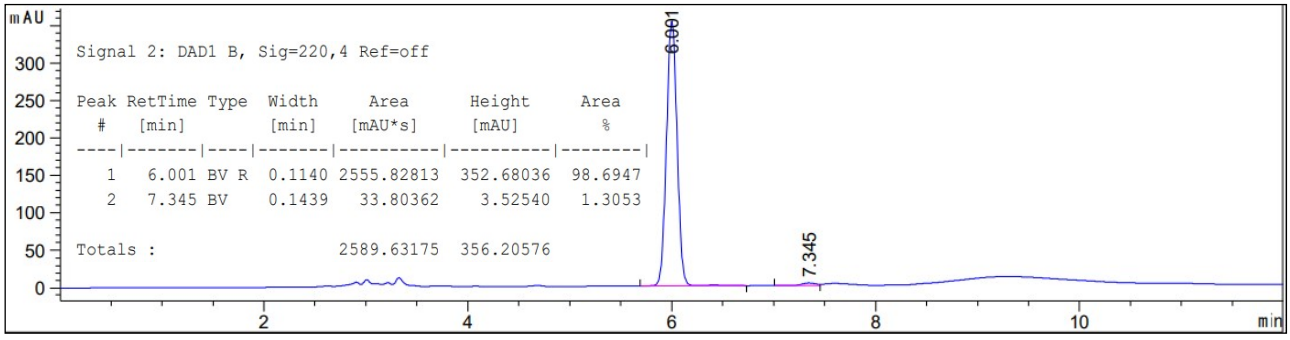
Colorless oil. 31.1 mg, 48% yield.

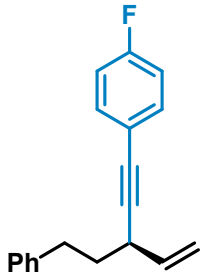
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 97% *ee* (t_R (major) = 6.00 min, t_R(minor) = 7.35 min).

Racemic



Enantioenriched





(*R*)-**3g**

Colorless oil. 27.5 mg, 26% yield. **[α]$^{20}_{D}$**: +3.4 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.12 (m, 3H), 6.94 (t, *J* = 8.7 Hz, 2H), 5.80 (ddd, *J* = 16.5, 10.0, 6.1 Hz, 1H), 5.36 – 5.27 (m, 1H), 5.10 (dd, *J* = 10.0, 1.5 Hz, 1H), 3.22 (q, *J* = 6.5 Hz, 1H), 2.84 – 2.70 (m, *J* = 7.5 Hz, 2H), 1.93 – 1.84 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.21 (d, *J* = 248.5 Hz), 141.69, 137.62, 133.44 (d, *J* = 8.1 Hz), 128.55, 128.41, 125.94, 119.75 (d, *J* = 3.4 Hz), 115.51, 115.45 (d, *J* = 21.9 Hz), 89.7, 83.05, 36.95, 35.48, 33.27.

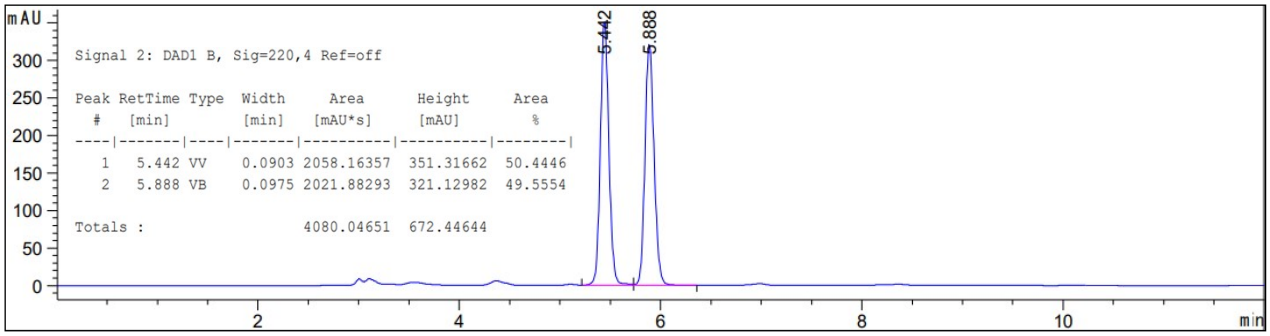
^{19}F NMR (376 MHz, $CDCl_3$): δ = -113.93.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{19}H_{17}F]^+$ 264.1309, found 264.1313.

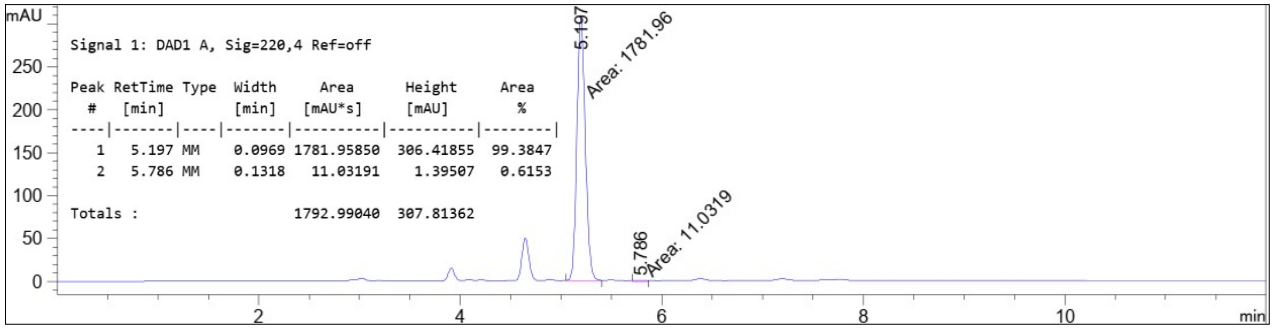
IR (neat): 3022, 2970, 2926, 2178, 1728, 1597, 1508, 1456, 1412, 1325, 1213, 1067, 750, 667 cm^{-1}

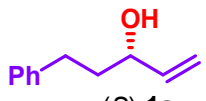
HPLC: Daicel Chiralcel® OJ-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 99% *ee* (t_R (major) = 5.20 min, t_R(minor) = 5.79 min).

Racemic



Enantioenriched





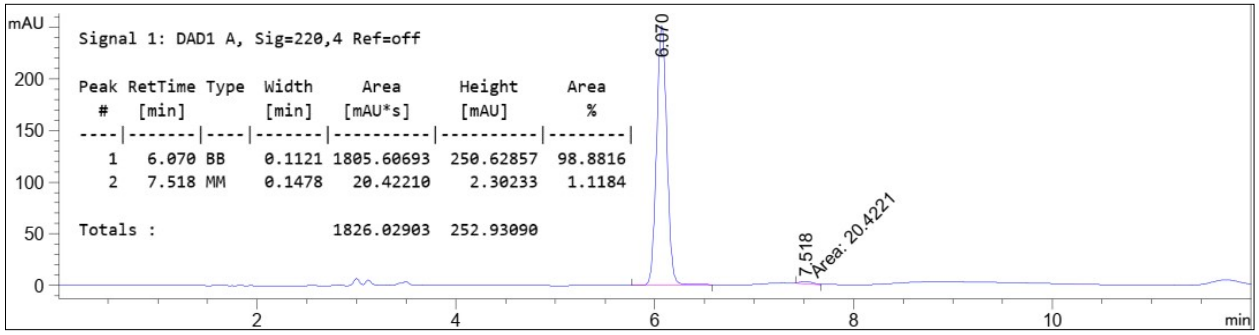
(*S*)-**1a** Obtained from the preparation of (*R*)-**3g**.

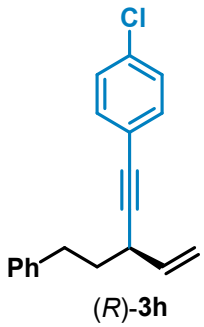
Colorless oil. 30.5 mg, 47% yield.

HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 6.07 min, t_R(minor) = 7.52 min).

Racemic

Enantioenriched





(*R*)-**3h**

Colorless oil. 25.8 mg, 23% yield. **[α]$^{20}_{D}$**: +4.5 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 7.34 – 7.27 (m, 4H), 7.22 (dd, *J* = 14.4, 6.6 Hz, 3H), 5.93 – 5.80 (m, 1H), 5.43 – 5.33 (m, 1H), 5.21 – 5.13 (m, 1H), 3.29 (q, *J* = 7.3, 6.7 Hz, 1H), 2.90 – 2.76 (m, 2H), 1.95 (q, *J* = 7.6 Hz, 2H).

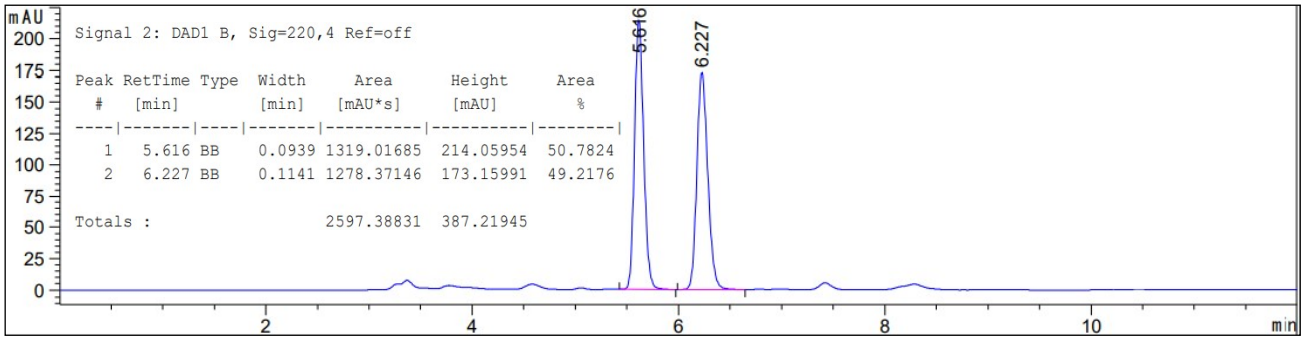
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.63, 137.48, 133.74, 132.87, 128.54, 128.42, 125.96, 122.19, 115.58, 91.13, 83.03, 36.89, 35.52, 33.26.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{19}H_{17}Cl]^+$ 280.1013, found 280.1004.

IR (neat): 3024, 2924, 2858, 2208, 1639, 1603, 1489, 1454, 1217, 1092, 1015, 920, 827, 752, 698 cm^{-1}.

HPLC: Daicel Chiralcel® OJ-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 98% *ee* (t_R (major) = 5.46 min, t_R(minor) = 6.18 min).

Racemic



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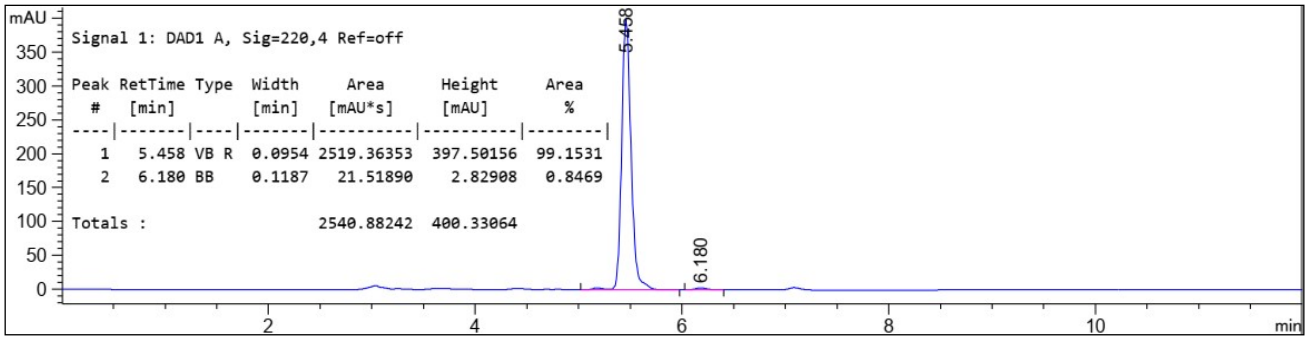
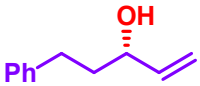


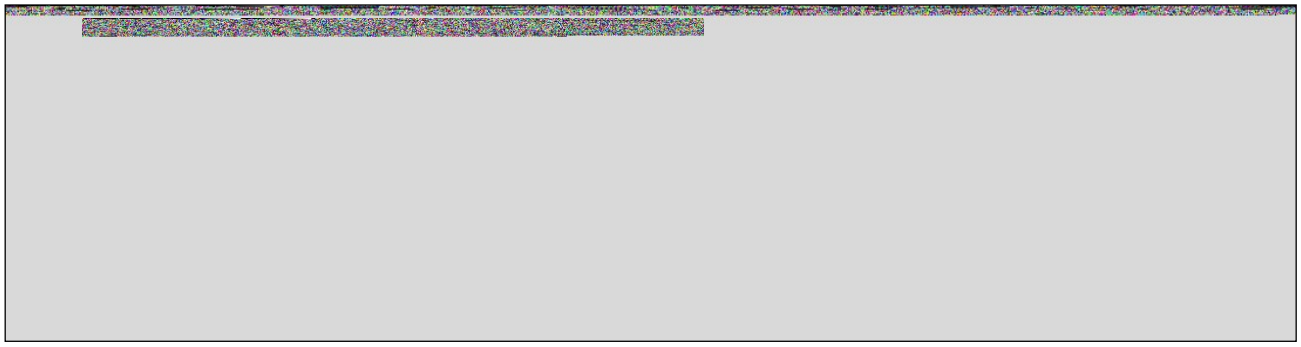


(*S*)-**1a** Obtained from the preparation of (*R*)-**3h**.

Colorless oil. 31.1 mg, 48% yield.

HPLC: Daicel Chiralcel® OD-H, 12 % ^{i}PrOH, 1.0 mL/min, 88% hexane, 35 °C, 220 nm; 98% *ee* (t_R (major) = 6.09 min, t_R(minor) = 7.50 min).

Racemic



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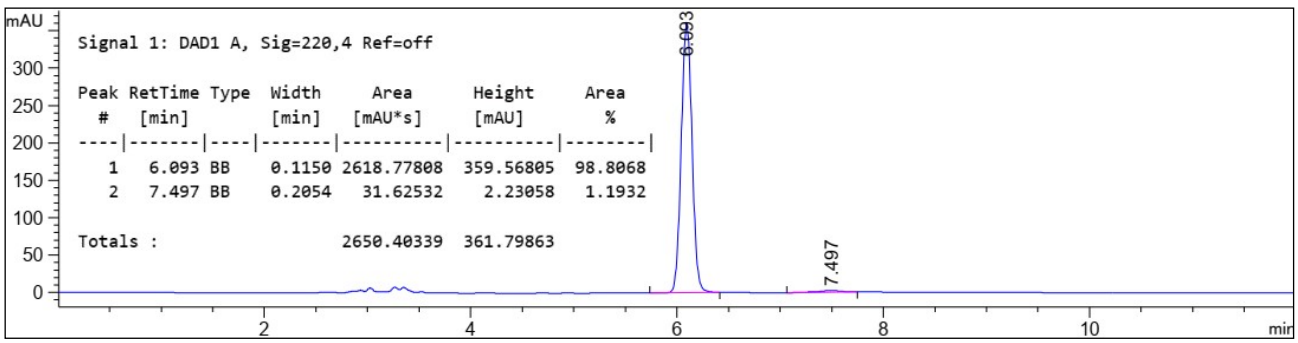
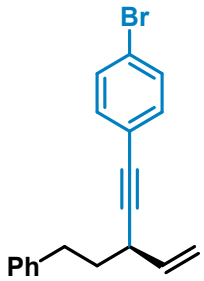




(*R*)-**3i**

Colorless oil. 33.7 mg, 26% yield. **[α]$^{20}_{D}$**: +3.3 (*c* = 0.5, $CHCl_3$).

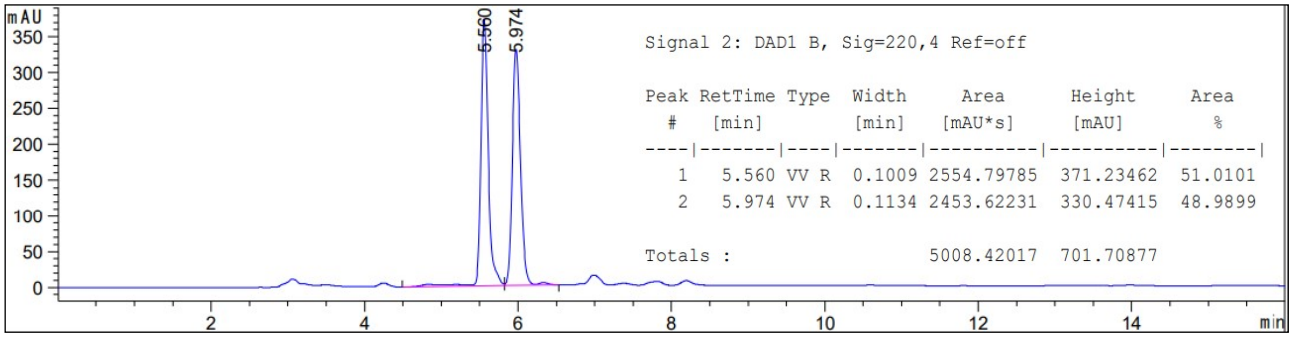
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.34 – 7.25 (m, 5H), 7.27 – 7.15 (m, 4H), 5.85 (ddd, *J* = 17.0, 10.0, 6.2 Hz, 1H), 5.36 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.16 (dt, *J* = 10.0, 1.4 Hz, 1H), 3.28 (q, *J* = 7.5, 6.9 Hz, 1H), 2.90 – 2.73 (m, 2H), 2.01 – 1.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.61, 137.43, 133.10, 131.46, 128.53, 128.41, 125.95, 122.66, 121.91, 115.59, 91.34, 83.08, 36.85, 35.54, 33.25.

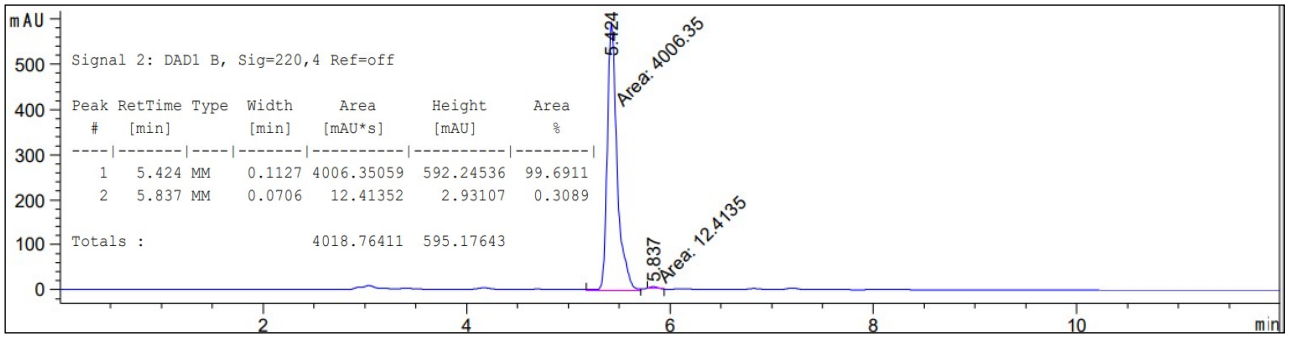
HRMS (APCI): $[M]^+$ Calcd. for $[C_{19}H_{17}Br]^+$ 324.0508, found 324.0512.

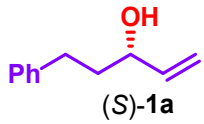
HPLC: Daicel Chiralcel® OJ-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 99% *ee* (t_R (major) = 5.42 min, t_R(minor) = 5.84 min).

Racemic



Enantioenriched



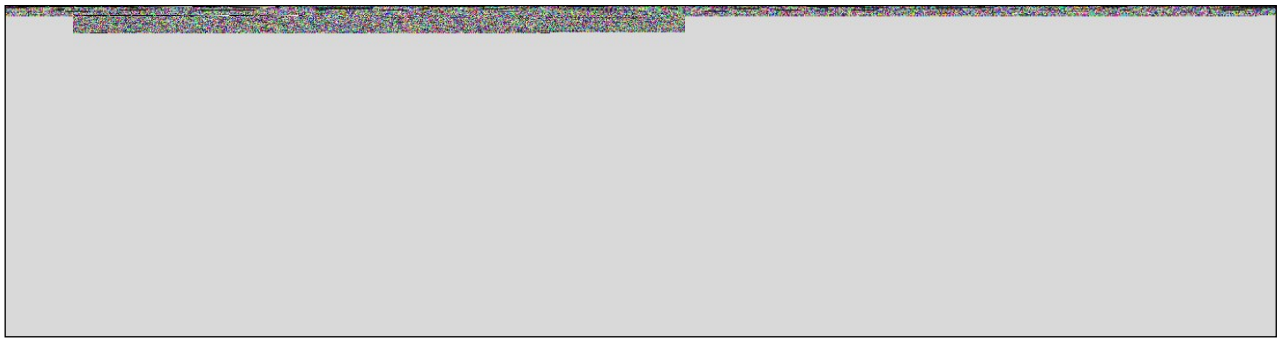


(*S*)-**1a** Obtained from the preparation of (*R*)-**3i**.

Colorless oil. 28.6 mg, 44% yield.

HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 96% *ee* (t_R (major) = 6.13 min, t_R(minor) = 7.53 min).

Racemic



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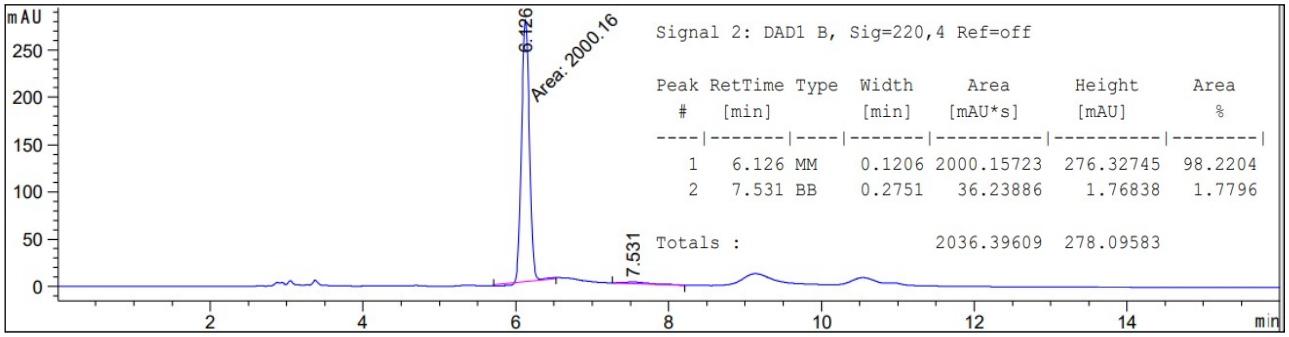
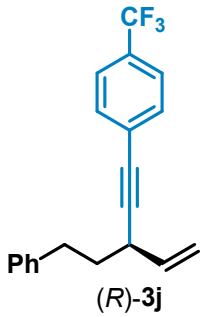




(*R*)-**3j**

Colorless oil. 33.9 mg, 27% yield. **[α]$^{20}_{D}$**: +0.6 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.16 – 7.07 (m, 3H), 5.76 (ddd, *J* = 17.0, 10.0, 6.1 Hz, 1H), 5.28 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.08 (dt, *J* = 10.1, 1.4 Hz, 1H), 3.22 (q, *J* = 6.4 Hz, 1H), 2.81 – 2.67 (m, 2H), 1.92 – 1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.54, 137.25, 131.89, 129.59 (q, *J* = 32.6 Hz), 128.55, 128.47, 127.56 (d, *J* = 1.6 Hz), 126.03, 125.18 (q, *J* = 3.9 Hz), 124.02 (q, *J* = 272.1 Hz), 115.77, 92.89, 82.96, 36.83, 35.54, 33.28.

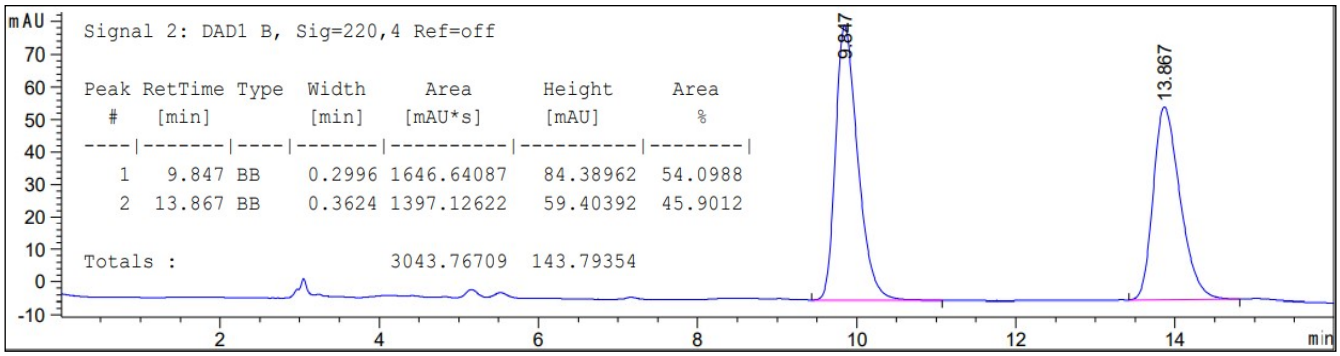
^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.75.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{20}H_{17}F_3]^+$ 314.1277, found 314.1283.

IR(neat): 3020, 2208, 1547, 1479, 1445, 1327, 1217, 1032, 932, 852, 773, 744, 669 cm^{-1}.

HPLC: Daicel Chiralcel® OJ-H, 0.5% ^{i}PrOH, 99.5% hexane, 1.0 mL/min, 40 °C, 220 nm; 92% *ee* (t_R (major) = 9.78 min, t_R(minor) = 13.87 min).

Racemic



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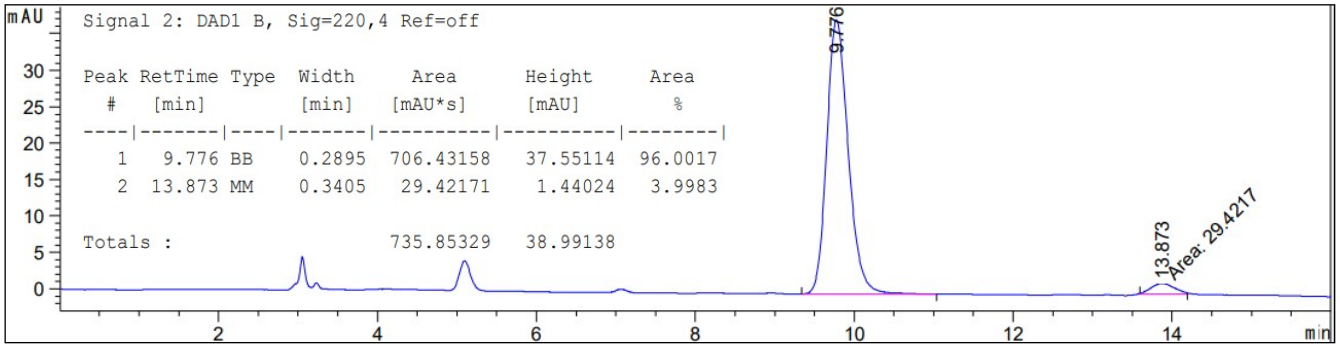
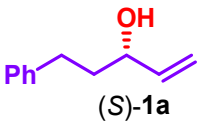


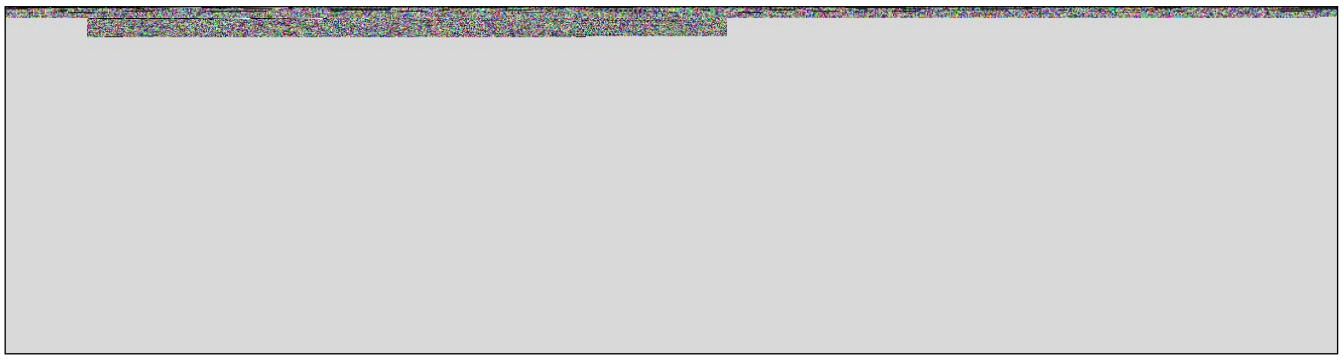


(*S*)-**1a** Obtained from the preparation of (*R*)-**3j**.

Colorless oil. 29.9 mg, 46% yield.

HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 90% *ee* (t_R (major) = 6.05 min, t_R(minor) = 7.46 min).

Racemic



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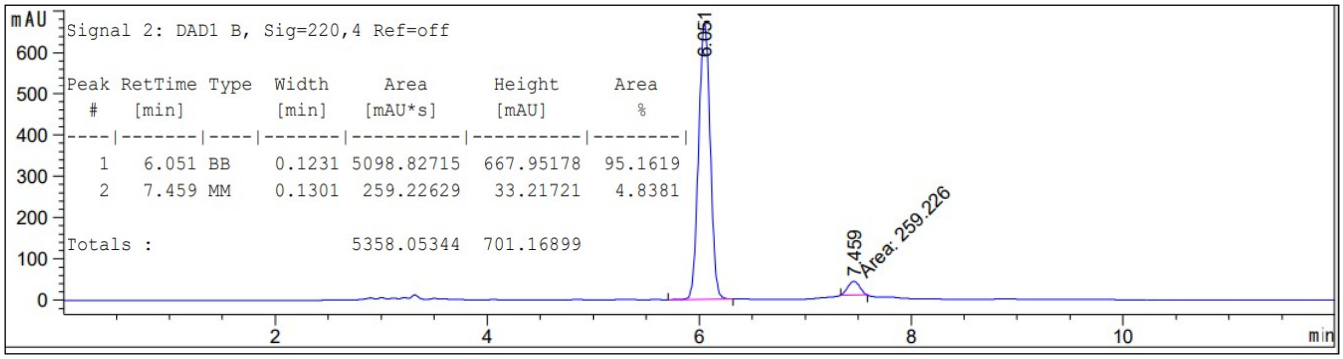
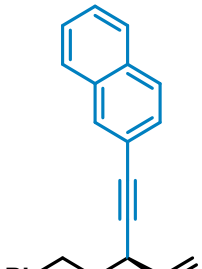




(*R*)-**3k**

Colorless oil. 35.5 mg, 30% yield. **[α]$^{20}_{D}$**: +4.6 (*c* = 0.5, $CHCl_3$).

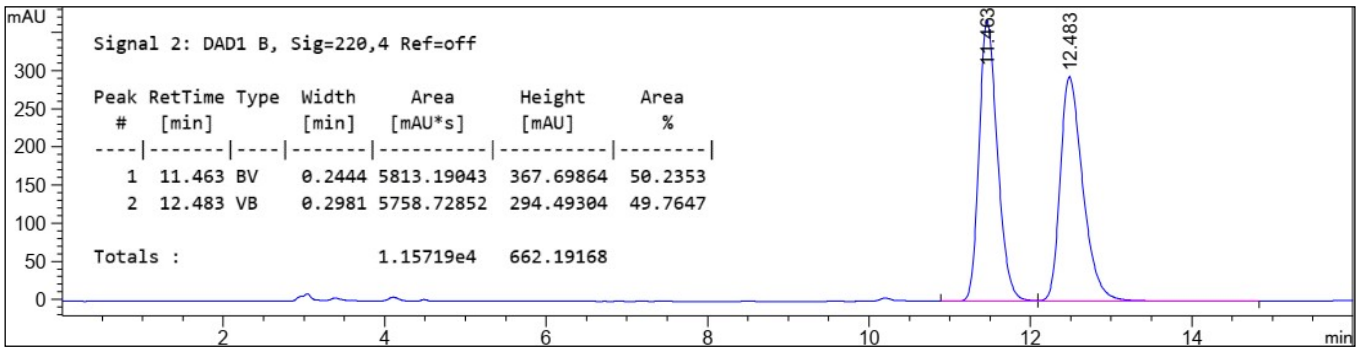
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.72 (dd, *J* = 14.0, 8.7 Hz, 3H), 7.48 – 7.36 (m, 3H), 7.27 – 7.16 (m, 4H), 7.16 – 7.11 (m, 1H), 5.83 (ddd, *J* = 17.0, 10.0, 6.1 Hz, 1H), 5.36 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.11 (dt, *J* = 10.0, 1.4 Hz, 1H), 3.28 (q, *J* = 6.6 Hz, 1H), 2.89 – 2.74 (m, 2H), 1.91 (q, *J* = 7.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.76, 137.71, 133.03, 132.59, 131.21, 128.72, 128.59, 128.42, 127.85, 127.72, 127.63, 126.43, 126.38, 125.93, 121.01, 115.55, 90.41, 84.48, 37.03, 35.64, 33.33.

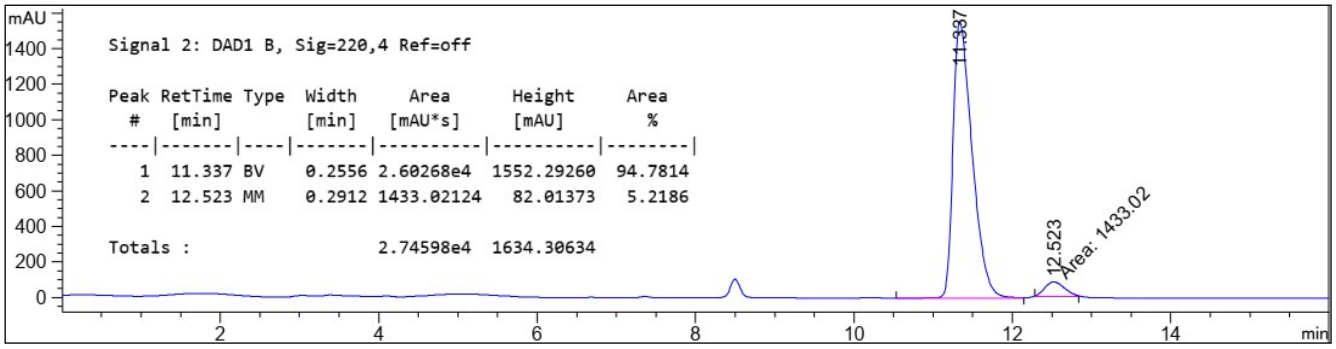
HRMS (APCI): $[M]^+$ Calcd. for $[C_{23}H_{20}]^+$ 296.1560, found 296.1568.

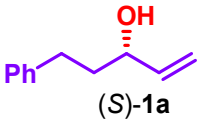
HPLC: Daicel Chiralcel® OJ-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 90% *ee* (t_R (major) = 11.34 min, t_R(minor) = 12.52 min).

Racemic



Enantioenriched



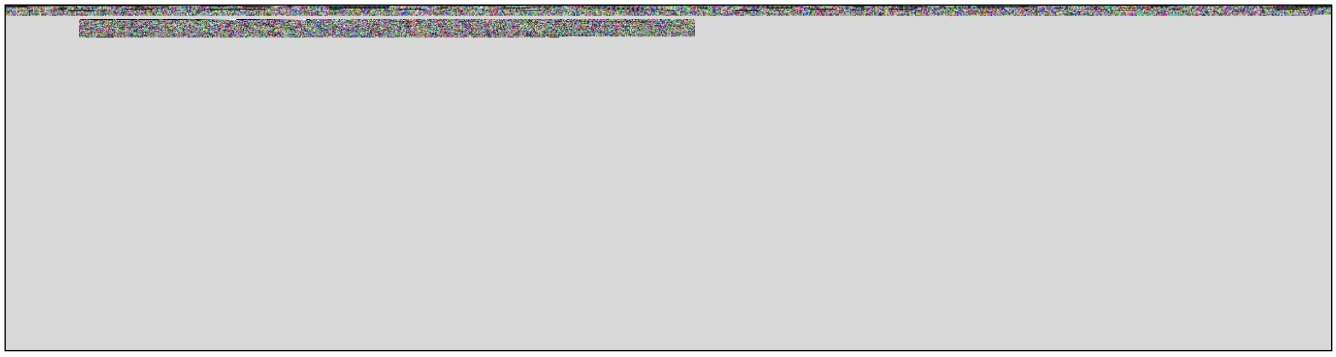


(*S*)-**1a** Obtained from the preparation of (*R*)-**3k**.

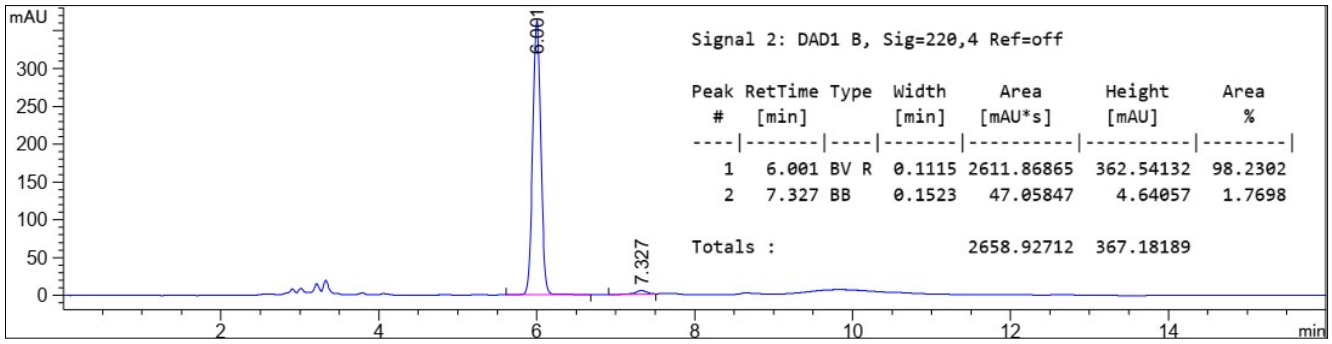
Colorless oil. 31.1 mg, 48% yield.

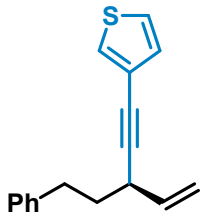
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 96% *ee* (t_R (major) = 6.00 min, t_R(minor) = 7.33 min).

Racemic



Enantioenriched





(*R*)-**3l**

Colorless oil. 25.2 mg, 25% yield. $[\alpha]^{20}_{D}$: -1.4 (*c* = 0.5, $CHCl_3$).

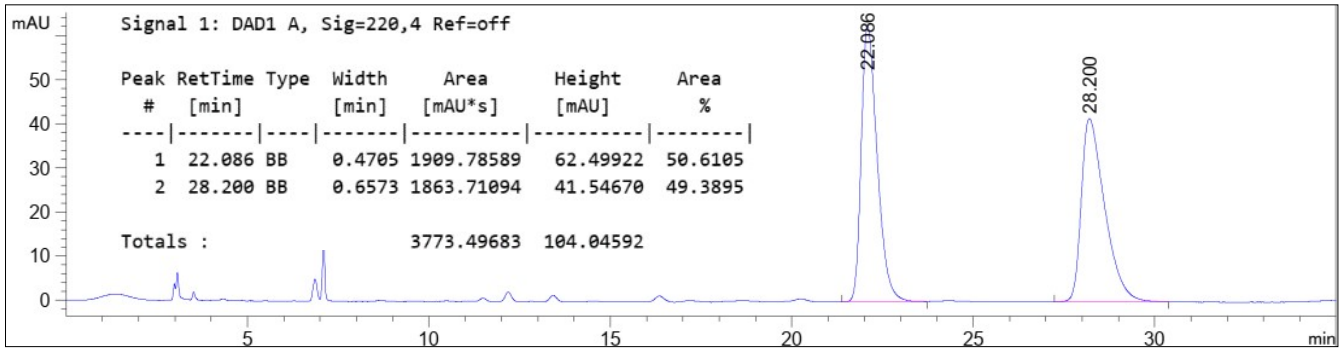
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 3.0, 1.0 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.20 – 7.11 (m, 4H), 7.05 (dd, *J* = 5.0, 1.1 Hz, 1H), 5.78 (ddd, *J* = 17.0, 10.0, 6.1 Hz, 1H), 5.30 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.08 (dt, *J* = 10.0, 1.4 Hz, 1H), 3.21 (q, *J* = 6.4 Hz, 1H), 2.83 – 2.69 (m, 2H), 1.91 – 1.82 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.73, 137.66, 130.06, 128.56, 128.39, 127.93, 125.91, 125.08, 122.64, 115.49, 89.54, 79.07, 36.94, 35.56, 33.27.

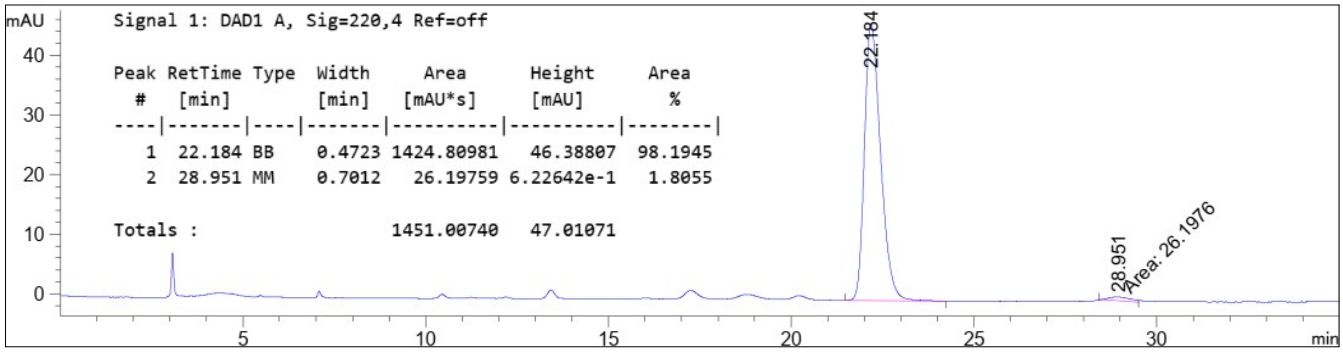
HRMS (APCI): $[M]^+$ Calcd. for $[C_{17}H_{16}S]^+$ 252.0967, found 252.0970.

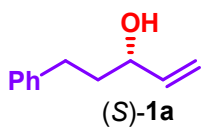
HPLC: Daicel Chiralcel® OJ-H, 0.5% ^{i}PrOH, 99.5% hexane, 1.0 mL/min, 40 °C, 220 nm; 96% *ee* (t_R (major) = 22.18 min, t_R(minor) = 28.95 min)

Racemic



Enantioenriched



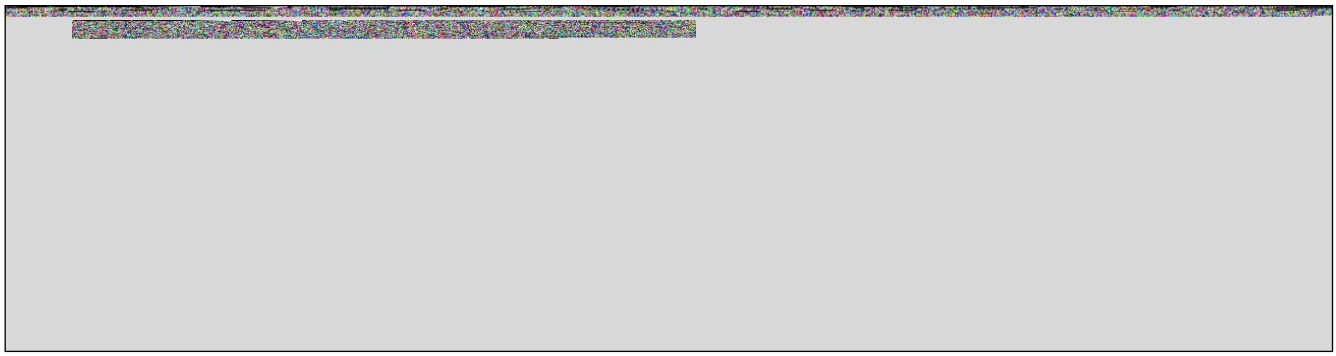


(*S*)-**1a** Obtained from the preparation of (*R*)-**3l**.

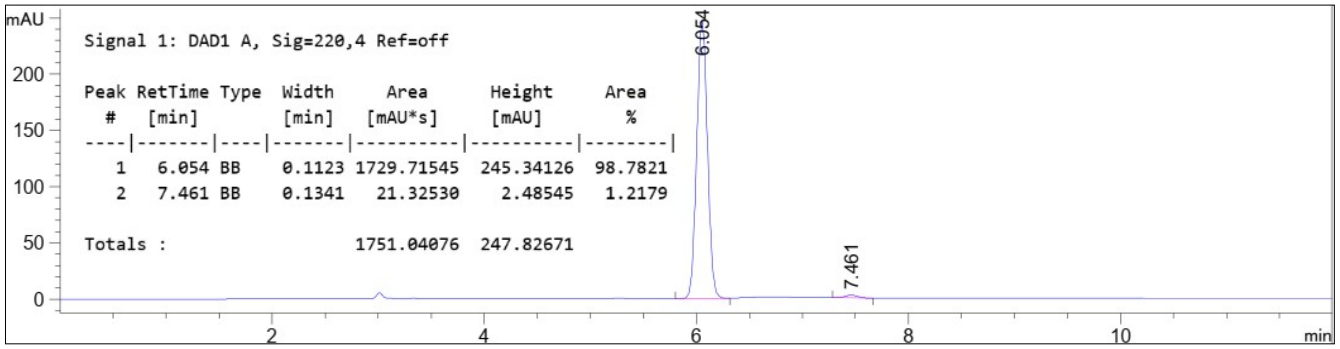
Colorless oil. 31.8 mg, 49% yield.

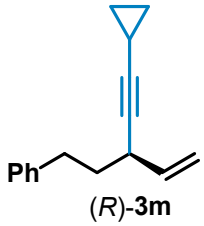
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 6.05 min, t_R(minor) = 7.46 min).

Racemic



Enantioenriched





(*R*)-**3m**

(*R*)-(3-(cyclopropylethynyl)pent-4-en-1-yl)benzene (3m).

Colorless oil. 26.9 mg, 32% yield. **[α]$^{20}_{D}$**: -4.3 (*c* = 1.0, $CHCl_3$).

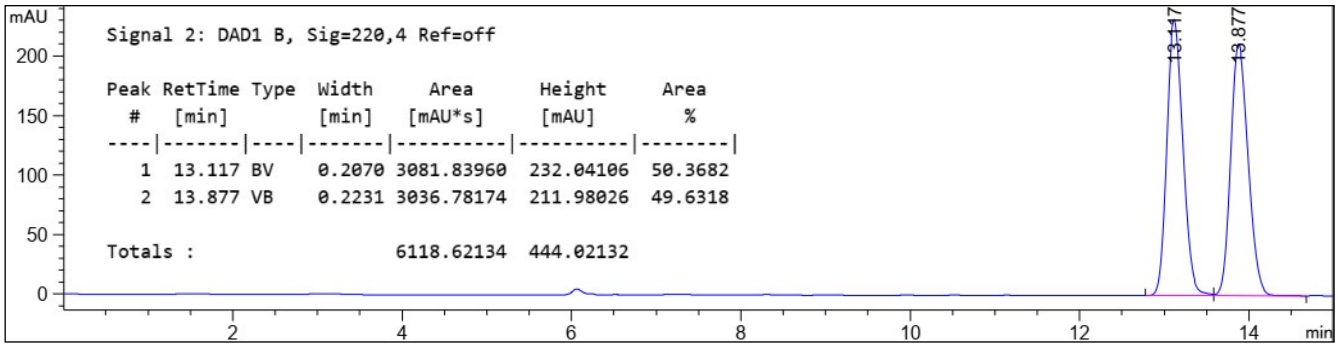
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.18 – 7.09 (m, 3H), 5.72 (ddd, *J* = 16.5, 10.0, 6.1 Hz, 1H), 5.22 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.02 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.01 – 2.91 (m, 1H), 2.77 – 2.61 (m, 2H), 1.82 – 1.68 (m, 2H), 1.27 – 1.20 (m, 1H), 0.75 – 0.67 (m, 2H), 0.66 – 0.58 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.32, 138.86, 128.88, 128.68, 126.15, 115.22, 87.50, 75.89, 37.57, 35.38, 33.59, 8.66, 8.62.

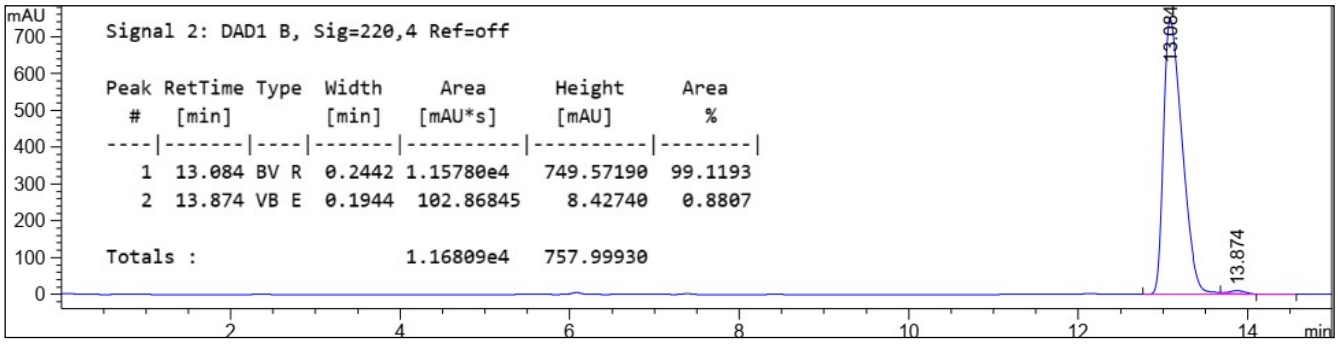
HRMS (APCI): $[M]^+$ Calcd. for $[C_{16}H_{18}]^+$ 210.1403, found 210.1403.

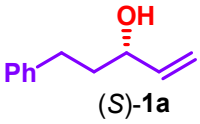
HPLC: Daicel Chiralcel® OJ-H, 100% hexane, 0.5 mL/min, 40 °C, 220 nm; 98% *ee* (t_R (major) = 13.08 min, t_R(minor) = 13.87 min).

Racemic



Enantioenriched



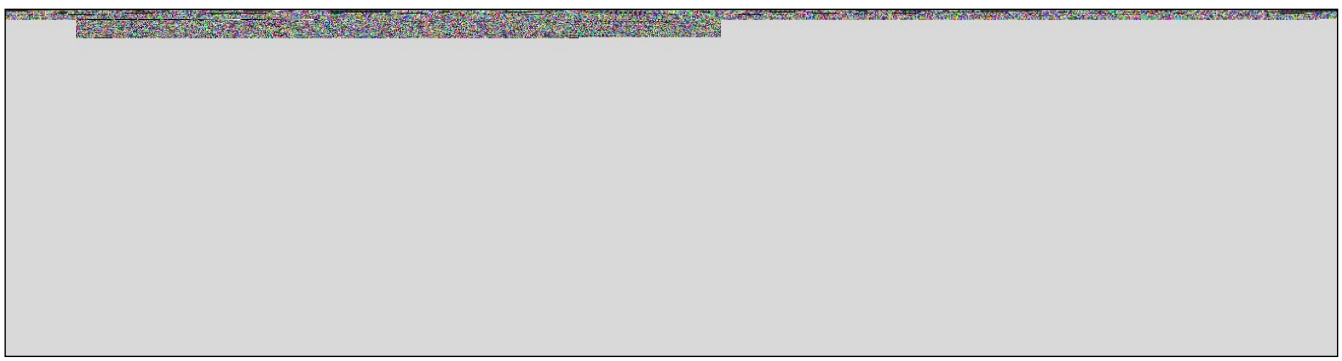


(*S*)-**1a** Obtained from the preparation of (*R*)-**3m**.

Colorless oil. 27.3 mg, 42% yield.

HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 96% *ee* (t_R (major) = 5.94 min, t_R(minor) = 7.24 min).

Racemic



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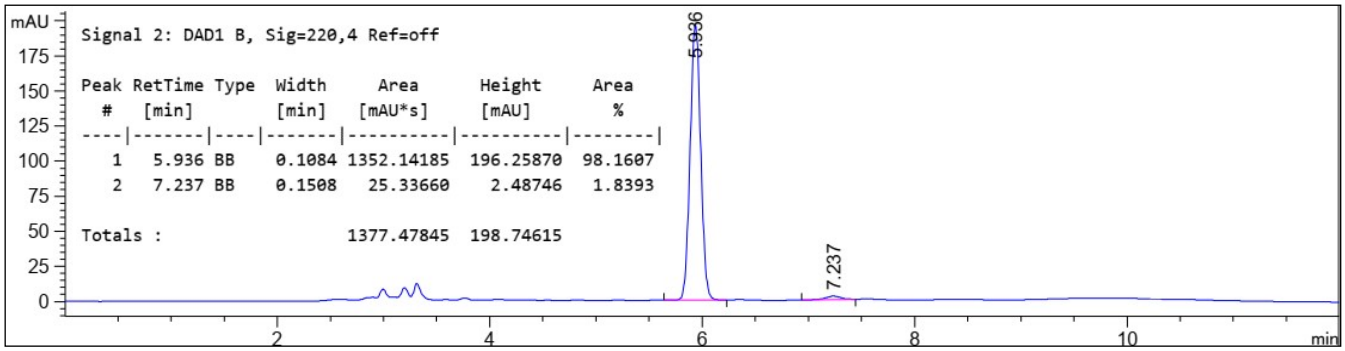
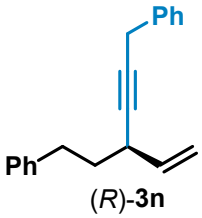




(*R*)-**3n**

Colorless oil. 18.8 mg, 18% yield. **[α]$^{20}_{D}$**: -7.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.25 (m, 3H), 7.22 (d, *J* = 7.5 Hz, 3H), 5.84 (ddd, *J* = 16.4, 10.1, 6.1 Hz, 1H), 5.35 (dq, *J* = 16.9, 1.5 Hz, 1H), 5.13 (dq, *J* = 10.0, 1.4 Hz, 1H), 3.70 (s, 2H), 3.20 – 3.10 (m, 1H), 2.88 – 2.73 (m, 2H), 1.95 – 1.82 (m, 2H).

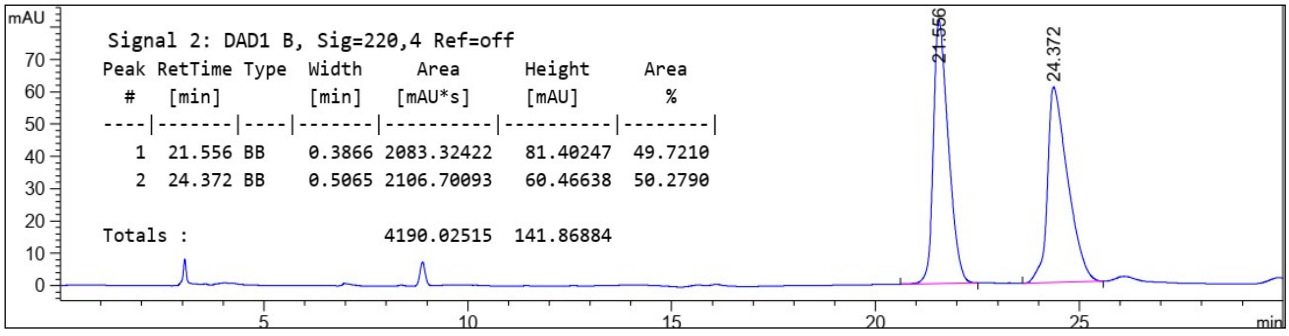
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.92, 138.31, 137.41, 128.56, 128.53, 128.47, 128.37, 127.87, 126.47, 125.85, 115.13, 82.68, 81.38, 37.25, 35.17, 33.30, 25.25.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{20}H_{20}]^+$ 260.1560, found 260.1562.

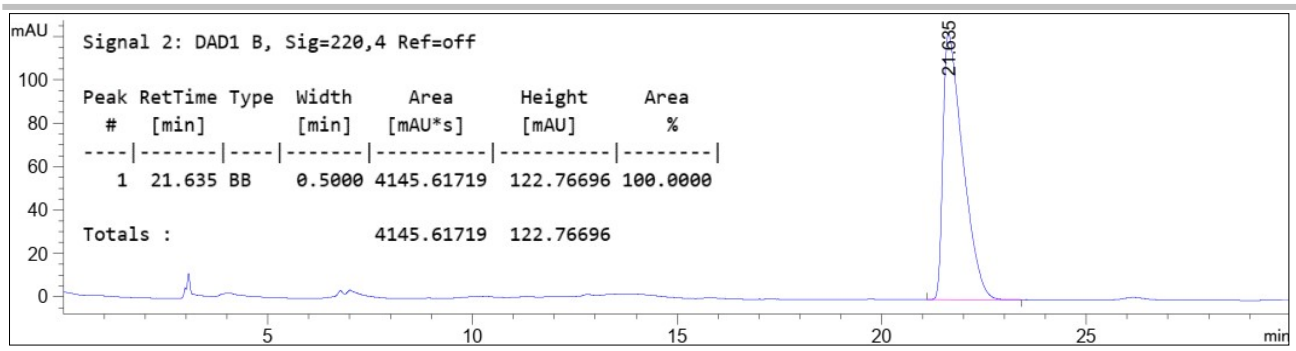
IR (neat): 3030, 2934, 2858, 2210, 1707, 1603, 1497, 1452, 1317, 1219, 1074, 1030, 933, 854, 771, 687, 673 cm^{-1}

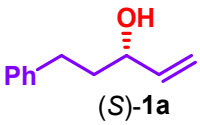
HPLC: Daicel Chiralcel® OJ-H, 0.5% ^{i}PrOH, 99.5% hexane, 1.0 mL/min, 40 °C, 220 nm; 99% *ee* (t_R (major) = 21.64 min).

Racemic



Enantioenriched





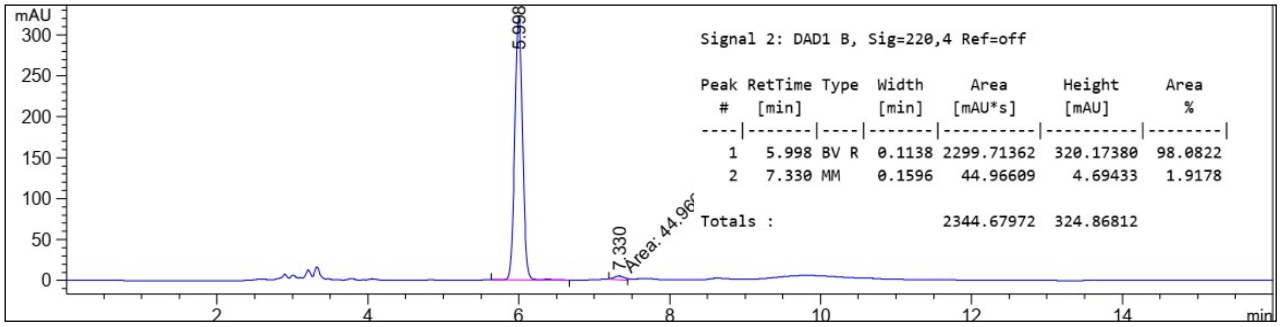
(*S*)-**1a** Obtained from the preparation of (*R*)-**3n**.

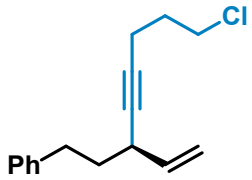
Colorless oil. 31.8 mg, 49% yield.

HPLC: Daicel Chiralcel® OD-H, 12.0% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 96% *ee* (t_R (major) = 6.00 min, t_R(minor) = 7.33 min).

Racemic

Enantioenriched





(*R*)-**3o**

Colorless oil. 25.7 mg, 26% yield. **[α]$^{20}_{D}$**: -8.0 (*c* = 0.5, $CHCl_3$).

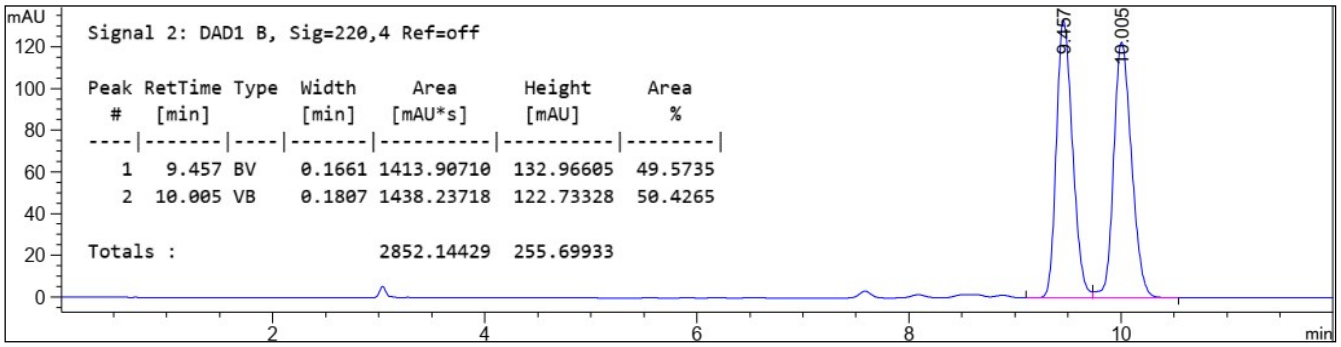
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 3H), 5.78 (ddd, *J* = 17.0, 10.0, 6.0 Hz, 1H), 5.29 (dt, *J* = 16.9, 1.6 Hz, 1H), 5.10 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.69 (t, *J* = 6.4 Hz, 2H), 3.10 – 3.01 (m, 1H), 2.83 – 2.68 (m, 2H), 2.45 (td, *J* = 6.8, 2.2 Hz, 2H), 1.99 (p, *J* = 6.6 Hz, 2H), 1.90 – 1.75 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.84, 138.33, 128.51, 128.37, 125.86, 114.98, 81.89, 81.45, 43.79, 37.18, 35.02, 33.26, 31.76, 16.31.

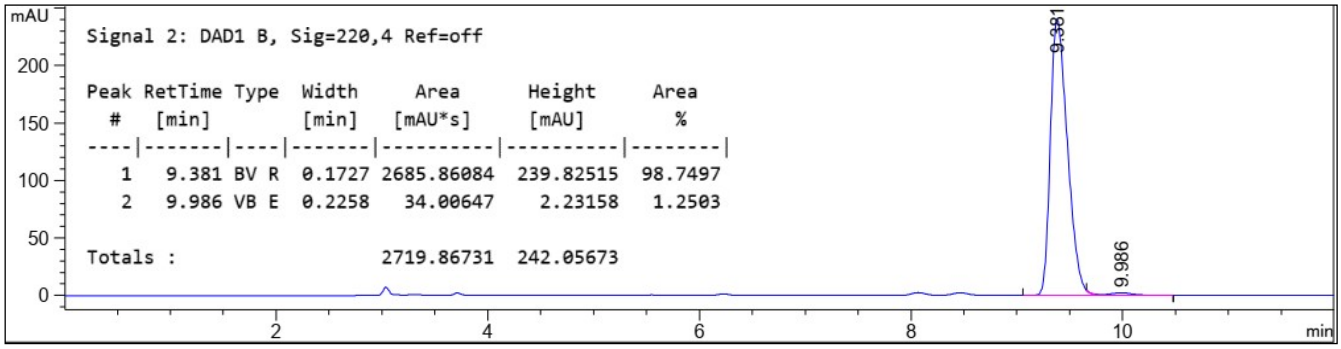
HRMS (APCI): $[M]^+$ Calcd. for $[C_{16}H_{19}Cl]^+$ 246.1170, found 246.1169.

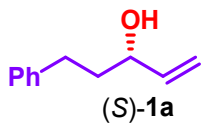
HPLC: Daicel Chiralcel® OJ-H, 100% hexane, 1.0 mL/min, 40 °C, 220 nm; 97% *ee* (t_R (major) = 9.38 min, t_R(minor) = 9.99 min).

Racemic



Enantioenriched



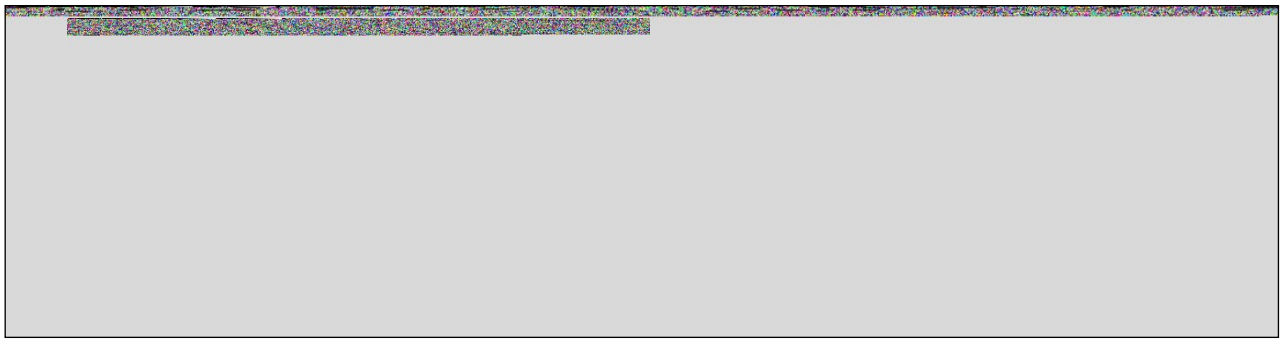


(*S*)-**1a** Obtained from the preparation of (*R*)-**3o**.

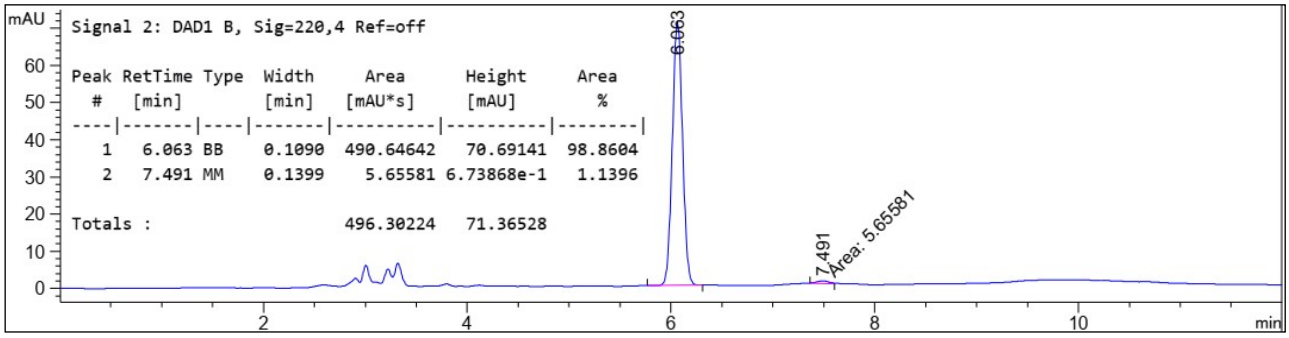
Colorless oil. 31.8 mg, 49% yield.

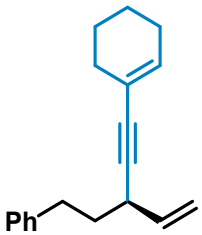
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 6.06 min, t_R(minor) = 7.49 min).

Racemic



Enantioenriched





(*R*)-**3p**

Colorless oil. 36.1mg, 36% yield. **[α]$^{20}_{D}$**: -3.6 (c = 1.0, $CHCl_3$).

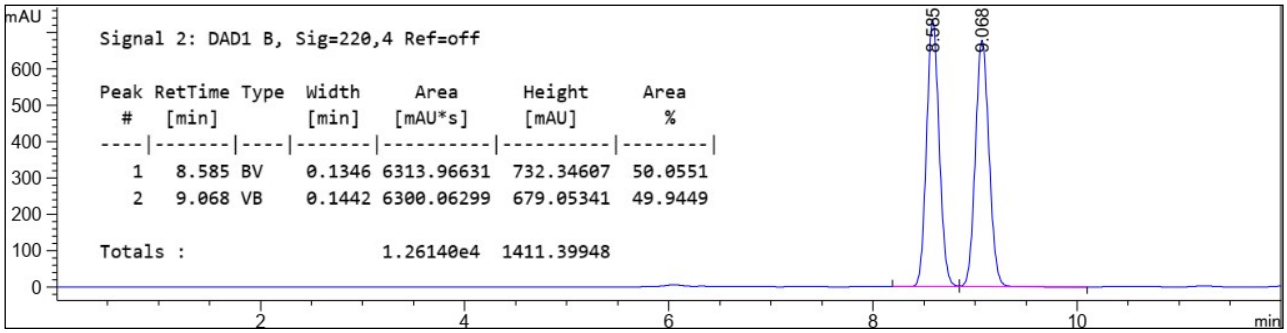
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (dd, *J* = 14.2, 7.1 Hz, 3H), 6.11 (dt, *J* = 4.1, 2.1 Hz, 1H), 5.82 (ddd, *J* = 16.4, 10.0, 6.0 Hz, 1H), 5.33 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 3.20 (q, *J* = 6.8 Hz, 1H), 2.88 – 2.72 (m, 2H), 2.23 – 2.08 (m, 4H), 1.94 – 1.80 (m, 2H), 1.71 – 1.57 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.92, 138.11, 133.71, 128.56, 128.35, 125.83, 120.87, 115.10, 87.07, 85.99, 37.16, 35.46, 33.27, 29.68, 25.61, 22.43, 21.62.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{19}H_{22}]^+$ 250.1716, found 250.1718.

HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 98% *ee* (t_R (major) = 8.64 min, t_R(minor) = 9.12 min).

Racemic



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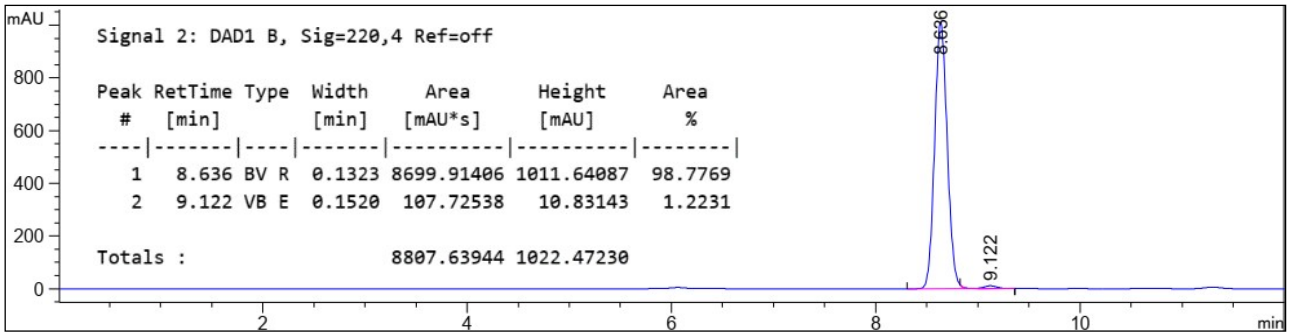
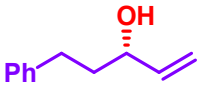


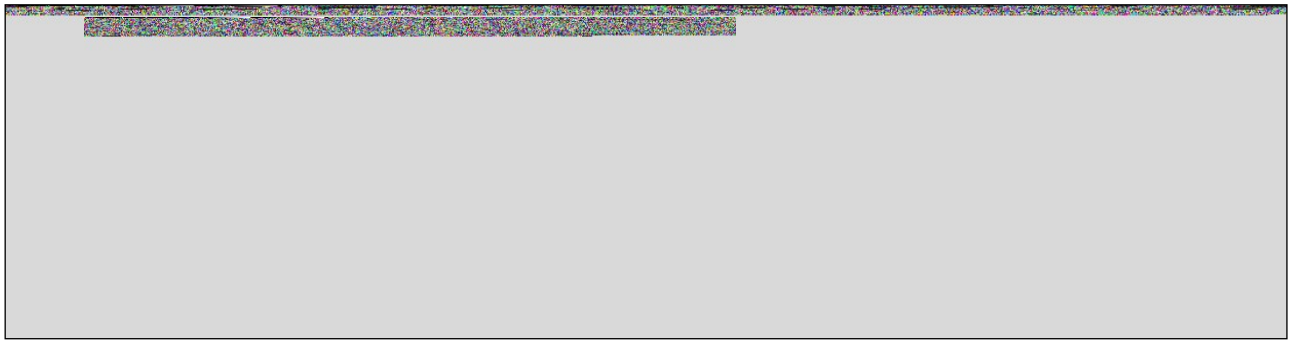


(*S*)-**1a** Obtained from the preparation of (*R*)-**3p**.

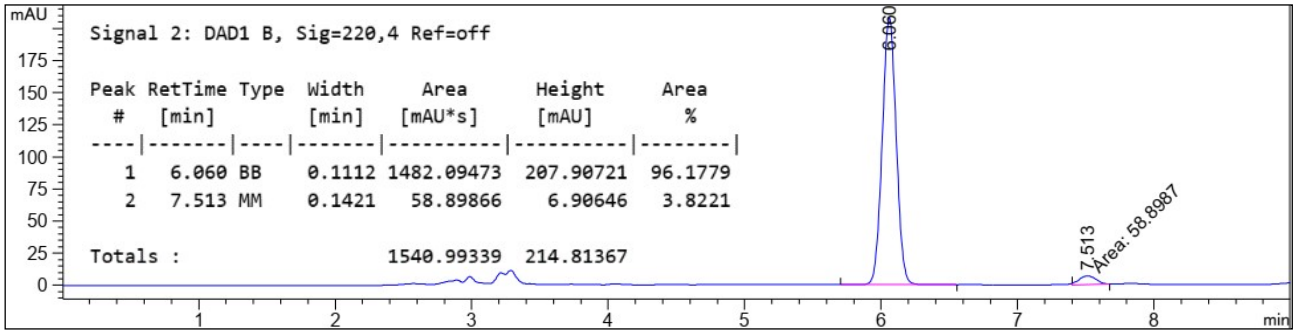
Colorless oil. 29.2 mg, 45% yield.

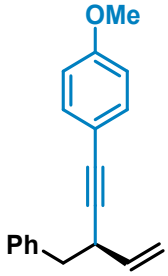
HPLC: Daicel Chiralcel® OD-H, 12% ^{i}PrOH, 88% hexane, 1.0 mL/min, 35 °C, 220 nm; 92% *ee* (t_R (major) = 6.06 min, t_R(minor) = 7.51 min).

Racemic



Enantioenriched





(*R*)-**4b**

Colorless oil. 23.1 mg, 22% yield. **[α]$^{20}_{D}$**: -2.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.13 (m, 7H), 6.74 (d, *J* = 8.8 Hz, 2H), 5.80 (ddd, *J* = 16.9, 10.0, 6.0 Hz, 1H), 5.28 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.05 (dt, *J* = 10.0, 1.4 Hz, 1H), 3.73 (s, 3H), 3.45 (q, *J* = 7.1 Hz, 1H), 2.91 – 2.79 (m, 2H).

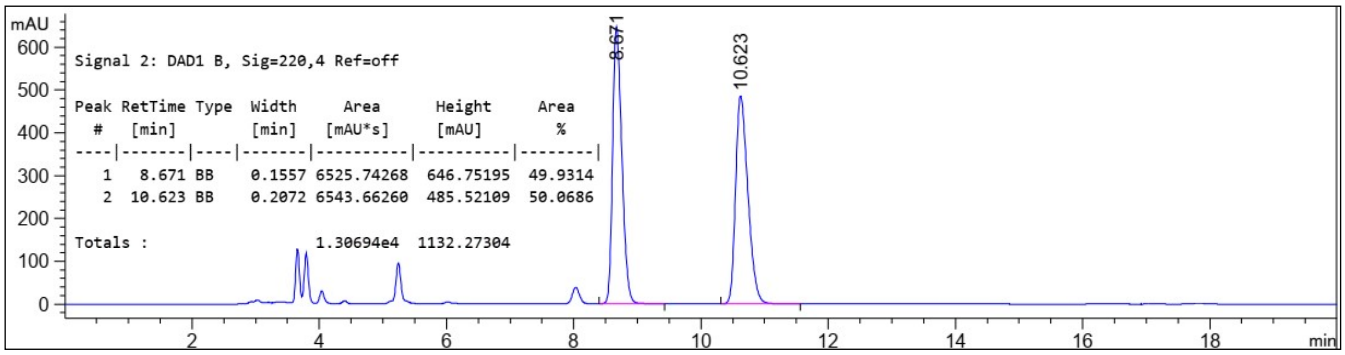
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.19, 138.98, 137.34, 132.89, 129.48, 128.11, 126.38, 115.81, 115.56, 113.79, 88.24, 84.37, 55.27, 42.08, 38.19.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{19}H_{19}O]^+$ 263.1430, found 263.1429.

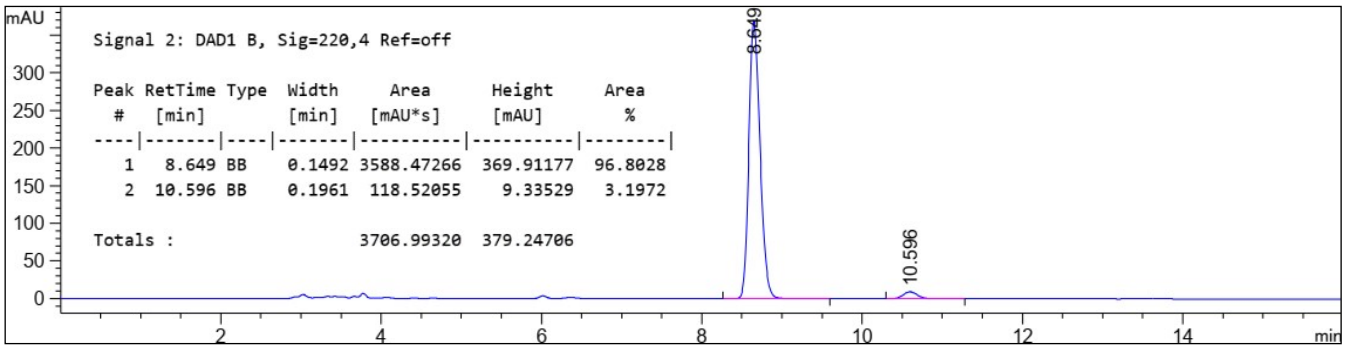
IR (neat): 3020, 2934, 2841, 2203, 1709, 1607, 1510, 1443, 1246, 1219, 1034, 924, 831, 771, 686, 673 cm^{-1}

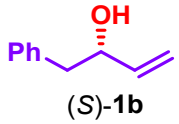
HPLC: Daicel Chiralcel® OJ-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 40 °C, 220 nm; 94% *ee* (t_R (major) = 8.65 min, t_R(minor) = 10.60 min).

