Electronic Supplementary Information

Copper/Ruthenium Relay Catalysis Enables 1,6-Double Chiral Inductions with Stereodivergence

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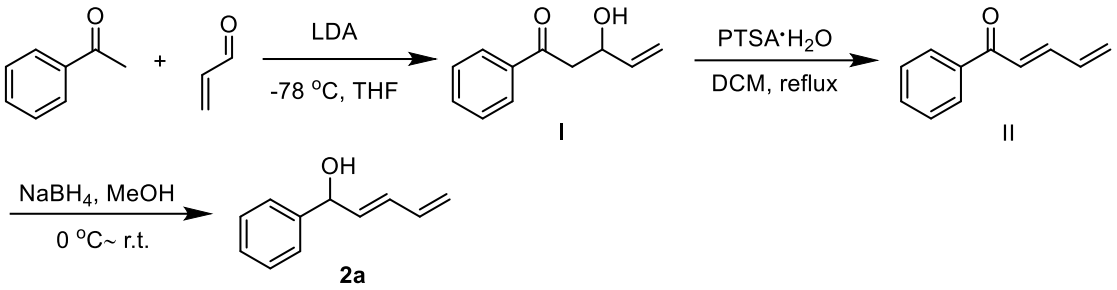
Content

1. General remarks

^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. ^{13}C NMR spectra were recorded on a Bruker 101 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. ^{19}F NMR spectra were recorded on a Bruker 376 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal CF_3COOH signal at -76.55 ppm. The data are reported as (s = single, d = double, t = triple, q = quarter, m = multiple or unresolved, br s = broad single, coupling constant(s) in Hz, integration). High resolution mass spectra (HR-MS) were recorded on a LTQ-Orbitrap Elite mass spectrometer with MeOH as solvent mixture for the measurements. Commercially obtained reagents were used without further purification. Solvents were purified prior to use according to the standard methods. Unless otherwise noted, all reactions were carried out under argon atmosphere. The enantiomeric excesses (ee) and diastereomeric ratio (dr) of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on Agilent 1200 and 1260 Series chromatographs using a Diacel chiral column (25 cm). Optical rotations were measured on a Rudolph Research Analytical Autopol VI polarimeter with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL. The racemic products were obtained by running reactions with racemic [Ru]-catalyst and racemic ligand. The chiral catalyst [Ru]-**1**[1] and [Ru]-**2**[1] and known chiral ligands **L1**[2], **L5**-**L9**[2] and ligand **L2**[3] and ligands **L4**,[4] **L10**-**L11**[4] were prepared according to the literature procedure. Commercially available chiral ligands (**L3**) were purchased and used without further purification. Diphenyl ketimine esters **1**, racemic 1,3-dienyl carbinols **2**[5] and 1,3,5-trienyl carbinols **4**[6] were prepared according to the literature procedure. The absolute configuration of (2*R*,7*S*,*E*)-*trans*-**10** and (2*R*,7*R*,*E*)-*cis*-**10** was determined by X-ray analysis, and those of other *trans*- and *cis*-products were deduced on the basis of these results.

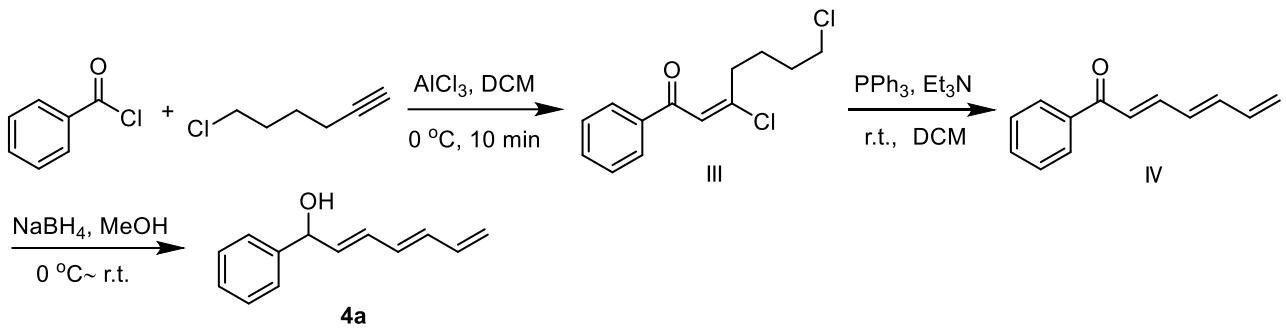
2. Preparation of racemic 1,3-dienyl carbinols and 1,3,5-trienyl carbinols



To a stirred solution of *i*-Pr_2NH (33 mmol, 1.1 eq.) in dry THF (33 mL), was add *n*-BuLi (33 mmol, 2.5 M in hexane, 1.1 eq.) dropwise at -78 °C. The mixture was stirred for 30 min at the same temperature then acetophenone (30 mmol, 1.0 eq.) in THF (10 mL) was added to the generated LDA solution at −78 °C and the reaction was allowed to stir for 30 min. A solution of acrolein in THF (10 mL) was added and the mixture was stirred for 1 h. The reaction was quenched with sat. aq. NH_4Cl solution when the starting material was completely consumed. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The alcohol product **I** was isolated via silica gel column chromatography as a yellow liquid in 75% yield.

To a solution of **I** (22 mmol, 1.0 eq.) in DCM (44 mL) at room temperature was added PTSA (11 mmol, 0.5 eq.). The reaction system was heated to 40 °C and refluxed for 3 h. The mixture was diluted with DCM and washed with water (2 × 40 mL). Dried organic layer was evaporated. The product **II** was isolated via silica gel column chromatography as a yellow liquid in 80% yield.

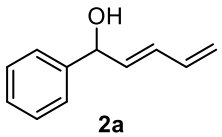
To a stirred solution of **II** (17.6 mmol, 1.0 eq.) in MeOH (40 mL), was added $CeCl_3 \cdot 7H_2O$. The mixture was cooled to 0 °C and $NaBH_4$ was added slowly at 0 °C. After stirring for 1 h, the reaction was quenched with H_2O and MeOH was removed in vacuo. The mixture was extracted with EtOAc (3 × 40 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The substrate **2a** was isolated via silica gel column chromatography as a yellow liquid in 90% yield.



Under Argon, to a suspension of $AlCl_3$ (33 mmol, 1.1 eq.) in dry DCM (30 mL) was added benzoyl chloride (30 mmol, 1.0 eq.) in DCM (10 mL) and 6-chloro-1-hexyne (30 mmol, 1.0 eq.) in DCM (10 mL) simultaneously at 0 °C. The reaction was quenched by H_2O after 15 min. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The product **III** was isolated via silica gel column chromatography as a yellow liquid in 65% yield.

A dry flask was charged with **III** (5 mmol, 1.0 eq.) and PPh_3 (0.5 mmol, 0.1 eq.) under argon. To this flask was added dry DCM (10 mL) followed by Et_3N (1.5 mmol, 1.5 eq.) at room temperature. The mixture was continued to stir until reaction was completed. The reaction was quenched with H_2O (10 mL), extracted with DCM (3 × 10 mL), and dried with Na_2SO_4. The product **IV** was isolated via silica gel column chromatography as a yellow liquid in 30% yield.

4a was synthesized from **IV** in the same method as that used for the substrate **2a** from **II**.

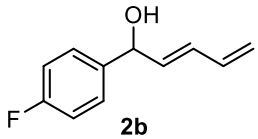


2a

(*E*)-1-phenylpenta-2,4-dien-1-ol (2a): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 6.33 – 6.22 (m, 2H), 5.89 – 5.77 (m, 1H), 5.23 – 5.15 (m, 2H), 5.09 – 5.02 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.7, 136.2, 135.5, 131.3, 128.6, 127.8, 126.3, 118.1, 74.7.



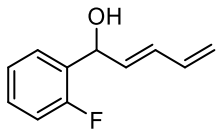
2b

(*E*)-1-(4-fluorophenyl)penta-2,4-dien-1-ol (2b): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 2H), 6.99 – 6.92 (m, 2H), 6.32 – 6.16 (m, 2H), 5.84 –5.69 (m, 1H), 5.22 – 5.13 (m, 2H), 5.09 – 5.03 (m, 1H), 2.05 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3 (d, *J* = 246.7 Hz), 138.4 (d, *J* = 3.4 Hz), 136.0, 135.2, 131.5, 128.0 (d, *J* = 8.3 Hz), 118.4, 115.4 (d, *J* = 21.3 Hz), 74.0.

^{19}F NMR (376 MHz, Chloroform-*d*) -114.76 – -114.78 (m).



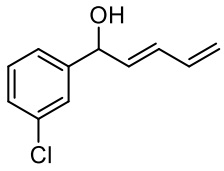
2c

(*E*)-1-(2-fluorophenyl)penta-2,4-dien-1-ol (2c): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 1H), 7.30 – 7.26 (m, 1H), 7.20 – 7.12 (m, 1H), 7.09 – 6.98 (m, 1H), 6.41 – 6.25 (m, 2H), 5.97 – 5.84 (m, 1H), 5.62 – 5.51 (m, 1H), 5.30 – 5.21 (m, 1H), 5.17 – 5.09 (m, 1H), 2.10 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.9 (d, *J* = 247.3 Hz), 136.0, 134.0, 131.5, 129.7 (d, *J* = 13.1 Hz), 129.2 (d, *J* = 8.2 Hz), 127.6 (d, *J* = 4.3 Hz), 124.4 (d, *J* = 3.6 Hz), 118.4, 115.4 (d, *J* = 21.5 Hz), 68.7 (d, *J* = 3.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.06 – -119.20 (m).

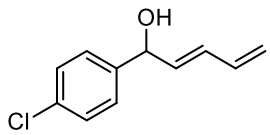


2d

(*E*)-1-(3-chlorophenyl)penta-2,4-dien-1-ol (2d): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.34 (m, 1H), 7.31-7.24 (m, 3H), 6.41 – 6.25 (m, 2H), 5.91 – 5.76 (m, 1H), 5.31 – 5.20 (m, 2H), 5.19 – 5.11 (m, 1H), 1.99 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 135.9, 134.7, 134.4, 131.9, 129.8, 127.8, 126.4, 124.4, 118.7, 74.1.

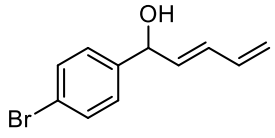


2e

(*E*)-1-(4-chlorophenyl)penta-2,4-dien-1-ol (2e): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.29 (m, 4H), 6.39 – 6.25 (m, 2H), 5.90 – 5.76 (m, 1H), 5.30 – 5.21 (m, 2H), 5.17 – 5.11 (m, 1H), 2.00 (s,1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.1, 135.9, 135.0, 133.4, 131.7, 128.7, 127.6, 118.6, 74.0.

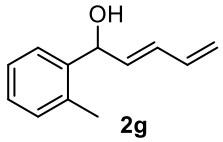


2f

(*E*)-1-(4-bromophenyl)penta-2,4-dien-1-ol (2f): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.44 (m, 2H), 7.29 – 7.24 (m, 2H), 6.42 – 6.22 (m, 2H), 5.91 – 5.74 (m, 1H), 5.31 – 5.19 (m, 2H), 5.18 – 5.11 (m, 1H), 2.00 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) 141.6, 135.9, 134.9, 131.8, 131.6, 128.0, 121.6, 118.6, 74.0.

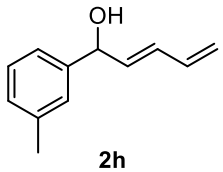


2g

(*E*)-1-(*o*-tolyl)penta-2,4-dien-1-ol (2g): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.43 (m, 1H), 7.24 – 7.10 (m, 3H), 6.39 – 6.22 (m, 2H), 5.86 (dd, *J* = 14.6, 6.2 Hz, 1H), 5.44 (d, *J* = 6.4 Hz, 1H), 5.22 (dd, *J* = 16.4, 2.0 Hz, 1H), 5.10 (dd, *J* = 9.8, 1.8 Hz, 1H), 2.34 (s, 3H), 1.94 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.6, 136.2, 135.2, 134.7, 131.3, 130.5, 127.6, 126.3, 125.8, 117.9, 71.4, 19.1.

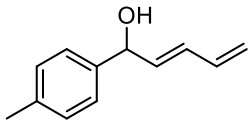


2h

(*E*)-1-(*m*-tolyl)penta-2,4-dien-1-ol (2h): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.21 (m, 1H), 7.19 – 7.14 (m, 2H), 7.12 – 7.08 (m, 1H), 6.40 – 6.28 (m, 2H), 5.93 – 5.84 (m, 1H), 5.28 – 5.20 (m, 2H), 5.14 – 5.09 (m, 1H), 2.36 (s, 3H), 1.96 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.7, 138.3, 136.2, 135.6, 131.1, 128.53, 128.50, 126.9, 123.3, 118.0, 74.7, 21.4.

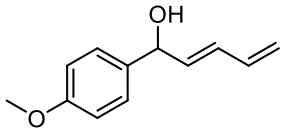


2i

(*E*)-1-(*p*-tolyl)penta-2,4-dien-1-ol (2i): white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.42 – 6.21 (m, 2H), 5.97 – 5.80 (m, 1H), 5.29 – 5.19 (m, 2H), 5.16 – 5.07 (m, 1H), 2.34 (s, 3H), 1.89 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.8, 137.5, 136.2, 135.6, 131.1, 129.3, 126.2, 117.9, 74.5, 21.1.

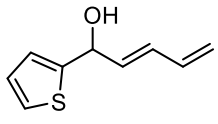


2j

(*E*)-1-(4-methoxyphenyl)penta-2,4-dien-1-ol (2j): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 2H), 6.33 – 6.19 (m, 2H), 5.87 – 5.76 (m, 1H), 5.21 – 5.12 (m, 2H), 5.07 – 5.01 (m, 1H), 3.73 (s, 3H), 1.84 (d, *J* = 3.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 136.2, 135.7, 135.0, 131.0, 127.6, 117.9, 114.0, 74.2, 55.3.

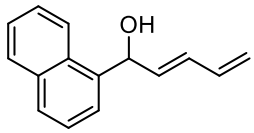


2k

(*E*)-1-(thiophen-2-yl)penta-2,4-dien-1-ol (2k): orange liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 1H), 7.02 – 6.92 (m, 2H), 6.45 – 6.30 (m, 2H), 6.03 – 5.86 (m, 1H), 5.47 (dd, *J* = 6.6, 3.8 Hz, 1H), 5.32 – 5.23 (m, 1H), 5.20 – 5.12 (m, 1H), 2.28 (d, *J* = 4.0 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.7, 135.9, 134.4, 131.8, 126.8, 125.2, 124.3, 118.6, 70.4.

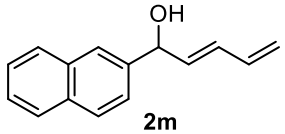


2l

(*E*)-1-(naphthalen-1-yl)penta-2,4-dien-1-ol (2l): sticky yellow liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.14 (m, 1H), 7.91 – 7.85 (m, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.55 – 7.45 (m, 3H), 6.46 – 6.30 (m, 2H), 6.15 – 6.04 (m, 1H), 6.02 – 5.97 (m, 1H), 5.28 – 5.19 (m, 1H), 5.15 – 5.08 (m, 1H), 2.12 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.2, 136.2, 135.0, 133.9, 131.7, 130.6, 128.8, 128.5, 126.2, 125.7, 125.4, 123.9, 123.7, 118.1, 71.7.

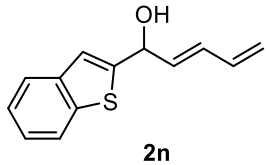


2m

(*E*)-1-(naphthalen-2-yl)penta-2,4-dien-1-ol (2m): white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.75 (m, 4H), 7.54 – 7.42 (m, 3H), 6.44 – 6.29 (m, 2H), 6.04 – 5.89 (m, 1H), 5.46 – 5.39 (m, 1H), 5.31 – 5.21 (m, 1H), 5.17 – 5.09 (m, 1H), 2.09 (d, *J* = 3.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.0, 136.2, 135.4, 133.3, 133.0, 131.5, 128.3, 128.0, 127.6, 126.2, 125.9, 124.8, 124.5, 118.2, 74.7.

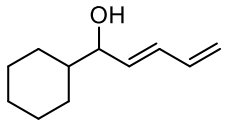


2n

(*E*)-1-(benzo[*b*]thiophen-2-yl)penta-2,4-dien-1-ol (2n): white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.68 (m, 1H), 7.67 – 7.60 (m, 1H), 7.29 – 7.20 (m, 2H), 7.13 (s, 1H), 6.38 – 6.25 (m, 2H), 5.98 – 5.84 (m, 1H), 5.51 – 5.43 (m, 1H), 5.27 – 5.18 (m, 1H), 5.15 – 5.08 (m, 1H), 2.19 (d, *J* = 4.4 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.4, 139.7, 139.5, 135.8, 133.8, 132.4, 124.30, 124.26, 123.6, 122.5, 120.7, 119.0, 71.1.

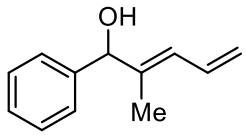


2q

(*E*)-1-cyclohexylpenta-2,4-dien-1-ol (2q): colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.42 – 6.28 (m, 1H), 6.25 – 6.14 (m, 1H), 5.72 (dd, *J* = 15.2, 7.2 Hz, 1H), 5.21 (dd, *J* = 16.8, 1.6 Hz, 1H), 5.09 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.89 (t, *J* = 6.6 Hz, 1H), 1.89 – 1.82 (m, 1H), 1.79 – 1.71 (m, 2H), 1.70 – 1.63 (m, 2H), 1.47 – 1.38 (m, 1H), 1.29 – 1.24 (m, 1H), 1.23 – 1.19 (m, 1H), 1.18 – 1.11 (m, 1H), 1.05 – 0.94 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.4, 135.3, 131.8, 117.3, 43.8, 28.8, 28.5, 26.5, 26.1, 26.0.

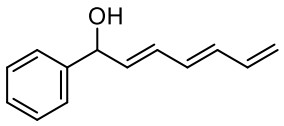


2s

(*E*)-2-methyl-1-phenylpenta-2,4-dien-1-ol (2s):

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 4H), 7.29 – 7.25 (m, 1H), 6.68 – 7.51 (m, 1H), 6.37 – 6.27 (m, 1H), 5.28 (dd, *J* = 16.4, 2.0 Hz, 1H), 5.20 – 5.08 (m, 2H), 1.99 (s, 1H), 1.63 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 139.6, 132.6, 128.4, 127.6, 126.4, 126.1, 117.7, 78.8, 12.8.

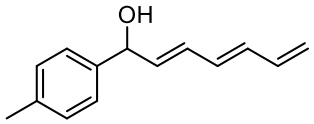


4a

(2*E*,4*E*)-1-phenylhepta-2,4,6-trien-1-ol (4a): white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 4H), 7.31 – 7.26 (m, 1H), 6.41 – 6.21 (m, 4H), 5.94 – 5.86 (m, 1H), 5.30 – 5.21 (m, 2H), 5.14 – 5.09 (m, 1H), 1.98 (d, *J* = 3.2 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.7, 136.7, 135.6, 134.1, 132.1, 130.6, 128.6, 127.8, 126.3, 117.8, 74.8.

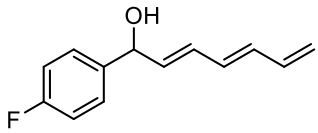


4b

(2*E*,4*E*)-1-(*p*-tolyl)hepta-2,4,6-trien-1-ol (4b): white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.43 – 6.19 (m, 4H), 5.89 (dd, *J* = 14.8, 6.8 Hz, 1H), 5.29 – 5.19 (m, 2H), 5.11 (dd, *J* = 10.0, 1.6 Hz, 1H), 2.34 (s, 3H), 1.90 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.8, 137.5, 136.8, 135.8, 133.9, 132.3, 130.3, 129.2, 126.2, 117.7, 74.6, 21.1.



4c

(2*E*,4*E*)-1-(4-fluorophenyl)hepta-2,4,6-trien-1-ol (4c): white solid.

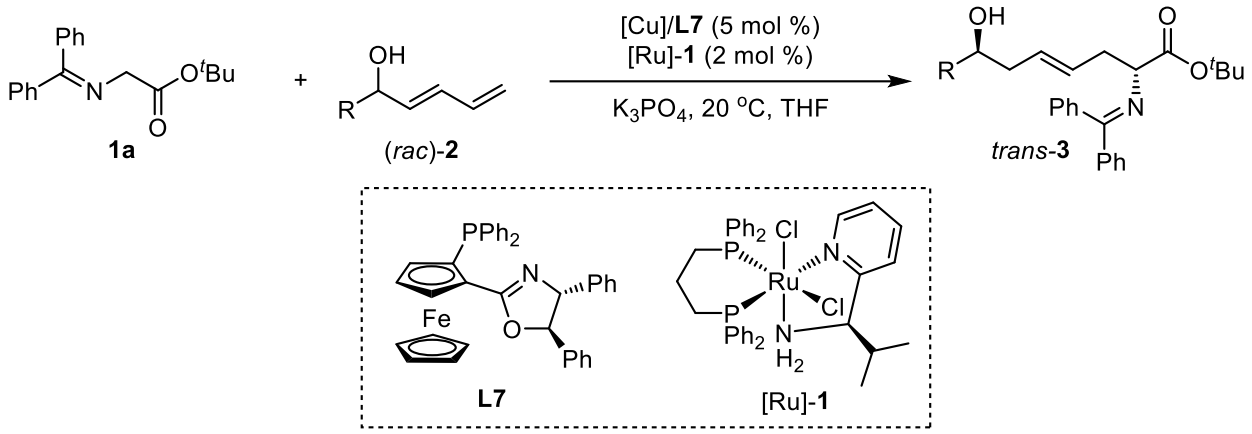
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.30 (m, 2H), 7.10 – 6.97 (m, 2H), 6.41 – 6.18 (m, 4H), 5.86 (dd, *J* = 14.6, 6.6 Hz, 1H), 5.30 – 5.21 (m, 2H), 5.13 (dd, *J* = 9.8, 1.4 Hz, 1H), 2.01 (brs, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.3 (d, *J* = 246.6 Hz), 138.4 (d, *J* = 3.0 Hz), 136.7, 135.3, 134.4, 131.9, 130.8, 128.0 (d, *J* = 8.2 Hz), 118.1, 115.4 (d, *J* = 21.4 Hz), 74.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.6 – -114.8 (m).

3. Typical procedure for stereodivergent synthesis of chiral ζ-hydroxy amino ester

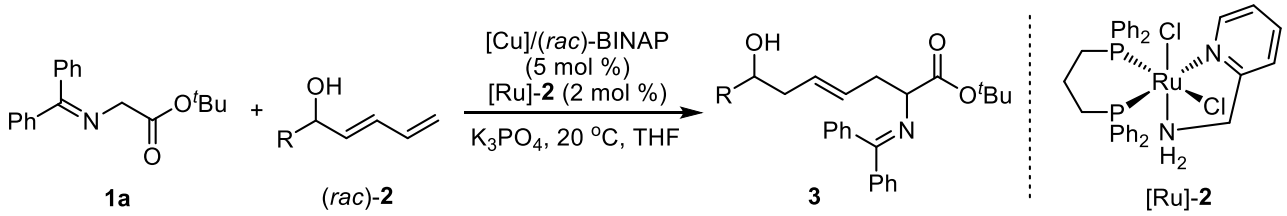
General procedure for preparation of enantiomeric products:



Under argon, to a flame dried Schlenk tube were added $Cu(MeCN)_4BF_4$ (0.01 mmol) and **L7** (0.011 mmol) and degassed THF (1 mL). The reaction mixture was stirred at 20 ºC for 30 min. Then, [Ru]-**1** complex (0.004 mmol), imino ester **1a** (0.20 mmol), dienyl carbinols **2** (0.60 mmol), K_3PO_4 (0.20 mmol) and THF (1 mL) were added into the Schlenk tube under argon. The reaction mixture was continuously stirred at 20 ºC. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography to give the desired *trans*-products, which were then directly analyzed by chiral HPLC to determine the dr value and the enantiomeric excess.

The corresponding *cis*-**3** was obtained by changing [Ru]-**1** with *ent*-[Ru]-**1** under otherwise identical conditions. Four stereodivergent products were produced with four different sets of catalyst combinations: [Cu/(*R*,*R*,R_p)-**L7**]/[Ru]-**1**; [Cu/(*R*,*R*,R_p)-**L7**]/*ent*-[Ru]-**1**; [Cu/(*S*,*S*,S_p)-**L7**]/[Ru]-**1**; [Cu/(*S*,*S*,S_p)-**L7**]/*ent*-[Ru]-**1**.

General procedure for preparation of racemic products:

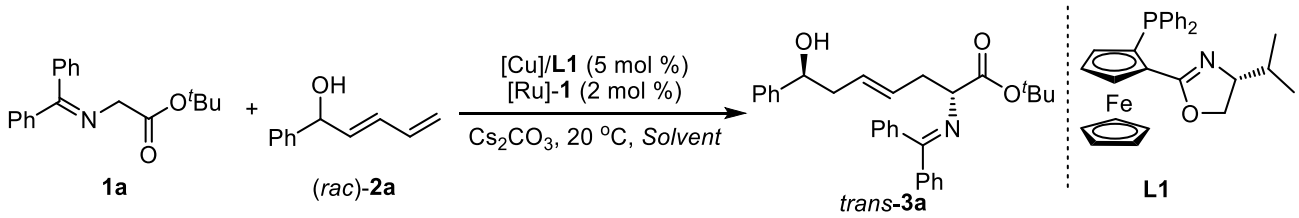


Under argon, to a flame dried Schlenk tube were added $Cu(MeCN)_4BF_4$ (0.01 mmol) and (*rac*)-BINAP (0.011 mmol) and degassed THF (1.0 mL). The reaction mixture was stirred at 20 ºC for 30

min. Then, [Ru]-**2** complex (0.004 mmol), imino ester **1a** (0.20 mmol), dienyl carbinols **2** (0.60 mmol), K_3PO_4 (0.20 mmol) and THF (1.0 mL) were added into the Schlenk tube under argon. The reaction mixture was continuously stirred at 20 ºC overnight. Then the organic solvent was removed and the residue was purified by column chromatography to give the desired *rac*-products.

4. Optimization of rection conditions

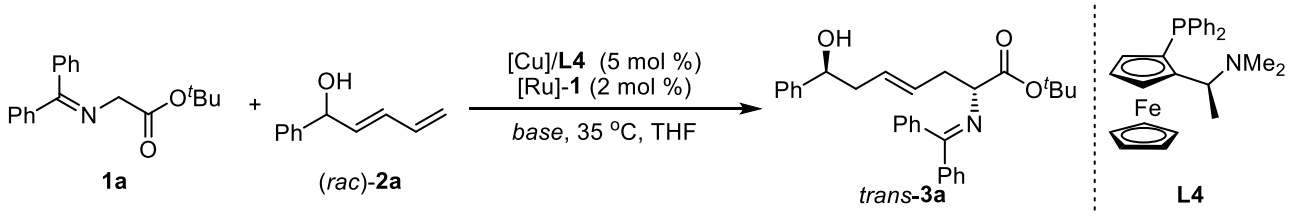
Table S1. Evaluation of solvent [a]



Solvent	yield (%) [b]	dr [c]	ee (%) [c]
THF	93	4:1	>99
Toluene	mess	-	-
DCM	70	4:1	98
1,4-Dioxane	mess	-	-
MTBE	83	2:1	96
Et_2O	64	1:1	91
2-Me-THF	45	1:1	33

[a] All reactions were carried out with 0.20 mmol of **1a**, 0.60 mmol of **2a**, 0.005 mmol of [Cu], 0.0055 mmol of **L1** and 0.20 mmol of Cs_2CO_3 in 2 mL of solvent at 20 ºC. The reaction was monitored by TLC. [Cu] = $Cu(MeCN)_4BF_4$. [b] Isolated yield. [c] The dr and ee values were determined by HPLC analysis.

Table S2. Evaluation of base [a]

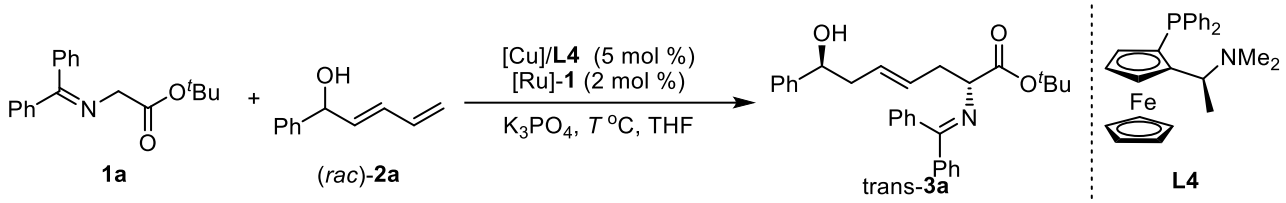


Base	yield (%)[b]	dr [c]	ee (%) [c]
^{t}BuOK	38	1:1	0
Cs_2CO_3	74	11:1	99
K_3PO_4	72	13:1	99
Na_2CO_3	-	-	-
Et_3N	-	-	-

DBU	trace	-	-

[a] All reactions were carried out with 0.20 mmol of **1a**, 0.60 mmol of **2a**, 0.005 mmol of [Cu], 0.0055 mmol of **L4** and 0.20 mmol of the base in 2 mL of THF at 35 °C. The reaction was monitored by TLC. [Cu] = $Cu(MeCN)_4BF_4$. [b] Isolated yield. [c] The dr and ee values were determined by HPLC analysis.