Racemic



Enantioenriched





(*S*)-**1b**

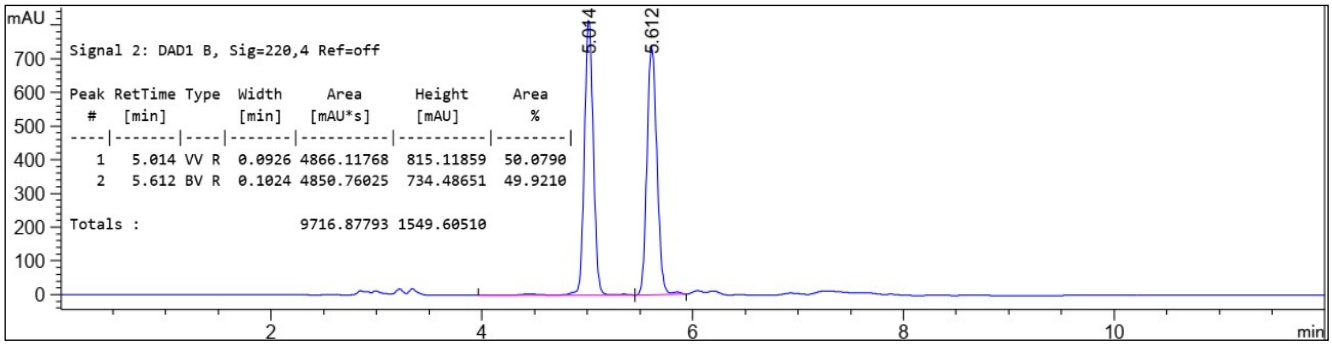
Colorless oil. 28.5 mg, 48% yield. **[α]$^{20}_{D}$**: +2.6 (*c* = 1.0, $CHCl_3$) (lit[9]: **[α]$^{25}_{D}$:** +12.7 (*c* = 1.0, $CHCl_3$)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.18 – 7.13 (m, 3H), 5.85 (ddd, *J* = 17.3, 10.5, 5.8 Hz, 1H), 5.16 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.04 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.29 – 4.22 (m, 1H), 2.82 – 2.67 (m, 2H).

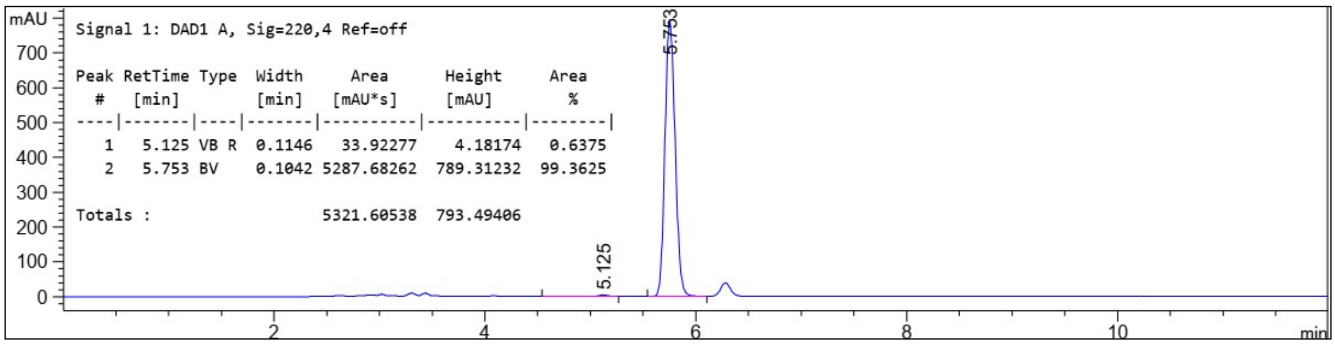
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.16, 137.75, 129.58, 128.50, 126.59, 114.98, 73.66, 43.85.

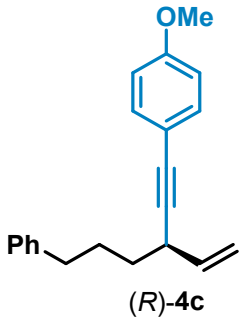
HPLC: Daicel Chiralcel® OD-H, 10% ^{i}PrOH, 90% hexane, 1.0 mL/min, 35 °C, 220 nm; 99% *ee* (t_R (major) = 5.75 min, t_R(minor) = 5.13 min).

Racemic



Enantioenriched





(*R*)-**4c**

Colorless oil. 38.3 mg, 33% yield. **[α]$^{20}_{D}$**: -25.4 (*c* = 1.0, $CHCl_3$) (lit[3b]: **[α]$^{25}_{D}$**: -2.6 (*c* = 0.5, $CHCl_3$)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 6.4 Hz, 1H), 7.24 – 7.15 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.83 (ddd, *J* = 16.5, 10.0, 6.1 Hz, 1H), 5.35 (dt, *J* =

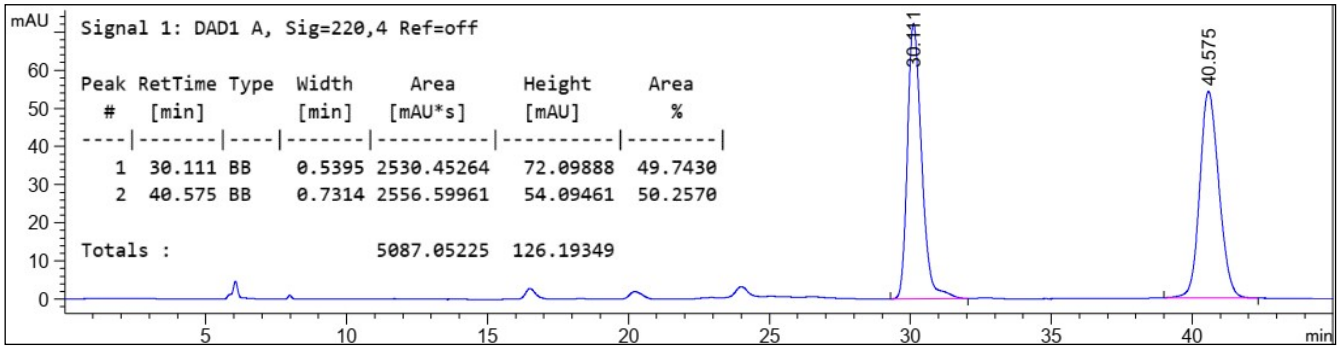
17.0, 1.5 Hz, 1H), 5.11 (dt, *J* = 10.0, 1.4 Hz, 1H), 3.80 (s, 3H), 3.29 (q, *J* = 6.4 Hz, 1H), 2.72 – 2.62 (m, 2H), 1.93 – 1.76 (m, 2H), 1.71 – 1.61 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.17, 142.36, 138.16, 132.96, 128.45, 128.32, 125.74, 115.94, 115.04, 113.82, 88.68, 83.48, 55.28, 36.03, 35.66, 34.97, 28.83.

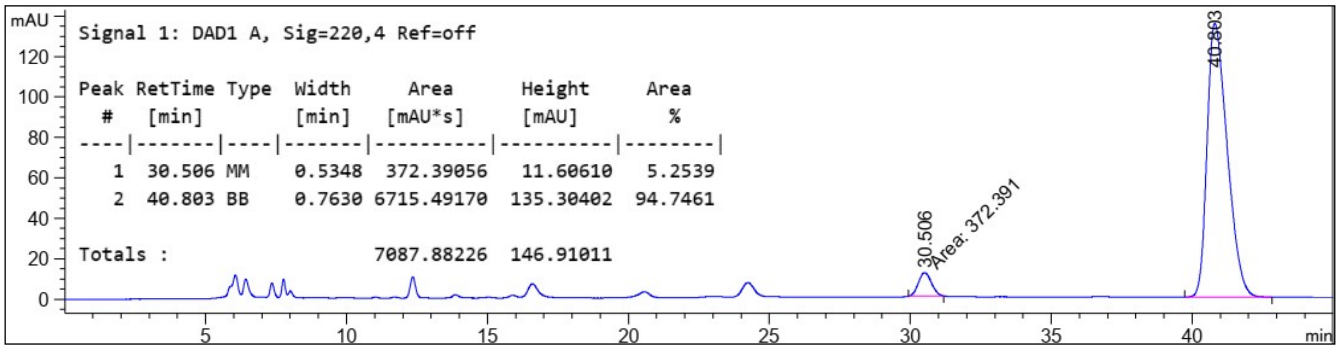
HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{21}H_{23}O]^+$ 291.1743, found 291.1741.

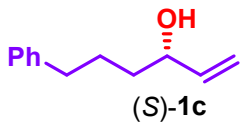
HPLC: Daicel Chiralcel® OJ-H, 10% ^{i}PrOH, 90% hexane, 0.5 mL/min, 40 °C, 220 nm; 89% *ee* (t_R (major) = 40.80 min, t_R(minor) = 30.51 min).

Racemic



Enantioenriched





(*S*)-**1c**

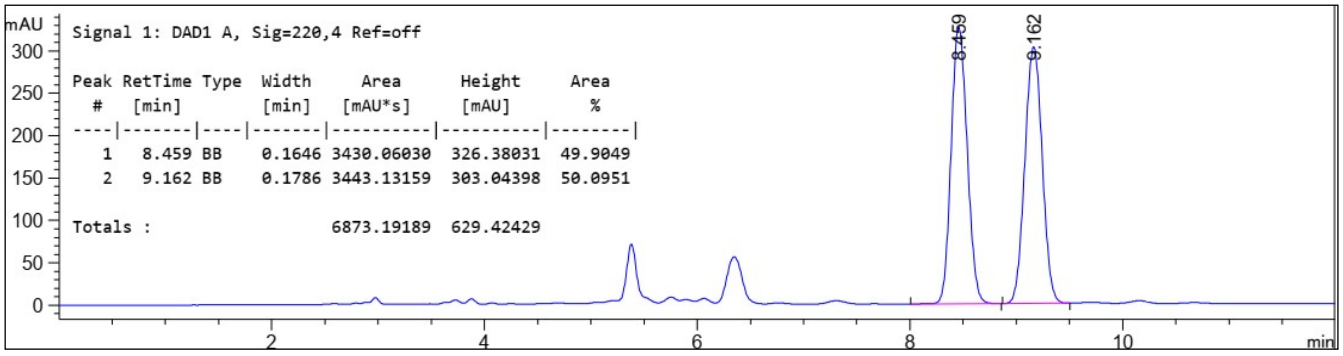
Colorless oil. 31.7 mg, 45% yield. **$[\alpha]^{20}_D$**: +3.7 (*c* = 1.0, $CHCl_3$) (lit[4]: **$[\alpha]^{20}_D$:** +6.9 (*c* = 0.48, $CHCl_3$)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.25 – 7.16 (m, 3H), 5.87 (ddd, *J* = 16.9, 10.4, 6.2 Hz, 1H), 5.23 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.12 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.12 (q, *J* = 6.3 Hz, 1H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.66 (m, 2H), 1.64 – 1.54 (m, 2H).

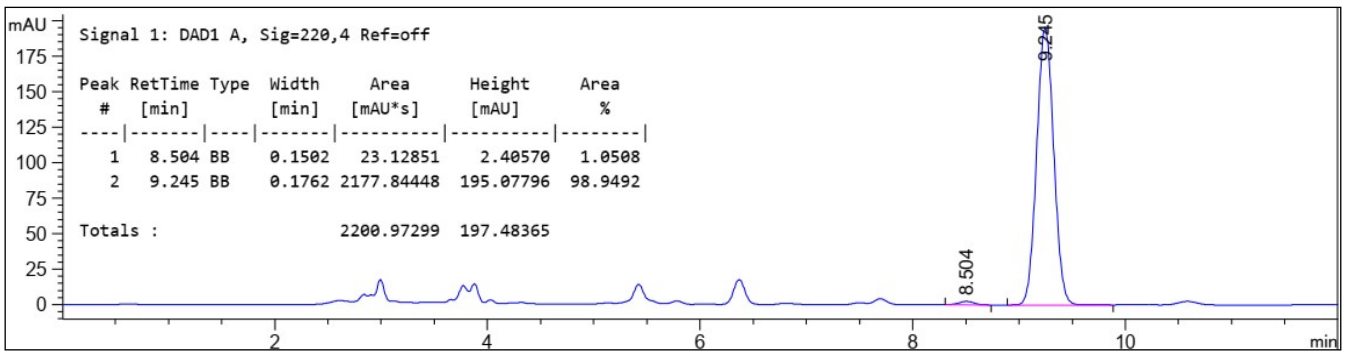
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.34, 141.16, 128.45, 128.33, 125.78, 114.75, 73.12, 36.56, 35.81, 27.20.

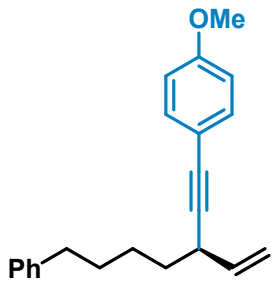
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 9.25 min, t_R(minor) = 8.50 min).

Racemic



Enantioenriched





(*R*)-**4d**

Colorless oil. 42.6 mg, 35% yield. $[\alpha]^{20}_{D}$: -25.1 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.23 – 7.13 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.84 (ddd, *J* = 21.0, 10.0, 6.2 Hz, 1H), 5.39 – 5.30 (m, 1H), 5.14 – 5.07 (m, 1H), 3.80 (s, 3H), 3.26 (q, *J* = 6.2 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.75 – 1.46 (m, 6H).

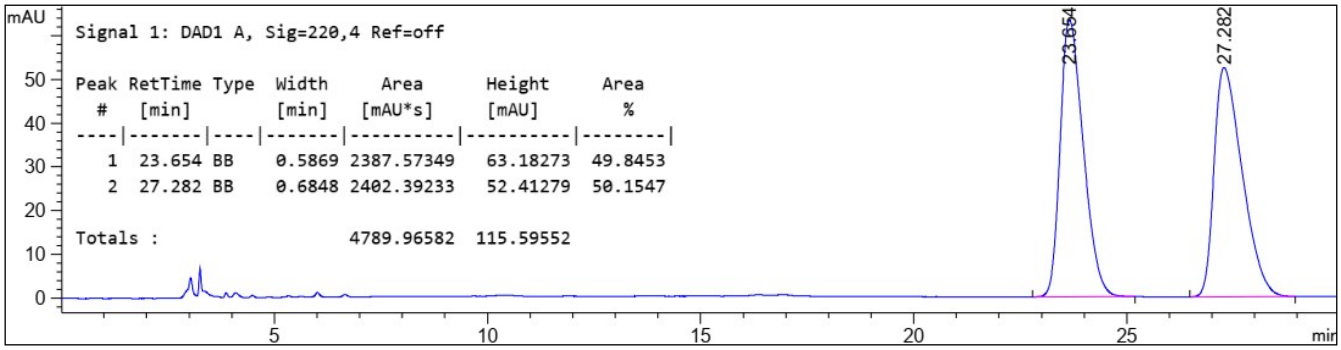
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.15, 142.67, 138.29, 132.97, 128.42, 128.27, 125.63, 115.96, 114.91, 113.79, 88.84, 83.39, 55.28, 36.09, 35.87, 35.33, 31.27, 26.78.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{22}H_{25}O]^+$ 305.1900, found 305.1898.

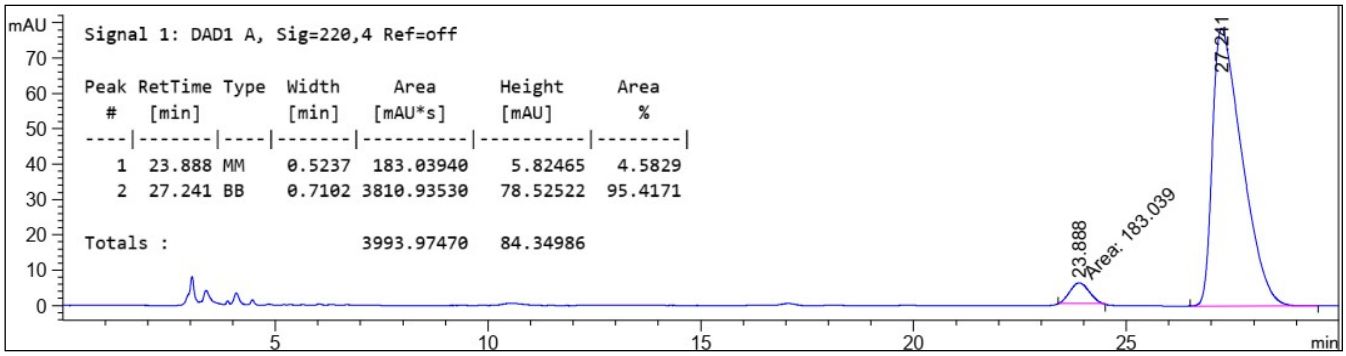
IR (neat): 3022, 2939, 2862, 2210, 1607, 1545, 1510, 1445, 1290, 1219, 1034, 926, 833, 773, 669 cm^{-1}.

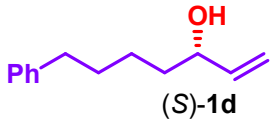
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 91% *ee* (t_R (major) = 27.24 min, t_R(minor) = 23.89 min).

Racemic



Enantioenriched





(*S*)-**1d**

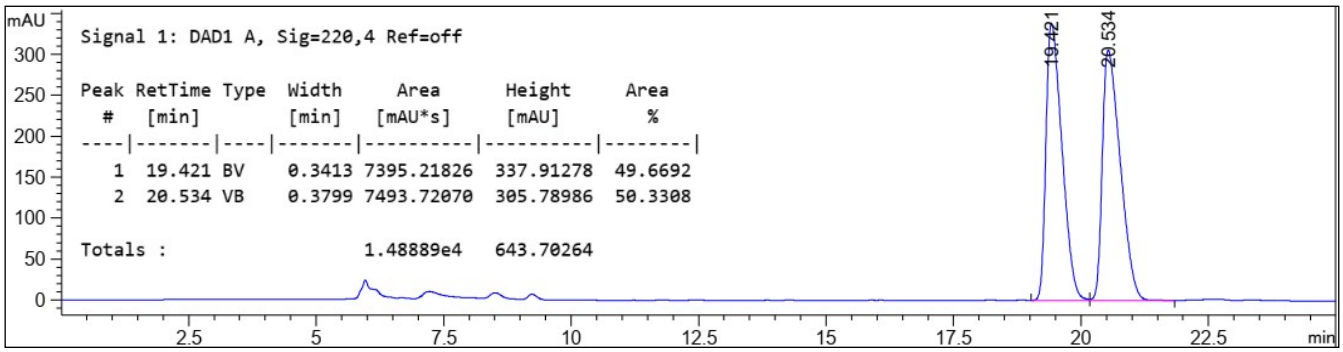
Colorless oil. 37.3 mg, 49% yield. $[\alpha]^{20}_{D}$: +2.2 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.15 (m, 3H), 5.87 (ddd, *J* = 16.9, 10.4, 6.2 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.11 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.10 (q, *J* = 6.1 Hz, 1H), 2.66 – 2.60 (m, 2H), 1.69 – 1.56 (m, 4H), 1.53 – 1.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.59, 141.25, 128.40, 128.29, 125.68, 114.65, 73.18, 36.89, 35.92, 31.44, 25.07.

HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 0.5 mL/min, 35 °C, 220 nm; 96% *ee* (t_R (major) = 19.43 min, t_R(minor) = 20.79 min).

Racemic



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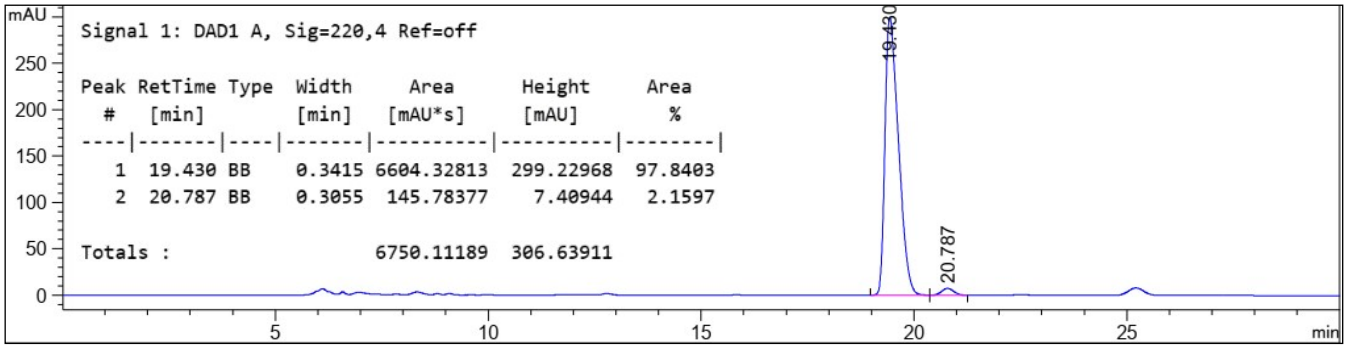
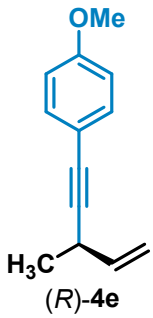




(*R*)-**4e**

Colorless oil. 23.8 mg, 32% yield. **[α]$^{20}_{D}$**: -61.1 (*c* = 1.0, $CHCl_3$).

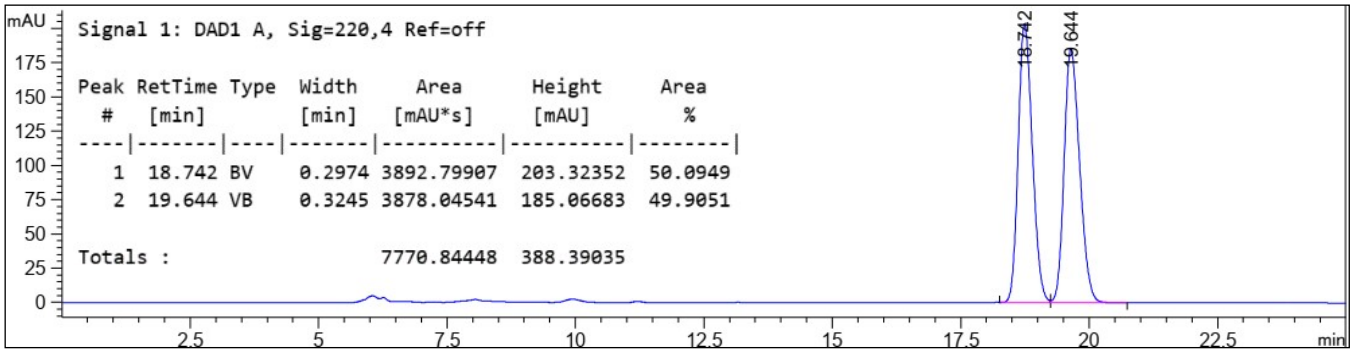
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.89 (ddd, *J* = 17.0, 10.0, 5.7 Hz, 1H), 5.34 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.08 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.36 (dt, *J* = 12.8, 6.4 Hz, 1H), 1.35 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.14, 139.49, 132.94, 115.89, 113.98, 113.79, 89.92, 82.34, 55.26, 30.21, 21.35.

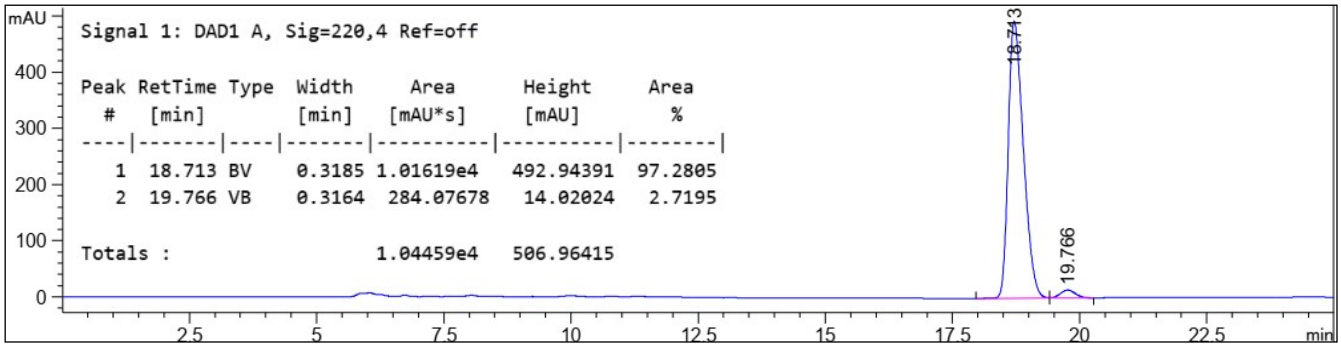
HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{13}H_{15}O]^+$ 187.1117, found 187.1116.

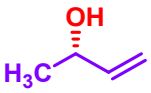
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 0.5 mL/min, 40 °C, 220 nm; 95% *ee* (t_R (major) = 18.71 min, t_R(minor) = 19.77 min).

Racemic



Enantioenriched



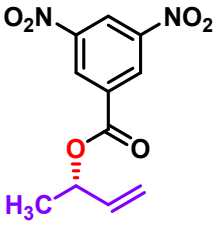


(*S*)-**1e**

Colorless oil. 13.5 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (ddd, *J* = 16.4, 10.4, 5.8 Hz, 1H), 5.19 (dt, *J* = 17.0, 1.3 Hz, 1H), 5.04 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.27 (p, *J* = 6.3 Hz, 1H), 2.06 – 1.92 (m, 1H), 1.25 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.33, 113.63, 68.99, 23.03.



(*S*)-**1e'**

White solid. 40.3 mg, 82% yield. mp: 54.2 – 54.9 °C. **[α]$^{20}_D$**: +16.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, *J* = 2.2 Hz, 1H), 9.16 (d, *J* = 2.1 Hz, 2H), 5.98 (ddd, *J* = 17.0, 10.5, 6.4 Hz, 1H), 5.68 (p, *J* = 6.5 Hz, 1H), 5.39 (dt, *J* = 17.1, 1.1 Hz, 1H), 5.29 (dt, *J* = 10.5, 1.1 Hz, 1H), 1.53 (d, *J* = 6.5 Hz, 3H).

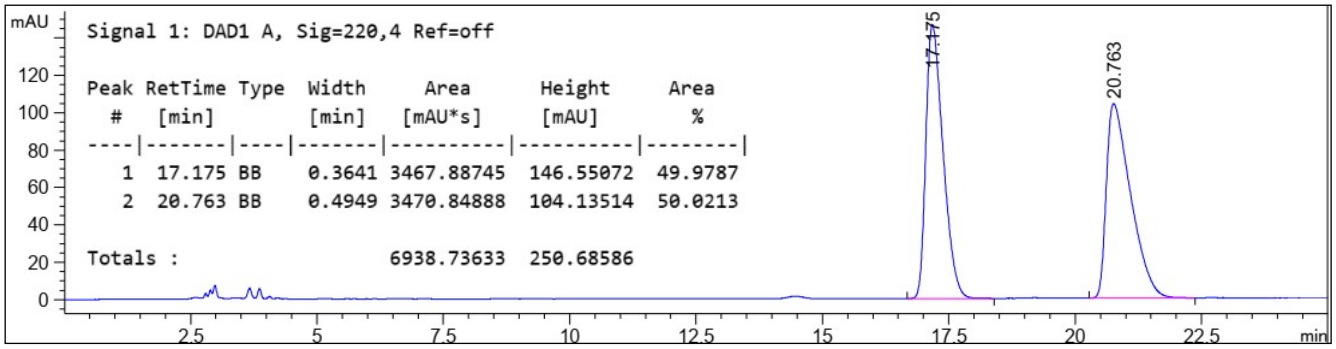
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.73, 148.65, 136.39, 134.31, 129.45, 122.33, 117.69, 74.31, 19.96.

HRMS (ESI): $[M-H]^-$ Calcd. for $[C_{11}H_9N_2O_6]^-$ 265.0466, found 265.0459.

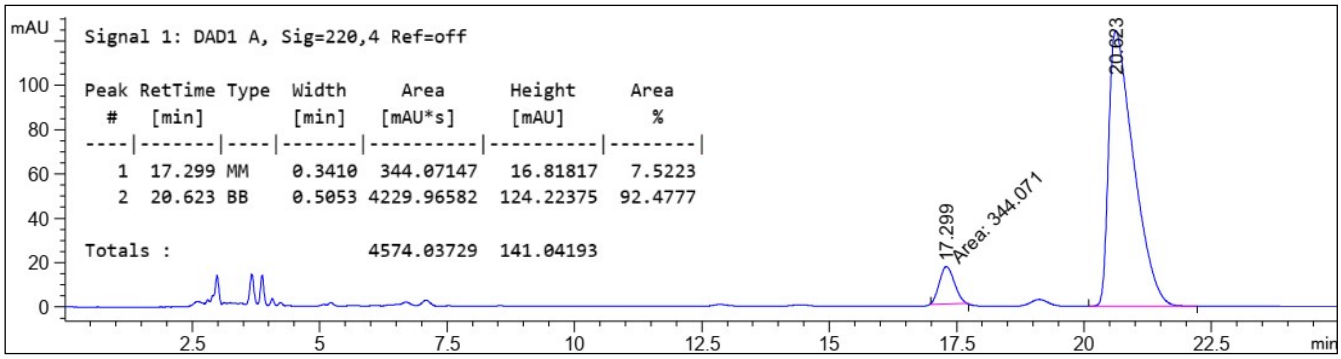
IR (neat): 3103, 3020, 1730,1630, 1549, 1460, 1425, 1346, 1277, 1215, 1076, 1042, 991, 926, 771, 744, 667 cm^{-1}.

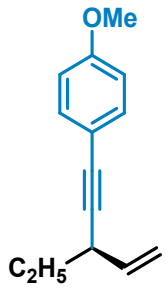
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 85% *ee* (t_R (major) = 20.62 min, t_R(minor) = 17.30 min).

Racemic



Enantioenriched





(*R*)-**4f**

Colorless oil. 27.2 mg, 34% yield. $[\alpha]^{20}_{D}$: -46.4 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.84 (ddd, *J* = 16.5, 10.0, 6.1 Hz, 1H), 5.36 (dt, *J* = 16.9, 1.6 Hz, 1H), 5.12 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.21 (q, *J* = 6.2 Hz, 1H), 1.74 – 1.59 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

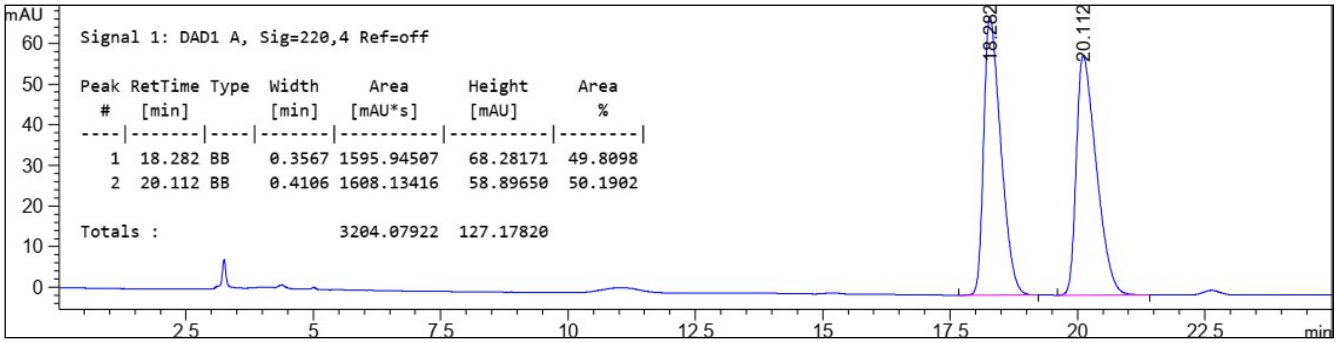
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.12, 138.10, 132.95, 116.02, 115.04, 113.79, 88.74, 83.41, 55.27, 37.64, 28.54, 11.46.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{14}H_{17}O]^+$ 201.1274, found 201.1272.

IR (neat): 3020, 2210, 1607, 1510, 1477, 1423, 1215, 1036, 930, 835, 744, 667 cm^{-1}.

HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 93% *ee* (t_R (major) = 17.96 min, t_R(minor) = 20.32 min).

Racemic



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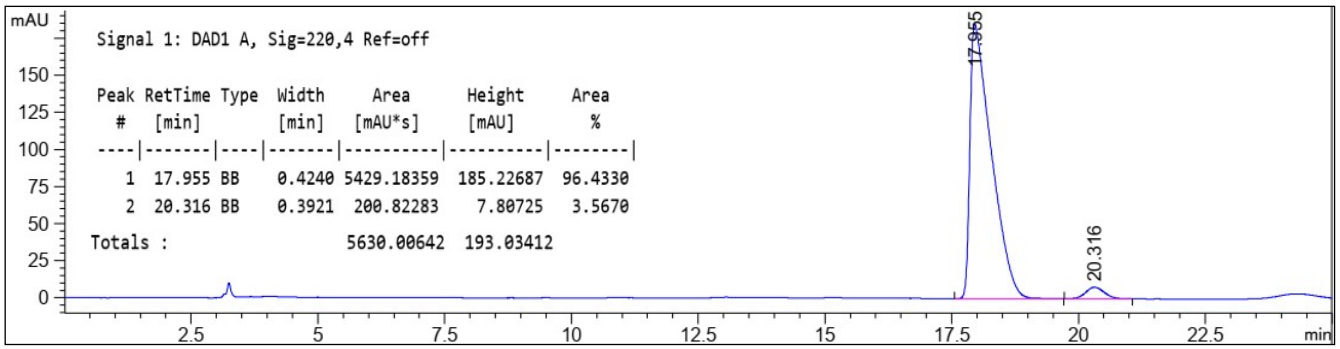
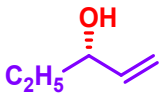


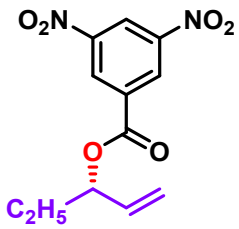


(*S*)-**1f**

Colorless oil. 15.8 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 16.8, 10.4, 6.2 Hz, 1H), 5.23 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.12 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.03 (q, *J* = 6.3 Hz, 1H), 1.85 (dd, *J* = 5.7, 2.3 Hz, 1H), 1.63 – 1.51 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.97, 114.73, 74.53, 29.83, 9.57.



(*S*)-**1f'**

White solid. 42.8 mg, 83% yield. mp: 65.5 – 66.4 °C. **[α]$^{20}_{D}$**: +23.0 (*c* = 0.2, $CHCl_3$) (lit[10]: **[α]$^{20}_{D}$**: +28.4 (*c* = 0.415, $CHCl_3$)).

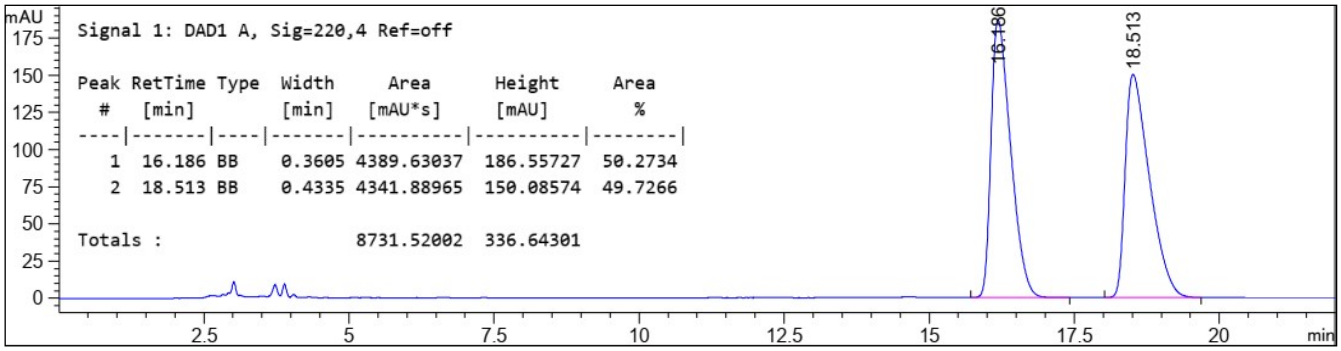
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, *J* = 2.1 Hz, 1H), 9.15 (d, *J* = 2.1 Hz, 2H), 5.90 (ddd, *J* = 17.3, 10.5, 6.9 Hz, 1H), 5.49 (q, *J* = 6.7 Hz, 1H), 5.38 (dt, *J* = 17.2, 1.1 Hz, 1H), 5.31 (dt, *J* = 10.5, 1.1 Hz, 1H), 1.96 – 1.77 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.81, 148.67, 135.06, 134.33, 129.40, 122.31, 118.68, 79.33, 27.20, 9.50.

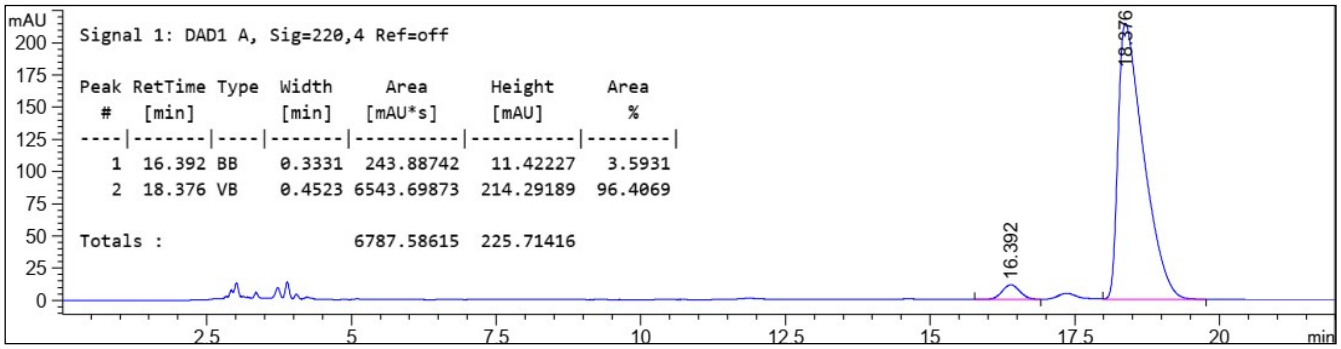
HRMS (ESI): $[M-H]^-$ Calcd for $[C_{12}H_{11}N_2O_6]^-$ 279.0623, found 279.0620.

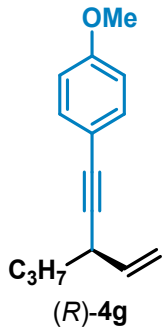
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 93% *ee* (t_R (major) = 18.38 min, t_R(minor) = 16.39 min).

Racemic



Enantioenriched





(*R*)-**4g**

Colorless oil. 30.0 mg, 35% yield. **$[\alpha]^{20}_D$**: -55.0 (*c* = 1.0, $CHCl_3$).

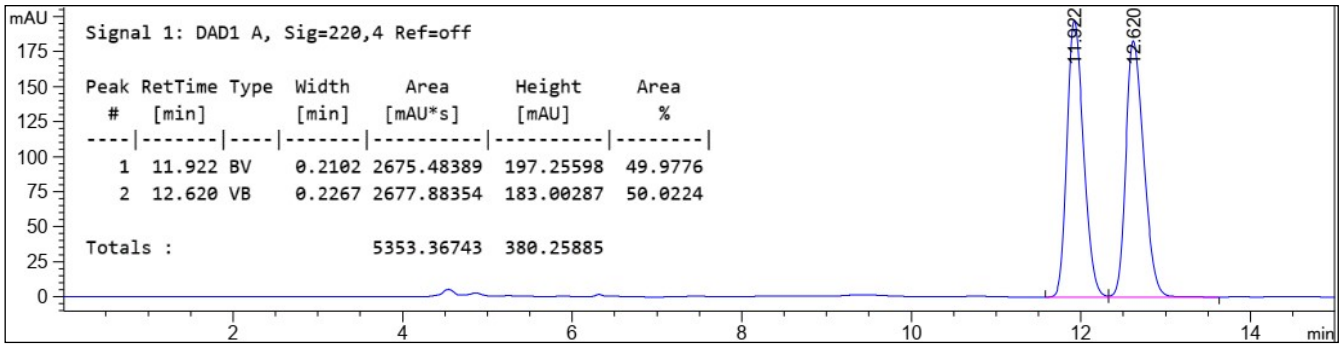
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.84 (ddd, *J* = 16.4, 10.0, 6.2 Hz, 1H), 5.35 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.11 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.27 (q, *J* = 6.4 Hz, 1H), 1.64 – 1.44 (m, 4H), 0.96 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.11, 138.40, 132.94, 116.02, 114.77, 113.79, 88.95, 83.23, 55.26, 37.64, 35.90, 20.29, 13.88.

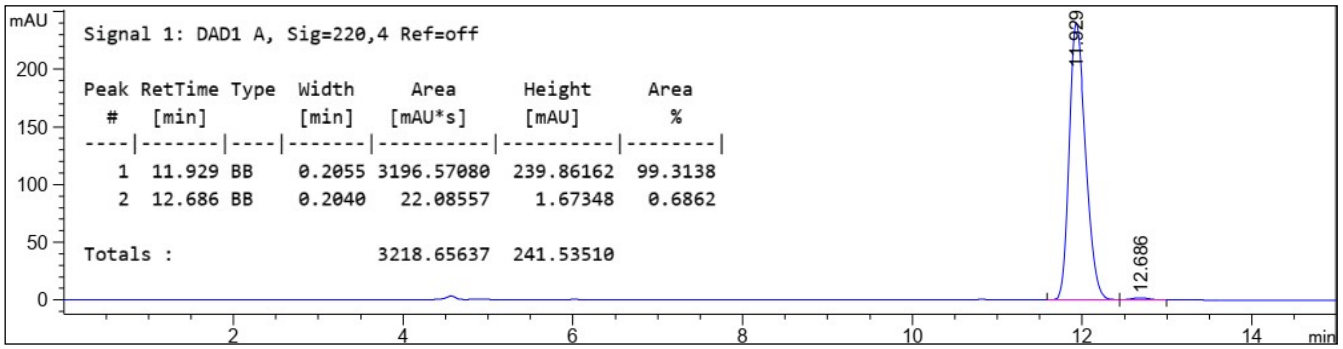
HRMS (ESI): $[M+H]^+$ Calcd for $[C_{15}H_{19}O]^+$ 215.1430, found 215.1429.

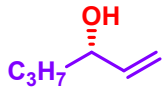
HPLC: Daicel Chiralcel® OJ-H, 1% *i*PrOH, 99% hexane, 0.7 mL/min, 40 °C, 220 nm; 99% *ee* (t_R (major) = 11.93 min, t_R(minor) = 12.69 min).

Racemic



Enantioenriched



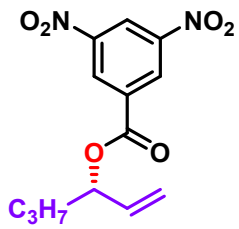


(*S*)-**1g**

Colorless oil. 19.6 mg, 49% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 17.0, 10.4, 6.3 Hz, 1H), 5.19 (d, *J* = 17.3 Hz, 1H), 5.07 (d, *J* = 10.4 Hz, 1H), 4.08 (q, *J* = 6.2 Hz, 1H), 1.91 (d, *J* = 4.7 Hz, 1H), 1.57 – 1.44 (m, 2H), 1.43 – 1.29 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.33, 114.43, 72.96, 39.14, 18.54, 13.95.



(*S*)-**1g'**

White solid. 45.6 mg, 79% yield. mp: 45.9 – 46,8 °C. **[α]$^{20}_D$**: +24.5 (*c* = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, *J* = 1.8 Hz, 1H), 9.15 (d, *J* = 2.0 Hz, 2H), 5.91 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.57 (q, *J* = 6.7 Hz, 1H), 5.38 (d, *J* = 17.0 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 1.92 – 1.81 (m, 1H), 1.81 – 1.71 (m, 1H), 1.50 – 1.36 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

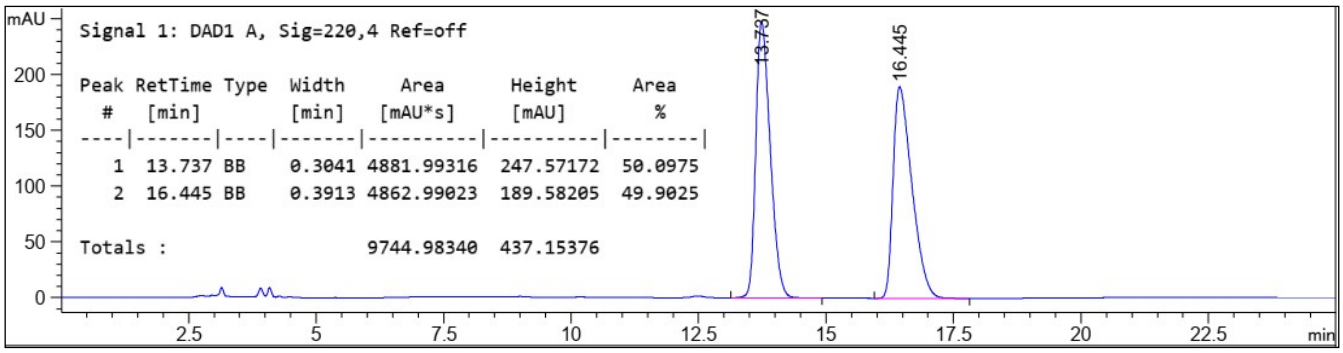
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.80, 148.67, 135.38, 134.33, 129.41, 122.30, 118.48, 77.94, 36.16, 18.43, 13.78.

HRMS (ESI): $[M-H]^-$ Calcd for $[C_{13}H_{13}N_2O_6]^-$ 293.0779, found 293.0778.

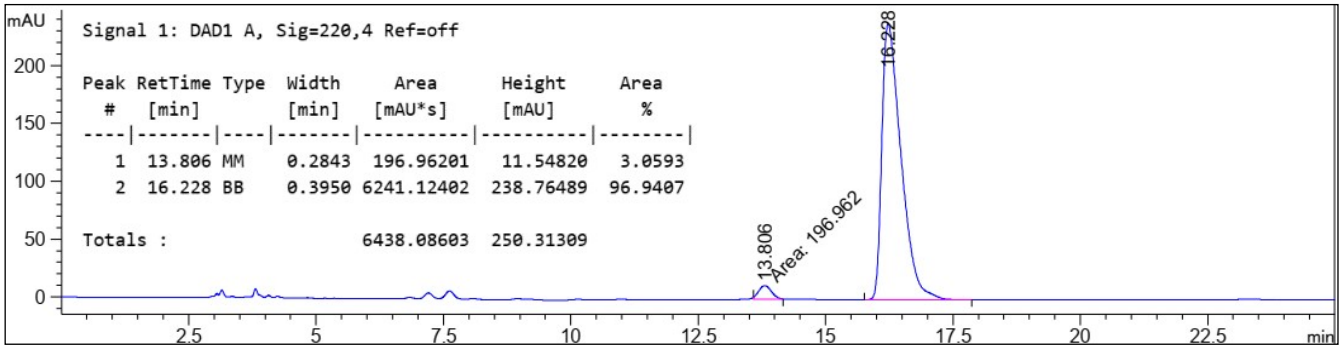
IR (neat): 3103, 3020, 2964, 2937, 2878, 1730, 1630, 1547, 1462, 1425, 1344, 1277, 1215, 1171, 1076, 926, 773, 744, 669 cm^{-1}.

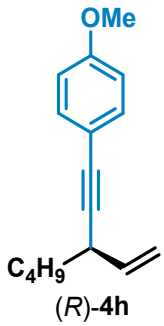
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 94% *ee* (t_R (major) = 16.23 min, t_R(minor) = 13.81 min).

Racemic



Enantioenriched





(*R*)-**4h**

Colorless oil. 31.2 mg, 34% yield. **[α]$^{20}_D$**: -50.1 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 5.77 (ddd, *J* = 16.5, 10.0, 6.2 Hz, 1H), 5.27 (d, *J* = 16.9 Hz, 1H), 5.03 (d, *J* = 10.0 Hz, 1H), 3.73 (s, 3H), 3.17 (q, *J* = 6.5 Hz, 1H), 1.59 – 1.50 (m, 2H), 1.46 – 1.35 (m, 2H), 1.33 – 1.23 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H).

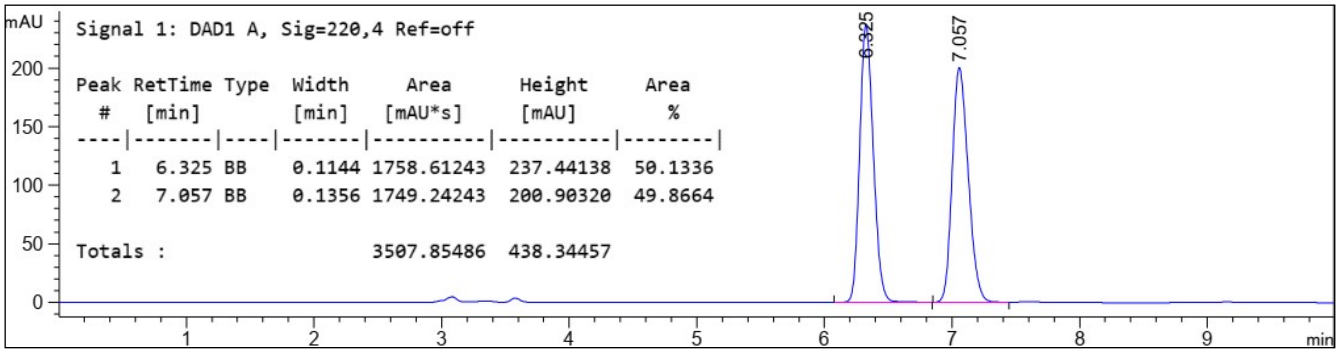
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.11, 138.42, 132.94, 116.03, 114.78, 113.78, 89.01, 83.22, 55.27, 36.11, 35.21, 29.27, 22.50, 14.05.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{16}H_{21}O]^+$ 229.1587, found 229.1585.

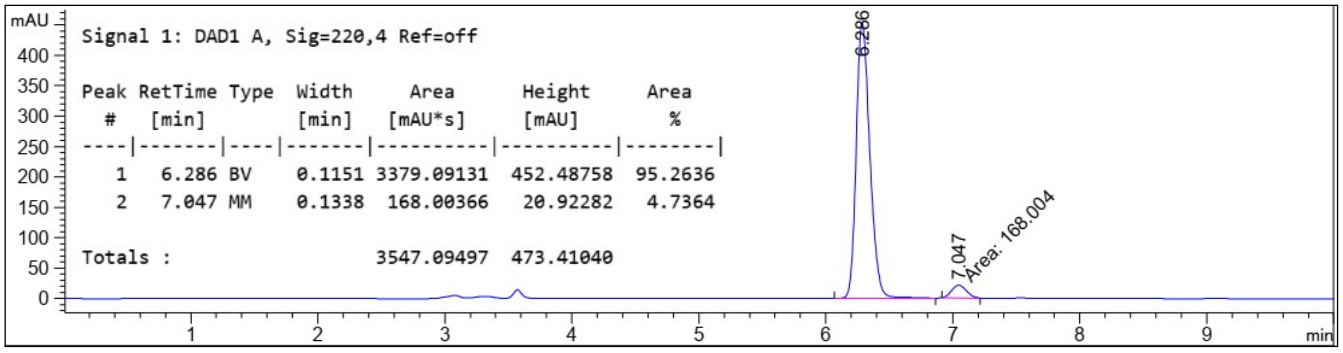
IR (neat): 3020, 2206, 1607, 1547, 1510, 1445, 1290, 1219, 1109, 1036, 930, 854, 773, 669 cm^{-1}.

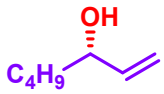
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 91% *ee* (t_R (major) = 6.29 min, t_R(minor) = 7.05 min).

Racemic



Enantioenriched



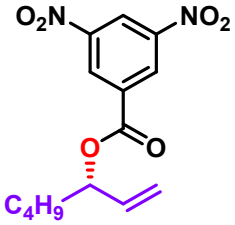


(*S*)-**1h**

Colorless oil. 22.4 mg, 49% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (ddd, *J* = 16.8, 10.4, 6.3 Hz, 1H), 5.18 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 4.05 (q, *J* = 6.5 Hz, 1H), 2.02 (s, 1H), 1.57 – 1.43 (m, 2H), 1.39 – 1.24 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (10 MHz, $CDCl_3$) δ 141.35, 114.43, 73.21, 36.70, 27.49, 22.60, 13.99.



(*S*)-**1h'**

White solid. 49.5 mg, 82% yield. mp: 60.1 – 60.9 °C. $[\alpha]^{20}_{D}$: +22.5 (*c* = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, *J* = 2.1 Hz, 1H), 9.16 (d, *J* = 2.1 Hz, 2H), 5.91 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.56 (q, *J* = 6.9 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 1.93 – 1.73 (m, 2H), 1.45 – 1.32 (m, 4H), 0.97 – 0.87 (m, 3H).

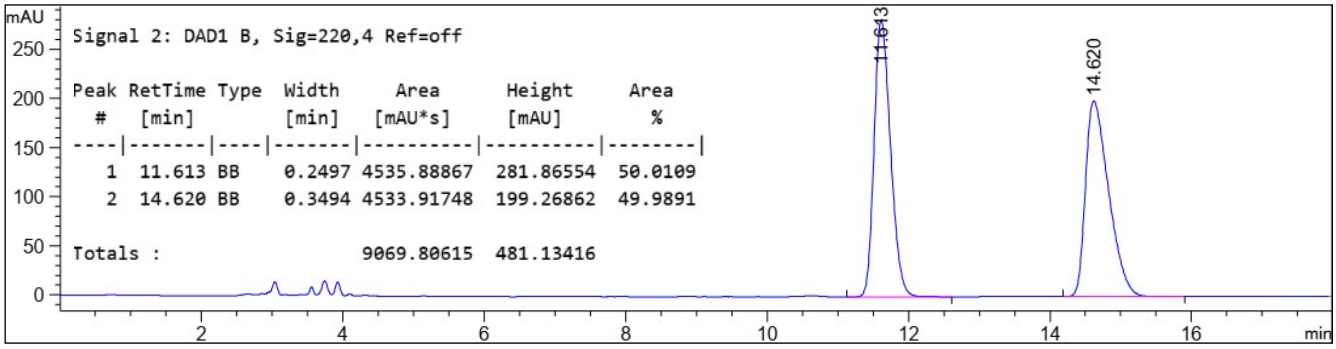
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.80, 148.67, 135.39, 134.35, 129.41, 122.30, 118.53, 78.21, 33.81, 27.26, 22.40, 13.93.

HRMS (ESI): $[M-H]^-$ Calcd. for $[C_{14}H_{15}N_2O_6]^-$ 307.0936, found 307.0937.

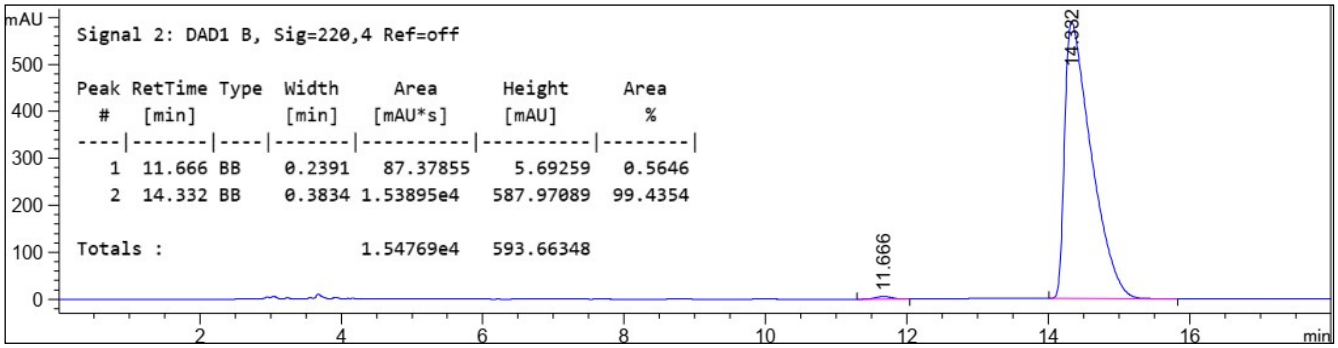
IR (neat): 3103, 3020, 2961, 2934, 2864, 1730, 1630, 1547, 1462, 1425, 1346, 1274, 1215, 1169, 1076, 961, 926, 750, 667 cm^{-1}.

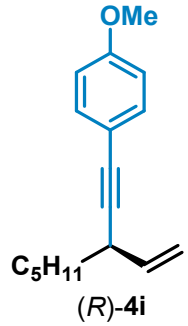
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 99% *ee* (t_R (major) = 14.33 min, t_R(minor) = 11.67 min).

Racemic



Enantioenriched





(*R*)-**4i**

Colorless oil. 34.0 mg, 35% yield. **[α]$^{20}_{D}$**: -34.2 (*c* = 1.0, $CHCl_3$).

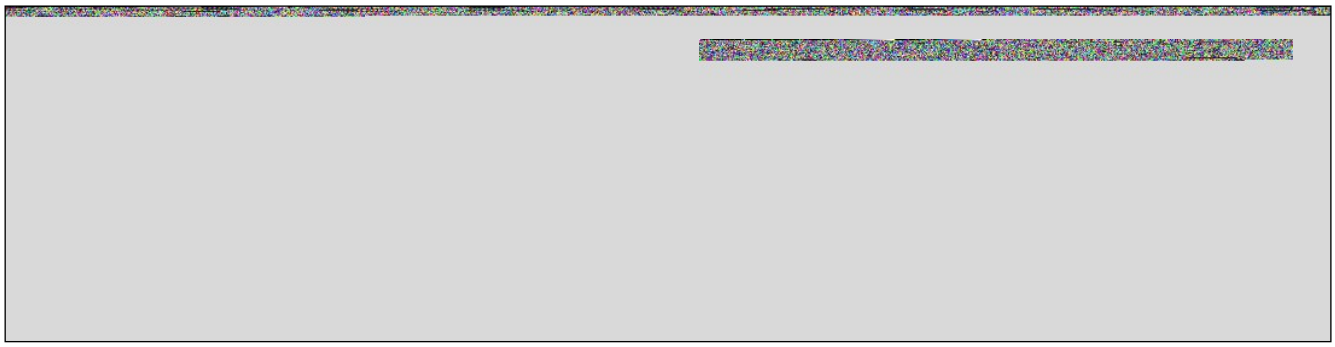
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.84 (ddd, *J* = 16.5, 10.0, 6.2 Hz, 1H), 5.34 (d, *J* = 16.9 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.25 (q, *J* = 6.5 Hz, 1H), 1.64 – 1.57 (m, 2H), 1.55 – 1.42 (m, 2H), 1.37 – 1.28 (m, 4H), 0.90 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.10, 138.42, 132.94, 116.04, 114.78, 113.78, 89.01, 83.22, 55.27, 36.14, 35.46, 31.61, 26.74, 22.59, 14.08.

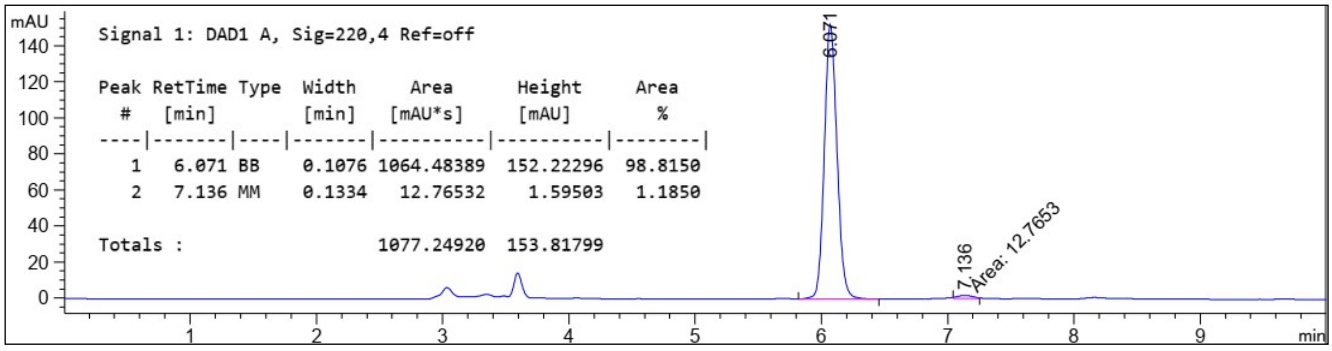
HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{17}H_{23}O]^+$ 243.1743, found 243.1741.

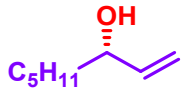
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 98% *ee* (t_R (major) = 6.07 min, t_R(minor) = 7.14 min).

Racemic



Enantioenriched



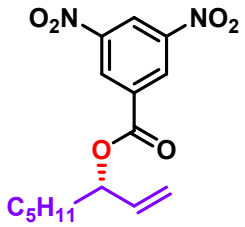


(*S*)-**1i**

Colorless oil. 23.8 mg, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, *J* = 16.9, 10.4, 6.3 Hz, 1H), 5.20 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.08 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.08 (q, *J* = 6.3 Hz, 1H), 1.73 (s, 1H), 1.57 – 1.44 (m, 2H), 1.42 – 1.23 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.33, 114.51, 73.28, 37.00, 31.76, 25.01, 22.60, 14.03.



(*S*)-**1i'**

White solid. 48.5 mg, 80% yield. mp: 63.1 – 63.8 °C. **[α]$^{20}_D$**: +22.1 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (t, *J* = 2.0 Hz, 1H), 9.16 (d, *J* = 2.0 Hz, 2H), 5.90 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.55 (q, *J* = 6.8 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.5 Hz, 1H), 1.92 – 1.73 (m, 2H), 1.44 – 1.27 (m, 6H), 0.89 (t, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.81, 148.67, 135.38, 134.34, 129.43, 122.32, 118.56, 78.24, 34.05, 31.46, 24.79, 22.49, 13.98.

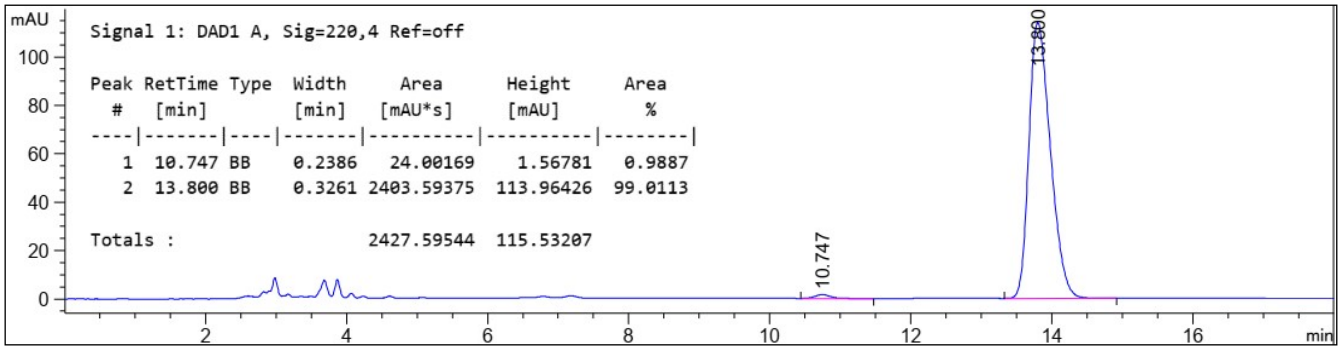
HRMS (ESI): $[M-H]^-$ Calcd. for $[C_{15}H_{17}N_2O_6]^-$ 321.1092, found 321.1084.

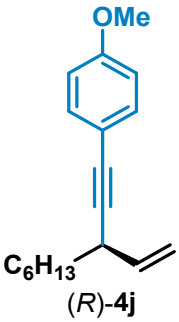
IR (neat): 3020, 1728, 1630, 1549, 1522, 1477, 1427, 1344, 1277, 1215, 928, 744, 669 cm^{-1}.

HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 13.80 min, t_R(minor) = 10.75 min).

Racemic

Enantioenriched





(*R*)-**4j**

Colorless oil. 35.9 mg, 35% yield. **[α]$^{20}_{D}$**: -33.5 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.84 (ddd, *J* = 16.4, 10.0, 6.2 Hz, 1H), 5.34 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.10 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.24 (q, *J* = 6.4 Hz, 1H), 1.65 – 1.58 (m, 2H), 1.54 – 1.39 (m, 2H), 1.36 – 1.27 (m, 6H), 0.91 – 0.86 (m, 3H).

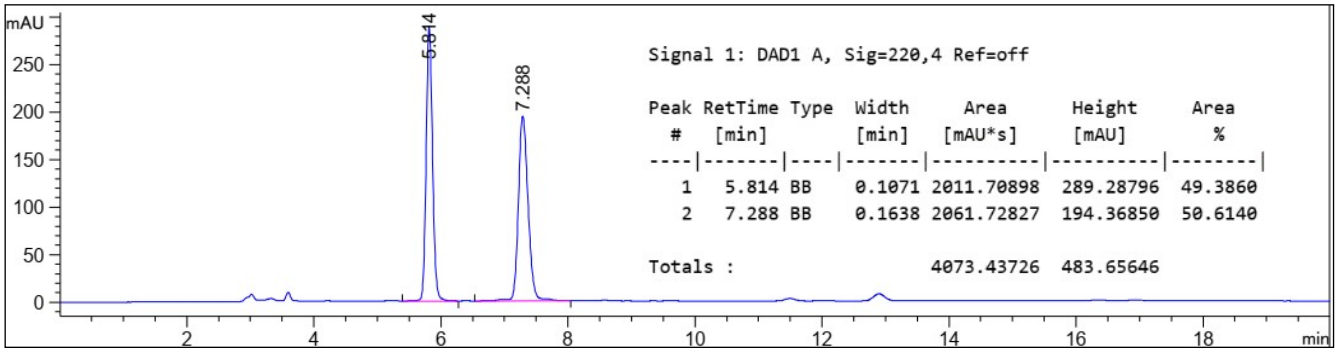
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.10, 138.43, 132.94, 116.03, 114.77, 113.78, 89.02, 83.21, 55.27, 36.13, 35.50, 31.78, 29.07, 27.03, 22.64, 14.10.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{18}H_{25}O]^+$ 257.1900, found 257.1898.

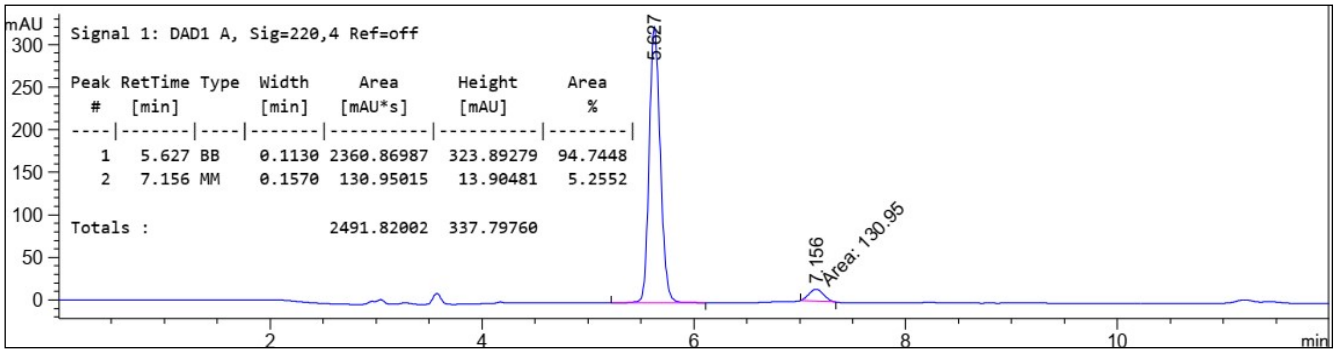
IR (neat): 3020, 2957, 2934, 2860, 2210, 1607, 1549, 1512, 1445, 1219, 1173, 1034, 932, 854, 773, 744, 669 cm^{-1}.

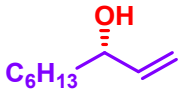
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 89% *ee* (t_R (major) = 5.63 min, t_R(minor) = 7.16 min).

Racemic



Enantioenriched



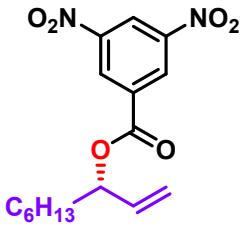


(*S*)-**1j**

Colorless oil. 26.2 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 16.9, 10.4, 6.2 Hz, 1H), 5.21 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.09 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.09 (q, *J* = 6.3 Hz, 1H), 1.59 (s, 1H), 1.56 – 1.45 (m, 2H), 1.43 – 1.24 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H)..

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.34, 114.52, 73.29, 37.06, 31.79, 29.22, 25.29, 22.60, 14.07.



(*S*)-**1j'**

White solid. 51.2 mg, 81% yield. mp: 58.5 – 59.5 °C. **[α]$^{20}_D$**: +15.0 (*c* = 0.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, *J* = 2.1 Hz, 1H), 9.15 (d, *J* = 2.1 Hz, 2H), 5.90 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.55 (q, *J* = 7.0 Hz, 1H), 5.37 (dt, *J* = 17.1, 1.2 Hz, 1H), 5.29 (dt, *J* = 10.4, 1.1 Hz, 1H), 1.92 – 1.72 (m, 2H), 1.42 – 1.23 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H).

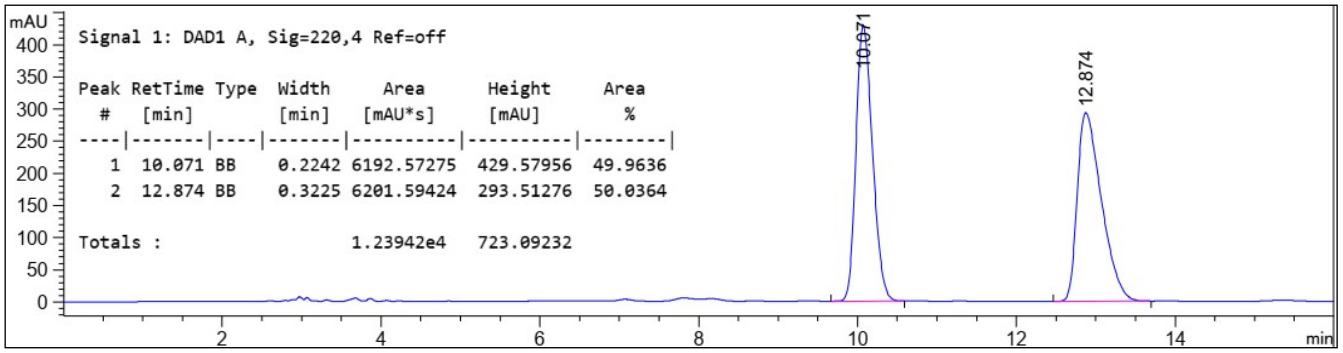
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.80, 148.66, 135.40, 134.33, 129.42, 122.31, 118.51, 78.22, 34.09, 31.64, 28.96, 25.08, 22.55, 14.04.

HRMS (ESI): $[M-H]^-$ Calcd for $[C_{16}H_{19}N_2O_6]^-$ 335.1249, found 335.1222.

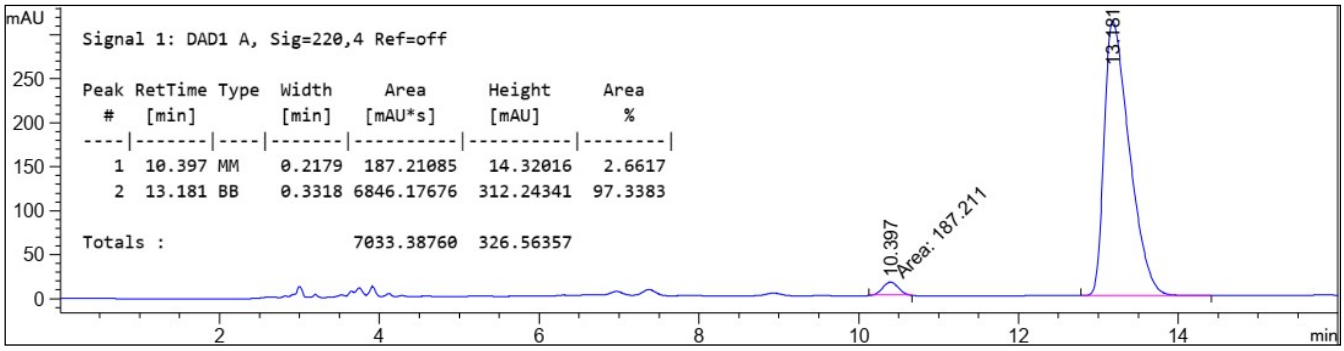
IR (neat): 3103, 3020, 2930, 2858, 1730, 1630, 1549, 1460, 1427, 1344, 1275, 1215, 1171, 1076, 991, 924, 754, 669 cm^{-1}.

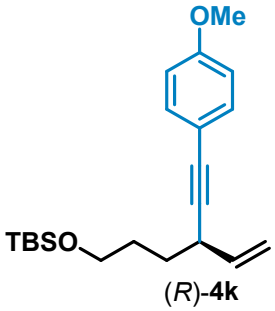
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 95% *ee* (t_R (major) = 13.18 min, t_R(minor) = 10.40 min).

Racemic



Enantioenriched





(*R*)-**4k**

Colorless oil. 49.6 mg, 36% yield. **[α]$^{20}_{D}$**: -26.7 (*c* = 1.0, $CHCl_3$).

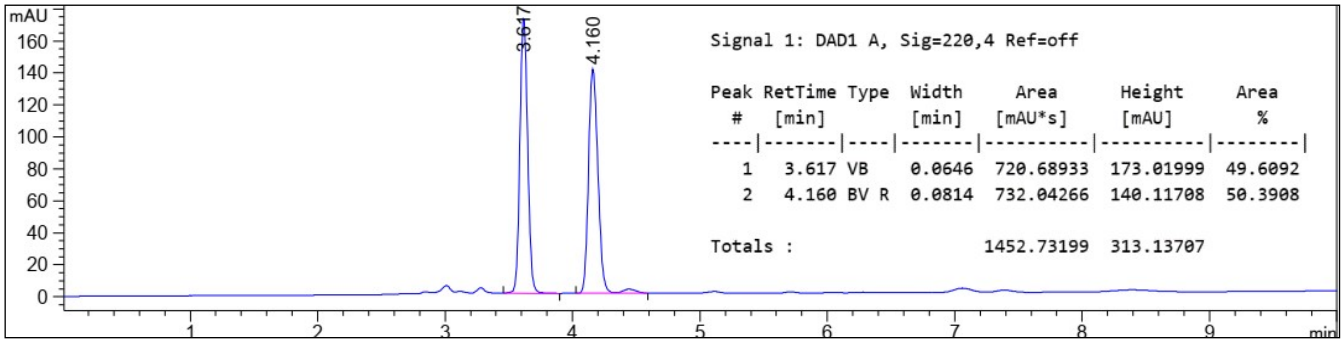
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.84 (ddd, *J* = 16.3, 10.0, 6.1 Hz, 1H), 5.36 (d, *J* = 16.9 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.67 (t, *J* = 5.8 Hz, 2H), 3.34 – 3.24 (m, 1H), 1.80 – 1.61 (m, 4H), 0.90 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.11, 138.23, 132.95, 115.93, 115.00, 113.77, 88.70, 83.46, 62.94, 55.28, 35.85, 31.81, 30.29, 26.00, 18.39, -5.23.

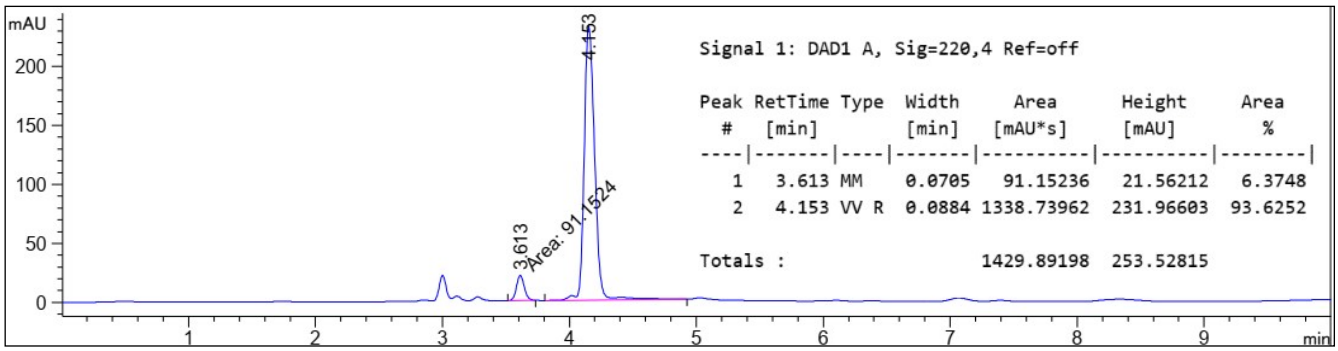
HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{21}H_{33}O_2Si]^+$ 345.2244, found 345.2244.

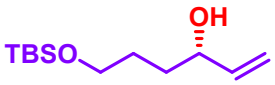
HPLC: Daicel Chiralcel® OJ-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 40 °C, 220 nm; 87% *ee* (t_R (major) = 4.15 min, t_R(minor) = 3.61 min).

Racemic



Enantioenriched



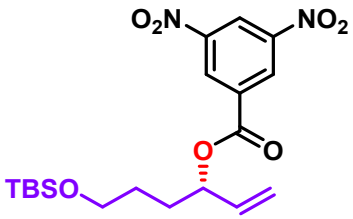


(*S*)-**1k**

Colorless oil. 42.4 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.6 Hz, 1H), 5.08 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.11 (q, *J* = 6.4, 5.7 Hz, 1H), 3.65 (t, *J* = 5.7 Hz, 2H), 2.74 (s, 1H), 1.70 – 1.54 (m, 4H), 0.89 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.23, 114.29, 72.64, 63.38, 34.38, 28.74, 25.93, 18.33, -5.38.



(*S*)-**1k'**

Colorless oil. 60.9 mg, 78% yield. **[α]$^{20}_D$**: +8.0 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (t, *J* = 2.1 Hz, 1H), 9.16 (d, *J* = 2.1 Hz, 2H), 5.91 (ddd, *J* = 17.3, 10.4, 6.9 Hz, 1H), 5.60 (q, *J* = 6.8 Hz, 1H), 5.39 (d, *J* = 17.3 Hz, 1H), 5.31 (d, *J* = 10.5 Hz, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 1.98 – 1.83 (m, 2H), 1.68 – 1.59 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H).

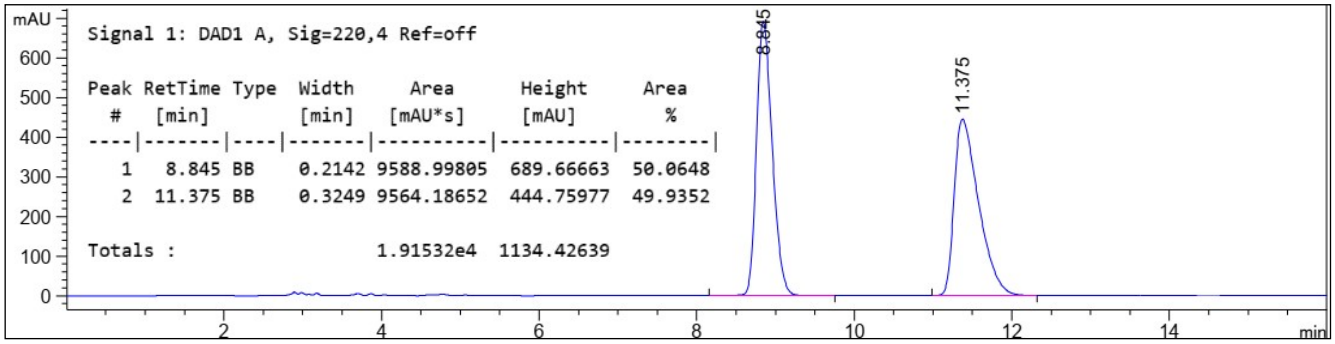
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.77, 148.65, 135.26, 134.27, 129.44, 122.35, 118.69, 77.98, 62.42, 30.63, 28.33, 25.93, 18.34, -5.31.

HRMS (ESI): $[M-H]^-$ Calcd. for $[C_{19}H_{27}N_2O_7Si]^-$ 423.1593, found 423.1581.

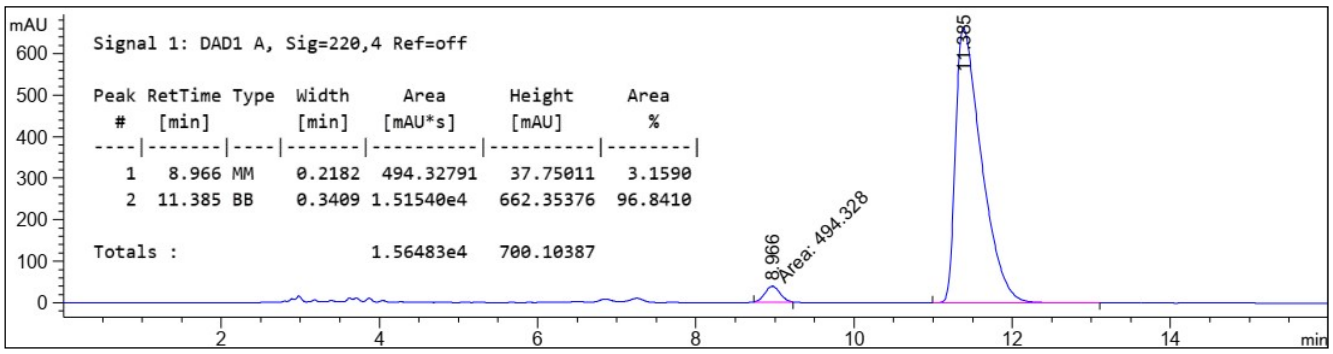
IR (neat): 3105, 2955, 2930, 2887, 2858, 1730, 1630, 1547, 1460, 1344, 1275, 1169, 1099, 986, 920, 835, 775, 721 cm^{-1}.

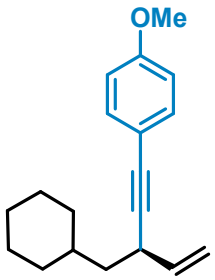
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 94% *ee* (t_R (major) = 11.39 min, t_R(minor) = 8.97 min).

Racemic



Enantioenriched





(*R*)-**4l**

Colorless oil. 39.7 mg, 37% yield. **[α]$^{20}_D$**: -39.7 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 5.83 (ddd, *J* = 16.6, 10.0, 6.3 Hz, 1H), 5.34 (d, *J* = 17.0 Hz, 1H), 5.09 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.34 (q, *J* = 6.5 Hz, 1H), 1.83 (d, *J* = 12.7 Hz, 1H), 1.78 – 1.65 (m, 4H), 1.55 – 1.50 (m, 1H), 1.47 – 1.40 (m, 1H), 1.28 – 1.15 (m, 3H), 1.05 – 0.79 (m, 3H).

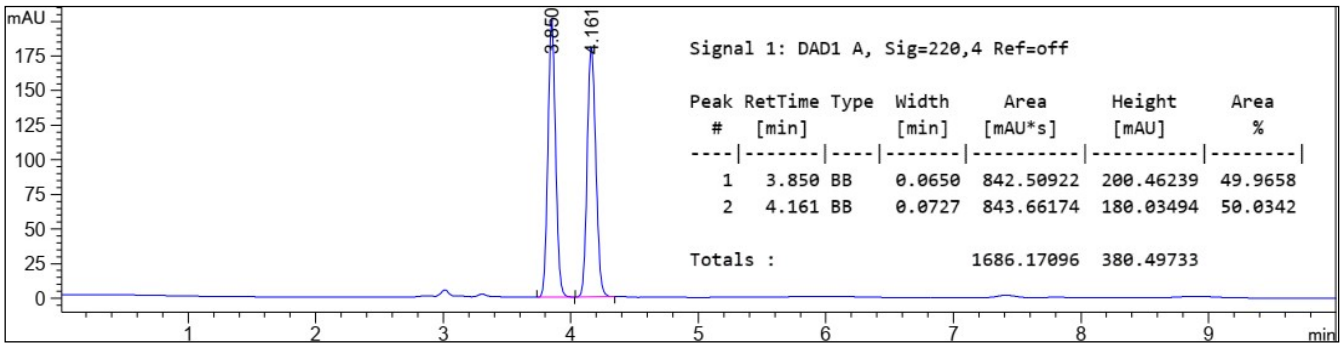
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.10, 138.74, 132.94, 116.08, 114.55, 113.79, 89.19, 83.01, 55.27, 43.24, 35.27, 33.61, 33.53, 32.80, 26.65, 26.29, 26.27.

HRMS (APCI): $[M]^+$ Calcd. for $[C_{19}H_{24}O]^+$ 268.1822, found 268.1830.

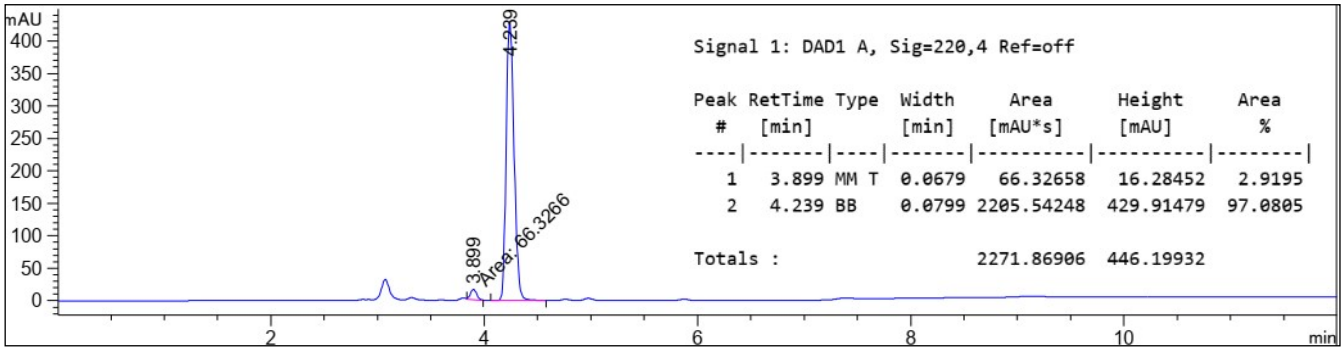
IR (neat): 3020, 2210, 1607, 1547, 1512, 1445, 1290, 1219, 1107, 1034, 931, 854, 733, 667 cm^{-1}.

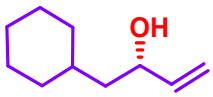
HPLC: Daicel Chiralcel® OD-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 35 °C, 220 nm; 94% *ee* (t_R (major) = 4.24 min, t_R(minor) = 3.90 min).

Racemic



Enantioenriched



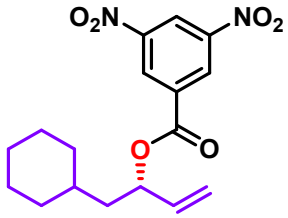


(*S*)-**1l**

Colorless oil. 25.9 mg, 42% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, *J* = 16.9, 10.4, 6.3 Hz, 1H), 5.20 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.07 (dt, *J* = 10.4, 1.4 Hz, 1H), 4.19 (q, *J* = 6.4 Hz, 1H), 1.77 (d, *J* = 12.6 Hz, 1H), 1.73 – 1.60 (m, 5H), 1.49 – 1.37 (m, 2H), 1.37 – 1.27 (m, 1H), 1.27 – 1.08 (m, 3H), 0.98 – 0.84 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.78, 114.26, 70.82, 44.86, 33.93, 33.85, 33.08, 26.57, 26.30, 26.20.



(*S*)-**1l'**

White solid. 43.9 mg, 75% yield. mp 74.2 – 75.0 ℃. **[α]$^{20}_{D}$**: -1.0 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (t, *J* = 2.2 Hz, 1H), 9.15 (d, *J* = 2.2 Hz, 2H), 5.90 (ddd, *J* = 17.3, 10.4, 7.0 Hz, 1H), 5.67 (q, *J* = 7.1 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.28 (d, *J* = 10.3 Hz, 1H), 1.85 – 1.59 (m, 7H), 1.44 – 1.32 (m, 1H), 1.27 – 1.13 (m, 3H), 1.06 – 0.92 (m, 2H).

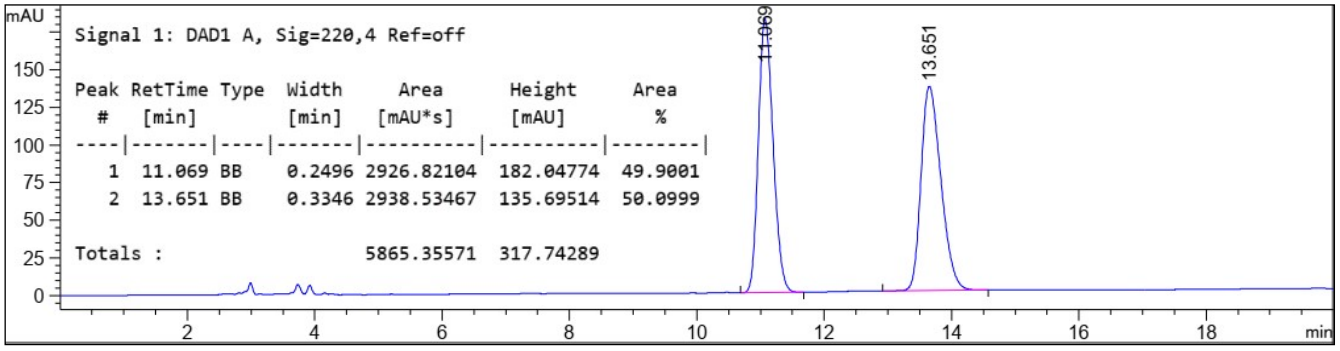
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.79, 148.69, 135.71, 134.36, 129.43, 122.30, 118.43, 76.26, 41.69, 33.95, 33.35, 33.11, 26.36, 26.09, 26.07.

HRMS (ESI): $[M-H]^-$ Calcd for $[C_{17}H_{19}N_2O_6]^-$ 347.1249, found 347.1253.

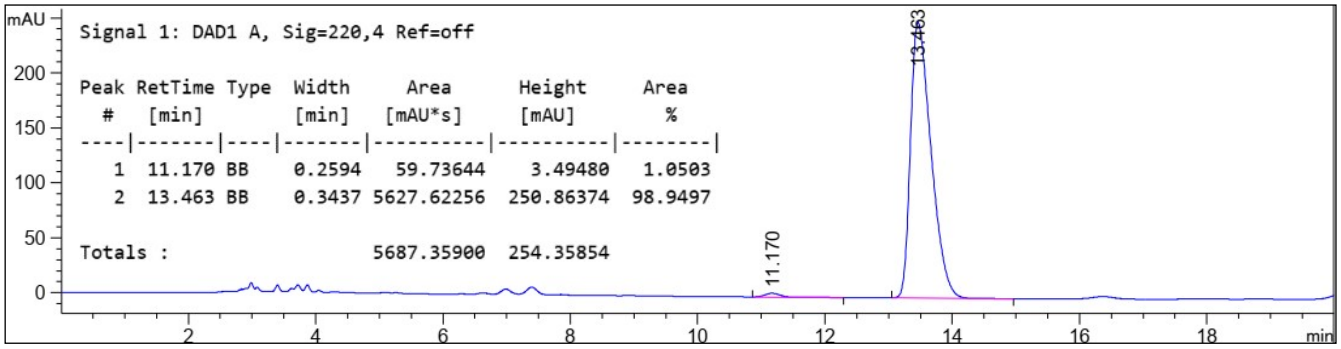
IR (neat): 3105, 2922, 2853, 1717, 1630, 1541, 1460, 1342, 1283, 1173, 1072, 993, 949, 918, 824, 775, 729, 719, 689 cm^{-1}.

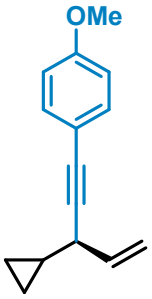
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 98% *ee* (t_R (major) = 13.46 min, t_R(minor) = 11.17 min).

Racemic



Enantioenriched





(*R*)-**4m**

Colorless oil. 28.1 mg, 33% yield. **[α]$^{20}_{D}$**: -6.5 (*c* = 1.0, $CHCl_3$).

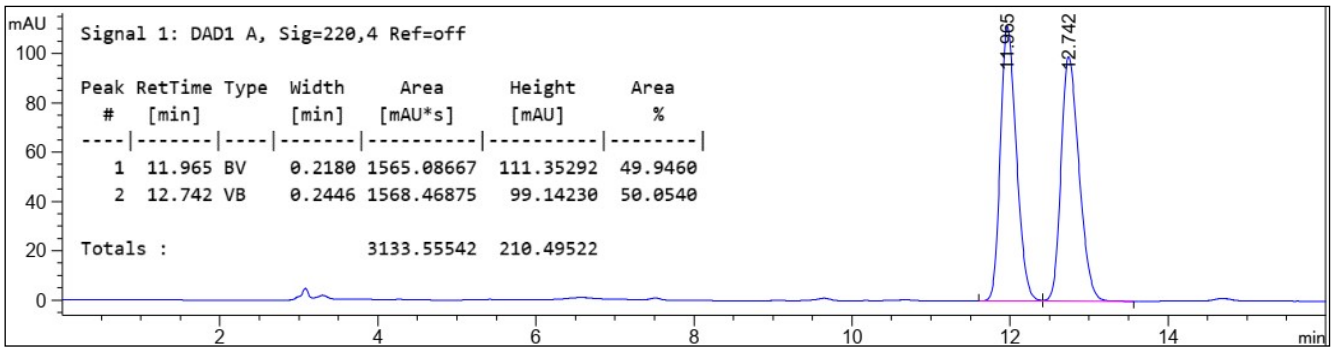
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.96 (ddd, *J* = 16.7, 10.0, 5.9 Hz, 1H), 5.39 (dt, *J* = 17.0, 1.6 Hz, 1H), 5.14 (dt, *J* = 10.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.02 (t, *J* = 6.4 Hz, 1H), 1.07 – 0.97 (m, 1H), 0.58 – 0.49 (m, 2H), 0.48 – 0.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.19, 137.71, 133.01, 115.83, 114.73, 113.80, 86.95, 83.36, 55.26, 39.44, 15.21, 3.37, 2.75.

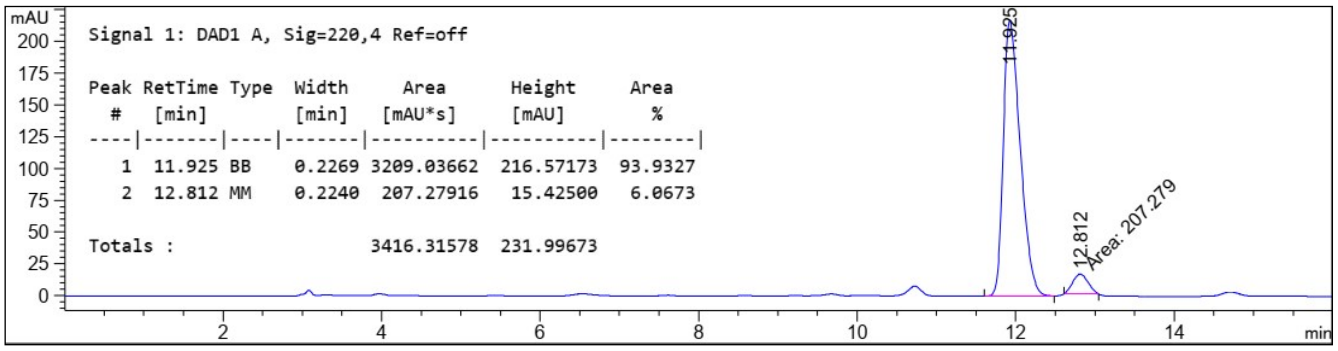
HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{15}H_{17}O]^+$ 213.1274, found 213.1273.

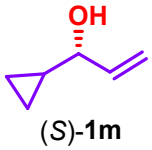
HPLC: Daicel Chiralcel® OD-H, 1% ^{i}PrOH, 99% hexane, 1.0 mL/min, 35 °C, 220 nm; 88% *ee* (t_R (major) = 11.93 min, t_R(minor) = 12.81 min).

Racemic



Enantioenriched



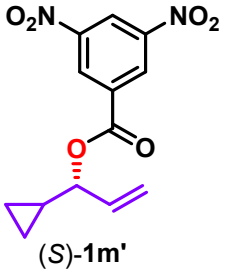


(*S*)-**1m**

Colorless oil. 14.5 mg, 37% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddd, *J* = 17.4, 10.4, 5.8 Hz, 1H), 5.23 (d, *J* = 17.3 Hz, 1H), 5.08 (d, *J* = 10.5 Hz, 1H), 3.45 (t, *J* = 6.9 Hz, 1H), 2.01 (s, 1H), 1.01 – 0.90 (m, 1H), 0.56 – 0.45 (m, 2H), 0.38 – 0.28 (m, 1H), 0.28 – 0.18 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.73, 114.64, 77.21, 17.35, 3.13, 2.04.



(*S*)-**1m'**

White solid. 31.5 mg, 73% yield. mp 77.1 – 78.1 °C. **[α]$^{20}_D$**: +0.8 (*c* = 0.5, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (t, *J* = 2.1 Hz, 1H), 9.19 (d, *J* = 2.1 Hz, 2H), 5.99 (ddd, *J* = 17.1, 10.5, 6.4 Hz, 1H), 5.41 (d, *J* = 17.1 Hz, 1H), 5.30 (d, *J* = 10.5 Hz, 1H), 5.06 – 4.97 (m, 1H), 1.33 – 1.24 (m, 1H), 0.76 – 0.62 (m, 2H), 0.57 – 0.49 (m, 1H), 0.48 – 0.41 (m, 1H).

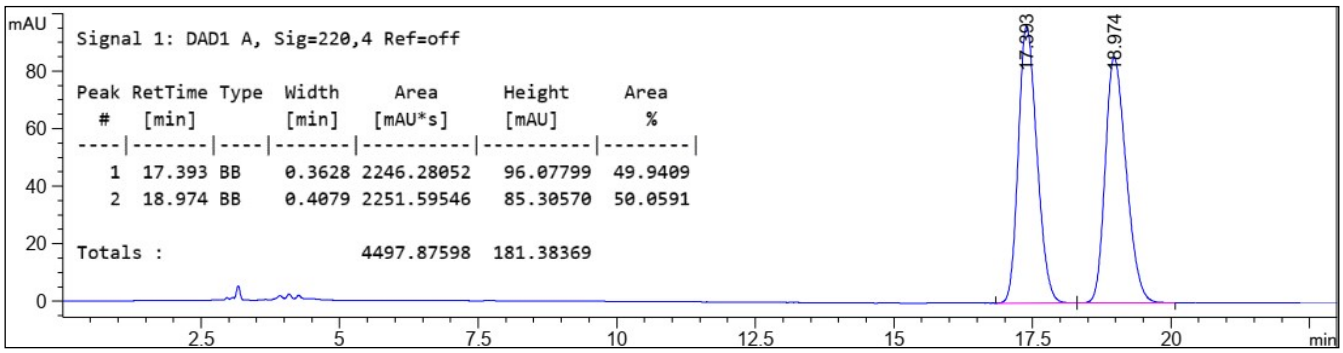
^{13}C NMR (100 MHz, $CDCl_3$) δ 161.90, 148.66, 134.40, 129.52, 122.29, 118.27, 82.29, 14.59, 4.03, 2.92.

HRMS (ESI): $[M-H]^-$ Calcd. for $[C_{13}H_{11}N_2O_6]^-$ 291.0623, found 291.0622.

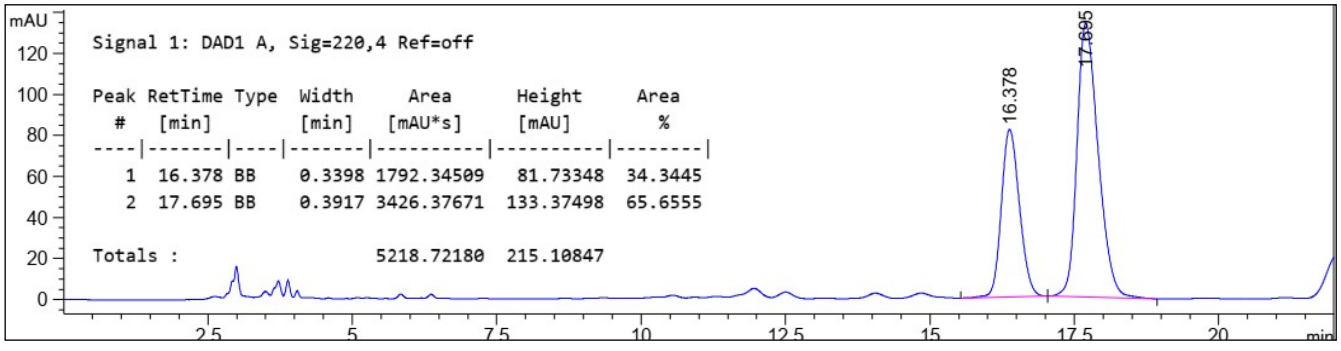
IR (neat): 3105, 2922, 2855, 1720, 1630, 1543, 1460, 1429, 1342, 1277, 1200, 1165, 1074, 1032, 989, 934, 920, 889, 820, 775, 717, 681 cm^{-1}.

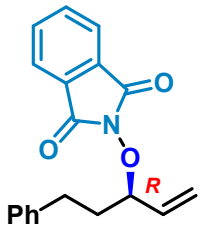
HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 35 °C, 220 nm; 31% *ee* (t_R (major) = 17.70 min, t_R(minor) = 16.38 min).

Racemic



Enantioenriched





(*R*)-5

Colorless oil. 103.3 mg, 84% yield. **[α]$^{20}_{D}$**: +51.4 (*c* = 1.0, $CHCl_3$).

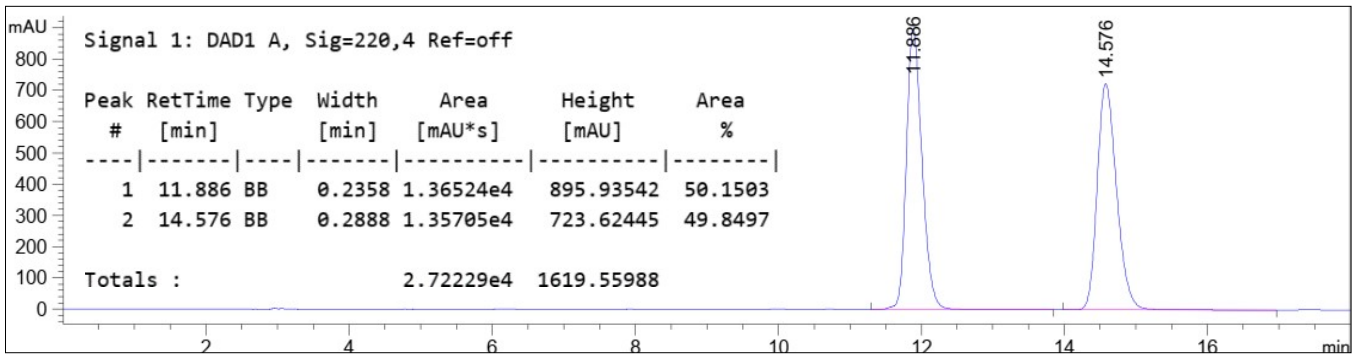
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 –7.72 (m, 2H), 7.68 – 7.64 (m, 2H), 7.25 – 7.17 (m, 4H), 7.15 – 7.11 (m, 1H), 5.95 – 5.86 (m, 1H), 5.19 – 5.10 (m, 2H), 4.62 (dt, *J* = 9.2, 6.6 Hz, 1H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.25 – 2.16 (m, 1H), 1.97 – 1.88 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.98, 141.29, 135.89, 134.36, 128.83, 128.52, 128.45, 126.02, 123.44, 121.66, 88.74, 34.90, 31.33.

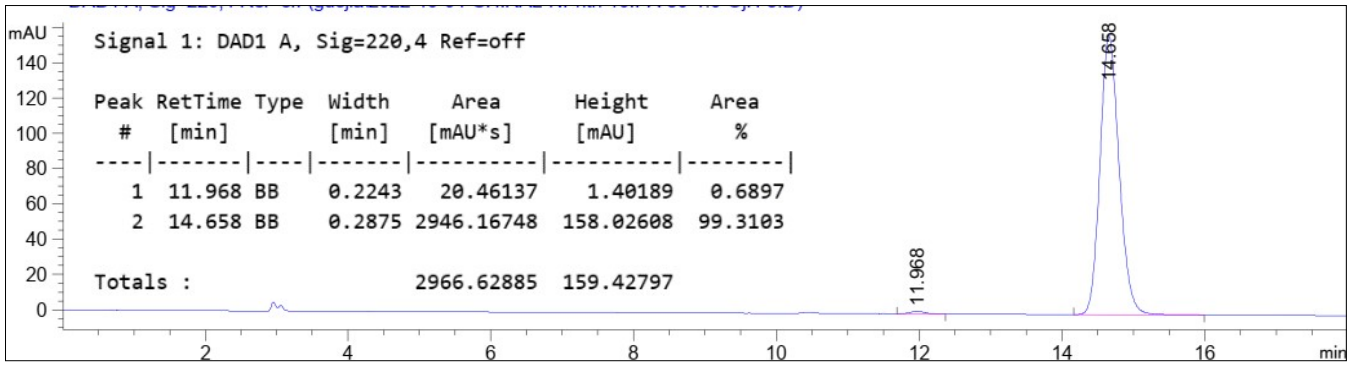
HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{19}H_{18}NO_3]^+$ 308.1282, found 308.1271.

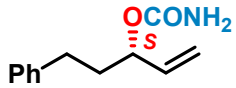
HPLC: Daicel Chiralcel® OJ-H, 10% ^{i}PrOH, 90% hexane, 1.0 mL/min, 30 °C, 220 nm; 99% *ee* (t_R (major) = 14.66 min, t_R(minor) = 11.97 min).

Racemic



Enantioenriched





(*S*)-6

White solid. 69.6 mg, 85% yield. mp: 54.2-55.0°C. $[\alpha]^{20}_{D}$: +3.9 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.19 (m, 2H), 7.13 – 7.10 (m, 3H), 5.80 – 5.71 (m, 1H), 5.21 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.14 – 5.07 (m, 2H), 4.63 (s, 2H), 2.67 – 2.54 (m, 2H), 1.96 – 1.79 (m, 2H).

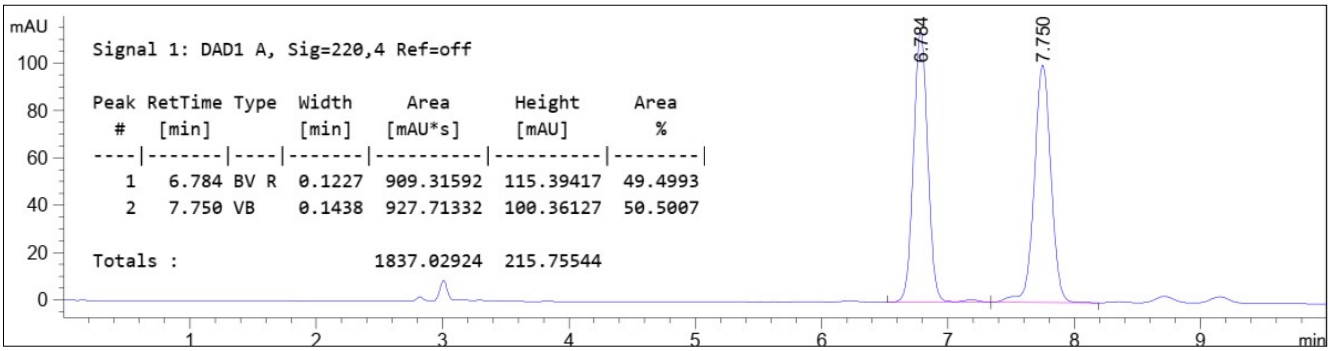
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.30, 141.46, 136.59, 128.43, 128.37, 125.95, 116.62, 75.02, 36.08, 31.41.

HRMS (ESI): $[M+Na]^+$ Calcd. for $[C_{12}H_{15}NO_2Na]^+$ 228.0995, found 228.0992.

IR (neat): 3435, 3342, 3028, 2949, 2860, 2361, 2340, 1705, 1603, 1497, 1454, 1385, 1313, 1219, 1109, 1040, 989, 928, 773, 700 cm^{-1}.

HPLC: Daicel Chiralcel® IA, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 30 °C, 220 nm; >99% *ee* (t_R (major) = 6.77 min).

Racemic



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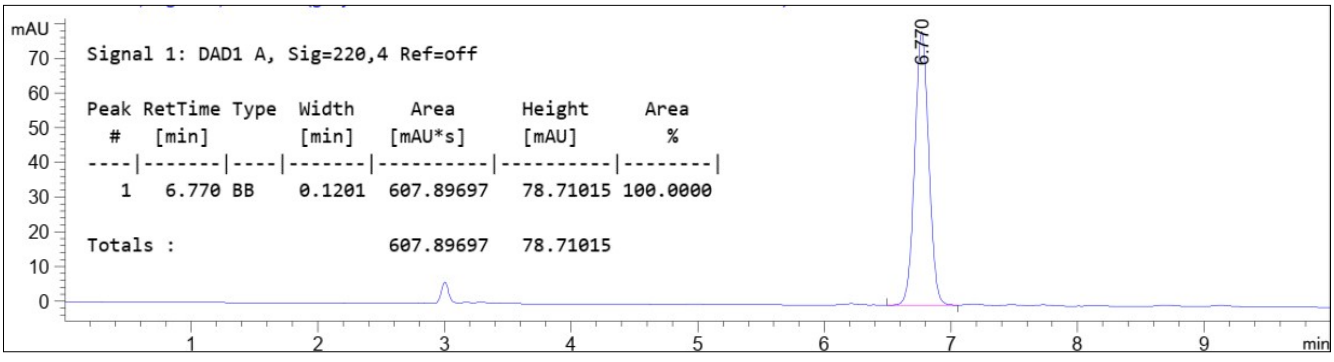
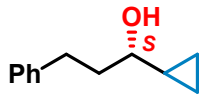




(*S*)-7

Colorless oil. 60.1 mg, 85% yield. **[α]$^{20}_{D}$**: -23.5 (*c* = 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 7.20 – 7.13 (m, 3H), 2.89 – 2.83 (m, 1H), 2.82 – 2.76 (m, 1H), 2.74 –2.66 (m, 1H), 1.93 – 1.87 (m, 2H), 1.58 (s, 1H), 0.96 –0.87 (m, 1H), 0.54 – 0.44 (m, 2H), 0.27 – 0.22 (m, 1H), 0.20 – 0.15 (m, 1H).

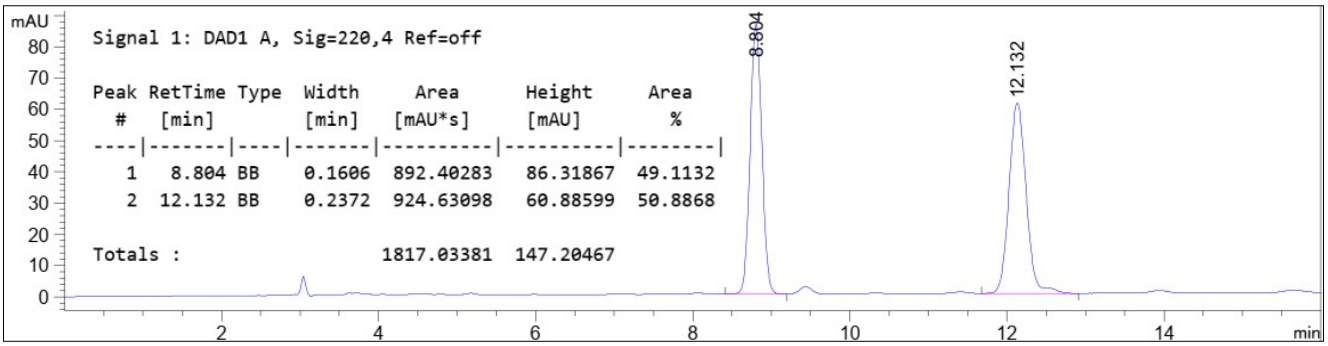
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.26, 128.41, 128.36, 125.75, 76.17, 38.71, 32.05, 18.05, 2.76, 2.58.

HRMS (ESI): $[M+H]^+$ Calcd. for $[C_{12}H_{17}O]^+$ 177.1274, found 177.1273.

IR (neat): 3387, 3081, 3026, 3003, 2926, 2862, 1603, 1497, 1454, 1221, 1074, 1042, 955, 914, 824, 770, 746, 689 cm^{-1}.

HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 30 °C, 220 nm; 99% *ee* (t_R (major) = 8.79 min, t_R(minor) = 12.11 min).

Racemic



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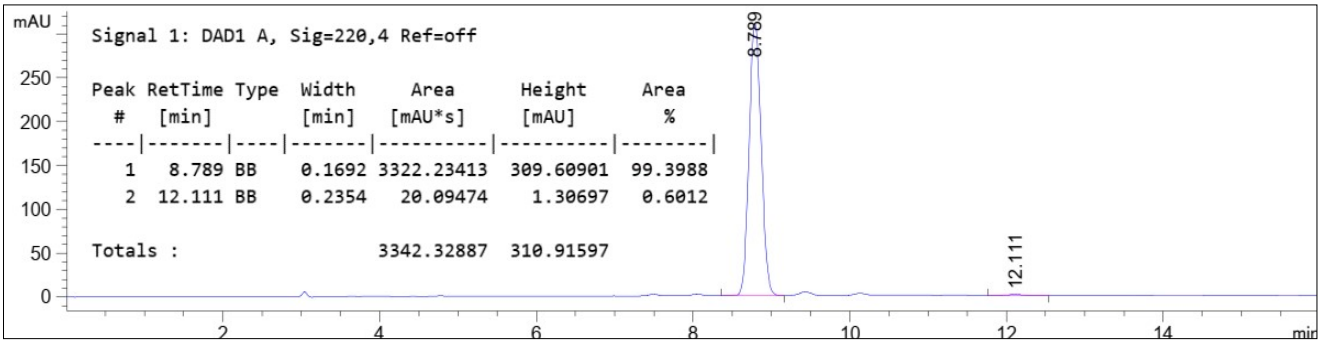
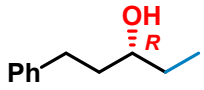




(*R*)-8

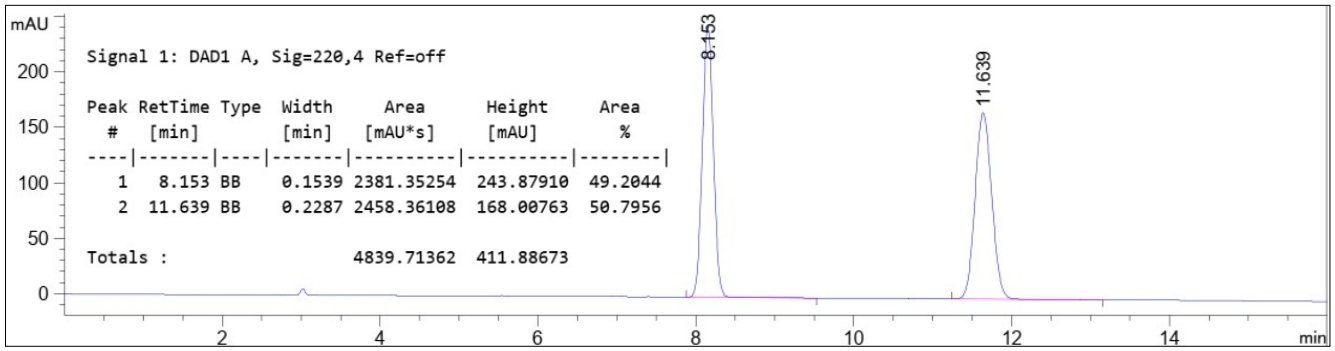
White solid. 63.6 mg, 98% yield. mp: 32.9-33.7 °C. **[α]$^{20}_{D}$**: -20.6 (*c* = 1.0, $CHCl_3$). (lit[7]: **[α]$^{22}_{D}$**: -21.0 (*c* = 1.0, $CHCl_3$)).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.30 – 7.21 (m, 3H), 3.67 – 3.58 (m, 1H), 2.91 – 2.81 (m, 1H), 2.78 – 2.68 (m, 1H), 1.91 – 1.74 (m, 2H), 1.67 – 1.55 (m, 2H), 1.54 – 1.47 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

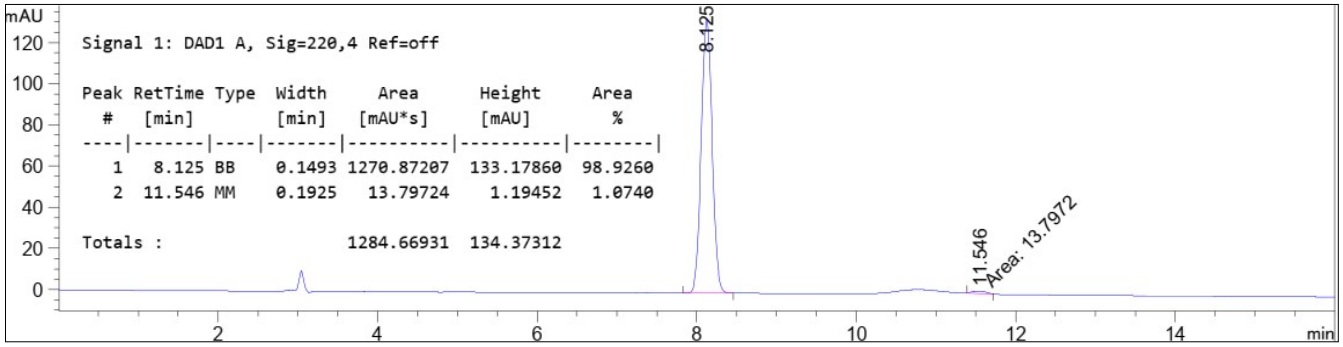
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.22, 128.42, 128.40, 125.80, 72.69, 38.61, 32.09, 30.32, 9.85.

HPLC: Daicel Chiralcel® OD-H, 5% ^{i}PrOH, 95% hexane, 1.0 mL/min, 30 °C, 220 nm; 98% *ee* (t_R (major) = 8.13 min, t_R(minor) = 11.55 min).

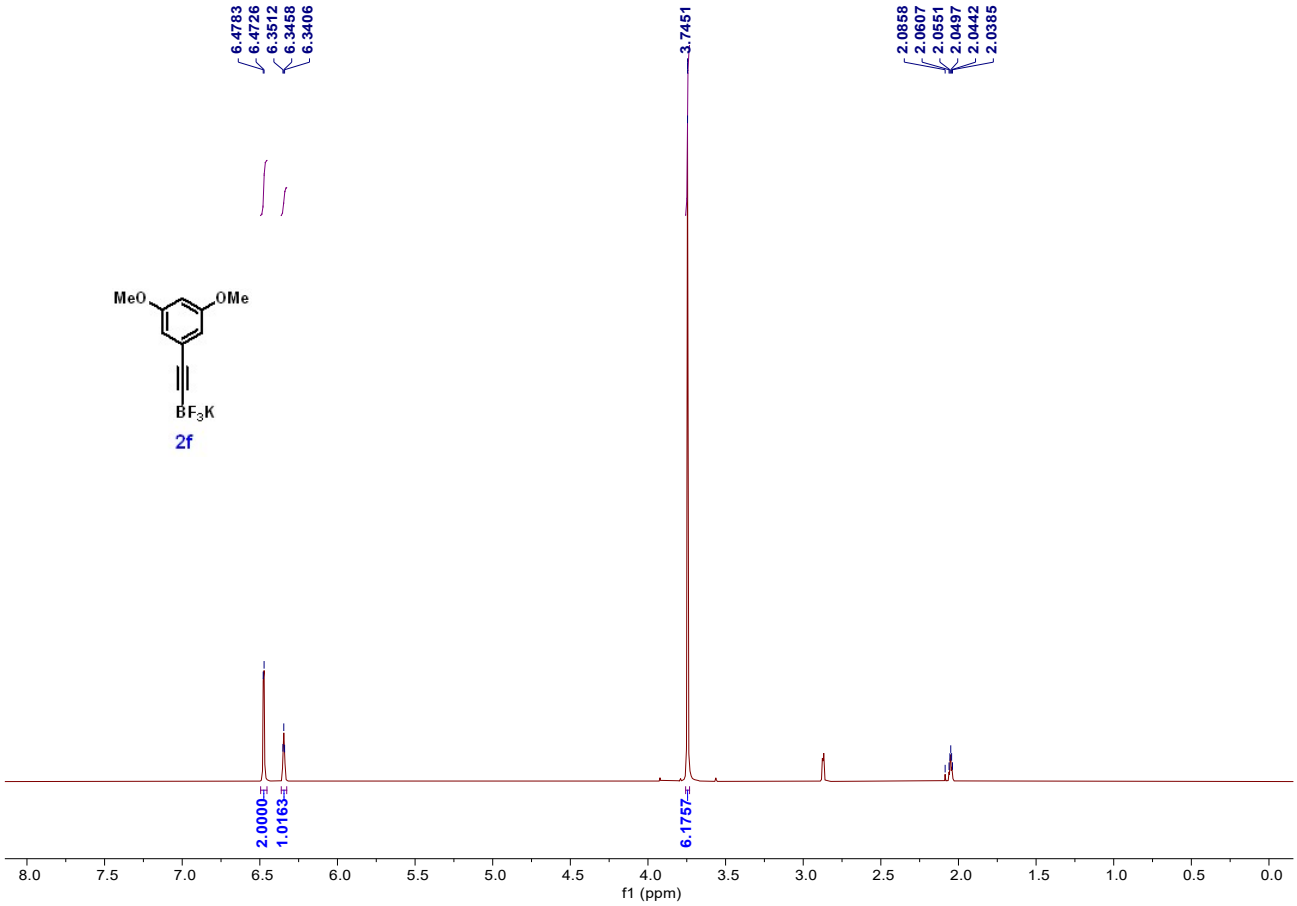
Racemic



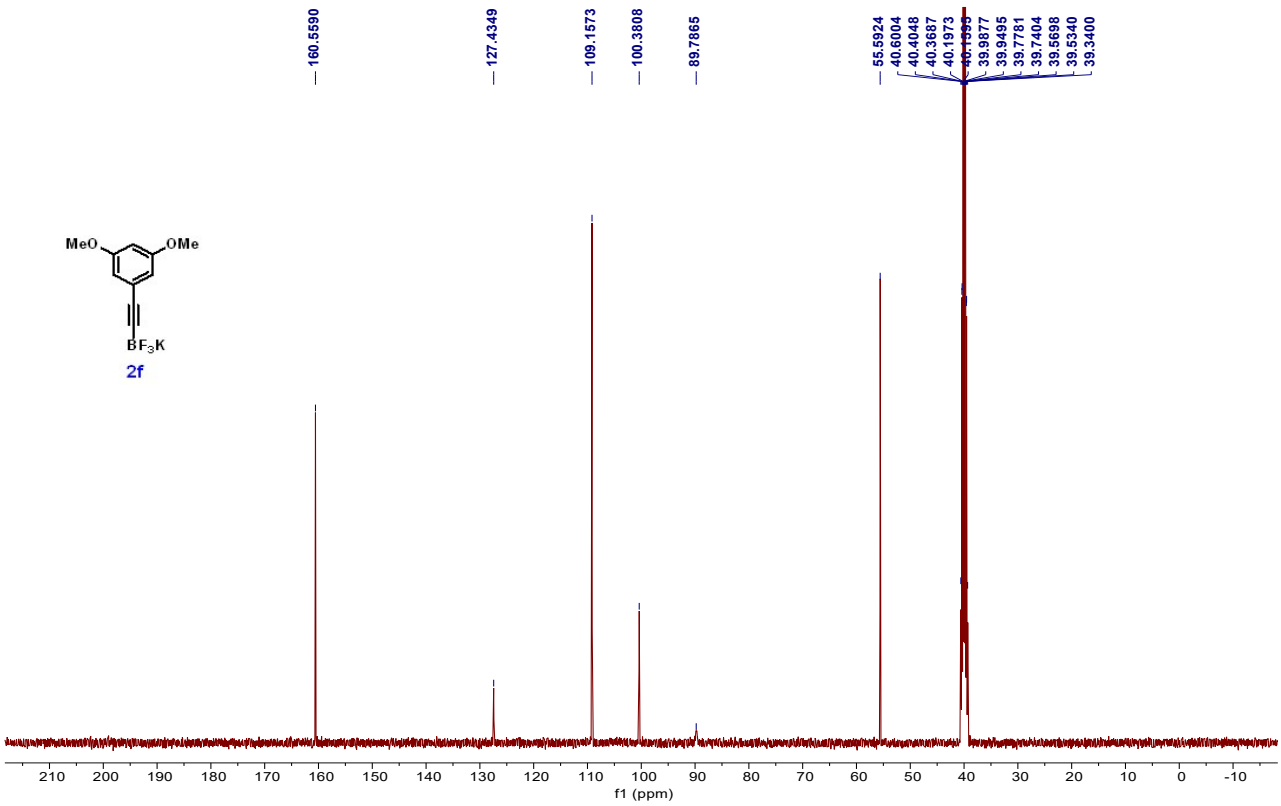
Enantioenriched



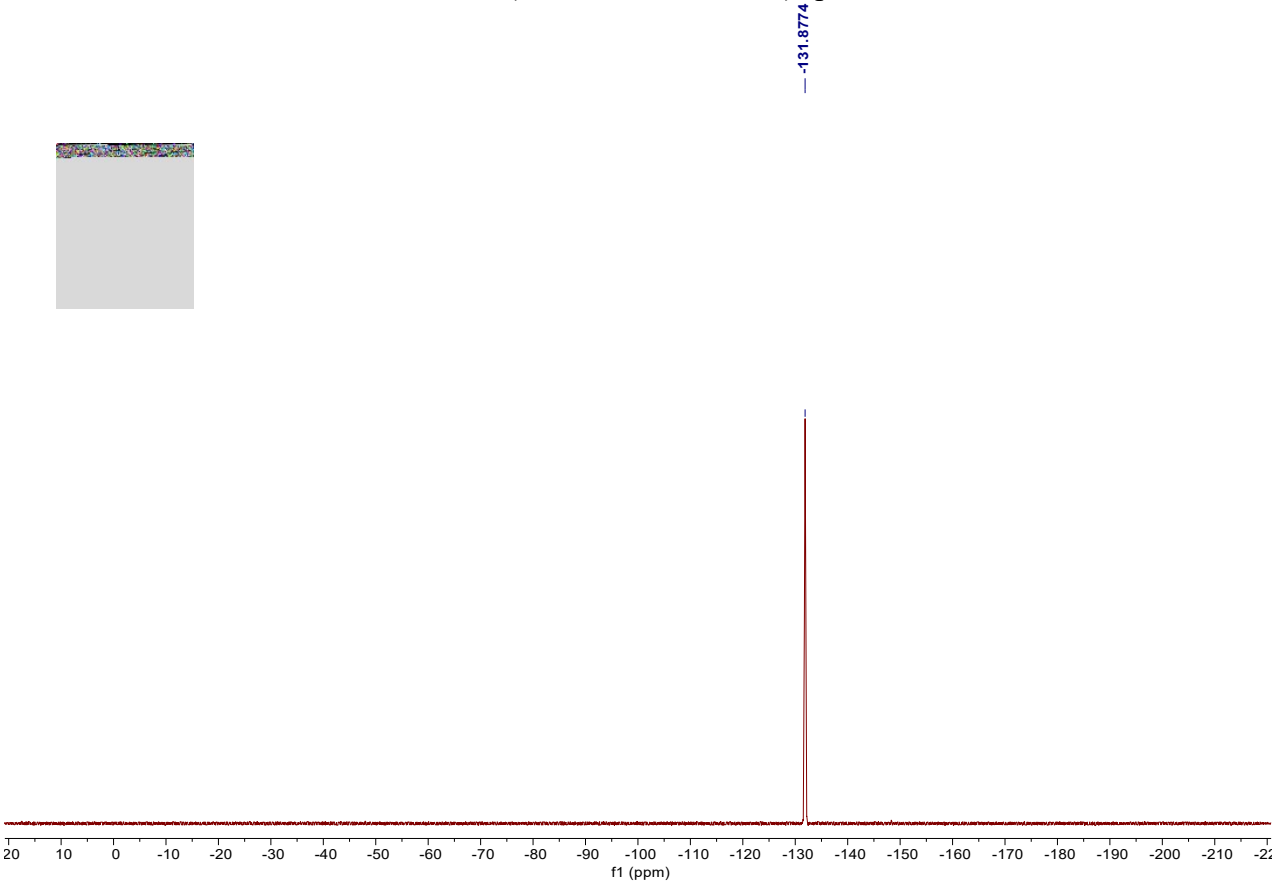
NMR Spectra



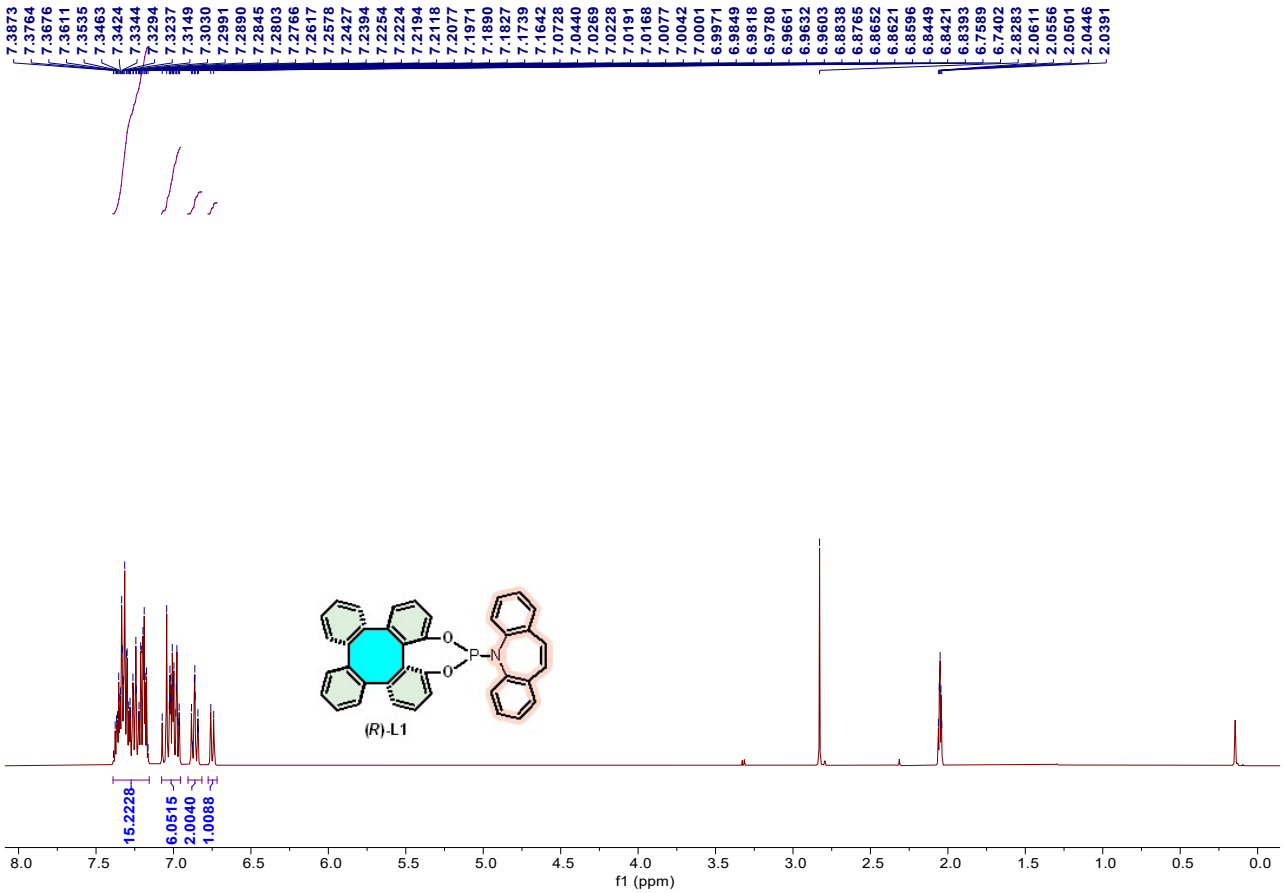
^{1}H NMR (400 MHz, Acetone-d_6) spectrum of **2f**



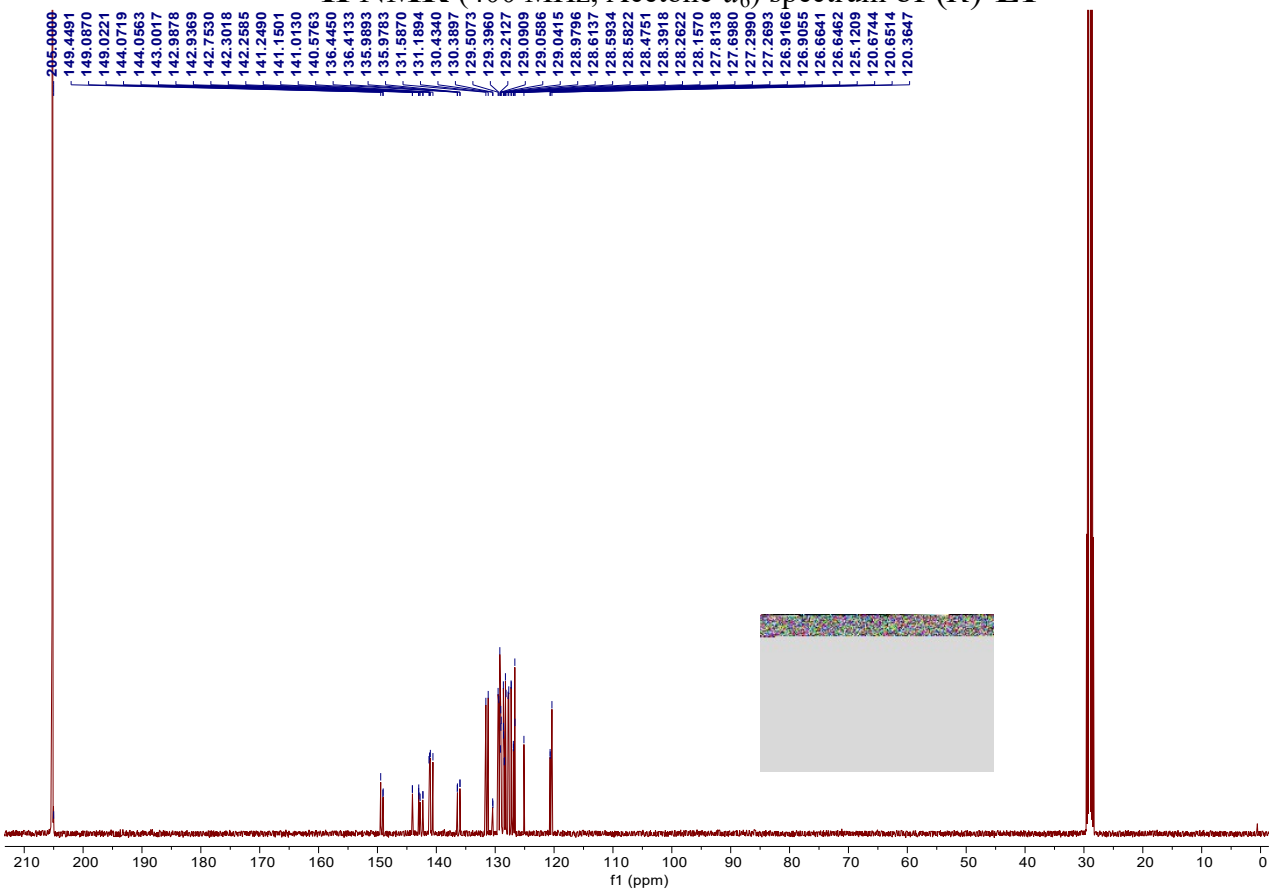
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **2f**



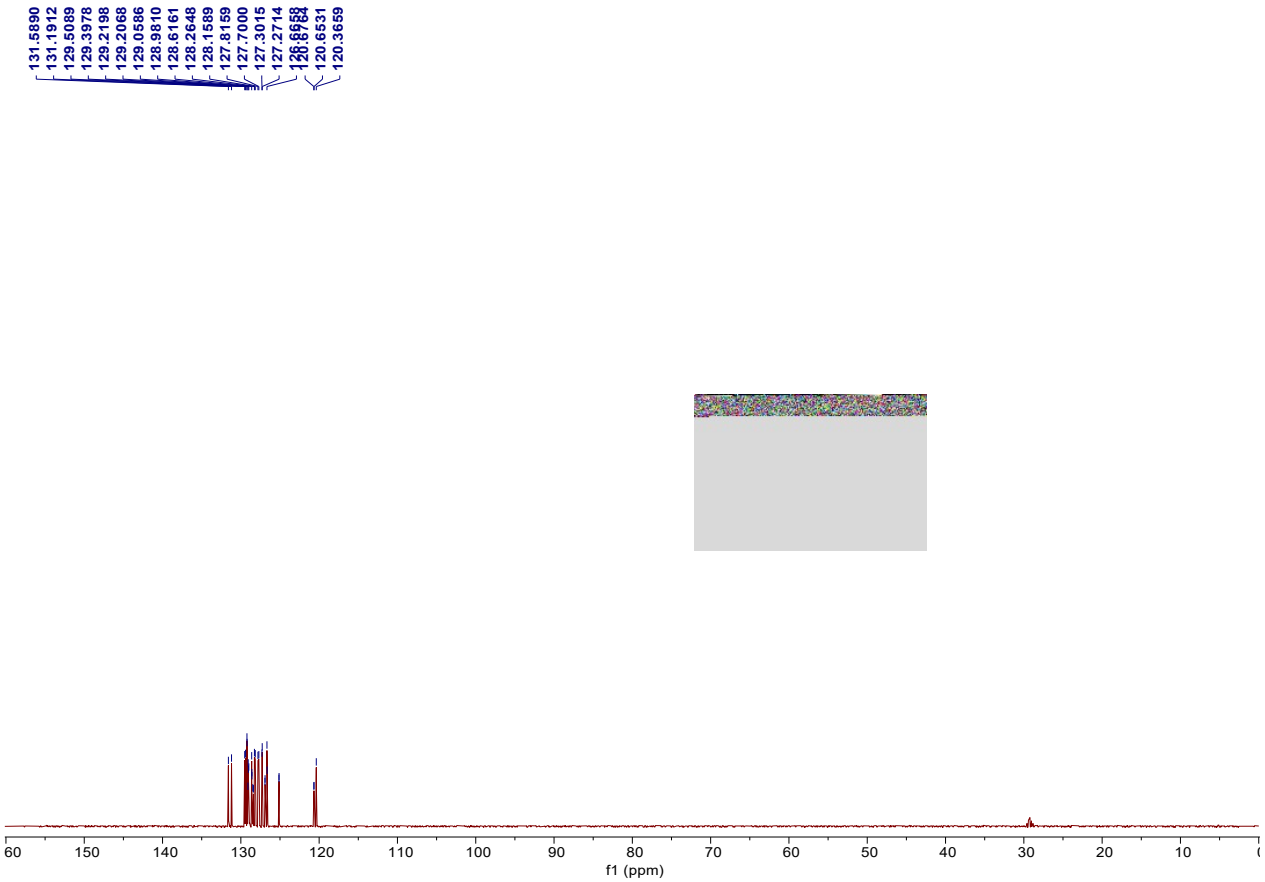
^{19}F NMR (376 MHz; DMSO-d_6) spectrum of **2f**



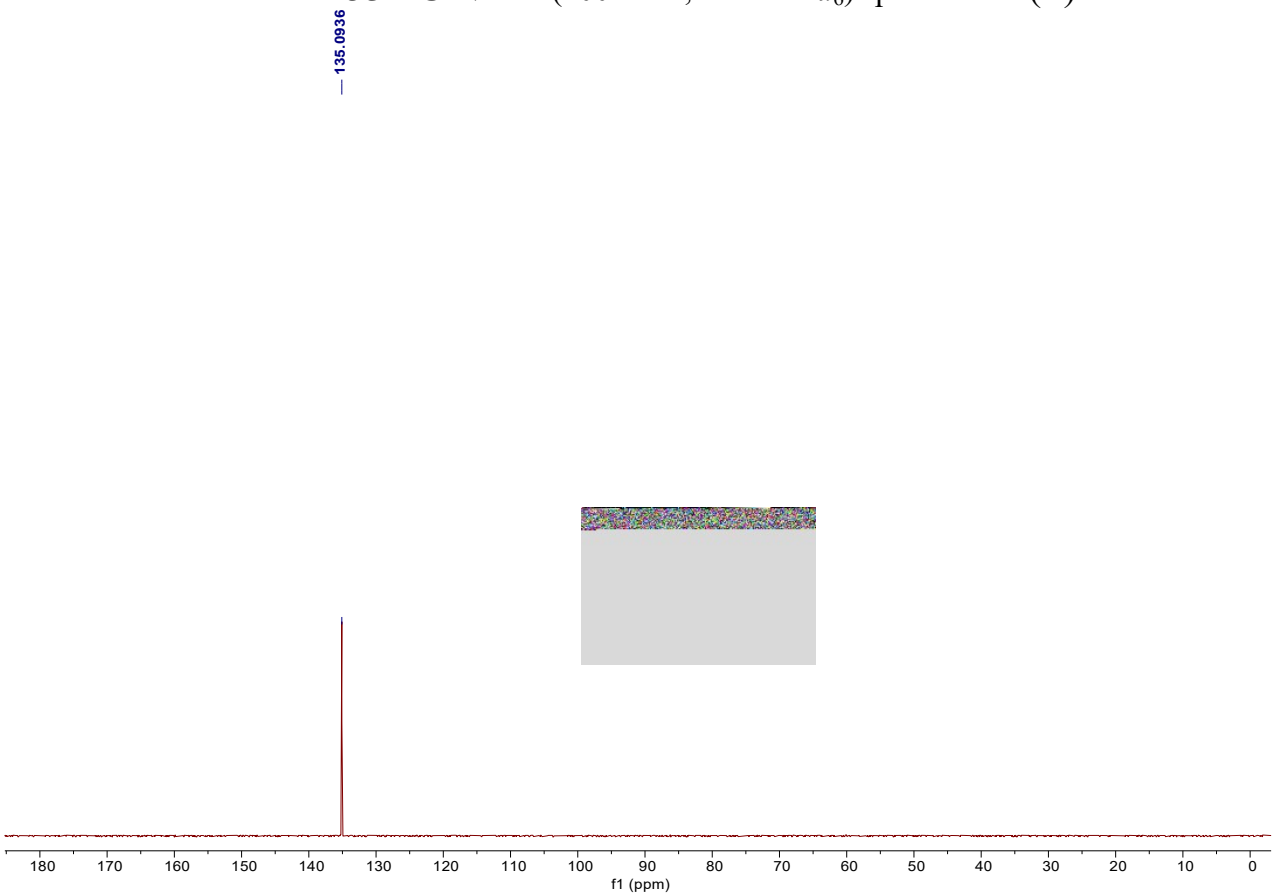
^{1}H NMR (400 MHz, Acetone-d_6) spectrum of (*R*)-**L1**



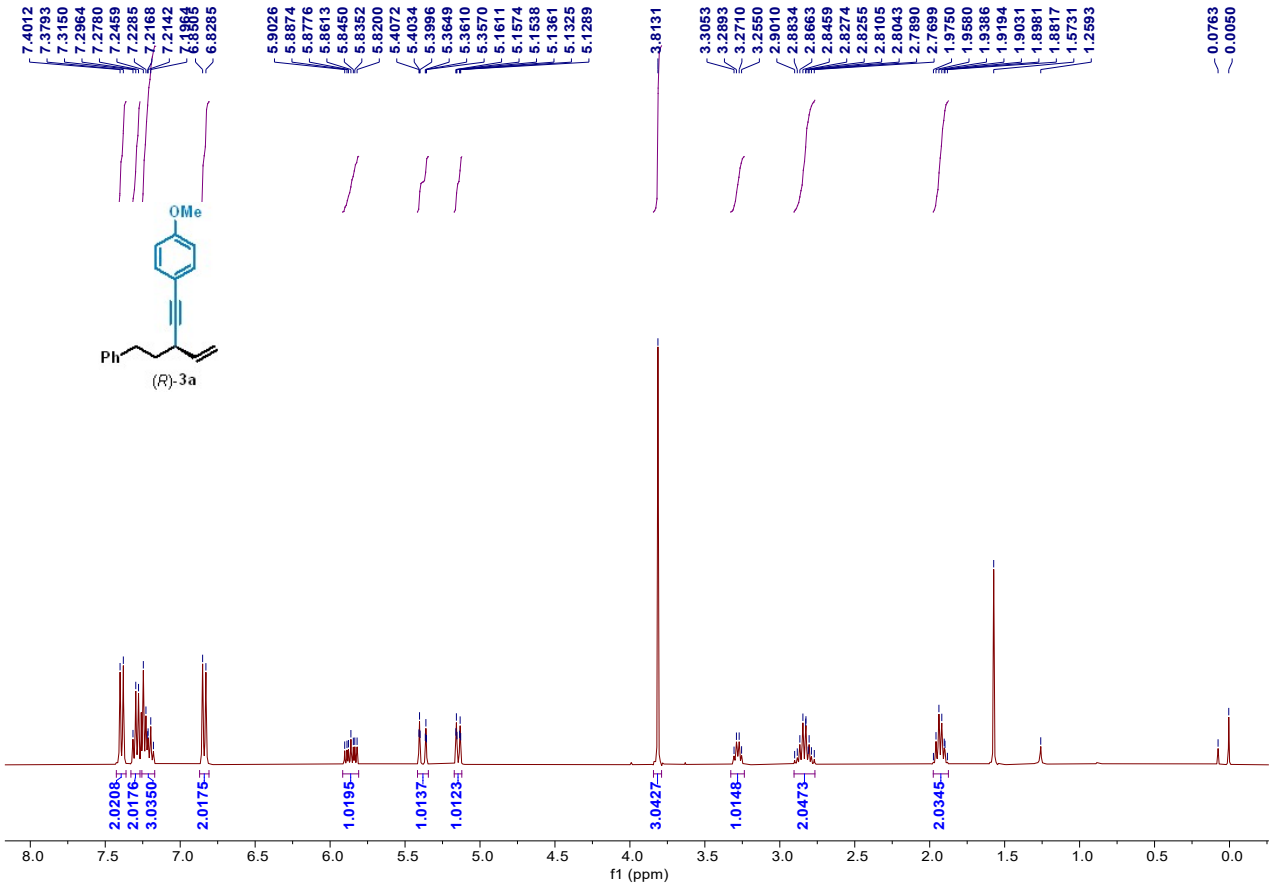
^{13}C NMR (100 MHz, Acetone-d_6) spectrum of (*R*)-**L1**



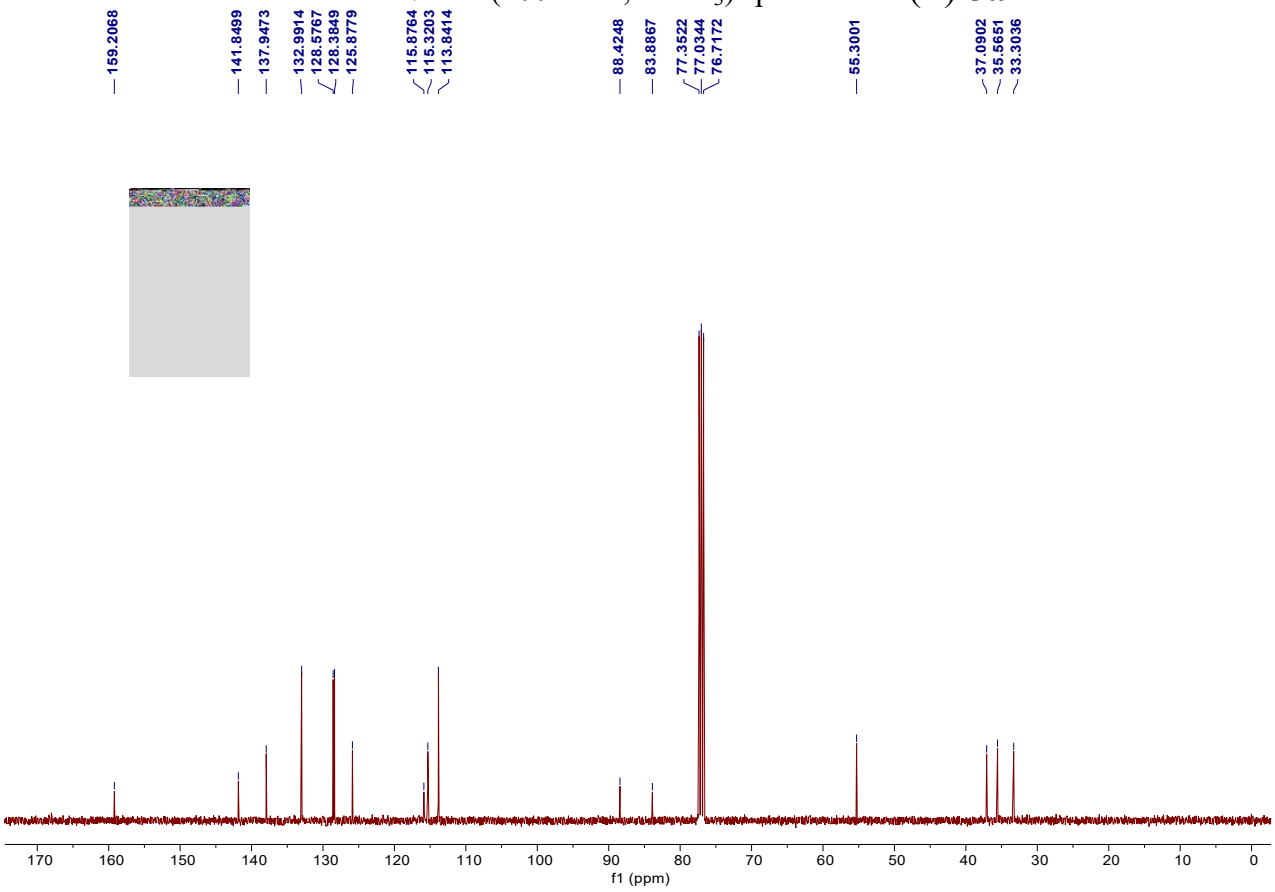
DEPT-135 ^{13}C NMR (100 MHz, Acetone-d_6) spectrum of (*R*)-**L1**



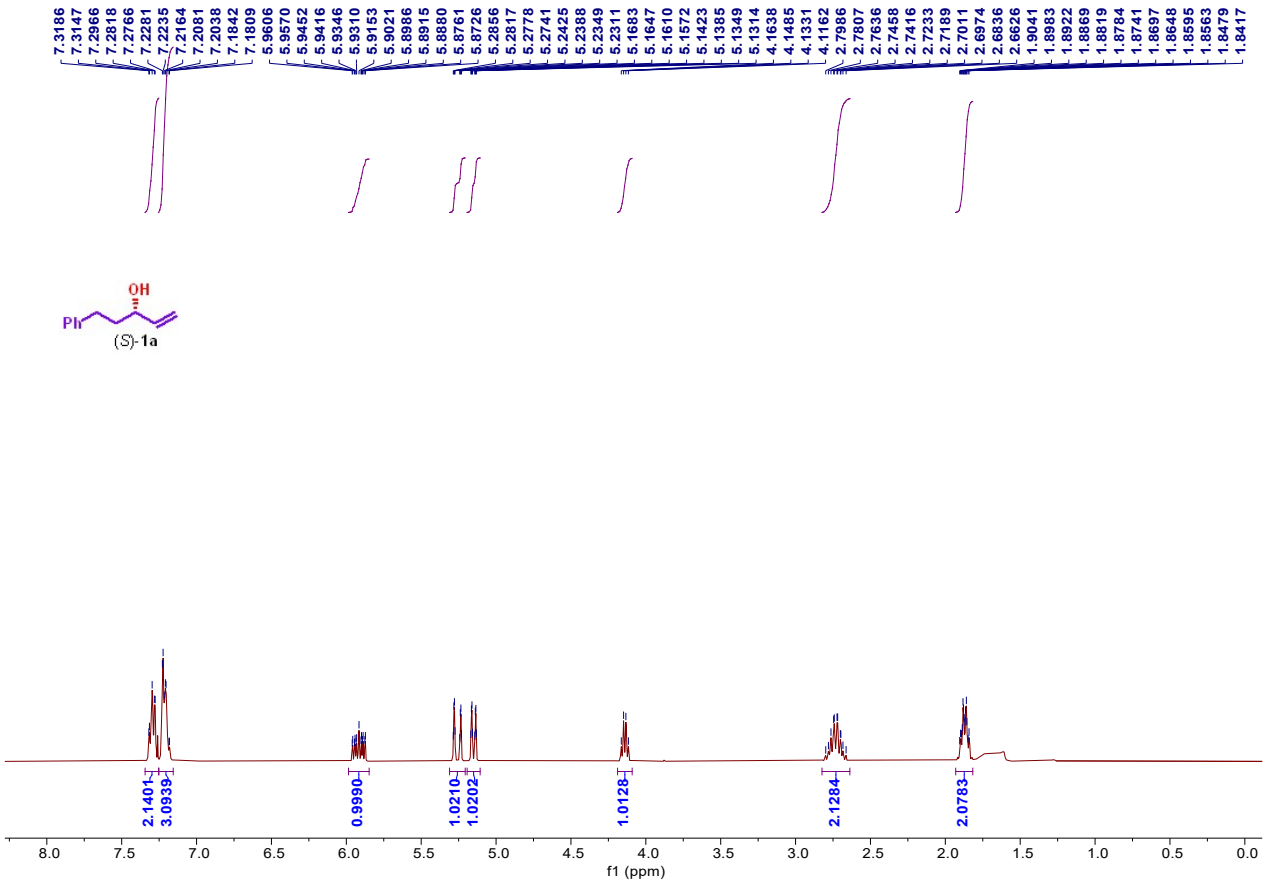
^{31}P NMR (162 MHz, Acetone-d_6) spectrum of (*R*)-**L1**



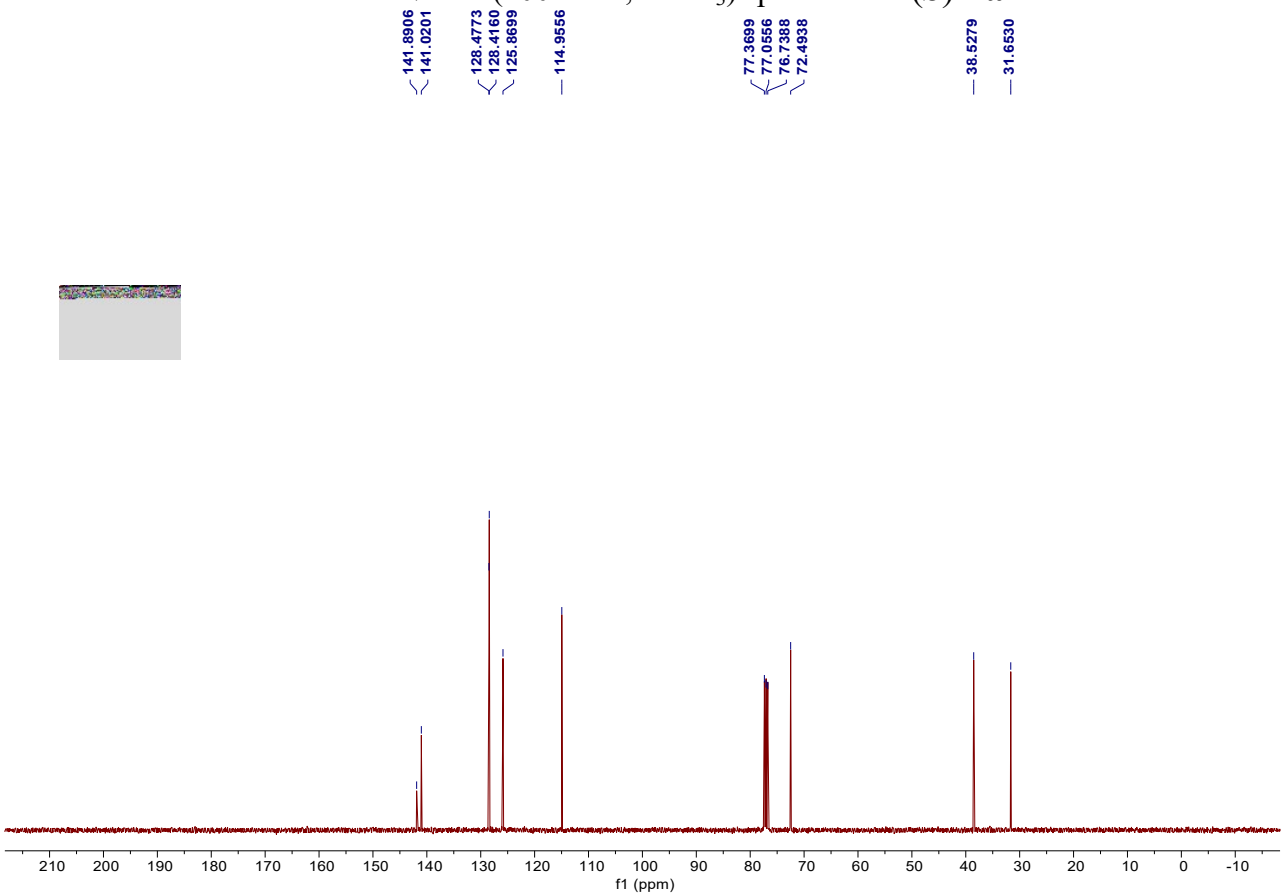
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3a**