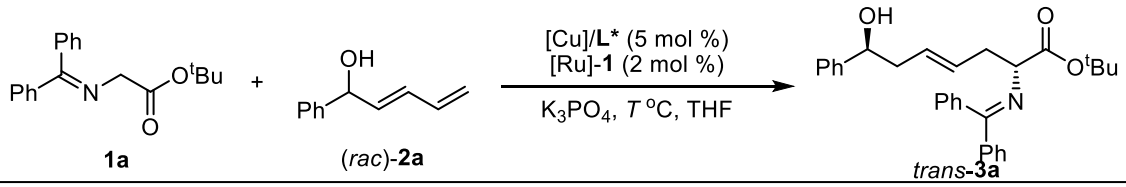
Table S3. Evaluation of temperature [a]

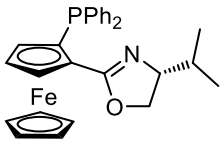


T (°C)	yield (%) [b]	dr [c]	ee (%) [c]
0	17	16:1	99
20	72	9:1	97
35	42	4:1	96

[a] All reactions were carried out with 0.20 mmol of **1a**, 0.60 mmol of **2a**, 0.005 mmol of [Cu], 0.0055 mmol of **L4** and 0.20 mmol of K_3PO_4 in 2 mL of THF at T °C. The reaction was monitored by TLC. [Cu] = $Cu(MeCN)_4BF_4$. [b] Isolated yield. [c] The dr and ee values were determined by HPLC analysis.

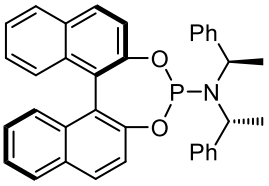
Table S4. Evaluation of chiral ligand





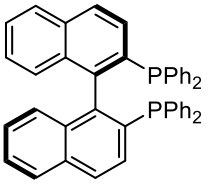
(R,R_p)-**L1**

20 °C, [Ru]-**1**, 93% yield, 4:1 dr, >99% ee
20 °C, *ent*-[Ru]-**1**, 82% yield, 1:4 dr, >99% ee



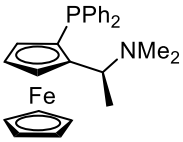
(R,R,R_p)-**L2**

35 °C, [Ru]-**1**, 56% yield, 1:1 dr



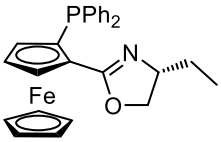
(R)-**L3**

35 °C, [Ru]-**1**, 60% yield, 1:1 dr



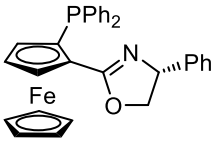
(S,R_p)-**L4**

20 °C, [Ru]-**1**, 72% yield
13:1 dr, >99% ee



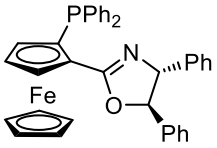
(R,R_p)-**L5**

20 °C, [Ru]-**1**, 93% yield
4:1 dr, >99% ee



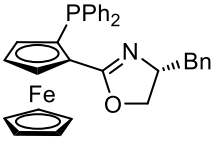
(R,R_p)-**L6**

20 °C, [Ru]-**1**, 99% yield
6:1 dr, >99% ee



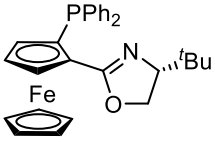
(R,R,R_p)-**L7**

20 °C, [Ru]-**1**, 99% yield
24:1 dr, >99% ee
20 °C, *ent*-[Ru]-**1**, 99% yield
1:23 dr, >99% ee



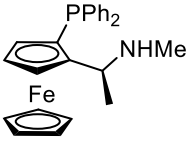
(R,R_p)-**L8**

20 °C, [Ru]-**1**, 65% yield
3:1 dr, 98% ee



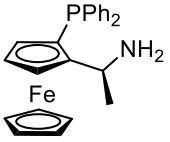
(R,R_p)-**L9**

20 °C, [Ru]-**1**, 42% yield
5:1 dr, 98% ee



(S,R_p)-**L10**

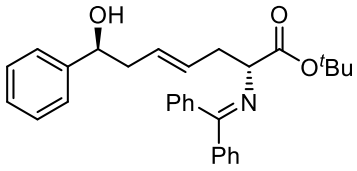
20 °C, [Ru]-**1**, 89% yield
2:1 dr, 96% ee



(S,R_p)-**L11**

20 °C, [Ru]-**1**, 85% yield
6:1 dr, 99% ee

5. Characterization data for the products



(2*R*,7*S*,*E*)-**3a**

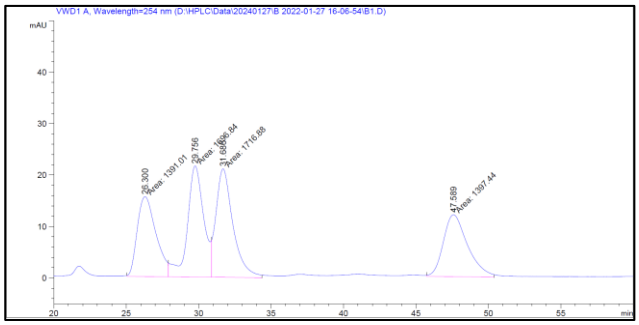
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoate ((2*R*,7*S*,*E*)-3a)**: yield (90 mg, 99%); colorless oil; $[\alpha]^{20}_{D}$ = +24.8 (*c* 0.48, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 26.30, 29.76, 31.69 and 47.59 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.67 – 7.41 (m, 3H), 7.40 – 7.28 (m, 7H), 7.25 – 7.19 (m, 1H), 7.17 – 7.11 (m, 2H), 5.58 – 5.39 (m, 2H), 4.62 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.99 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.69 – 2.53 (m, 2H), 2.48 – 2.41 (m, 1H), 2.41 – 2.31 (m, 1H), 1.44 (s, 9H).

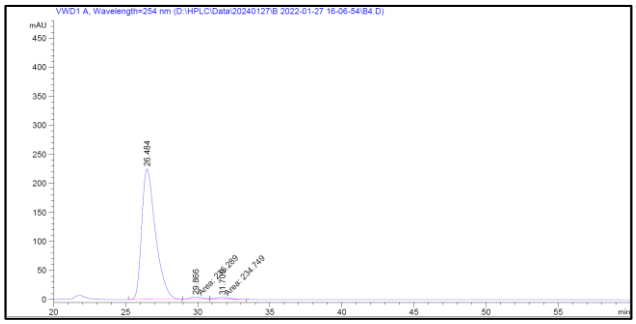
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.1, 143.9, 139.6, 136.6, 130.5, 130.2, 128.8, 128.7, 128.5, 128.4, 128.3, 128.0, 127.8, 127.3, 125.7, 81.1, 73.0, 66.0, 43.0, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{30}H_{34}NO_3$ ($[M+H]^+$): 456.2533, found: 456.2540.

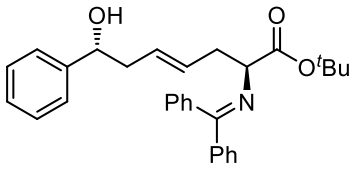
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.300	MF	1.4934	1391.01367	15.52366	22.4279
2	29.756	MF	1.3096	1696.83582	21.59413	27.3588
3	31.686	FM	1.3572	1716.87903	21.08306	27.6819
4	47.589	MM	1.9347	1397.43835	12.03840	22.5315



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.484	BB	1.0018	1.48875e4	224.75534	96.9394
2	29.866	MF	1.0623	235.28857	3.69139	1.5321
3	31.709	FM	1.2477	234.74864	3.13584	1.5286

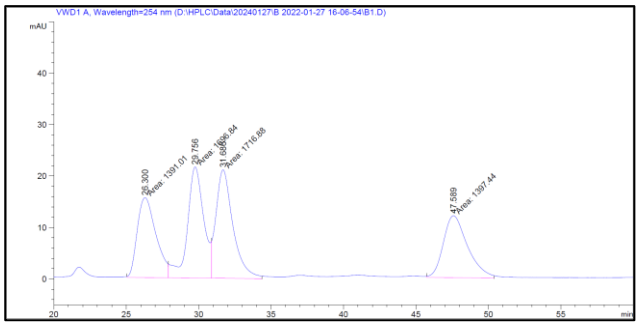


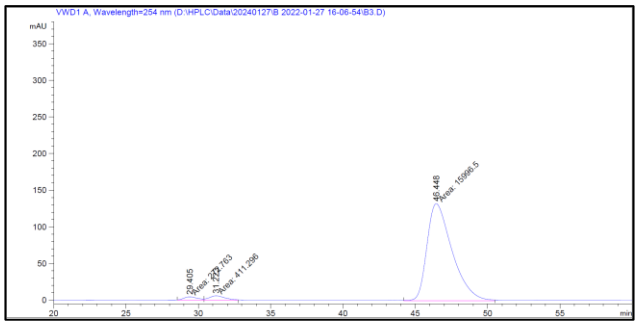
(2*S*,7*R*,*E*)-**3a**

***tert*-butyl (2*S*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoate ((2*S*,7*R*,*E*)-3a)**: yield (90 mg, 99%); colorless oil; $[\alpha]^{20}_D$ = -24.6 (*c* 0.68, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 26.30, 29.76, 31.69 and 47.59 min.

HRMS (ESI+) calcd. For $C_{30}H_{34}NO_3$ ($[M+H]^+$): 456.2533, found: 456.2539.

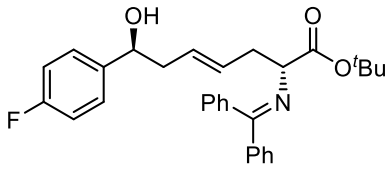
HPLC chromatogram of compound (2*S*,7*R*,*E*)-3a





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.300	MF	1.4934	1391.01367	15.52366	22.4279
2	29.756	MF	1.3096	1696.83582	21.59413	27.3588
3	31.686	FM	1.3572	1716.87903	21.08306	27.6819
4	47.589	MM	1.9347	1397.43835	12.03840	22.5315

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.405	MF	1.0665	272.76273	4.26271	1.6352
2	31.223	FM	1.2144	411.29568	5.64460	2.4657
3	46.448	MM	2.0112	1.59965e4	132.56378	95.8991



(2*R*,7*S*,*E*)-**3b**

***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-(4-fluorophenyl)-7-hydroxyhept-4-enoate ((2*R*,7*S*,*E*)-3b)**: yield (89 mg, 94%); colorless oil; $[\alpha]^{15}_D$ = +17.5 (*c* 0.58, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 19:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 17.36, 19.09, 20.90 and 29.52 min.

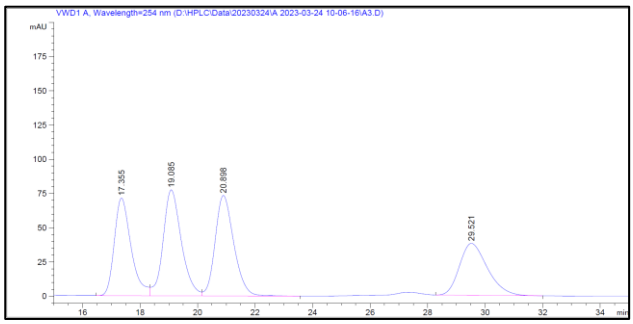
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 2H), 7.46 – 7.37 (m, 4H), 7.35 – 7.30 (m, 2H), 7.28 – 7.24 (m, 2H), 7.17 – 7.11 (m, 2H), 7.00 – 6.93 (m, 2H), 5.55 – 5.41 (m, 2H), 4.60 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.98 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.65 – 2.54 (m, 2H), 2.44 – 2.38 (m, 1H), 2.37 – 2.33 (m, 1H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 162.0 (d, *J* = 245.9 Hz), 139.6 (d, *J* = 3.0 Hz), 139.5, 136.5, 130.8, 130.3, 128.8, 128.6, 128.5, 128.4, 128.0, 127.7, 127.3 (d, *J* = 8.0 Hz), 115.0 (d, *J* = 21.4 Hz), 81.2, 72.3, 65.9, 43.1, 37.1, 28.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.41 – -115.69 (m).

HRMS (ESI+) calcd. For $C_{30}H_{33}FNO_3$ ([M+H]$^+$): 474.2439, found: 474.2440.

HPLC chromatogram of compound (2*R*,7*S*,*E*)-3b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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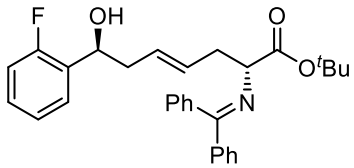
2	19.085	VV	0.6637	3398.20605	77.33379	27.9559
3	20.898	VB	0.6902	3307.86353	73.34522	27.2127
4	29.521	BB	1.0322	2560.06177	37.89103	21.0608

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.329	MF	0.6053	1.02302e4	281.68924	95.1457
2	17.920	FM	0.6381	335.59995	8.76516	3.1212
3	19.617	BB	0.6070	186.34337	4.58619	1.7331



(2*R*,7*S*,*E*)-**3c**

***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-(2-fluorophenyl)-7-hydroxyhept-4-enoate ((2*R*,7*S*,*E*)-3c)**: yield (91 mg, 96%); colorless oil; $[\alpha]^{20}_D$ = +13.6 (*c* 0.52, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 11:1 dr, 99% ee (Chiralpak IF + Chiralpak IF, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.77, 19.68, 20.47 and 22.37 min.

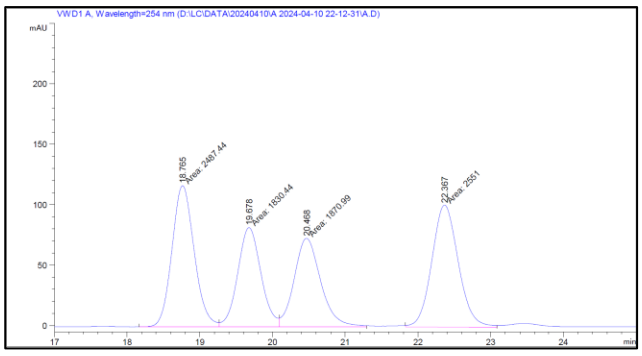
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 2H), 7.47 – 7.41 (m, 4H), 7.40 – 7.31 (m, 3H), 7.23 – 7.14 (m, 3H), 7.12 – 7.07 (m, 1H), 7.00 – 6.93 (m, 1H), 5.57 – 5.45 (m, 2H), 4.95 (dd, *J* = 8.6, 4.2 Hz, 1H), 4.00 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.67 – 2.57 (m, 2H), 2.44 – 2.26 (m, 2H), 1.45 (s, 9H).

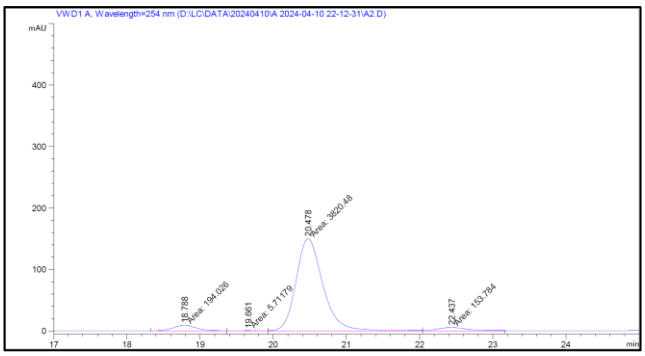
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 160.0 (d, *J* = 123.2 Hz), 139.5, 136.6, 131.0, 130.8, 130.8, 130.3, 128.8, 128.6, 128.53, 128.47, 128.0, 127.8, 127.1 (d, *J* = 4.4 Hz), 124.1 (d, *J* = 3.6 Hz), 115.1 (d, *J* = 21.4 Hz), 81.2, 67.0, 66.0, 41.7, 37.1, 28.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.64 – -119.87 (m).

HRMS (ESI+) calcd. For $C_{30}H_{33}FNO_3$ ([M+H]$^+$): 474.2439, found: 474.2443.

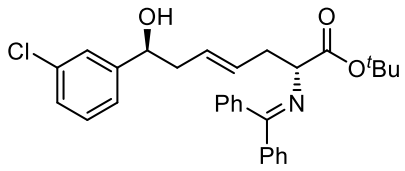
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3c





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.765	MF	0.3547	2487.43530	116.87381	28.4608
2	19.678	MF	0.3709	1830.43713	82.25761	20.9436
3	20.468	MF	0.4250	1870.98657	73.37386	21.4075
4	22.367	FM	0.4213	2550.99854	100.91523	29.1881

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.788	MF	0.3540	194.02628	9.13515	4.6484
2	19.661	MF	0.3721	5.71179	2.55812e-1	0.1368
3	20.478	MF	0.4252	3820.47852	149.75595	91.5304
4	22.437	FM	0.4623	153.78445	5.54425	3.6843



(2*R*,7*S*,*E*)-**3d**

***tert*-butyl (2*R*,7*S*,*E*)-7-(3-chlorophenyl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*S*,*E*)-3d)**: yield (90 mg, 92%); colorless oil; $[\alpha]^{15}_D$ = +16.3 (*c* 0.61, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.04, 22.19, 24.45 and 52.05 min.

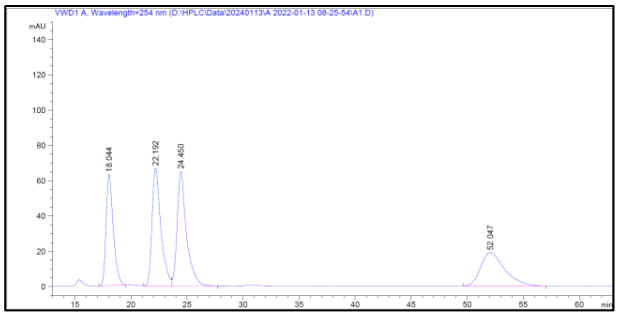
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 2H), 7.48 – 7.41 (m, 3H), 7.40 – 7.36 (m, 1H),

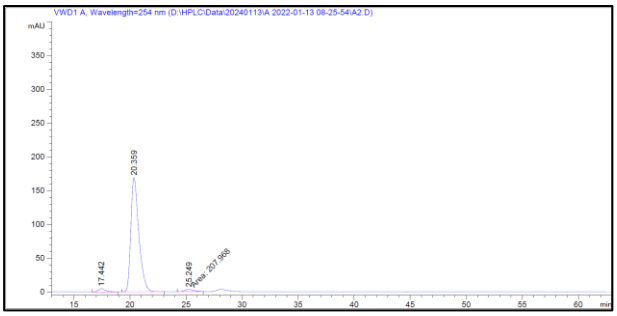
7.36 – 7.30 (m, 3H), 7.22 – 7.12 (m, 5H), 5.61 – 5.35 (m, 2H), 4.60 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.99 (dd, *J* = 6.4, 6.0 Hz, 1H), 2.64 – 2.54 (m, 2H), 2.46 – 2.41 (m, 1H), 2.36 – 2.28 (m, 1H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 146.0, 139.5, 136.6, 134.2, 131.1, 130.3, 129.5, 128.8, 128.6, 128.5, 128.3, 128.0, 127.7, 127.3, 125.9, 123.9, 81.2, 72.2, 65.9, 43.0, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{30}H_{33}ClNO_3$ ([M+H]$^+$): 490.2143, found: 490.2147.

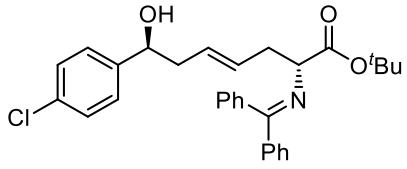
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3d





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.044	BB	0.6686	2799.91260	62.98667	21.5644
2	22.192	BV	0.8148	3652.05640	66.69958	28.1275
3	24.450	VB	0.8407	3734.44385	64.96114	28.7620
4	52.047	BB	1.8575	2797.53638	18.81717	21.5461

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.442	BB	0.6057	193.48793	4.66641	2.2110
2	20.359	BB	0.7419	8349.81445	168.84679	95.4126
3	25.249	MF	0.9822	207.96782	3.52879	2.3764



(2*R*,7*S*,*E*)-**3e**

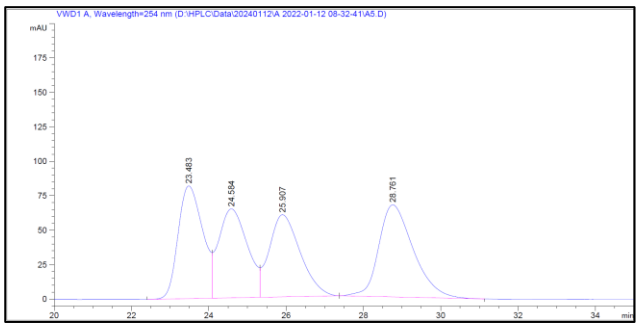
***tert*-butyl (2*R*,7*S*,*E*)-7-(4-chlorophenyl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*S*,*E*)-3e)**: yield (80 mg, 82%); colorless oil; $[\alpha]^{15}_D$ = +18.1 (*c* 0.53, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 23.48, 24.58, 25.91 and 28.76 min.

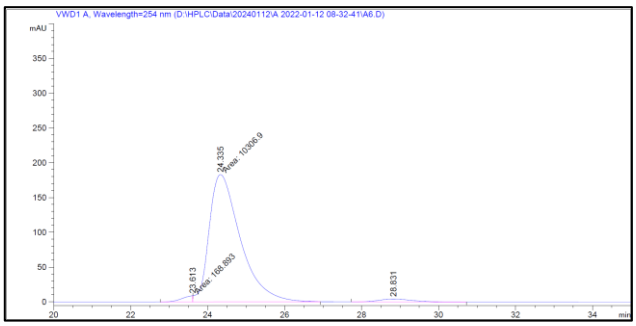
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.29 (m, 1H), 7.28 – 7.23 (m, 2H), 7.19 – 7.15 (m, 4H), 7.09 – 7.03 (m, 2H), 5.50 – 5.32 (m, 2H), 4.53 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.91 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.58 – 2.47 (m, 2H), 2.38 – 2.32 (m, 1H), 2.28 – 2.22 (m, 1H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 142.4, 139.5, 136.6, 132.9, 131.0, 130.3, 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.8, 127.1, 81.2, 72.3, 65.9, 43.0, 37.1, 28.1.

HRMS (ESI+) calcd. For $C_{30}H_{33}ClNO_3$ ([M+H]$^+$): 490.2143, found: 490.2146.

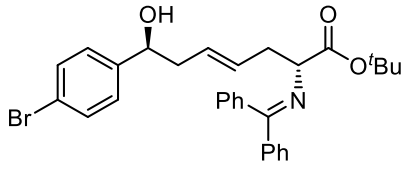
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3e





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.483	BV	0.6857	3619.99219	81.73204	25.0628
2	24.584	VV	0.7862	3358.27295	64.52159	23.2508
3	25.907	VB	0.8367	3323.45581	59.58376	23.0097
4	28.761	BB	0.9501	4141.96729	66.82352	28.6767

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.613	MF	0.3146	168.89313	8.94613	1.5754
2	24.335	FM	0.9385	1.03069e4	183.04245	96.1425
3	28.831	BB	0.8208	244.64882	4.21133	2.2821



(2*R*,7*S*,*E*)-**3f**

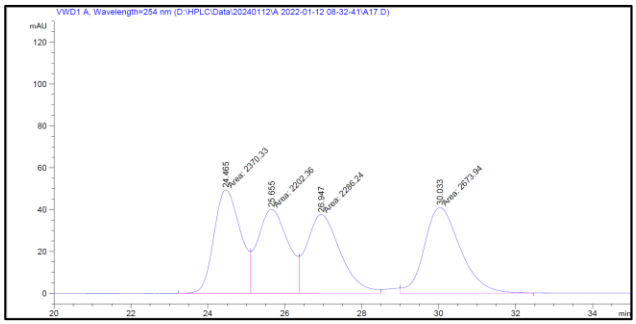
***tert*-butyl (2*R*,7*S*,*E*)-7-(4-bromophenyl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*S*,*E*)-3f)**: yield (98 mg, 92%); colorless oil; $[\alpha]^{15}_D$ = +9.4 (*c* 0.47, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 24.47, 25.66, 26.95 and 30.03 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.2 1H), 7.46 – 7.37 (m, 6H), 7.36 – 7.31 (m, 2H), 7.19 – 7.11 (m, 4H), 5.56 – 5.40 (m, 2H), 4.59 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.98 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.65 – 2.54 (m, 2H), 2.45 – 2.38 (m, 1H), 2.35 – 2.30 (m, 1H), 1.44 (s, 9H).

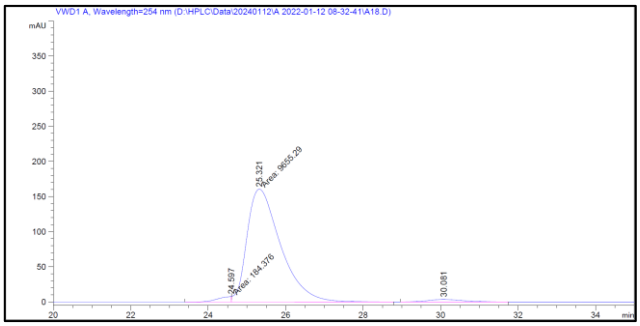
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.2, 142.9, 139.5, 136.5, 131.3, 131.0, 130.3, 128.8, 128.6, 128.5, 128.3, 128.0, 127.7, 127.5, 121.0, 81.2, 72.3, 65.9, 43.0, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{30}H_{33}BrNO_3$ ([M+H]$^+$): 534.1638, found: 534.1644.

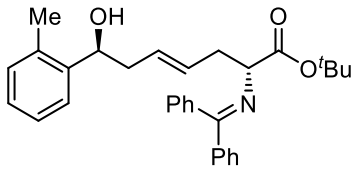
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3f



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.465	MF	0.7993	2370.32544	49.42738	24.8648
2	25.655	FM	0.9153	2202.36450	40.10333	23.1028
3	26.947	FM	1.0117	2286.24121	37.66394	23.9827
4	30.033	FM	1.0899	2673.94165	40.88910	28.0497



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.597	MF	0.3902	184.37611	7.87496	1.8353
2	25.321	FM	1.0022	9655.29395	160.57590	96.1114
3	30.081	BB	0.7977	206.27431	3.40067	2.0533



(2*R*,7*S*,*E*)-**3g**

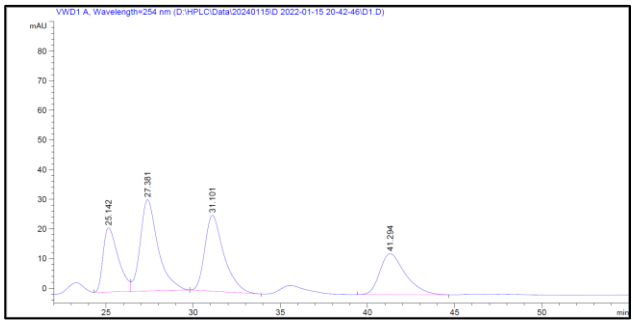
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(*o*-tolyl)hept-4-enoate ((2*R*,7*S*,*E*)-3g)**: yield (88 mg, 94%); colorless oil; $[\alpha]^{15}_{D}$ = +18.4 (*c* 0.48, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 19:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 25.14, 27.38, 31.10 and 41.29 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.62 (m, 2H), 7.47 – 7.41 (m, 4H), 7.39 – 7.30 (m, 3H), 7.20 – 7.11 (m, 4H), 7.09 – 7.05 (m, 1H), 5.56 – 5.47 (m, 2H), 4.84 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.00 (dd, *J* = 6.4, 6.0 Hz, 1H), 2.68 – 2.57 (m, 2H), 2.45 – 2.38 (m, 1H), 2.34 – 2.28 (m, 1H), 2.26 (s, 3H), 1.45 (s, 9H).