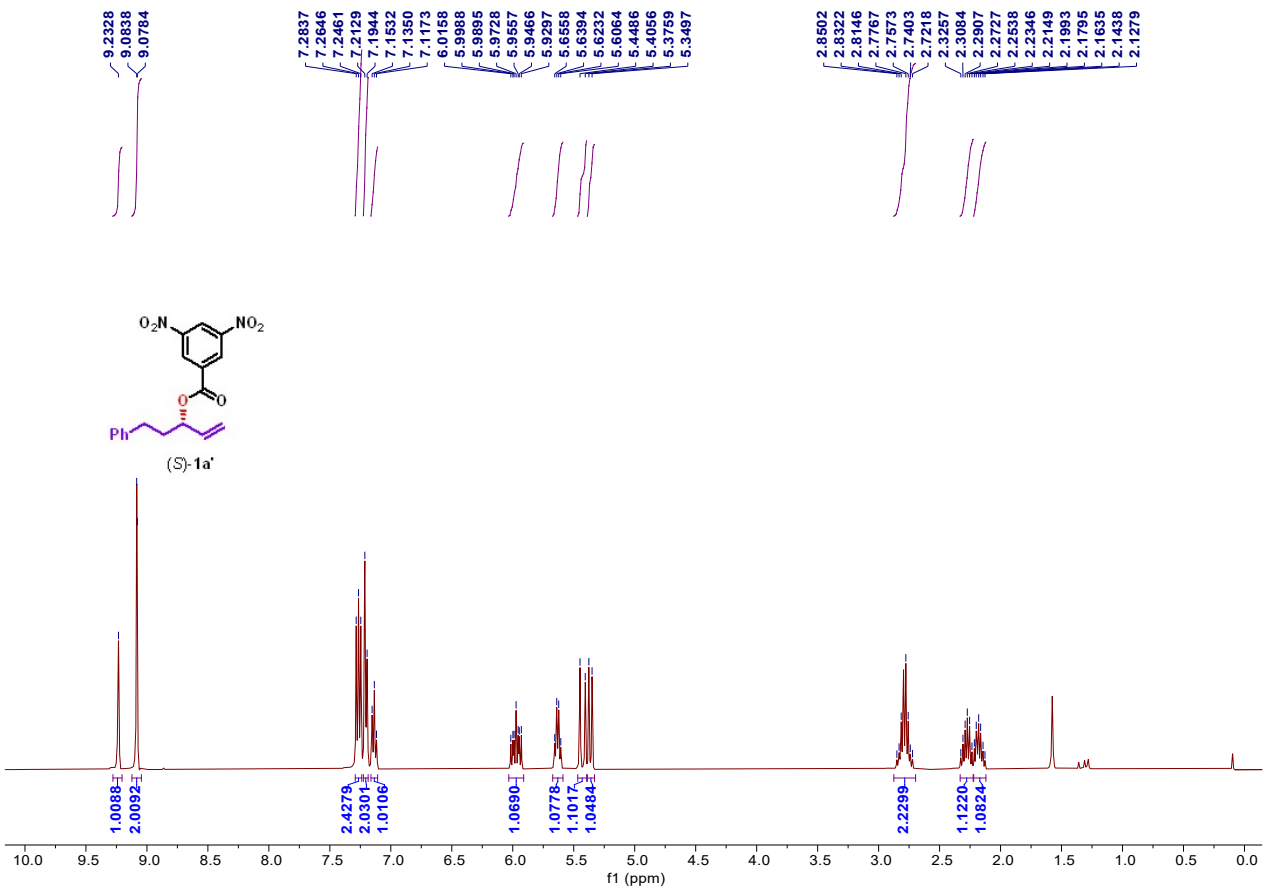
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3a**



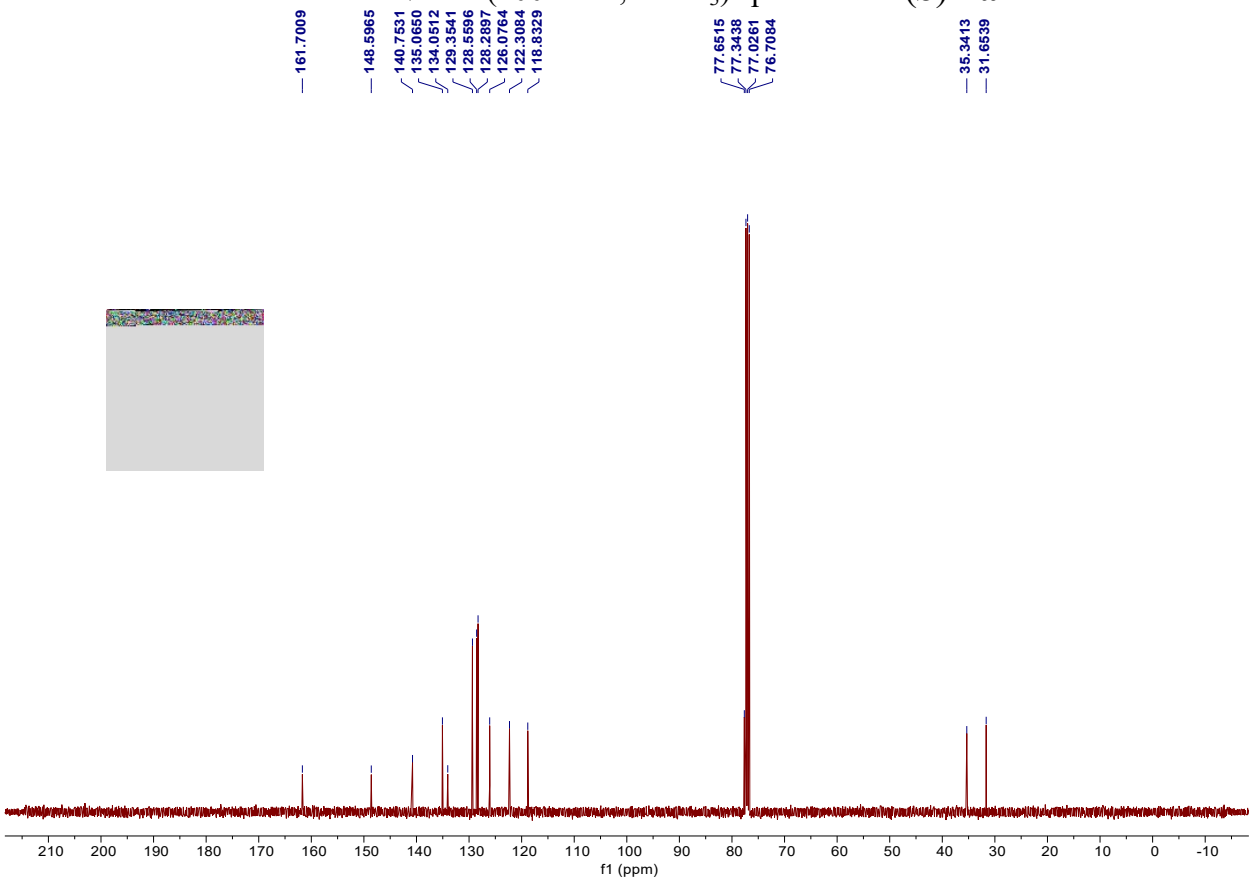
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1a**



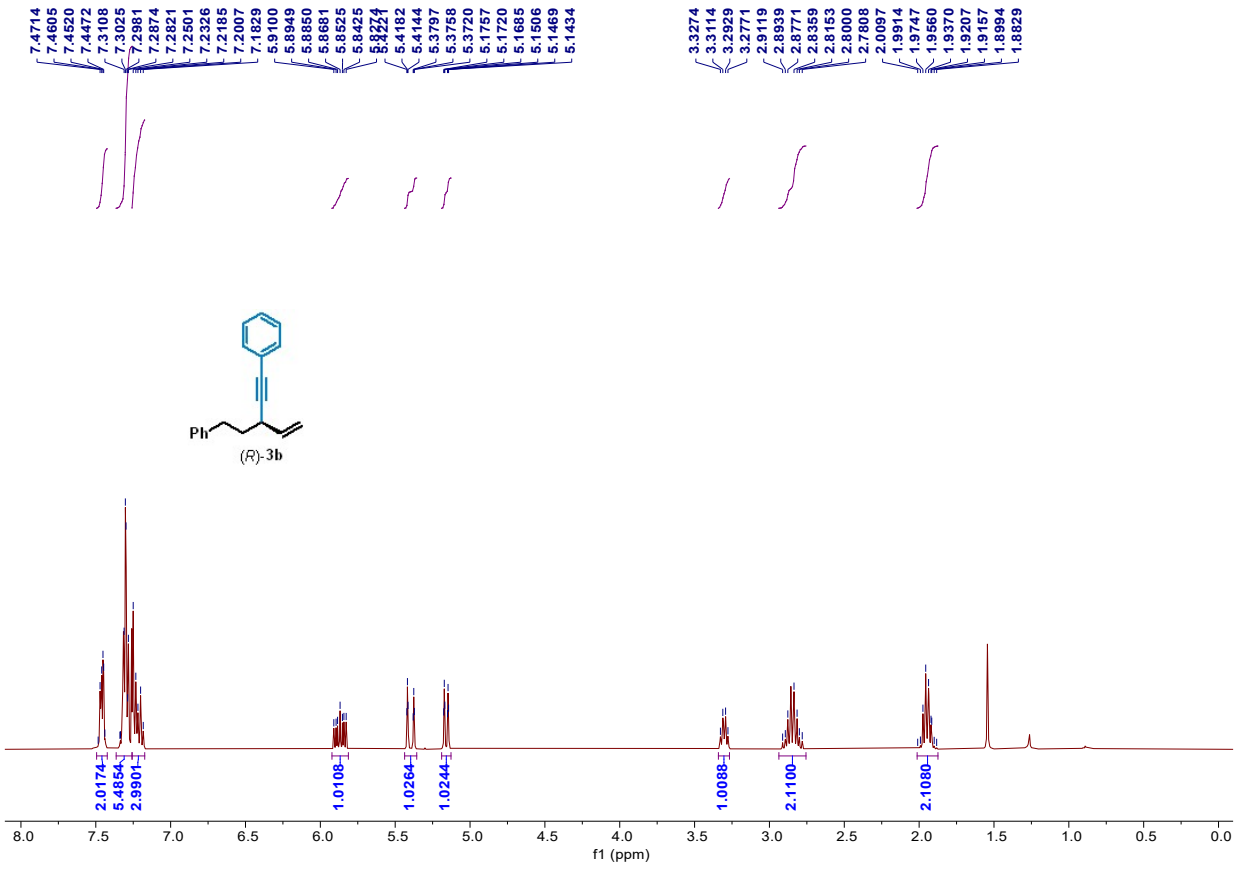
^{13}C NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1a**



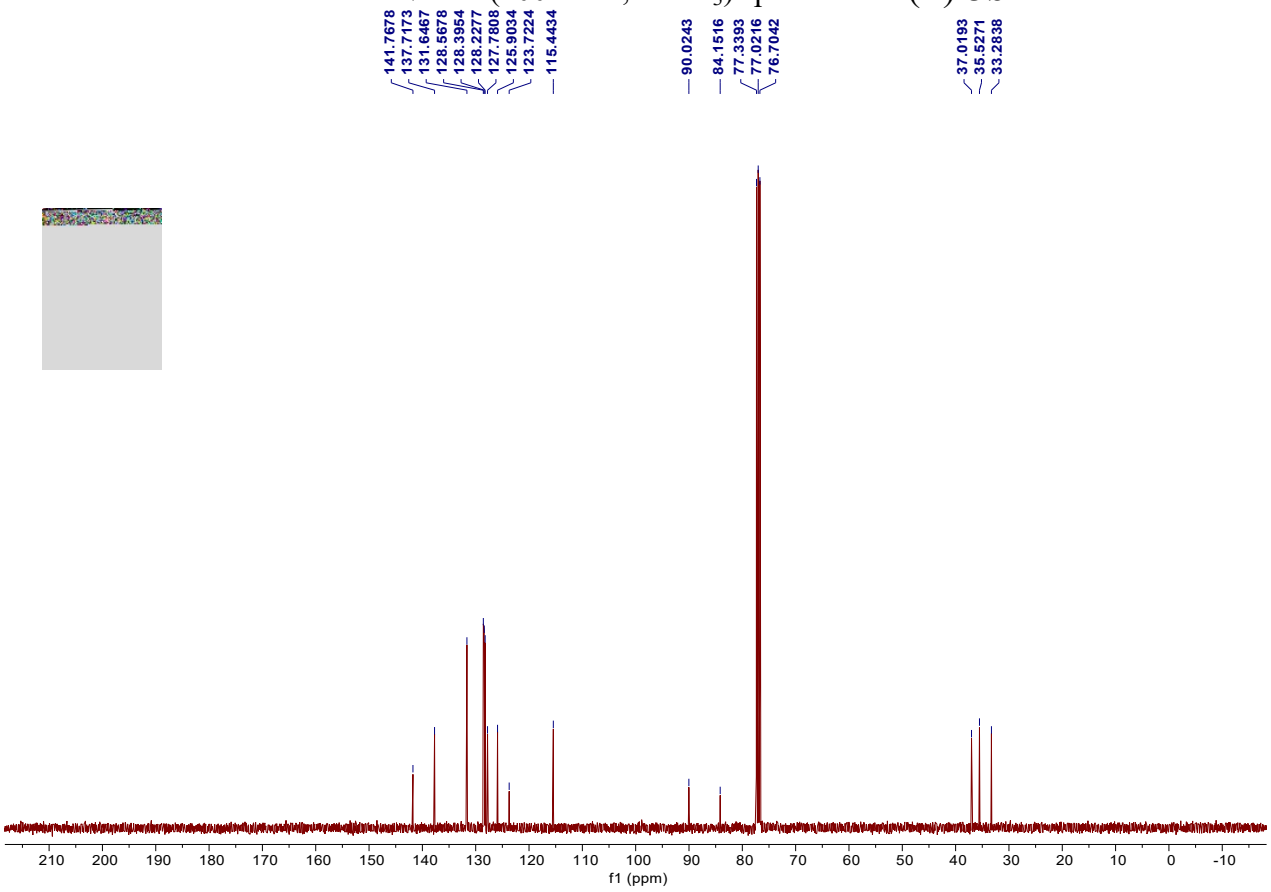
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1a'**



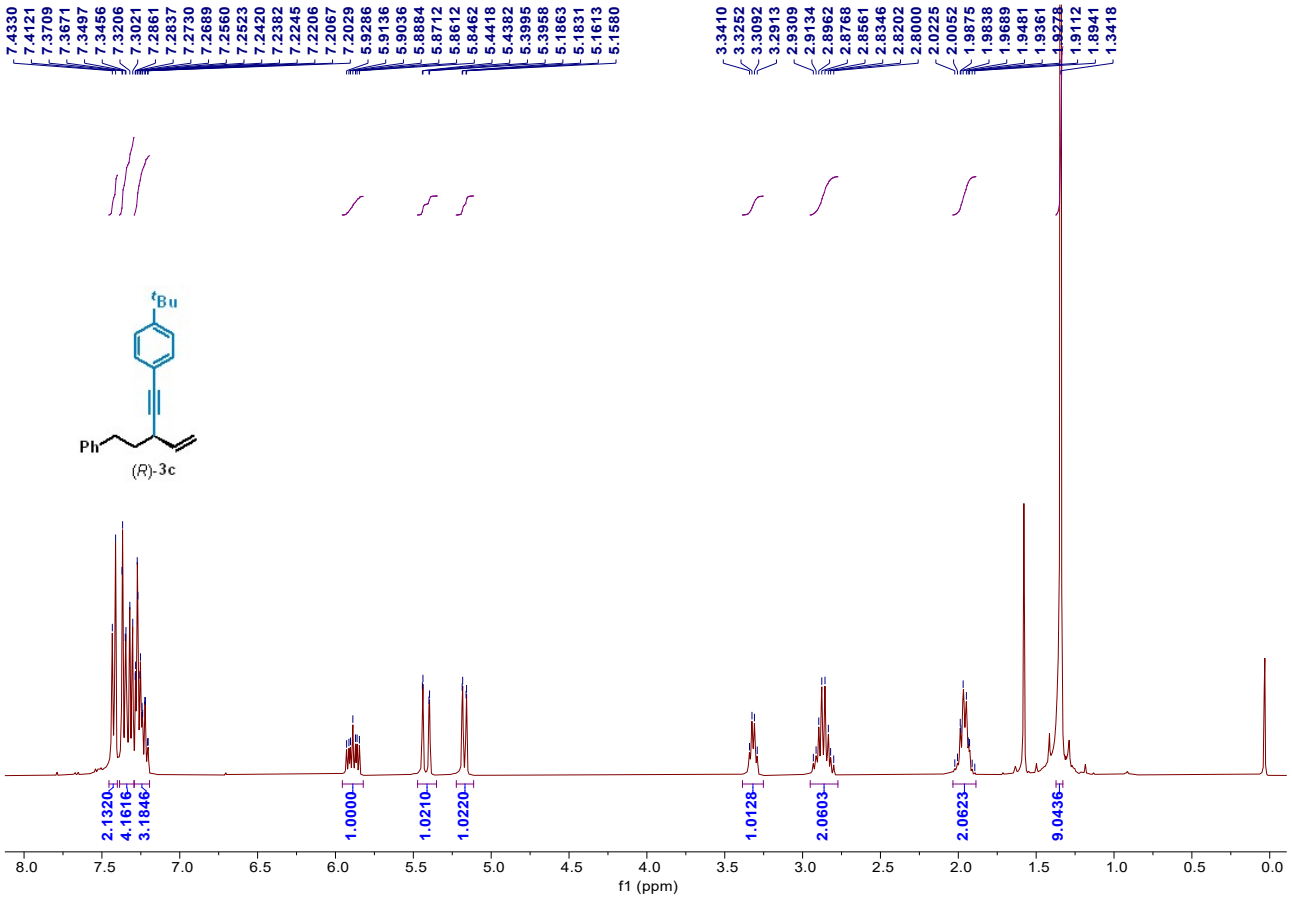
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1a'**



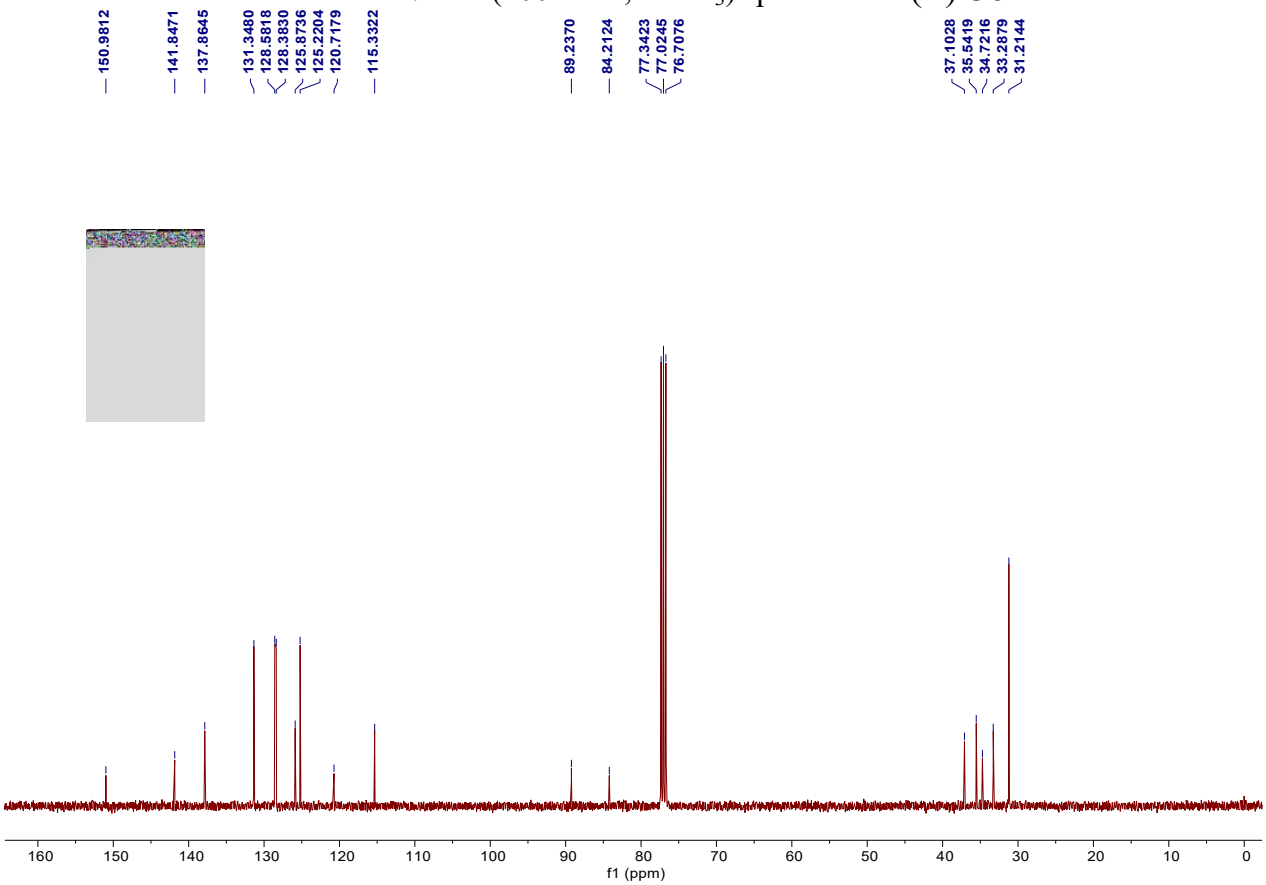
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3b**



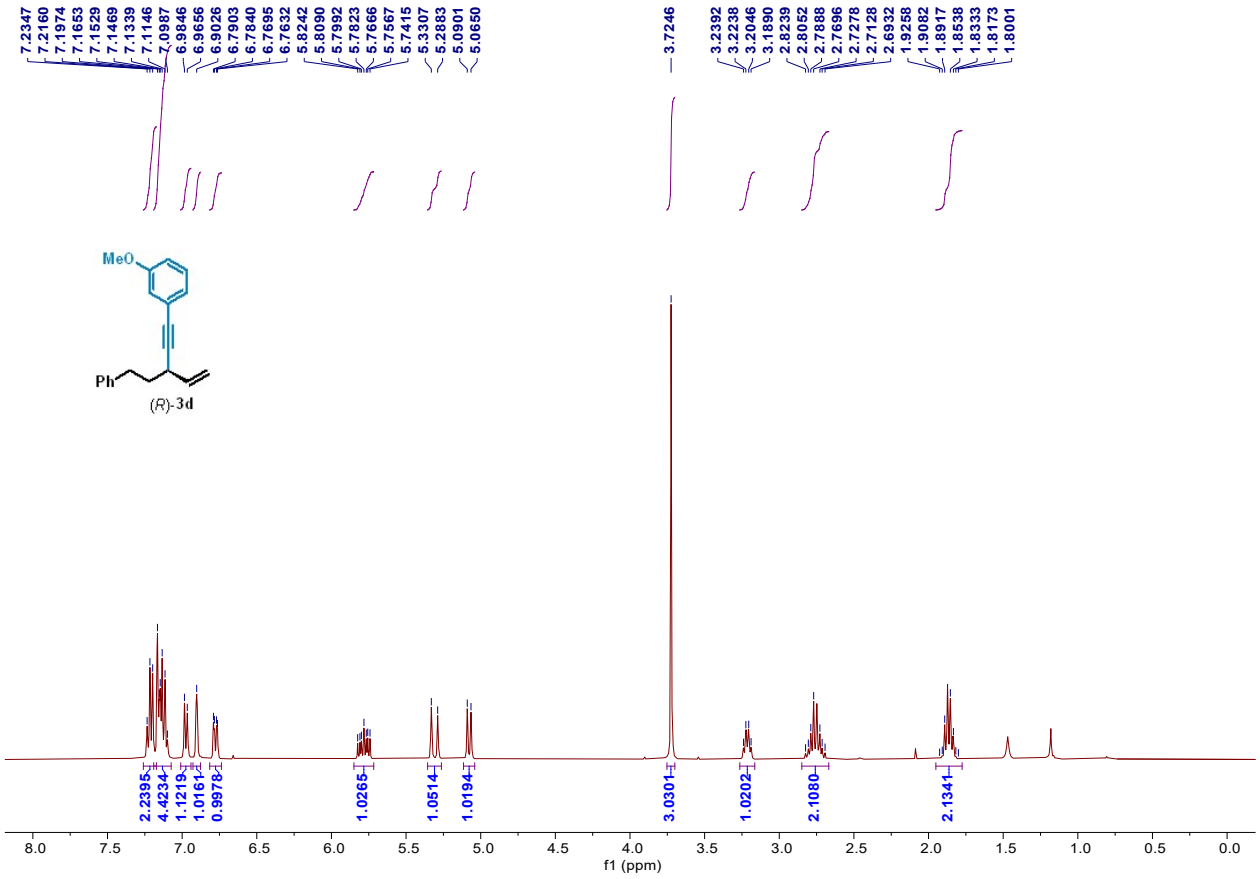
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3b**



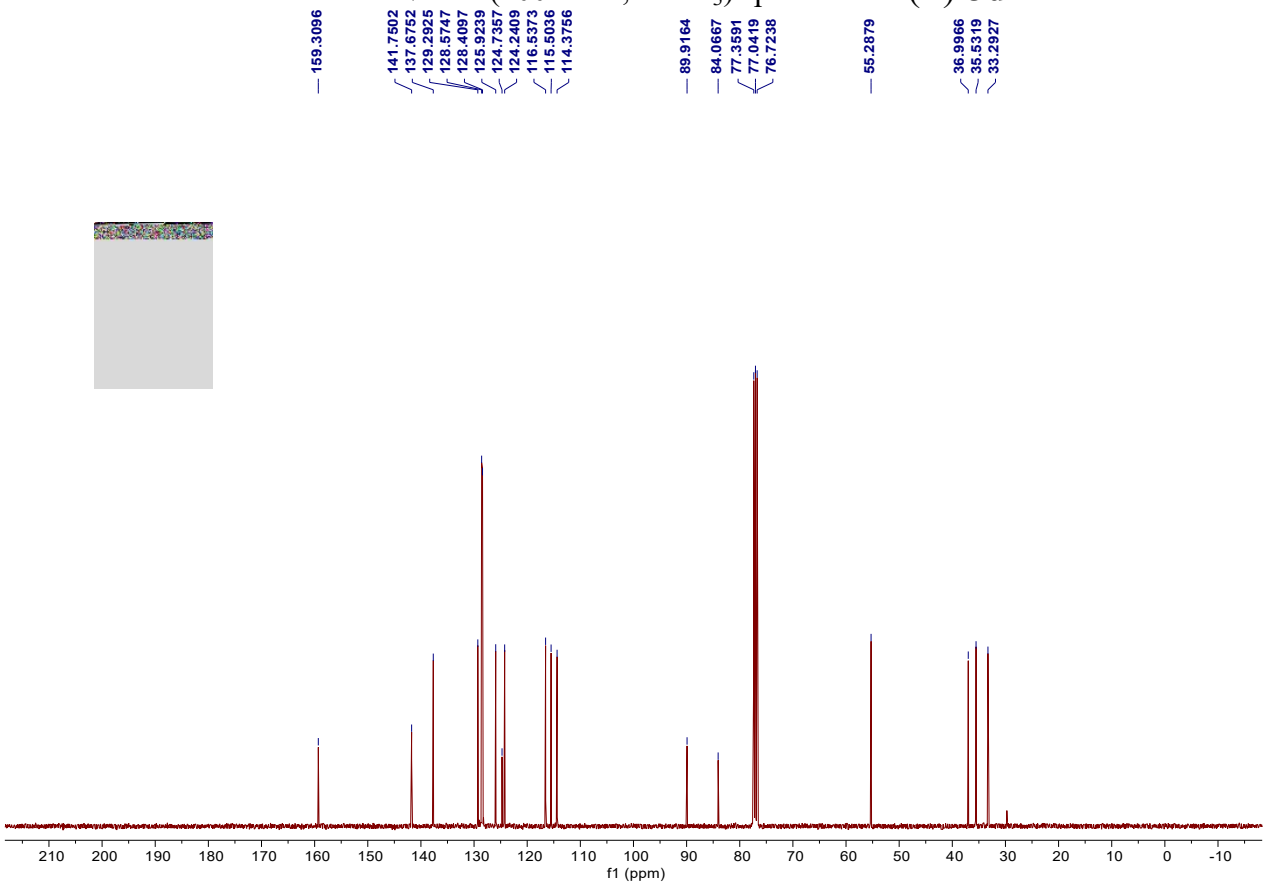
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3c**



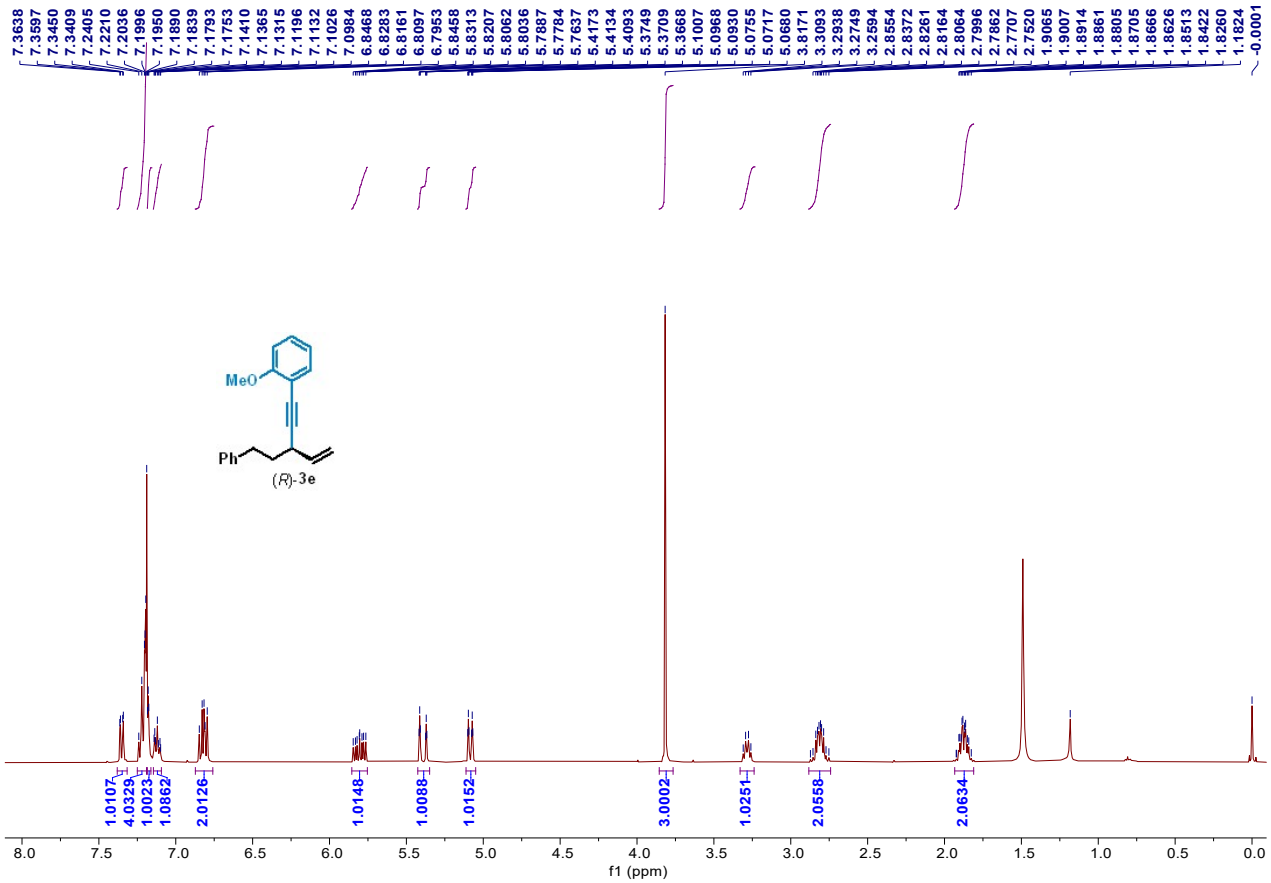
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3c**



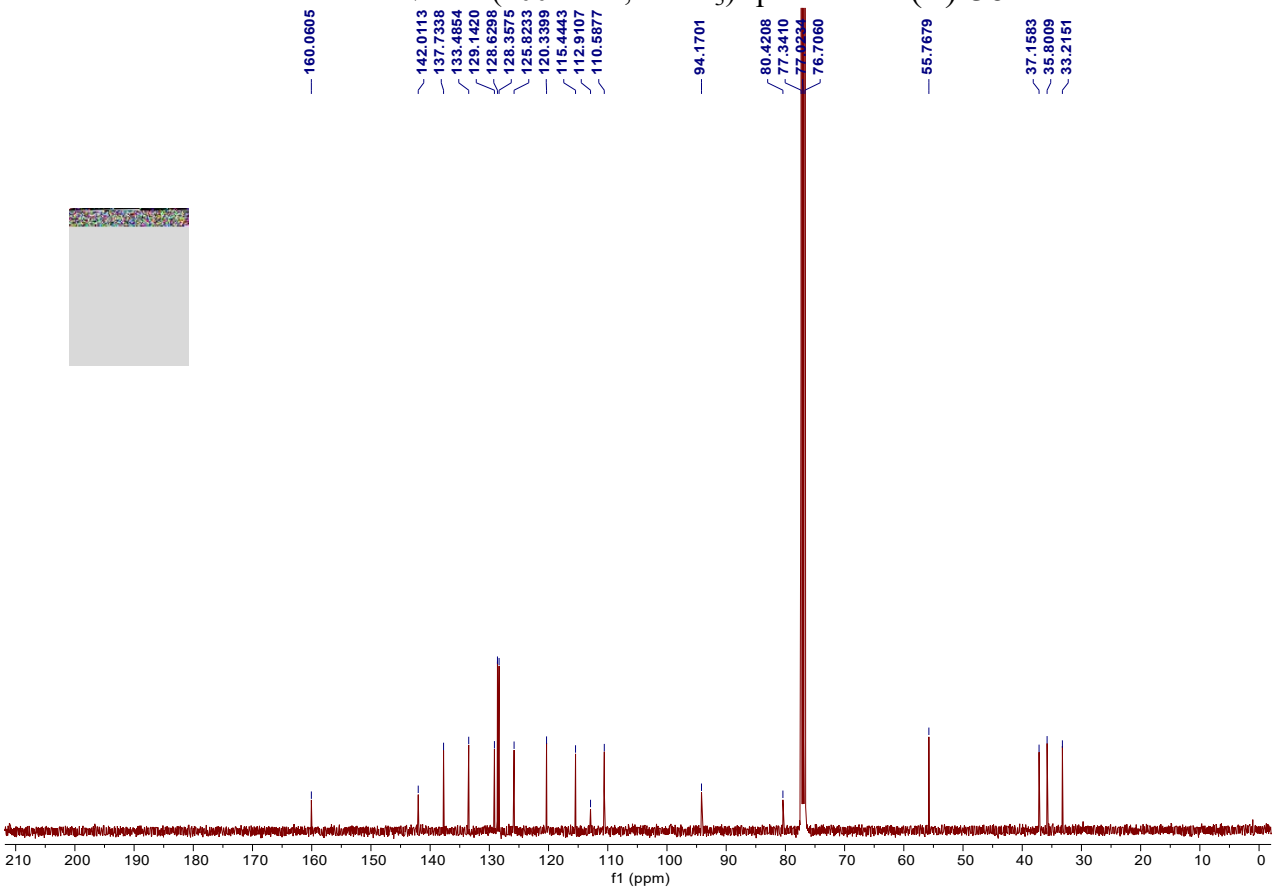
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3d**



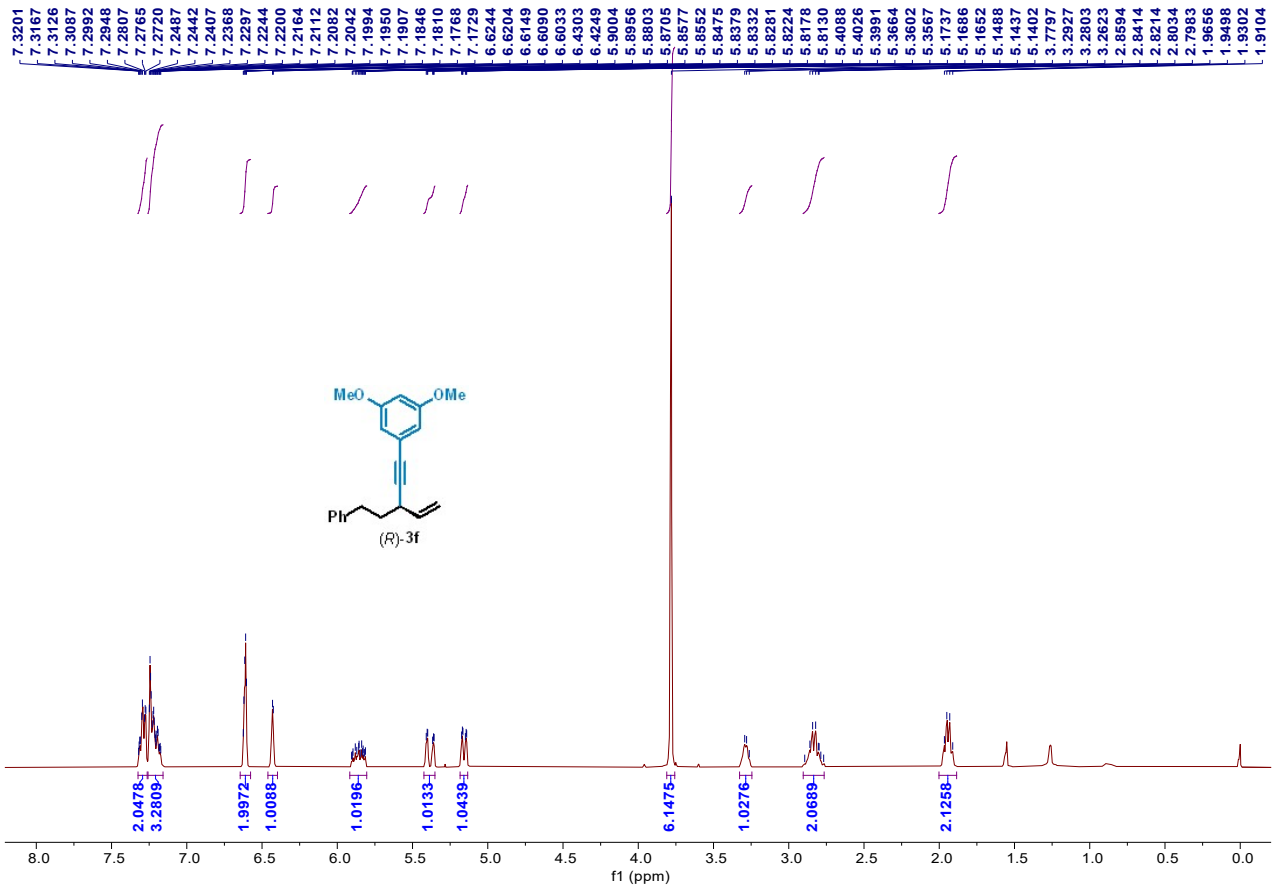
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3d**



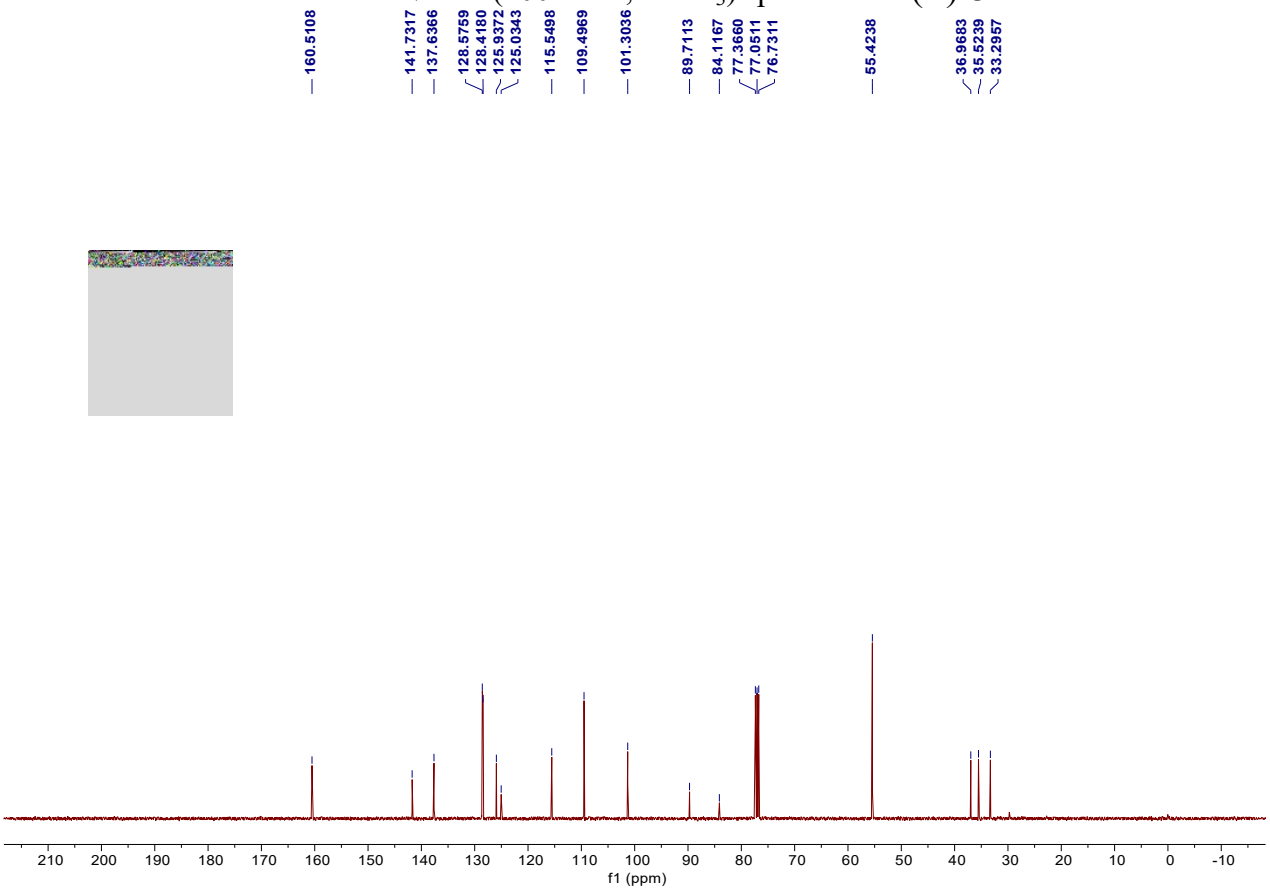
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3e**



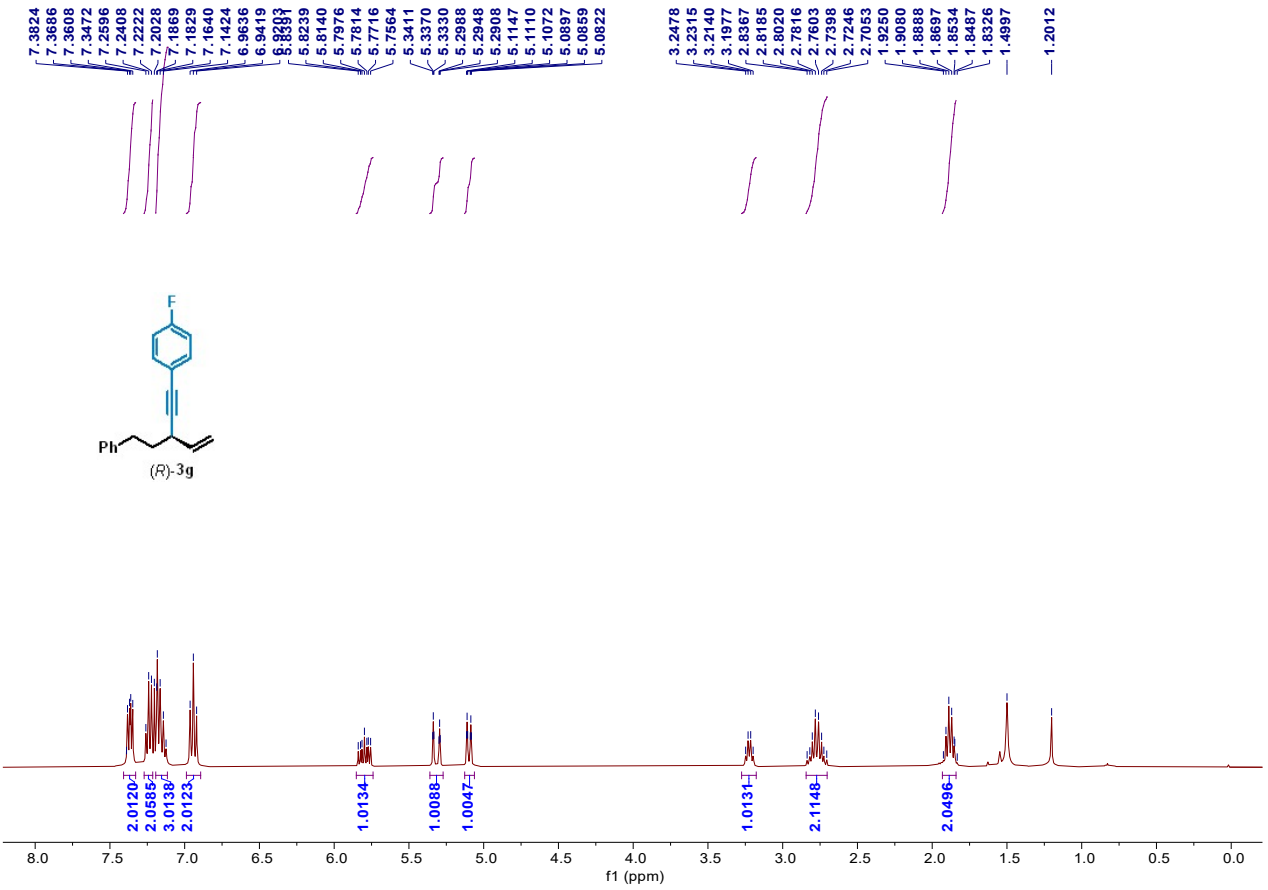
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3e**



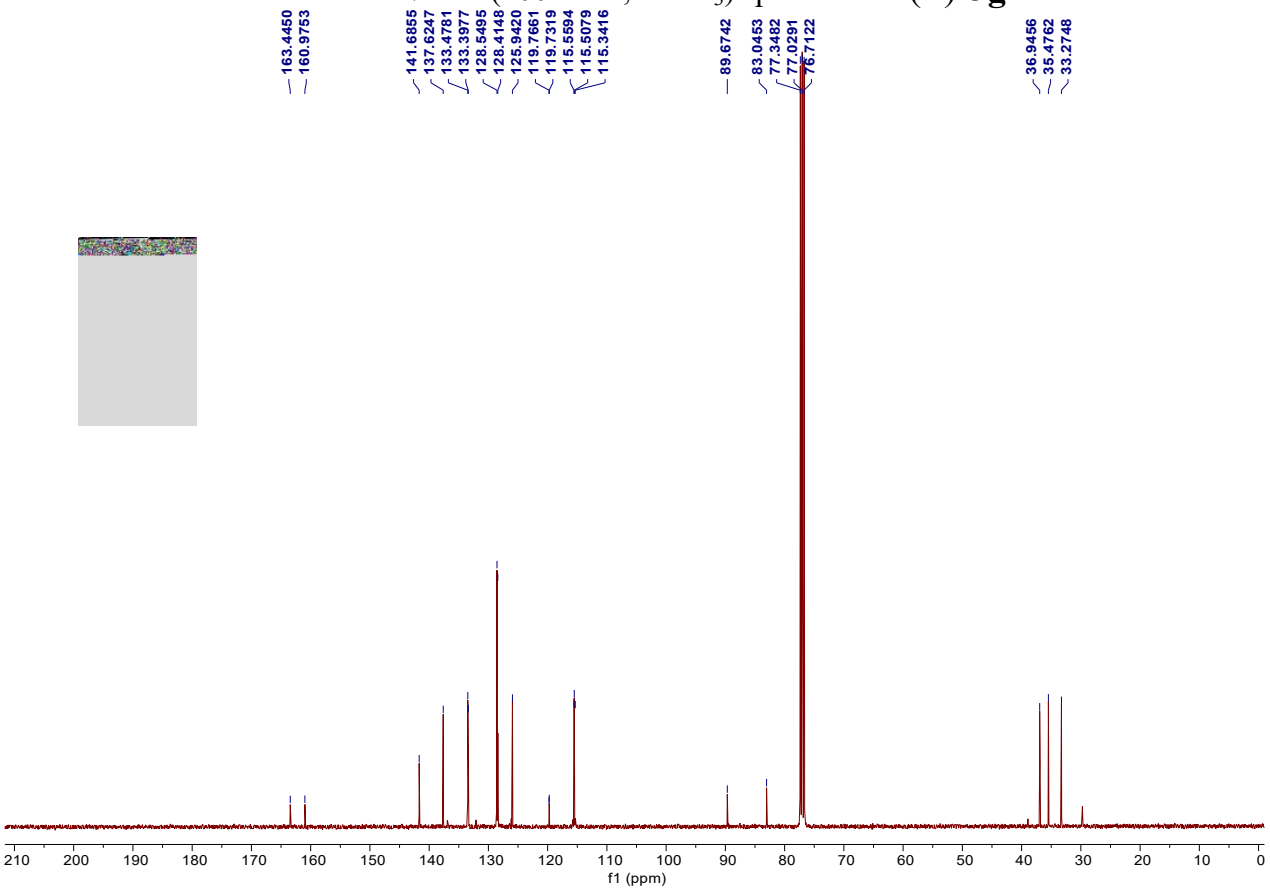
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3f**



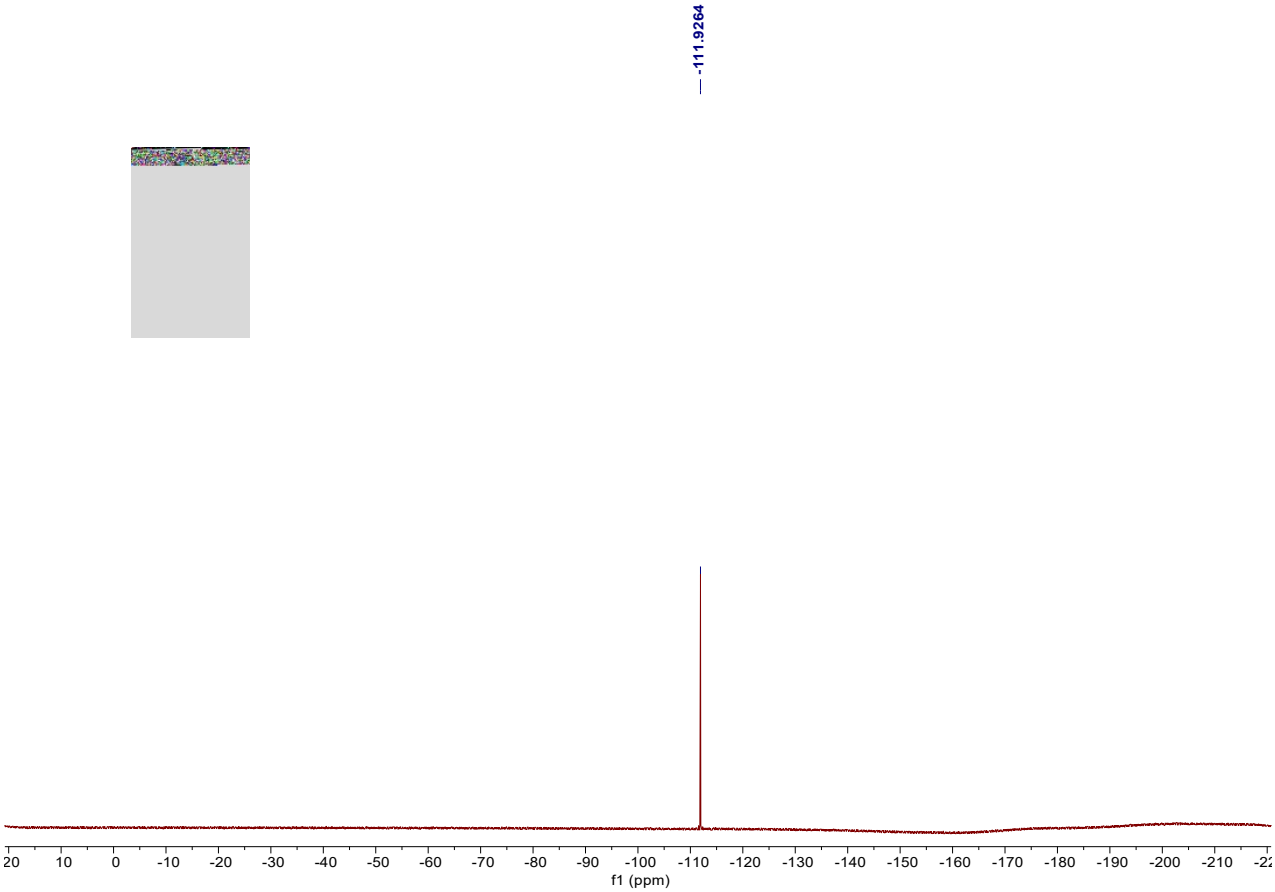
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3f**



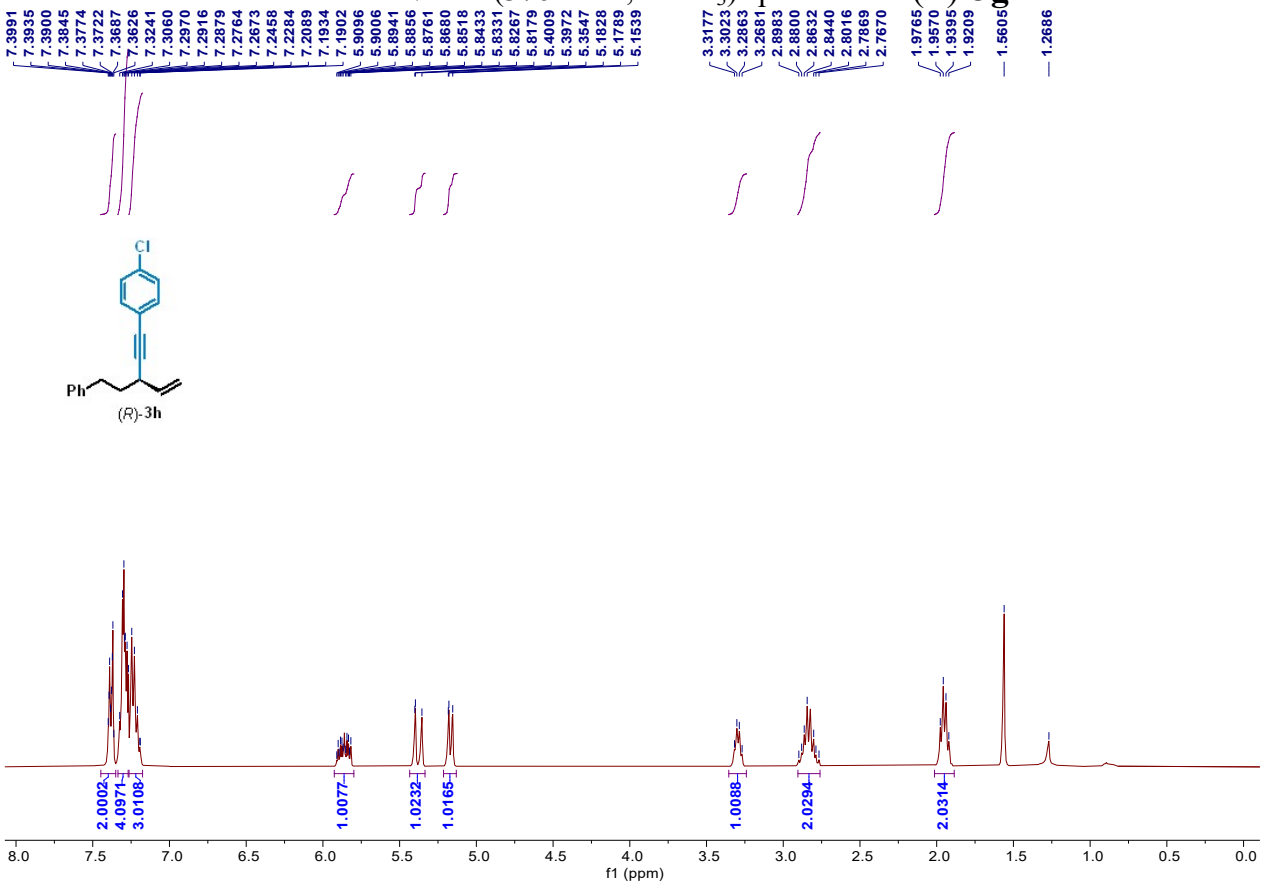
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3g**



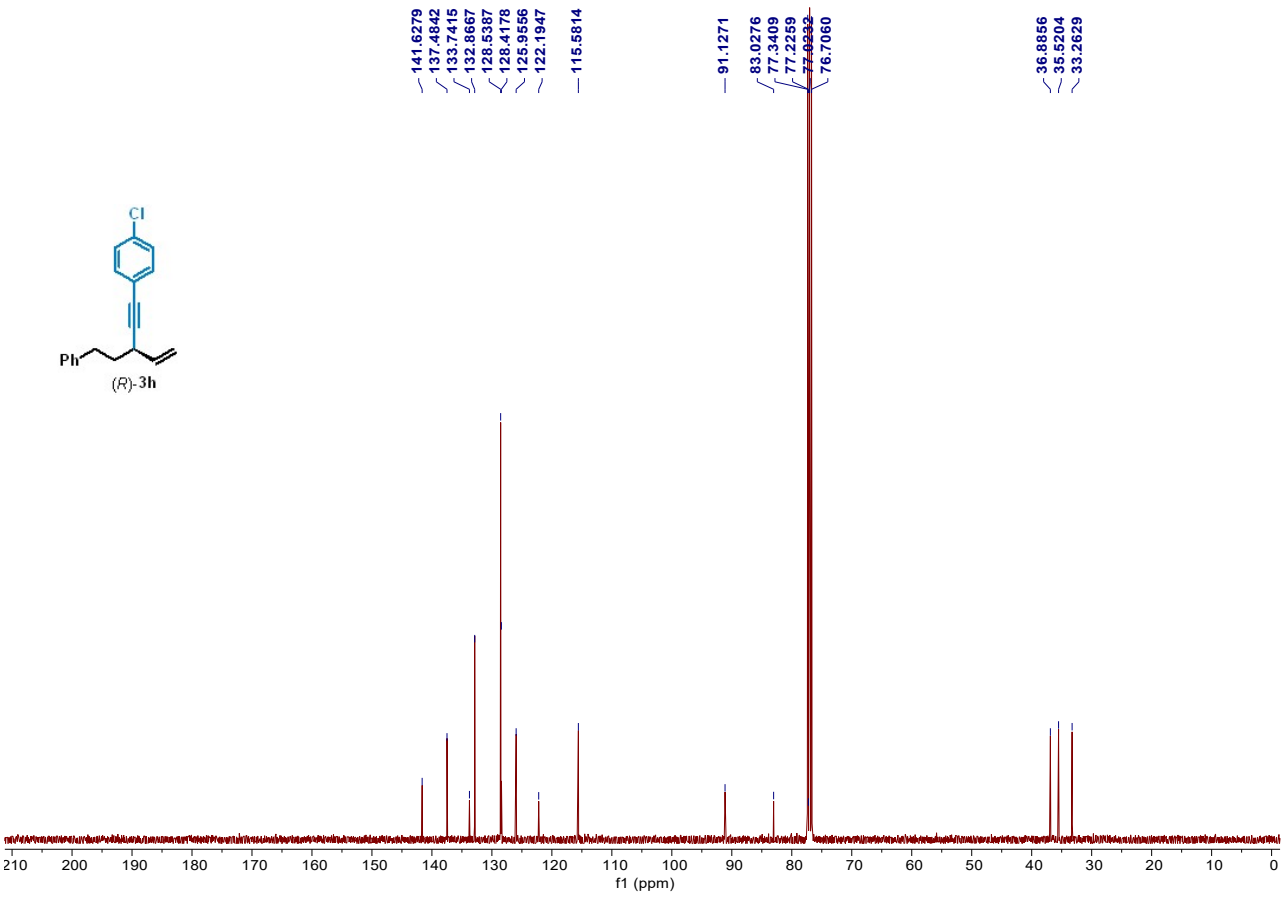
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3g**



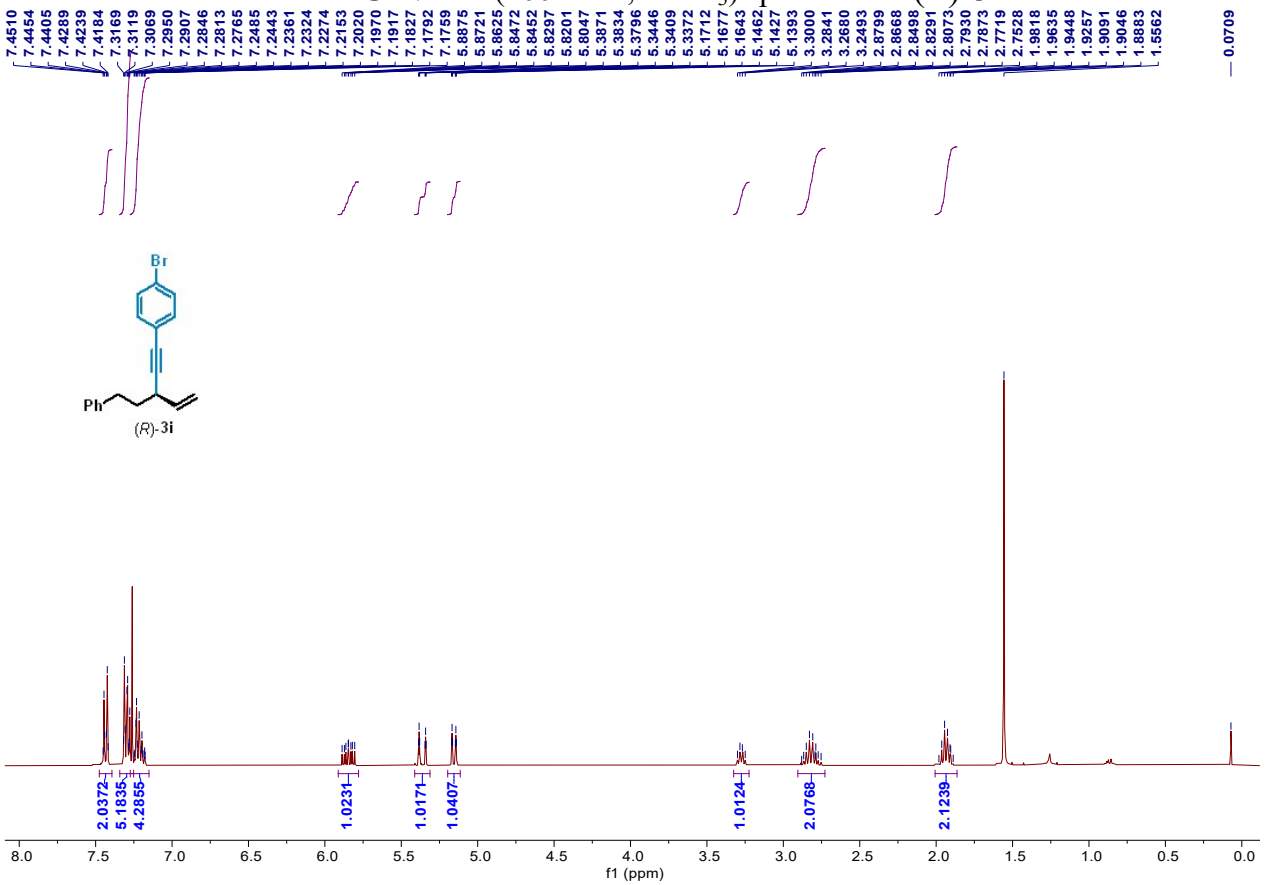
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (*R*)-**3g**



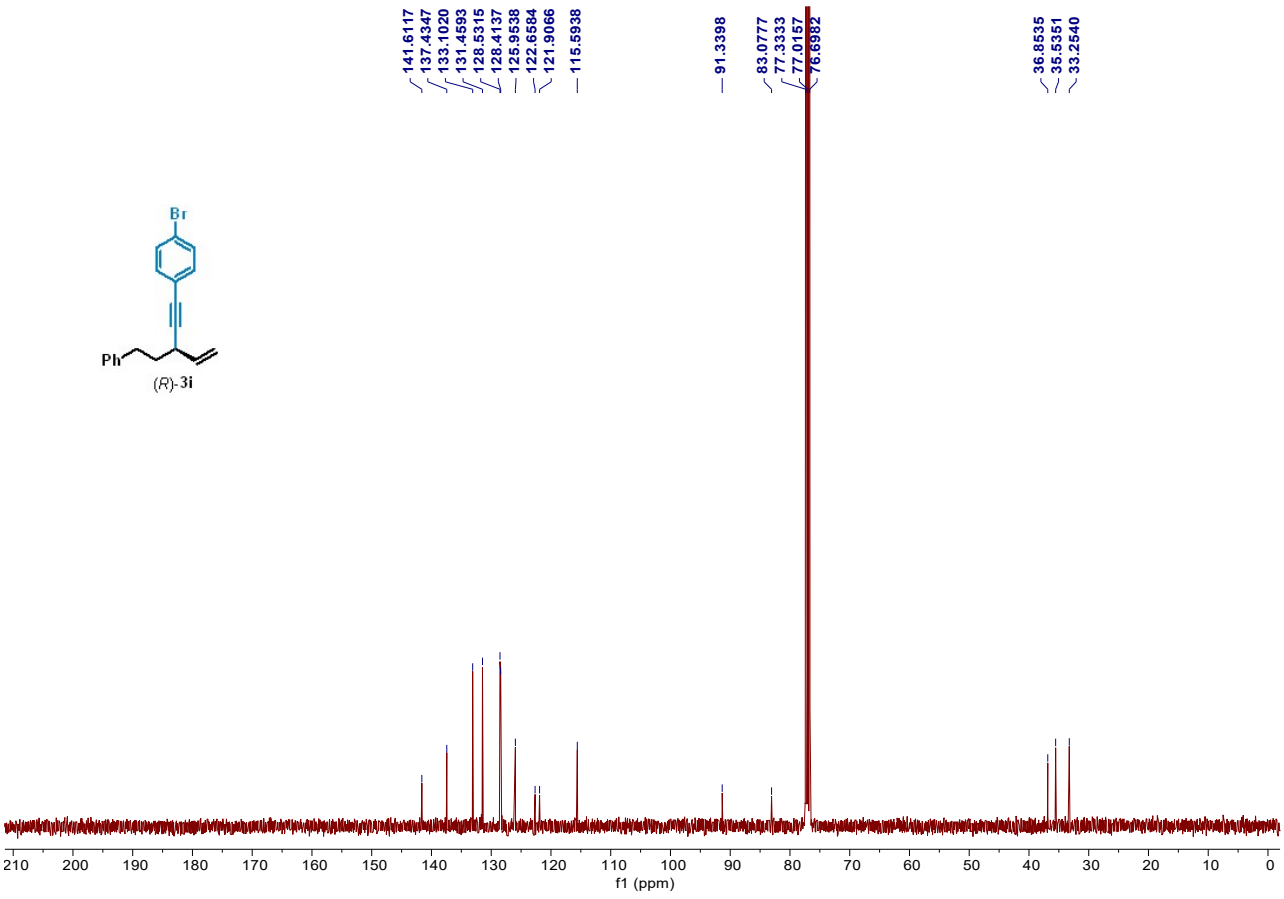
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3h**



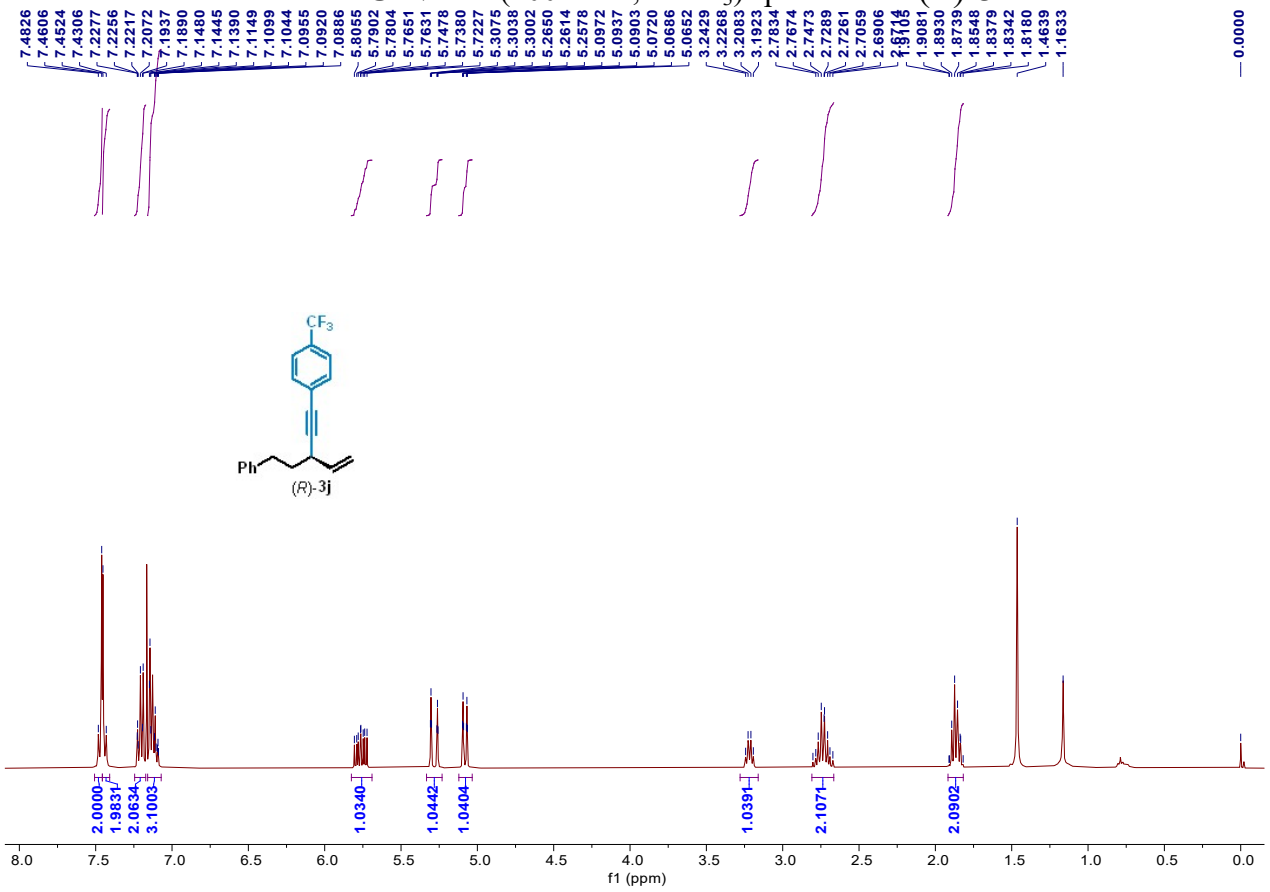
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3h**



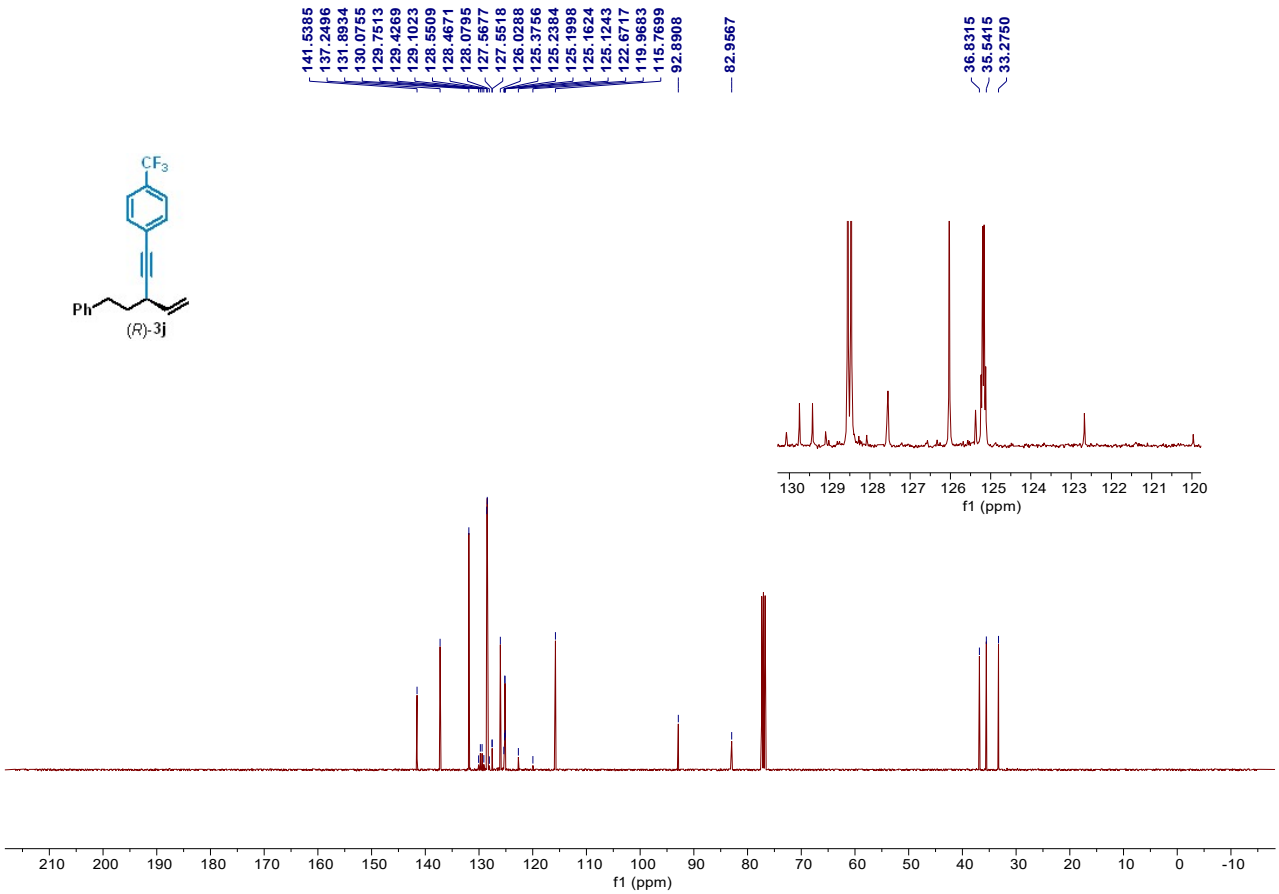
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3i**



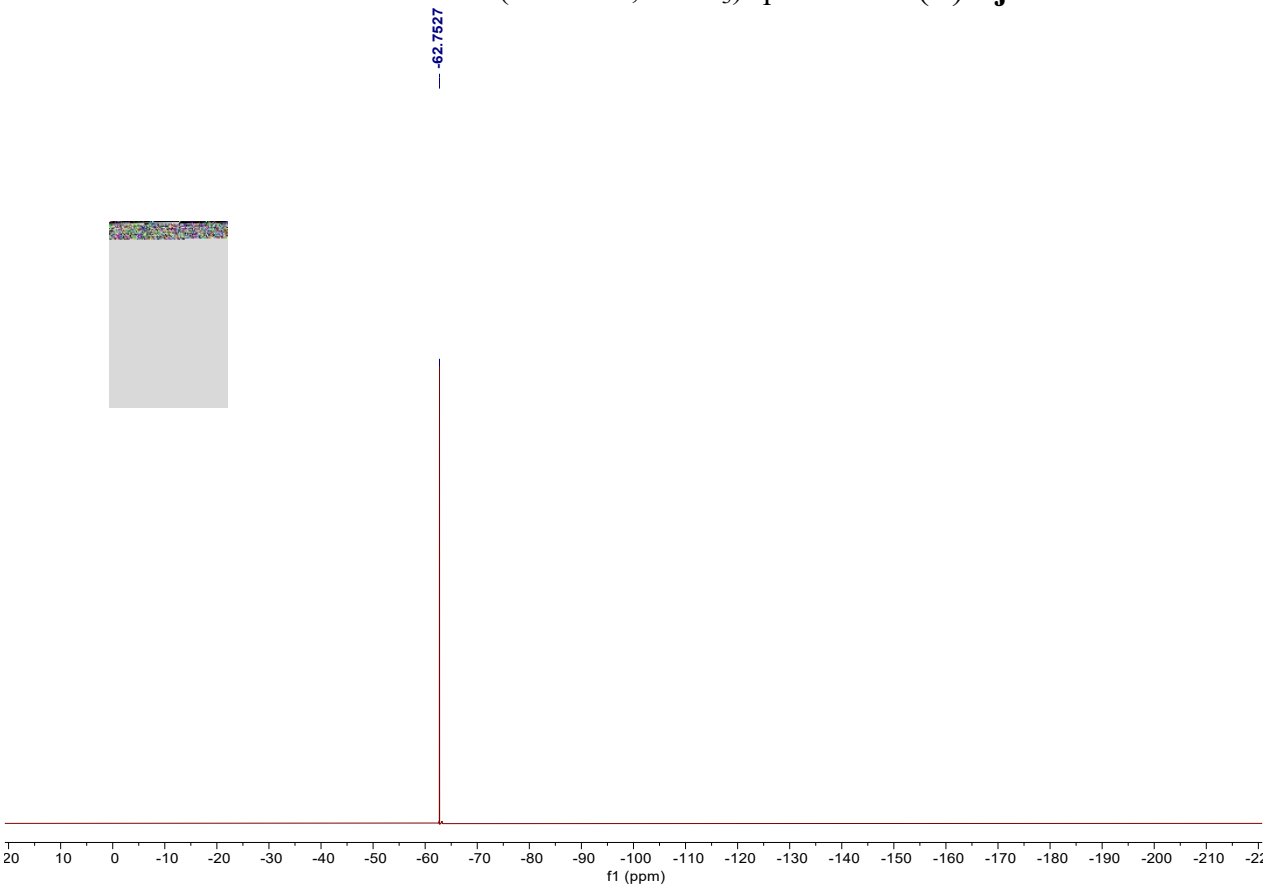
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3i**



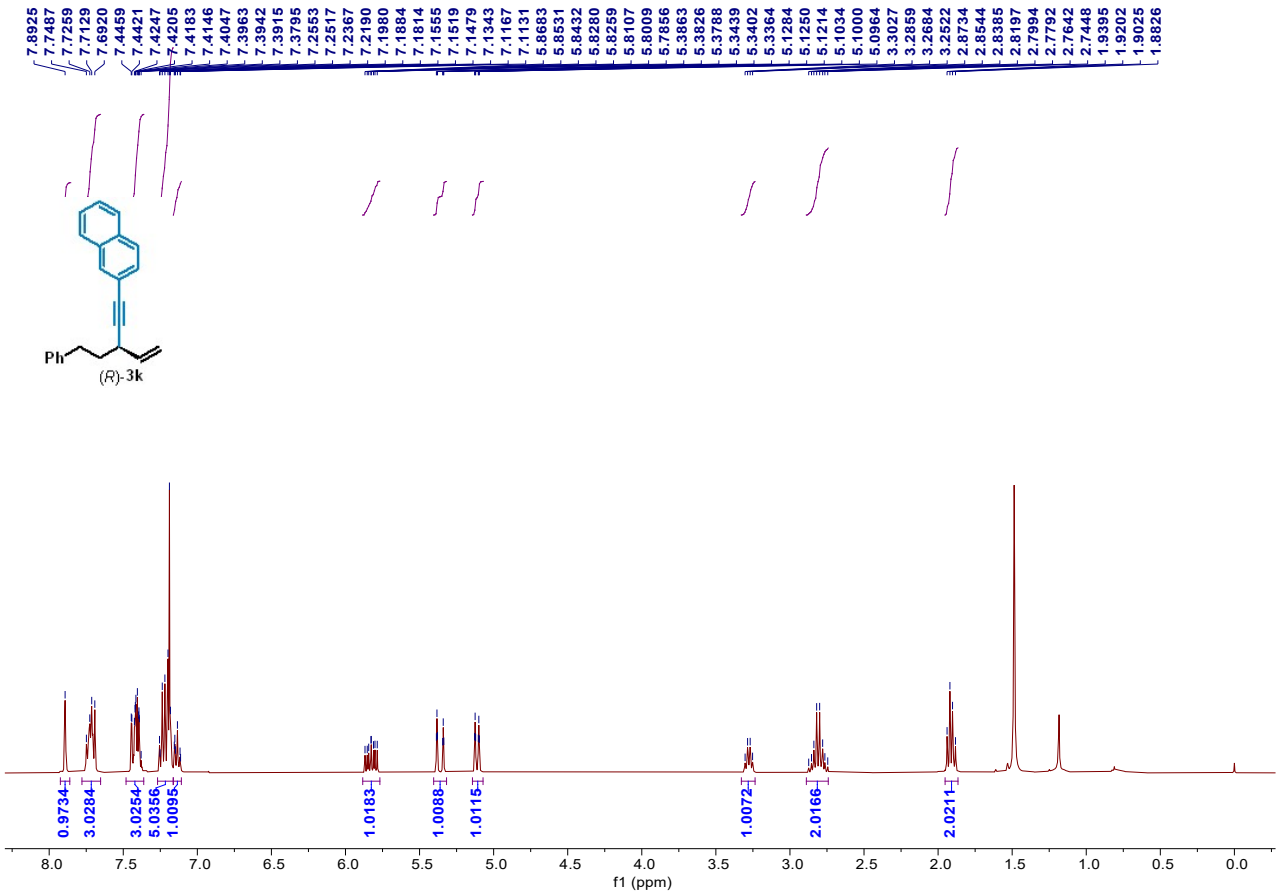
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3j**



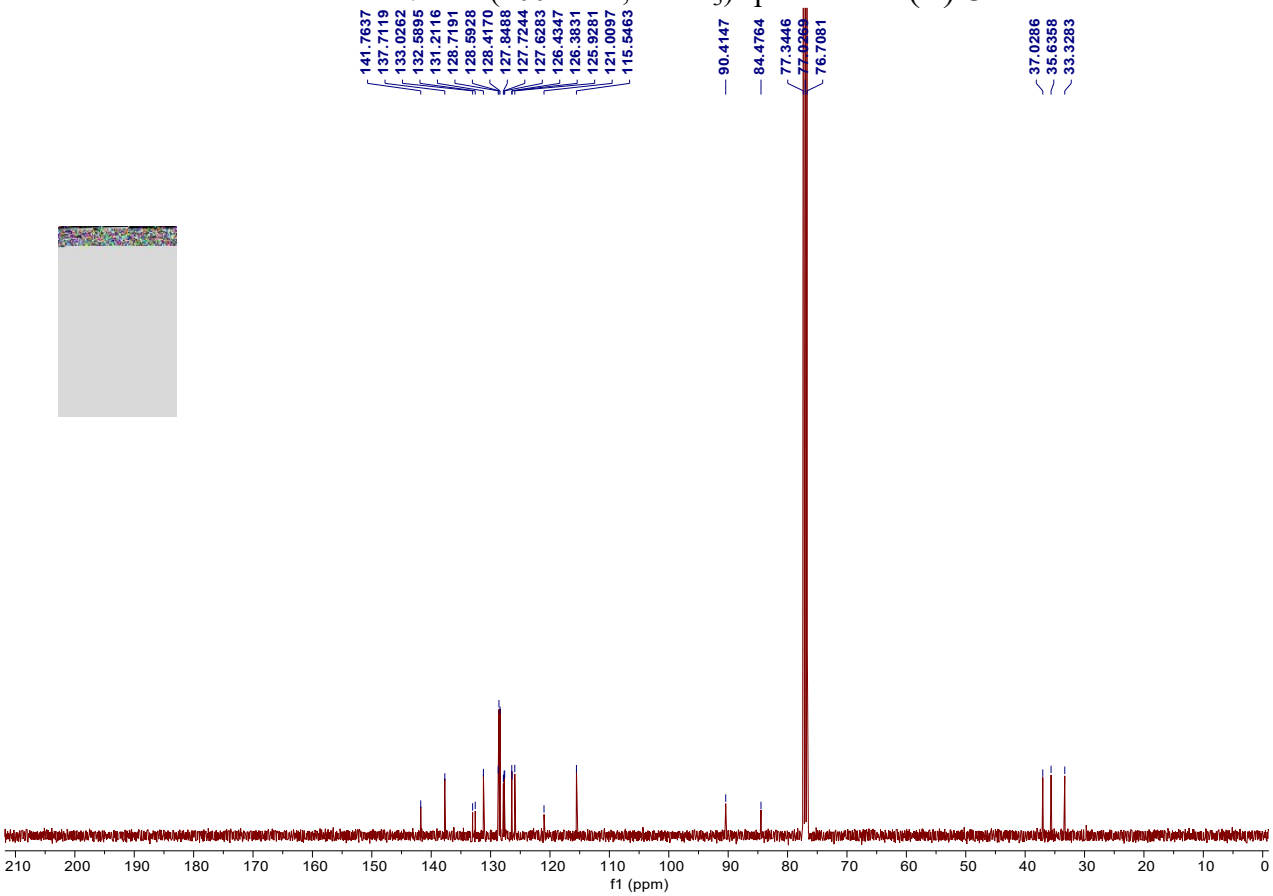
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3j**



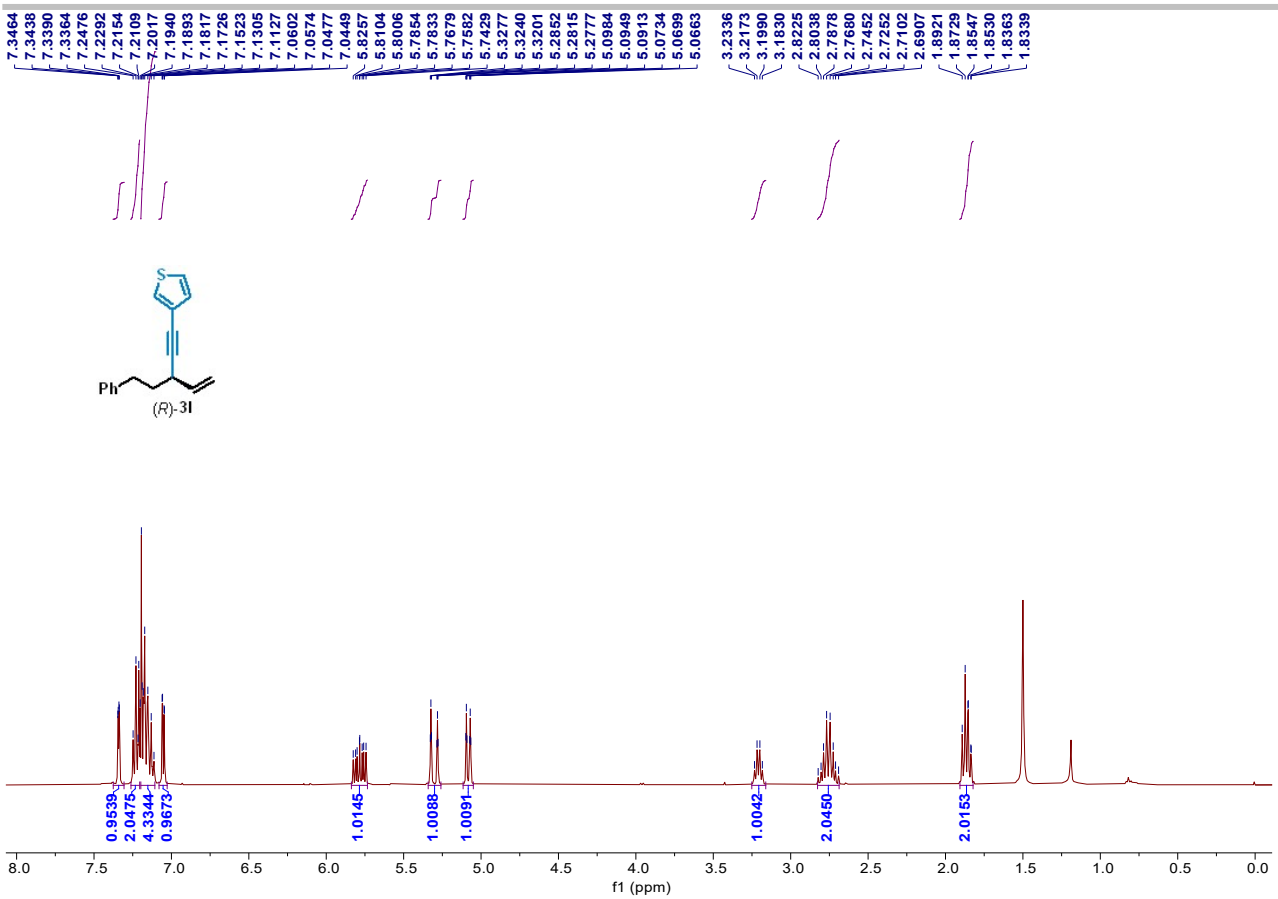
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of (*R*)-**3j**



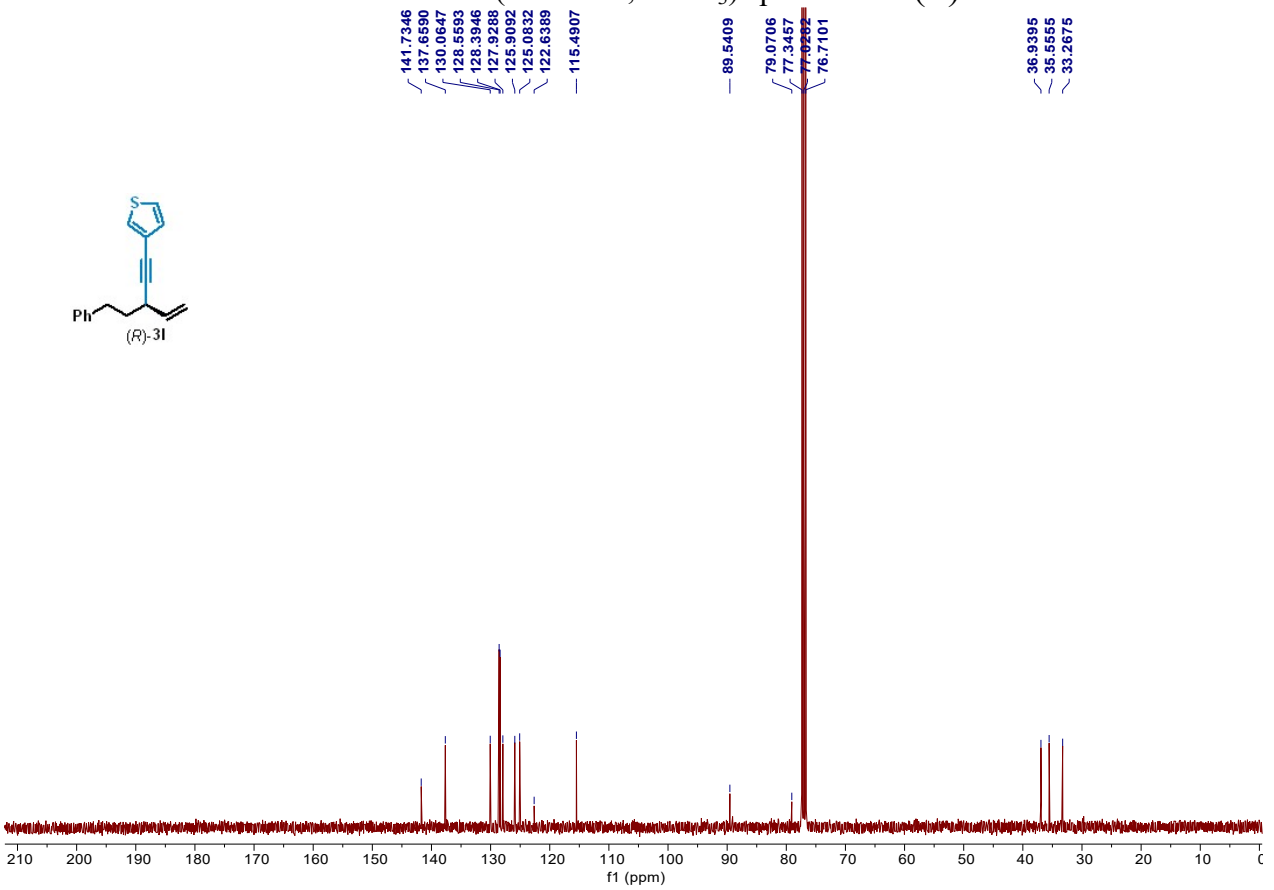
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3k**



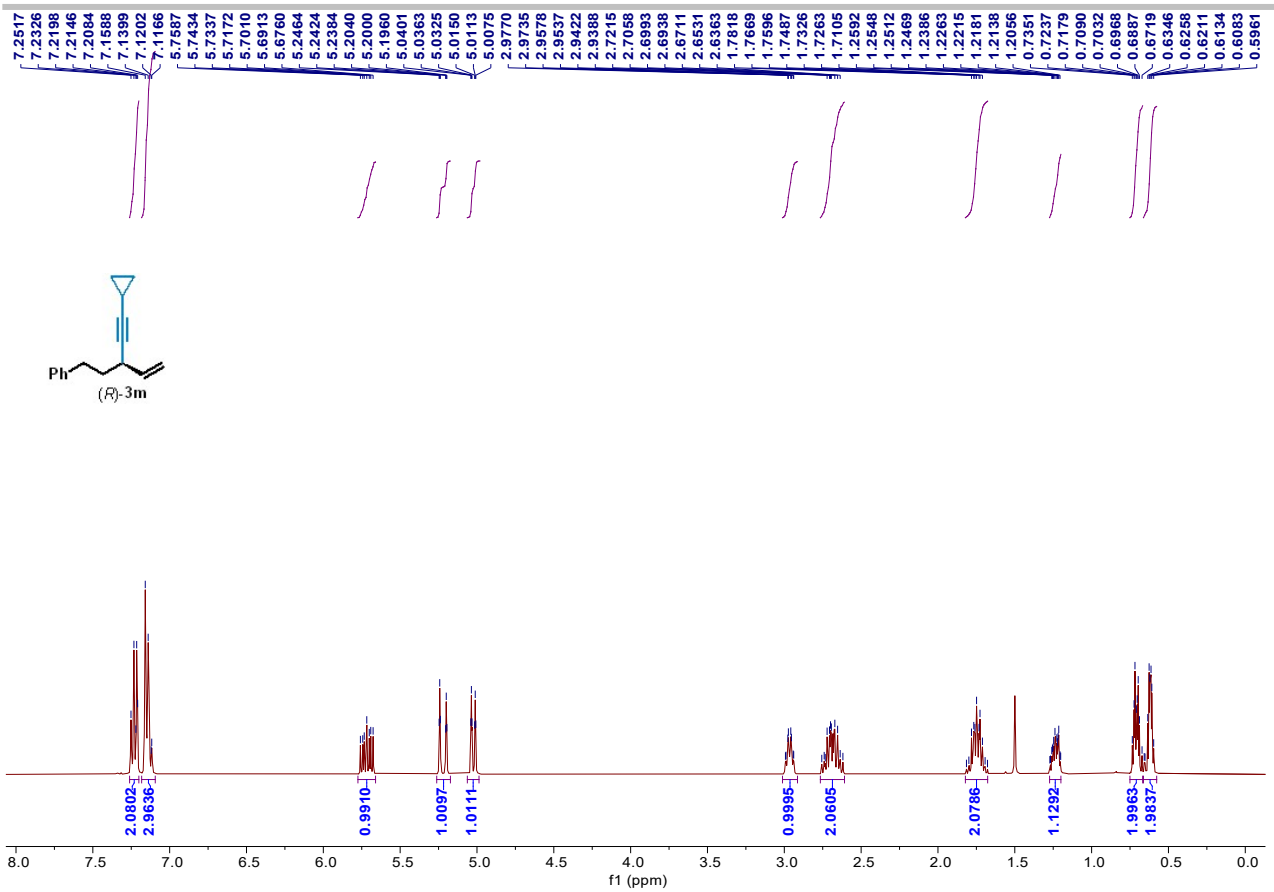
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3k**



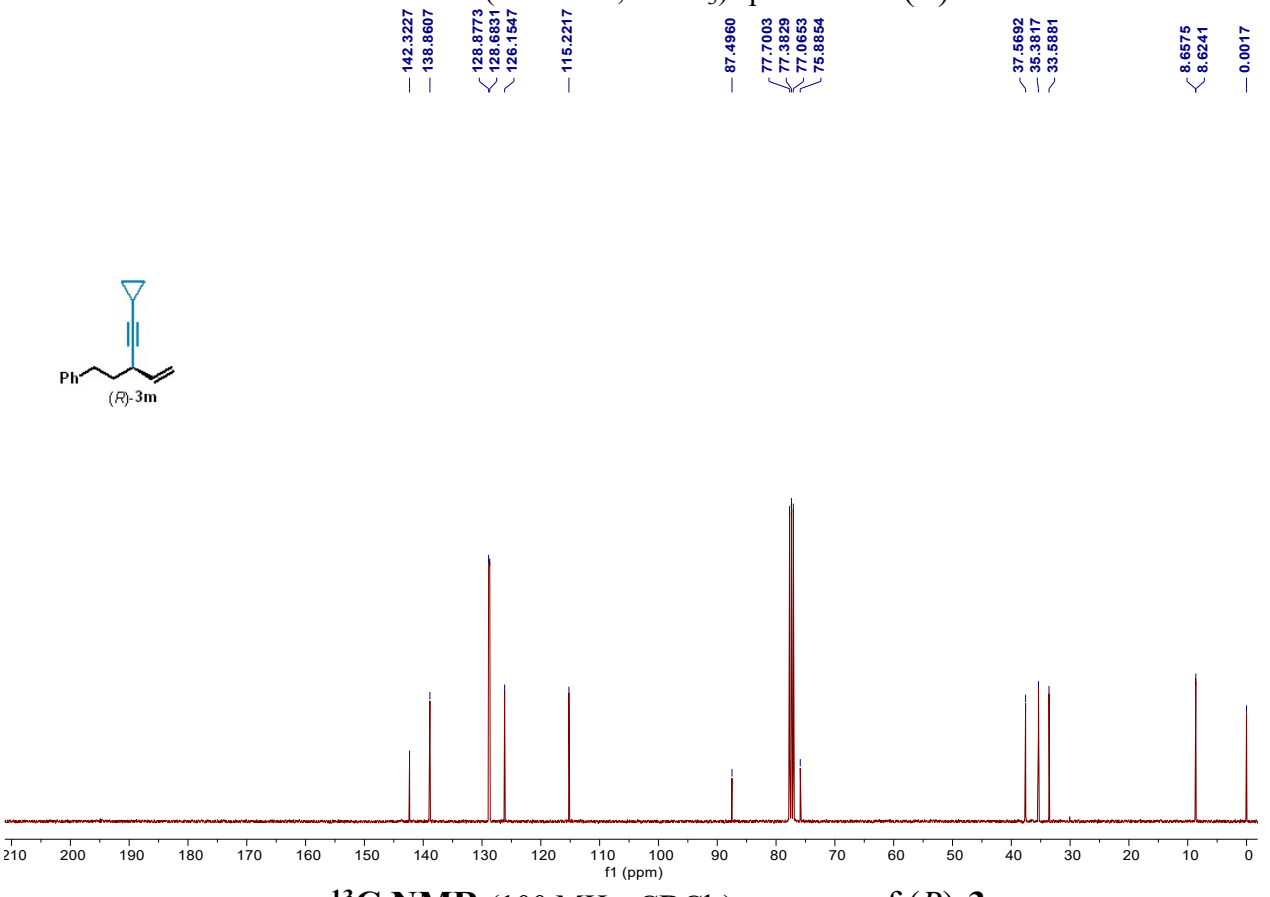
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3l**



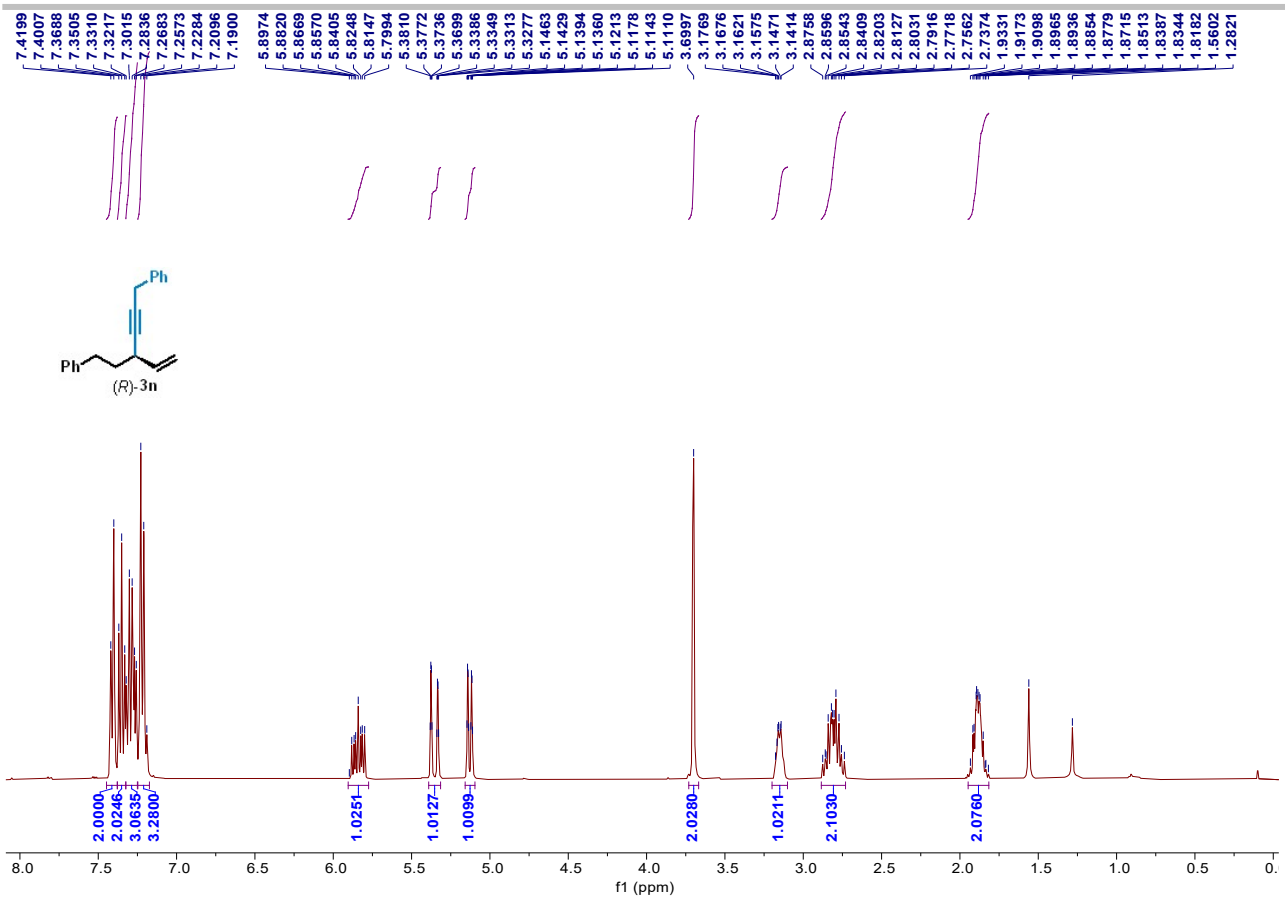
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3l**



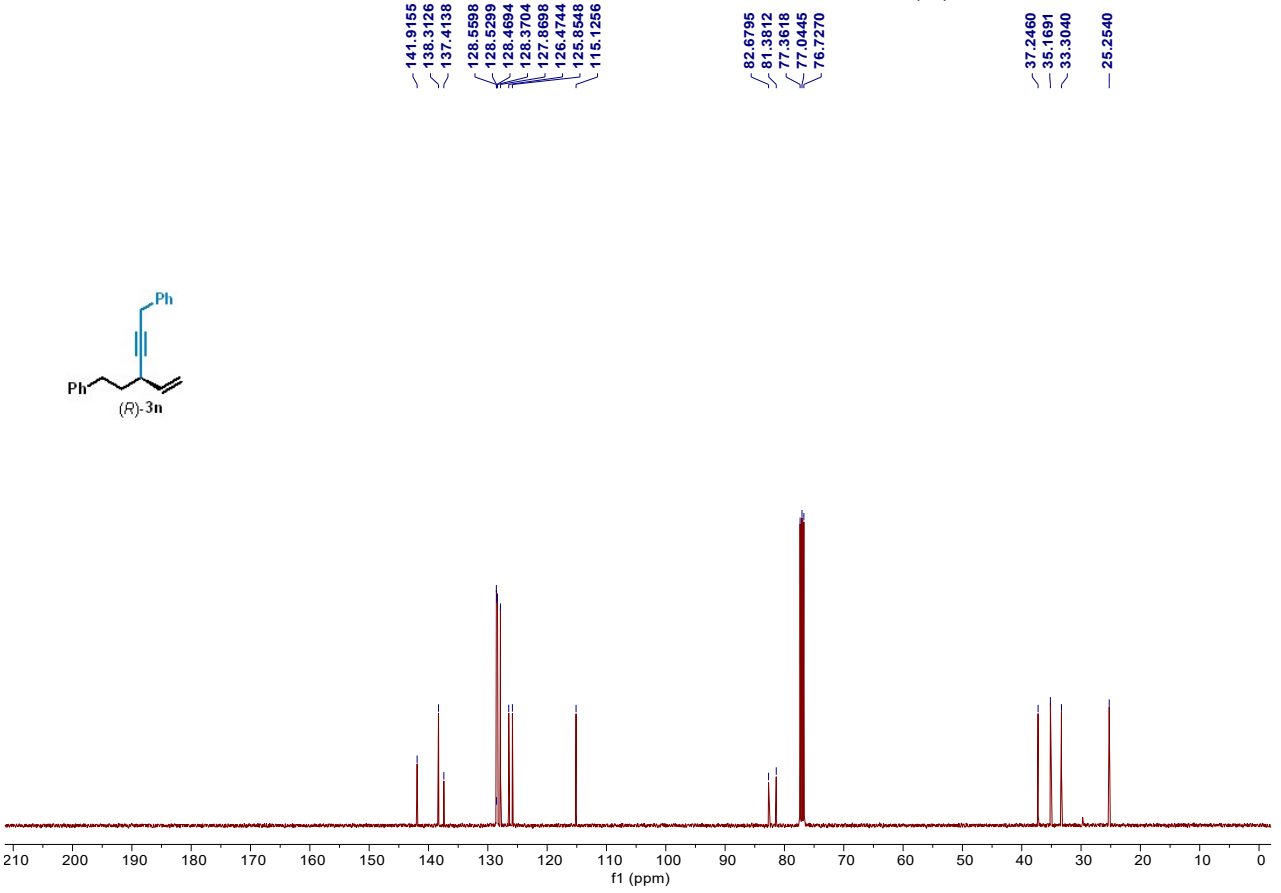
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3m**



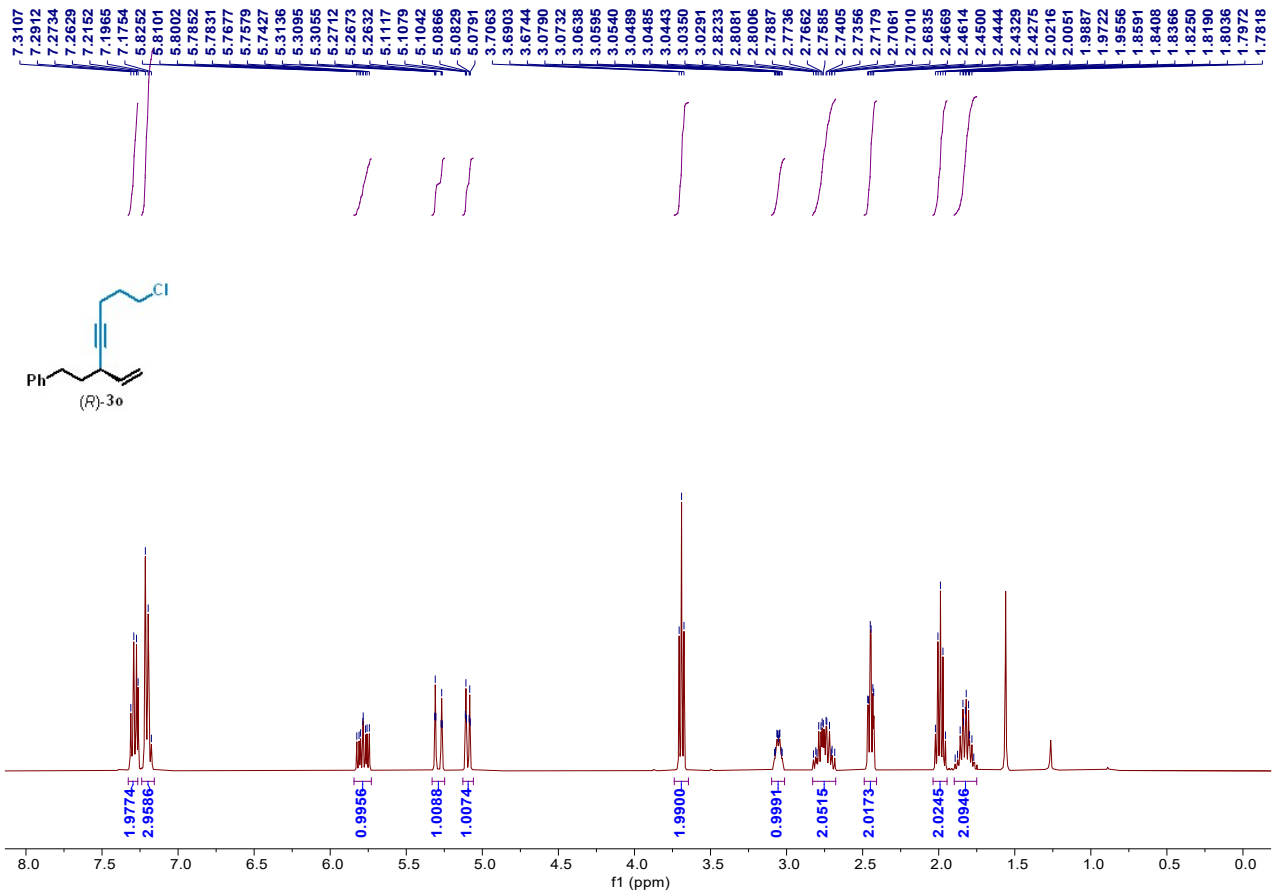
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3m**



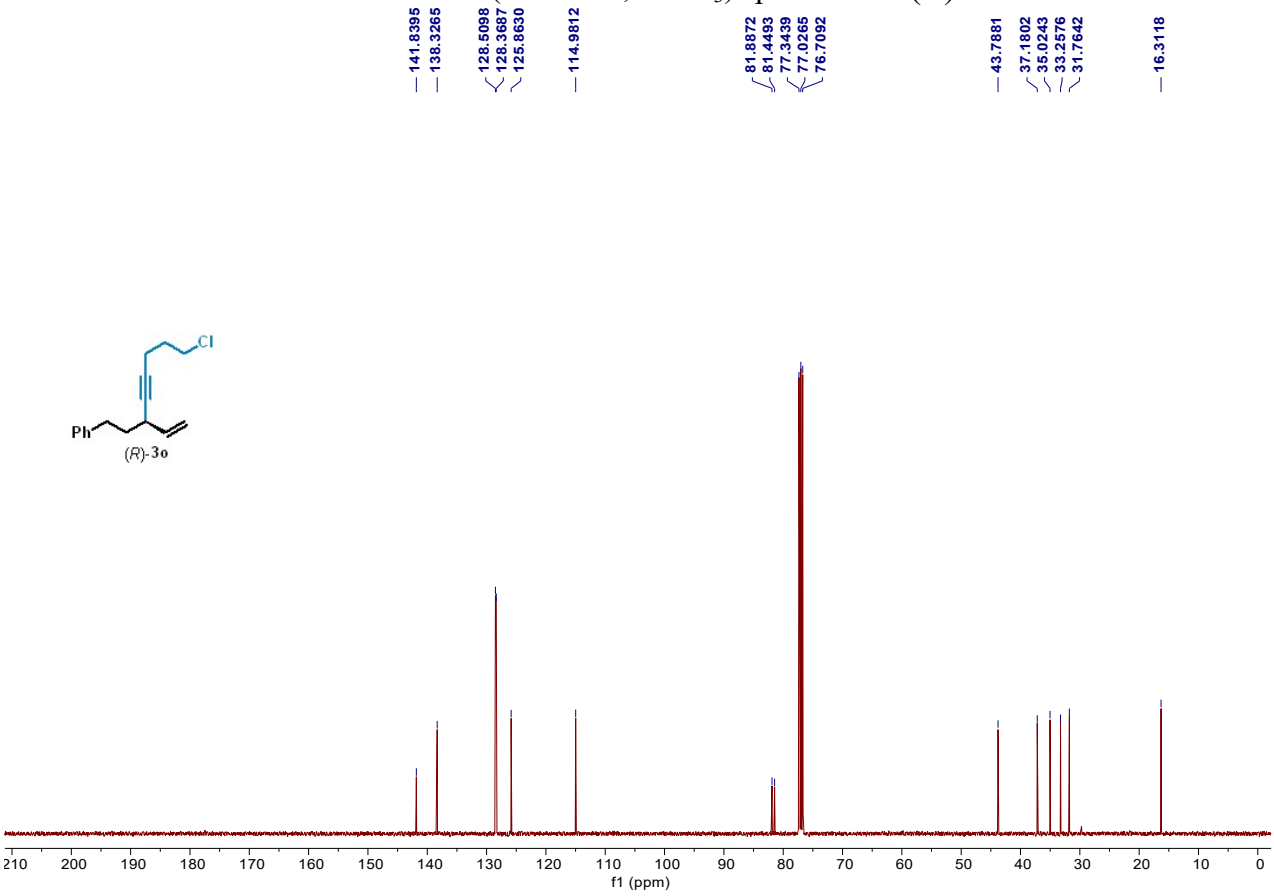
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3n**



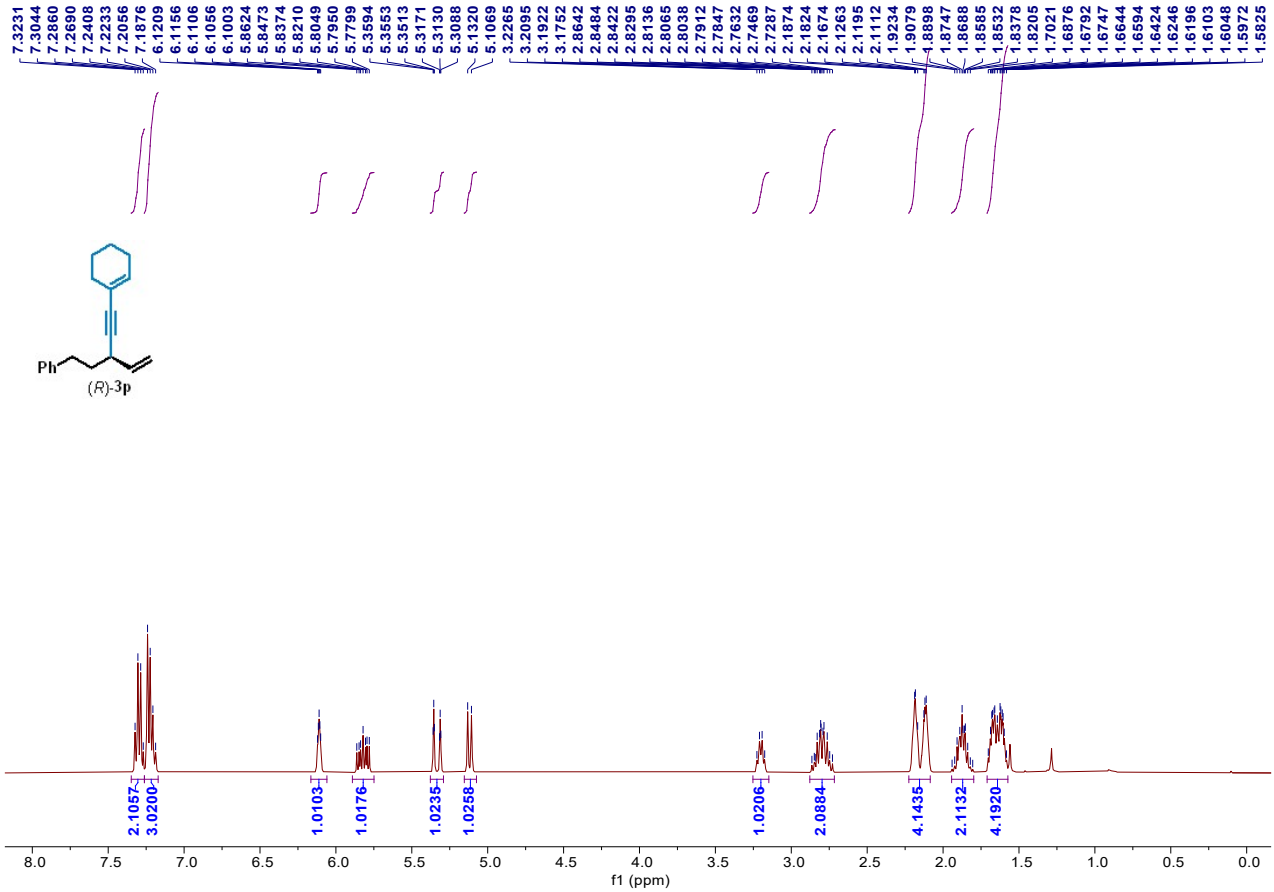
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3n**



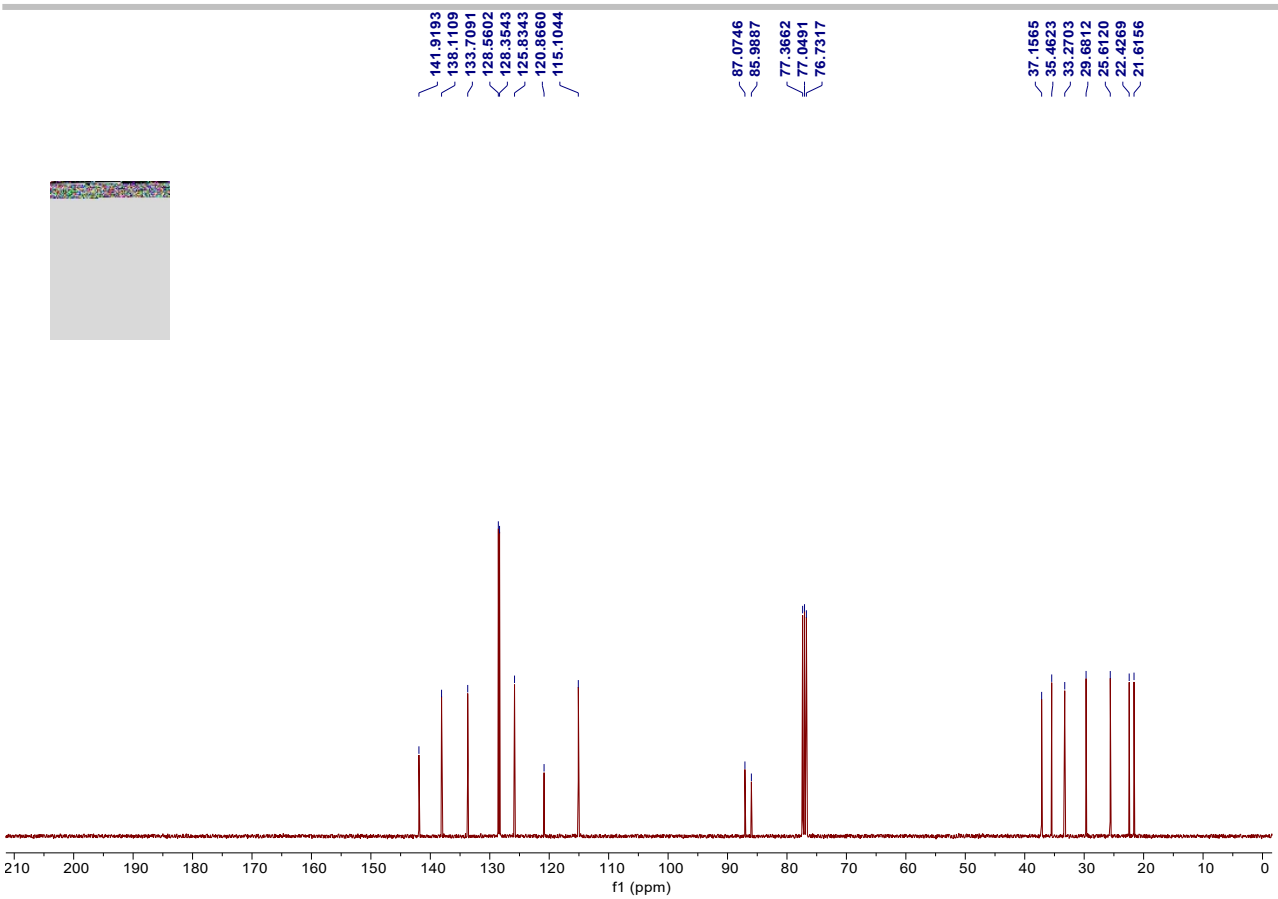
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3o**



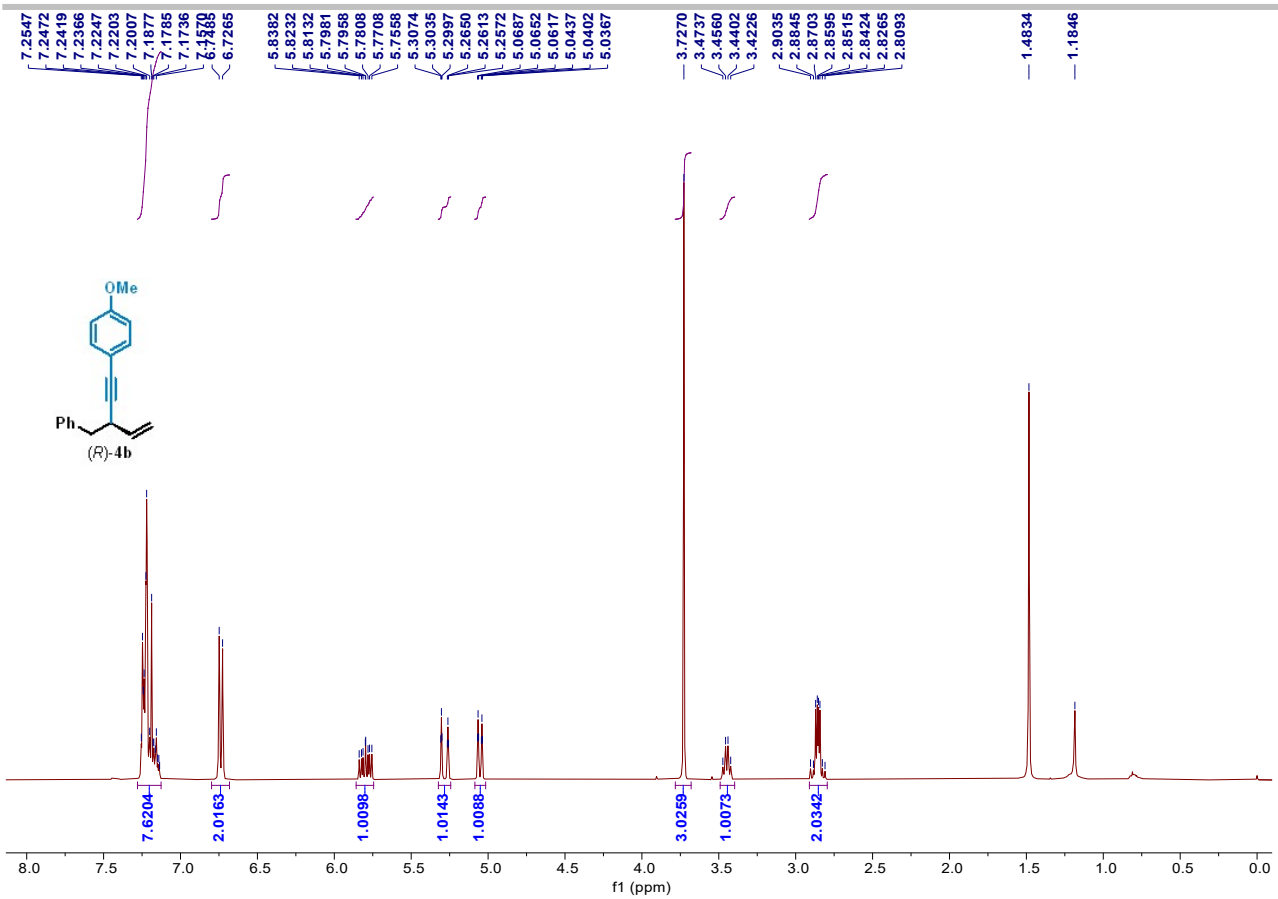
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3o**



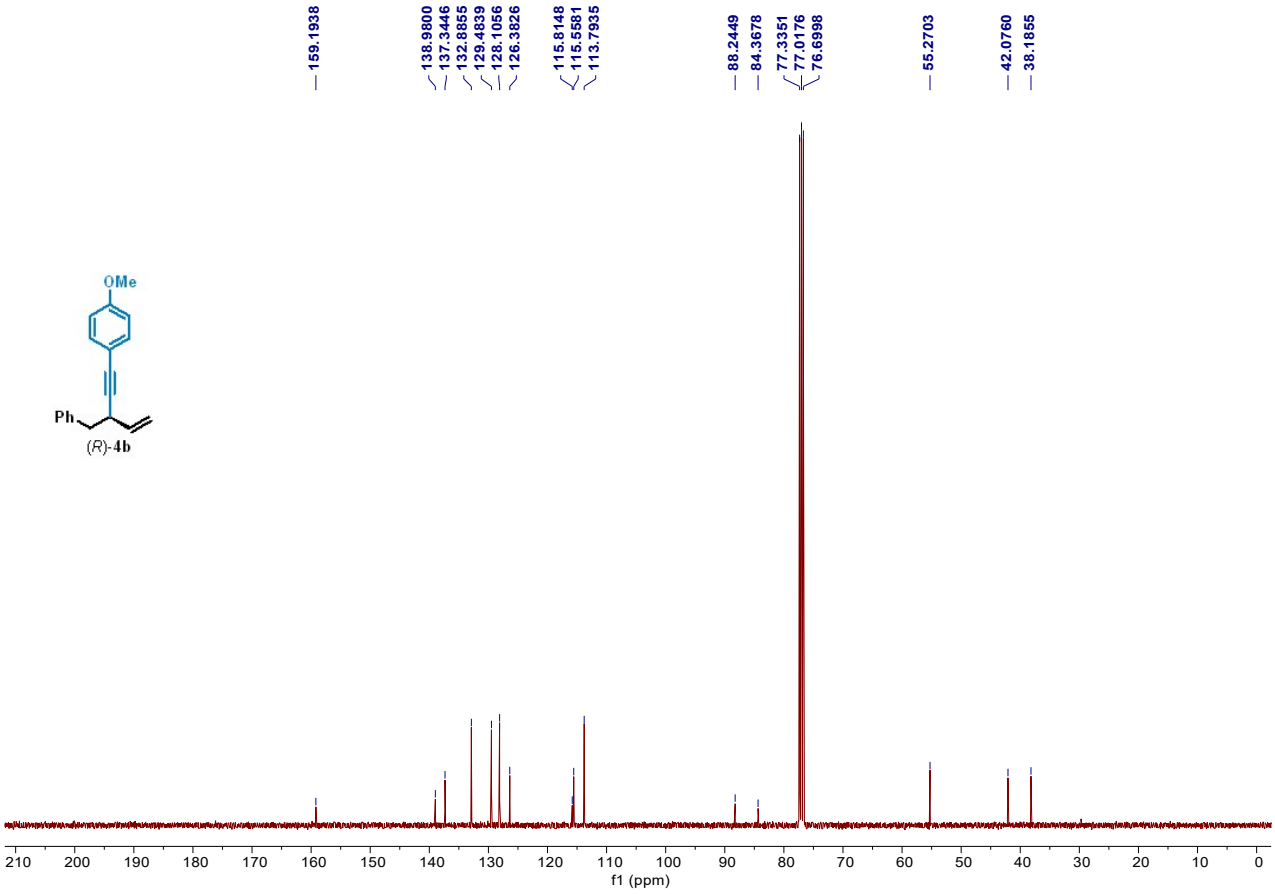
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**3p**



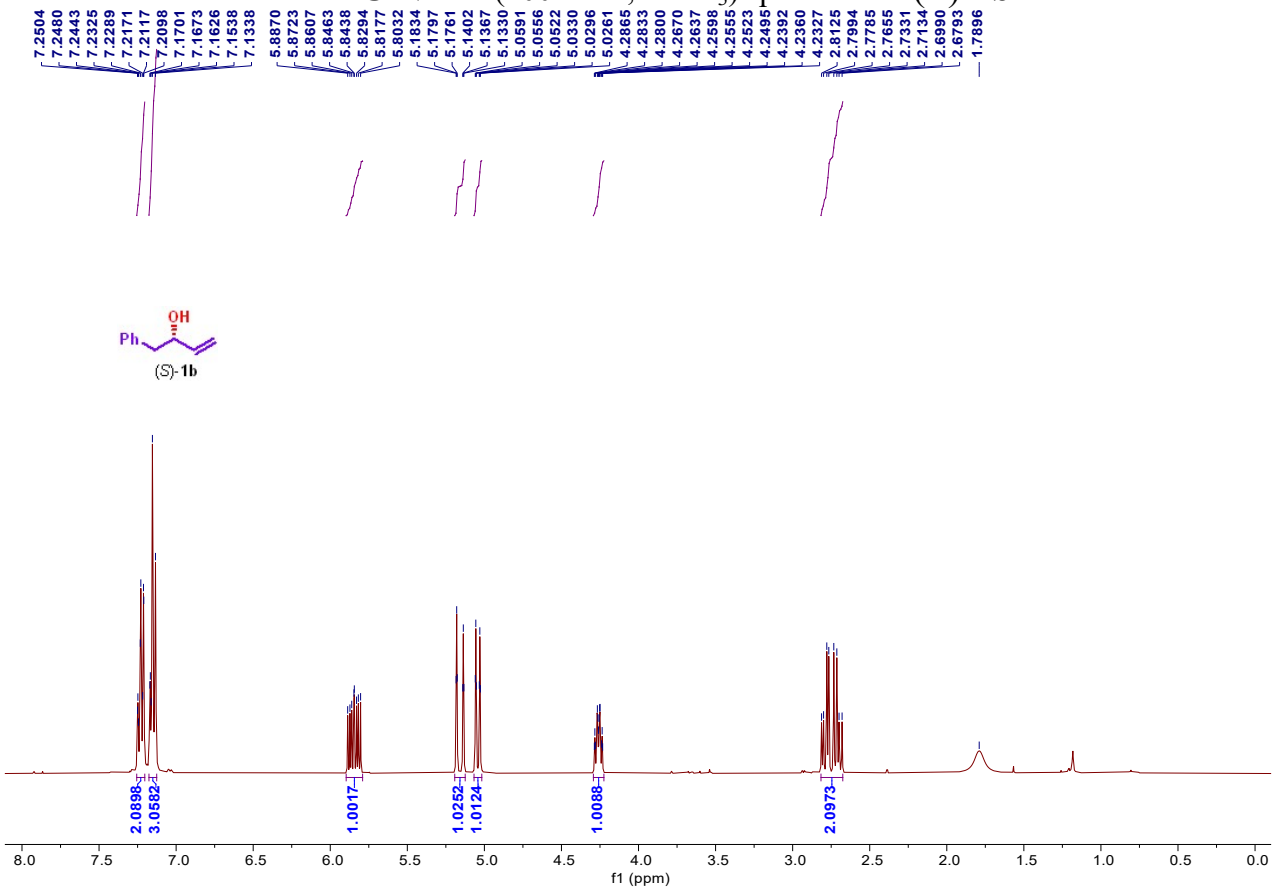
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**3p**



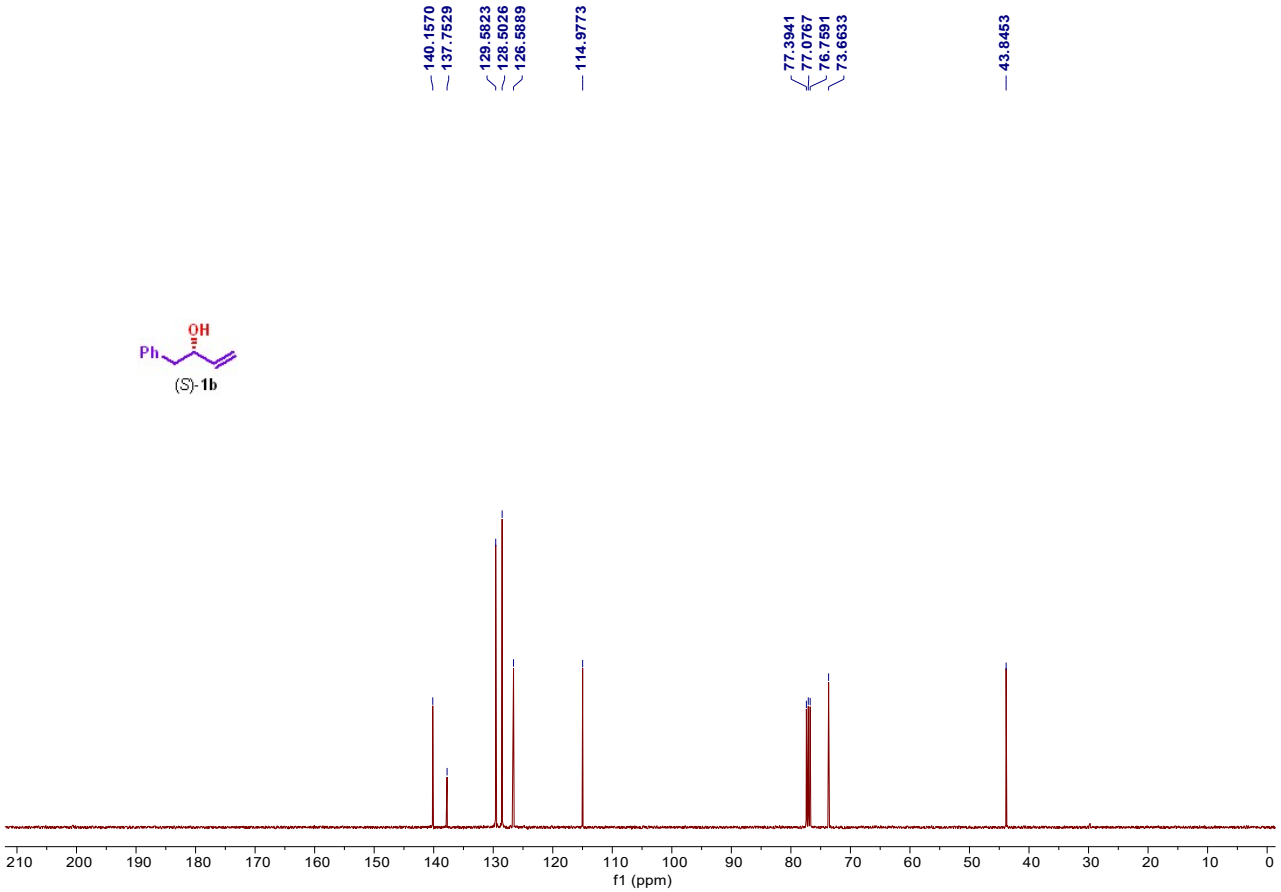
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4b**



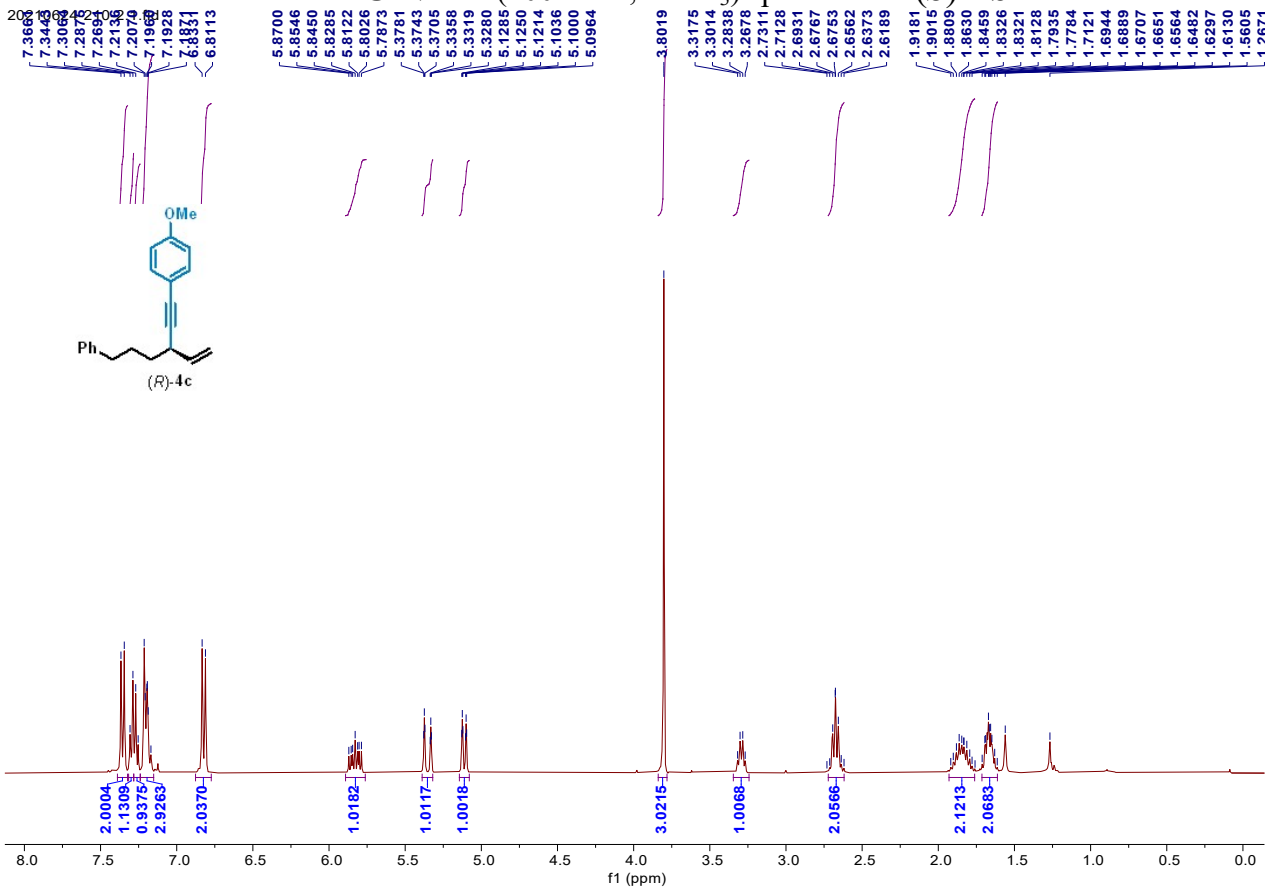
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4b**



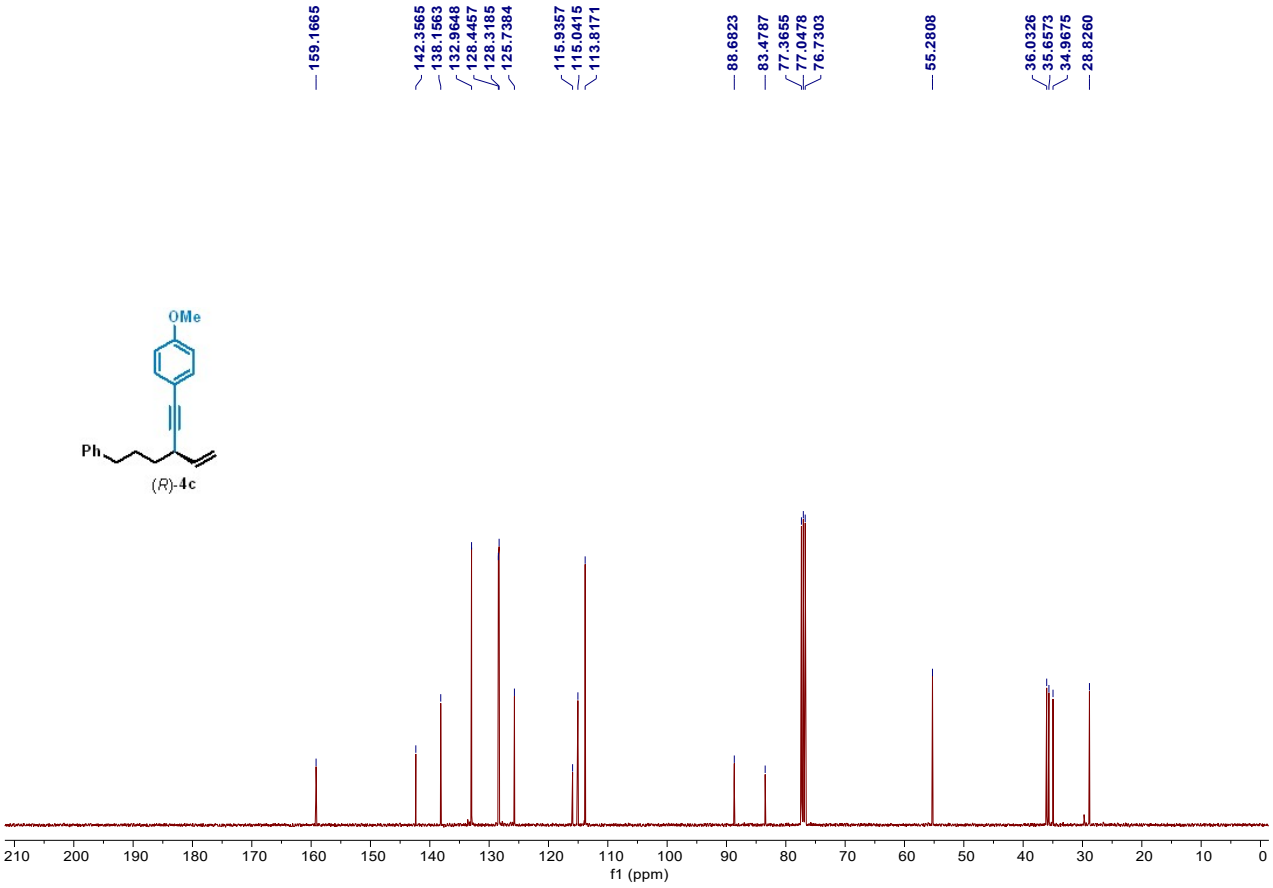
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1b**



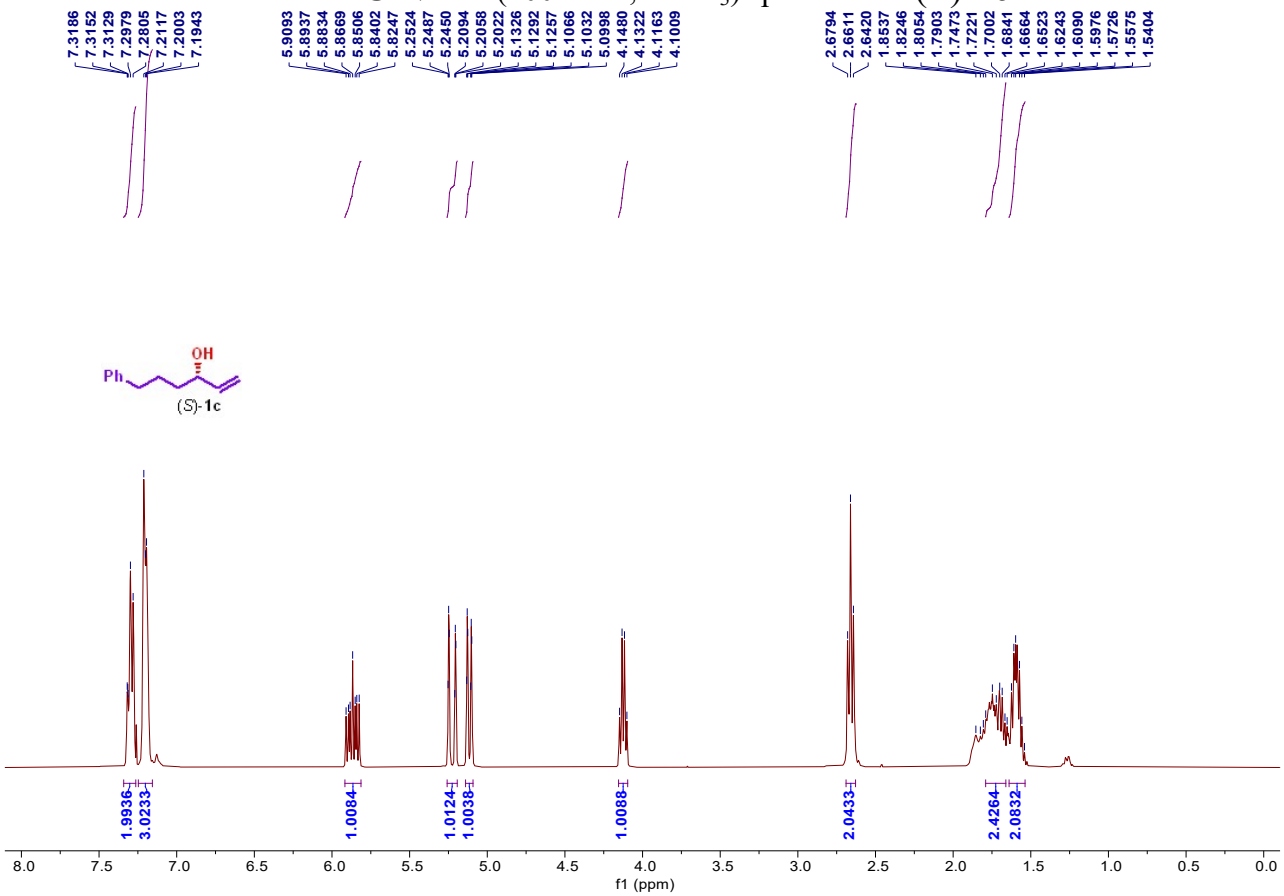
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1b**



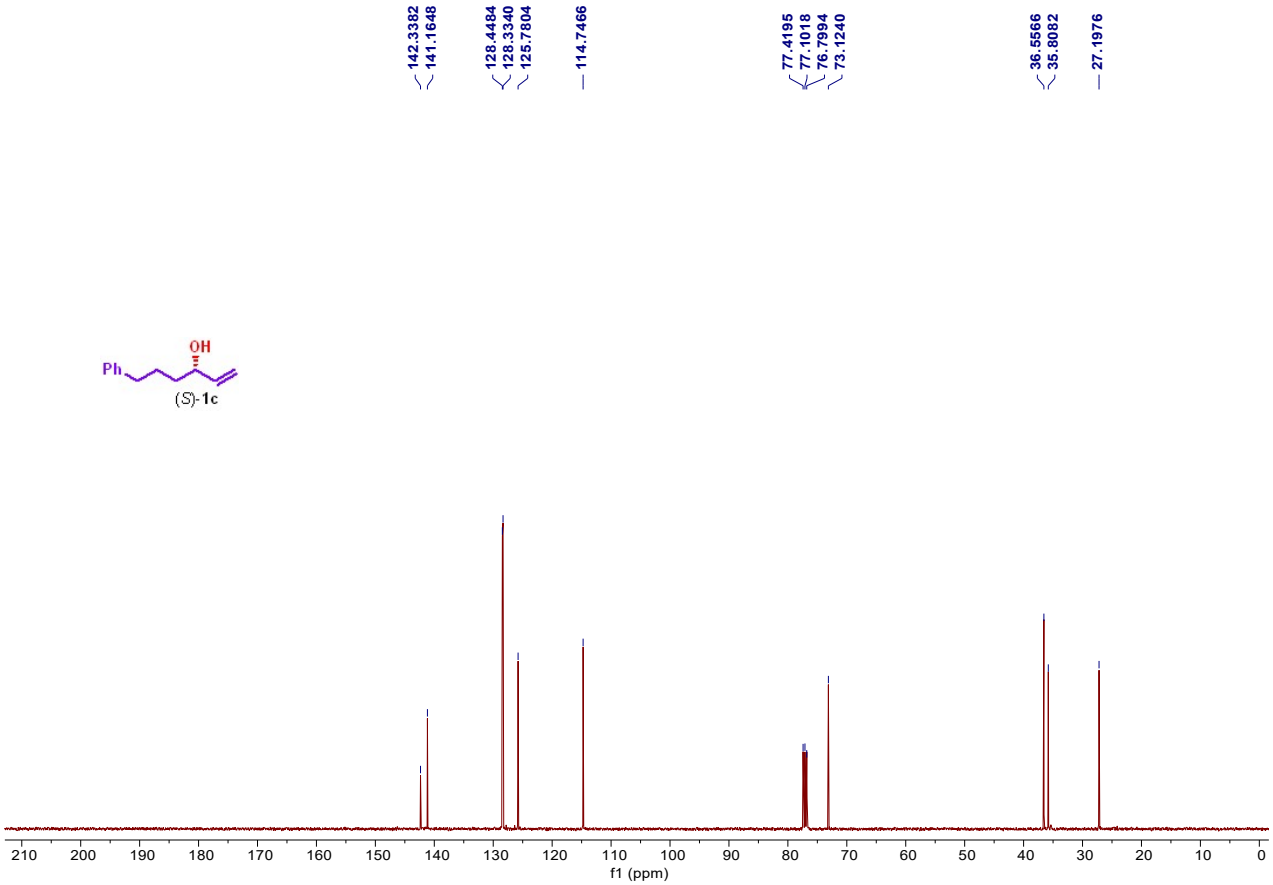
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4c**



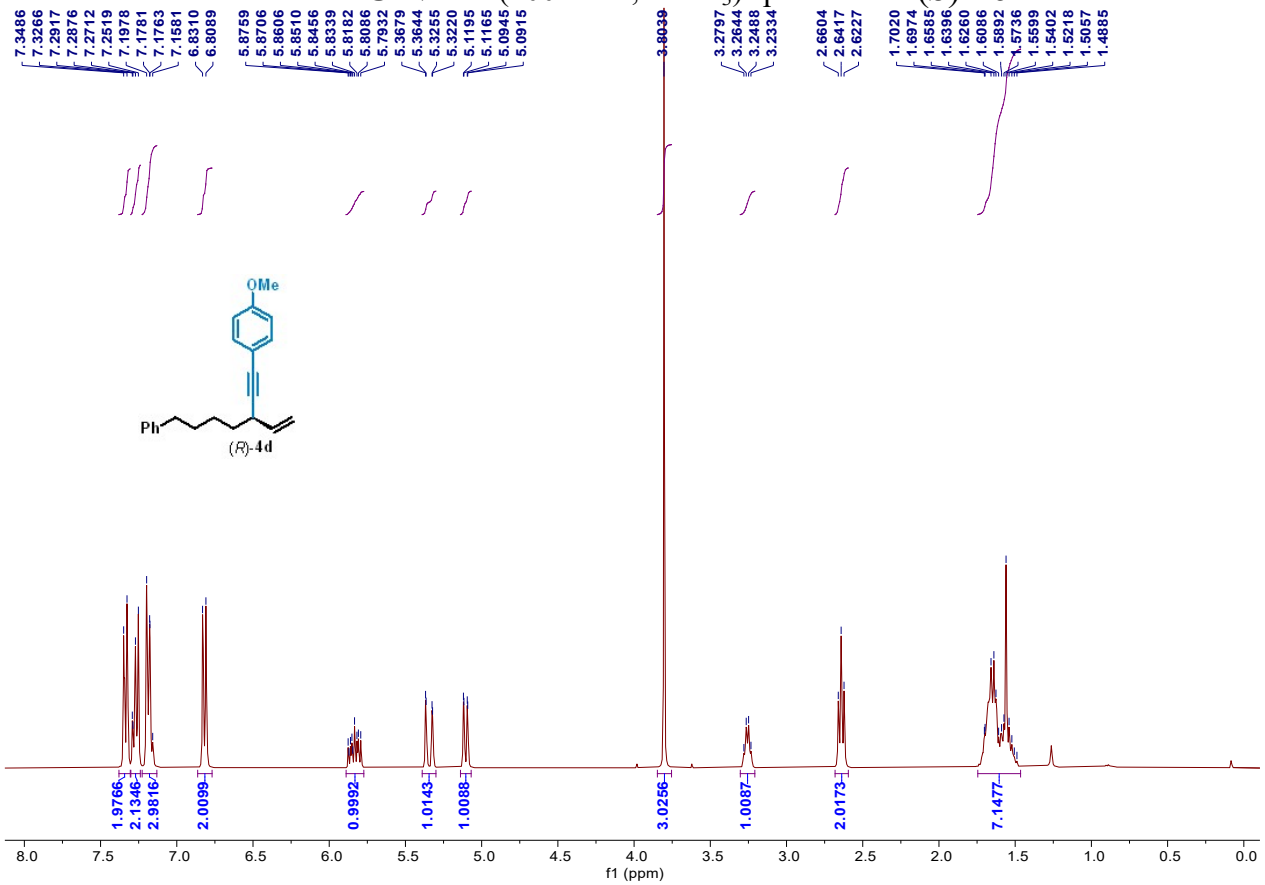
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4c**



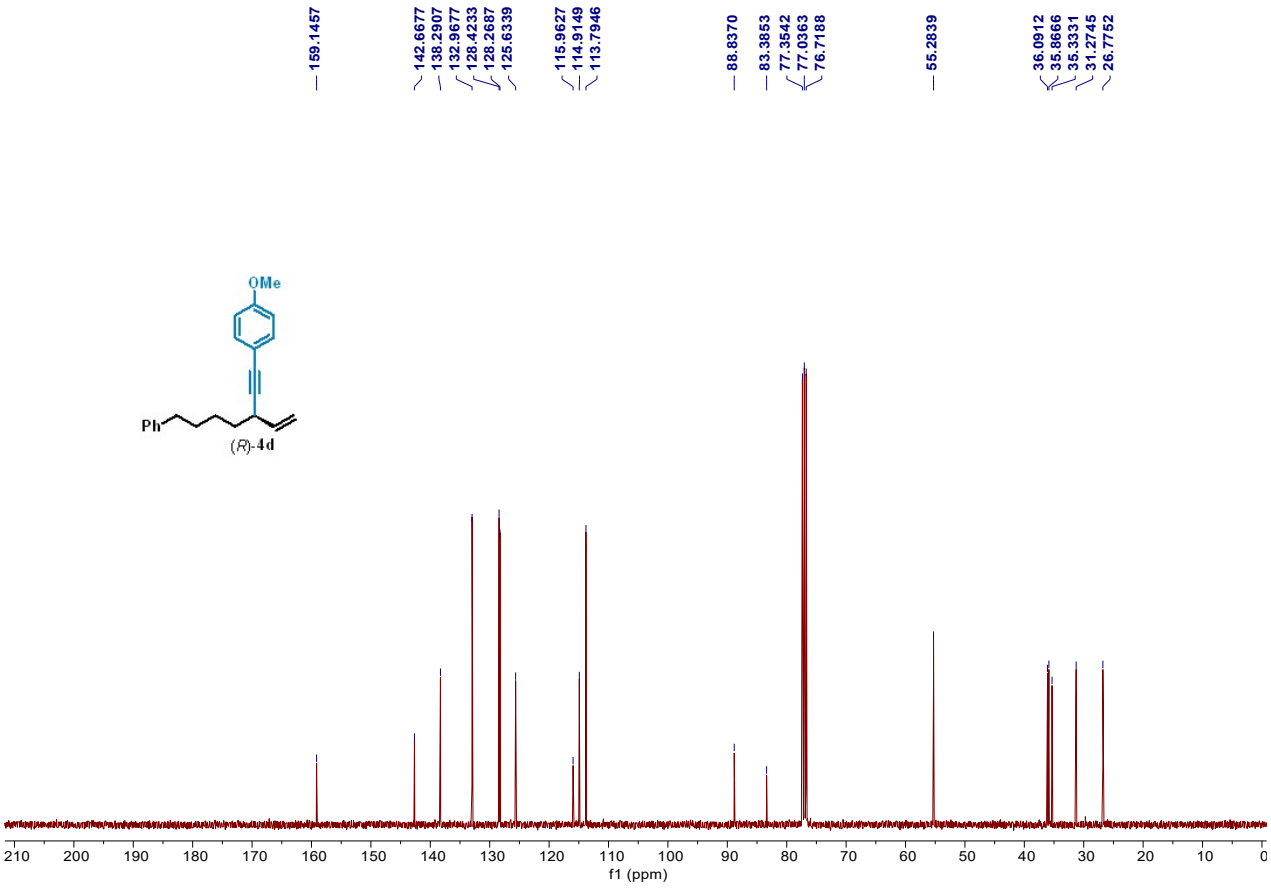
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1c**



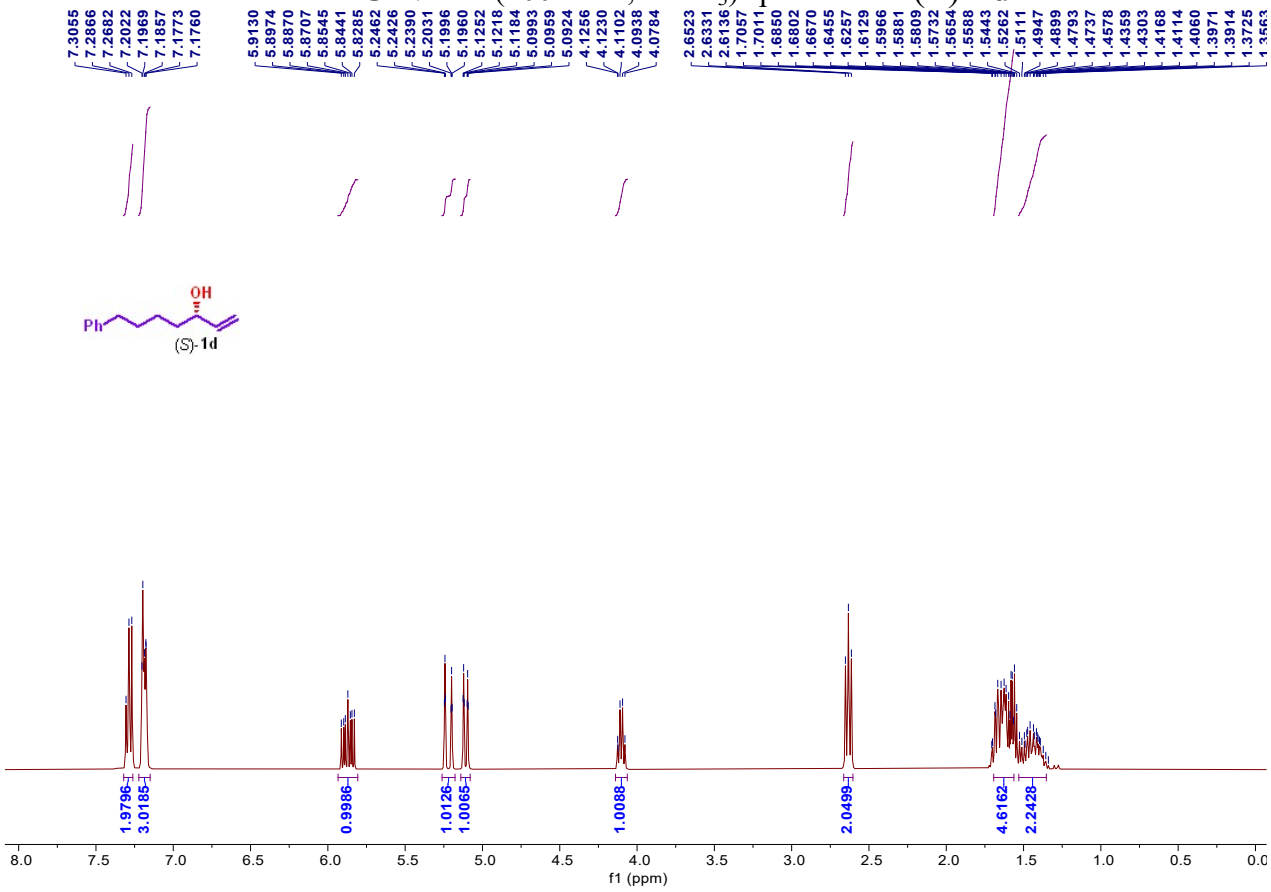
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1c**