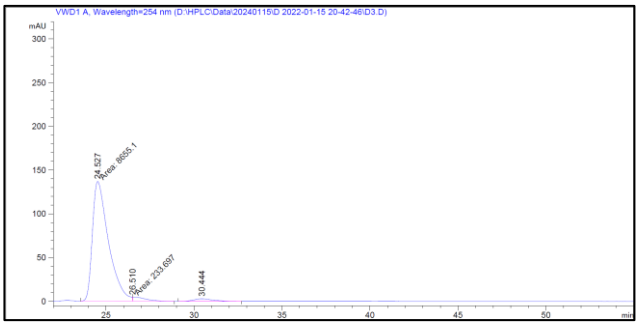
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.1, 142.0, 139.5, 136.6, 134.2, 130.34, 130.25, 130.2, 129.1, 128.8, 128.6, 128.4, 128.0, 127.8, 127.0, 126.2, 125.1, 81.1, 69.5, 65.9, 41.7, 37.1, 28.0, 19.0.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2691.

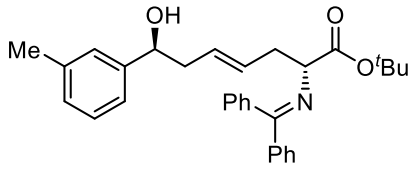
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3g



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.142	BV	0.9046	1314.24036	21.63872	19.1849
2	27.381	VB	1.0323	2185.32861	30.78133	31.9008
3	31.101	BB	1.1250	1943.81995	25.59508	28.3753
4	41.294	BB	1.4303	1406.99451	13.83712	20.5389



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.527	MF	1.0551	8655.09570	136.72385	95.2062
2	26.510	FM	0.8466	233.69702	4.60074	2.5707
3	30.444	BB	0.8716	202.10471	2.78842	2.2232



(2*R*,7*S*,*E*)-**3h**

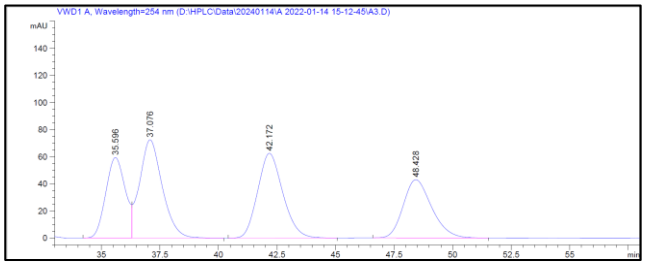
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(*m*-tolyl)hept-4-enoate ((2*R*,7*S*,*E*)-3h)**: yield (88 mg, 94%); colorless oil; $[\alpha]^{20}_D$ = +22.9 (*c* 0.62, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 19:1 dr, > 99% ee (Chiralpak IC + Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 0.75 mL/min, λ = 254 nm); t_r = 35.60, 37.08, 42.17 and 48.43 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.47 – 7.41 (m, 3H), 7.39 – 7.35 (m, 1H), 7.35 – 7.29 (m, 2H), 7.20 – 7.12 (m, 4H), 7.10 – 7.03 (m, 2H), 5.56 – 5.43 (m, 2H), 4.59 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.99 (dd, *J* = 7.0, 5.4 Hz, 1H), 2.66 – 2.54 (m, 2H), 2.47 – 2.41 (m, 1H), 2.40 – 2.34 (m, 1H), 2.33 (s, 3H), 1.44 (s, 9H).

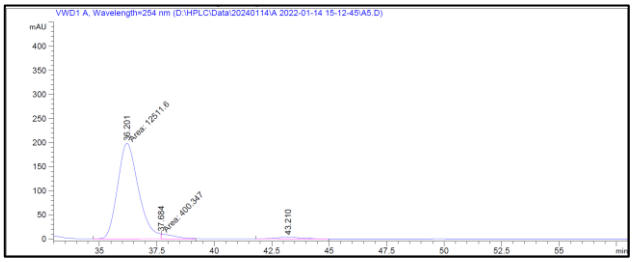
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.1, 143.9, 139.6, 137.9, 136.6, 130.4, 130.2, 128.9, 128.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 126.4, 122.8, 81.1, 73.1, 66.0, 43.0, 37.1, 28.0, 21.4.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2693.

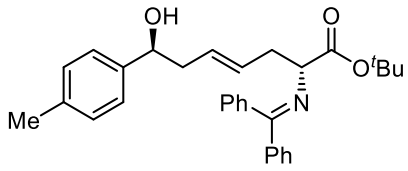
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3h



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.596	BV	0.8829	3422.52173	59.34138	20.6241
2	37.076	VB	0.9937	4889.97803	72.42786	29.4670
3	42.172	BB	1.1217	4668.31738	62.47826	28.1313
4	48.428	BB	1.2574	3613.95337	42.91986	21.7777



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.201	MF	1.0514	1.25116e4	198.32797	95.0704
2	37.684	FM	0.6492	400.34705	10.27870	3.0421
3	43.210	BB	0.9008	248.40707	3.33951	1.8875



(2*R*,7*S*,*E*)-**3i**

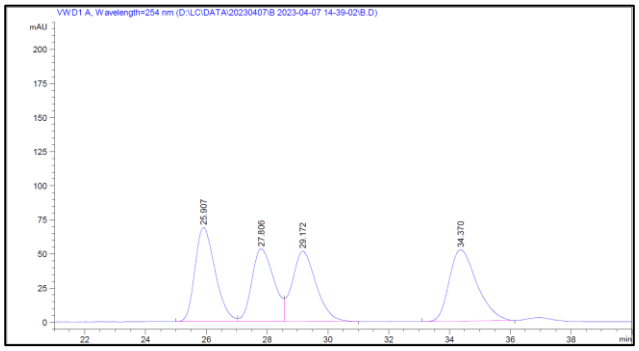
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(*p*-tolyl)hept-4-enoate ((2*R*,7*S*,*E*)-3i)**: yield (90 mg, 96%); colorless oil; $[\alpha]^{15}_{D}$ = +7.1 (*c* 0.70, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 17:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 25.91, 27.81, 29.17 and 34.37 min.

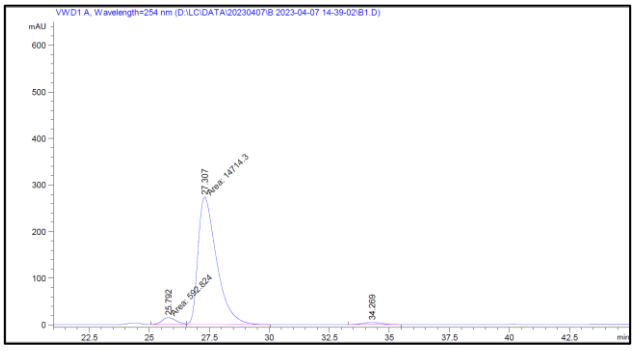
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.38 – 7.33 (m, 3H), 7.32 – 7.22 (m, 3H), 7.14 – 7.10 (m, 2H), 7.08 – 7.00 (m, 4H), 5.47 – 5.35 (m, 2H), 4.52 (dd, *J* = 8.2, 4.6 Hz, 1H), 3.90 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.58 – 2.46 (m, 2H), 2.39 – 2.32 (m, 1H), 2.32 – 2.27 (m, 1H), 2.24 (s, 3H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.1, 141.0, 139.6, 136.9, 136.6, 130.4, 130.2, 129.0, 128.9, 128.8, 128.5, 128.4, 128.0, 127.8, 125.7, 81.1, 73.0, 66.0, 42.9, 37.1, 28.0, 21.1.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2697.

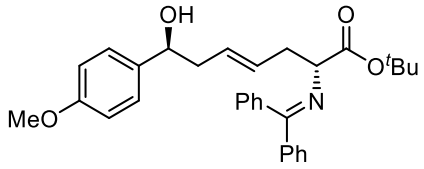
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3i





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.907	BV	0.6941	3178.03271	68.87778	26.5391
2	27.806	VV	0.7500	2674.96216	53.30546	22.3381
3	29.172	VV R	0.7896	2815.60278	51.59161	23.5125
4	34.370	BB	0.9142	3306.31348	52.36954	27.6103

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.792	MF	0.6774	592.82404	14.58477	3.8072
2	27.307	FM	0.8967	1.47143e4	273.47815	94.4974
3	34.269	BB	0.6827	263.98740	4.59955	1.6954



(2*R*,7*S*,*E*)-**3j**

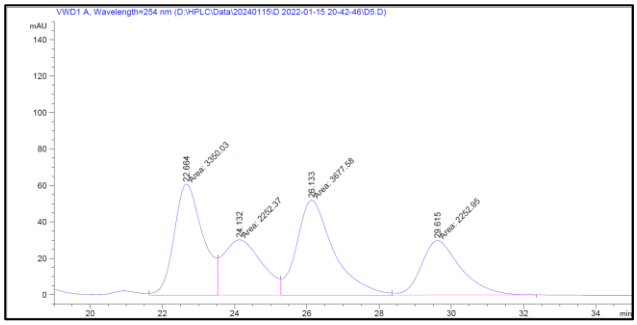
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(4-methoxyphenyl)hept-4-enoate ((2*R*,7*S*,*E*)-3j)**: yield (84 mg, 86%); colorless oil; $[\alpha]^{15}_{D}$ = +28.1 (*c* 0.51, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 19:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 22.66, 24.13, 26.13 and 29.62 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.46 – 7.41 (m, 3H), 7.40 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 7.24 – 7.20 (m, 2H), 7.17 – 7.10 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 5.54 – 5.42 (m, 2H), 4.58 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.98 (dd, *J* = 7.0, 5.4 Hz, 1H), 3.78 (s, 3H), 2.66 – 2.54 (m, 2H), 2.45 – 2.33 (m, 2H), 1.44 (s, 9H).

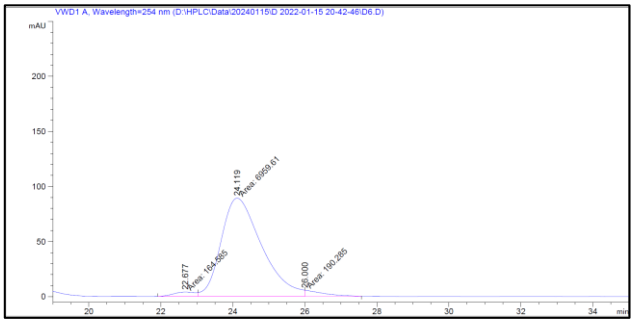
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.1, 158.9, 139.6, 136.6, 136.1, 130.4, 130.2, 128.9, 128.8, 128.6, 128.4, 128.0, 127.8, 127.0, 113.7, 81.1, 72.7, 66.0, 55.2, 42.9, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_4$ ($[M+H]^+$): 486.2639, found: 486.2641.

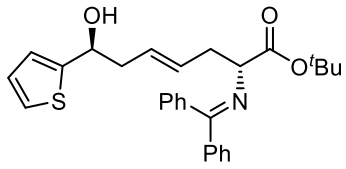
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3j



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.664	MF	0.9178	3350.02563	60.83315	29.0475
2	24.132	FM	1.2391	2252.37036	30.29615	19.5299
3	26.133	MF	1.1783	3677.58057	52.02008	31.8877
4	29.615	FM	1.2585	2252.94653	29.83608	19.5349



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.677	MF	0.7042	164.58478	3.89514	2.2501
2	24.119	MF	1.3014	6959.60693	89.13271	95.1484
3	26.000	FM	0.5723	190.28525	5.54150	2.6015



(2*R*,7*S*,*E*)-**3k**

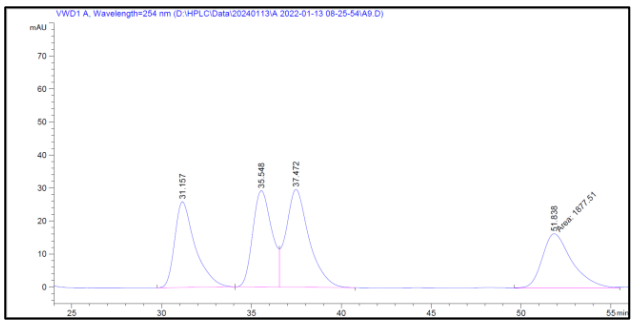
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(thiophen-2-yl)hept-4-enoate ((2*R*,7*S*,*E*)-3k)**: yield (81 mg, 88%); colorless oil; $[\alpha]^{15}_{D}$ = +45.4 (*c* 0.48, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 4:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 31.16, 35.55, 37.47 and 51.84 min.

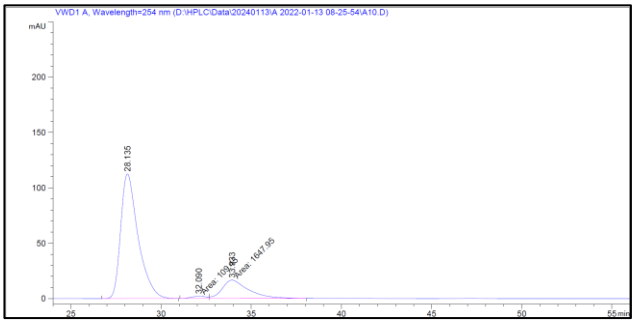
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 2H), 7.37 – 7.23 (m, 6H), 7.14 – 7.10 (m, 1H), 7.09 – 7.05 (m, 2H), 6.85 – 6.81 (m, 2H), 5.50 – 5.39 (m, 2H), 4.81 (dd, *J* = 7.6, 4.8 Hz, 1H), 3.91 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.55 – 2.49 (m, 2H), 2.48 – 2.39 (m, 2H), 1.36 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 147.9, 139.5, 136.6, 131.0, 130.3, 128.8, 128.6, 128.4, 128.1, 128.0, 127.8, 126.5, 124.3, 123.4, 81.4, 69.3, 65.9, 42.9, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{28}H_{32}NO_3S$ ($[M+H]^+$): 462.2097, found: 462.2100.

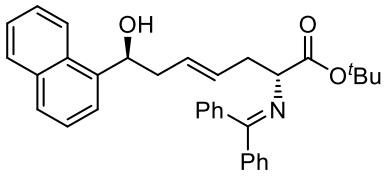
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3k





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.157	BB	1.1441	2053.90918	25.98606	23.5017
2	35.548	BV	1.1126	2153.87036	29.19880	24.6455
3	37.472	VB	1.2723	2654.13403	29.65247	30.3697
4	51.838	MF	1.9049	1877.50952	16.42696	21.4832

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.135	BB	1.0004	7548.41748	112.55023	81.1150
2	32.090	MF	0.9747	109.44960	1.87144	1.1761
3	33.933	FM	1.6682	1647.95313	16.46454	17.7088



(2*R*,7*S*,*E*)-**3l**

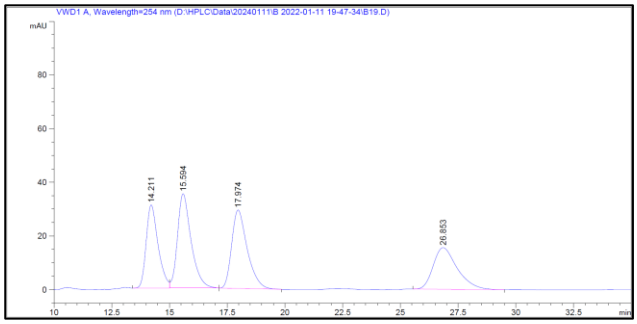
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(naphthalen-1-yl)hept-4-enoate ((2*R*,7*S*,*E*)-3l)**: yield (83 mg, 82%); colorless oil; $[\alpha]^{15}_{D}$ = +4.1 (*c* 0.51, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 17:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 14.21, 15.59, 17.97 and 26.85 min.

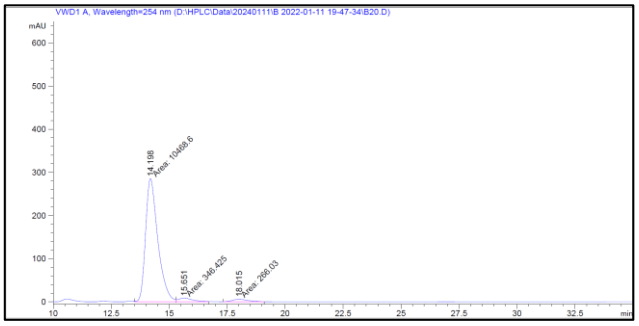
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.95 (m, 1H), 7.87 – 7.82 (m, 1H), 7.77 – 7.72 (m, 1H), 7.68 – 7.59 (m, 3H), 7.47 – 7.40 (m, 6H), 7.39 – 7.30 (m, 3H), 7.19 – 7.13 (m, 2H), 5.65 – 5.51 (m, 2H), 5.40 (dd, *J* = 8.8, 3.6 Hz, 1H), 4.02 (dd, *J* = 6.4, 6.4 Hz, 1H), 2.66 – 2.61 (m, 2H), 2.54 – 2.39 (m, 2H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 139.5, 139.4, 136.6, 133.7, 130.5, 130.3, 130.2, 129.2, 128.9, 128.8, 128.6, 128.5, 128.0, 127.8, 127.7, 125.9, 125.4, 125.4, 123.0, 122.8, 81.2, 69.9, 66.0, 42.0, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{34}H_{36}NO_3$ ($[M+H]^+$):506.2690, found: 506.2694.

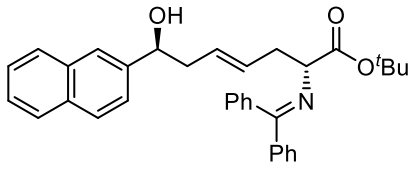
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3l





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.211	BV	0.5389	1112.84277	30.99708	22.0764
2	15.594	VB	0.6128	1443.15125	35.16558	28.6290
3	17.974	BB	0.7040	1367.06213	29.21193	27.1196
4	26.853	BB	1.0606	1117.81140	15.51426	22.1750

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.198	FM	0.6112	1.04686e4	285.47696	94.4729
2	15.651	MF	0.7044	346.42462	8.19645	3.1263
3	18.015	MF	0.7661	266.02963	5.78735	2.4008



(2*R*,7*S*,*E*)-**3m**

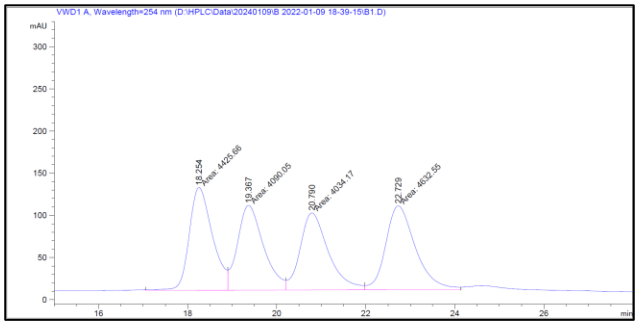
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(naphthalen-2-yl)hept-4-enoate ((2*R*,7*S*,*E*)-3m)**: yield (77 mg, 76%); colorless oil; $[\alpha]^{15}_{D}$ = +6.3 (*c* 0.53, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 13:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.25, 19.37, 20.79 and 22.73 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 4H), 7.67 – 7.62 (m, 2H), 7.46 – 7.37 (m, 7H), 7.35 – 7.30 (m, 2H), 7.16 – 7.11 (m, 2H), 5.59 – 5.46 (m, 2H), 4.80 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.99 (dd, *J* = 7.0, 5.4 Hz, 1H), 2.65 – 2.57 (m, 2H), 2.57 – 2.51 (m, 1H), 2.48 – 2.42 (m, 1H), 1.44 (s, 9H).

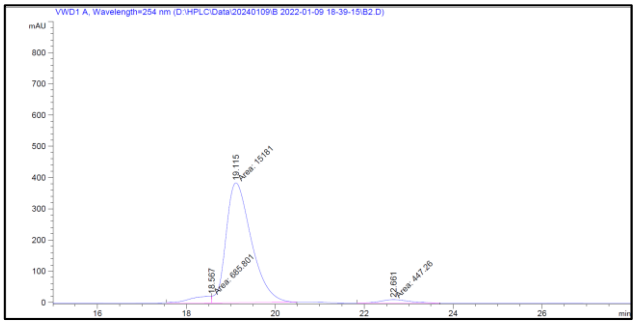
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 141.3, 139.5, 136.6, 133.2, 132.8, 130.7, 130.3, 128.8, 128.7, 128.6, 128.4, 128.0, 127.9, 127.8, 127.8, 127.6, 126.0, 125.7, 124.3, 124.1, 81.2, 73.1, 65.9, 42.9, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{34}H_{36}NO_3$ ($[M+H]^+$):506.2690, found: 506.2697.

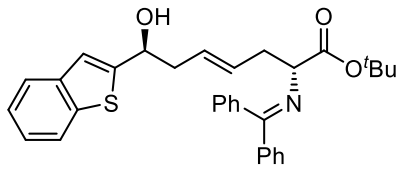
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3m



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.254	MF	0.6059	4425.66406	121.72798	25.7569
2	19.367	MF	0.6782	4090.05396	100.51357	23.8037
3	20.790	MF	0.7357	4034.16553	91.39146	23.4784
4	22.729	FM	0.7762	4632.55078	99.46693	26.9610



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.567	MF	0.5434	685.80139	21.03318	4.2037
2	19.115	MF	0.6598	1.51810e4	383.45770	93.0547
3	22.661	MF	0.7137	447.25961	10.44433	2.7416



(2*R*,7*S*,*E*)-**3n**

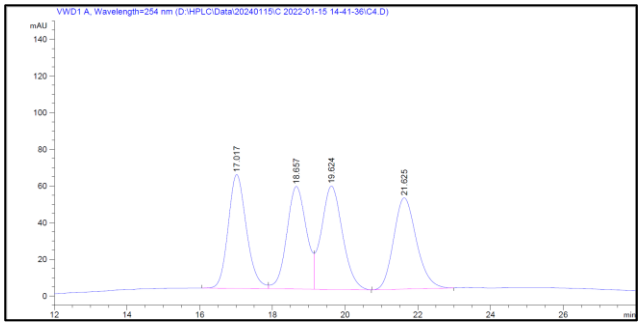
***tert*-butyl (2*R*,7*S*,*E*)-7-(benzo[*b*]thiophen-2-yl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*S*,*E*)-3n)**: yield (85 mg, 87%); colorless oil; $[\alpha]^{15}_{D}$ = +17.2 (*c* 0.50, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 6:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 17.02, 18.66, 19.62 and 21.63 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.68 (m, 1H), 7.60 – 7.54 (m, 3H), 7.36 – 7.29 (m, 4H), 7.27 – 7.19 (m, 4H), 7.07 – 7.02 (m, 3H), 5.55 – 5.40 (m, 2H), 4.87 (dd, *J* = 7.6, 4.4 Hz, 1H), 3.91 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.55 – 2.52 (m, 2H), 2.51 – 2.43 (m, 2H), 1.35 (s, 9H).

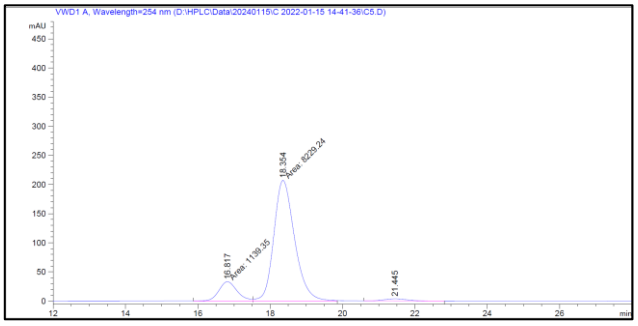
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 148.6, 139.5, 139.3, 136.6, 131.38, 131.35, 130.3, 128.8, 128.6, 128.5, 128.0, 127.8, 127.7, 124.2, 124.0, 123.4, 122.4, 119.9, 81.2, 69.7, 65.9, 42.5, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{32}H_{34}NO_3S$ ($[M+H]^+$): 512.2254, found: 512.2255.

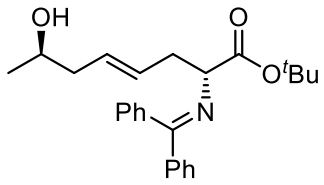
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3n



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.017	BV	0.5347	2170.81860	62.12012	24.8817
2	18.657	VV	0.5731	2095.96045	55.94752	24.0236
3	19.624	VB	0.6149	2289.83154	56.36955	26.2458
4	21.625	BB	0.6723	2167.96558	49.75972	24.8490



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.817	MF	0.5770	1139.34851	32.91150	11.9556
2	18.354	MF	0.6635	8229.24219	206.70213	86.3522
3	21.445	BB	0.6324	161.27008	3.75248	1.6923



(2*R*,7*R*,*E*)-**3o**

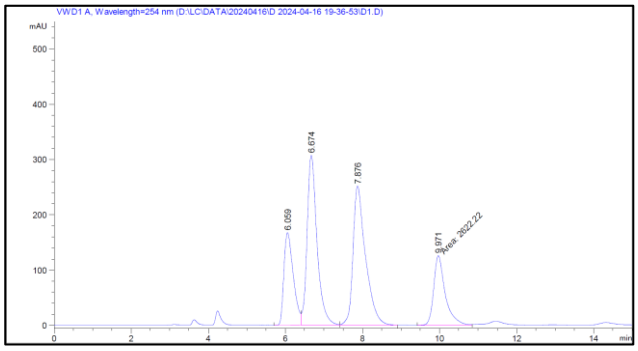
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxyoct-4-enoate ((2*R*,7*R*,*E*)-3o):** yield (62 mg, 79%); colorless oil; $[\alpha]^{25}_{D}$ = +78.0 (*c* 0.42, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 1.7:1 dr, 98% ee (Chiralpak AD-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 6.06, 6.67, 7.88 and 9.97 min.

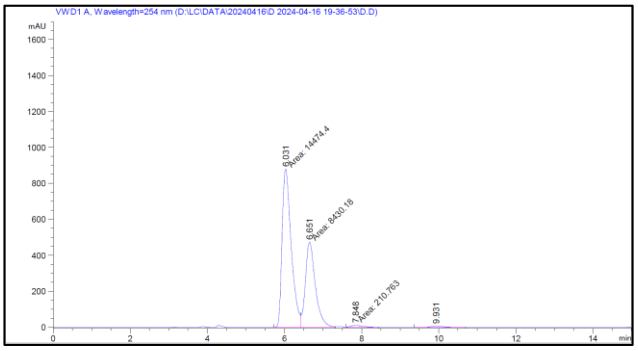
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.58 (m, 2H), 7.48 – 7.39 (m, 3H), 7.39 – 7.28 (m, 3H), 7.21 – 7.09 (d, *J* = 6.6 Hz, 2H), 5.53 – 5.37 (m, 2H), 4.05 – 3.92 (m, 1H), 3.82 – 3.65 (m, 1H), 2.70 – 2.51 (m, 2H), 2.22 – 2.11 (m, 1H), 2.11 – 2.00 (m, 1H), 1.442 (s, 2.83H, minor), 1.436 (s, 6.02H, major), 1.14 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.9, 170.11, 170.06, 139.59, 139.57, 136.6, 130.2, 130.1, 130.0, 129.1, 129.0, 128.7, 128.55, 128.52, 128.43, 128.41, 128.0, 127.81, 127.77, 81.1, 81.0, 67.0, 66.9, 66.0, 42.5, 37.1, 28.1, 22.6.

HRMS (ESI+) calcd. For $C_{25}H_{32}NO_3$ ($[M+H]^+$): 394.2377, found: 394.2378.

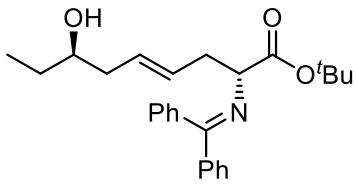
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3o





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.059	BV	0.2591	2837.15674	167.20161	17.0600
2	6.674	VV	0.2688	5511.17139	307.41818	33.1390
3	7.876	VB	0.3251	5659.89893	251.51981	34.0334
4	9.971	MF	0.3471	2622.21802	125.90105	15.7676

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.031	MF	0.2742	1.44744e4	879.72296	62.2570
2	6.651	FM	0.2967	8430.17676	473.49783	36.2596
3	7.848	FM	0.3423	210.76344	10.26361	0.9065
4	9.931	BB	0.3222	134.12590	6.09728	0.5769



(2*R*,7*R*,*E*)-**3p**

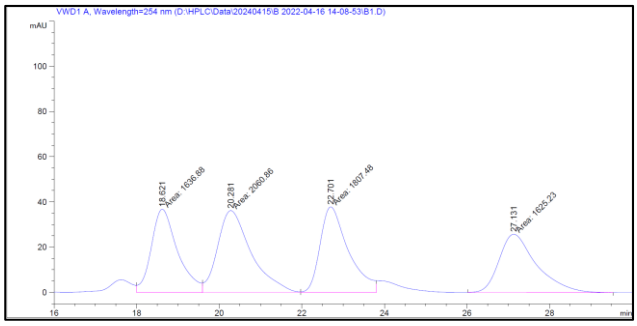
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxynon-4-enoate ((2*R*,7*R*,*E*)-3p)**: yield (57 mg, 70%); colorless oil; $[\alpha]^{25}_{D}$ = +57.0 (*c* 0.41, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 1:1 dr, 91% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.62, 20.28, 22.70 and 27.13 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.60 (m, 2H), 7.48 – 7.41 (m, 3H), 7.39 – 7.28 (m, 3H), 7.20 – 7.12 (m, 2H), 5.56 – 5.39 (m, 2H), 4.05 – 3.94 (m, 1H), 3.53 – 3.39 (m, 1H), 2.68 – 2.46 (m, 2H), 2.26 – 2.18 (m, 1H), 2.10 – 1.99 (m, 1H), 1.50 – 1.46 (m, 2H), 1.443 (s, 4.15H, minor), 1.437 (s, 5.08H, major), 0.93 – 0.86 (m, 3H).

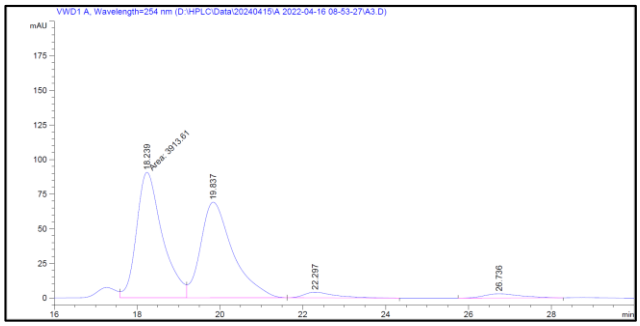
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.99, 170.96, 170.10, 170.05, 139.6, 136.6, 130.2, 129.9, 129.2, 129.0, 128.8, 128.5, 128.43, 128.41, 128.0, 127.82, 127.79, 81.07, 81.03, 72.1, 72.0, 66.1, 66.0, 40.3, 40.2, 37.2, 37.1, 29.4, 28.1, 10.0.

HRMS (ESI+) calcd. For $C_{26}H_{34}NO_3$ ($[M+H]^+$): 408.2533, found: 408.2534.

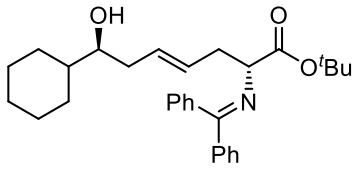
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3p



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.621	FM	0.7406	1636.87512	36.83912	22.9561
2	20.281	MF	0.9477	2060.85889	36.24128	28.9022
3	22.701	FM	0.7950	1807.48132	37.89495	25.3488
4	27.131	FM	1.0496	1625.23206	25.80704	22.7928



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.239	FM	0.7197	3913.60840	90.63604	48.7228
2	19.837	VB	0.8040	3721.80762	69.03400	46.3350
3	22.297	BB	0.7227	211.43172	4.12692	2.6322
4	26.736	BB	0.8473	185.54526	3.04313	2.3100



(2*R*,7*S*,*E*)-**3q**

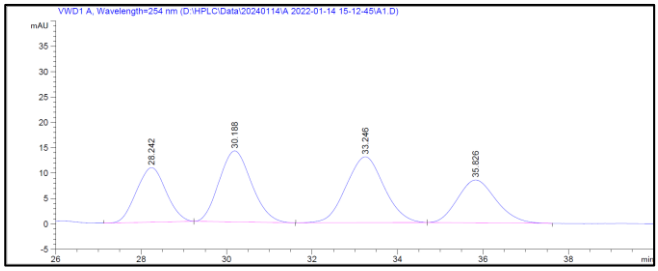
***tert*-butyl (2*R*,7*S*,*E*)-7-cyclohexyl-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*S*,*E*)-3q)**: yield (74 mg, 80%); colorless oil; $[\alpha]^{20}_D$ = +30.4 (*c* 0.56, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 6:1 dr, > 99% ee (Chiralpak IC + Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 0.75 mL/min, λ = 254 nm); t_r = 28.24, 30.19, 33.25 and 35.83 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.47 – 7.41 (m, 3H), 7.39 – 7.29 (m, 3H), 7.19 – 7.13 (m, 2H), 5.53 – 5.40 (m, 2H), 3.98 (dd, *J* = 6.8, 5.6 Hz, 1H), 3.33 – 3.23 (m, 1H), 2.67 – 2.54 (m, 2H), 2.26 – 2.19 (m, 1H), 2.08 – 1.98 (m, 1H), 1.84 – 1.61 (m, 7H), 1.44 (s, 9H), 1.20 – 1.14 (m, 2H), 1.07 – 0.95 (m, 2H).

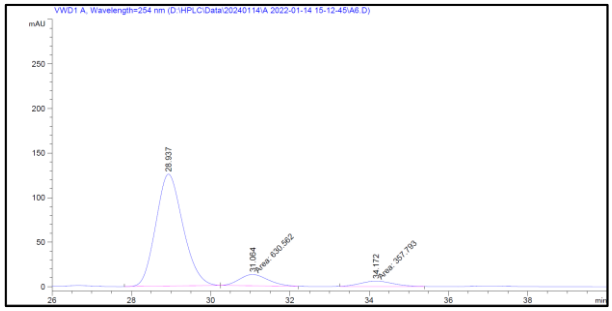
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.1, 139.6, 136.6, 130.2, 129.9, 129.7, 128.8, 128.5, 128.4, 128.0, 127.8, 81.1, 74.7, 66.0, 42.9, 37.5, 37.2, 29.1, 28.2, 28.1, 26.5, 26.2, 26.1.

HRMS (ESI+) calcd. For $C_{30}H_{40}NO_3$ ($[M+H]^+$): 462.3003, found: 462.3010.

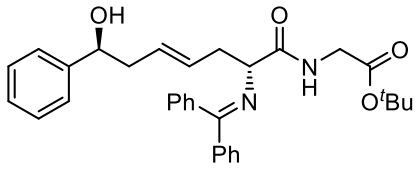
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3q



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.242	BB	0.7407	518.53638	10.75115	20.0971
2	30.188	BB	0.7958	736.80237	13.98249	28.5566
3	33.246	BB	0.9167	798.75641	12.96627	30.9578
4	35.826	BB	0.9223	526.05438	8.42655	20.3885



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.937	BB	0.7279	5970.22949	125.52958	85.7966
2	31.064	MF	0.8330	630.56183	12.61577	9.0616
3	34.172	FM	0.9700	357.79272	6.14756	5.1417



(2*R*,7*S*,*E*)-Gly-Gly-**3r**

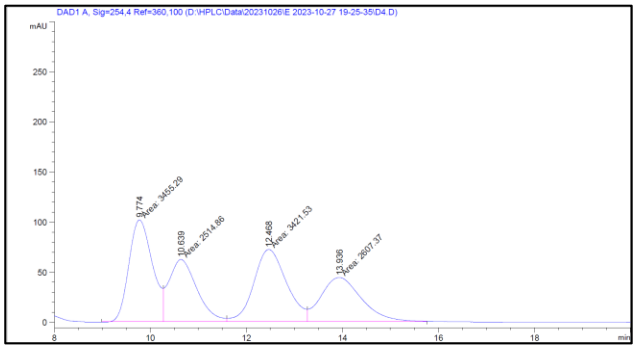
***tert*-butyl ((2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)glycinate ((2*R*,7*S*,*E*)-Gly-Gly-3r)**: yield (78 mg, 76%); colorless oil; $[\alpha]^{20}_{D}$ = -85.0 (*c* 0.62, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralcel OD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 9.77, 10.64, 12.47 and 13.94 min.

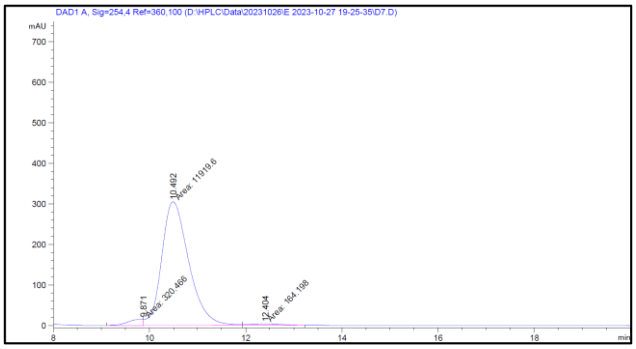
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.66 (m, 2H), 7.53 – 7.48 (m, 1H), 7.46 – 7.41 (m, 4H), 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 7.14 – 7.09 (m, 2H), 5.54 – 5.38 (m, 2H), 4.59 (dd, *J* = 9.0, 3.8 Hz, 1H), 4.11 – 4.03 (m, 2H), 3.92 (dd, *J* = 18.0, 5.2 Hz, 1H), 2.54 – 2.41 (m, 3H), 2.33 – 2.24 (m, 1H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 169.5, 168.8, 144.1, 139.1, 135.6, 130.7, 130.0, 129.3, 128.9, 128.73, 128.67, 128.2, 127.6, 127.1, 125.6, 82.0, 72.6, 65.8, 43.4, 41.6, 39.1, 28.0.

HRMS (ESI+) calcd. For $C_{32}H_{37}N_2O_4$ ($[M+H]^+$): 513.2748, found: 513.2749.

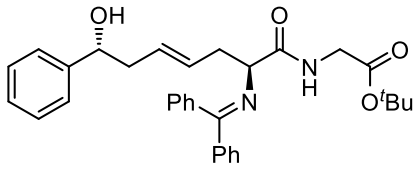
HPLC chromatogram of compound (2*R*,7*S*,*E*)-Gly-Gly-3r





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.774	MF	0.5676	3455.29468	101.46545	28.7964
2	10.639	FM	0.6758	2514.85864	62.02573	20.9588
3	12.468	FM	0.7920	3421.53467	72.00500	28.5150
4	13.936	FM	0.9849	2607.36938	44.12298	21.7298

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.871	MF	0.3590	320.46637	14.87823	2.5835
2	10.492	FM	0.6514	1.19196e4	304.97012	96.0928
3	12.404	FM	0.7856	164.19832	3.48343	1.3237

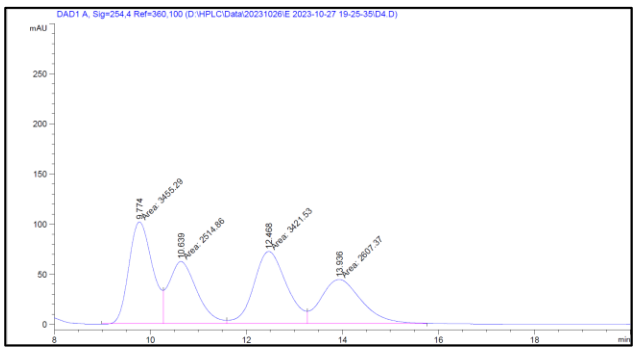


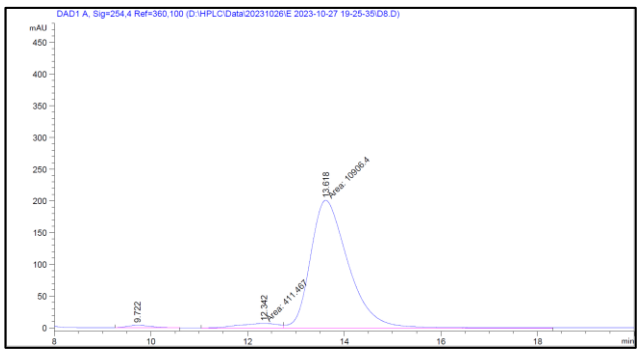
(2*S*,7*R*,*E*)-Gly-Gly-**3r**

***tert*-butyl ((2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)glycinate ((2*S*,7*R*,*E*)-Gly-Gly-3r)**: yield (79 mg, 77%); colorless oil; $[\alpha]^{20}_{D}$ = +86.1 (*c* 0.45, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralcel OD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 9.77, 10.64, 12.47 and 13.94 min.

HRMS (ESI+) calcd. For $C_{32}H_{37}N_2O_4$ ($[M+H]^+$): 513.2748, found: 513.2747.

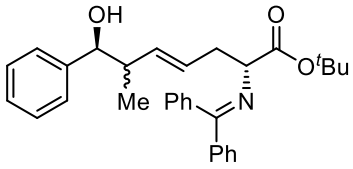
HPLC chromatogram of compound (2*S*,7*R*,*E*)-Gly-Gly-3r





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.774	MF	0.5676	3455.29468	101.46545	28.7964
2	10.639	FM	0.6758	2514.85864	62.02573	20.9588
3	12.468	FM	0.7920	3421.53467	72.00500	28.5150
4	13.936	FM	0.9849	2607.36938	44.12298	21.7298

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.722	BB	0.3939	128.06172	3.82186	1.1188
2	12.342	MF	0.9489	411.46701	7.22736	3.5949
3	13.618	FM	0.9027	1.09064e4	201.37543	95.2863



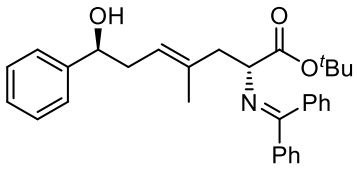
(2*R*,7*S*,*E*)-**3s**

***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-6-methyl-7-phenylhept-4-enoate ((2*R*,7*S*,*E*)-3s)**: yield (70 mg, 75%); colorless oil; $[\alpha]^{25}_D$ = +12.1 (*c* 0.42, CH_2Cl_2); The product was analyzed by ^{1}H NMR to determine the dr value: 1.3:1 dr.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.59 (m, 2H), 7.49 – 7.40 (m, 3H), 7.39 – 7.28 (m, 5H), 7.25 – 7.11 (m, 5H), 5.64 – 5.51 (m, 0.59H, minor), 5.49 – 5.35 (m, 1.42H, major), 4.56 (d, *J* = 5.2 Hz, 0.38H, minor), 4.22 (d, *J* = 8.4 Hz, 0.57H, major), 4.02 (dd, *J* = 7.2, 5.6 Hz, 0.58H, major), 3.96 (dd, *J* = 7.2, 5.6 Hz, 0.42H, minor), 2.67 – 2.52 (m, 2H), 2.46 – 2.28 (m, 1H), 1.45 (s, 4.52H, major), 1.44 (s, 4.02H, minor), 0.90 (d, *J* = 6.8 Hz, 1.29H), 0.77 (d, *J* = 6.8 Hz, 1.72H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.1, 170.0, 142.4, 142.3, 139.61, 139.57, 136.6, 135.3, 134.7, 130.3, 130.2, 129.1, 128.8, 128.6, 128.54, 128.51, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.54, 127.49, 127.1, 127.0, 126.4, 81.2, 81.1, 77.9, 76.9, 66.2, 65.9, 45.8, 43.7, 37.3, 37.1, 28.1, 16.8, 14.0.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2689.



(2*R*,7*S*,*E*)-**3t**

***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-4-methyl-7-phenylhept-4-enoate ((2*R*,7*S*,*E*)-3t)**: yield (67 mg, 71%); colorless oil; $[\alpha]^{25}_D$ = +54.4 (*c* 0.41, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee

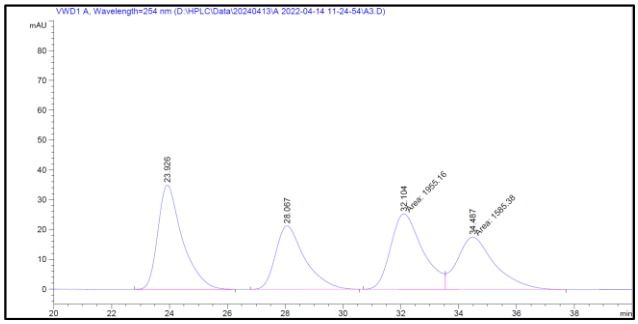
(Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 23.93, 28.07, 32.10 and 34.49 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.58 (m, 2H), 7.44 – 7.39 (m, 3H), 7.39 – 7.26 (m, 7H), 7.24 – 7.21 (m, 1H), 7.14 – 7.06 (m, 2H), 5.25 (dd, *J* = 7.6 , 7.6 Hz, 1H), 4.61 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.06 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.64 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.53 (dd, *J* = 13.2, 8.0 Hz, 1H), 2.47 – 2.33 (m, 2H), 1.45 (s, 9H), 1.40 (s, 3H).

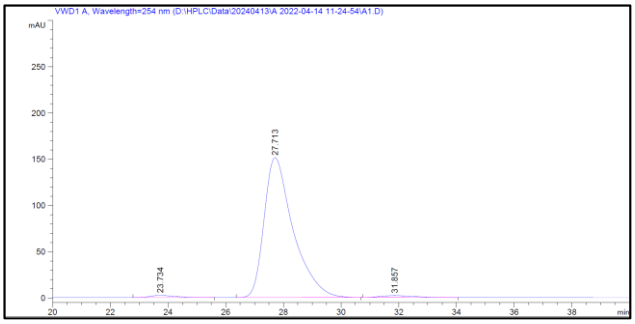
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 169.7, 144.1, 139.7, 136.4, 135.5, 130.2, 128.7, 128.5, 128.3, 128.3, 128.0, 127.9, 127.3, 125.7, 123.2, 81.1, 73.6, 64.9, 44.0, 38.4, 28.1, 16.5.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ([M+H]$^+$): 470.2690, found: 470.2691.

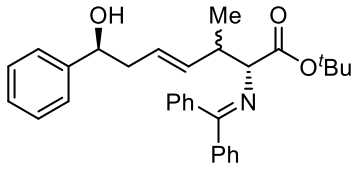
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3t



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.926	BB	0.8571	2047.70337	34.97396	28.9281
2	28.067	BB	1.0231	1490.34656	21.28062	21.0543
3	32.104	MF	1.2867	1955.16443	25.32477	27.6208
4	34.487	FM	1.5080	1585.38269	17.52140	22.3968



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.734	BB	0.7510	130.68596	2.28919	1.2109
2	27.713	BB	1.0329	1.05208e4	151.18086	97.4860
3	31.857	BB	0.8839	140.63211	1.88178	1.3031



(2*R*,7*S*,*E*)-**3u**

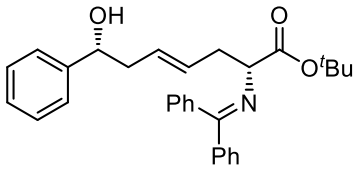
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-3-methyl-7-phenylhept-4-enoate ((2*R*,7*S*,*E*)-3u):** yield (62 mg, 66%); colorless oil; $[\alpha]^{25}_D$ = +34.6 (*c* 0.46, CH_2Cl_2); The product was analyzed by ^{1}H NMR to determine the dr value: 2.5:1 dr.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.60 (m, 2H), 7.45 – 7.39 (m, 3H), 7.39 – 7.27 (m, 7H), 7.25 – 7.23 (m, 1H), 7.16 – 7.07 (m, 2H), 5.84 – 5.72 (m, 0.67H, minor), 5.60 – 5.39 (m, 1.30H, major), 4.68 (dd, *J* = 8.4, 4.0 Hz, 0.66H, major), 4.61 (dd, *J* = 8.8, 4.0 Hz, 0.31H, minor), 3.83 (d, *J* = 5.2 Hz, 0.64H, major), 3.79 (d, *J* = 6.8 Hz, 0.29H, minor), 2.95 – 2.77 (m, 1H), 2.63 – 2.45 (m, 1H), 2.45 – 2.17 (m, 2H), 1.44 (s, 2.31H, minor), 1.43 (s, 6.68H, major), 1.05 (d, *J* = 6.8 Hz, 0.82H, minor),

0.98 (d, J = 6.8 Hz, 2.13H, major).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.7, 170.4, 170.1, 144.1, 144.0, 139.6, 137.1, 136.8, 136.6, 130.2, 128.8, 128.51, 128.46, 128.42, 128.40, 128.3, 128.0, 127.8, 127.2, 126.3, 126.2, 125.8, 125.7, 81.1, 81.0, 73.0, 72.9, 71.0, 70.8, 43.2, 42.9, 41.2, 40.8, 28.1, 17.4, 16.7.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ([M+H]$^+$): 470.2690, found: 470.2696.



(2*R*,7*R*,*E*)-**3a**

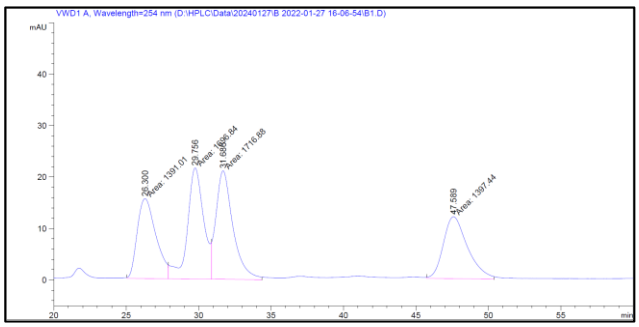
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoate ((2*R*,7*R*,*E*)-3a)**: yield (87 mg, 96%); colorless oil; $[\alpha]^{20}_D$ = +78.7 (*c* 0.57, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 26.30, 29.76, 31.69 and 47.59 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, J = 7.6 Hz, 2H), 7.46 – 7.29 (m, 10H), 7.25 – 7.22 (m, 1H), 7.19 – 7.13 (m, 2H), 5.59 – 5.43 (m, 2H), 4.63 (dd, J = 8.2, 4.6 Hz, 1H), 4.00 (t, J = 6.4 Hz, 1H), 2.66 – 2.55 (m, 2H), 2.48 – 2.35 (m, 2H), 1.43 (s, 9H).

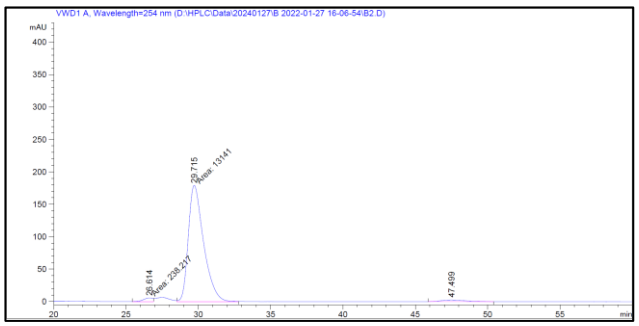
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.1, 143.9, 139.6, 136.6, 130.7, 130.2, 128.8, 128.5, 128.4, 128.3, 128.0, 127.8, 127.3, 125.7, 81.1, 73.1, 66.0, 42.9, 37.0, 28.0.

HRMS (ESI+) calcd. For $C_{30}H_{34}NO_3$ ([M+H]$^+$): 456.2533, found: 456.2540.

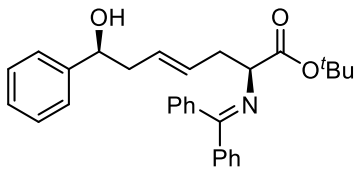
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.300	MF	1.4934	1391.01367	15.52366	22.4279
2	29.756	MF	1.3096	1696.83582	21.59413	27.3588
3	31.686	FM	1.3572	1716.87903	21.08306	27.6819
4	47.589	MM	1.9347	1397.43835	12.03840	22.5315



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.614	MF	0.7280	238.21719	5.45374	1.7430
2	29.715	FM	1.2220	1.31410e4	179.22752	96.1510
3	47.499	BB	1.3212	287.82278	2.59463	2.1060

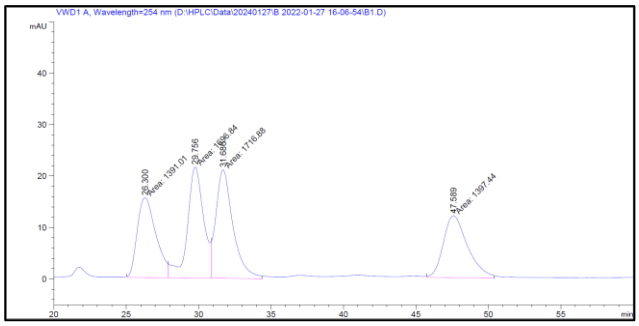


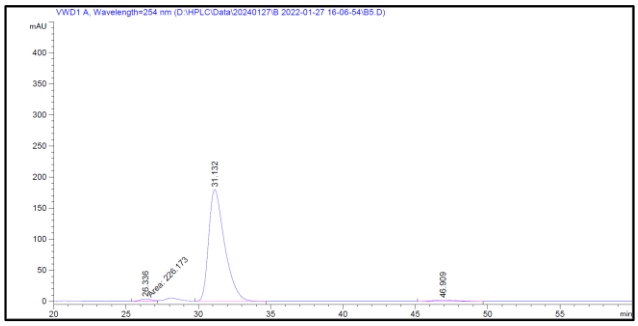
(2*S*,7*S*,*E*)-**3a**

***tert*-butyl (2*S*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoate ((2*S*,7*S*,*E*)-3a)**: yield (86 mg, 96%); colorless oil; $[\alpha]^{20}_{D}$ = -77.6 (*c* 0.57, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 26.30, 29.76, 31.69 and 47.59 min.

HRMS (ESI+) calcd. For $C_{30}H_{34}NO_3$ ($[M+H]^+$): 456.2533, found: 456.2537.

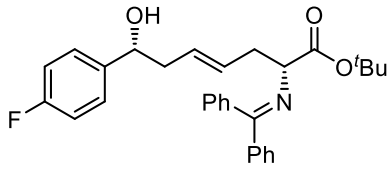
HPLC chromatogram of compound (2*S*,7*S*,*E*)-3a





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.300	MF	1.4934	1391.01367	15.52366	22.4279
2	29.756	MF	1.3096	1696.83582	21.59413	27.3588
3	31.686	FM	1.3572	1716.87903	21.08306	27.6819
4	47.589	MM	1.9347	1397.43835	12.03840	22.5315

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.336	MF	0.9886	226.17250	3.81289	1.5918
2	31.132	BB	1.1521	1.37537e4	179.87622	96.7981
3	46.909	BB	1.3099	228.77431	2.04857	1.6101



(2*R*,7*R*,*E*)-**3b**

***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-(4-fluorophenyl)-7-hydroxyhept-4-enoate ((2*R*,7*R*,*E*)-3b)**: yield (77 mg, 81%); colorless oil; $[\alpha]^{15}_{D}$ = +87.1 (*c* 0.52, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 12:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.31, 20.12,

22.05 and 30.93 min.

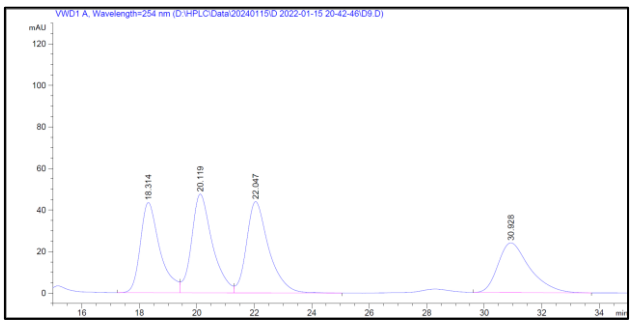
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.60 (m, 2H), 7.45 – 7.30 (m, 6H), 7.28 – 7.25 (m, 2H), 7.17 – 7.13 (m, 2H), 7.00 – 6.94 (m, 2H), 5.60 – 5.40 (m, 2H), 4.61 (dd, *J* = 7.8, 4.6 Hz, 1H), 4.00 (t, *J* = 6.2 Hz, 1H), 2.65 – 2.53 (m, 2H), 2.46 – 2.31 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.2, 162.0 (d, *J* = 245.7 Hz), 139.6 (d, *J* = 2.9 Hz), 139.6, 136.6, 130.9, 130.3, 128.8, 128.5, 128.4, 128.2, 128.0, 127.8, 127.4 (d, *J* = 8.0 Hz), 115.1 (d, *J* = 21.2 Hz), 81.1, 77.2, 72.5, 65.9, 42.9, 37.0, 28.1.

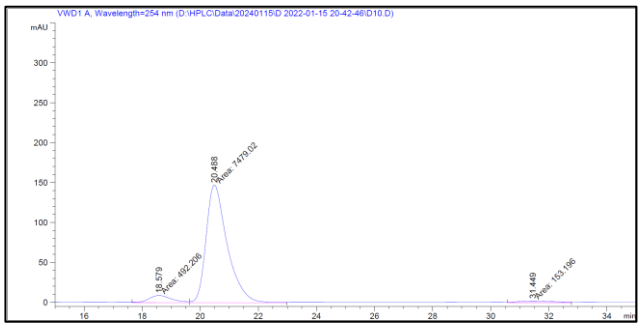
^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.42 – -115.64 (m).

HRMS (ESI+) calcd. For $C_{30}H_{33}FNO_3$ ([M+H]$^+$): 474.2439, found: 474.2432.