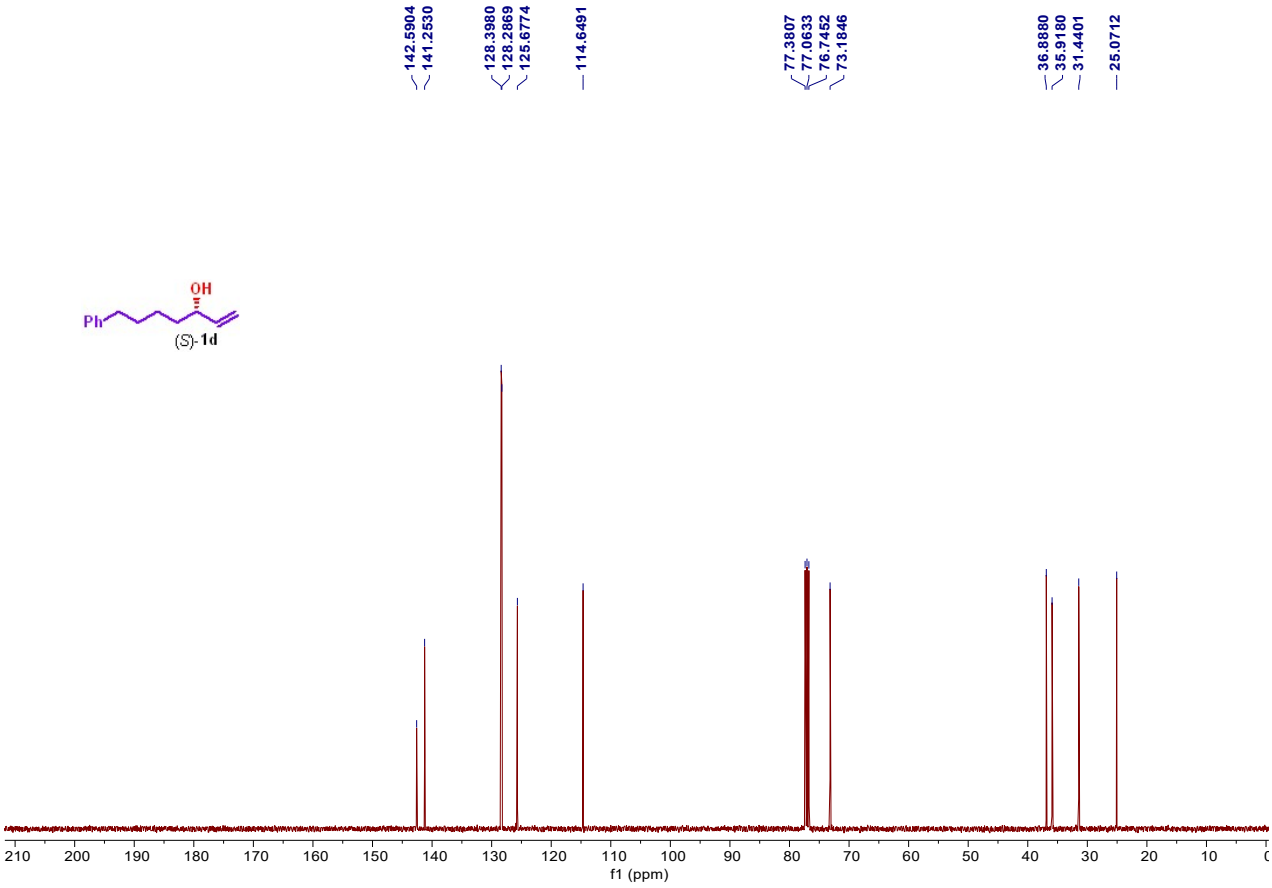
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4d**



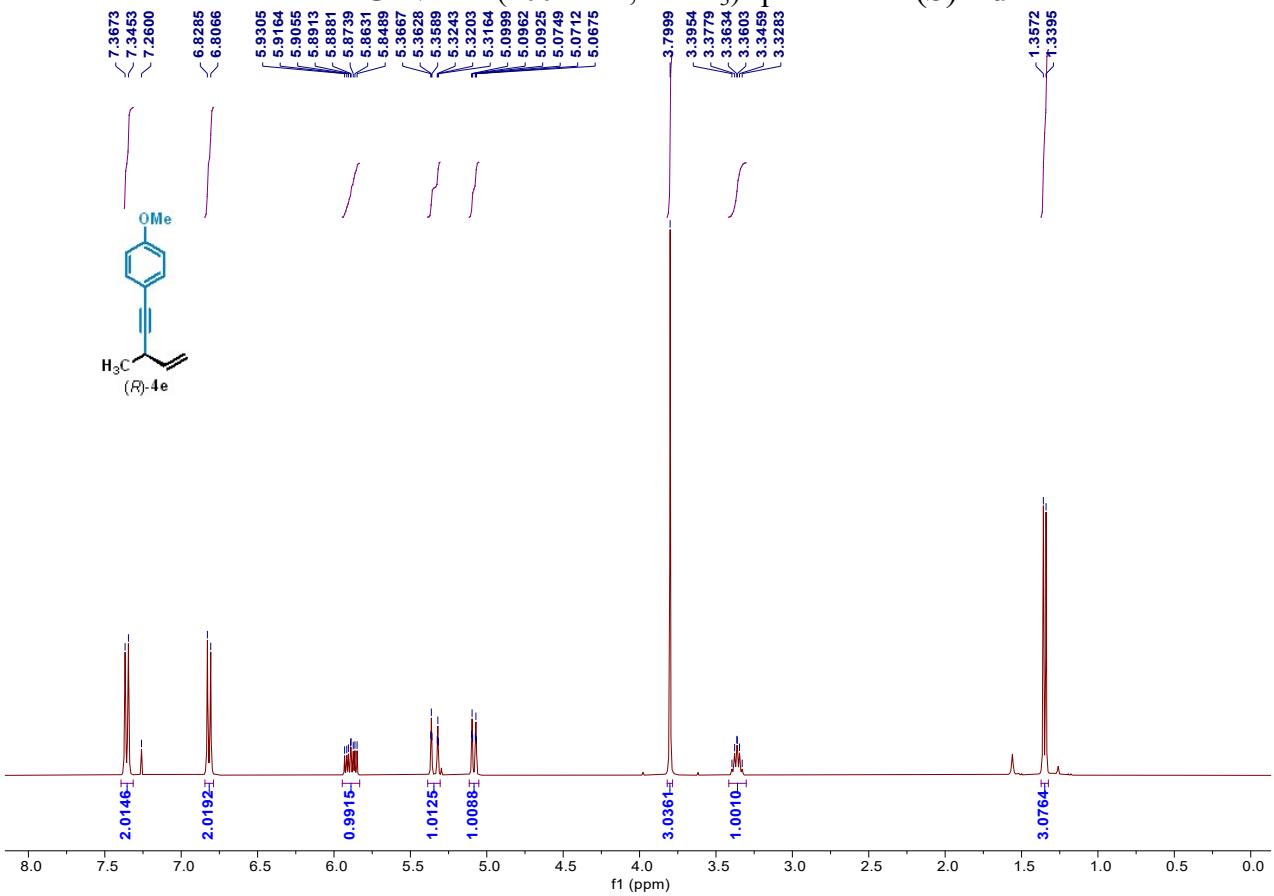
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4d**



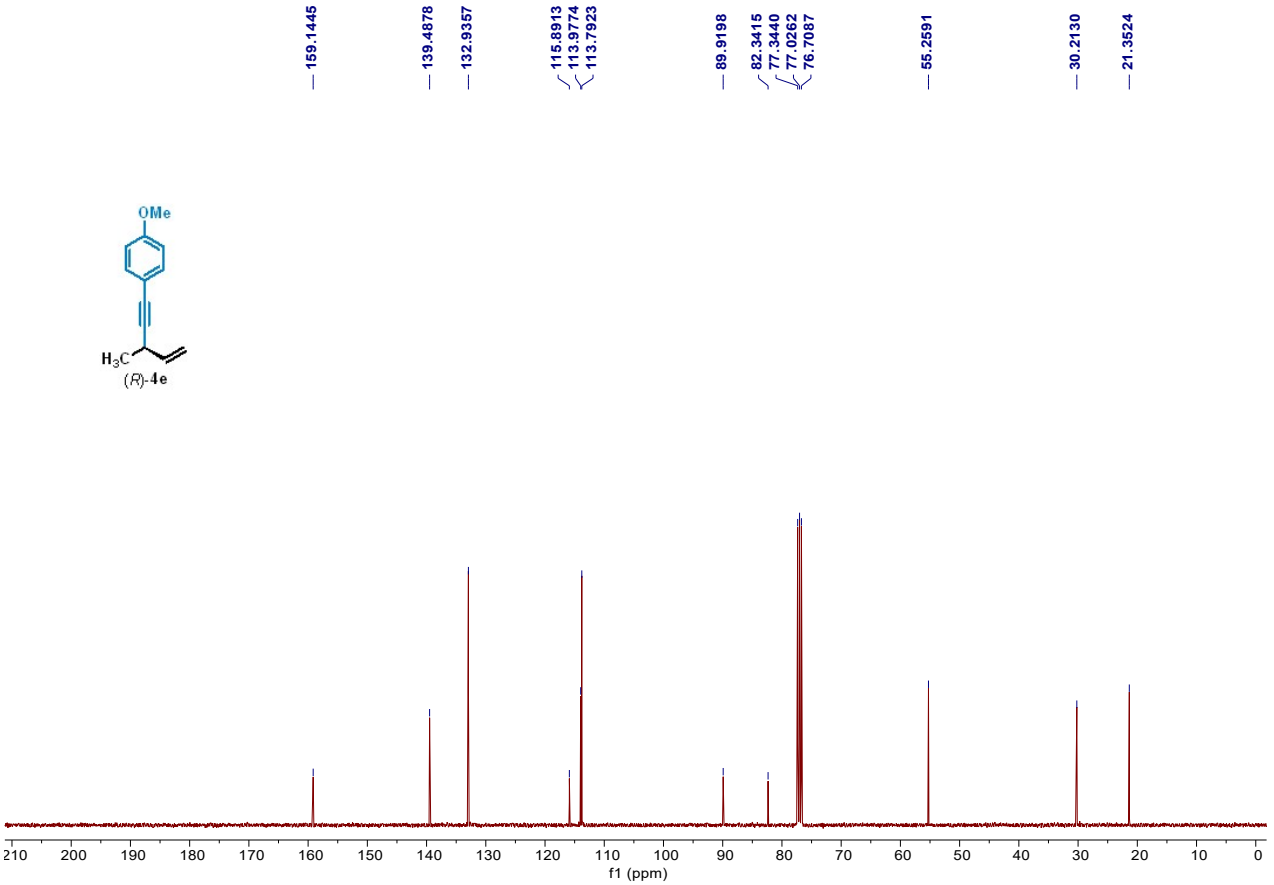
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1d**



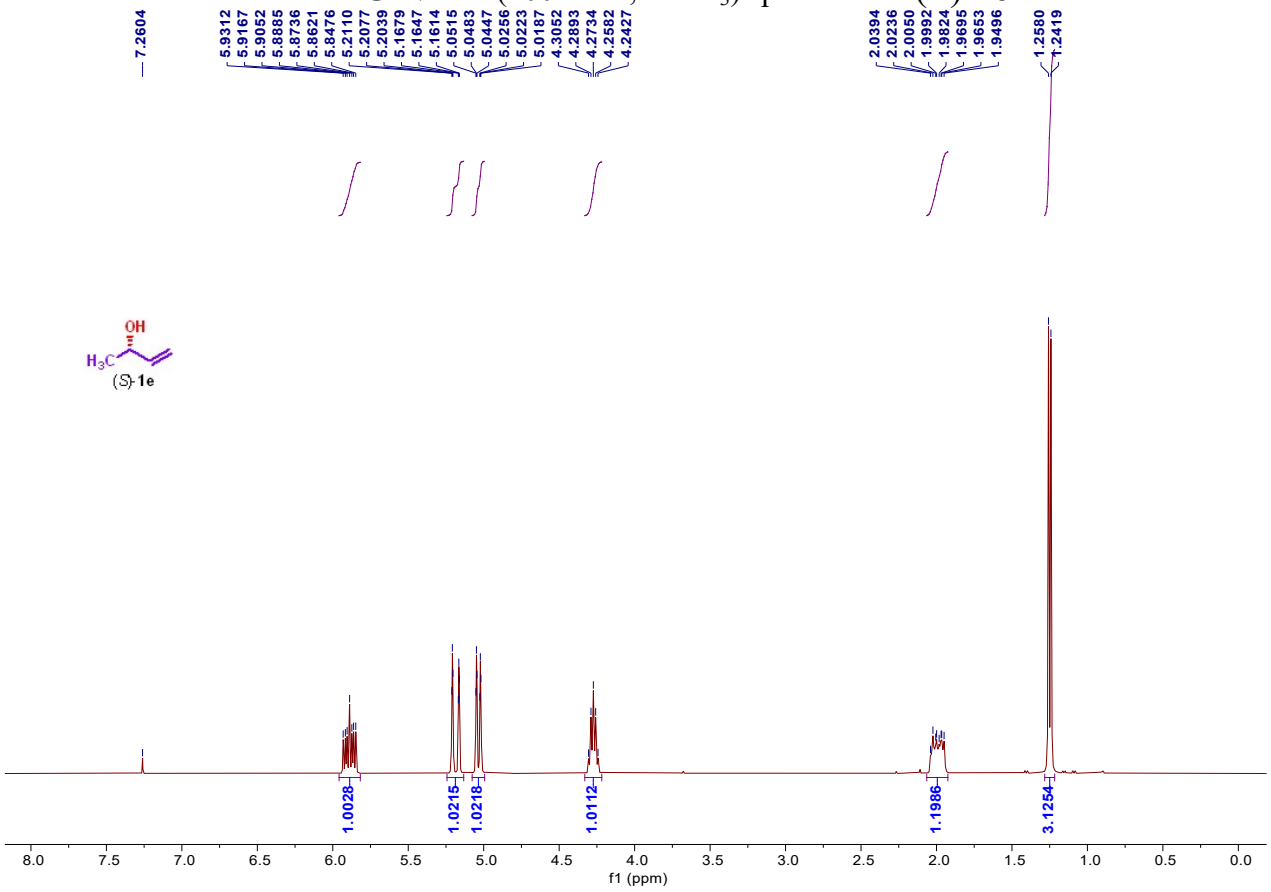
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1d**



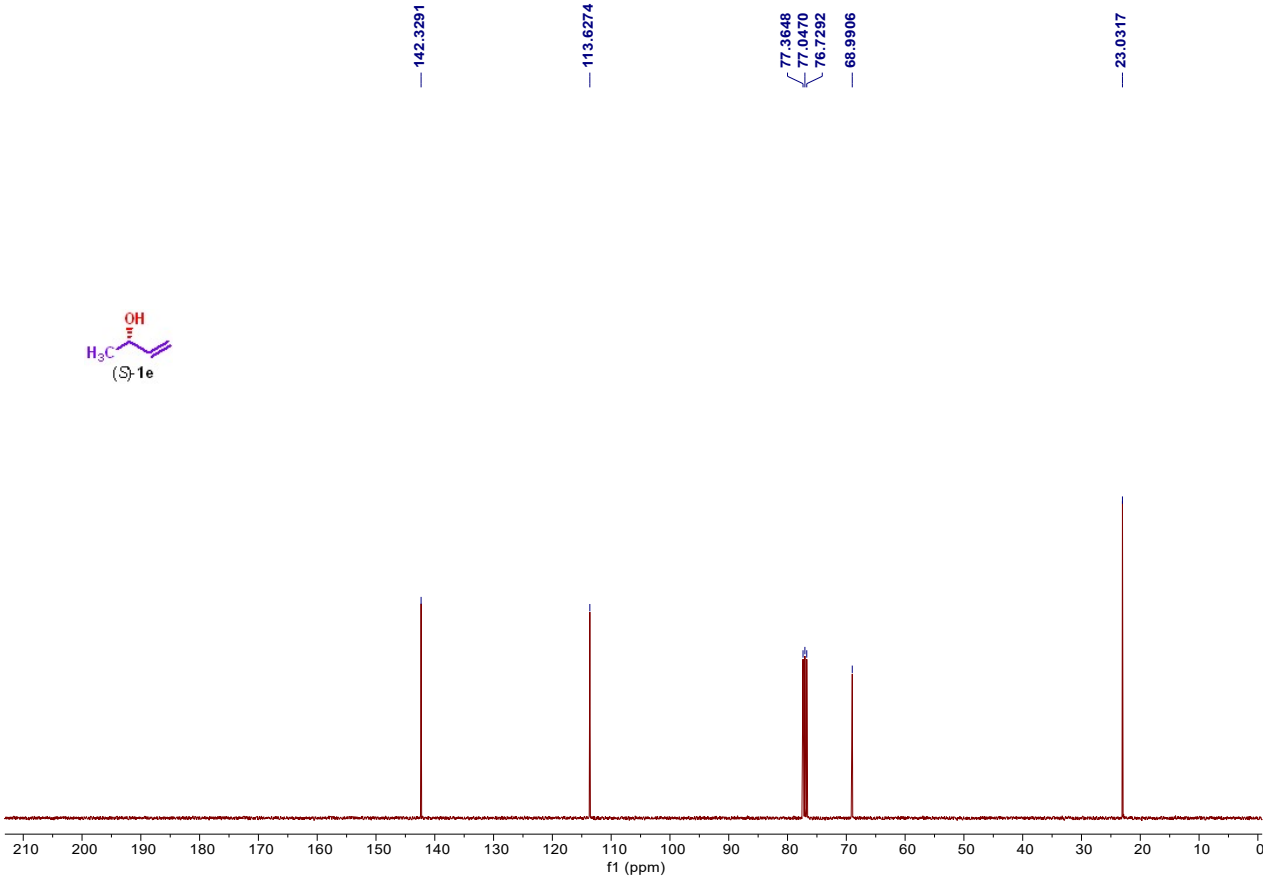
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4e**



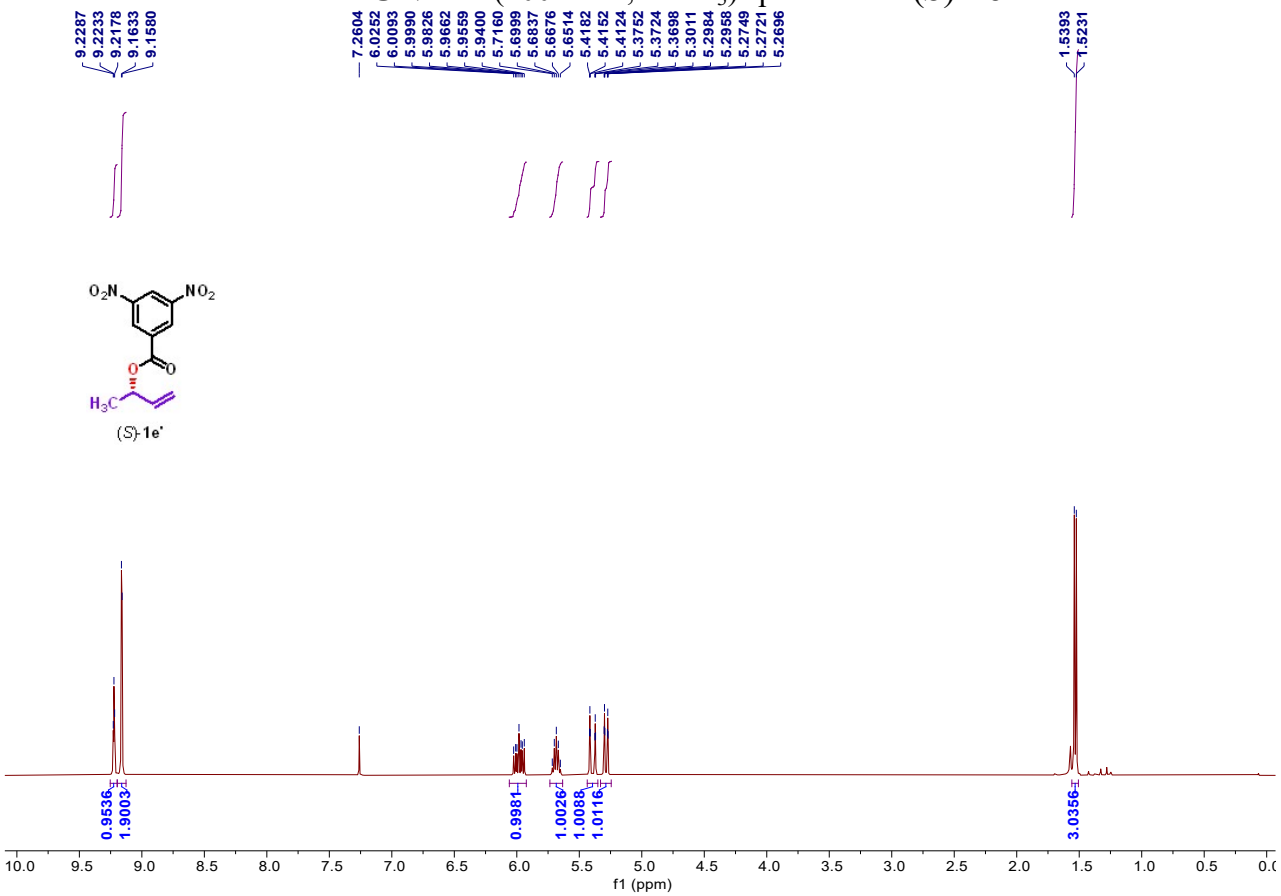
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4e**



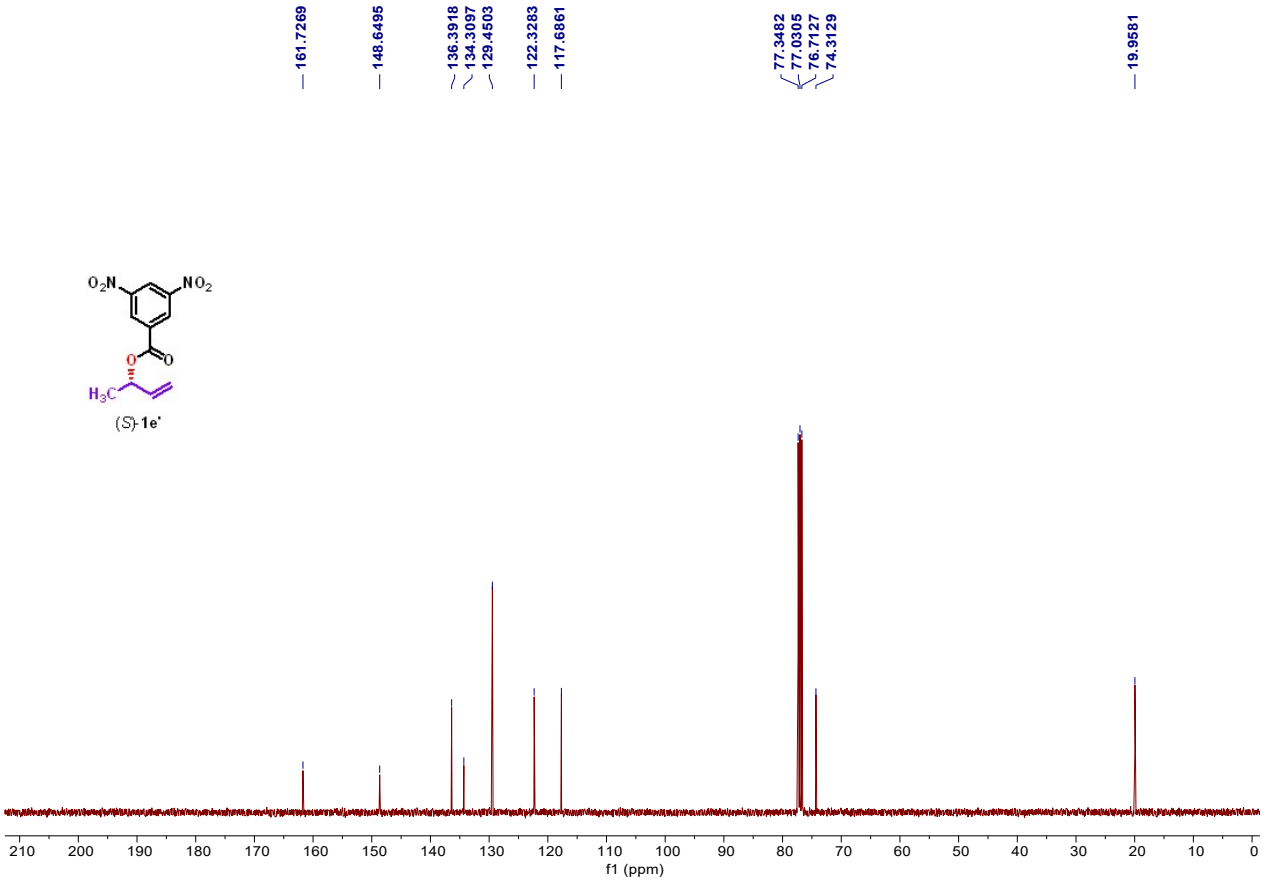
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1e**



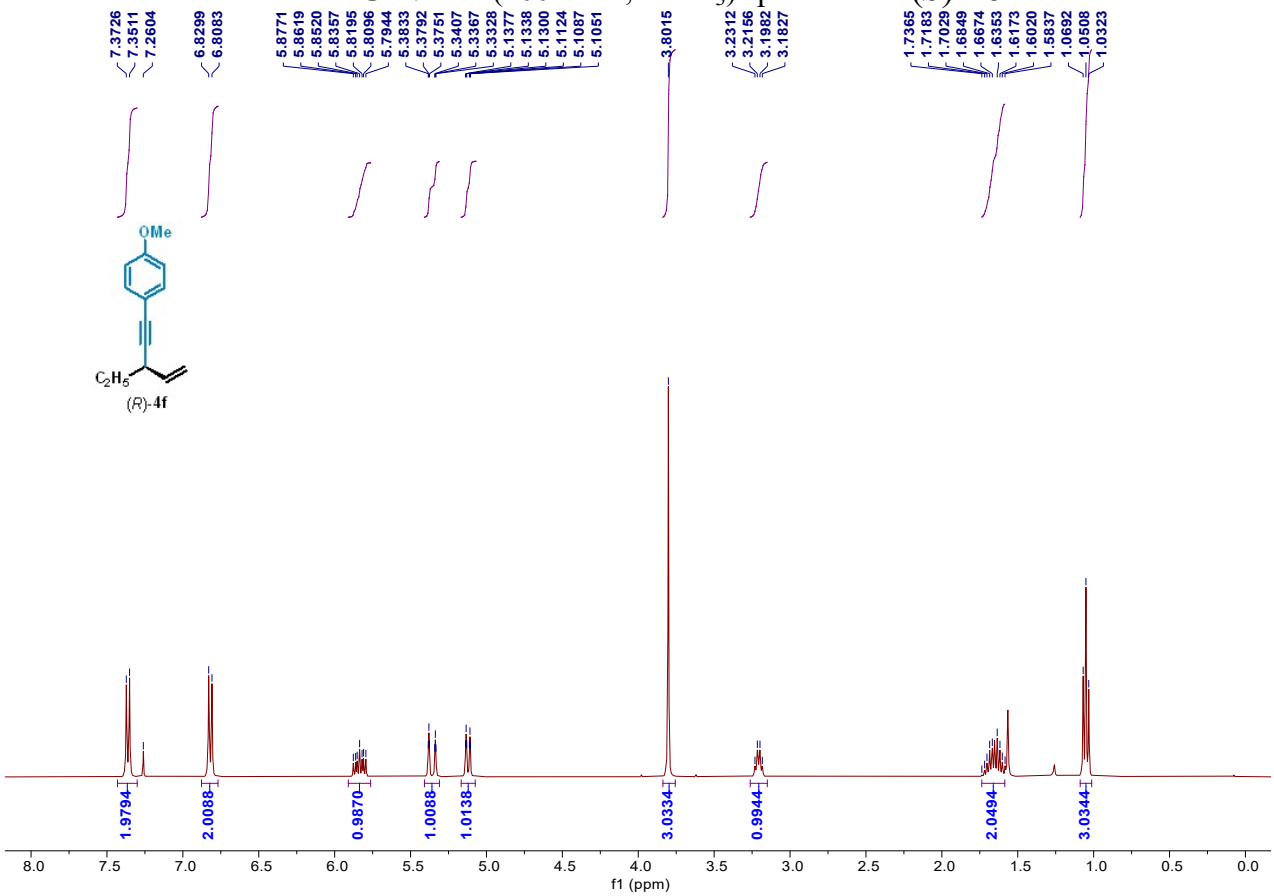
^{13}CNMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1e**



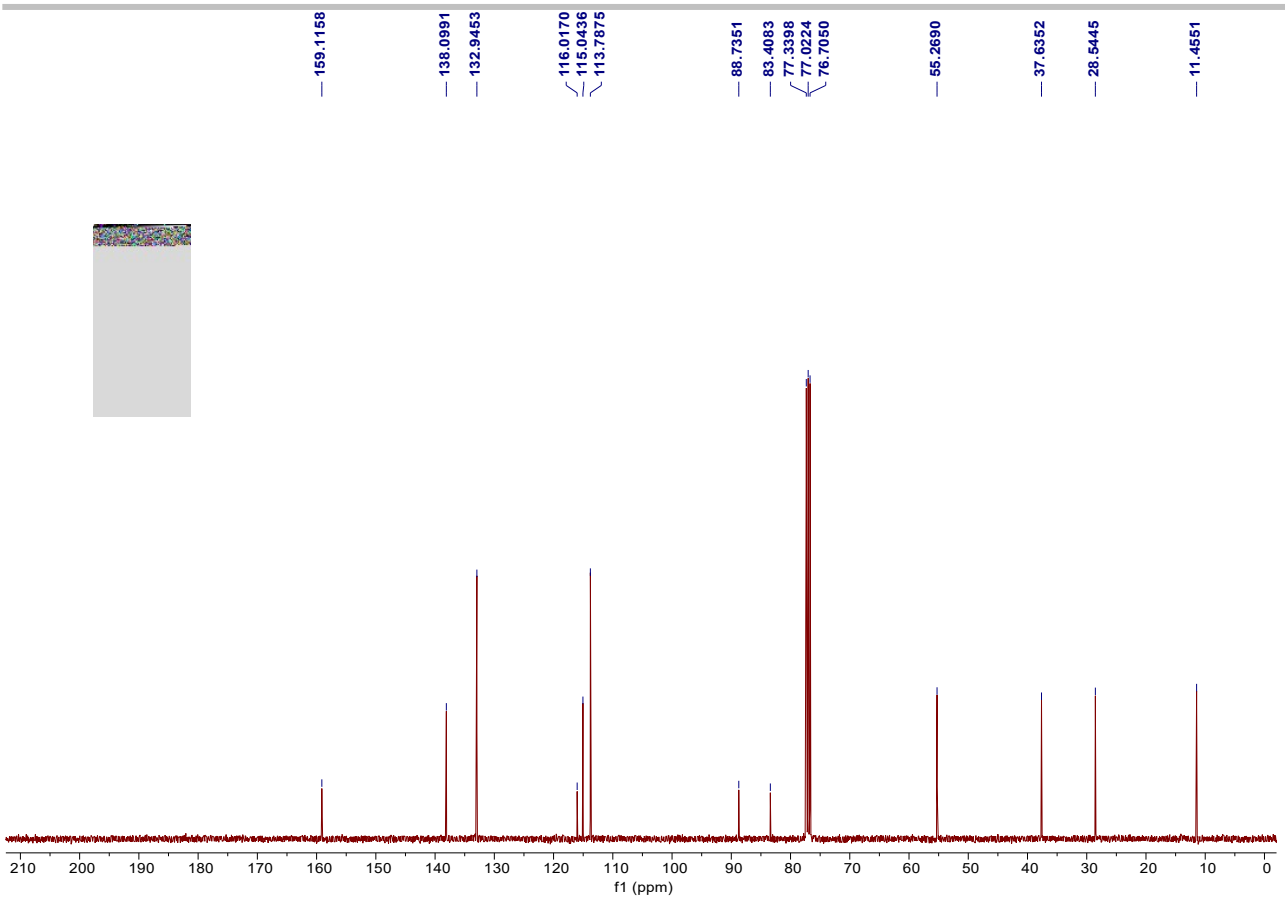
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1e'**



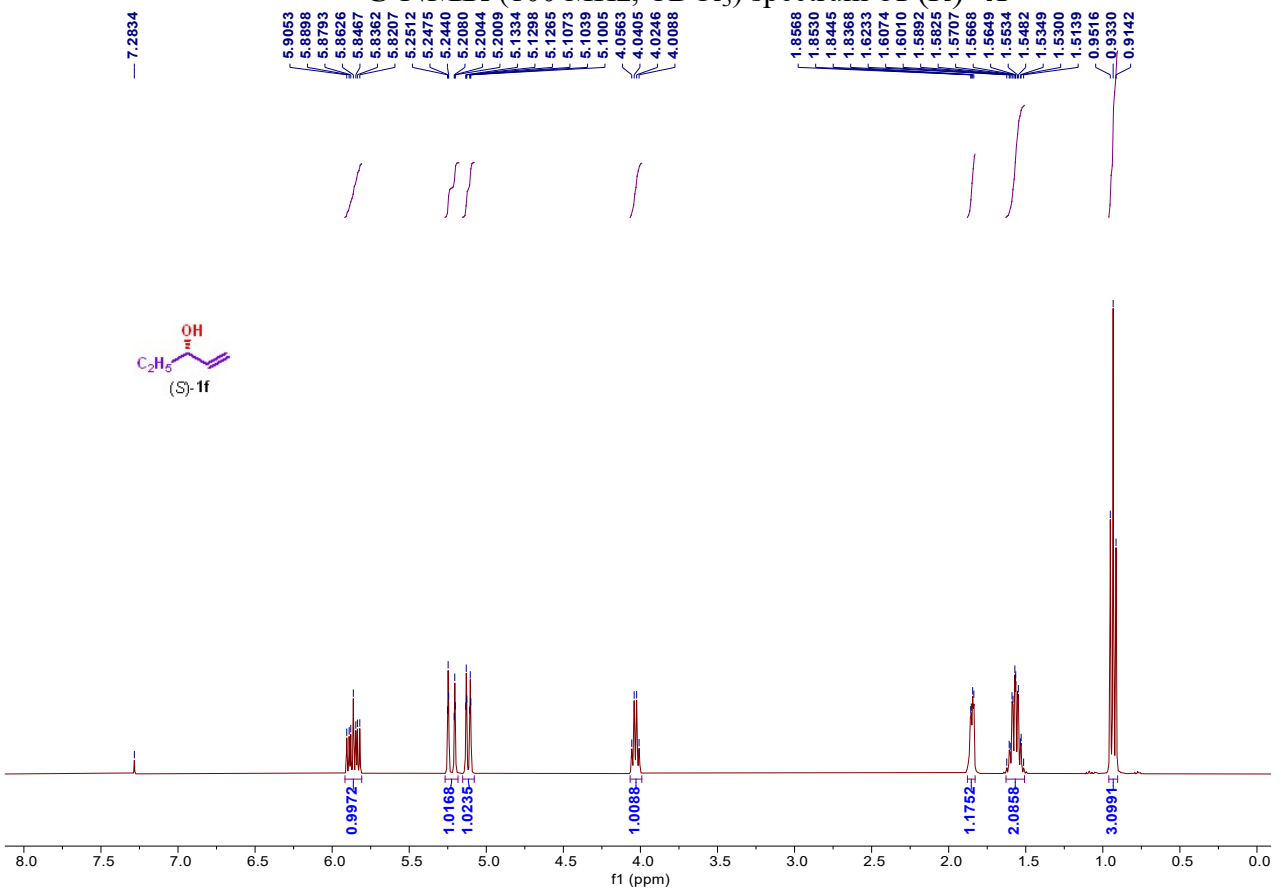
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1e'**



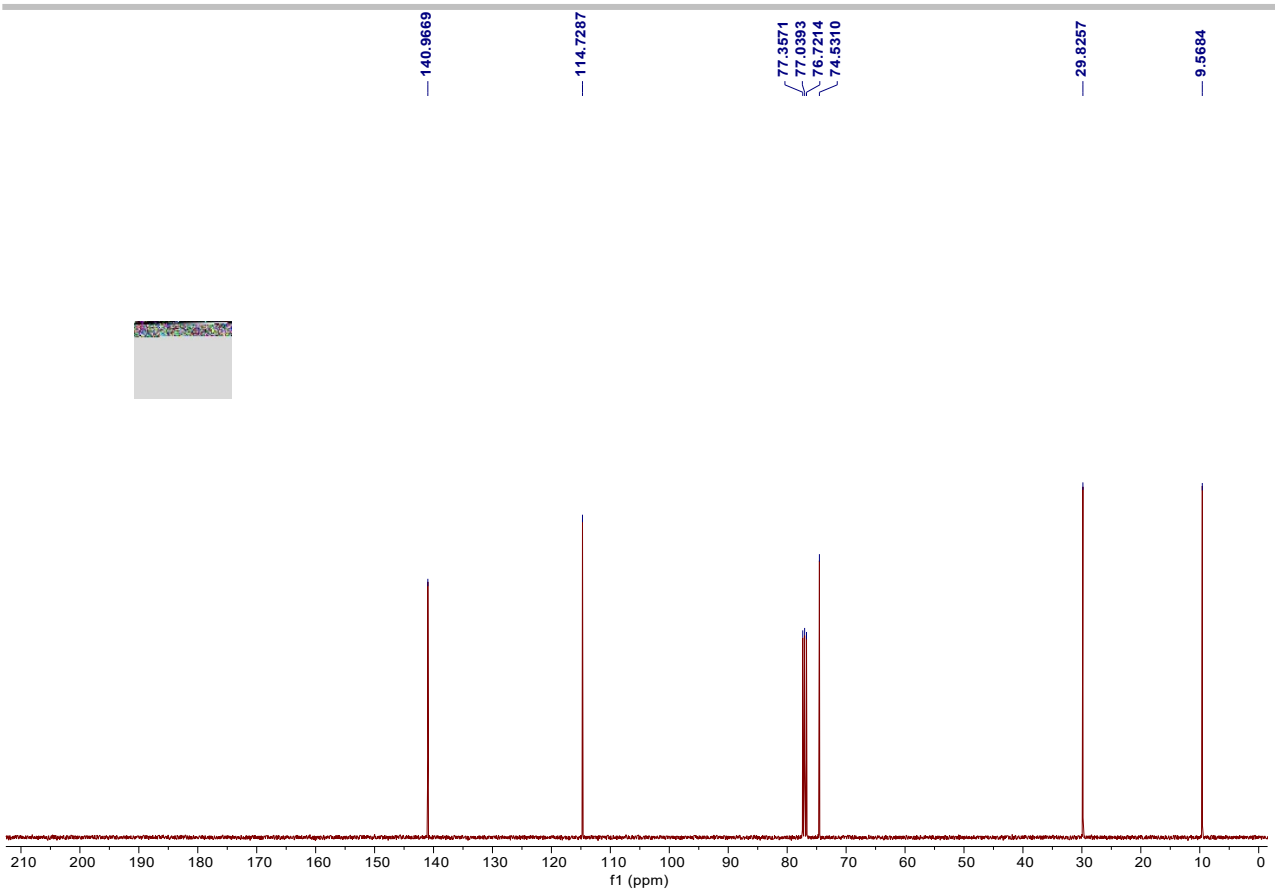
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4f**



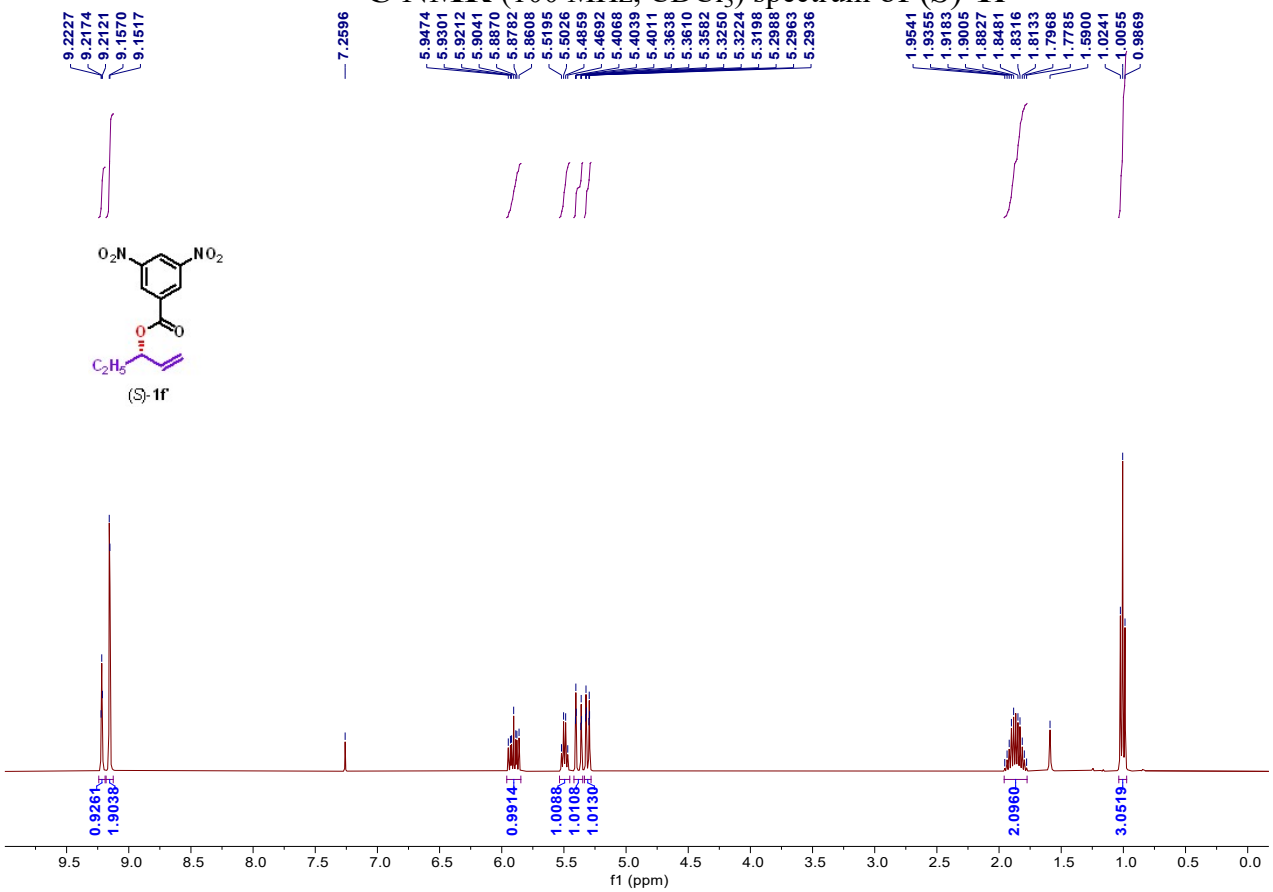
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4f**



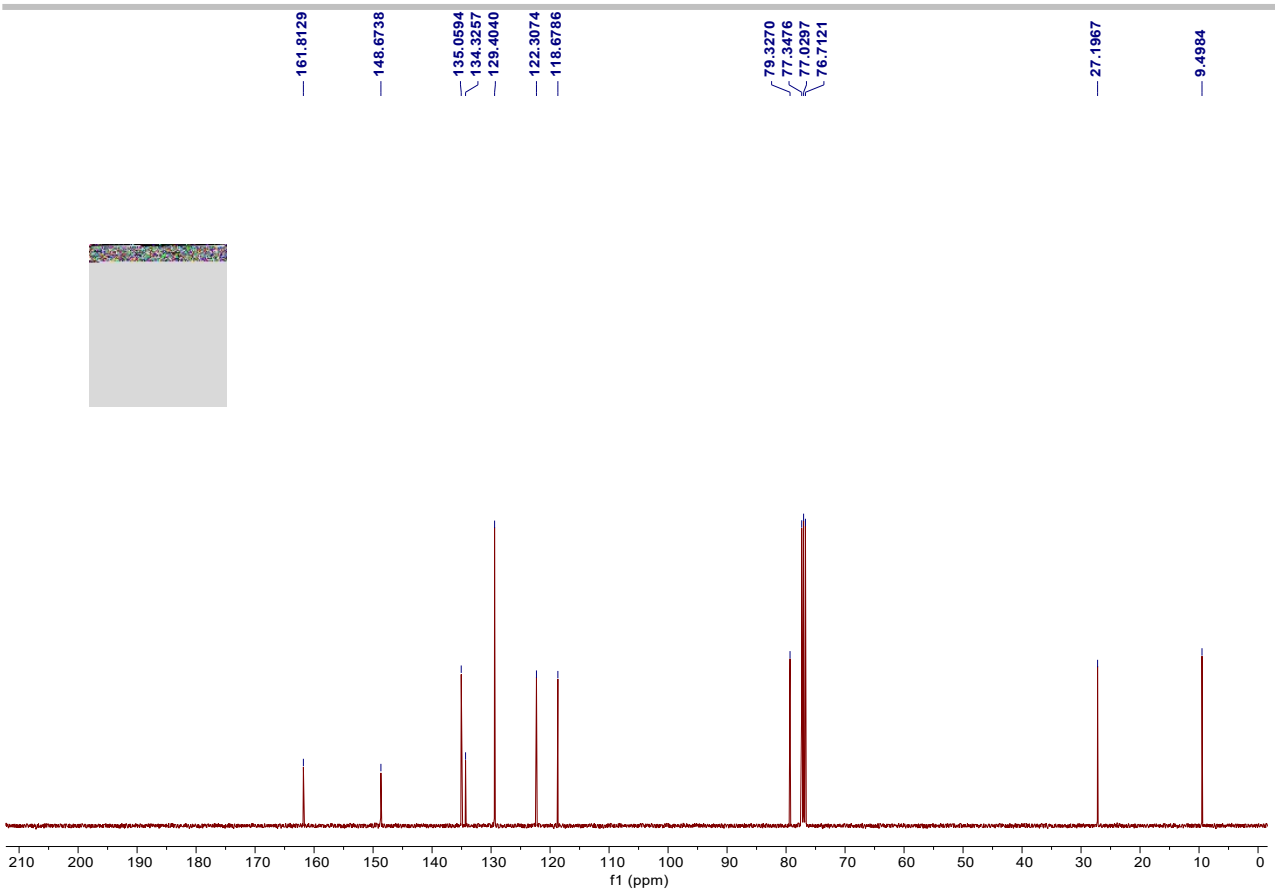
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1f**



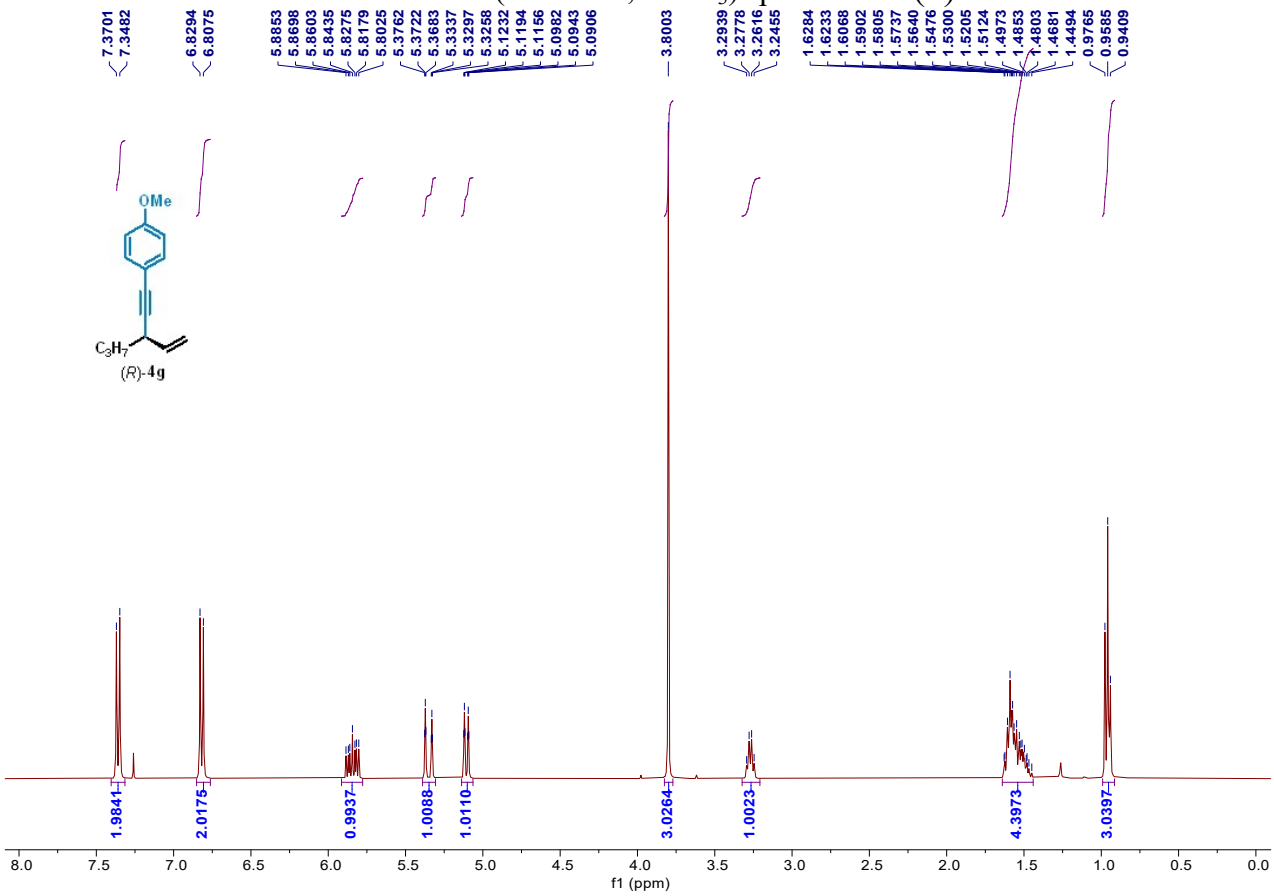
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1f**



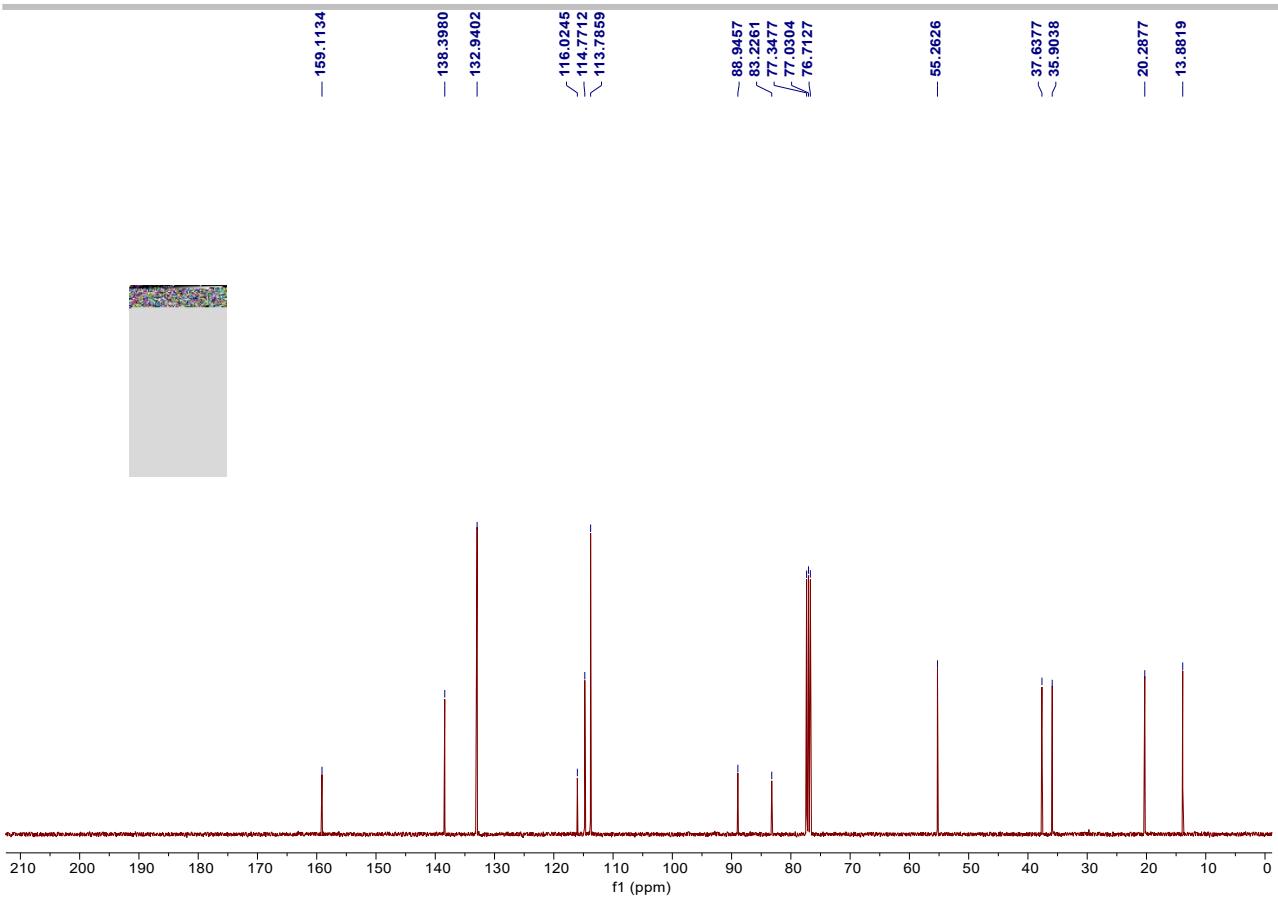
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1f'**



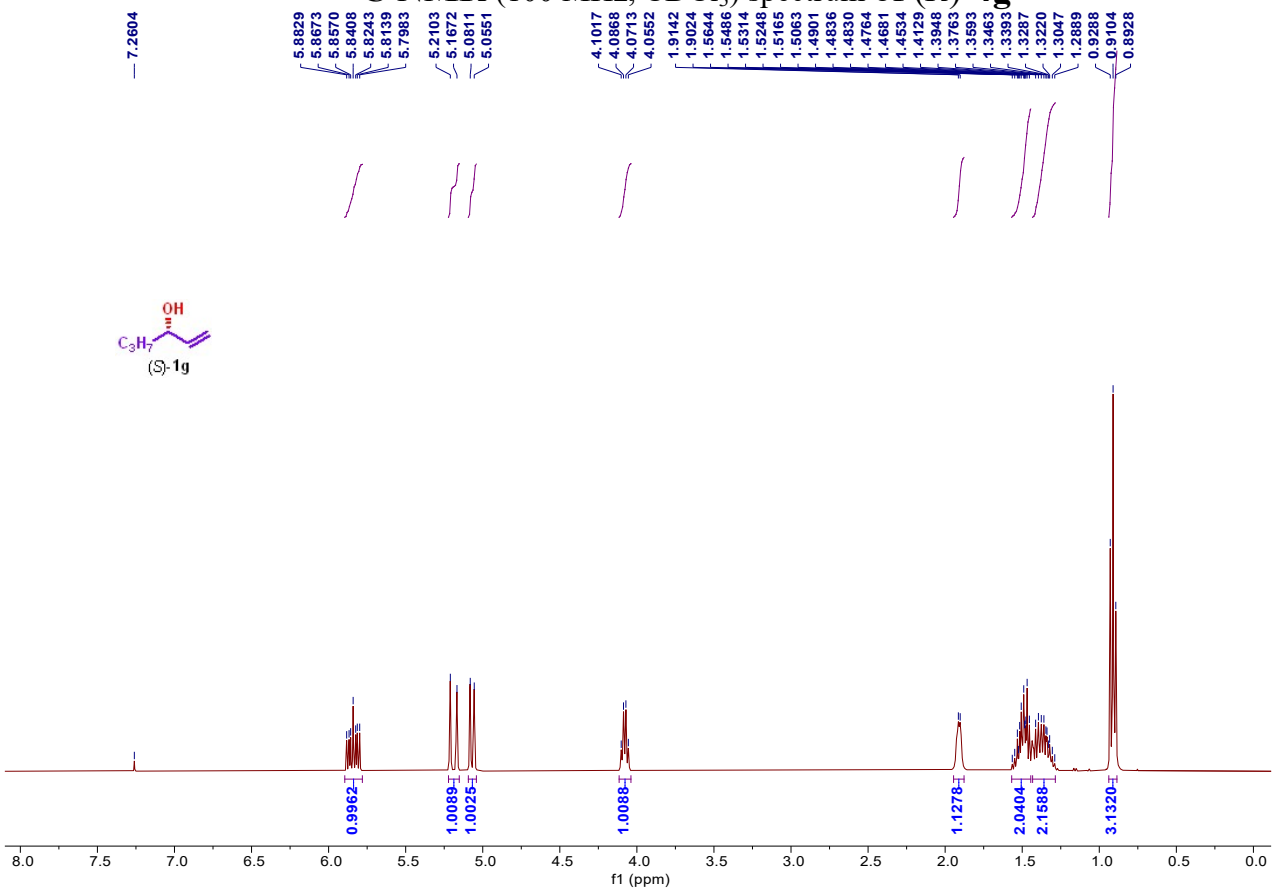
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1f'**



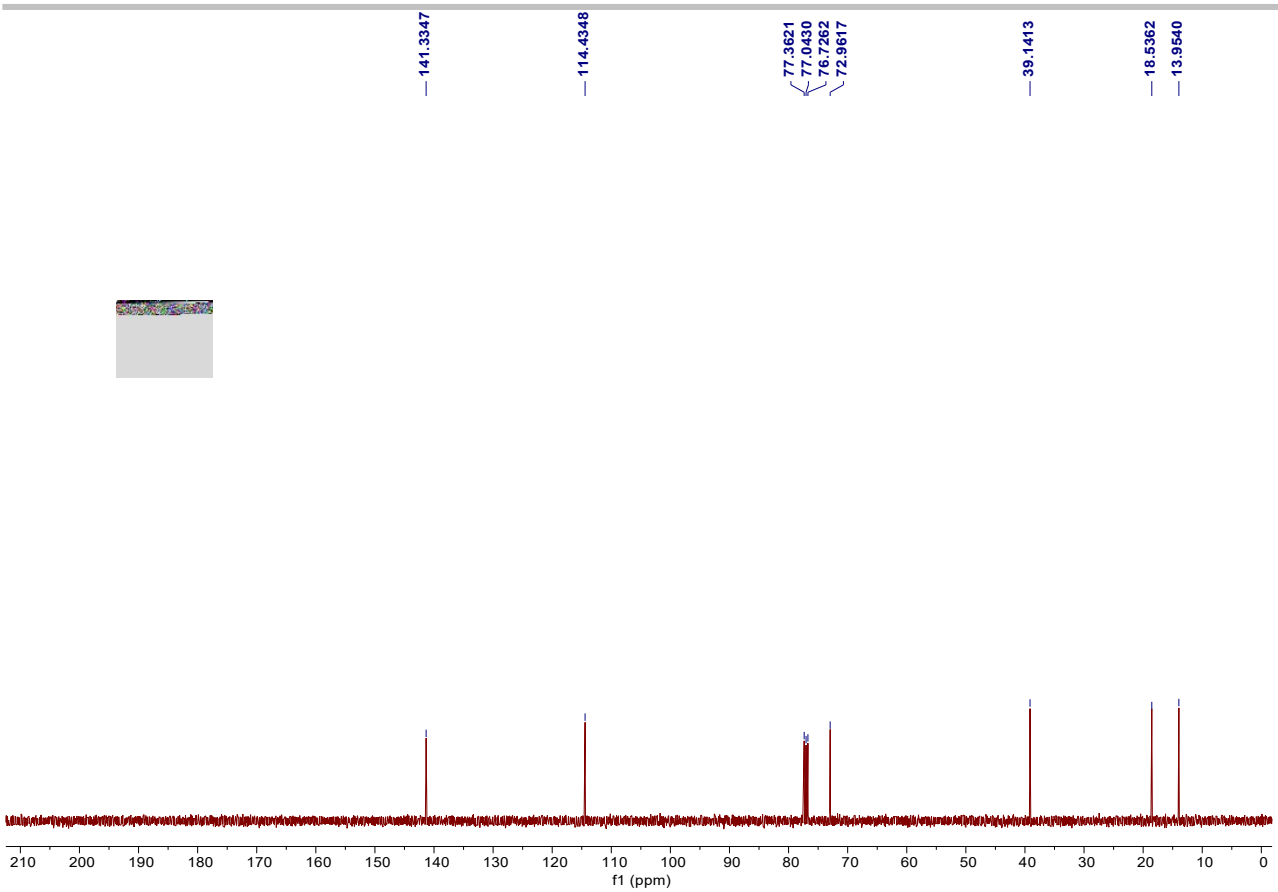
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4g**



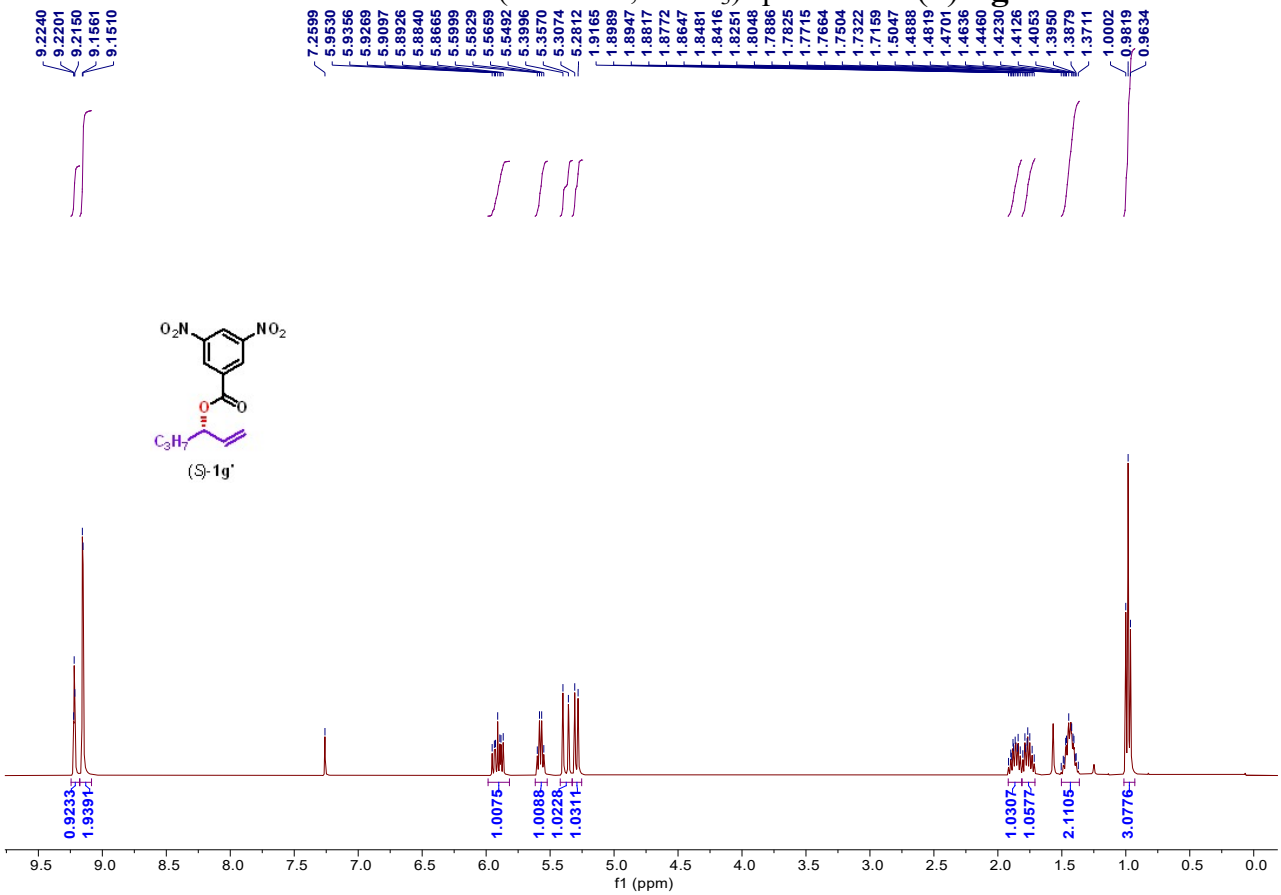
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4g**



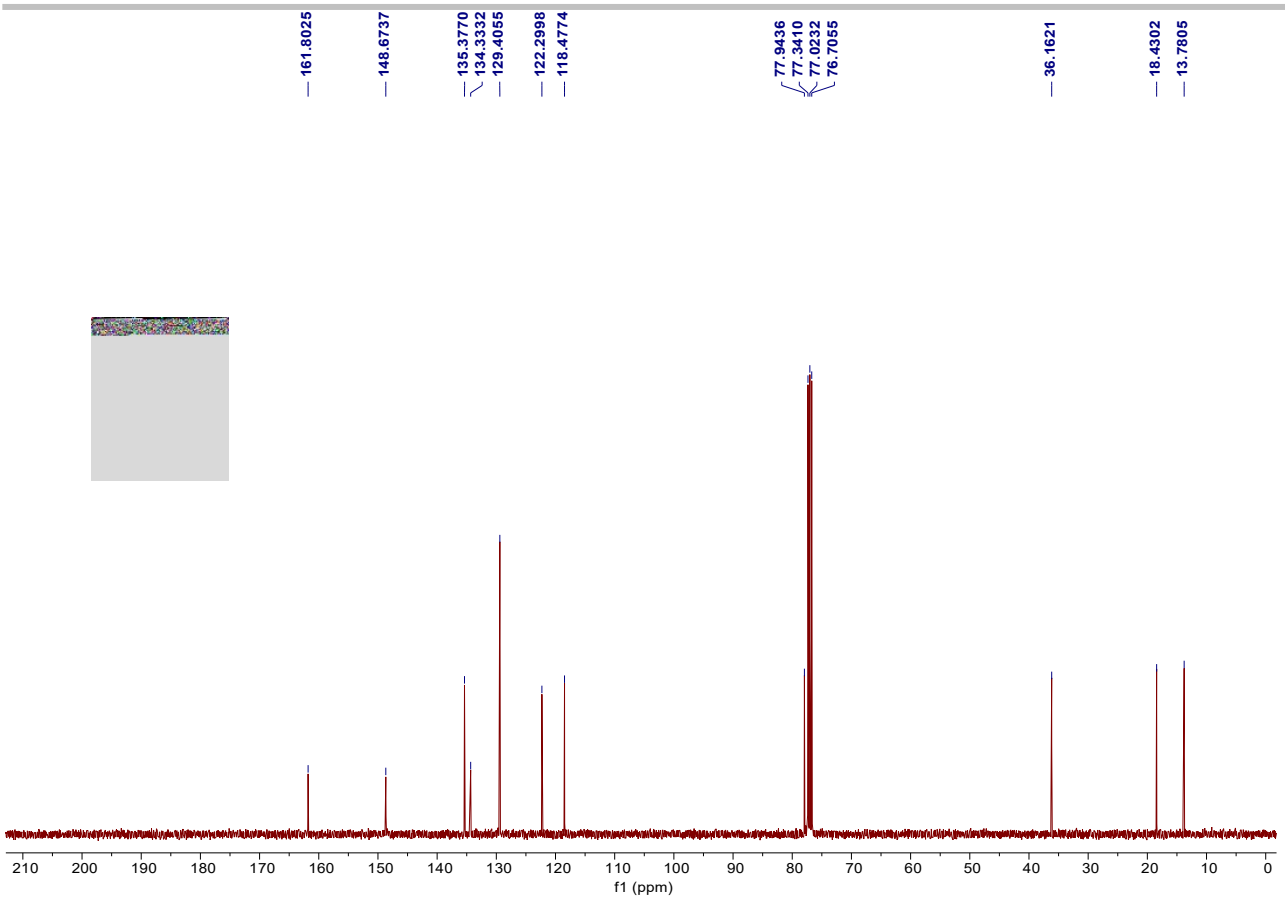
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1g**



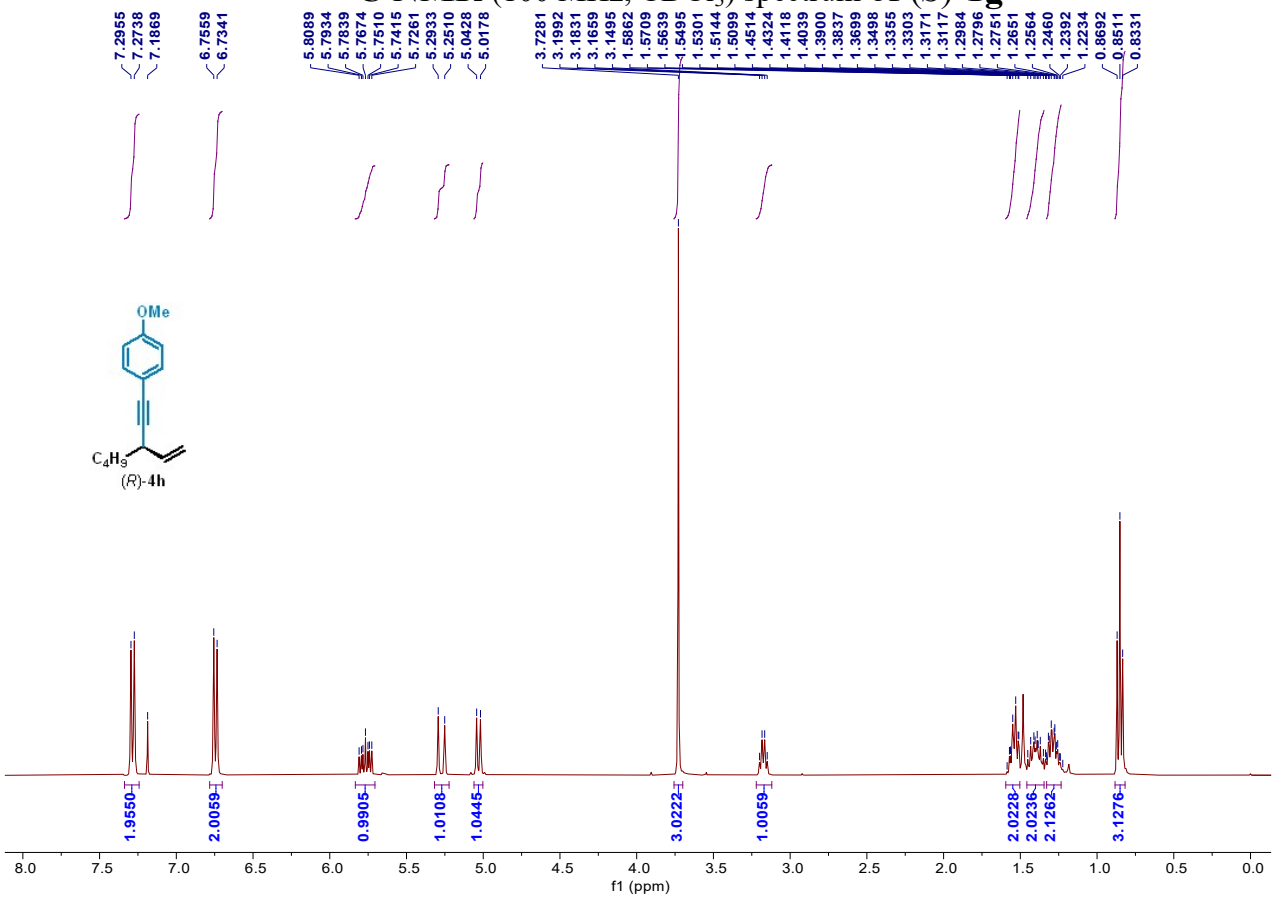
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1g**



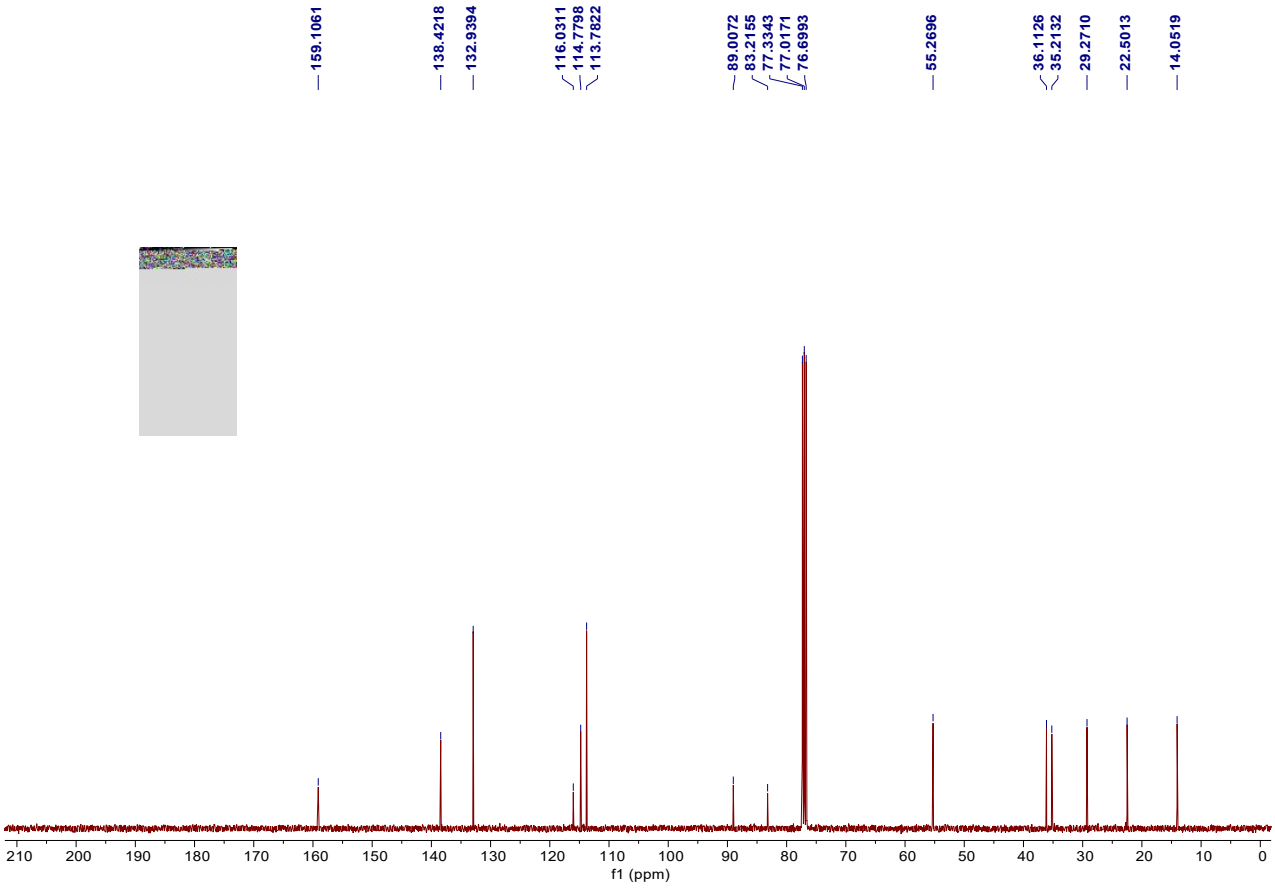
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1g'**



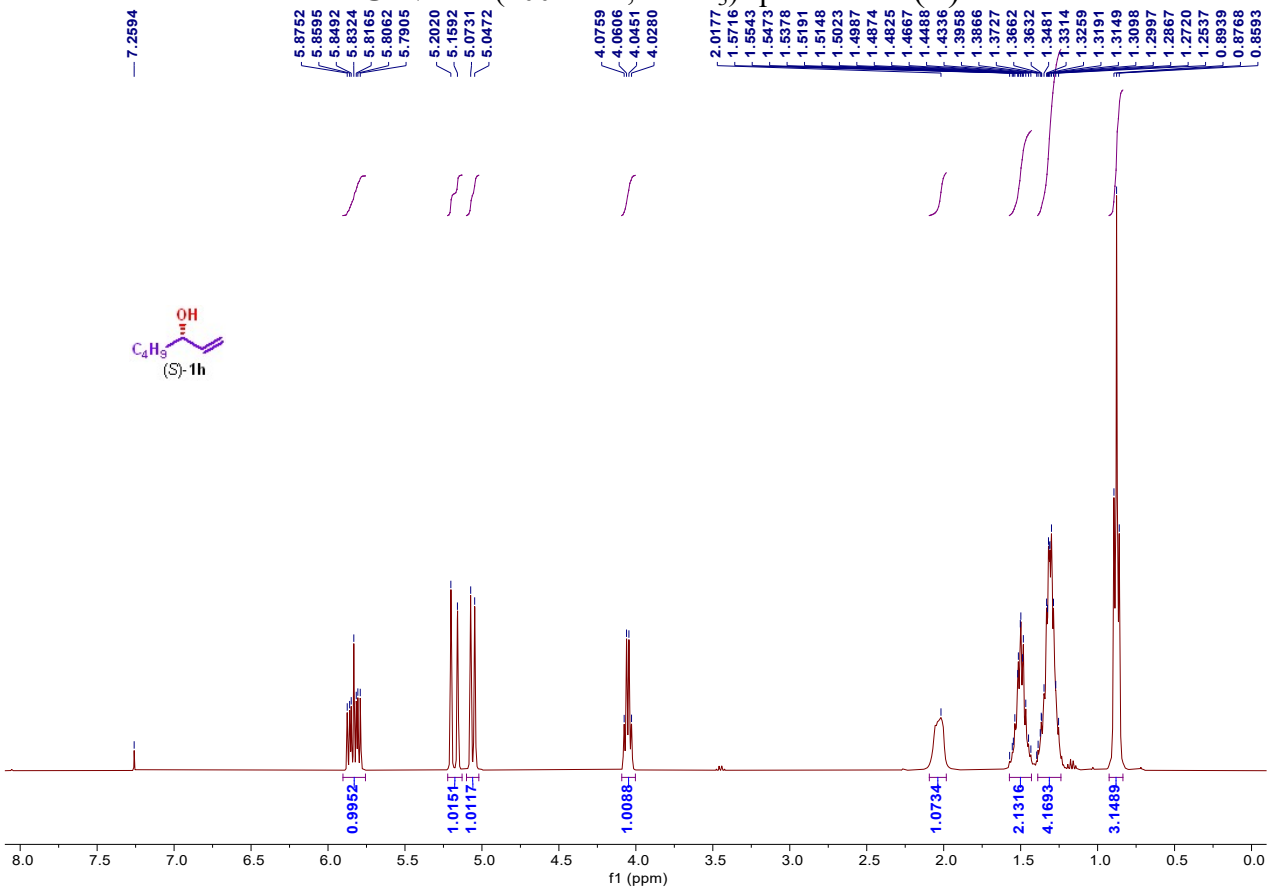
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1g'**