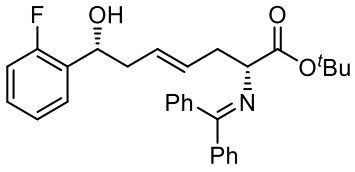
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.314	BV	0.7014	2052.49683	43.42568	23.7587
2	20.119	VV	0.7415	2388.60449	47.51143	27.6493
3	22.047	VB	0.7982	2367.23413	43.96163	27.4019
4	30.928	BB	1.1339	1830.59253	23.94411	21.1900



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.579	MF	0.9187	492.20605	8.92935	6.0583
2	20.488	FM	0.8453	7479.02393	147.46727	92.0560
3	31.449	MM	1.3189	153.19603	1.93593	1.8856



(2*R*,7*R*,*E*)-**3c**

***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-(2-fluorophenyl)-7-hydroxyhept-4-enoate ((2*R*,7*R*,*E*)-3c)**: yield (76 mg, 80%); colorless oil; $[\alpha]^{15}_{D}$ = +86.9 (*c* 0.53, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 11:1 dr, 99% ee (Chiralpak IF + Chiralpak IF, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.77, 19.68, 20.47 and 22.37 min.

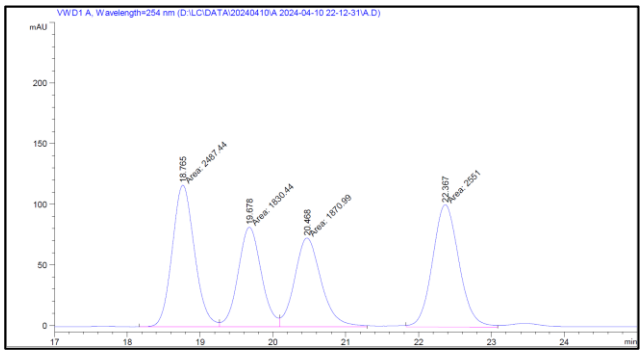
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.62 (m, 2H), 7.45 – 7.36 (m, 5H), 7.35 – 7.30 (m, 2H), 7.23 – 7.19 (m, 1H), 7.18 – 7.15 (m, 2H), 7.10 – 7.05 (m, 1H), 7.01 – 6.95 (m, 1H), 5.60 – 5.45 (m, 2H), 4.96 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.00 (dd, *J* = 7.0, 5.4 Hz, 1H), 2.62 – 2.47 (m, 3H), 2.39 – 2.32 (m, 1H), 1.44 (s, 9H).

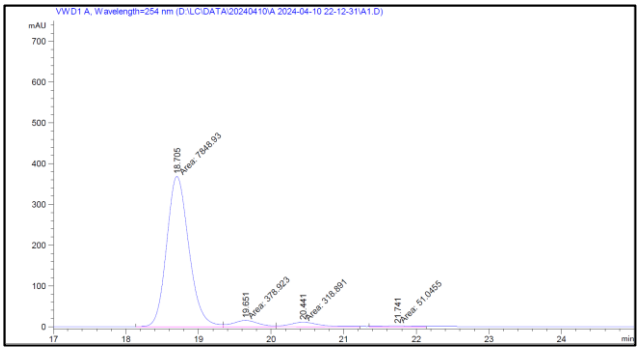
^{13}C NMR (101 MHz, Chloroform-*d*) 171.0, 170.1, 159.6 (d, *J* = 246.4 Hz), 139.6, 136.6, 131.0, 130.2, 128.8, 128.6, 128.5, 128.4, 128.2, 128.0, 127.8, 127.2 (d, *J* = 4.4 Hz), 124.1 (d, *J* = 3.5 Hz), 115.1 (d, *J* = 21.9 Hz), 81.1, 67.0 (d, *J* = 2.5 Hz), 66.0, 41.5, 37.0, 28.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.69 – -119.81 (m).

HRMS (ESI+) calcd. For $C_{30}H_{33}FNO_3$ ([M+H]$^+$): 474.2439, found: 474.2437.

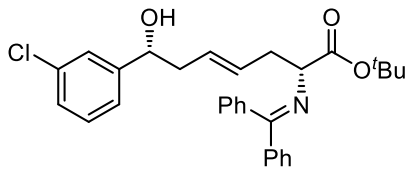
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3c





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.765	MF	0.3547	2487.43530	116.87381	28.4608
2	19.678	MF	0.3709	1830.43713	82.25761	20.9436
3	20.468	MF	0.4250	1870.98657	73.37386	21.4075
4	22.367	FM	0.4213	2550.99854	100.91523	29.1881

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.705	MF	0.3545	7848.92578	368.96945	91.2901
2	19.651	MF	0.4049	378.92328	15.59919	4.4072
3	20.441	FM	0.4698	318.89145	11.31284	3.7090
4	21.741	FM	0.4322	51.04554	1.96861	0.5937



(2*R*,7*R*,*E*)-**3d**

***tert*-butyl (2*R*,7*R*,*E*)-7-(3-chlorophenyl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate((2*R*,7*R*,*E*)-3d)**: yield (95 mg, 97%); colorless oil; $[\alpha]^{15}_D$ = +73.0 (*c* 0.57, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 17:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.04, 22.19,

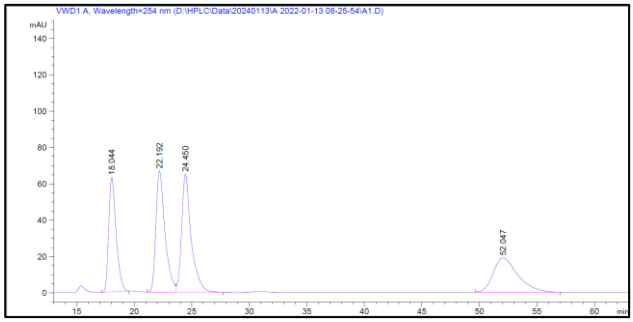
24.45 and 52.05 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.46 – 7.30 (m, 7H), 7.23 – 7.13 (m, 5H), 5.62 – 5.40 (m, 2H), 4.60 (dd, *J* = 8.2, 4.2 Hz, 1H), 4.01 (t, *J* = 6.0 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.48 – 2.41 (m, 1H), 2.34 – 2.30 (m, 1H), 1.43 (s, 9H).

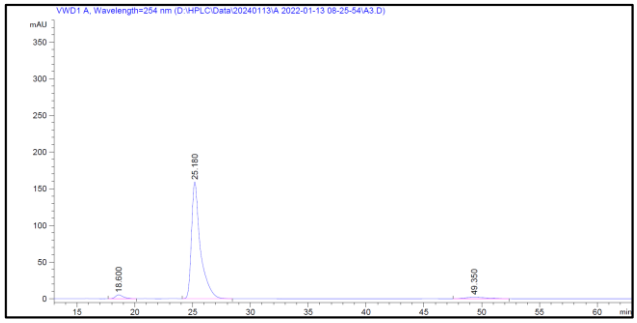
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.2, 146.1, 139.5, 136.6, 134.2, 131.3, 130.3, 129.5, 128.8, 128.6, 128.4, 128.0, 127.8, 127.4, 125.9, 123.9, 81.1, 72.3, 65.9, 42.8, 37.0, 28.1.

HRMS (ESI+) calcd. For $C_{30}H_{33}ClNO_3$ ([M+H]$^+$): 490.2143, found: 490.2147.

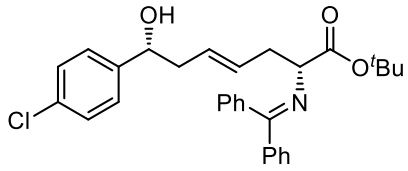
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.044	BB	0.6686	2799.91260	62.98667	21.5644
2	22.192	BV	0.8148	3652.05640	66.69958	28.1275
3	24.450	VB	0.8407	3734.44385	64.96114	28.7620
4	52.047	BB	1.8575	2797.53638	18.81717	21.5461



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.600	BB	0.6752	242.17767	5.25941	2.7063
2	25.180	BB	0.7705	8464.11133	158.89493	94.5857
3	49.350	BB	1.3725	242.32547	2.08561	2.7080



(2*R*,7*R*,*E*)-**3e**

***tert*-butyl (2*R*,7*R*,*E*)-7-(4-chlorophenyl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*R*,*E*)-3e)**: yield (91 mg, 93%); colorless oil; $[\alpha]^{15}_D$ = +82.8 (*c* 0.53, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 12:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 23.48, 24.58, 25.91 and 28.76 min.

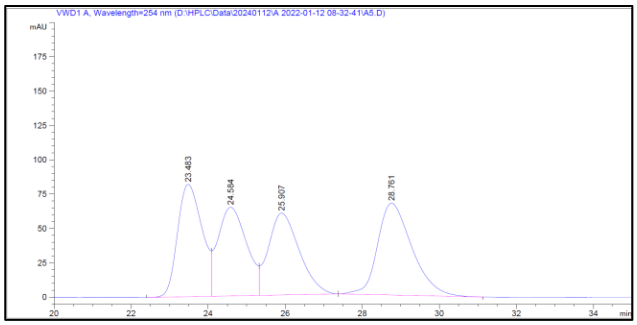
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.46 – 7.41 (m, 3H), 7.41 – 7.36 (m, 1H), 7.41 – 7.36 (m, 2H), 7.26 – 7.21 (m, 4H), 7.18 – 7.12 (m, 2H), 5.60 – 5.39 (m, 2H), 4.61 (dd, *J* = 8.0,

4.4 Hz, 1H), 4.00 (t, *J* = 6.2 Hz, 1H), 2.63 – 2.54 (m, 2H), 2.46 – 2.39 (m, 1H), 2.36 – 2.31 (m, 1H), 1.43 (s, 9H).

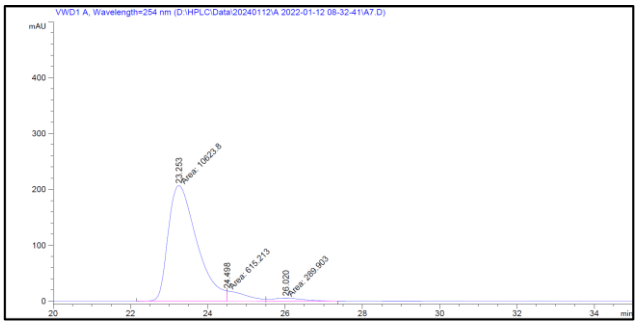
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.2, 142.4, 139.5, 136.6, 132.8, 131.1, 130.3, 128.8, 128.6, 128.43, 128.38, 128.0, 127.8, 127.1, 81.1, 72.3, 65.9, 42.8, 37.0, 28.0.

HRMS (ESI+) calcd. For $C_{30}H_{33}ClNO_3$ ([M+H]$^+$): 490.2143, found: 490.2140.

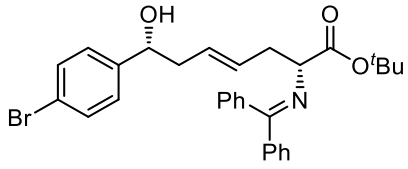
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3e



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.483	BV	0.6857	3619.99219	81.73204	25.0628
2	24.584	VV	0.7862	3358.27295	64.52159	23.2508
3	25.907	VB	0.8367	3323.45581	59.58376	23.0097
4	28.761	BB	0.9501	4141.96729	66.82352	28.6767



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.253	MF	0.8573	1.06238e4	206.54178	92.1492
2	24.498	MF	0.4165	615.21277	18.35585	5.3363
3	26.020	FM	0.9477	289.90277	5.09849	2.5146



(2*R*,7*R*,*E*)-**3f**

***tert*-butyl (2*R*,7*R*,*E*)-7-(4-bromophenyl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*R*,*E*)-3f)**: yield (100 mg, 94%); colorless oil; $[\alpha]^{15}_D$ = +85.0 (*c* 0.44, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 12:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 24.47, 25.66, 26.95 and 30.03 min.

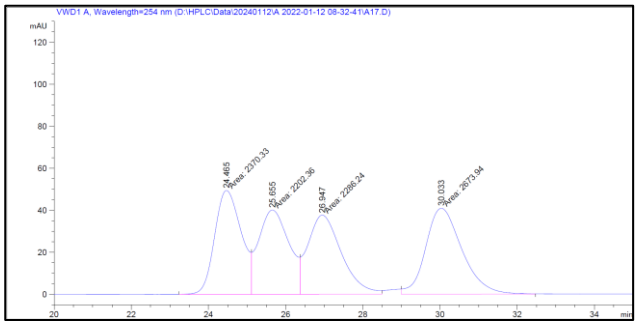
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.46 – 7.31 (m, 8H), 7.20 – 7.11 (m, 4H), 5.60 – 5.38 (m, 2H), 4.59 (dd, *J* = 7.8, 4.6 Hz, 1H), 4.00 (t, *J* = 6.2 Hz, 1H), 2.64 –2.52 (m, 2H), 2.46 –2.39 (m, 1H), 2.37 –2.31 (m, 1H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.2, 142.9, 139.5, 136.6, 131.3, 131.1, 130.3, 128.8,

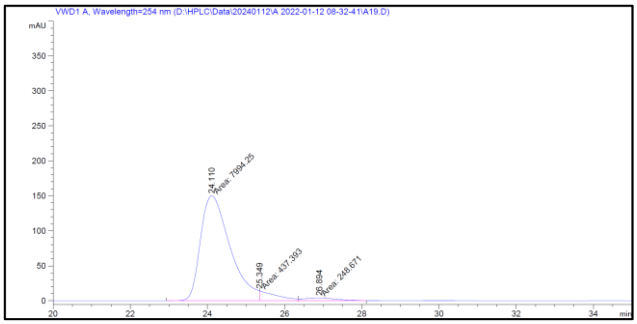
128.6, 128.4, 128.02, 127.99, 127.8, 127.5, 121.0, 81.1, 72.4, 65.9, 42.8, 37.0, 28.0.

HRMS (ESI+) calcd. For $C_{30}H_{33}BrNO_3$ ($[M+H]^+$): 534.1638, found: 534.1633.

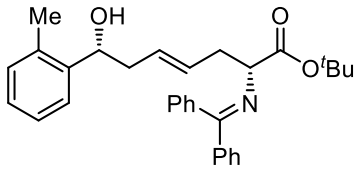
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3f



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.465	MF	0.7993	2370.32544	49.42738	24.8648
2	25.655	FM	0.9153	2202.36450	40.10333	23.1028
3	26.947	FM	1.0117	2286.24121	37.66394	23.9827
4	30.033	FM	1.0899	2673.94165	40.88910	28.0497



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.110	MF	0.8874	7994.24707	150.14470	92.0963
2	25.349	MF	0.3982	437.39340	14.20834	5.0389
3	26.894	FM	1.0130	248.67134	4.09144	2.8648



(2*R*,7*R*,*E*)-**3g**

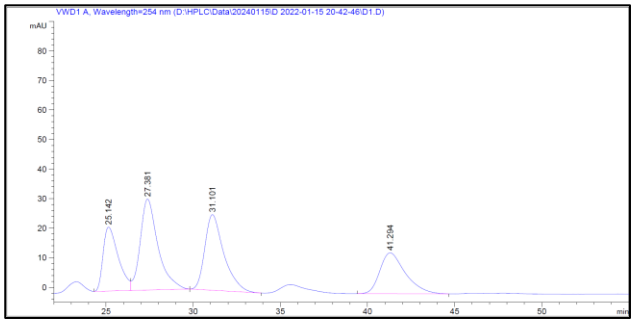
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(*o*-tolyl)hept-4-enoate ((2*R*,7*R*,*E*)-3g)**: yield (70 mg, 75%); colorless oil; $[\alpha]^{15}_D$ = +85.5 (*c* 0.48, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 17:1 dr, 98% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 25.14, 27.38, 31.10 and 41.29 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 2H), 7.45 – 7.40 (m, 4H), 7.39 – 7.30 (m, 3H), 7.21 – 7.13 (m, 4H), 7.12 – 7.09 (m, 1H), 5.60 – 5.48 (m, 2H), 4.85 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.01 (dd, *J* = 7.4, 5.4 Hz, 1H), 2.67 – 2.56 (m, 2H), 2.45 – 2.39 (m, 1H), 2.35 – 2.30 (m, 1H), 2.28 (s, 3H), 1.44 (s, 9H).

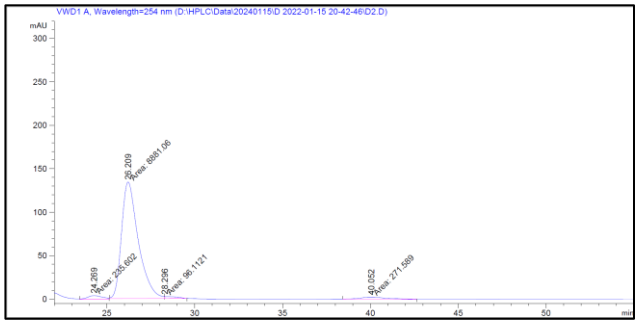
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.1, 142.0, 139.6, 136.6, 134.2, 130.5, 130.2, 128.9, 128.8, 128.5, 128.4, 128.0, 127.8, 127.0, 126.2, 125.1, 81.1, 69.6, 66.0, 41.5, 37.1, 28.1, 19.0.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2694.

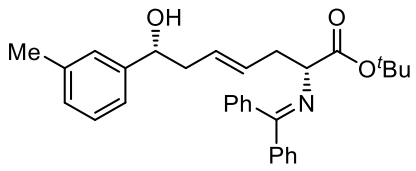
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3g



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.142	BV	0.9046	1314.24036	21.63872	19.1849
2	27.381	VB	1.0323	2185.32861	30.78133	31.9008
3	31.101	BB	1.1250	1943.81995	25.59508	28.3753
4	41.294	BB	1.4303	1406.99451	13.83712	20.5389



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.269	MM	0.9643	235.60226	4.07226	2.4841
2	26.209	MF	1.1042	8881.05566	134.05222	93.6390
3	28.296	FM	0.7892	96.11207	2.02963	1.0134
4	40.052	MM	1.9306	271.58871	2.34461	2.8635



(2*R*,7*R*,*E*)-**3h**

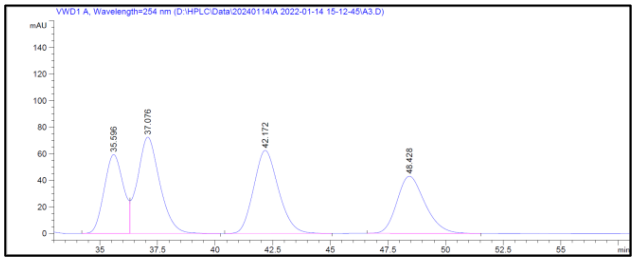
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(*m*-tolyl)hept-4-enoate ((2*R*,7*R*,*E*)-3h)**: yield (75 mg, 80%); colorless oil; $[\alpha]^{15}_{D}$ = +86.7 (*c* 0.50, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 19:1 dr, > 99% ee (Chiralpak IC + Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 0.75 mL/min, λ = 254 nm); t_r = 35.60, 37.08, 42.17 and 48.43 min.

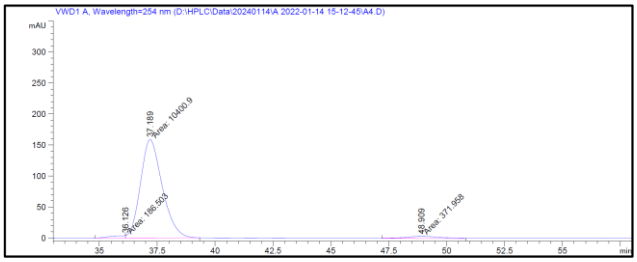
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.46 – 7.40 (m, 3H), 7.39 – 7.30 (m, 3H), 7.21 – 7.13 (m, 4H), 7.10 – 7.04 (m, 2H), 5.58 – 5.43 (m, 2H), 4.59 (dd, *J* = 8.2, 4.6 Hz, 1H), 4.00 (dd, *J* = 7.2, 5.6 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.49 – 2.36 (m, 2H), 2.33 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.1, 143.9, 139.6, 137.9, 136.6, 130.5, 130.2, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 126.4, 122.8, 81.0, 73.2, 66.0, 42.8, 37.0, 28.1, 21.4.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2696.

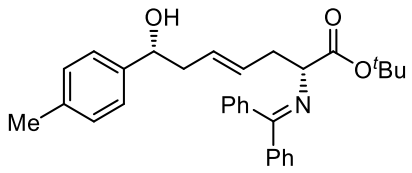
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3h





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.596	BV	0.8829	3422.52173	59.34138	20.6241
2	37.076	VB	0.9937	4889.97803	72.42786	29.4670
3	42.172	BB	1.1217	4668.31738	62.47826	28.1313
4	48.428	BB	1.2574	3613.95337	42.91986	21.7777

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.126	FM	0.7375	186.50298	4.21450	1.7018
2	37.189	FM	1.0929	1.04009e4	158.61198	94.9043
3	48.909	MF	1.7696	371.95813	3.50319	3.3940



(2*R*,7*R*,*E*)-**3i**

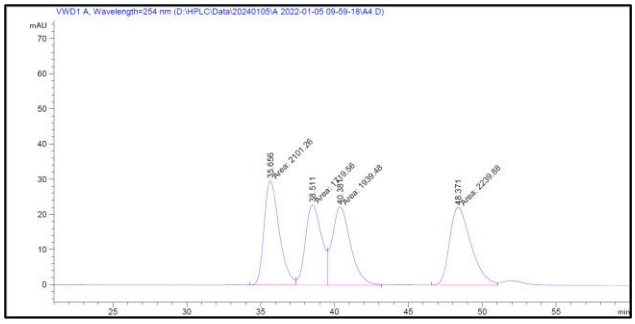
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(*p*-tolyl)hept-4-enoate ((2*R*,7*R*,*E*)-3i)**: yield (83 mg, 88%); colorless oil; $[\alpha]^{15}_{D}$ = +77.6 (*c* 0.52, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 12:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 35.66, 38.51, 40.38 and 48.37 min.

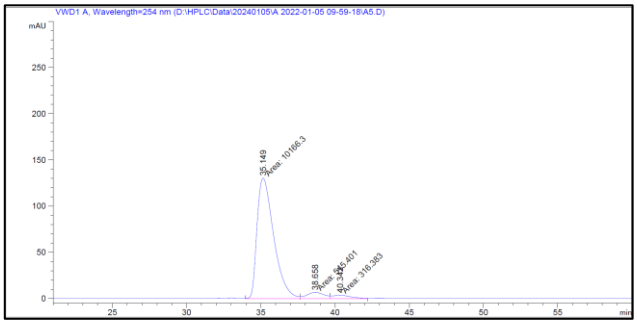
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.45 – 7.40 (m, 3H), 7.39 – 7.30 (m, 3H), 7.20 – 7.13 (m, 4H), 7.12 – 7.09 (m, 2H), 5.57 – 5.42 (m, 2H), 4.59 (dd, *J* = 7.8, 5.0 Hz, 1H), 3.99 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.65 – 2.55 (m, 2H), 2.45 – 2.35 (m, 2H), 2.32 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.1, 141.0, 139.6, 136.9, 136.7, 130.4, 130.2, 129.0, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 125.7, 81.0, 73.1, 66.0, 42.8, 37.0, 28.0, 21.0.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2688.

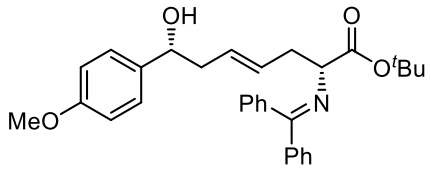
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3i





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.656	MF	1.1812	2101.25537	29.64985	26.2651
2	38.511	MF	1.2568	1719.55811	22.80326	21.4940
3	40.381	FM	1.4531	1939.48169	22.24508	24.2430
4	48.371	MF	1.6876	2239.87817	22.12046	27.9979

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.149	MF	1.2991	1.01663e4	130.42726	92.1855
2	38.658	MF	1.3508	545.40112	6.72925	4.9456
3	40.342	FM	1.4511	316.38281	3.63393	2.8689



(2*R*,7*R*,*E*)-**3j**

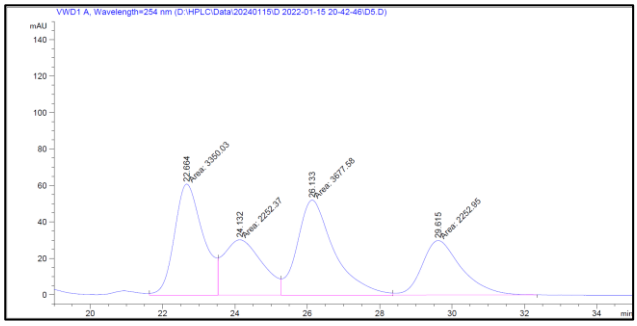
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(4-methoxyphenyl)hept-4-enoate ((2*R*,7*R*,*E*)-3j)**: yield (81 mg, 84%); colorless oil; $[\alpha]^{15}_{D}$ = +79.3 (*c* 0.47, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 17:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 22.66, 24.13, 26.13 and 29.62 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.40 (m, 3H), 7.39 – 7.30 (m, 3H), 7.24 – 7.20 (m, 2H), 7.18 – 7.13 (m, 2H), 6.83(d, *J* = 8.4 Hz, 2H), 5.57 – 5.41 (m, 2H), 4.58 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 1H), 3.78 (s, 3H), 2.64 – 2.54 (m, 2H), 2.45 – 2.34 (m, 2H), 1.43 (s, 9H).

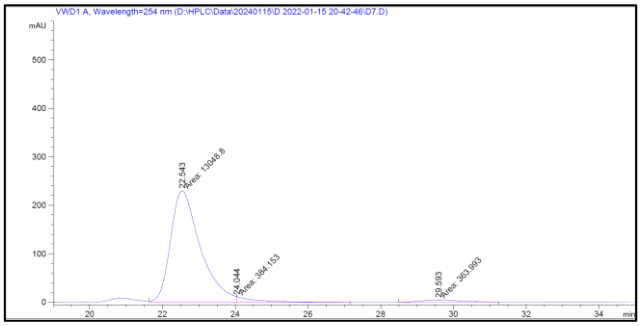
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.1, 158.9, 139.6, 136.6, 136.1, 130.4, 130.2, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 127.0, 113.7, 81.0, 72.9, 66.0, 55.2, 42.7, 37.0, 28.0.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_4$ ($[M+H]^+$): 486.2639, found: 486.2645.

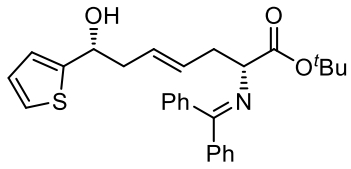
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3j



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.664	MF	0.9178	3350.02563	60.83315	29.0475
2	24.132	FM	1.2391	2252.37036	30.29615	19.5299
3	26.133	MF	1.1783	3677.58057	52.02008	31.8877
4	29.615	FM	1.2585	2252.94653	29.83608	19.5349



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.543	FM	0.9455	1.30488e4	230.02109	94.5775
2	24.044	FM	0.5661	384.15259	11.30920	2.7843
3	29.593	MM	1.2420	363.99332	4.88440	2.6382



(2*R*,7*R*,*E*)-**3k**

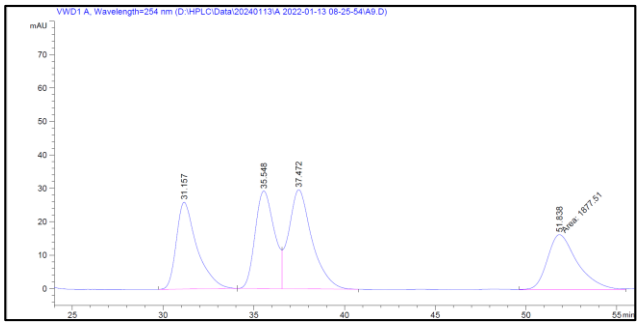
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(thiophen-2-yl)hept-4-enoate ((2*R*,7*R*,*E*)-3k)**: yield (83 mg, 90%); colorless oil; $[\alpha]^{15}_{D}$ = +72.5 (*c* 0.56, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 9:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 31.16, 35.55, 37.47 and 51.84 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 2H), 7.46 – 7.30 (m, 6H), 7.22 – 7.18 (m, 1H), 7.17 – 7.12 (m, 2H), 6.94 – 6.89 (m, 2H), 5.61 – 5.45 (m, 2H), 4.92 – 4.85 (m, 1H), 4.00 (dd, *J* = 7.0, 5.4 Hz, 1H), 2.64 – 2.57 (m, 2H), 2.57 – 2.45 (m, 2H), 1.43 (s, 9H).

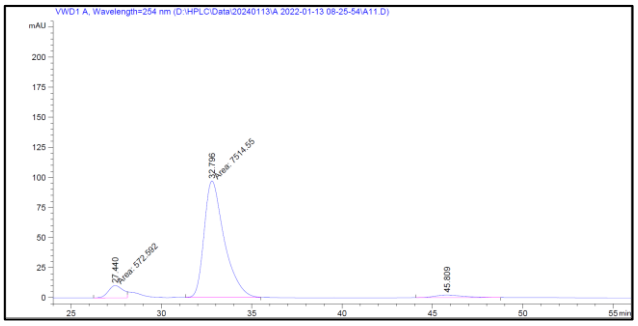
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.2, 147.9, 139.6, 136.6, 131.1, 130.2, 128.8, 128.5, 128.4, 128.0, 127.9, 127.8, 126.5, 124.4, 123.5, 81.1, 69.3, 65.9, 42.7, 37.0, 28.0.

HRMS (ESI+) calcd. For $C_{28}H_{32}NO_3S$ ($[M+H]^+$): 462.2097, found: 462.2090.

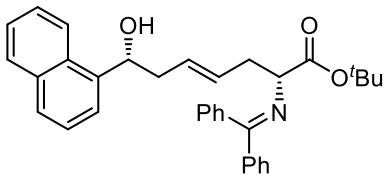
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3k



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.157	BB	1.1441	2053.90918	25.98606	23.5017
2	35.548	BV	1.1126	2153.87036	29.19880	24.6455
3	37.472	VB	1.2723	2654.13403	29.65247	30.3697
4	51.838	MF	1.9049	1877.50952	16.42696	21.4832



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.440	MF	0.9355	572.59235	10.20103	6.8773
2	32.796	MM	1.2927	7514.54736	96.88213	90.2553
3	45.809	BB	1.2687	238.74200	2.20232	2.8675



(2*R*,7*R*,*E*)-**3l**

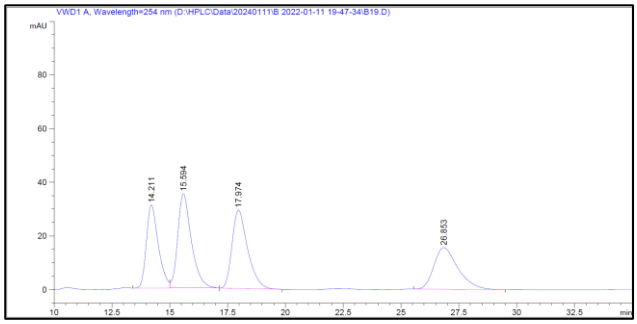
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(naphthalen-1-yl)hept-4-enoate ((2*R*,7*R*,*E*)-3l)**: yield (86 mg, 85%); colorless oil; $[\alpha]^{15}_{D}$ = +96.2 (*c* 0.61, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 17:1 dr, 98% ee (Chiralpak IC, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 14.21, 15.59, 17.97 and 26.85 min.

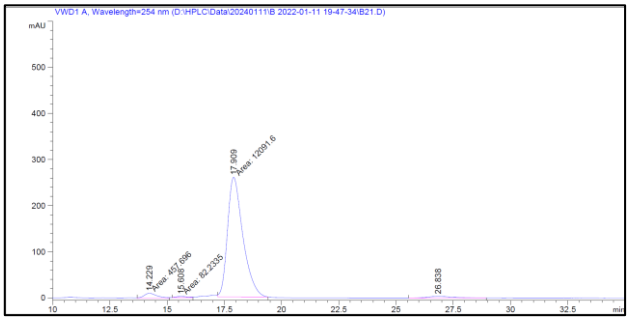
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.98 (m, 1H), 7.87 – 7.83 (m, 1H), 7.77 – 7.72 (m, 1H), 7.68 – 7.59 (m, 3H), 7.49 – 7.40 (m, 6H), 7.39 – 7.30 (m, 3H), 7.19 – 7.13 (m, 1H), 5.65 – 5.54 (m, 2H), 5.42 (dd, *J* = 8.6, 3.8 Hz, 1H), 4.02 (t, *J* = 6.2 Hz, 1H), 2.72 – 2.58 (m, 3H), 2.53 – 2.45 (m, 1H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.2, 139.6, 139.4, 136.6, 133.7, 130.6, 130.25, 130.22, 128.9, 128.8, 128.5, 128.4, 128.0, 127.8, 127.7, 125.9, 125.42, 125.37, 123.0, 122.8, 81.1, 69.9, 66.0, 41.8, 37.1, 28.1.

HRMS (ESI+) calcd. For $C_{34}H_{36}NO_3$ ($[M+H]^+$):506.2690, found: 506.2686.

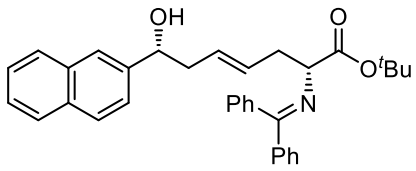
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3l





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.211	BV	0.5389	1112.84277	30.99708	22.0764
2	15.594	VB	0.6128	1443.15125	35.16558	28.6290
3	17.974	BB	0.7040	1367.06213	29.21193	27.1196
4	26.853	BB	1.0606	1117.81140	15.51426	22.1750

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.229	MM	0.6837	457.69583	11.15800	3.5553
2	15.608	MF	0.5426	82.23348	2.52602	0.6388
3	17.909	MM	0.7773	1.20916e4	259.27725	93.9251
4	26.838	BB	0.8597	242.12468	3.39656	1.8808



(2*R*,7*R*,*E*)-**3m**

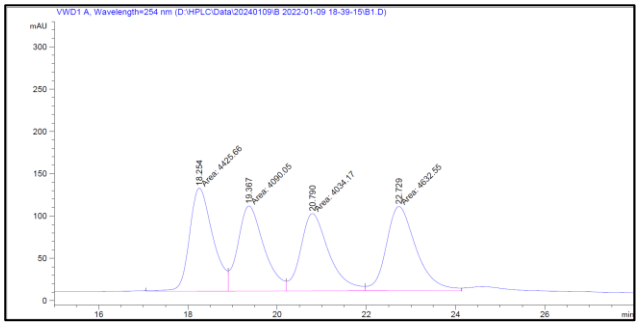
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-(naphthalen-2-yl)hept-4-enoate ((2*R*,7*R*,*E*)-3m)**: yield (86 mg, 85%); colorless oil; $[\alpha]^{15}_{D}$ = +80.8 (*c* 0.58, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 10:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.25, 19.37, 20.79 and 22.73 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 4H), 7.67 – 7.63 (m, 2H), 7.47 – 7.37 (m, 7H), 7.35 – 7.30 (m, 2H), 7.17 – 7.13 (m, 2H), 5.63 – 5.45 (m, 2H), 4.80 (dd, *J* = 8.0, 4.4 Hz, 1H), 4.00 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.64 – 2.57 (m, 2H), 2.57 – 2.51 (m, 1H), 2.51 – 2.42 (m, 1H), 1.43 (s, 9H).

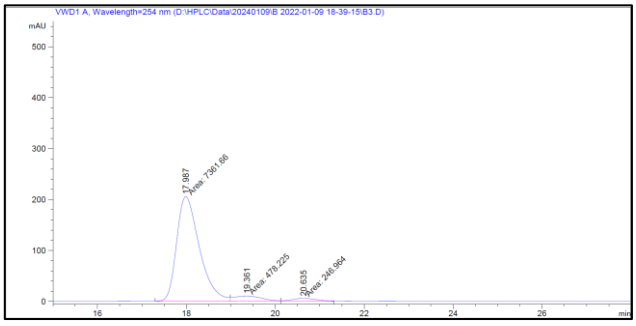
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.2, 141.4, 139.6, 136.6, 133.2, 132.8, 130.8, 130.3, 128.8, 128.5, 128.4, 128.04, 128.01, 127.9, 127.8, 127.6, 126.0, 125.7, 124.3, 124.0, 81.1, 73.2, 65.9, 42.8, 37.1, 28.0.

HRMS (ESI+) calcd. For $C_{34}H_{36}NO_3$ ($[M+H]^+$):506.2690, found: 506.2688.

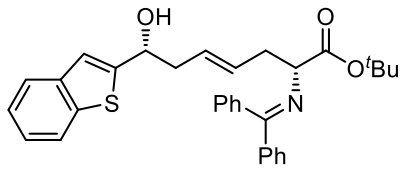
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3m



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.254	MF	0.6059	4425.66406	121.72798	25.7569
2	19.367	MF	0.6782	4090.05396	100.51357	23.8037
3	20.790	MF	0.7357	4034.16553	91.39146	23.4784
4	22.729	FM	0.7762	4632.55078	99.46693	26.9610



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.987	FM	0.5960	7361.66309	205.85715	91.0325
2	19.361	MF	0.7500	478.22534	10.62706	5.9136
3	20.635	FM	0.6850	246.96399	6.00870	3.0539



(2*R*,7*R*,*E*)-**3n**

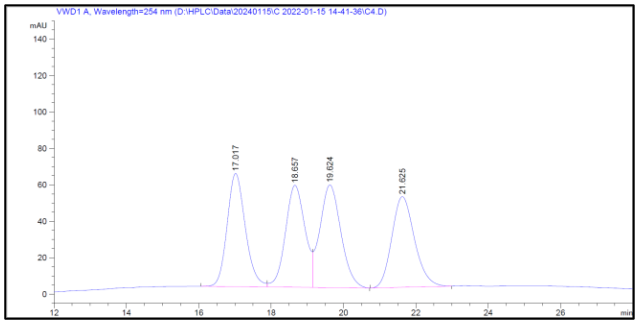
***tert*-butyl (2*R*,7*R*,*E*)-7-(benzo[b]thiophen-2-yl)-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*R*,*E*)-3n)**: yield (96 mg, 94%); colorless oil; $[\alpha]^{15}_{D}$ = +67.1 (*c* 0.56, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 6:1 dr, > 99% ee (Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 17.02, 18.66, 19.62 and 21.63 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.60 (m, 3H), 7.44 – 7.36 (m, 4H), 7.35 – 7.26 (m, 4H), 7.17 – 7.09 (m, 3H), 5.66 – 5.46 (m, 2H), 4.95 (t, *J* = 6.2 Hz, 1H), 4.00 (t, *J* = 6.2 Hz, 1H), 2.62 – 2.57 (m, 3H), 2.56 – 2.50 (m, 1H), 1.42 (s, 9H).

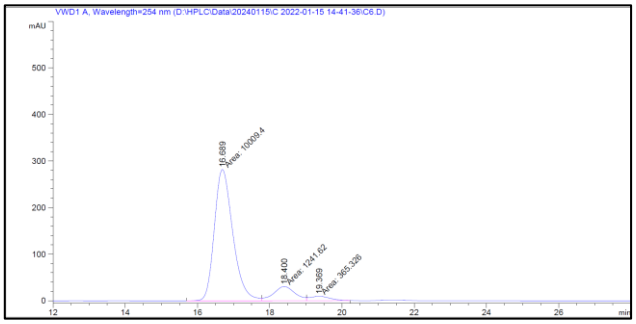
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.9, 170.2, 148.6, 139.6, 139.5, 139.3, 136.6, 131.4, 130.3, 128.8, 128.5, 128.4, 128.0, 127.8, 127.5, 124.1, 124.0, 123.4, 122.4, 119.9, 81.1, 69.7, 65.8, 42.4, 37.0, 28.0.

HRMS (ESI+) calcd. For $C_{32}H_{34}NO_3S$ ($[M+H]^+$): 512.2254, found: 512.2255.

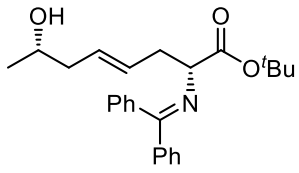
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3n



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.017	BV	0.5347	2170.81860	62.12012	24.8817
2	18.657	VV	0.5731	2095.96045	55.94752	24.0236
3	19.624	VB	0.6149	2289.83154	56.36955	26.2458
4	21.625	BB	0.6723	2167.96558	49.75972	24.8490



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.689	MF	0.5916	1.00094e4	281.99188	86.1665
2	18.400	MF	0.6789	1241.61768	30.47942	10.6885
3	19.369	FM	0.6596	365.32611	9.23127	3.1449



(2*R*,7*S*,*E*)-**3o**

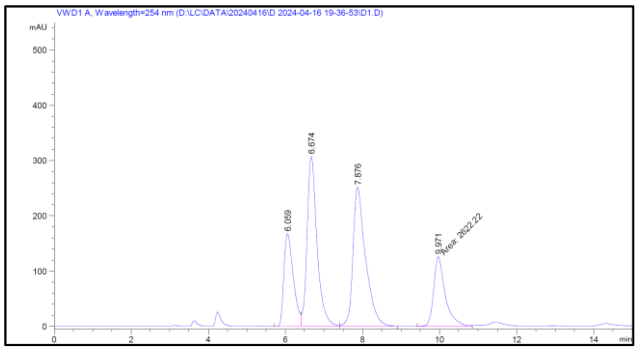
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxyoct-4-enoate ((2*R*,7*S*,*E*)-3o)**: yield (42 mg, 53%); colorless oil; $[\alpha]^{25}_{D}$ = +69.7 (*c* 0.47, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 1.3:1 dr, 98% ee (Chiralpak AD-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 6.06, 6.67, 7.88 and 9.97 min.

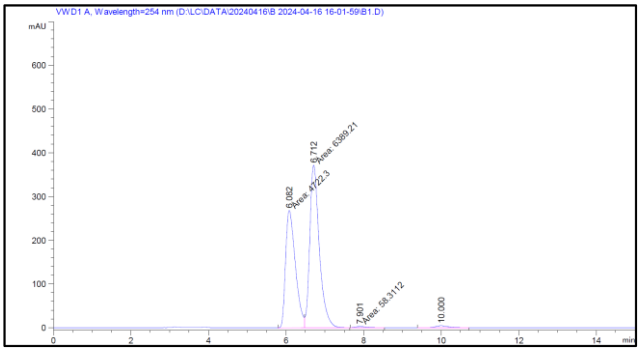
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.57 (m, 2H), 7.48 – 7.40 (m, 3H), 7.37 (d, *J* = 7.0 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.21 – 7.09 (m, 2H), 5.54 – 5.39 (m, 2H), 4.04 – 3.94 (m, 1H), 3.79 – 3.66 (m, 1H), 2.67 – 2.51 (m, 2H), 2.21 – 2.13 (m, 1H), 2.11 – 1.99 (m, 1H), 1.442 (s, 4.81H, major), 1.436 (s, 3.99H, minor), 1.14 (d, *J* = 6.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.9, 170.11, 170.06, 139.60, 139.57, 136.6, 130.2, 130.1, 130.0, 129.1, 129.0, 128.7, 128.5, 128.43, 128.411, 128.0, 127.81, 127.77, 81.1, 81.0, 67.0, 66.9, 66.0, 42.6, 42.5, 37.13, 37.10, 28.1, 22.6.

HRMS (ESI+) calcd. For $C_{25}H_{32}NO_3$ ($[M+H]^+$): 394.2377, found: 394.2382.

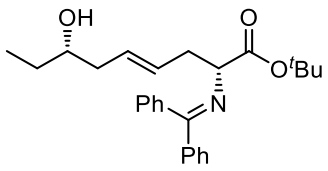
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3o





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.059	BV	0.2591	2837.15674	167.20161	17.0600
2	6.674	VV	0.2688	5511.17139	307.41818	33.1390
3	7.876	VB	0.3251	5659.89893	251.51981	34.0334
4	9.971	MF	0.3471	2622.21802	125.90105	15.7676

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.082	MF	0.2934	4722.30469	268.28632	41.8783
2	6.712	FM	0.2866	6389.21484	371.52213	56.6608
3	7.901	FM	0.3403	58.31115	2.85550	0.5171
4	10.000	VB R	0.3171	106.41431	4.82227	0.9437



(2*R*,7*S*,*E*)-**3p**

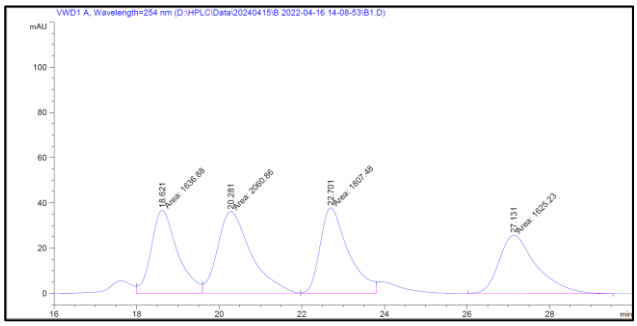
***tert*-butyl (2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxynon-4-enoate ((2*R*,7*S*,*E*)-3p)**: yield (53 mg, 65%); colorless oil; $[\alpha]^{25}_{D}$ = +52.3 (*c* 0.44, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 1.6:1 dr, 97% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 18.62, 20.28, 22.70 and 27.13 min.

^{1}H NMR (400 MHz, Chloroform-*d*) 7.69 – 7.64 (m, 2H), 7.48 – 7.41 (m, 3H), 7.40 – 7.30 (m, 3H), 7.20 – 7.12 (m, 2H), 5.54 – 5.41 (m, 2H), 4.06 – 3.91 (m, 1H), 3.56 – 3.40 (m, 1H), 2.68 – 2.55 (m, 2H), 2.24 – 2.17 (m, 1H), 2.12 – 2.01 (m, 1H), 1.49 – 1.47 (m, 2H), 1.440 (s, 5.93H, major), 1.435 (s, 2.95H, minor),.

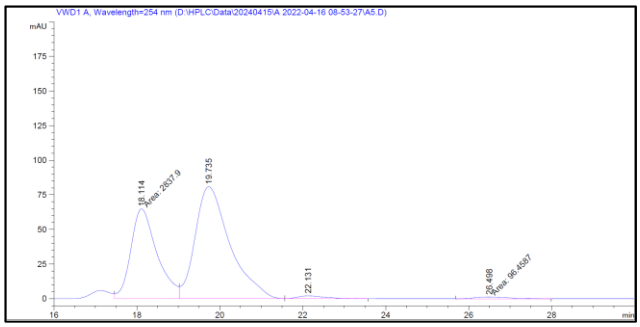
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.99, 170.96, 170.11, 170.06, 139.6, 136.6, 130.2, 129.9, 129.2, 129.0, 128.7, 128.530, 128.526, 128.43, 128.40, 128.0, 127.81, 127.78, 81.1, 81.0, 72.1, 72.0, 66.1, 66.0, 40.3, 40.2, 37.2, 37.1, 29.4, 28.1, 9.9.

HRMS (ESI+) calcd. For $C_{26}H_{34}NO_3$ ($[M+H]^+$): 408.2533, found: 408.2535.

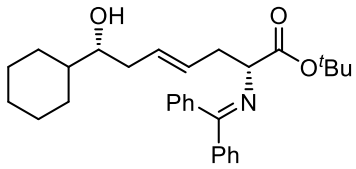
HPLC chromatogram of compound (2*R*,7*S*,*E*)-3p



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.621	FM	0.7406	1636.87512	36.83912	22.9561
2	20.281	MF	0.9477	2060.85889	36.24128	28.9022
3	22.701	FM	0.7950	1807.48132	37.89495	25.3488
4	27.131	FM	1.0496	1625.23206	25.80704	22.7928



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.114	FM	0.7301	2837.89990	64.78103	36.8076
2	19.735	VB	0.8701	4692.49414	80.72861	60.8618
3	22.131	BB	0.6278	83.23144	1.91992	1.0795
4	26.498	MM	1.1292	96.45875	1.42376	1.2511



(2*R*,7*R*,*E*)-**3q**

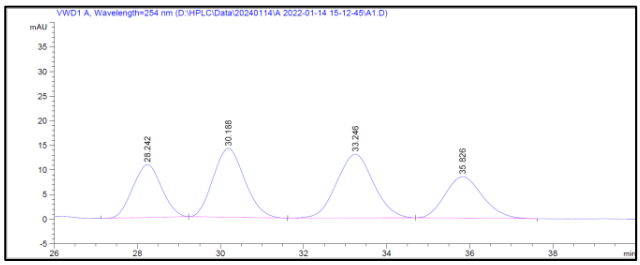
***tert*-butyl (2*R*,7*R*,*E*)-7-cyclohexyl-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*R*,7*R*,*E*)-3q)**: yield (60 mg, 65%); colorless oil; $[\alpha]^{15}_{D}$ = +61.7 (*c* 0.60, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 11:1 dr, > 99% ee (Chiralpak IC + Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 0.75 mL/min, λ = 254 nm); t_r = 28.24, 30.19, 33.25 and 35.83 min.

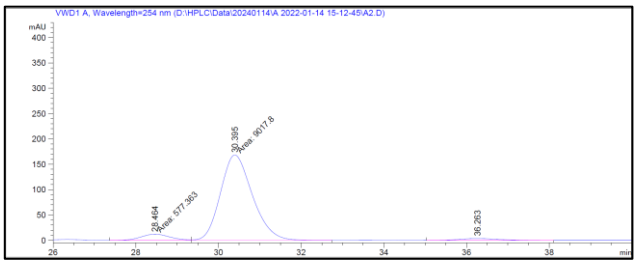
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.45 – 7.40 (m, 3H), 7.40 – 7.29 (m, 3H), 7.19 – 7.13 (m, 2H), 5.53 – 5.44 (m, 2H), 3.99 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.31 – 3.24 (m, 1H), 2.67 – 2.55 (m, 2H), 2.26 – 2.19 (m, 1H), 2.09 – 2.01 (m, 1H), 1.85 – 1.59 (m, 7H), 1.44 (s, 9H), 1.19 – 1.13 (m, 2H), 1.04 – 0.93 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.0, 139.6, 136.7, 130.2, 129.9, 129.5, 128.7, 128.5, 128.4, 128.0, 127.8, 81.0, 77.2, 74.9, 66.1, 42.8, 37.5, 37.1, 29.0, 28.2, 28.1, 26.5, 26.2, 26.1.

HRMS (ESI+) calcd. For $C_{30}H_{40}NO_3$ ($[M+H]^+$): 462.3003, found: 462.3002.

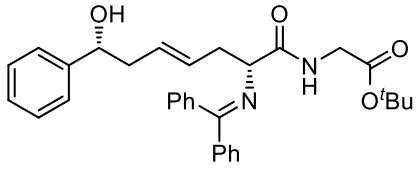
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3q





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.242	BB	0.7407	518.53638	10.75115	20.0971
2	30.188	BB	0.7958	736.80237	13.98249	28.5566
3	33.246	BB	0.9167	798.75641	12.96627	30.9578
4	35.826	BB	0.9223	526.05438	8.42655	20.3885

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.464	MF	0.7882	577.36255	12.20912	5.8762
2	30.395	FM	0.8932	9017.79980	168.26625	91.7799
3	36.263	BB	0.8212	230.30092	3.68481	2.3439



(2*R*,7*R*,*E*)-Gly-Gly-**3r**

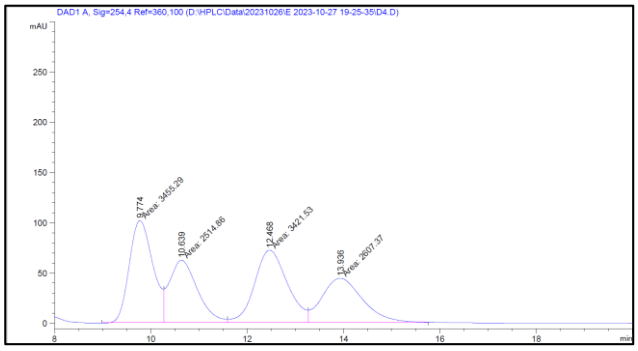
***tert*-butyl ((2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)glycinate ((2*R*,7*R*,*E*)-Gly-Gly-3r)**: yield (69 mg, 73%); colorless oil; $[\alpha]^{20}_{D}$ = -6.0 (*c* 0.44, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 13:1 dr, > 99% ee (Chiralcel OD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 9.77, 10.64, 12.47 and 13.94 min.

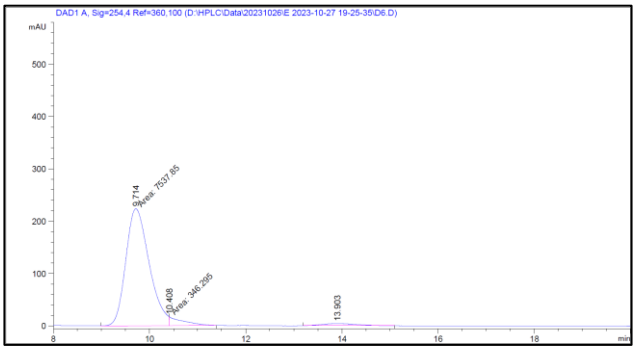
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.57 (m, 2H), 7.45 – 7.27 (m, 8H), 7.24 – 7.21 (m, 3H), 7.17 – 7.14 (m, 1H), 7.11 – 7.00 (m, 2H), 5.47 – 5.39 (m, 1H), 5.37 – 5.20 (d, *J* = 7.5 Hz, 1H), 4.59 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.00 (t, *J* = 6.2 Hz, 1H), 3.91 (dd, *J* = 5.6, 2.8 Hz, 1H), 2.47 – 2.27 (m, 4H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 169.7, 168.8, 144.1, 139.1, 135.7, 132.4, 130.7, 130.0, 129.9, 128.8, 128.7, 128.2, 127.6, 127.1, 125.7, 82.1, 72.8, 65.8, 42.5, 41.7, 38.7, 28.0.

HRMS (ESI+) calcd. For $C_{32}H_{37}N_2O_4$ ($[M+H]^+$): 513.2748, found: 513.2749.

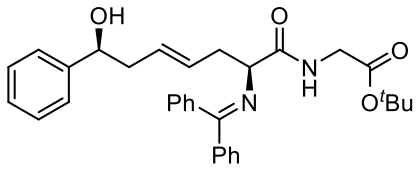
HPLC chromatogram of compound (2*R*,7*R*,*E*)-Gly-Gly-3r





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.774	MF	0.5676	3455.29468	101.46545	28.7964
2	10.639	FM	0.6758	2514.85864	62.02573	20.9588
3	12.468	FM	0.7920	3421.53467	72.00500	28.5150
4	13.936	FM	0.9849	2607.36938	44.12298	21.7298

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.714	MF	0.5622	7537.85400	223.44754	93.0862
2	10.408	FM	0.3393	346.29477	17.00795	4.2764
3	13.903	BB	0.5977	213.56754	4.20403	2.6374

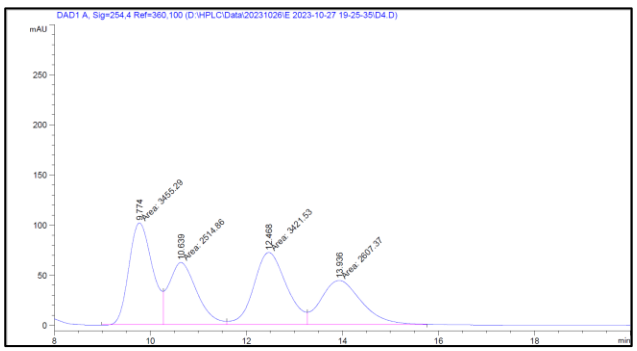


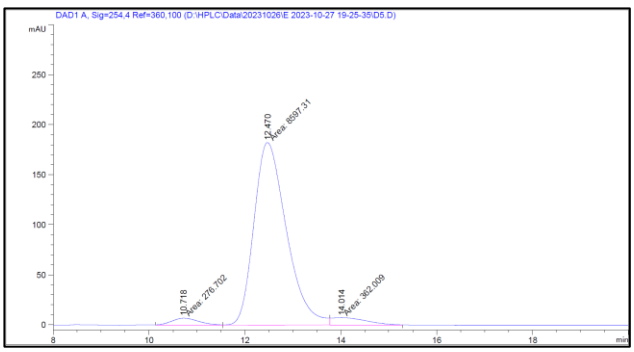
(2*S*,7*S*,*E*)-2-Gly-Gly-**3r**

***tert*-butyl (2*S*,7*S*,*E*)-7-cyclohexyl-2-((diphenylmethylene)amino)-7-hydroxyhept-4-enoate ((2*S*,7*S*,*E*)-Gly-Gly-3r)**: yield (72 mg, 70%); colorless oil; $[\alpha]^{20}_D$ = +6.2 (*c* 0.69, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 13:1 dr, > 99% ee (Chiralcel OD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 9.77, 10.64, 12.47 and 13.94 min.

HRMS (ESI+) calcd. For $C_{32}H_{37}N_2O_4$ ($[M+H]^+$): 513.2748, found: 513.2742.