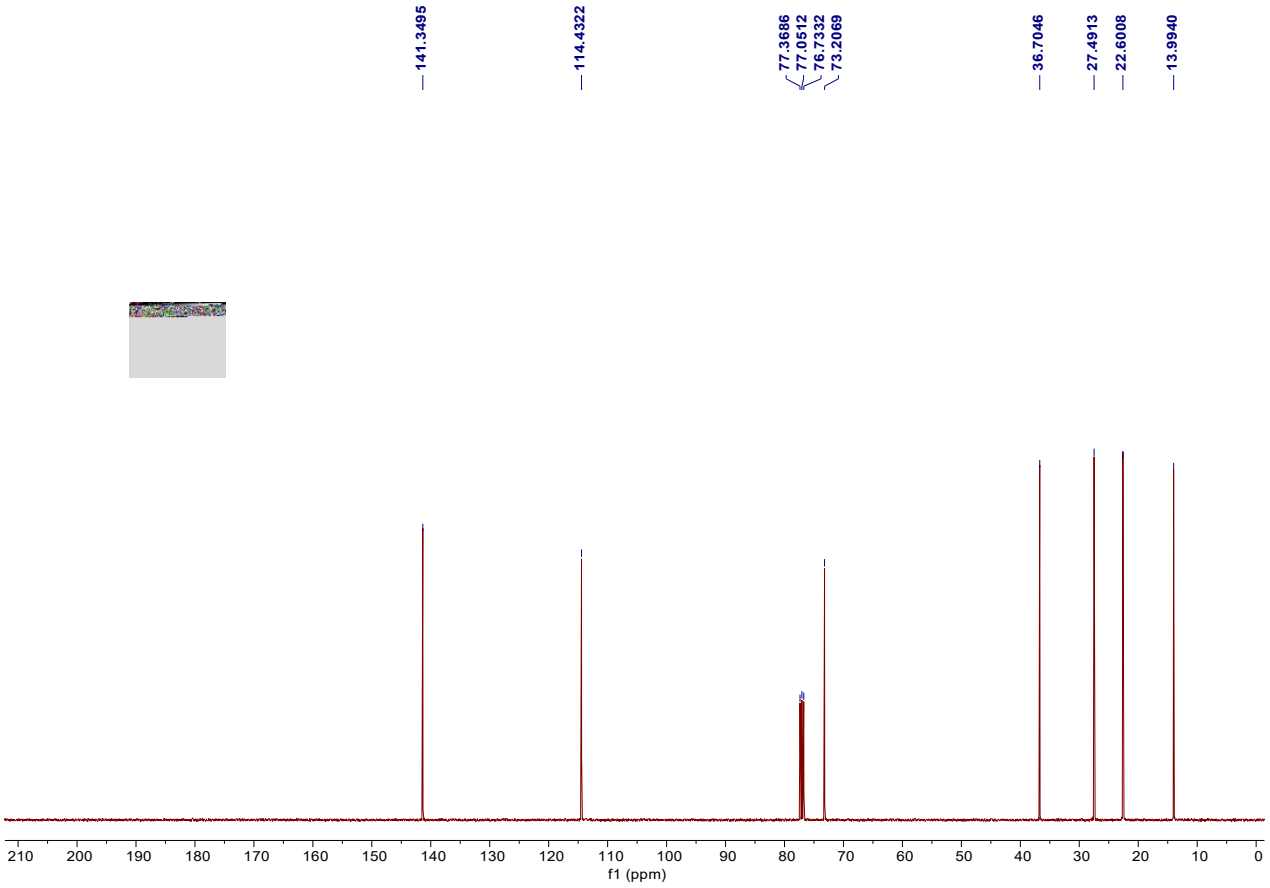
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4h**



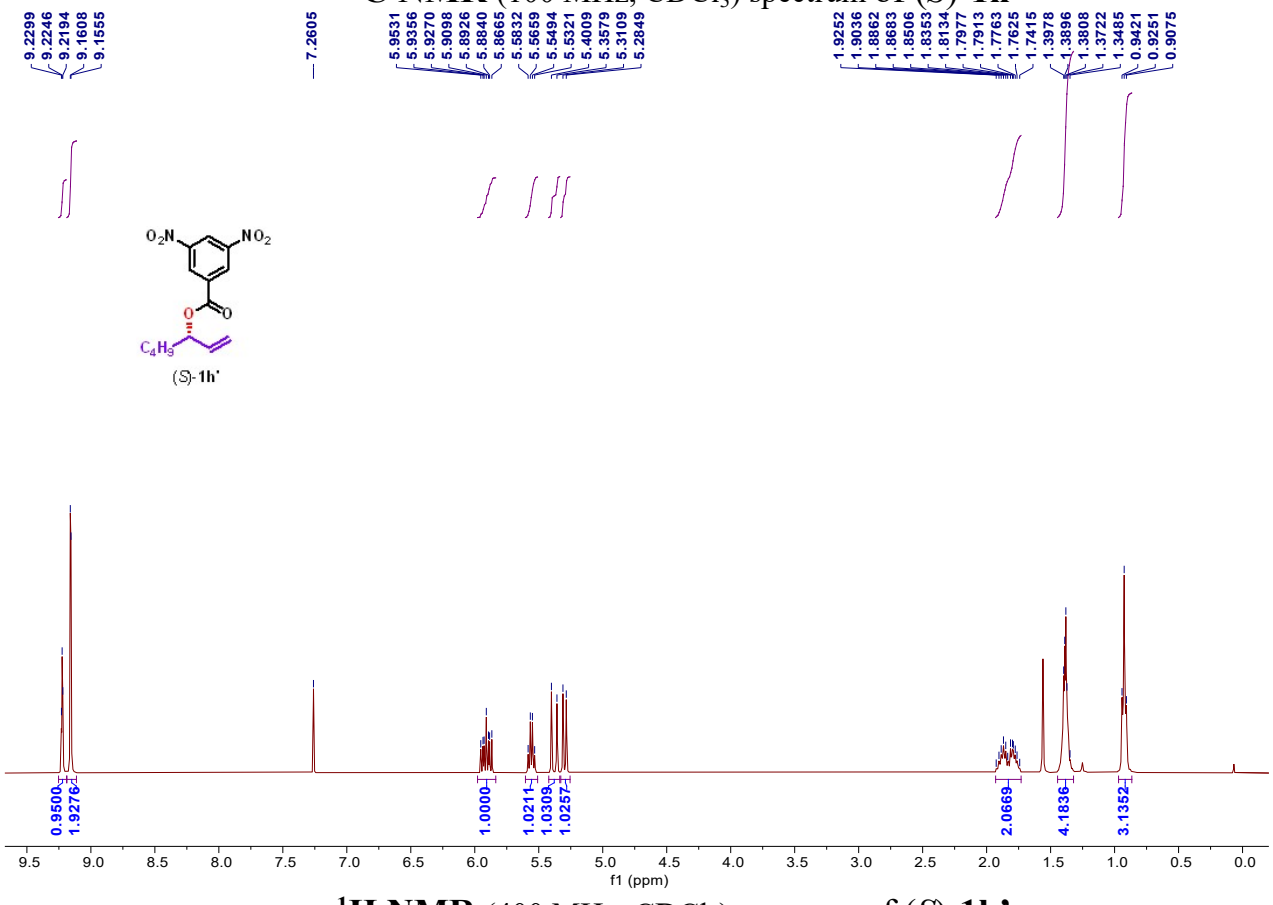
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4h**



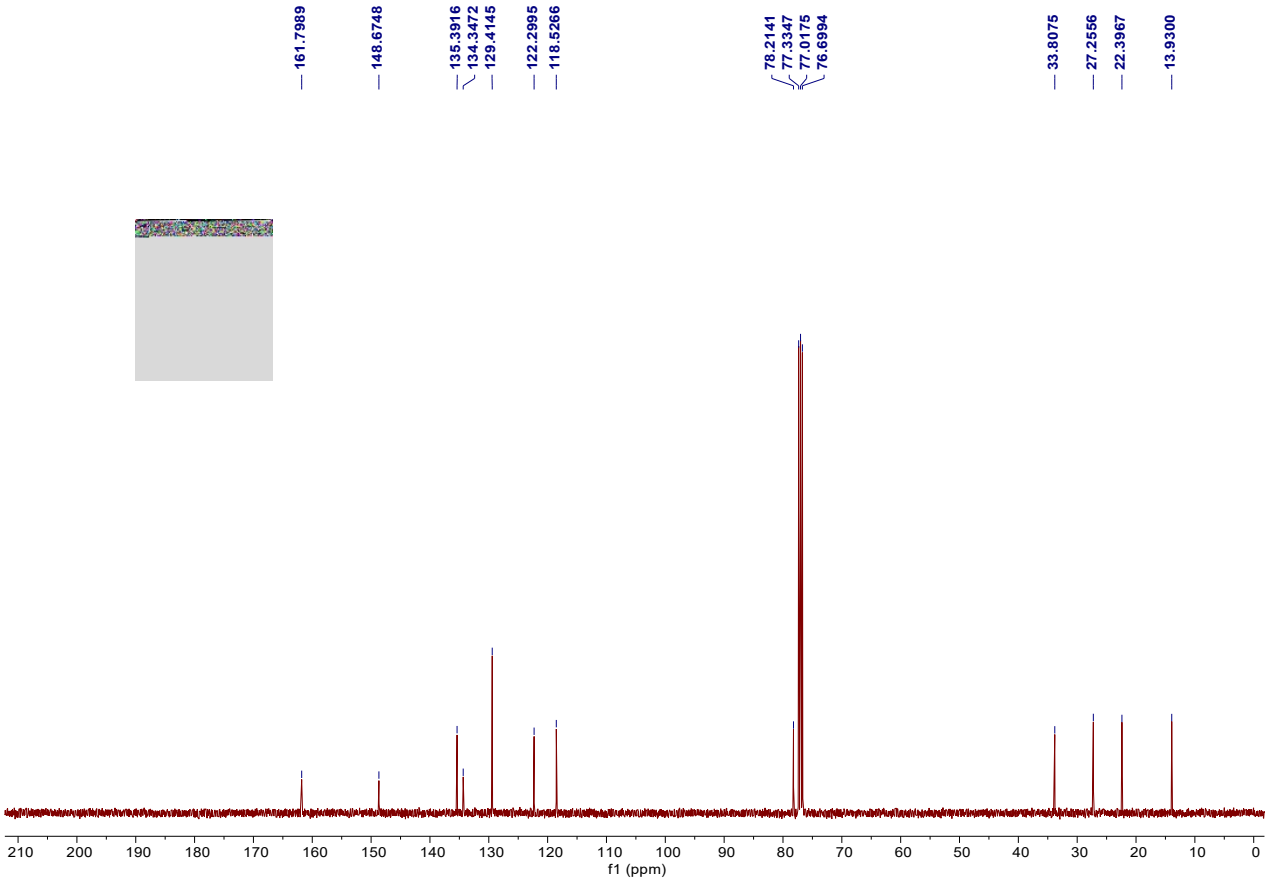
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1h**



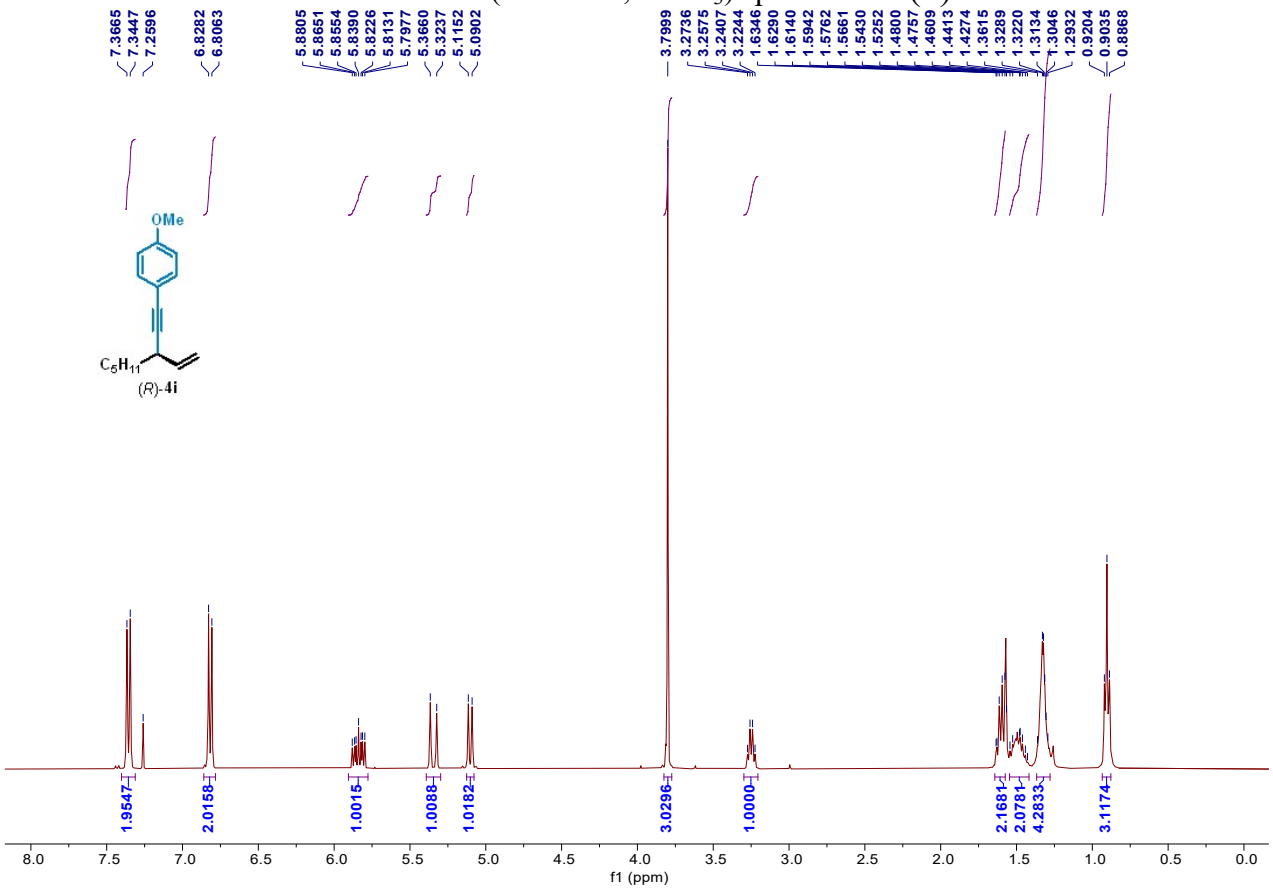
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1h**



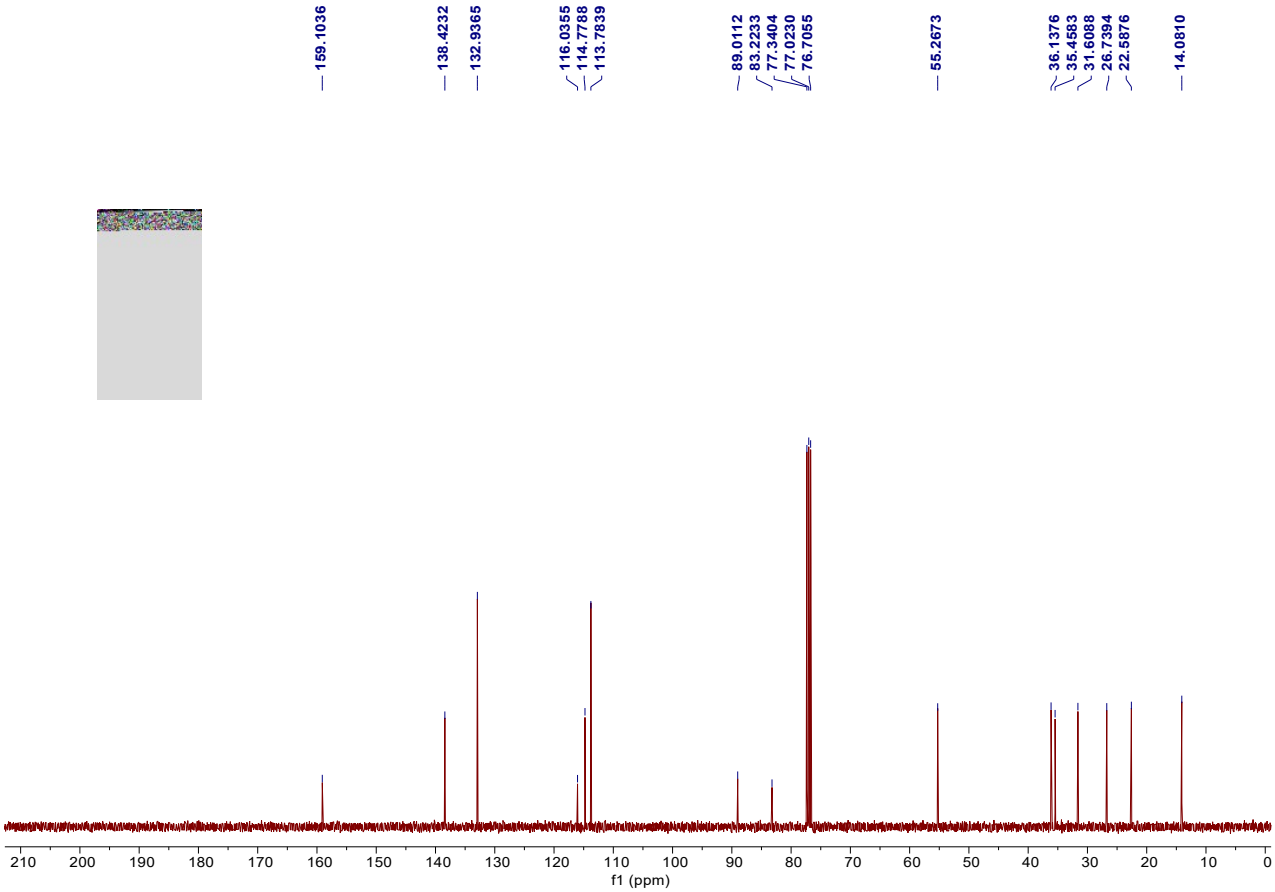
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1h'**



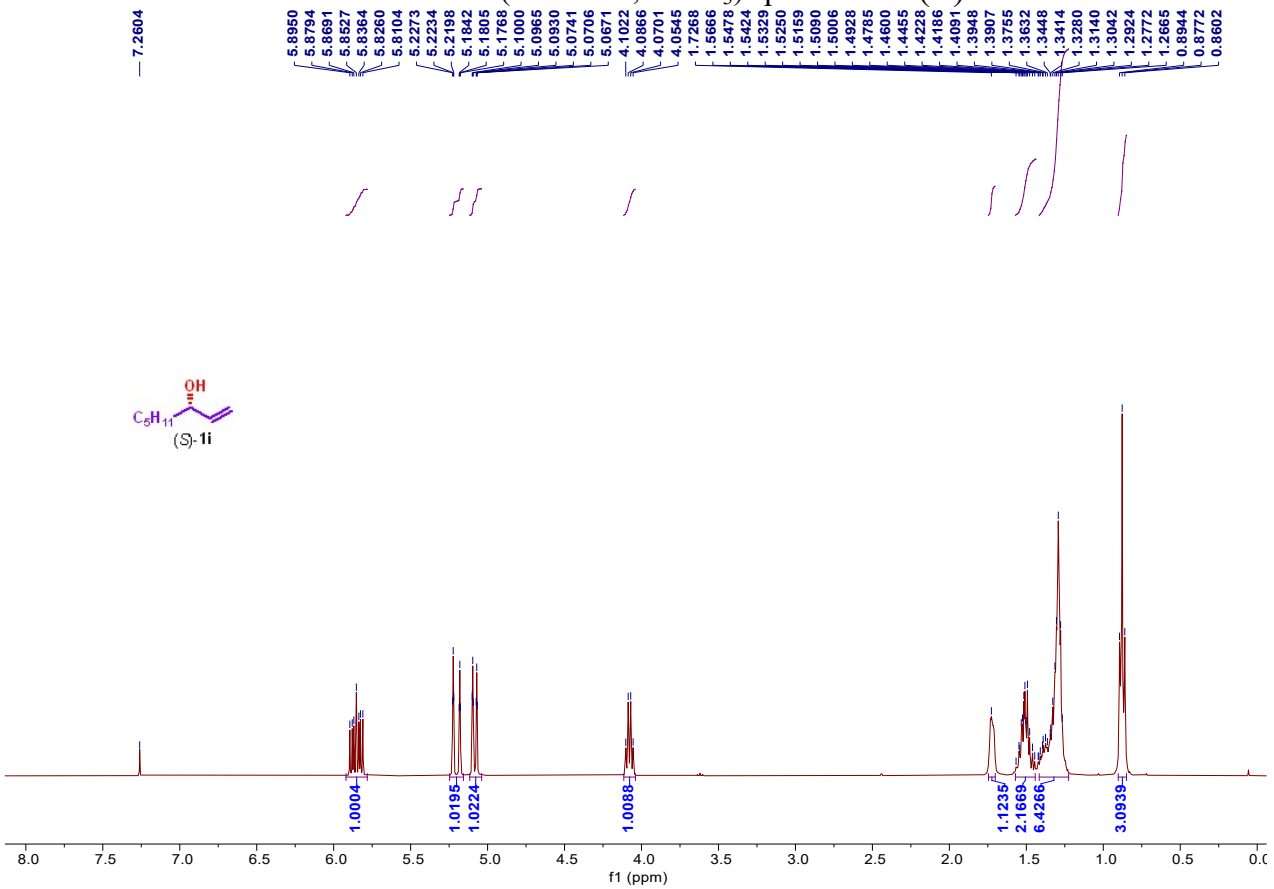
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1h'**



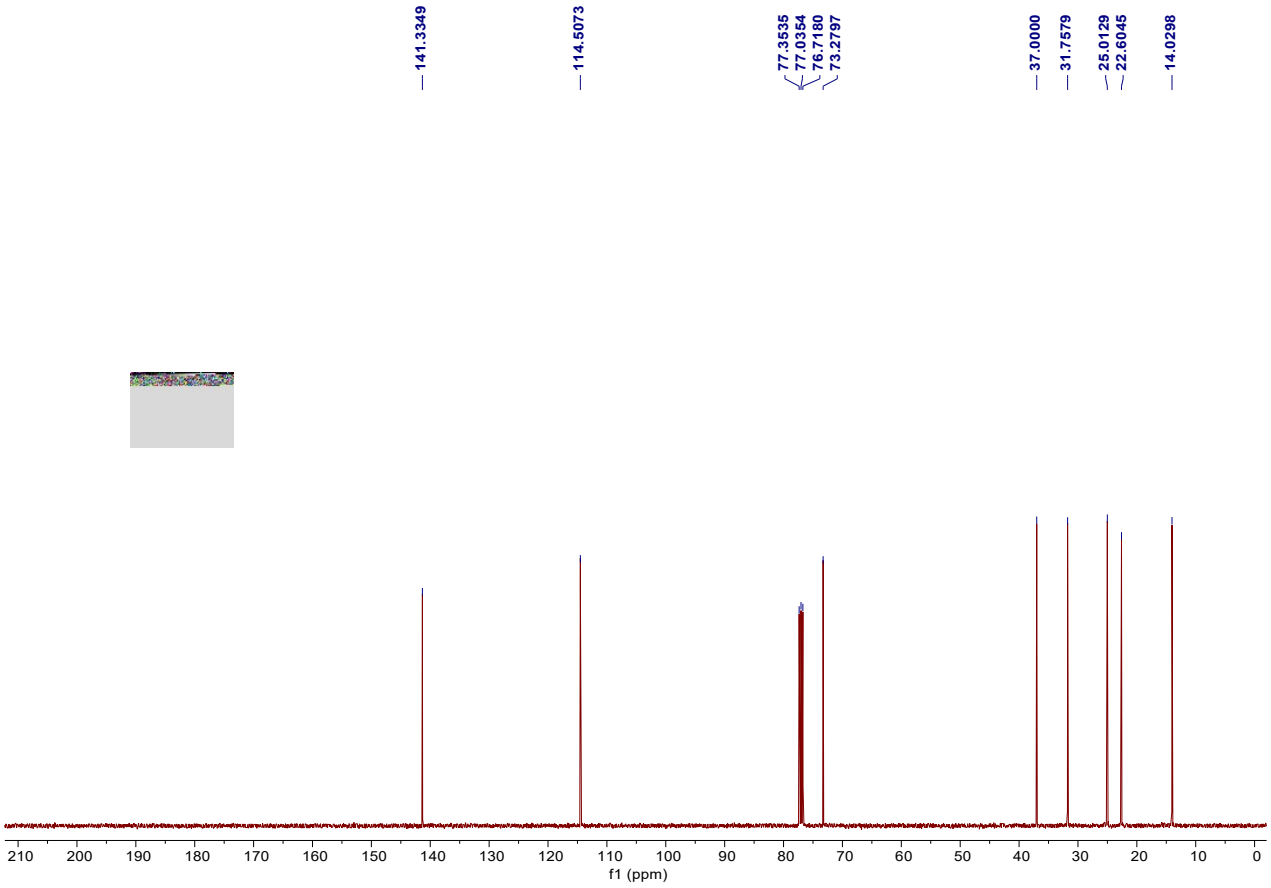
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4i**



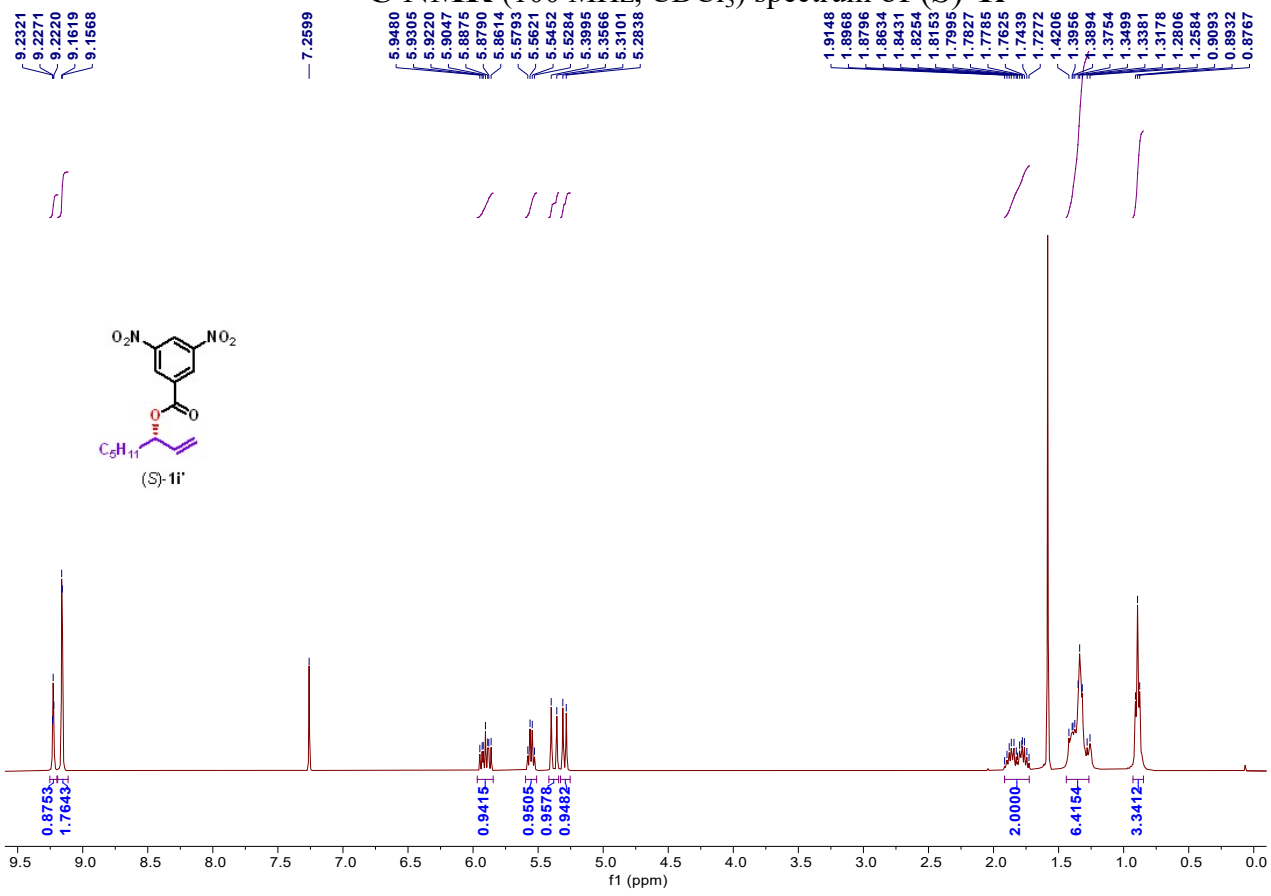
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4i**



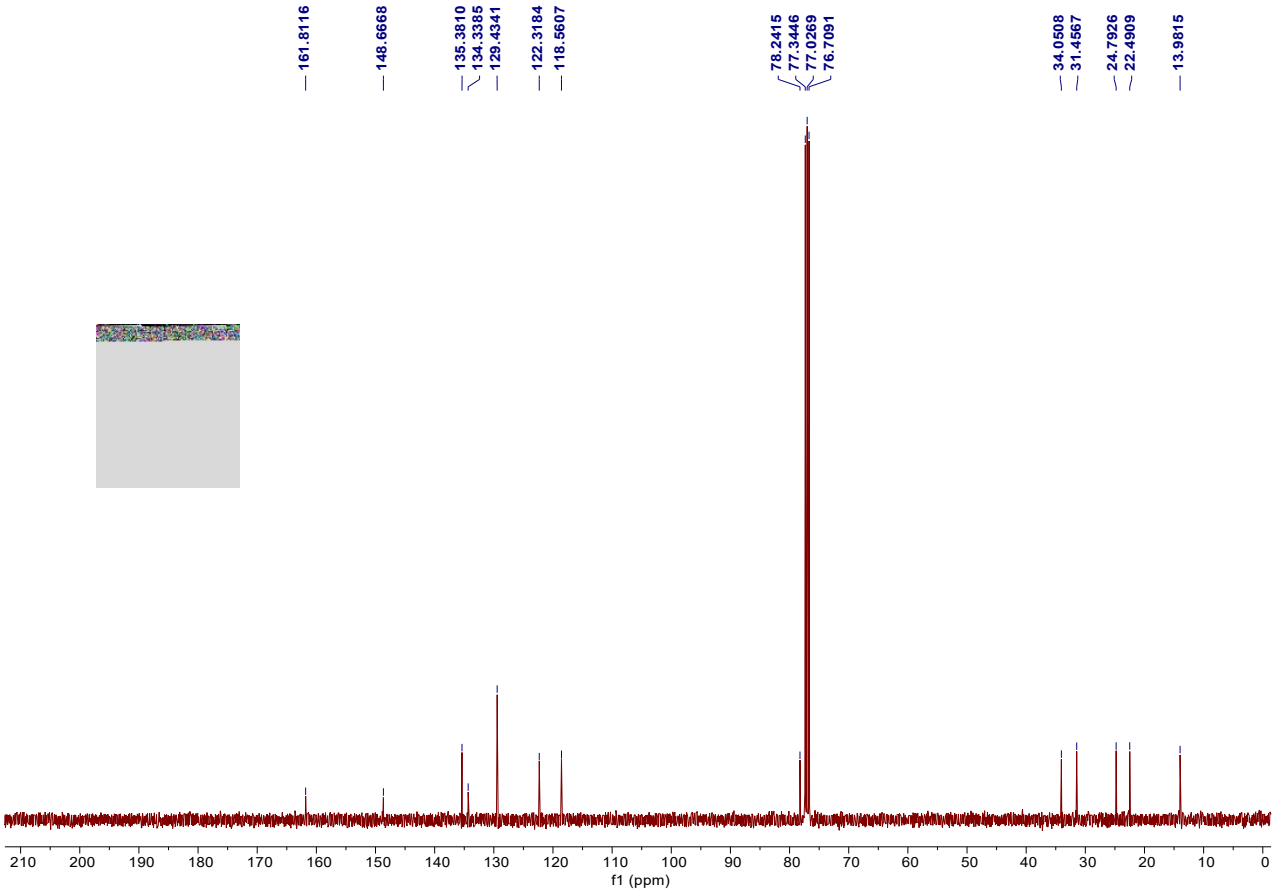
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1i**



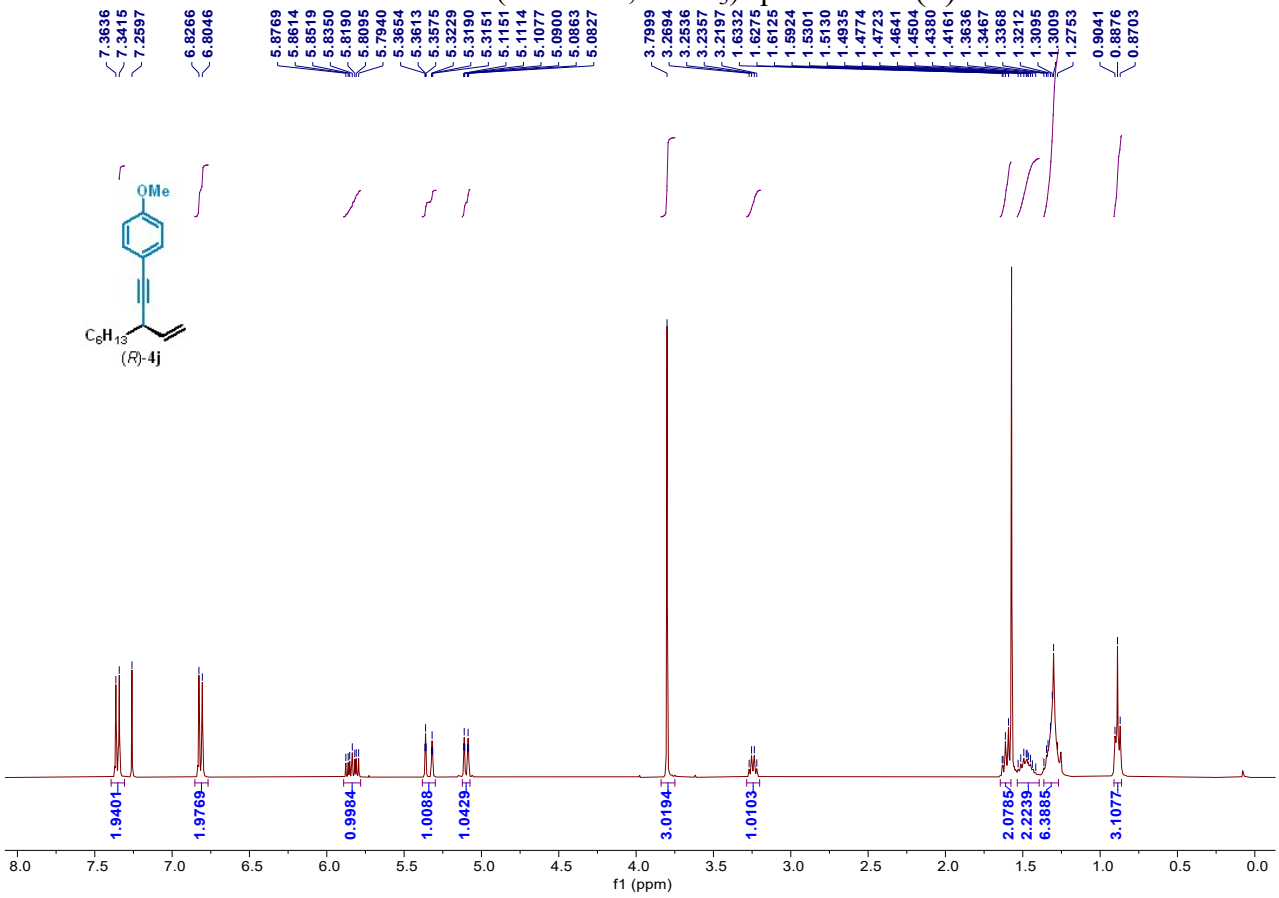
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1i**



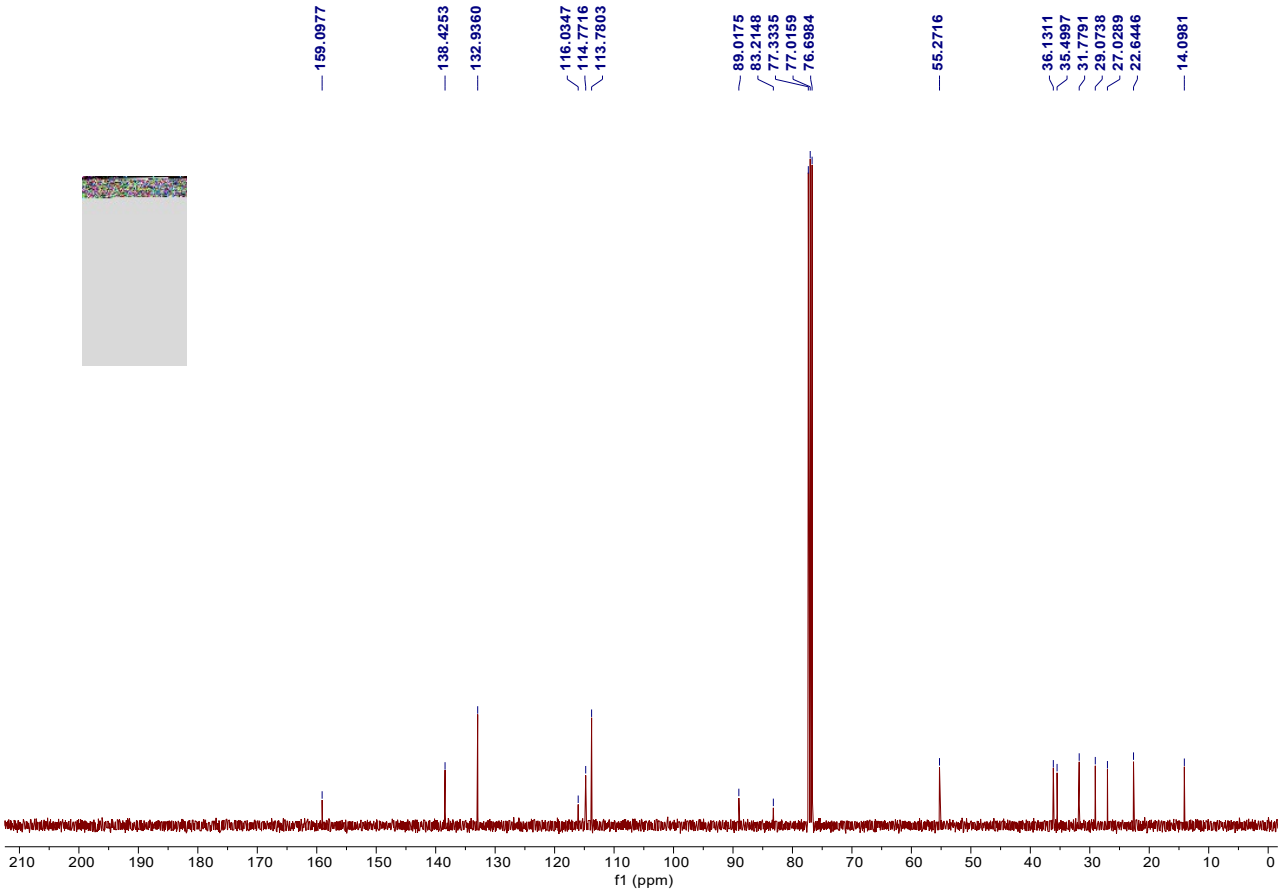
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1i'**



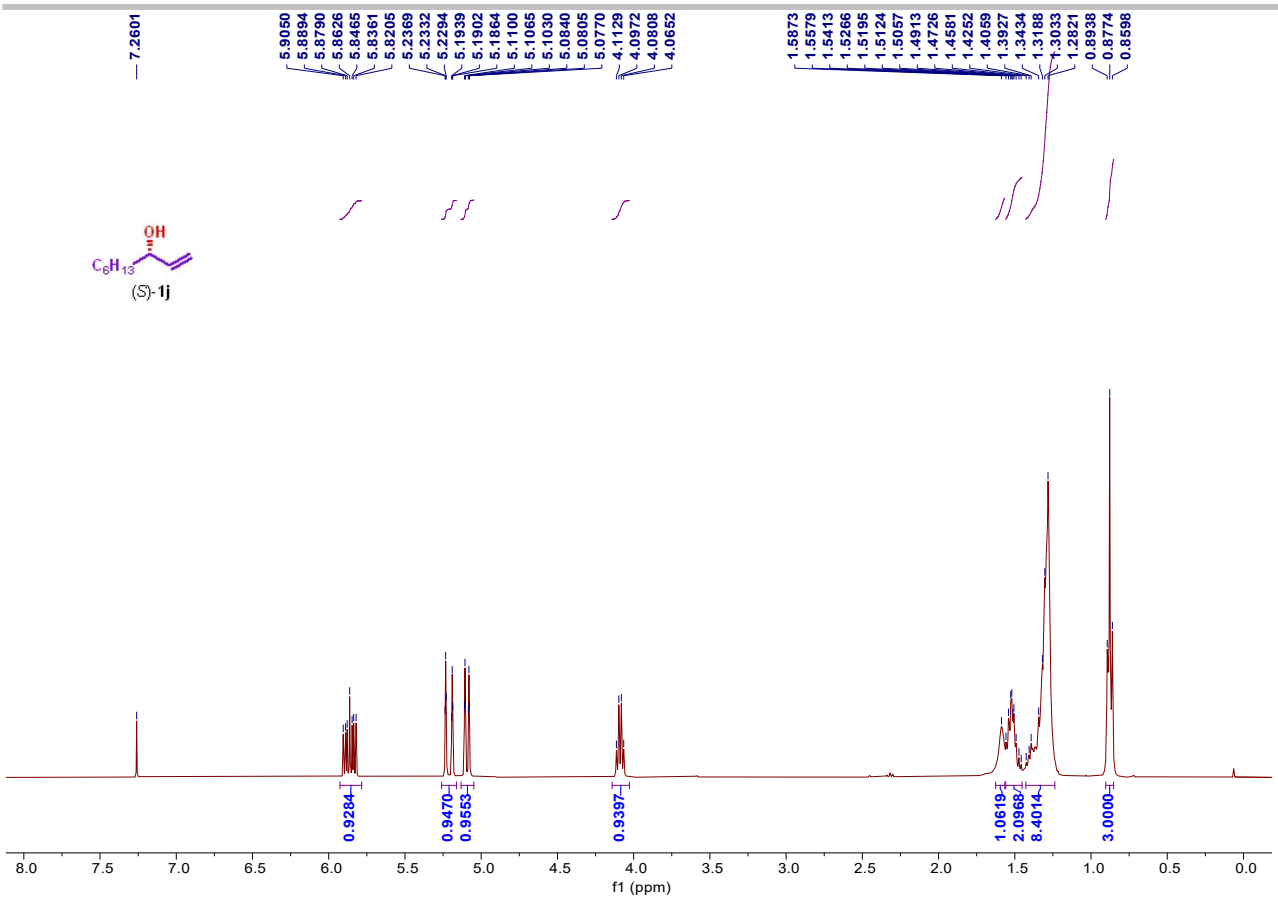
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1i'**



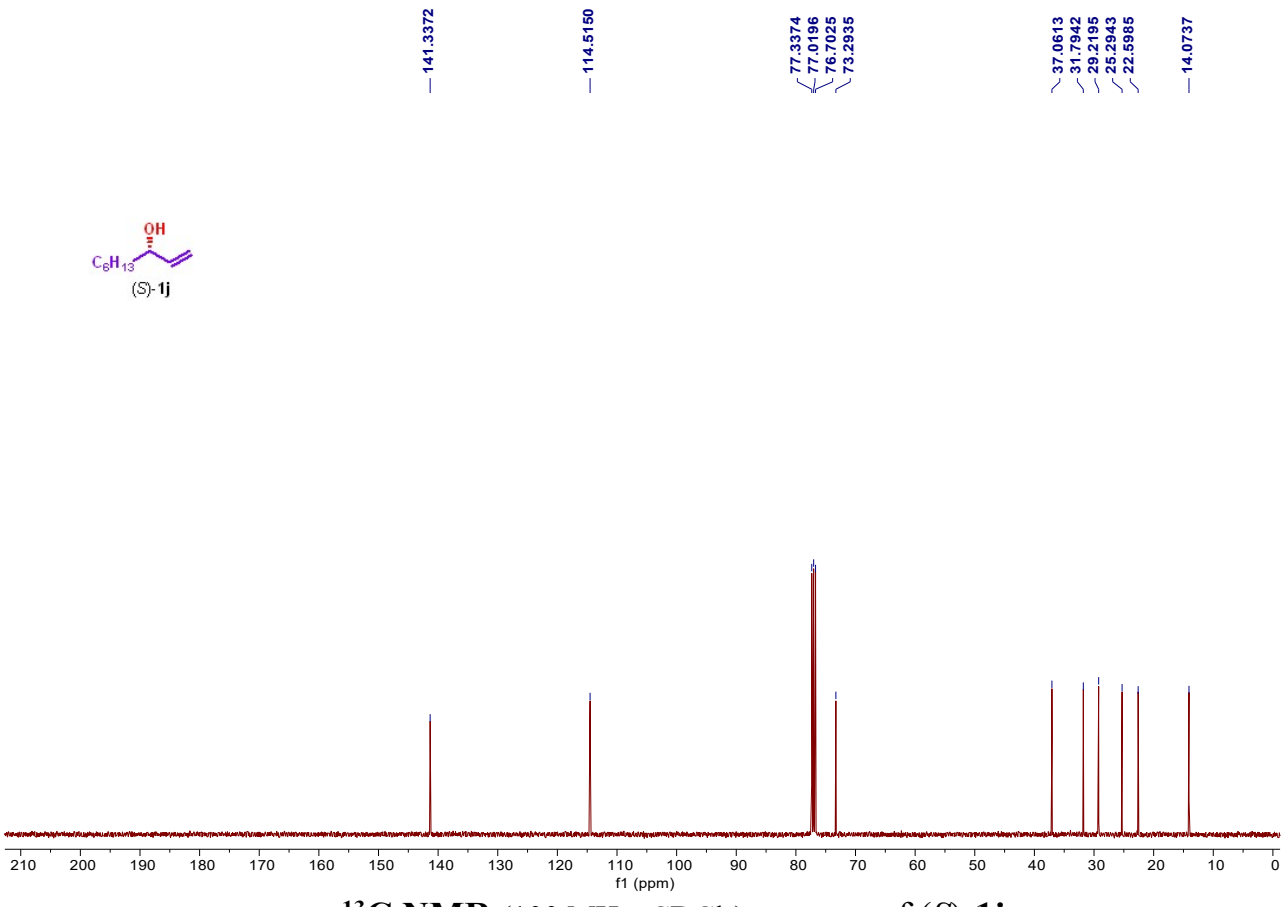
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4j**



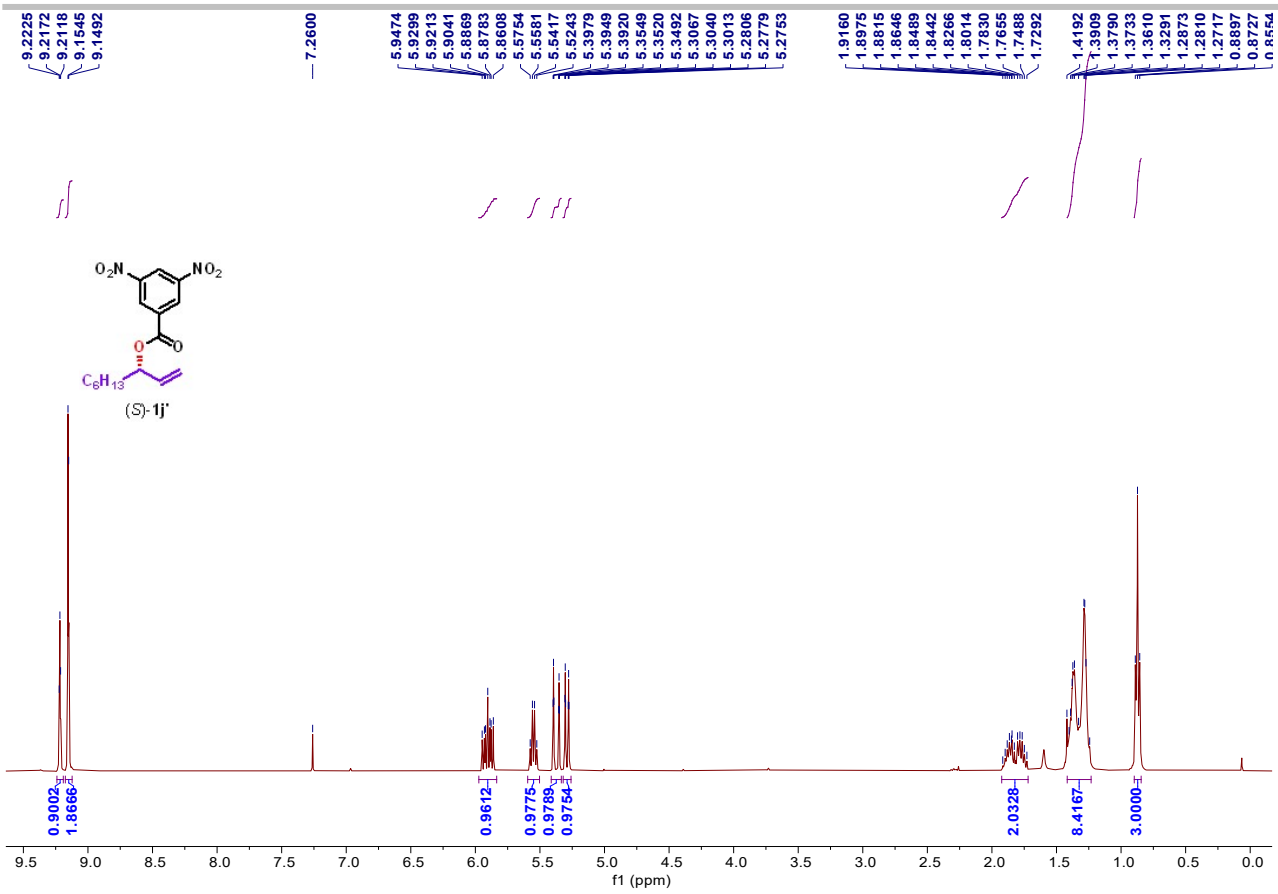
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4j**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1j**

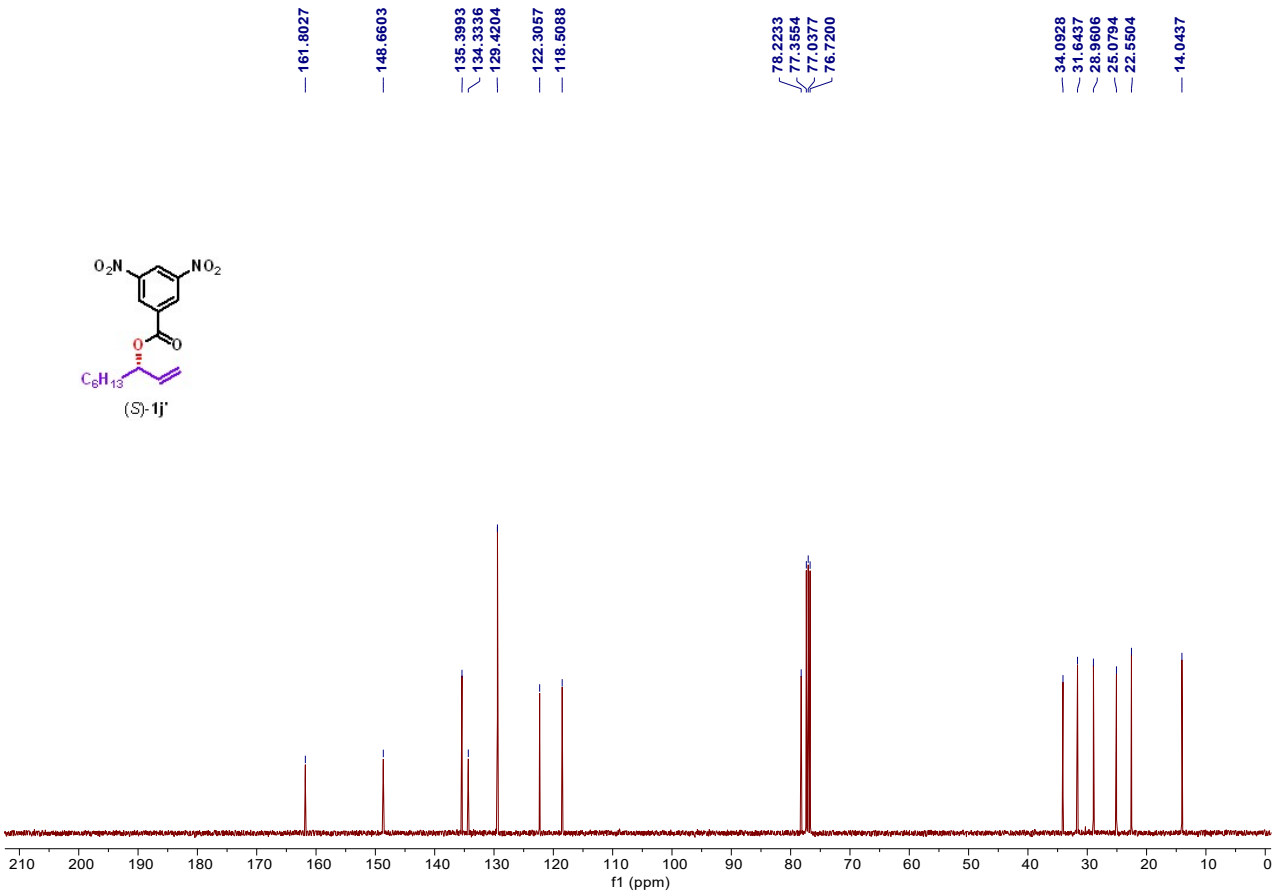


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1j**



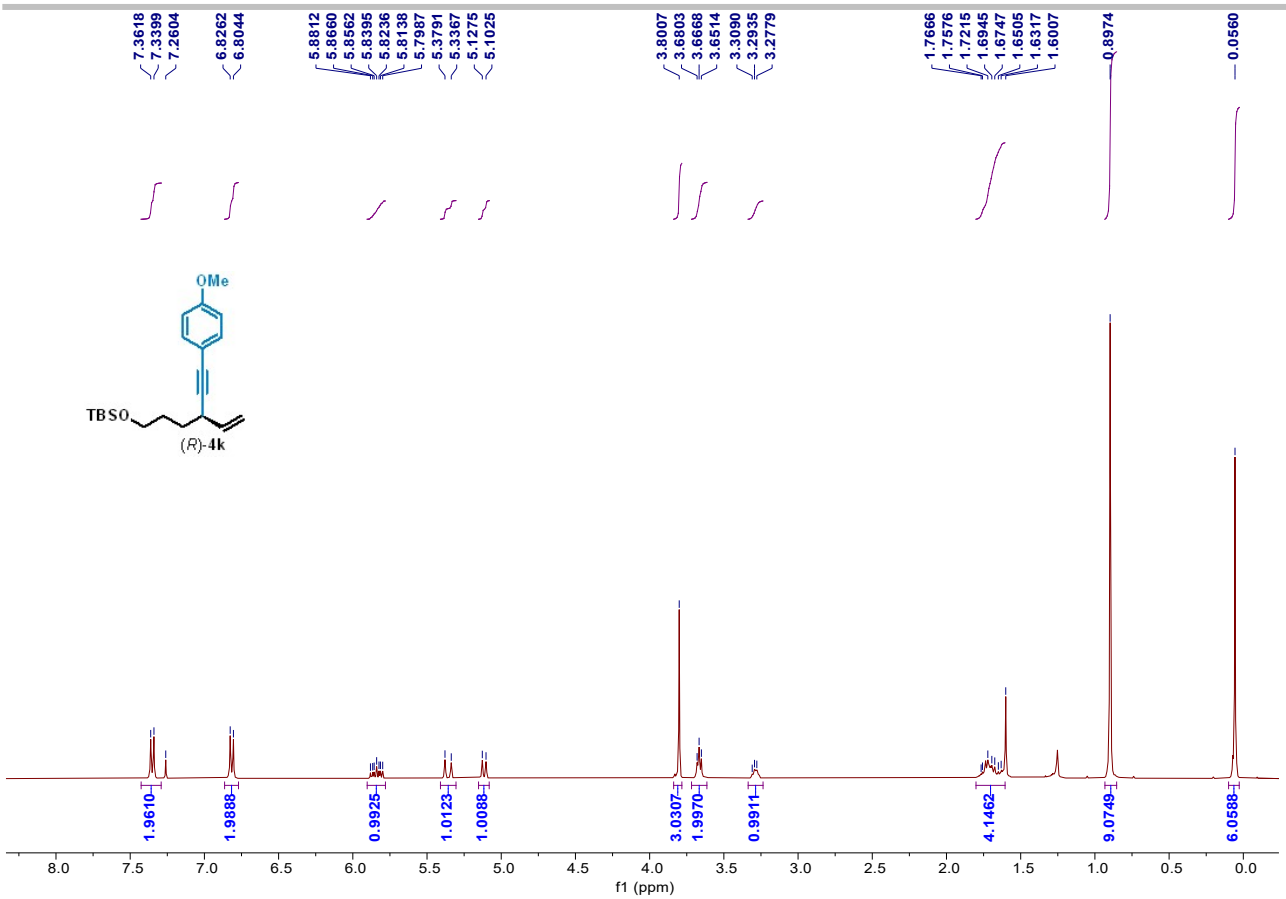
(*S*)-**1j'**

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1j'**

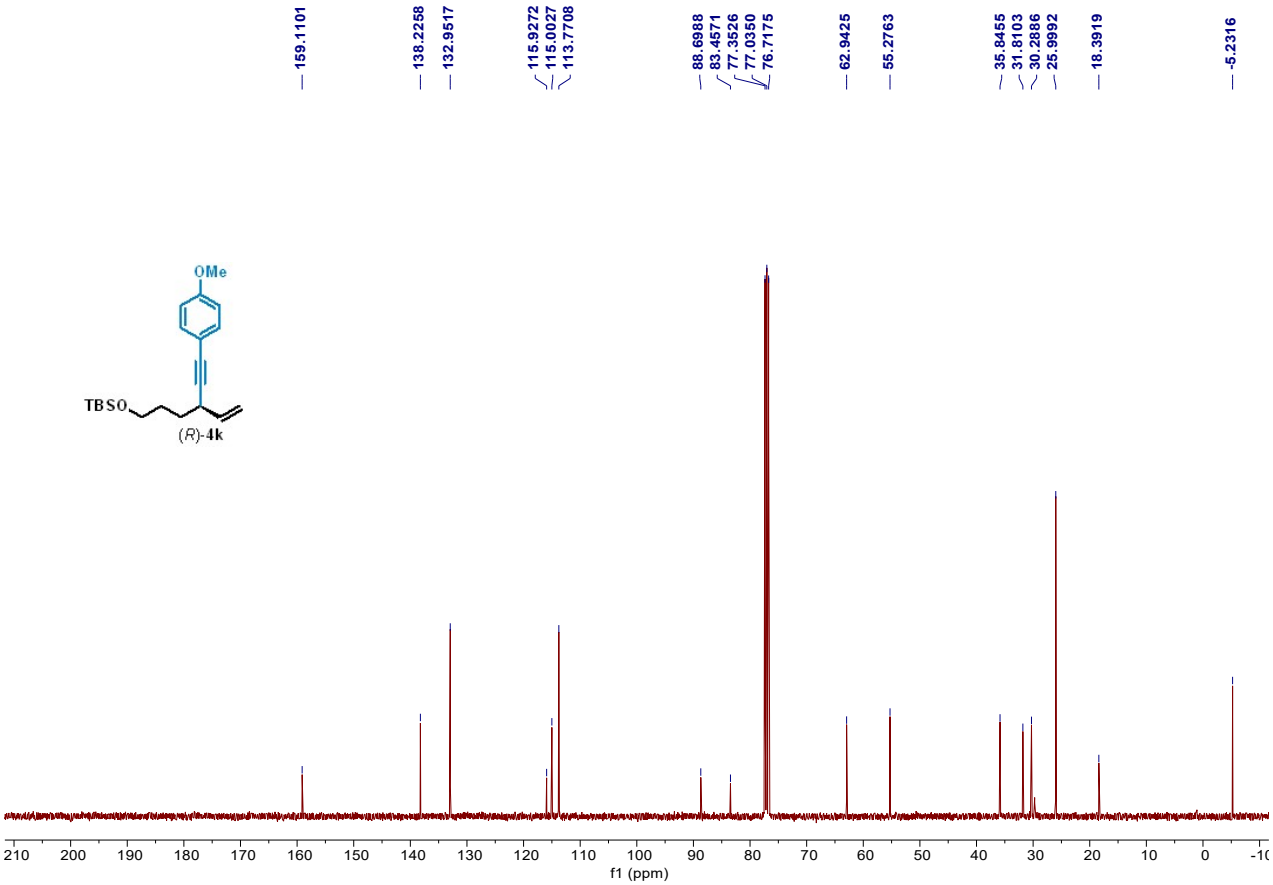


(*S*)-**1j'**

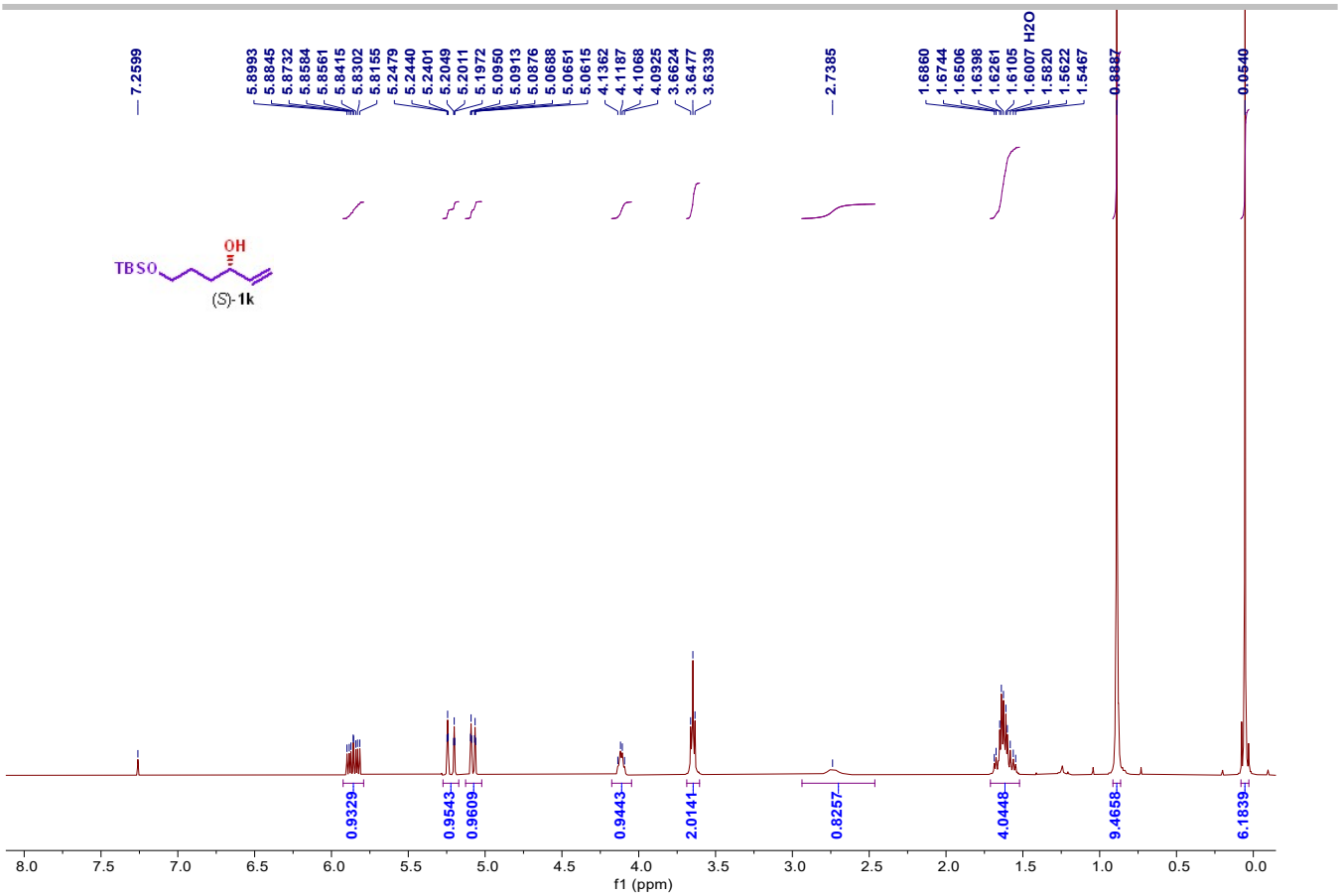
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1j'**



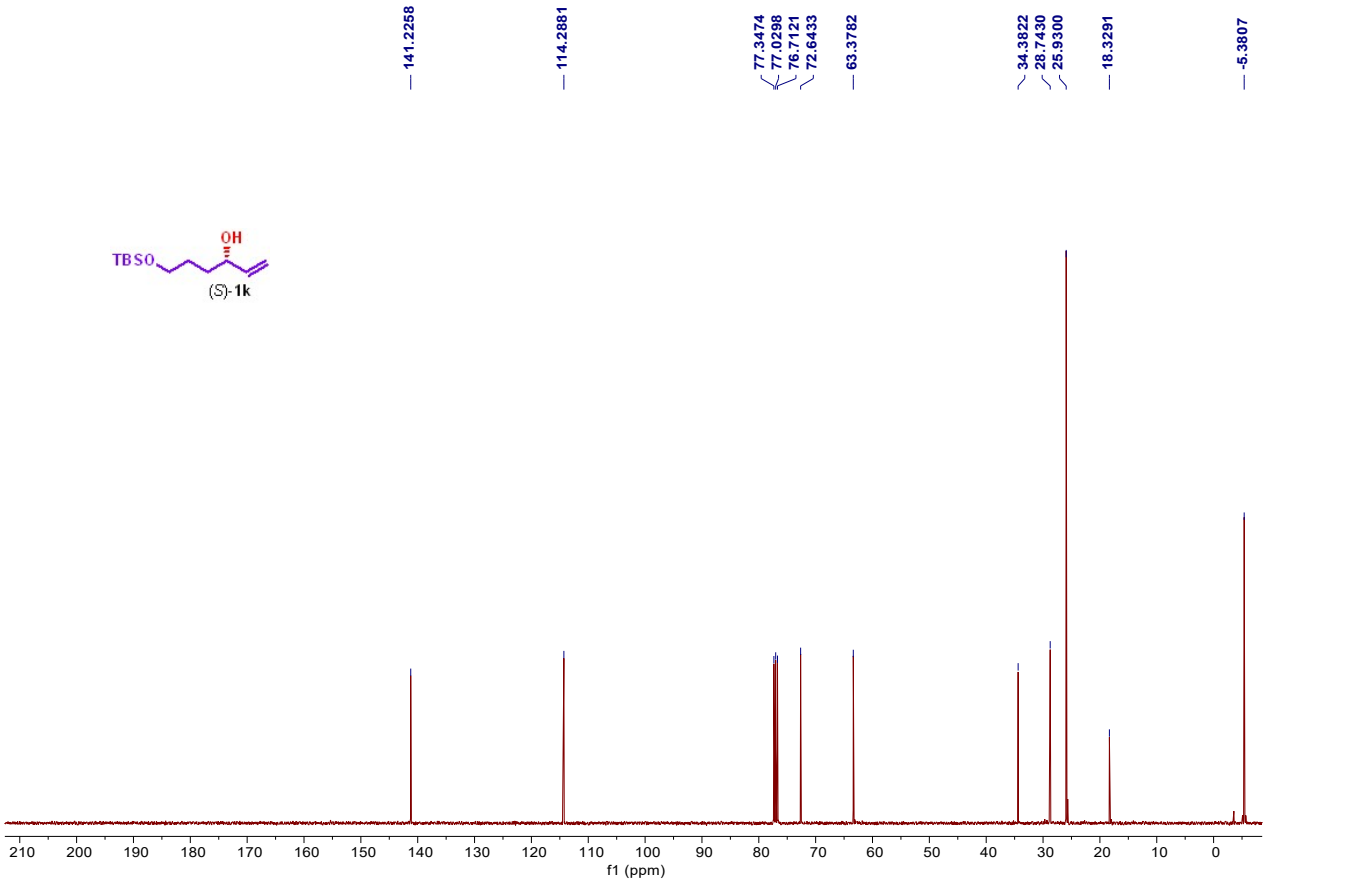
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4k**



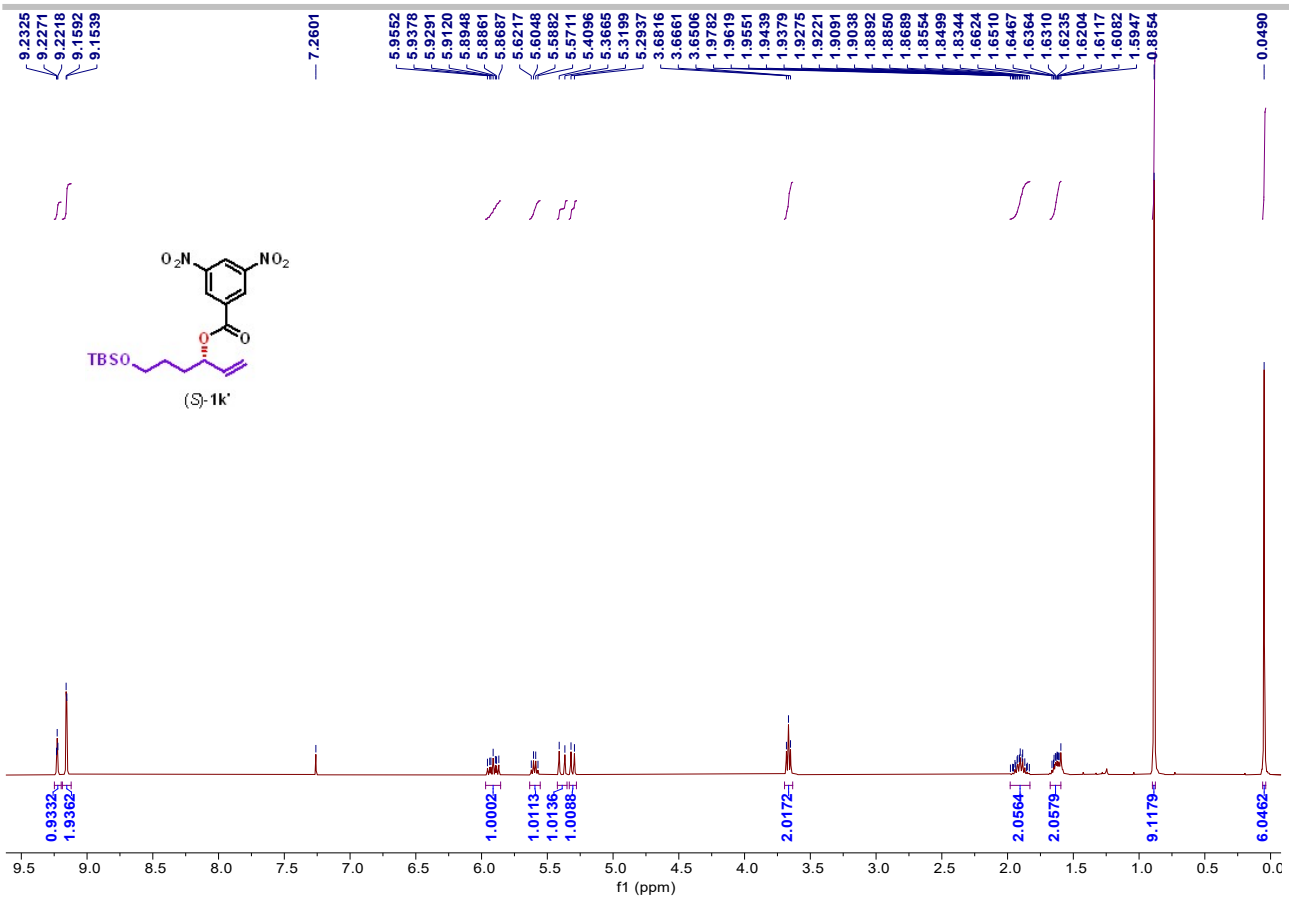
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4k**



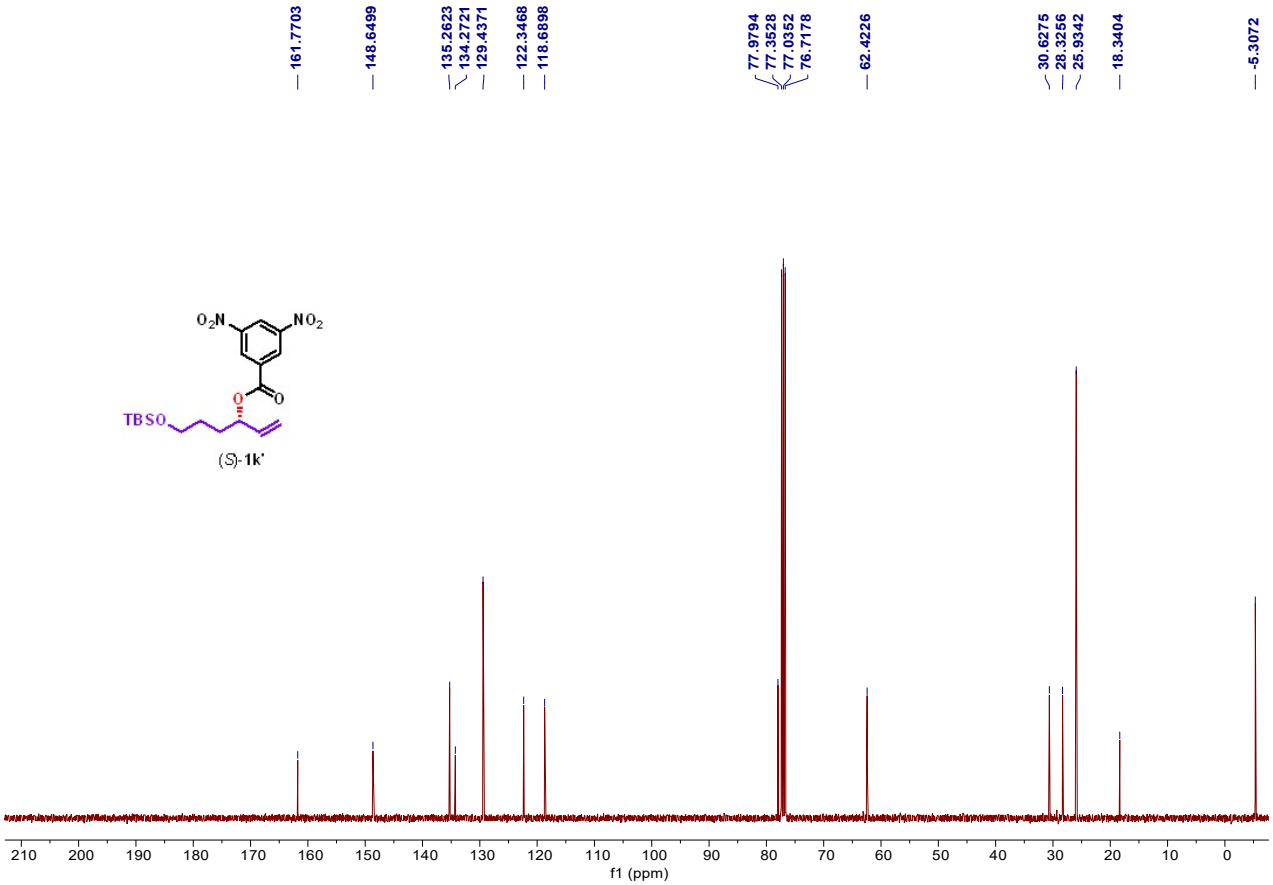
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1k**



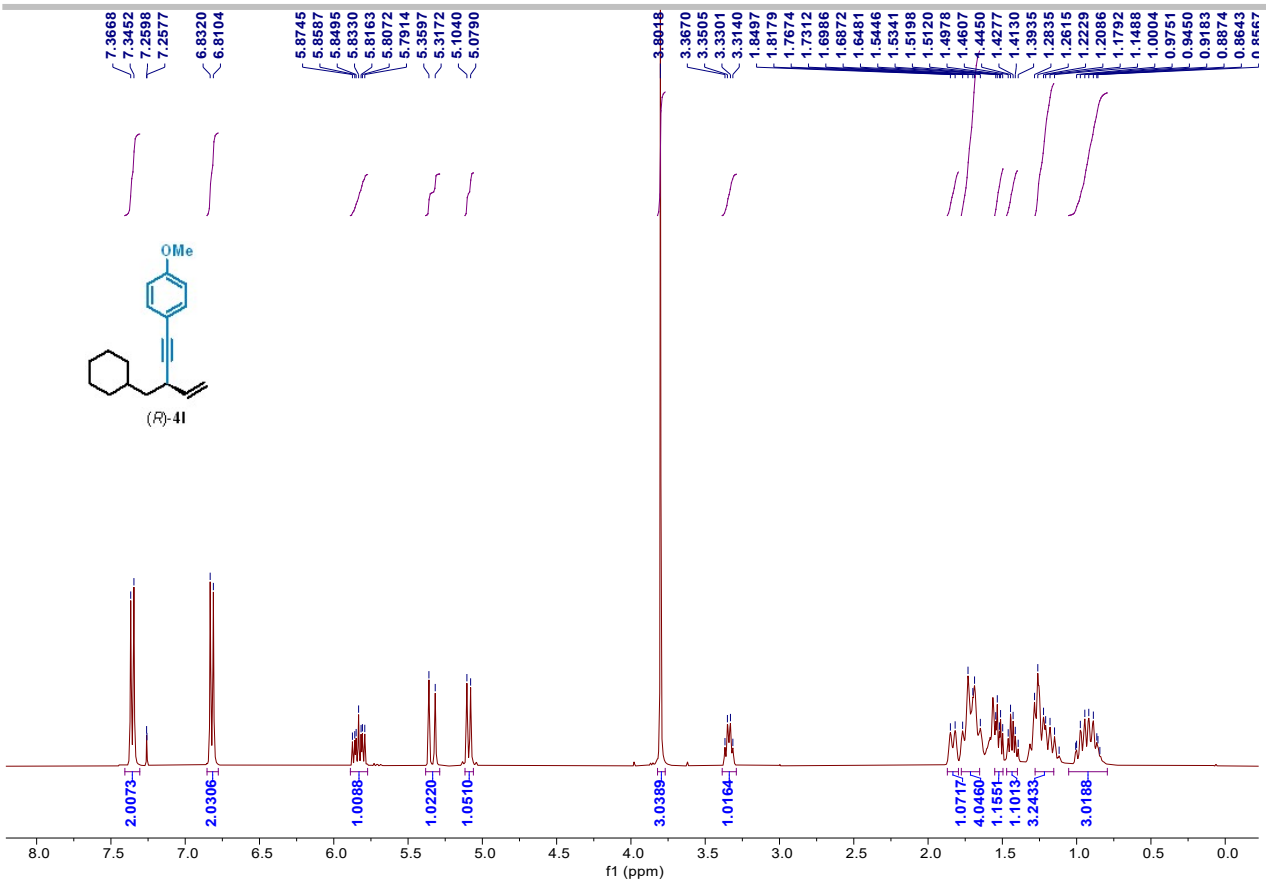
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1k**