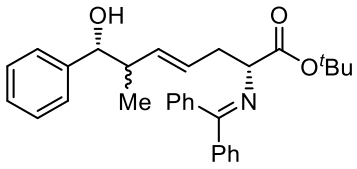
HPLC chromatogram of compound (2*S*,7*S*,*E*)-Gly-Gly-3r





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.774	MF	0.5676	3455.29468	101.46545	28.7964
2	10.639	FM	0.6758	2514.85864	62.02573	20.9588
3	12.468	FM	0.7920	3421.53467	72.00500	28.5150
4	13.936	FM	0.9849	2607.36938	44.12298	21.7298

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.718	MF	0.6552	276.70209	7.03890	2.9959
2	12.470	MF	0.7852	8597.31250	182.48773	93.0846
3	14.014	FM	0.8213	362.00897	7.34606	3.9195



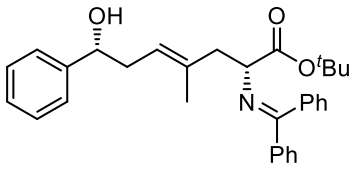
(2*R*,7*R*,*E*)-**3s**

***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-6-methyl-7-phenylhept-4-enoate ((2*R*,7*R*,*E*)-3s)**: yield (74 mg, 79%); colorless oil; $[\alpha]^{25}_D$ = +74.3 (*c* 0.39, CH_2Cl_2); The product was analyzed by ^{1}H NMR to determine the dr value and the enantiomeric excess: 1:1 dr.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.57 (m, 2H), 7.48 – 7.40 (m, 3H), 7.39 – 7.35 (m, 1H), 7.35 – 7.28 (m, 3H), 7.27 – 7.20 (m, 4H), 7.19 – 7.12 (m, 2H), 5.67 – 5.53 (m, 0.50H, minor), 5.49 – 5.31 (m, 1.47H, major), 4.56 (d, *J* = 4.8 Hz, 0.45H, minor), 4.23 (d, *J* = 8.0 Hz, 0.47H, major), 4.07 – 3.91 (m, 1H), 2.67 – 2.51 (m, 2H), 2.45 – 2.21 (m, 1H), 1.44 (s, 4.21H, minor), 1.43 (s, 4.39H, major), 0.89 (d, *J* = 6.8 Hz, 1.51H), 0.80 (d, *J* = 6.8 Hz, 1.50H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.9, 170.2, 170.1, 142.44, 142.41, 139.64, 139.56, 136.7, 136.6, 134.9, 134.5, 130.3, 130.2, 129.2, 128.8, 128.5, 128.4, 128.1, 128.01, 127.98, 127.90, 127.8, 127.6, 127.5, 127.1, 126.9, 126.4, 81.1, 81.0, 77.9, 66.1, 66.0, 45.6, 43.6, 37.13, 37.06, 28.1, 16.9, 14.1.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2691.



(2*R*,7*R*,*E*)-**3t**

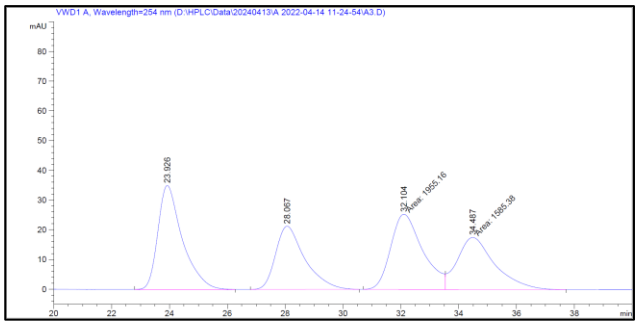
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-4-methyl-7-phenylhept-4-enoate ((2*R*,7*R*,*E*)-3t)**: yield (76 mg, 81%); colorless oil; $[\alpha]^{25}_D$ = +105.5 (*c* 0.41, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak IC, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 23.93, 28.07, 32.10 and 34.49 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.0 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.39 – 7.26 (m, 7H), 7.22 (q, *J* = 3.8 Hz, 1H), 7.14 (dd, *J* = 6.5, 2.9 Hz, 2H), 5.30 – 5.13 (m, 1H), 4.60 (dd, *J* = 8.0, 5.1 Hz, 1H), 4.06 (dd, *J* = 8.1, 5.2 Hz, 1H), 2.62 (dd, *J* = 13.4, 5.3 Hz, 1H), 2.55 (dd, *J* = 13.4, 8.0 Hz, 1H), 2.49 – 2.31 (m, 2H), 1.44 (s, 9H), 1.42 (s, 3H).

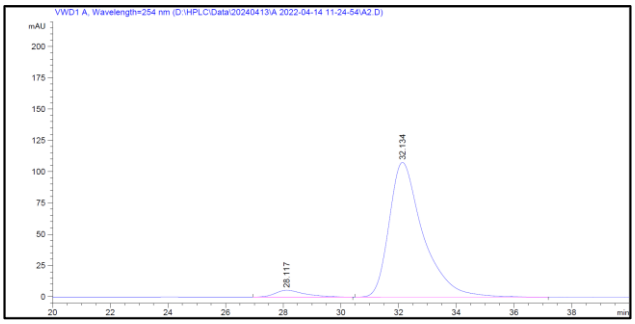
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.3, 169.8, 144.1, 139.6, 136.4, 135.4, 130.2, 128.7, 128.5, 128.32, 128.28, 128.0, 127.9, 127.3, 125.7, 123.2, 81.0, 73.7, 64.9, 43.89, 38.3, 28.0, 16.6.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ([M+H]$^+$): 470.2690, found: 470.2690.

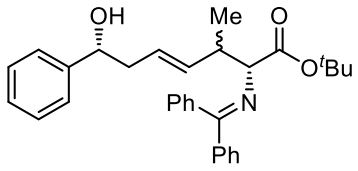
HPLC chromatogram of compound (2*R*,7*R*,*E*)-3t



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.926	BB	0.8571	2047.70337	34.97396	28.9281
2	28.067	BB	1.0231	1490.34656	21.28062	21.0543
3	32.104	MF	1.2867	1955.16443	25.32477	27.6208
4	34.487	FM	1.5080	1585.38269	17.52140	22.3968



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.117	BB	0.9447	374.76321	5.41353	4.0979
2	32.134	BB	1.2027	8770.46875	107.62825	95.9021



(2*R*,7*R*,*E*)-**3u**

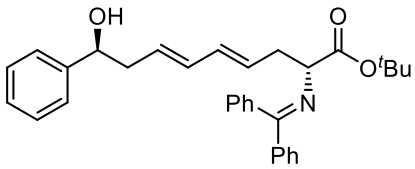
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-3-methyl-7-phenylhept-4-enoate ((2*R*,7*R*,*E*)-3u)**: yield (81 mg, 86%); colorless oil; $[\alpha]^{25}_D$ = +108.2 (*c* 0.46, CH_2Cl_2); The product was analyzed by ^{1}H NMR to determine the dr value: 2:1 dr.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.62 (m, 2H), 7.46 – 7.44 (m, 3H), 7.39 – 7.29 (m, 7H), 7.25 – 7.21 (d, *J* = 6.5 Hz, 1H), 7.17 – 7.07 (m, 2H), 5.86 – 5.76 (m, 0.64H, minor), 5.55 – 5.39 (m, 1.32H, major), 4.63 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.85 (d, *J* = 4.8 Hz, 0.62H, major), 3.81 (d, *J* = 6.4 Hz, 0.33H, minor), 2.94 – 2.78 (m, 1H), 2.64 – 2.17 (m, 3H), 1.43 (s, 6.04H, major), 1.42 (s, 3.00H, minor), 1.07 (d, *J* = 6.8 Hz, 0.98H, minor), 0.96 (d, *J* = 6.8 Hz, 3H, major).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.6, 170.5, 170.3, 144.1, 144.0, 139.64, 139.59,

137.03, 136.98, 136.8, 136.7, 130.2, 128.8, 128.5, 128.44, 128.39, 128.35, 128.28, 128.23, 128.0, 127.8, 127.3, 127.2, 126.2, 125.9, 125.8, 125.7, 81.0, 73.1, 72.9, 71.0, 70.9, 43.2, 42.8, 41.2, 40.9, 28.1, 17.8, 16.5.

HRMS (ESI+) calcd. For $C_{31}H_{36}NO_3$ ($[M+H]^+$): 470.2690, found: 470.2692.



(2*R*,4*E*,6*E*,9*S*)-**5a**

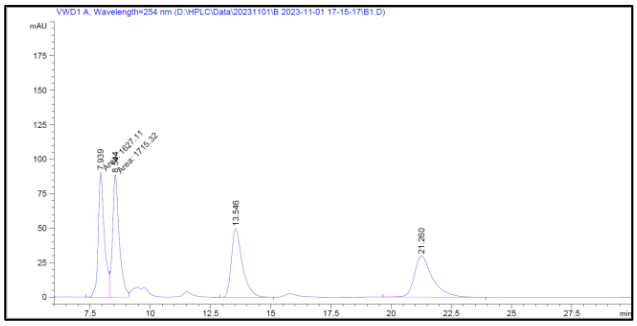
***tert*-butyl (2*R*,4*E*,6*E*,9*S*)-2-((diphenylmethylene)amino)-9-hydroxy-9-phenylnona-4,6-dienoate ((2*R*,4*E*,6*E*,9*S*)-5a)**: yield (91 mg, 94%); colorless oil; $[\alpha]^{20}_D$ = +10.2 (*c* 0.45, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 16:1 dr, > 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.94, 8.54, 13.55 and 21.26 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.37 – 7.22 (m, 10H), 7.19 – 7.16 (m, 1H), 7.10 – 7.02 (m, 2H), 6.05 – 5.89 (m, 2H), 5.52 – 5.34 (m, 2H), 4.61 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.92 (dd, *J* =7.4, 5.4 Hz, 1H), 2.63 – 2.49 (m, 2H), 2.47 – 2.36 (m, 2H), 1.36 (s, 9H).

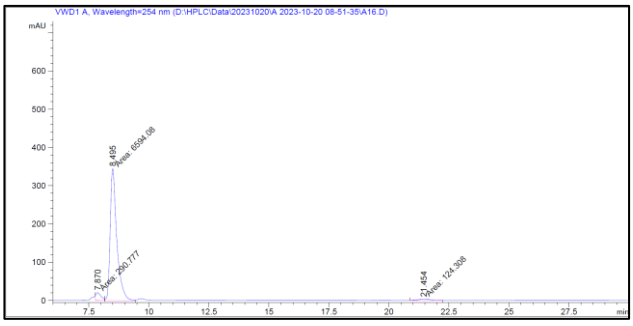
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.2, 143.8, 139.7, 136.6, 133.7, 132.5, 130.2, 129.1, 128.8, 128.5, 128.3, 128.0, 127.9, 127.7, 127.5, 125.7, 81.0, 73.6, 66.0, 42.7, 36.9, 28.0.

HRMS (ESI+) calcd. For $C_{32}H_{36}NO_3$ ($[M+H]^+$): 482.2690, found: 482.2695.

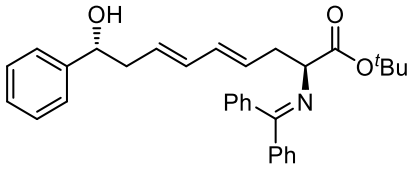
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*S*)-5a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.939	MF	0.2998	1627.10864	90.44197	25.0979
2	8.544	FM	0.3227	1715.32166	88.60120	26.4586
3	13.546	BB	0.4673	1576.58984	49.81060	24.3187
4	21.260	BB	0.7761	1564.02295	29.66586	24.1248



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.870	FM	0.2394	290.77689	20.24337	4.1485
2	8.495	MM	0.3187	6594.08301	344.87564	94.0780
3	21.454	MM	0.7147	124.30778	2.89887	1.7735

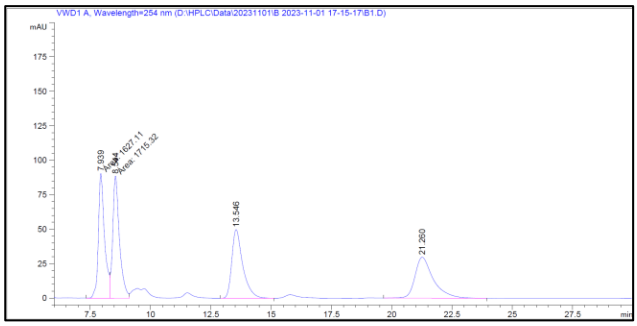


(2*S*,4*E*,6*E*,9*R*)-**5a**

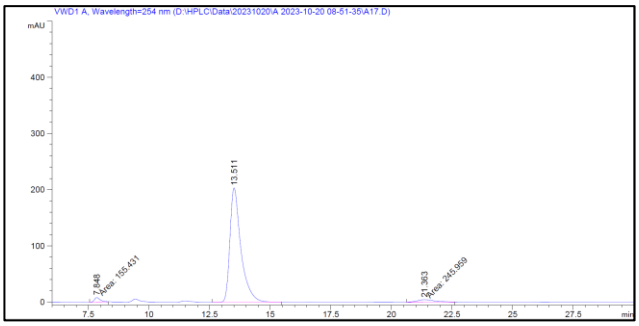
***tert*-butyl (2*S*,4*E*,6*E*,9*R*)-2-((diphenylmethylene)amino)-9-hydroxy-9-phenylnona-4,6-dienoate ((2*S*,4*E*,6*E*,9*R*)-5a)**: yield (95 mg, 99%); colorless oil; $[\alpha]^{20}_D$ = -10.9 (*c* 0.64, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 16:1 dr, > 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.94, 8.54, 13.55 and 21.26 min.

HRMS (ESI+) calcd. For $C_{32}H_{36}NO_3$ ($[M+H]^+$): 482.2690, found: 482.2689.

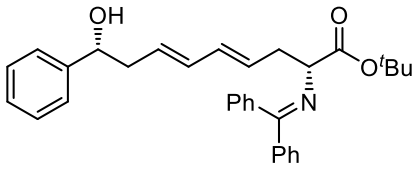
HPLC chromatogram of compound (2*S*,4*E*,6*E*,9*R*)-5a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.939	MF	0.2998	1627.10864	90.44197	25.0979
2	8.544	FM	0.3227	1715.32166	88.60120	26.4586
3	13.546	BB	0.4673	1576.58984	49.81060	24.3187
4	21.260	BB	0.7761	1564.02295	29.66586	24.1248



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.848	MM	0.3054	155.43135	8.48245	2.2926
2	13.511	BB	0.4633	6378.26465	203.12837	94.0795
3	21.363	MM	0.8900	245.95860	4.60619	3.6279



(2*R*,4*E*,6*E*,9*R*)-**5a**

***tert*-butyl (2*R*,4*E*,6*E*,9*R*)-2-((diphenylmethylene)amino)-9-hydroxy-9-phenylnona-4,6-dienoate ((2*R*,4*E*,6*E*,9*R*)-5a)**: yield (89 mg, 92%); colorless oil; $[\alpha]^{20}_D$ = +54.4 (*c* 0.66, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 13:1 dr, > 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r =7.94, 8.54,

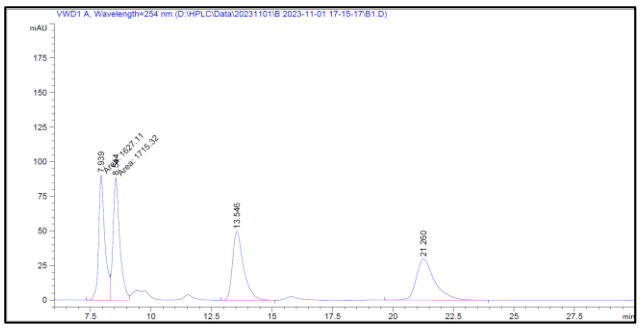
13.55 and 21.26 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 2H), 7.37 – 7.33 (m, 3H), 7.32 – 7.29 (m, 1H), 7.27 – 7.22 (m, 6H), 7.19 – 7.16 (m, 1H), 7.09 – 7.03 (m, 2H), 6.03 – 5.91 (m, 2H), 5.49 – 5.38 (m, 2H), 4.61 (dd, *J* = 7.6, 5.2 Hz, 1H), 3.92 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.63 – 2.50 (m, 2H), 2.46 – 2.36 (m, 2H), 1.36 (s, 9H).

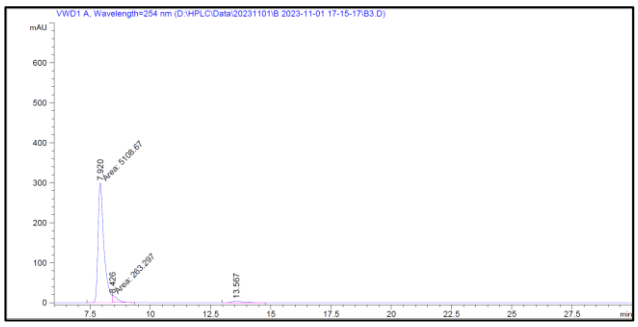
^{13}C NMR (101 MHz, Chloroform-*d*) 170.8, 170.2, 143.8, 139.6, 136.6, 133.7, 132.5, 130.2, 129.1, 128.8, 128.5, 128.4, 128.0, 127.9, 127.7, 127.5, 125.7, 81.0, 73.6, 66.0, 42.6, 36.9, 28.0.

HRMS (ESI+) calcd. For $C_{32}H_{36}NO_3$ ($[M+H]^+$): 482.2690, found: 482.2696.

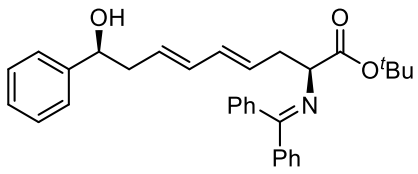
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*R*)-5a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.939	MF	0.2998	1627.10864	90.44197	25.0979
2	8.544	FM	0.3227	1715.32166	88.60120	26.4586
3	13.546	BB	0.4673	1576.58984	49.81060	24.3187
4	21.260	BB	0.7761	1564.02295	29.66586	24.1248



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.920	MF	0.2841	5108.66992	299.71225	93.0131
2	8.426	FM	0.2460	263.29657	17.84160	4.7938
3	13.567	BB	0.4561	120.45333	3.85956	2.1931

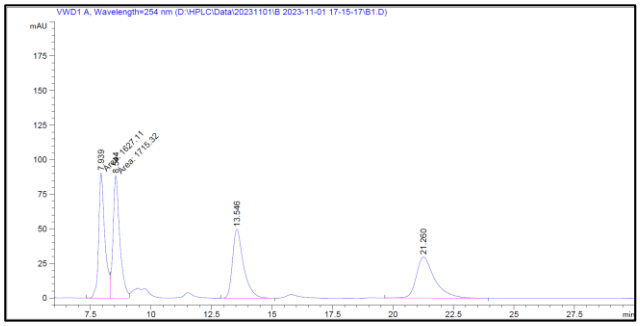


(2*S*,4*E*,6*E*,9*S*)-**5a**

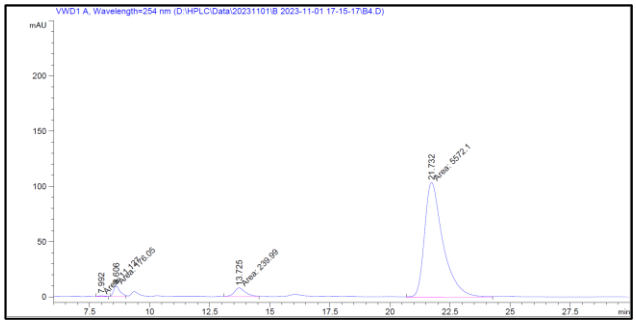
***tert*-butyl (2*S*,4*E*,6*E*,9*S*)-2-((diphenylmethylene)amino)-9-hydroxy-9-phenylnona-4,6-dienoate ((2*S*,4*E*,6*E*,9*S*)-5a)**: yield (89 mg, 92%); colorless oil; $[\alpha]^{20}_{D}$ = -54.6 (*c* 0.45, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 13:1 dr, 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.94, 8.54, 13.55 and 21.26 min.

HRMS (ESI+) calcd. For $C_{32}H_{36}NO_3$ ($[M+H]^+$): 482.2690, found: 482.2695.

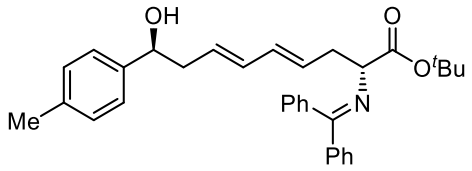
HPLC chromatogram of compound (2*S*,4*E*,6*E*,9*S*)-5a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.939	MF	0.2998	1627.10864	90.44197	25.0979
2	8.544	FM	0.3227	1715.32166	88.60120	26.4586
3	13.546	BB	0.4673	1576.58984	49.81060	24.3187
4	21.260	BB	0.7761	1564.02295	29.66586	24.1248



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.992	MF	0.2740	11.12695	6.76841e-1	0.1855
2	8.606	MF	0.3069	176.05025	9.56122	2.9345
3	13.725	MM	0.5199	239.99019	7.69322	4.0003
4	21.732	MM	0.8925	5572.09619	104.05132	92.8797



(2*R*,4*E*,6*E*,9*S*)-**5b**

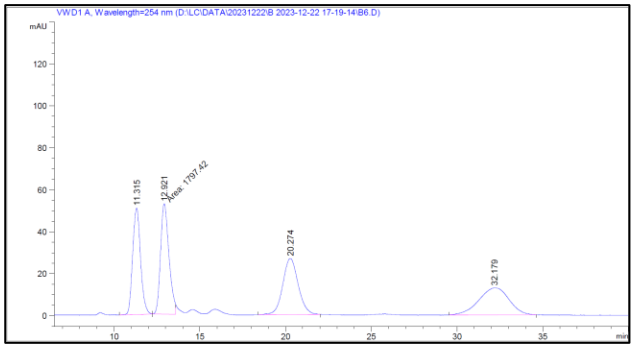
***tert*-butyl (2*R*,4*E*,6*E*,9*S*)-2-((diphenylmethylene)amino)-9-hydroxy-9-(*p*-tolyl)nona-4,6-dienoate ((2*R*,4*E*,6*E*,9*S*)-5b)**: yield (92 mg, 93%); colorless oil; $[\alpha]^{15}_{D}$ = +14.6 (*c* 0.52, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 11.32, 12.92, 20.27 and 32.18 min.

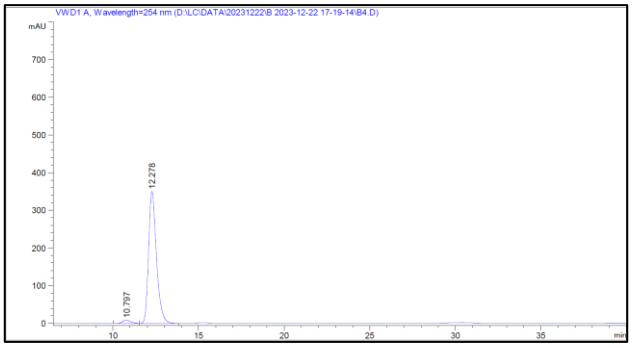
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.59 (m, 2H), 7.44 – 7.29 (m, 6H), 7.23 – 7.18 (m, 2H), 7.16 – 7.07 (m, 4H), 6.10 – 5.97 (m, 2H), 5.57 – 5.43 (m, 2H), 4.69 – 4.61 (m, 1H), 3.98 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.70 – 2.55 (m, 2H), 2.52 – 2.44 (m, 2H), 2.32 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.1, 140.9, 139.7, 137.1, 136.6, 133.6, 132.5, 130.2, 129.0, 128.8, 128.5, 128.4, 128.0, 127.92, 127.88, 125.7, 81.0 73.5, 66.0, 42.7, 36.9, 28.0, 21.1.

HRMS (ESI+) calcd. For $C_{33}H_{38}NO_3$ ($[M+H]^+$): 496.2846, found: 496.2843.

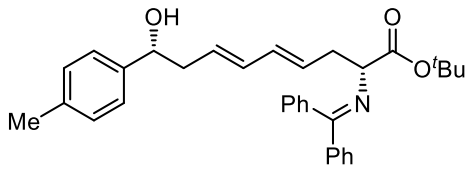
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*S*)-5b





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.315	BB	0.5045	1623.52759	50.71288	24.3512
2	12.921	MF	0.5698	1797.41577	52.57051	26.9594
3	20.274	BV R	0.8320	1676.85083	26.79663	25.1510
4	32.179	BB	1.4294	1569.33191	12.90098	23.5384

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.797	VV R	0.4894	272.22079	8.22655	2.3673
2	12.278	VB	0.4874	1.12268e4	350.38440	97.6327



(2*R*,4*E*,6*E*,9*R*)-**5b**

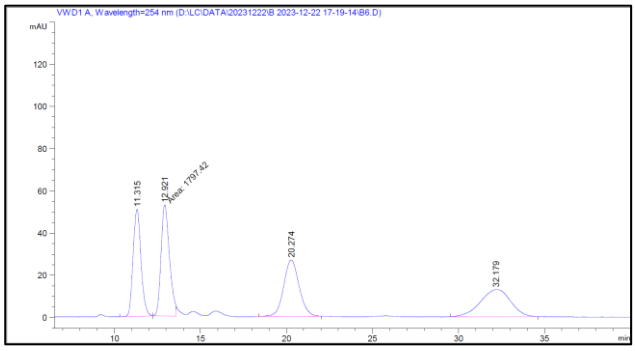
***tert*-butyl (2*R*,4*E*,6*E*,9*R*)-2-((diphenylmethylene)amino)-9-hydroxy-9-(p-tolyl)nona-4,6-dienoate ((2*R*,4*E*,6*E*,9*R*)-5b)**: yield (82 mg, 83%); colorless oil; $[\alpha]^{15}_{D}$ = +63.7 (*c* 0.52, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm); t_r = 11.32, 12.92, 20.27 and 32.18 min.

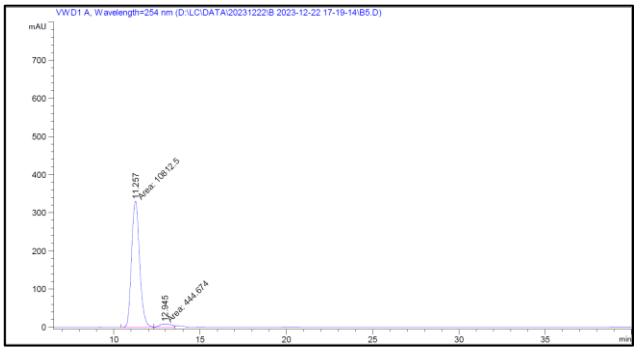
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.61 (m, 2H), 7.43 – 7.30 (m, 6H), 7.23 – 7.19 (m, 2H), 7.16 – 7.10 (m, 4H), 6.10 – 5.98 (m, 2H), 5.56 – 5.46 (m, 2H), 4.66 (t, *J* = 6.4 Hz, 1H), 3.99 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.70 – 2.57 (m, 2H), 2.53 – 2.44 (m, 2H), 2.33 (s, 3H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.1, 140.9, 139.6, 137.1, 136.6, 133.6, 132.5, 130.2, 129.03, 129.01, 128.8, 128.5, 128.4, 128.0, 127.89, 127.86, 125.7, 81.0, 73.5, 66.0, 42.6, 36.9, 28.0, 21.1.

HRMS (ESI+) calcd. For $C_{33}H_{38}NO_3$ ($[M+H]^+$): 496.2846, found: 496.2845.

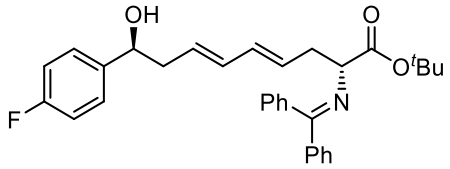
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*R*)-5b





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.315	BB	0.5045	1623.52759	50.71288	24.3512
2	12.921	MF	0.5698	1797.41577	52.57051	26.9594
3	20.274	BV R	0.8320	1676.85083	26.79663	25.1510
4	32.179	BB	1.4294	1569.33191	12.90098	23.5384

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.257	MF	0.5449	1.08125e4	330.74567	96.0499
2	12.945	MF	0.7911	444.67429	9.36854	3.9501



(2*R*,4*E*,6*E*,9*S*)-**5c**

***tert*-butyl (2*R*,4*E*,6*E*,9*S*)-2-((diphenylmethylene)amino)-9-(4-fluorophenyl)-9-hydroxynona-4,6-dienoate ((2*R*,4*E*,6*E*,9*S*)-5c)**: yield (95 mg, 95%); colorless oil; $[\alpha]^{15}_{D}$ = +18.1 (*c* 0.50, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 19:1 dr, > 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.63, 8.32, 12.19 and 18.41 min.

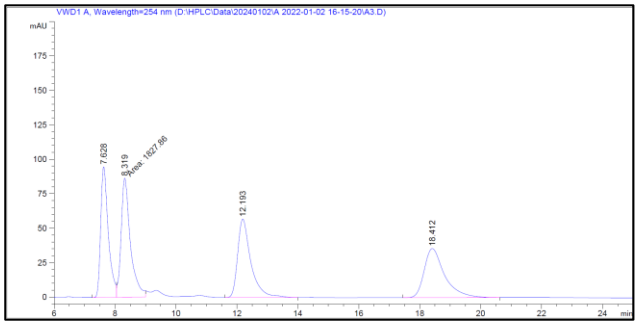
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.44 – 7.26 (m, 8H), 7.15 – 7.09 (m, 2H), 7.02 – 6.95 (m, 2H), 6.09 – 5.97 (m, 2H), 5.55 – 5.43 (m, 2H), 4.67 (t, *J* = 6.4 Hz, 1H), 3.99 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.69 – 2.56 (m, 2H), 2.50 – 2.41 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.2, 162.1 (d, *J* = 246.4 Hz), 139.7, 139.5 (d, *J* = 2.9 Hz), 136.6, 134.0, 132.4, 130.2, 129.4, 128.8, 128.5, 128.4, 128.0, 127.9, 127.4 (d, *J* = 8.1 Hz), 127.3, 115.1 (d, *J* = 21.2 Hz), 81.0, 72.9, 66.0, 42.8, 36.9, 28.0.