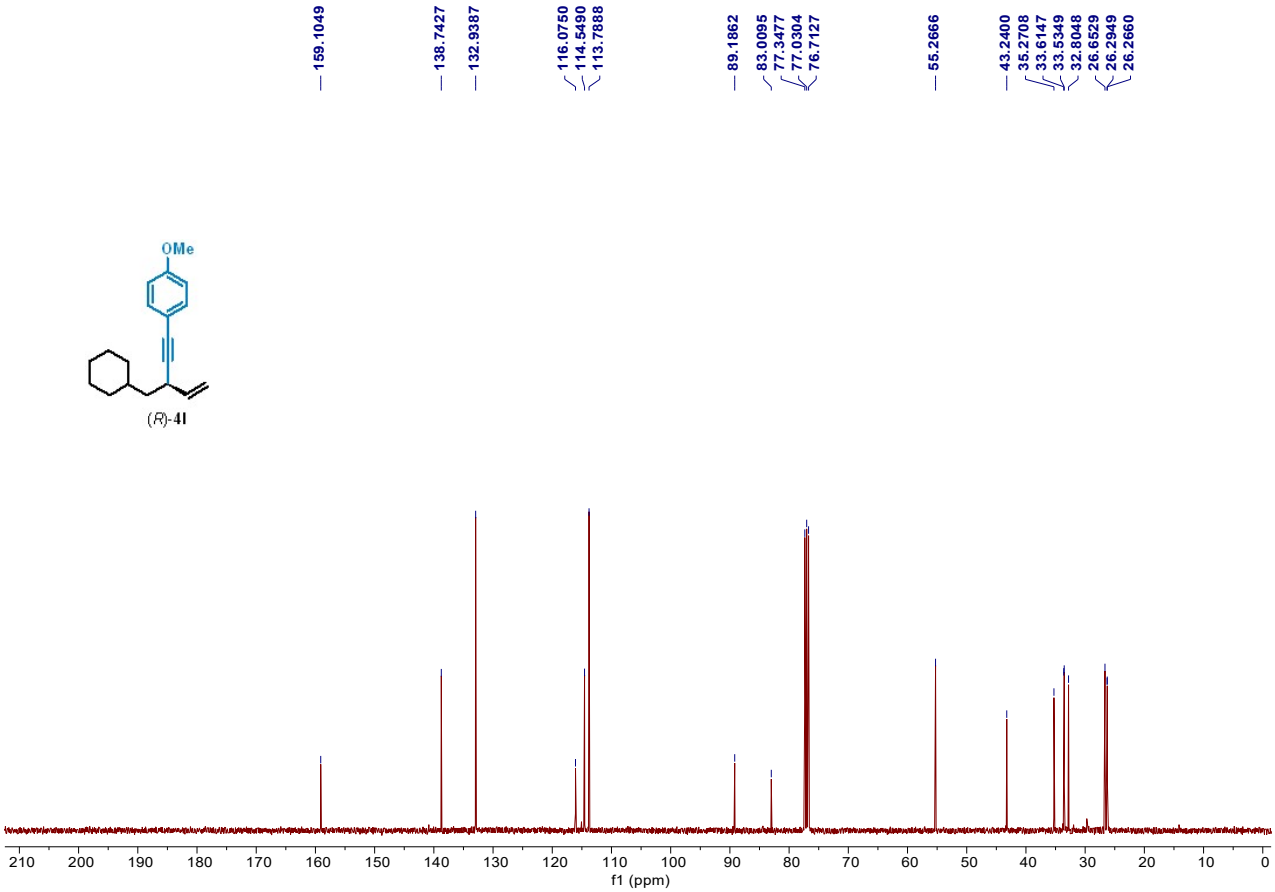
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1k'**



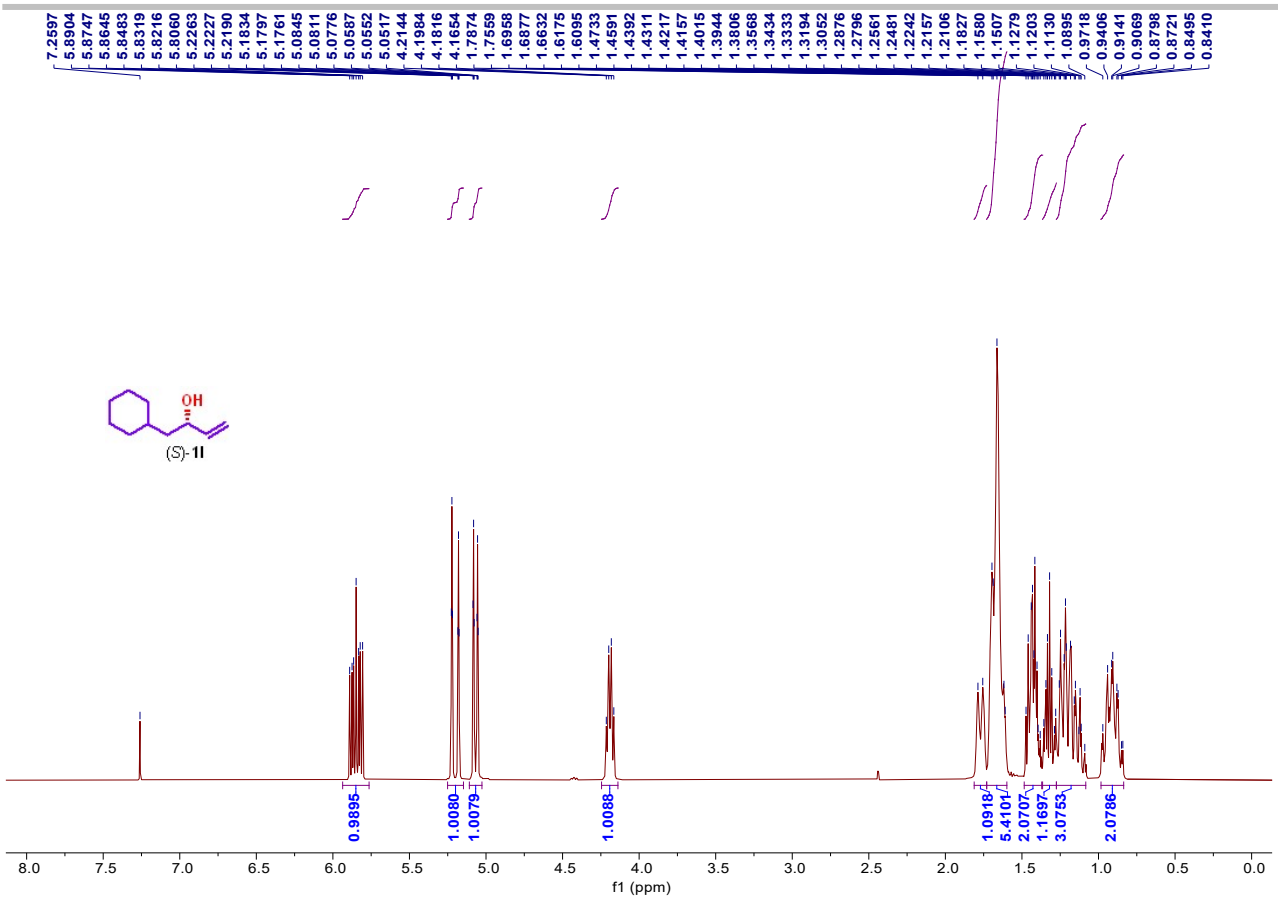
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1k'**



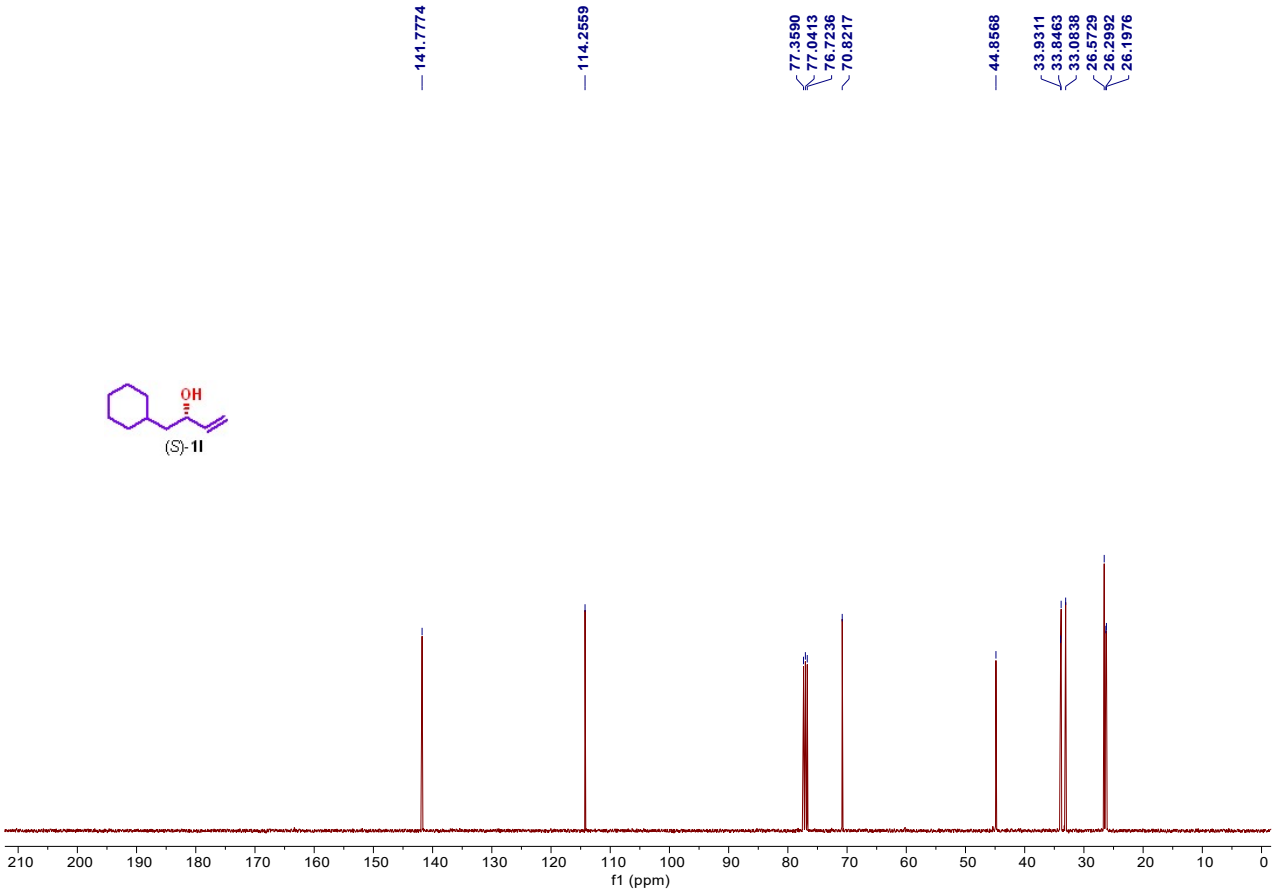
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4l**



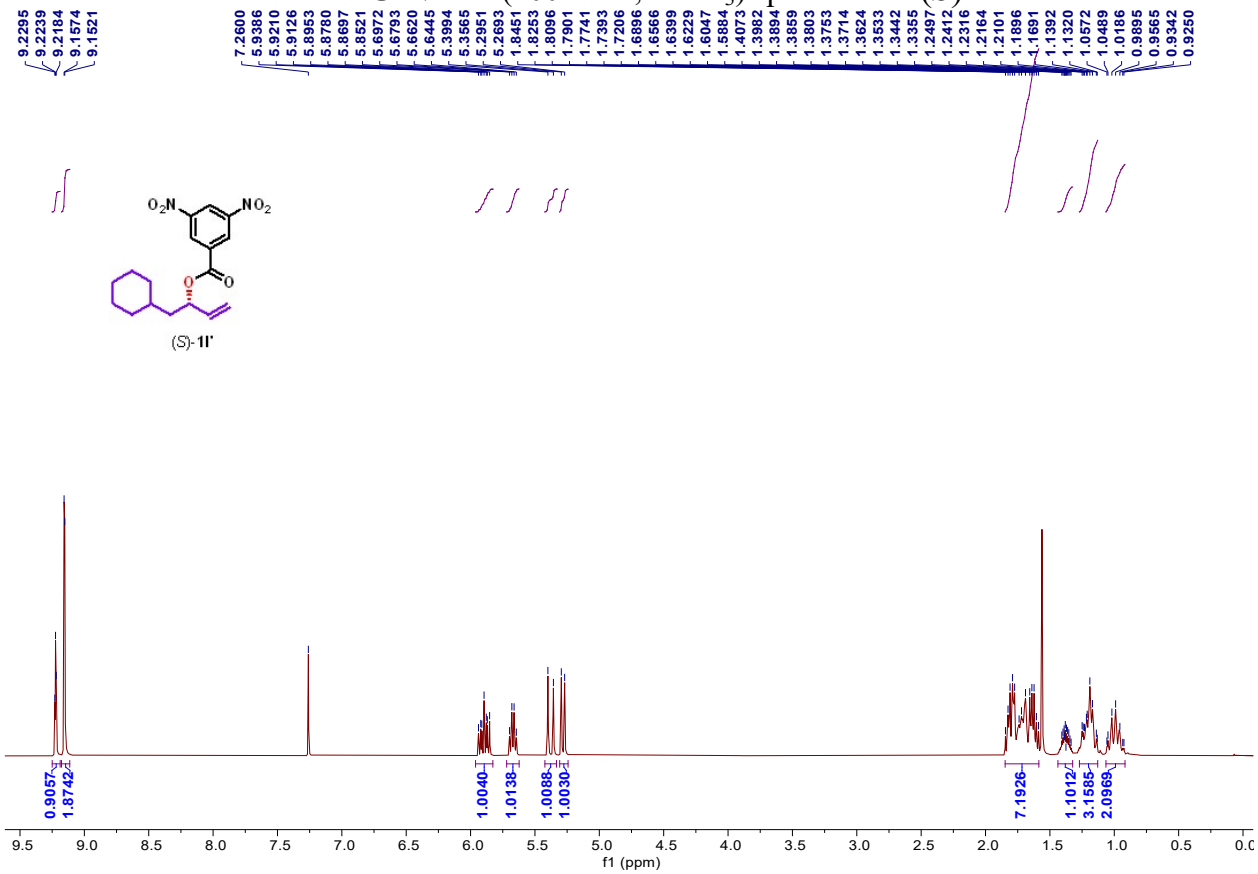
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4l**



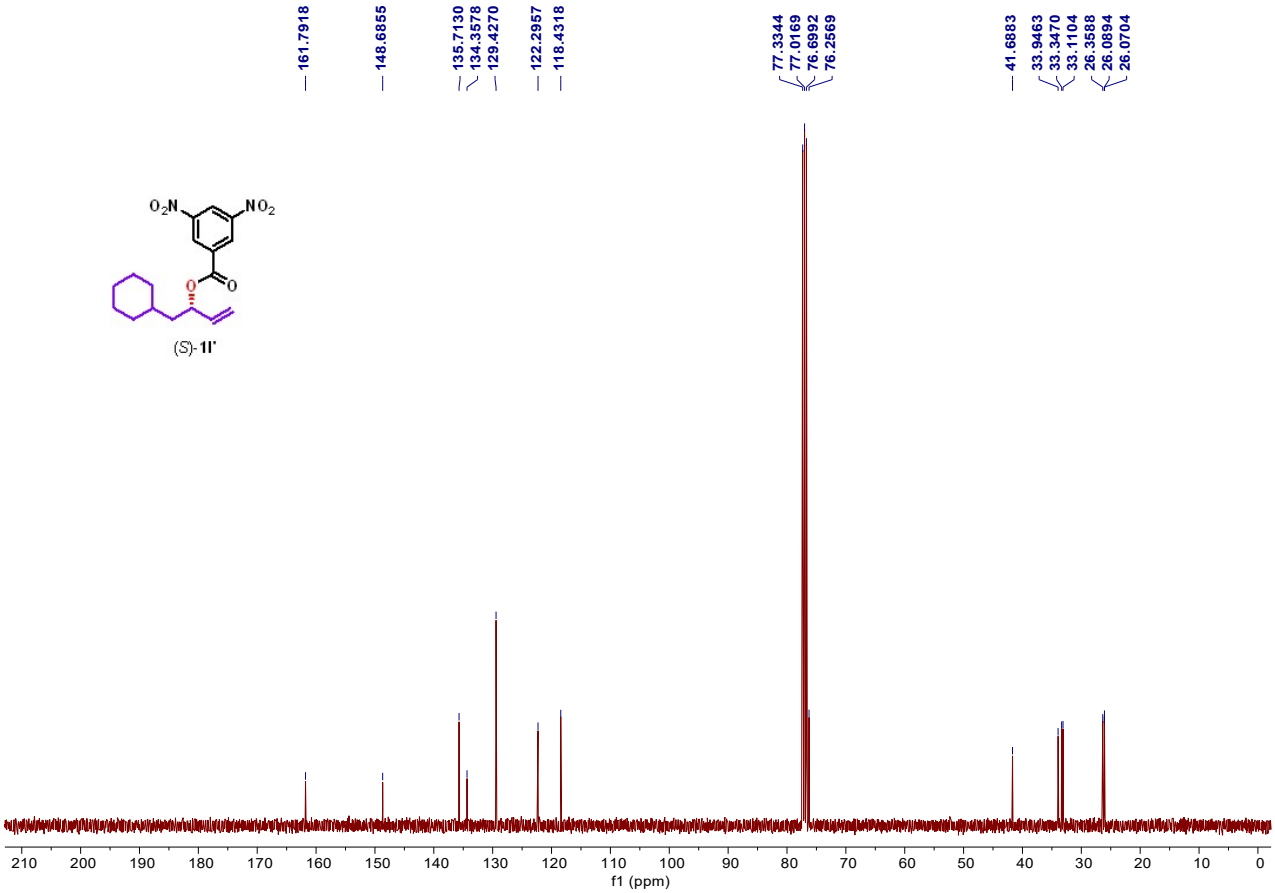
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1l**



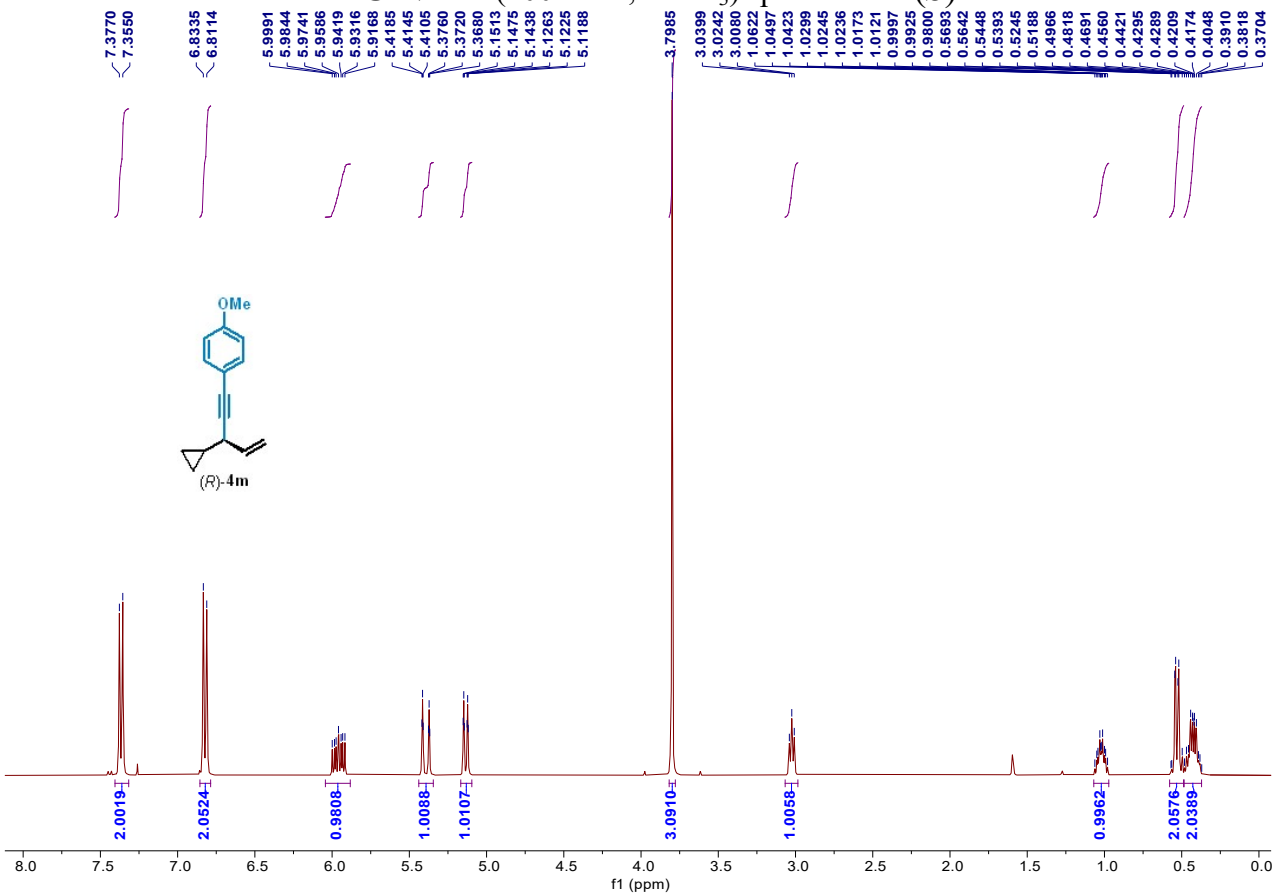
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1l**



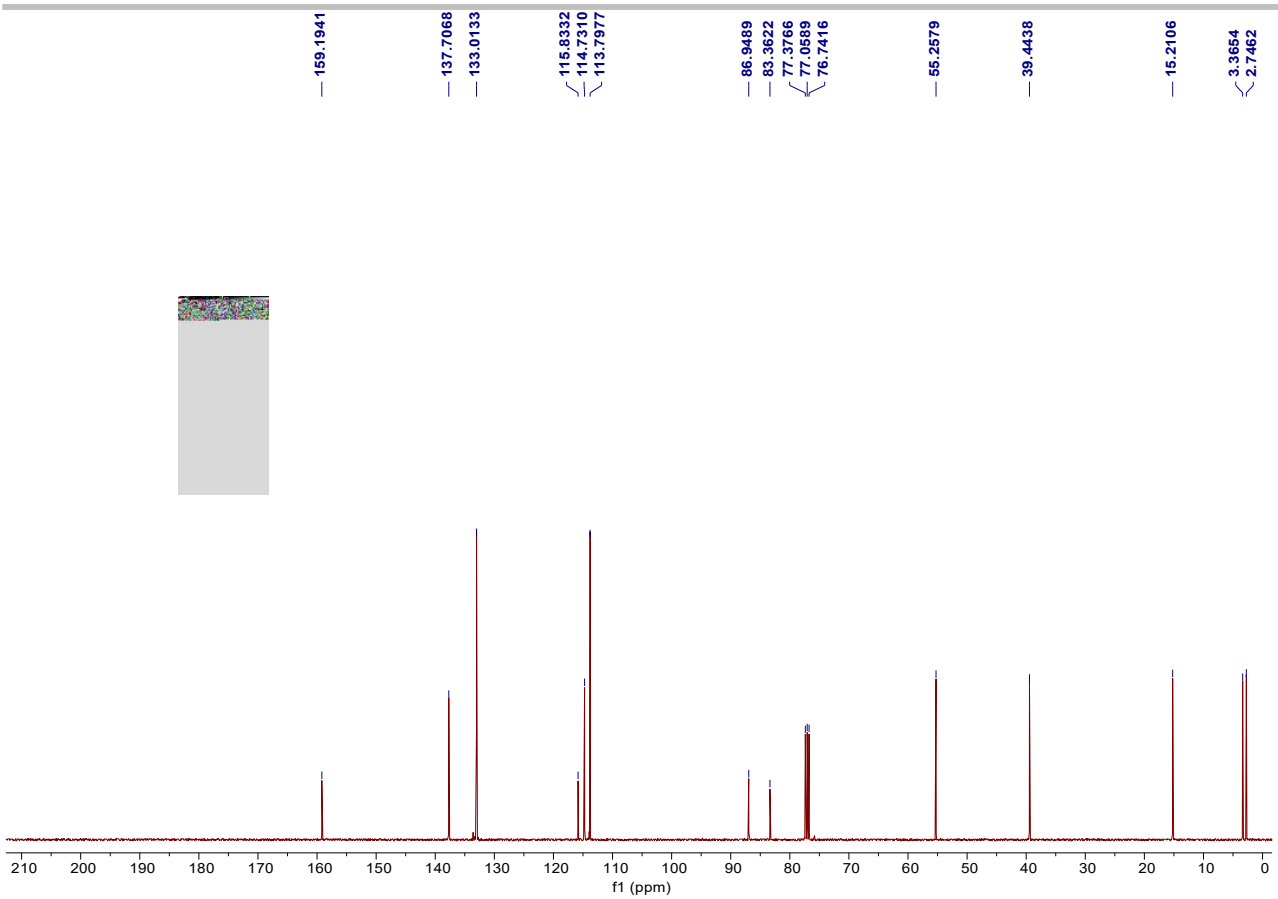
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1l'**



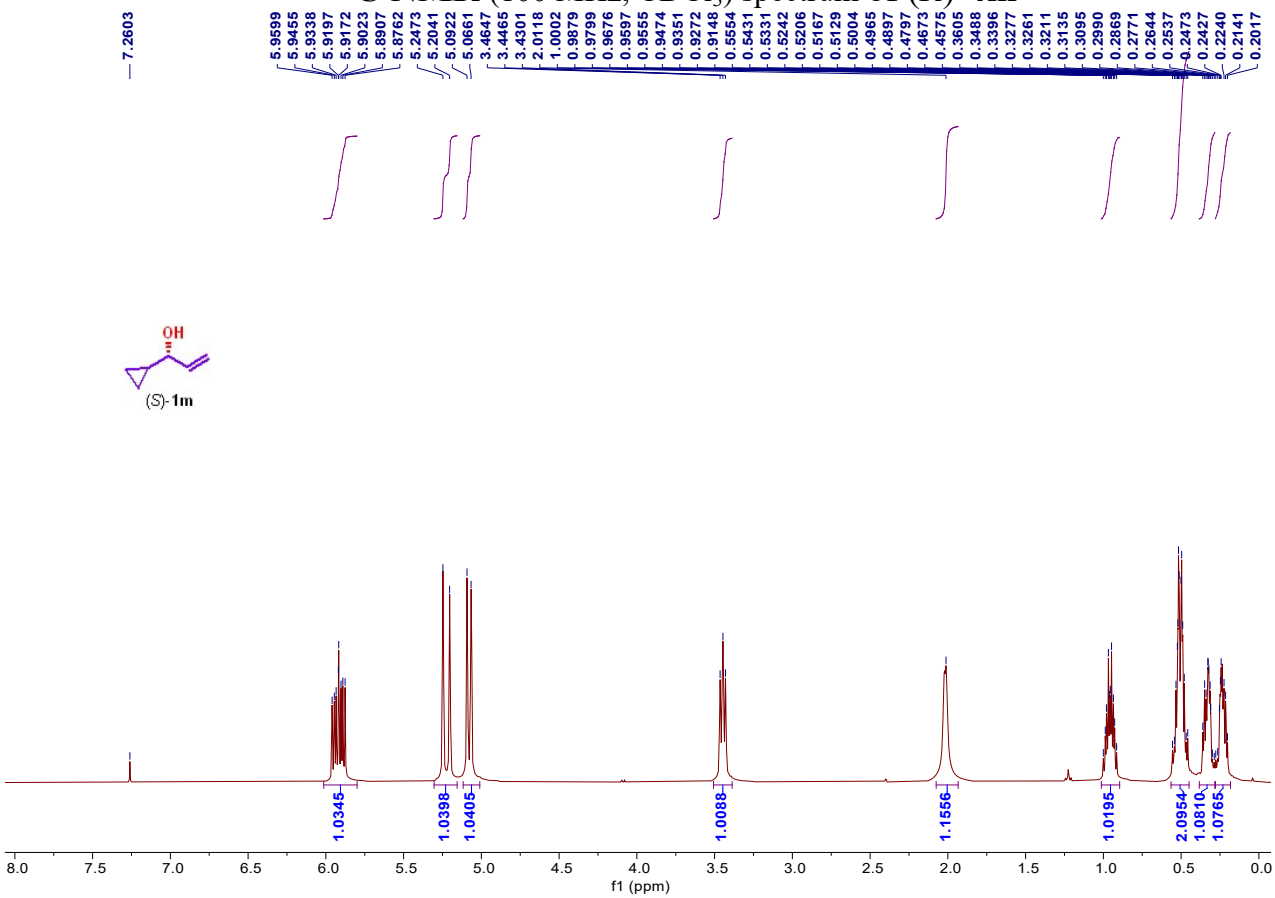
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1l'**



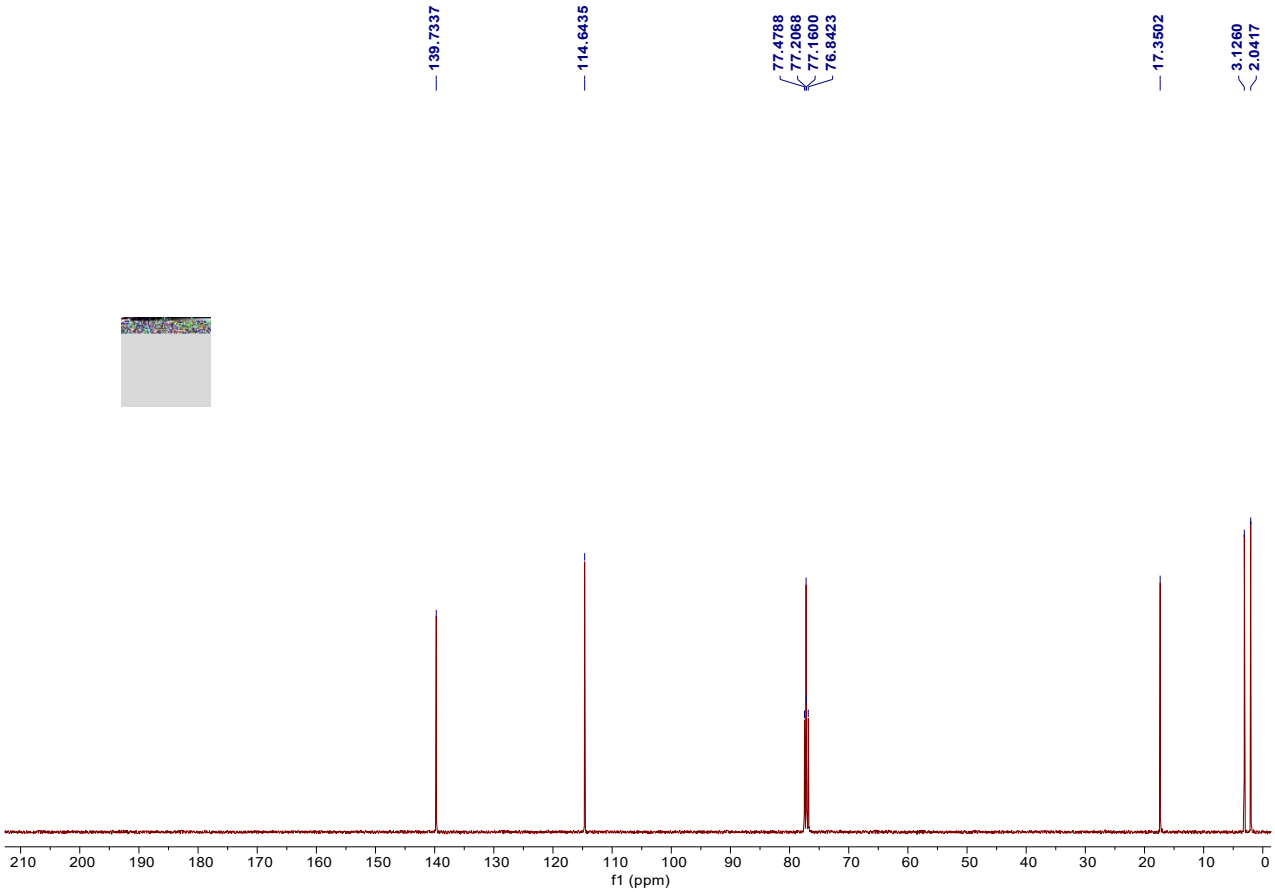
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**4m**



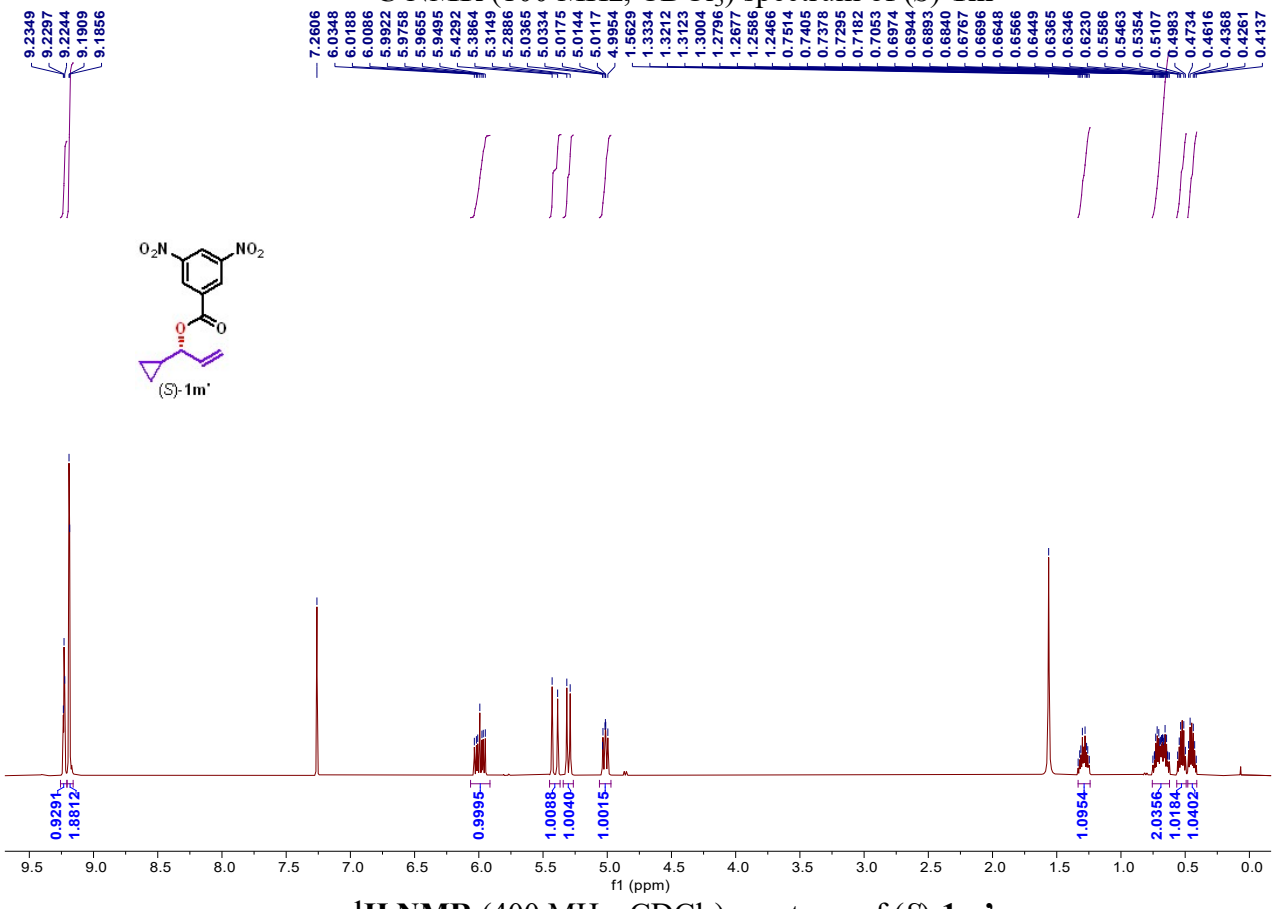
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**4m**



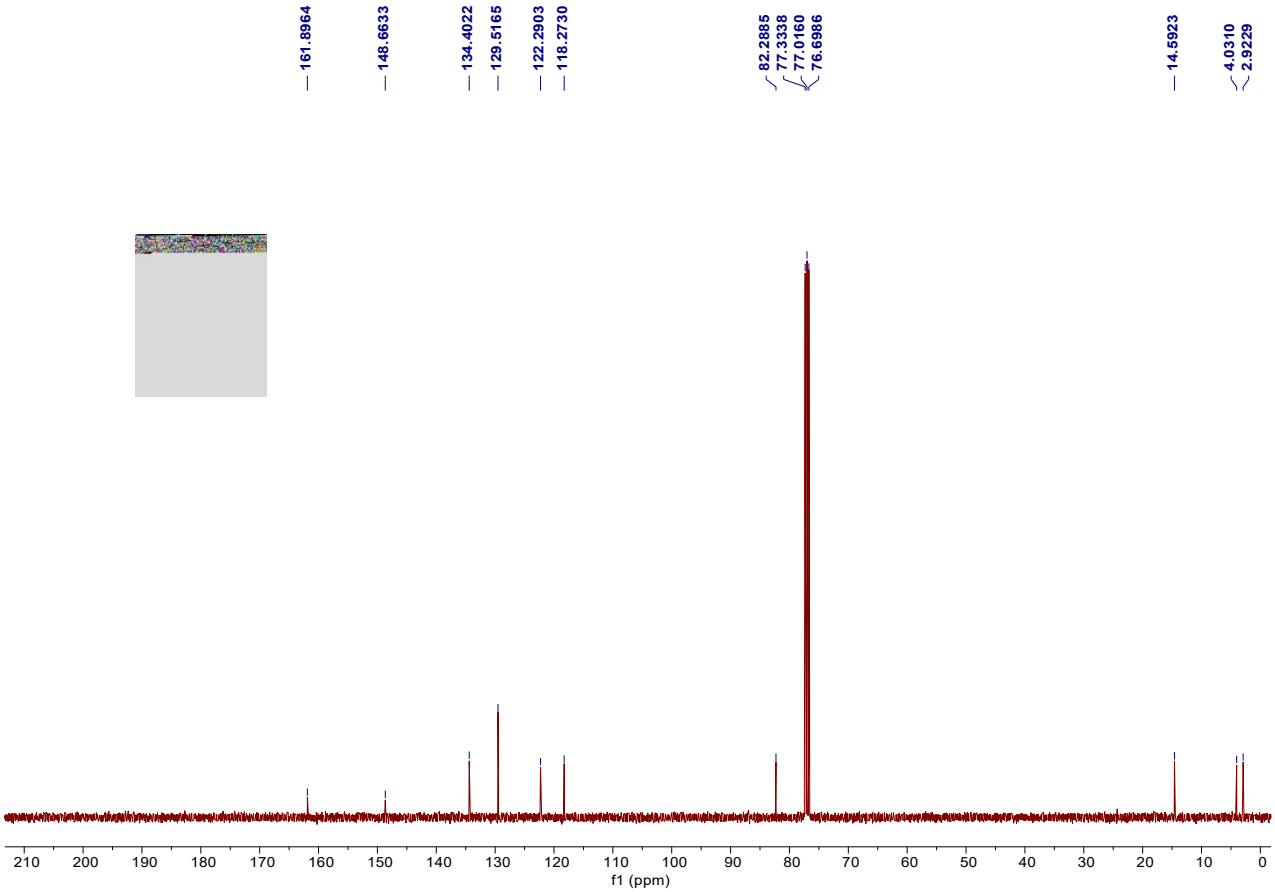
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1m**



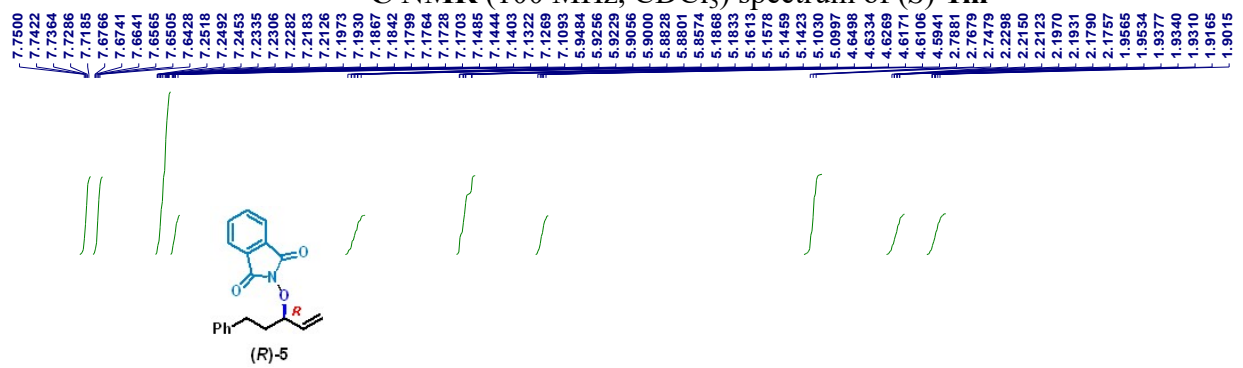
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1m**

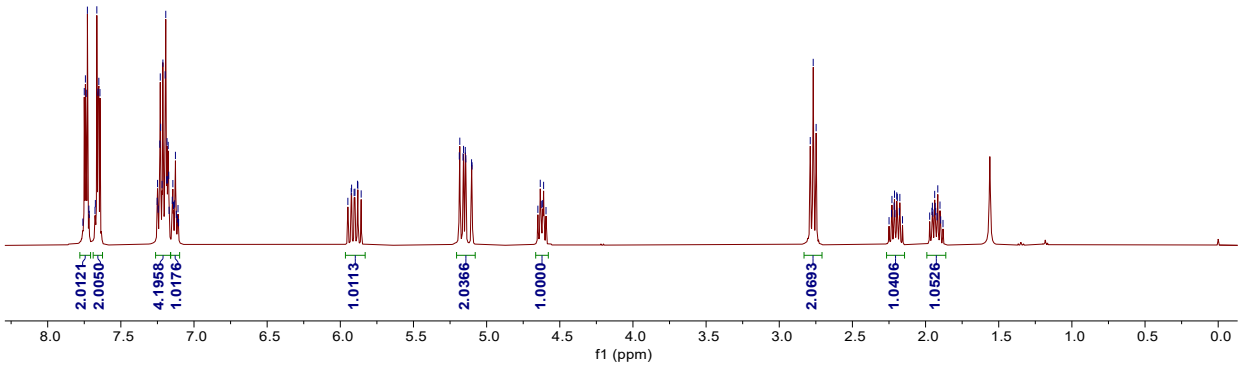


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**1m'**

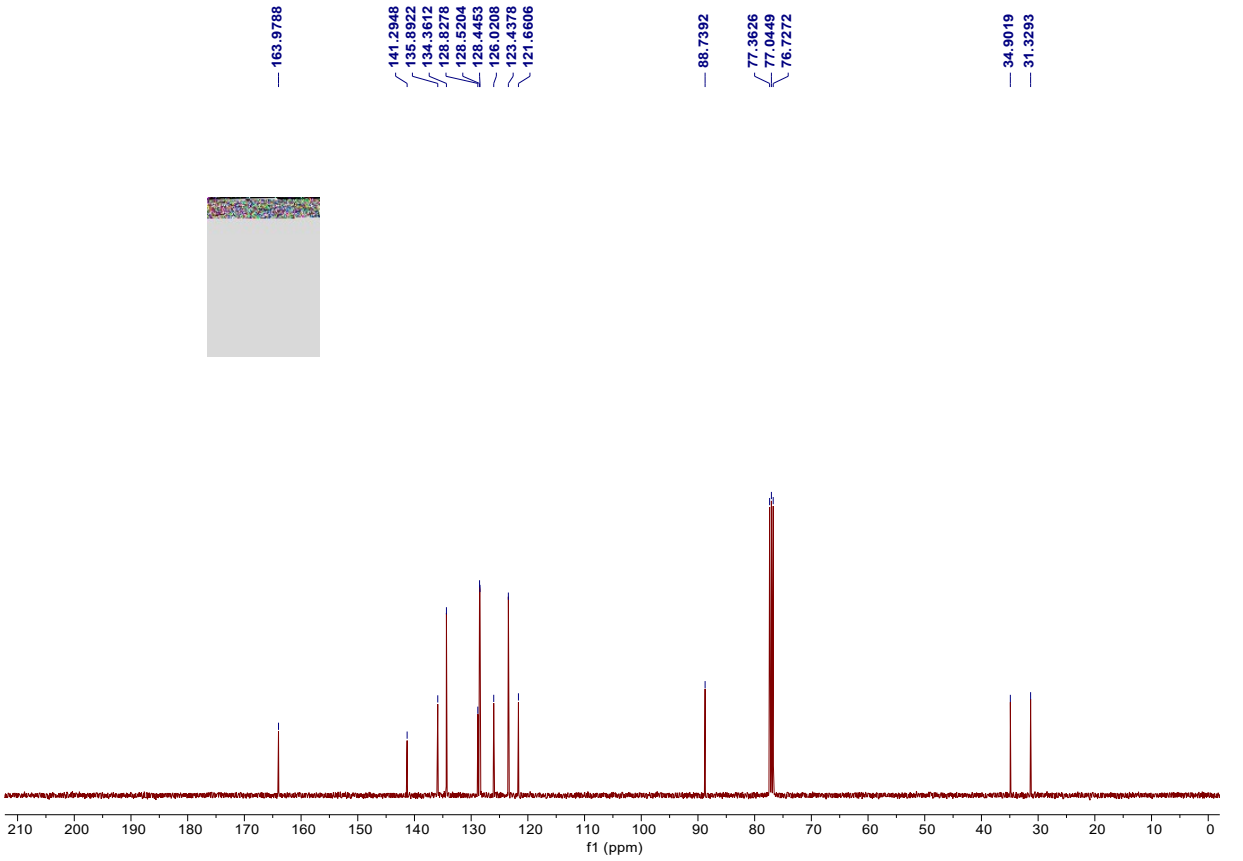


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**1m'**

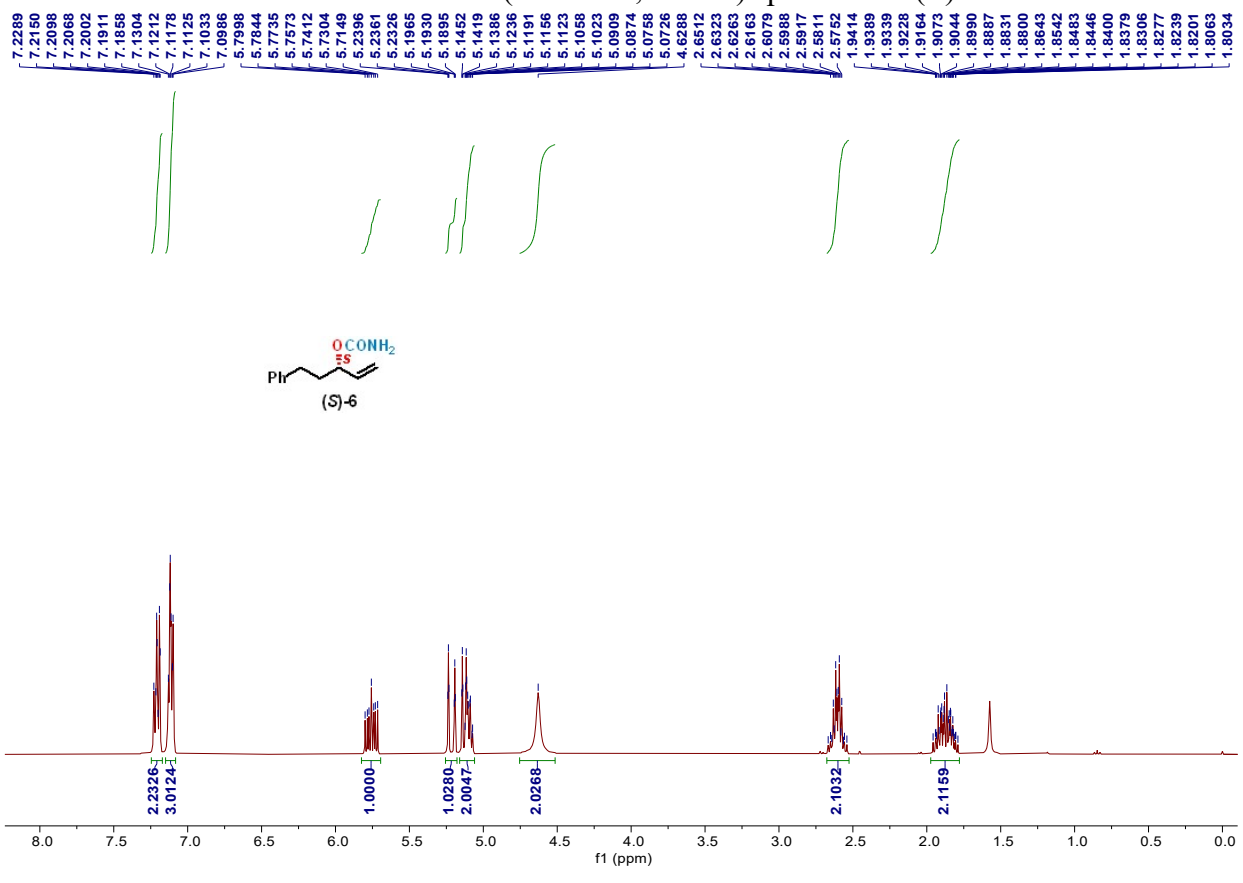




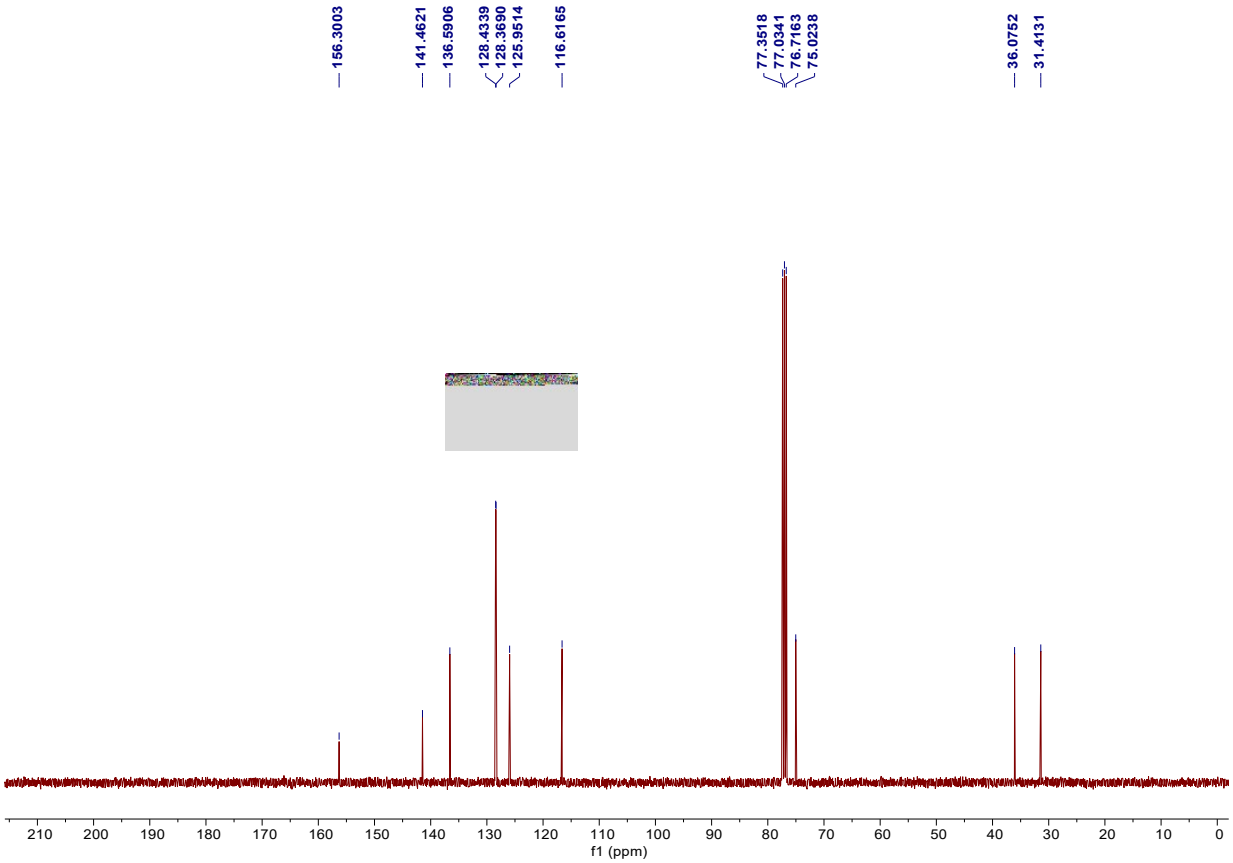
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**5**



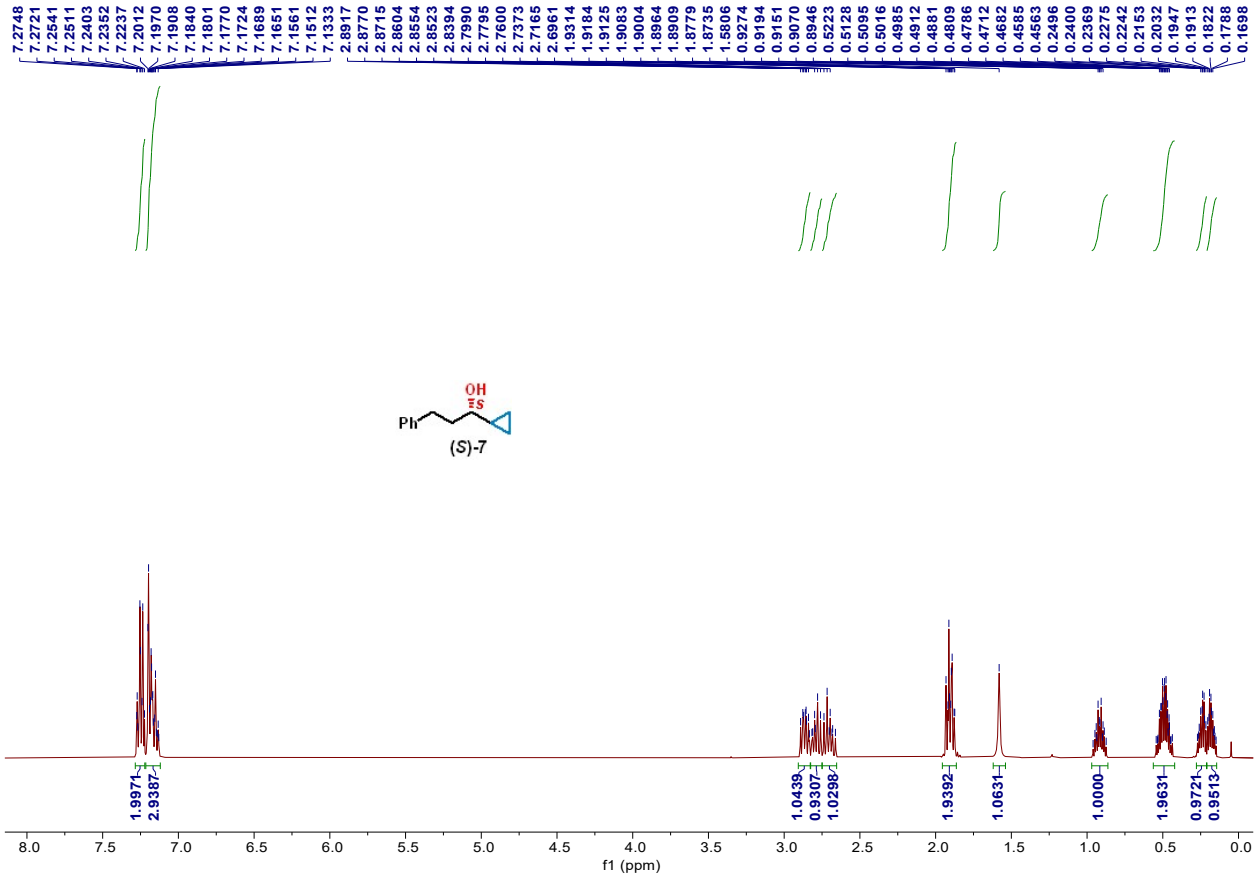
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**5**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**6**

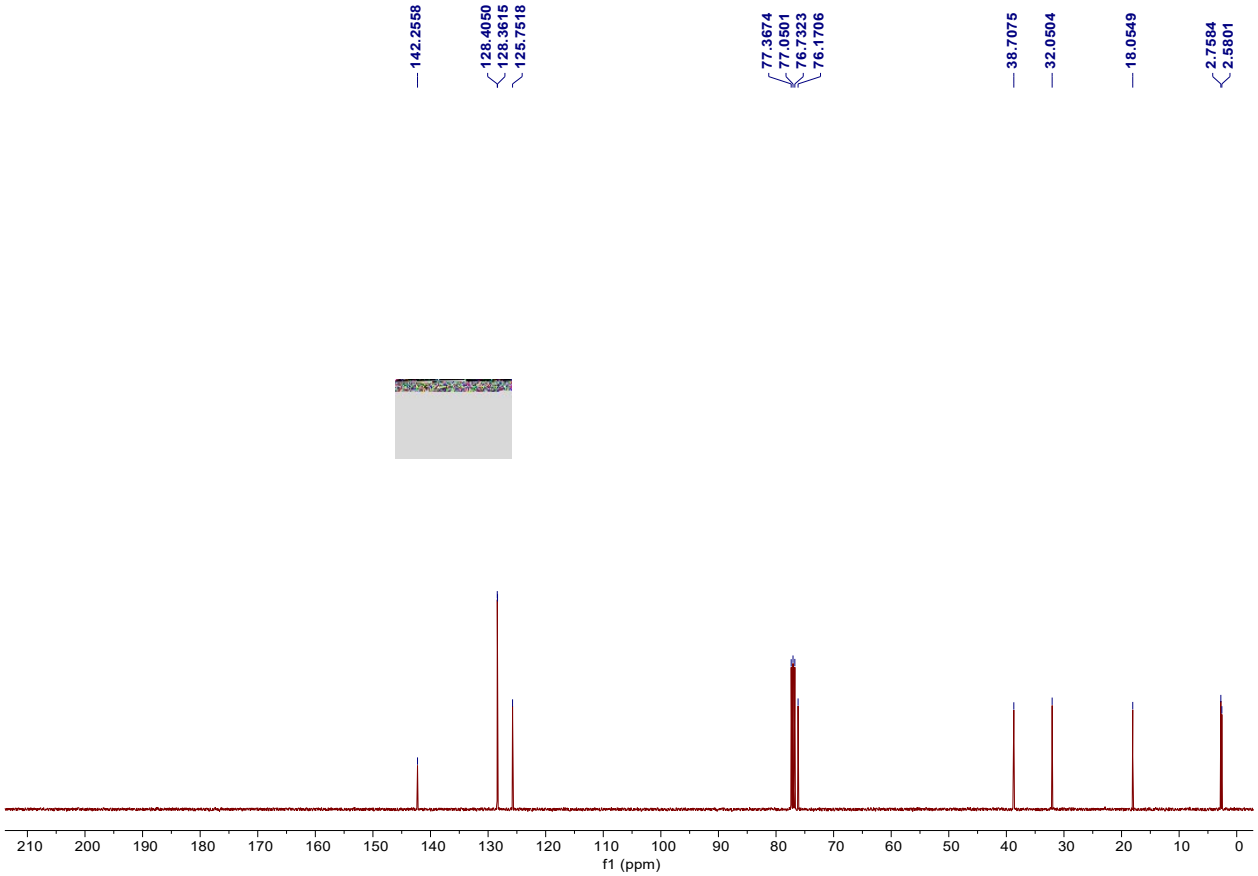


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**6**

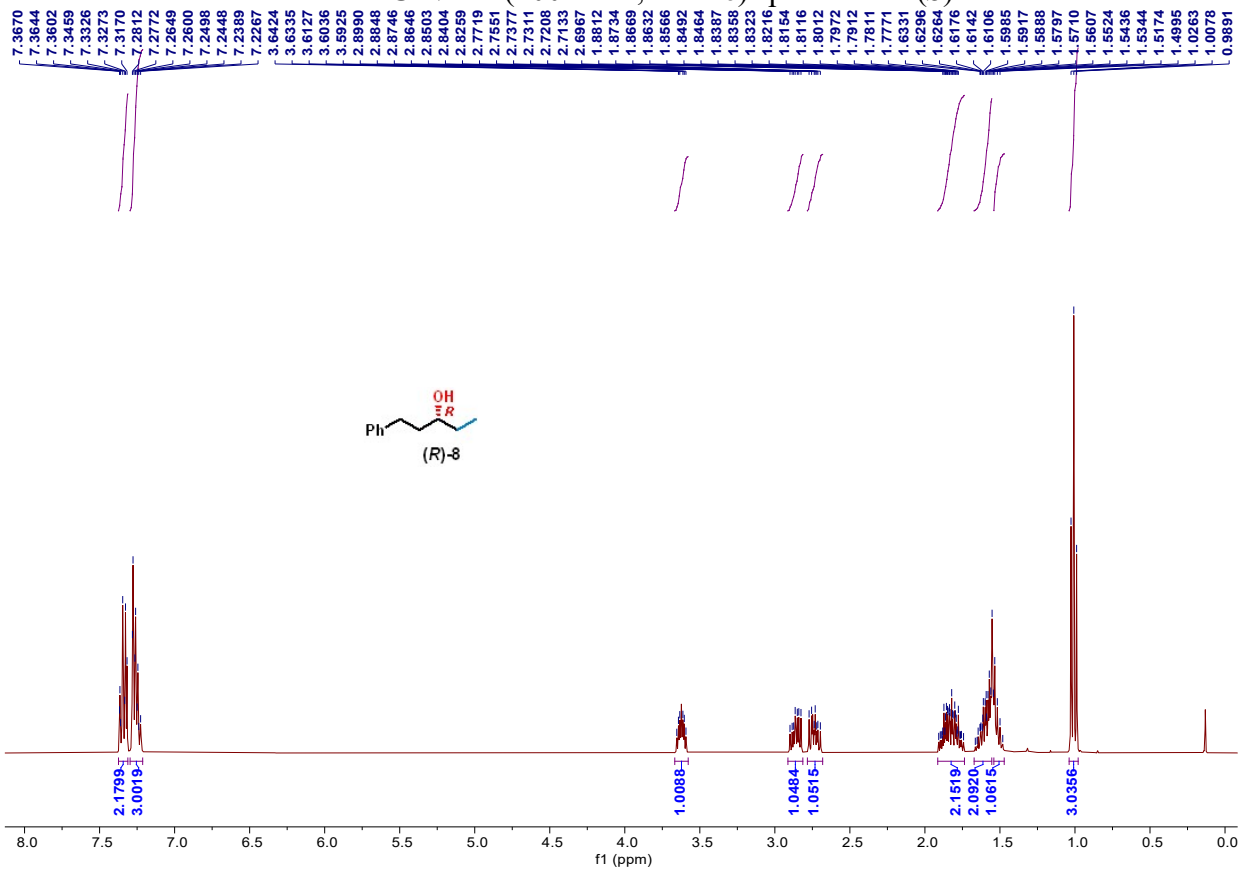


(*S*)-7

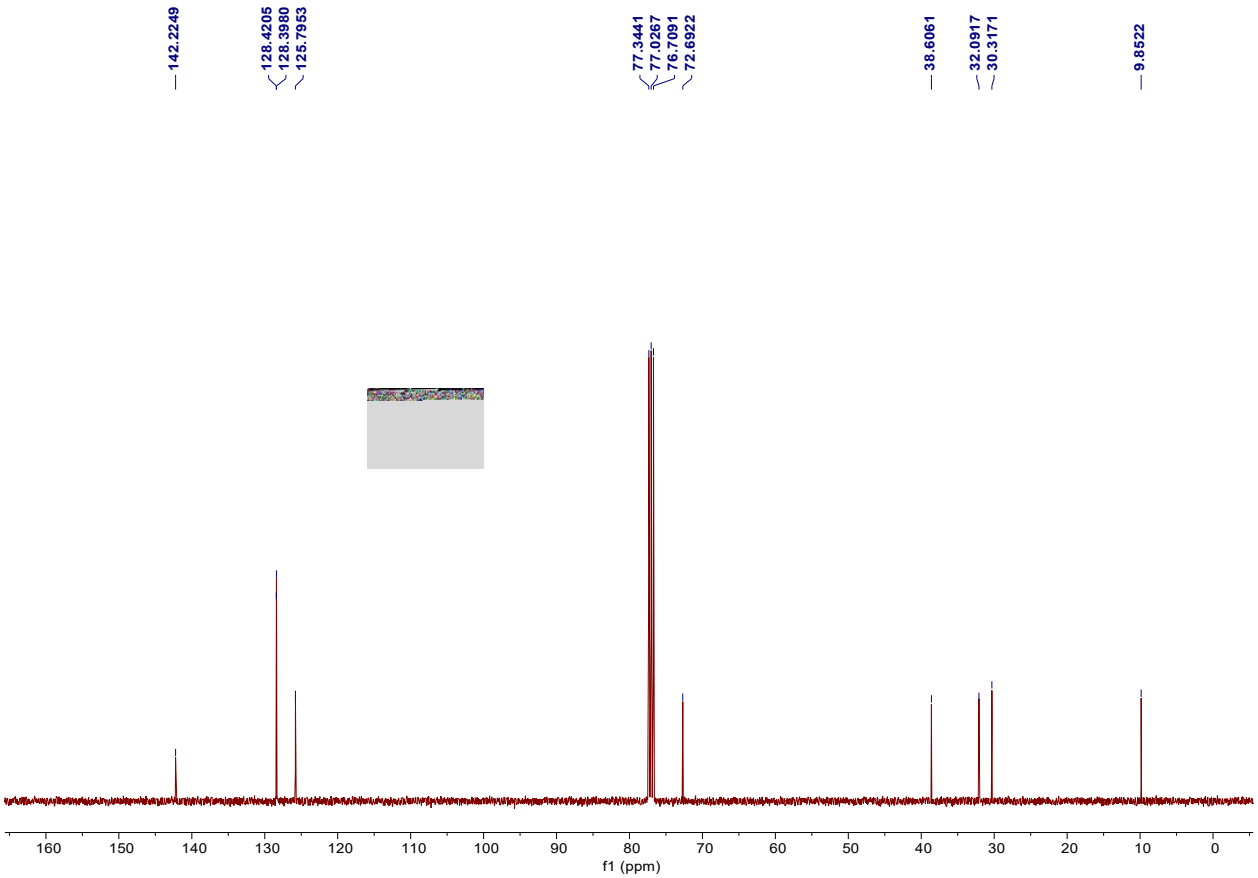
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*S*)-**7**



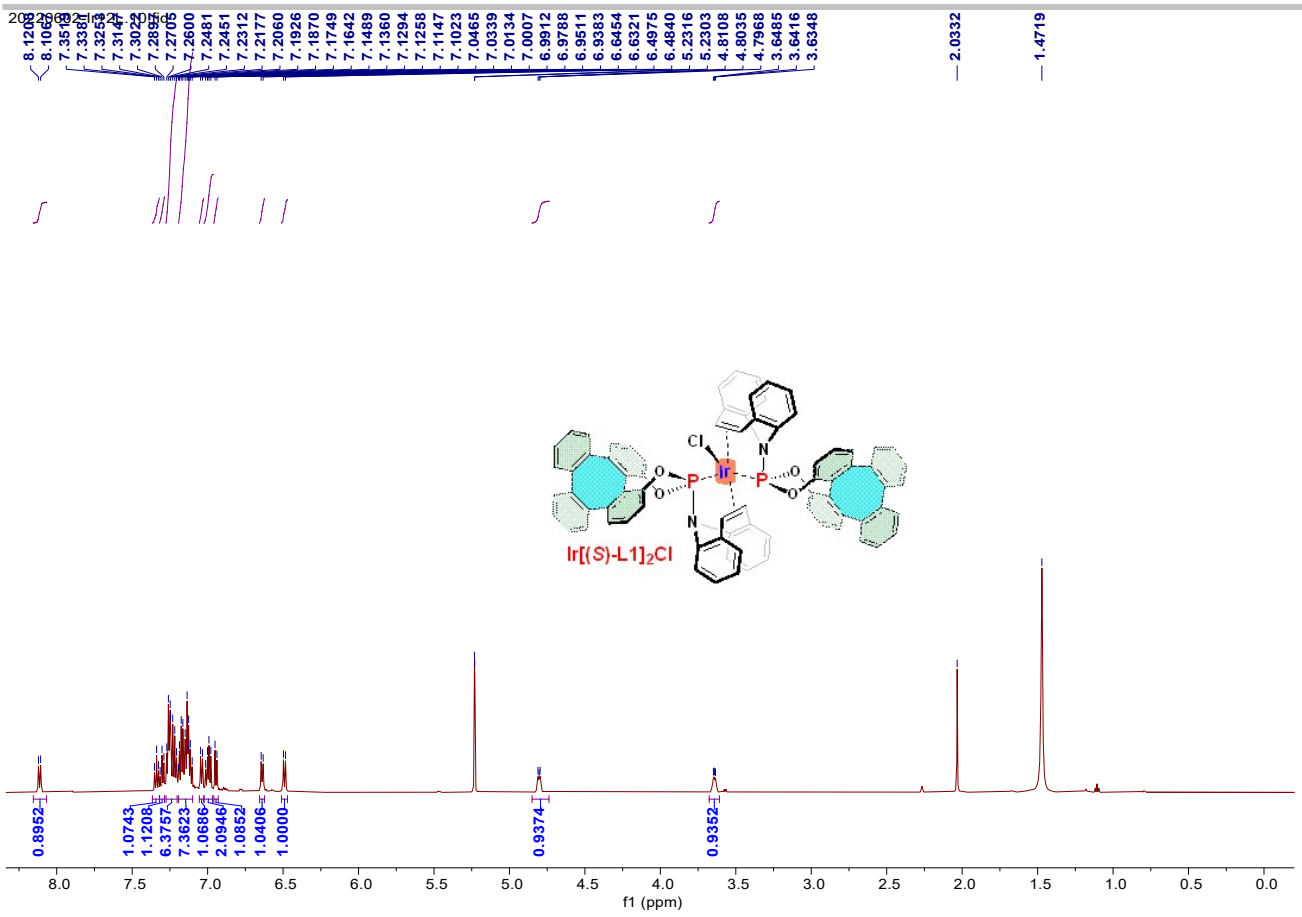
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*S*)-**7**



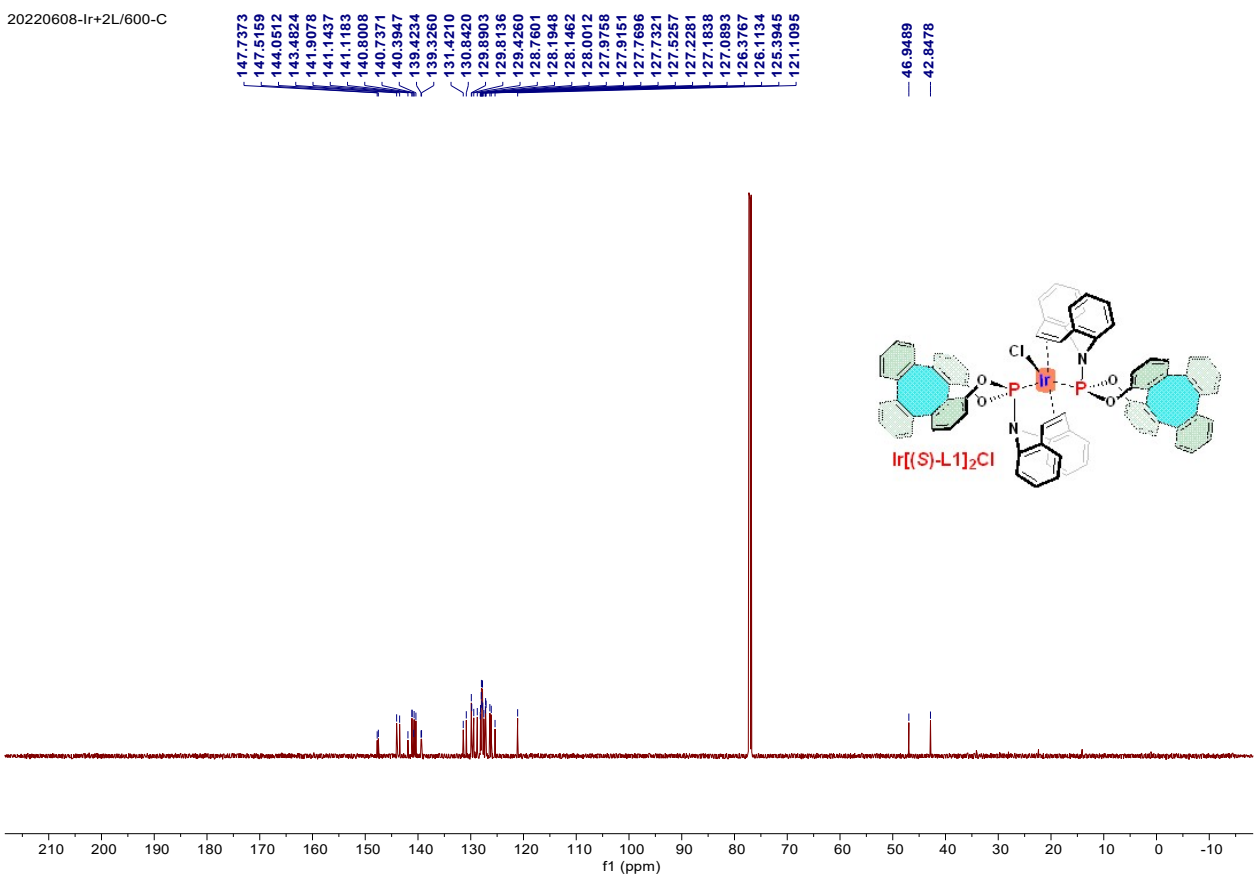
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-**8**



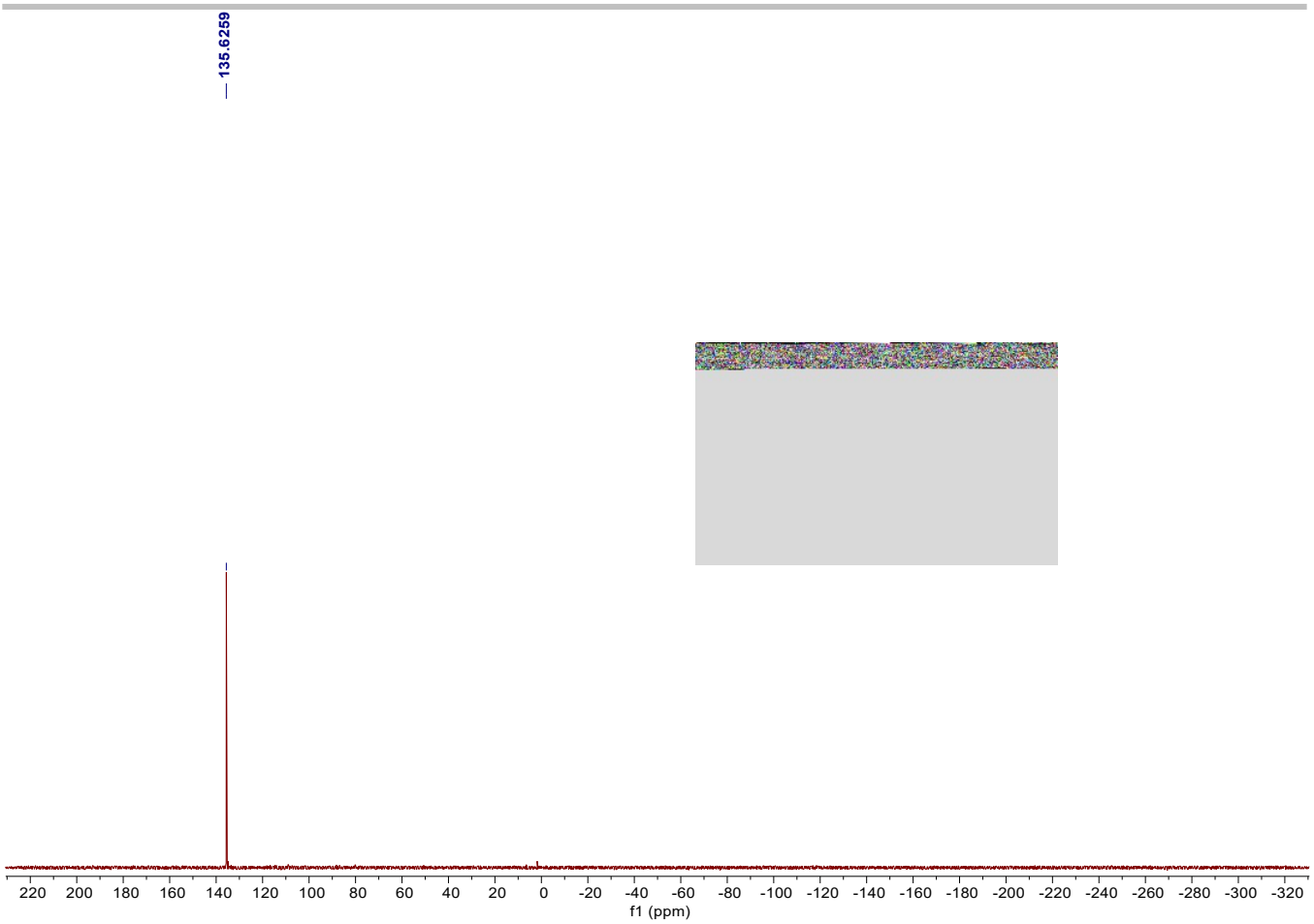
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-**8**



^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of **Ir[(*S*)-L1]$_2$Cl**



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **Ir[(*S*)-L1]$_2$Cl**



^{31}P NMR (162 MHz, $CDCl_3$) spectrum of **Ir[(*S*)-L1]$_2$Cl**

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