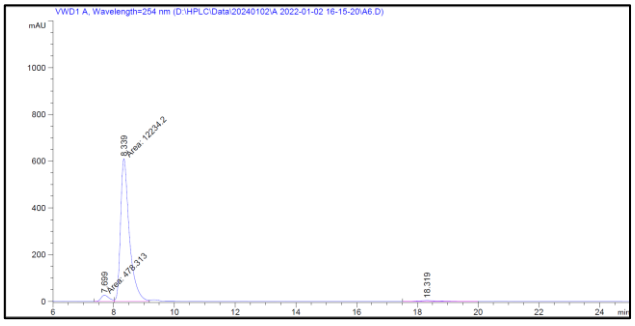
^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.12 – -115.28 (m).

HRMS (ESI+) calcd. For $C_{32}H_{35}FNO_3$ ($[M+H]^+$): 500.2595, found: 500.2602.

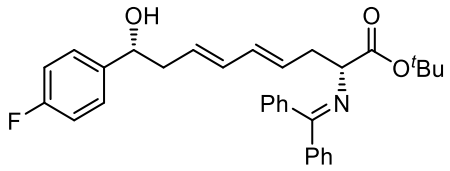
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*S*)-5c



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.628	BV	0.2591	1649.11743	94.72486	24.1325
2	8.319	MF	0.3529	1827.85608	86.33602	26.7481
3	12.193	BB	0.4424	1708.19067	56.87701	24.9970
4	18.412	BB	0.6866	1648.42371	35.57173	24.1224



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.699	MF	0.3041	478.31308	26.21165	3.7144
2	8.339	FM	0.3345	1.22342e4	609.56348	95.0071
3	18.319	BB	0.6340	164.62610	3.65858	1.2784



(2*R*,4*E*,6*E*,9*R*)-**5c**

***tert*-butyl (2*R*,4*E*,6*E*,9*R*)-2-((diphenylmethylene)amino)-9-(4-fluorophenyl)-9-hydroxynona-4,6-dienoate ((2*R*,4*E*,6*E*,9*R*)-5c)**: yield (87 mg, 87%); colorless oil; $[\alpha]^{15}_{D}$ = +60.4 (*c* 0.52, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: 13:1 dr, > 99% ee (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 7.63, 8.32, 12.19 and 18.41 min.

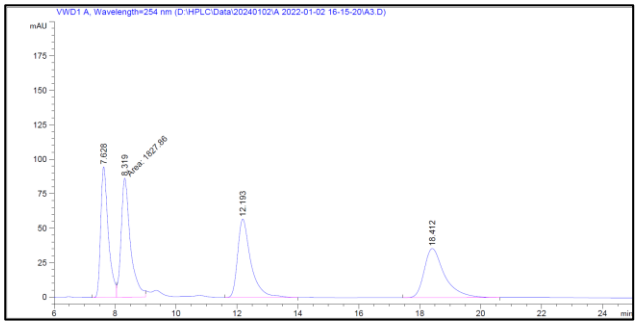
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 2H), 7.44 – 7.26 (m, 8H), 7.17 – 7.10 (m, 2H), 7.04 – 6.95 (m, 2H), 6.10 – 5.97 (m, 2H), 5.57 – 5.43 (m, 2H), 4.68 (dd, *J* = 7.4, 5.4 Hz, 1H), 3.99 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.70 – 2.56 (m, 2H), 2.53 – 2.41 (m, 2H), 1.43 (s, 9H).

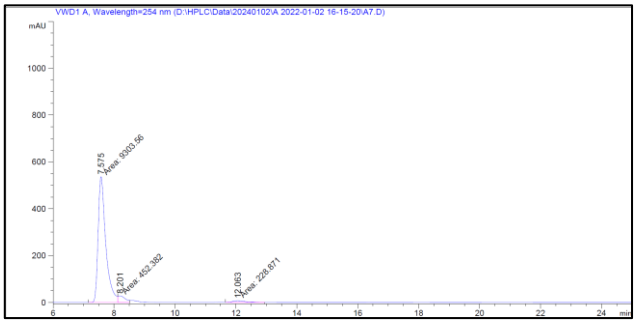
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.2, 162.1 (d, *J* = 245.9 Hz), 139.6, 139.5 (d, *J* = 3.0 Hz), 136.6, 134.0, 132.4, 130.2, 129.3, 128.8, 128.5, 128.4, 128.0, 127.9, 127.4 (d, *J* = 8.1 Hz), 127.3, 115.1 (d, *J* = 21.4 Hz), 81.0, 72.9, 66.0, 42.8, 36.9, 28.0.

^{19}F NMR (376 MHz, Chloroform-*d*) -115.09 – -115.31 (m).

HRMS (ESI+) calcd. For $C_{32}H_{35}FNO_3$ ($[M+H]^+$): 500.2595, found: 500.2600.

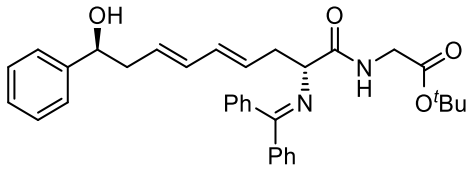
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*R*)-5c





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.628	BV	0.2591	1649.11743	94.72486	24.1325
2	8.319	MF	0.3529	1827.85608	86.33602	26.7481
3	12.193	BB	0.4424	1708.19067	56.87701	24.9970
4	18.412	BB	0.6866	1648.42371	35.57173	24.1224

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.575	MF	0.2891	9303.55664	536.36804	93.1771
2	8.201	FM	0.2732	452.38159	27.59366	4.5307
3	12.063	MF	0.4924	228.87100	7.74632	2.2922



(2*R*,4*E*,6*E*,9*S*)-Gly-Gly-**5d**

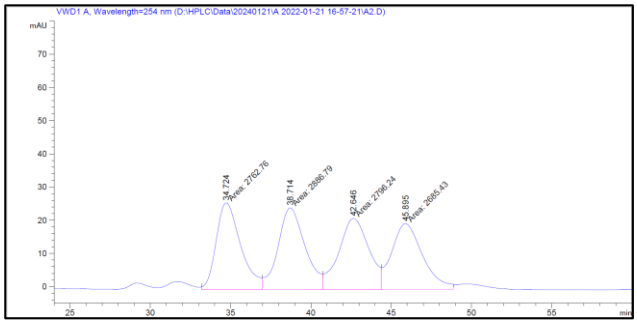
***tert*-butyl ((2*R*,4*E*,6*E*,9*S*)-2-((diphenylmethylene)amino)-9-hydroxy-9-phenylnona-4,6-dienoyl)glycinate ((2*R*,4*E*,6*E*,9*S*)-Gly-Gly-5d)**: yield (89 mg, 83%); colorless oil; $[\alpha]^{15}_{D}$ = -80.9 (*c* 0.53, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralcel IC-AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 34.72, 38.71, 42.65 and 45.90 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.46 – 7.39 (m, 5H), 7.38 – 7.35 (m, 2H), 7.32 – 7.27 (m, 4H), 7.25 – 7.20 (m, 1H), 7.08 – 7.02 (m, 2H), 6.07 – 5.91 (m, 2H), 5.53 – 5.35 (m, 2H), 4.71 – 4.64 (m, 1H), 4.09 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.01 (dd, *J* = 18.2, 5.4 Hz, 1H), 3.94 (dd, *J* = 18.0, 5.2 Hz, 1H), 2.58 – 2.44 (m, 4H), 1.47 (s, 9H).

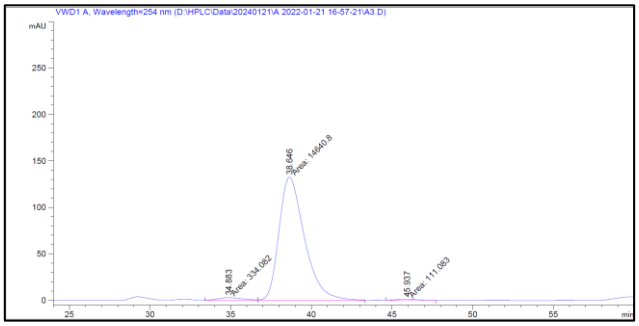
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 169.9, 168.7, 143.8, 139.3, 135.7, 133.6, 132.7, 130.6, 128.8, 128.71, 128.65, 128.6, 128.3, 128.1, 127.9, 127.8, 127.5, 125.7, 82.0, 73.5, 65.7, 42.8, 41.7, 38.6, 28.0.

HRMS (ESI+) calcd. For $C_{34}H_{39}N_2O_4$ ($[M+H]^+$): 539.2904, found: 539.2909.

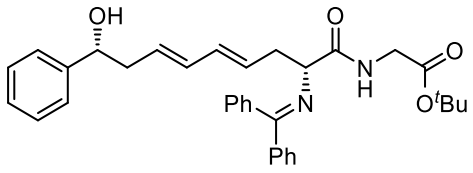
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*S*)-Gly-Gly-5d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.724	FM	1.7654	2762.76416	26.08285	24.8200
2	38.714	FM	1.9561	2886.78638	24.59692	25.9341
3	42.646	FM	2.1735	2796.24121	21.44174	25.1207
4	45.895	FM	2.2513	2685.42798	19.88074	24.1252



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.883	MF	1.8657	334.08203	2.98446	2.2145
2	38.646	FM	1.8392	1.46408e4	132.67056	97.0492
3	45.937	MM	1.8520	111.08257	9.99672e-1	0.7363



(2*R*,4*E*,6*E*,9*R*)-Gly-Gly-**5d**

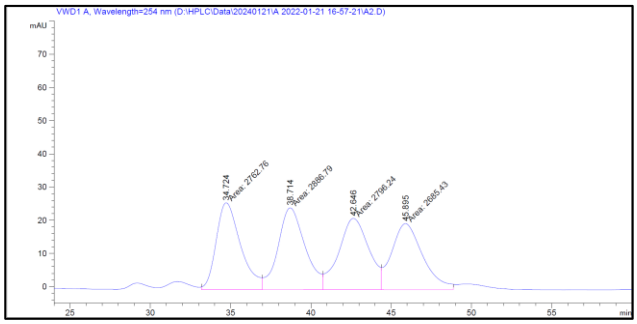
***tert*-butyl ((2*R*,4*E*,6*E*,9*R*)-2-((diphenylmethylene)amino)-9-hydroxy-9-phenylnona-4,6-dienoyl)glycinate ((2*R*,4*E*,6*E*,9*R*)-Gly-Gly-5d)**: yield (88 mg, 82%); colorless oil; $[\alpha]^{15}_{D}$ = -43.1 (*c* 0.50, CH_2Cl_2); The product was analyzed by HPLC to determine the dr value and the enantiomeric excess: > 20:1 dr, > 99% ee (Chiralcel IC-AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm); t_r = 34.72, 38.71, 42.65 and 45.90 min.

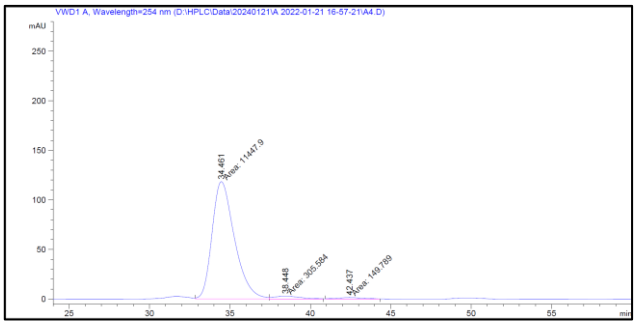
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.46 – 7.38 (m, 5H), 7.38 – 7.35 (m, 2H), 7.33 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 7.10 – 7.04 (m, 2H), 6.10 – 5.91 (m, 2H), 5.55 – 5.37 (m, 2H), 4.73 – 4.65 (m, 1H), 4.09 (dd, *J* = 6.4, 5.2 Hz, 1H), 4.02 (dd, *J* = 18.2, 5.4 Hz, 1H), 3.94 (dd, *J* = 18.2, 5.4 Hz, 1H), 2.58 – 2.41 (m, 4H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 169.8, 168.7, 143.8, 139.2, 135.7, 133.7, 132.7, 130.6, 128.8, 128.7, 128.6, 128.3, 128.2, 127.9, 127.8, 127.5, 125.7, 82.0, 73.6, 65.8, 42.7, 41.7, 38.6, 28.0.

HRMS (ESI+) calcd. For $C_{34}H_{39}N_2O_4$ ($[M+H]^+$): 539.2904, found: 539.2897.

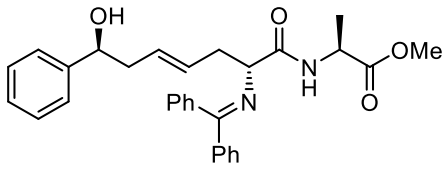
HPLC chromatogram of compound (2*R*,4*E*,6*E*,9*R*)-Gly-Gly-5d





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.724	FM	1.7654	2762.76416	26.08285	24.8200
2	38.714	FM	1.9561	2886.78638	24.59692	25.9341
3	42.646	FM	2.1735	2796.24121	21.44174	25.1207
4	45.895	FM	2.2513	2685.42798	19.88074	24.1252

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.461	FM	1.6152	1.14479e4	118.12802	96.1744
2	38.448	FM	1.8662	305.58432	2.72905	2.5672
3	42.437	MM	1.8444	149.78949	1.35354	1.2584



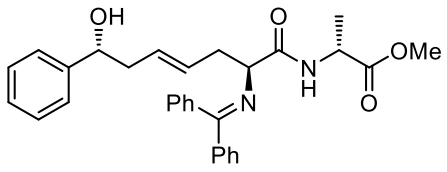
(2*R*,7*S*,*E*)-*L*-**3v**

methyl ((2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*L*-alaninate ((2*R*,7*S*,*E*)-*L*-3v): yield (48 mg, 50%); colorless oil; > 20:1 dr; $[\alpha]^{20}_{D}$ = -95.0 (*c* 0.54, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.57 (m, 2H), 7.55 – 7.46 (m, 1H), 7.44 – 7.23 (m, 9H), 7.21 –7.11 (m, 2H), 7.08 – 6.98 (m, 2H), 5.49 –5.32 (m, 2H), 4.60 – 4.47 (m, 2H), 3.96 (t, *J* = 6.4 Hz, 1H), 3.71 (s, 3H), 2.51 – 2.29 (m, 3H), 2.24 – 2.14 (m, 1H), 1.38 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 172.6, 169.2, 144.2, 139.0, 135.6, 130.7, 129.8, 129.5, 128.9, 128.8, 128.6, 128.25, 128.19, 127.5, 127.1, 125.6, 72.6, 65.6, 52.4, 47.6, 43.5, 39.1, 18.1.

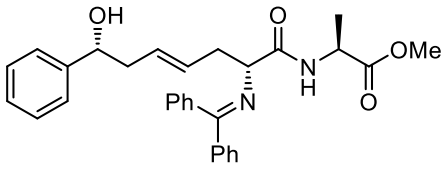
HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ($[M+H]^+$): 485.2435, found: 485.2440.



(2*S*,7*R*,*E*)-*D*-**3v**

methyl ((2*S*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*D*-alaninate ((2*S*,7*R*,*E*)-*D*-3v): yield (46 mg, 48%); colorless oil; > 20:1 dr; $[\alpha]^{20}_{D}$ = 95.6 (*c* 0.45, CH_2Cl_2).

HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ($[M+H]^+$): 485.2435, found: 485.2434.



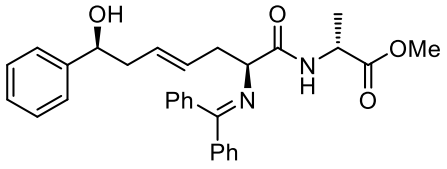
(2*R*,7*R*,*E*)-*L*-**3v**

methyl ((2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*L*-alaninate ((2*R*,7*R*,*E*)-*L*-3v): yield (45 mg, 47%); colorless oil; > 20:1 dr; $[\alpha]^{20}_{D}$ = -9.2 (*c* 0.53, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 – 7.42 (m, 4H), 7.41 – 7.36 (m, 2H), 7.33 – 7.26 (m, 4H), 7.25 – 7.18 (m, 1H), 7.16 – 7.06 (m, 2H), 5.56 – 5.47 (m, 1H), 5.44 – 5.30 (m, 1H), 4.71 – 4.57 (m, 2H), 4.04 (t, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 2.54 – 2.33 (m, 4H), 1.45 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4, 172.5, 169.4, 144.1, 139.0, 135.7, 130.7, 129.7, 128.85, 128.76, 128.7, 128.6, 128.3, 128.2, 127.5, 127.1, 125.6, 72.8, 65.6, 52.5, 47.7, 42.6, 38.7, 18.3.

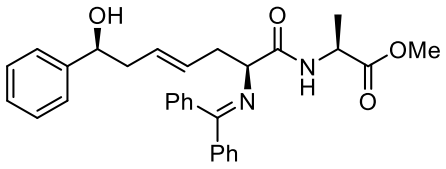
HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ($[M+H]^+$): 485.2435, found: 485.2434.



(2*S*,7*S*,*E*)-*D*-**3v**

methyl ((2*S*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*D*-alaninate ((2*S*,7*S*,*E*)-*D*-3v): yield (43 mg, 45%); colorless oil; > 20:1 dr; $[\alpha]^{20}_{D}$ = +9.9 (*c* 0.55, CH_2Cl_2).

HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ([M+H]$^+$): 485.2435, found: 485.2437.



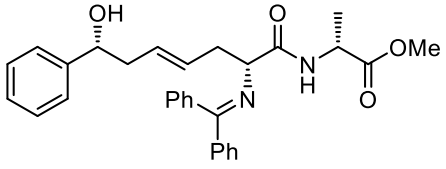
(2*S*,7*S*,*E*)-*L*-**3v**

methyl ((2*S*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*L*-alaninate ((2*S*,7*S*,*E*)-*L*-3v: yield (57 mg, 59%); colorless oil; 20:1 dr; $[\alpha]^{20}_D$ = +13.9 (*c* 0.59, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.55 (m, 2H), 7.48 – 7.29 (m, 7H), 7.25 – 7.19 (m, 4H), 7.18 – 7.01 (m, 3H), 5.47 – 5.37 (m, 1H), 5.37 – 5.20 (m, 1H), 4.65 – 4.49 (m, 2H), 3.94 (t, *J* = 6.2 Hz, 1H), 3.67 (s, 3H), 2.46 – 2.25 (m, 4H), 1.38 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 172.3, 170.0, 144.0, 139.1, 135.7, 130.7, 129.9, 128.9, 128.7, 128.6, 128.6, 128.2, 127.6, 127.2, 125.7, 72.8, 65.8, 52.4, 47.7, 42.4, 38.8, 18.6.

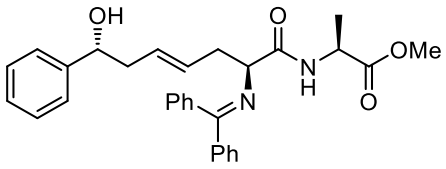
HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ([M+H]$^+$): 485.2435, found: 485.2440.



(2*R*,7*R*,*E*)-*D*-**3v**

methyl ((2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*D*-alaninate ((2*R*,7*R*,*E*)-*D*-3v): yield (58 mg, 60%); colorless oil; 20:1 dr; $[\alpha]^{20}_D$ = -14.2 (*c* 0.71, CH_2Cl_2).

HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ([M+H]$^+$): 485.2435, found: 485.2431.



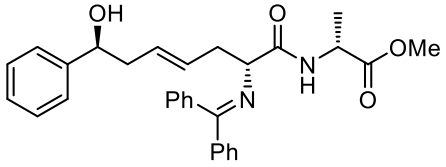
(2*S*,7*R*,*E*)-*L*-**3v**

methyl ((2*S*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*L*-alaninate ((2*S*,7*R*,*E*)-*L*-3v): yield (52 mg, 54%); colorless oil; 20:1 dr; $[\alpha]^{20}_{D}$ = +97.8 (*c* 0.52, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.53 (m, 3H), 7.42 – 7.29 (m, 6H), 7.27 – 7.20 (m, 4H), 7.18 – 7.12 (m, 1H), 7.10 – 6.99 (m, 2H), 5.48 – 5.29 (m, 2H), 4.61 – 4.49 (m, 2H), 3.94 (t, *J* = 6.6 Hz, 1H), 3.68 (s, 3H), 2.46 – 2.31 (m, 3H), 2.26 – 2.17 (m, 1H), 1.41 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 172.3, 169.8, 144.0, 139.1, 135.7, 130.7, 130.1, 129.2, 128.9, 128.7, 128.6, 128.2, 127.5, 127.2, 125.6, 72.6, 65.7, 52.4, 47.7, 43.4, 39.2, 18.7.

HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ($[M+H]^+$): 485.2435, found: 485.2441.



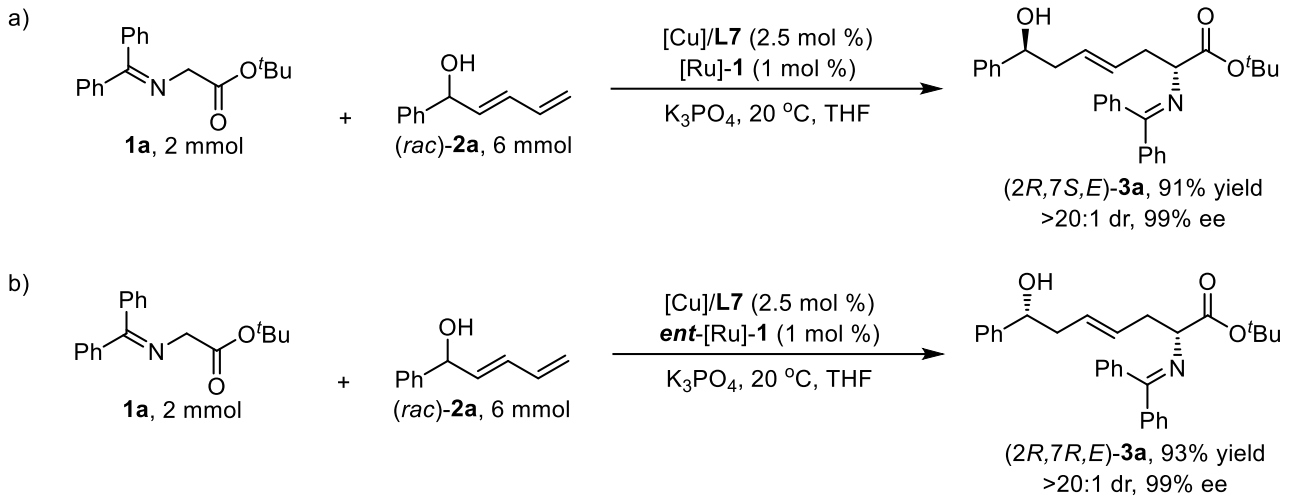
(2*R*,7*S*,*E*)-*D*-**3v**

methyl ((2*R*,7*S*,*E*)-2-((diphenylmethylene)amino)-7-hydroxy-7-phenylhept-4-enoyl)-*D*-alaninate ((2*R*,7*S*,*E*)-*D*-3v): yield (55 mg, 57%); colorless oil; 20:1 dr; $[\alpha]^{20}_{D}$ = -98.9 (*c* 0.54, CH_2Cl_2).

HRMS (ESI+) calcd. For $C_{30}H_{33}N_2O_4$ ($[M+H]^+$): 485.2435, found: 485.2436.

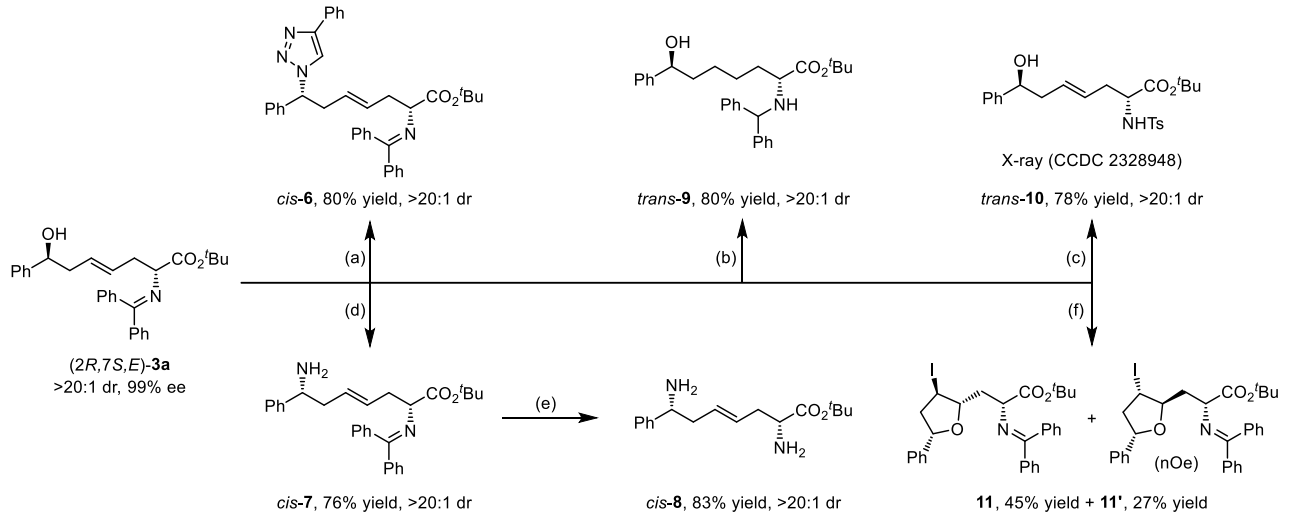
6. Scale-up experiments and synthetic transformations

Scheme S1. Scale-up experiments.



Under argon, to a flame dried Schlenk tube were added $Cu(MeCN)_4BF_4$ (0.05 mmol) and **L7** (0.055 mmol) and degassed THF (10 mL). The reaction mixture was stirred at 20 ºC for 30 min. Then, [Ru]-**1** or *ent*-[Ru]-**1** complex (0.02 mmol), imino ester **1a** (2 mmol), dienyl carbinol **2a** (6 mmol), K_3PO_4 (2 mmol) and THF (10 mL) were added into the Schlenk tube under argon. The reaction mixture was continuously stirred at 20 ºC. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography to give the desired enolate products, which were then directly analyzed by chiral HPLC to determine the dr value and the enantiomeric excess.

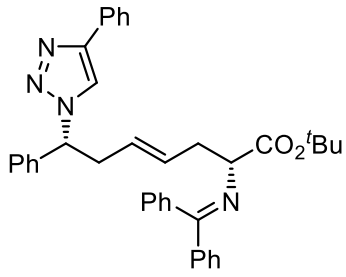
Scheme S2. Synthetic transformations.



Reaction conditions: (a) i. DIAD, DPPA, PPh_3, THF, ii. DIPEA, CuI, DMF, phenylacetylene; (b) Pd/C, H_2, EtOAc; (c) i. 15% citric acid, THF, ii. TsCl, Et_3N, DMAP; (d) i. DIAD, DPPA, PPh_3, THF, ii. PPh_3, THF, H_2O; (e) 15% citric acid, THF, H_2O; (f) I_2, $NaHCO_3$, MeCN, -20 °C.

(2*R*,7*S*,*E*)-**3a** (76 mg, 0.2 mmol) and PPh_3 (105 mg, 0.4 mmol) were dissolved in dry THF (5 mL) under an argon atmosphere, DIAD (81 mg, 0.4 mmol) was added dropwise under 0 ℃ and stirred for 10 min. Then DPPA (111 mg, 0.4 mmol) was added dropwise at the same time. The reaction mixture was stirred at room temperature for 16 h. Then the solution was concentrated under reduced pressure. The crude product was obtained by silica-gel column chromatography.

Another flame-dried Schlenk tube was cooled to room temperature and evacuated and backfilled with argon for three times. To this Schlenk tube were added the crude product (96 mg, 0.2 mmol), Phenylacetylene (27 mg, 0.26 mmol), CuI (3.8 mg, 0.02 mmol), DIPEA (52 mg, 0.4 mmol) and degassed DMF (2 mL). The mixture was stirred overnight at 30 ℃. And then the mixture was concentrated in vacuo and purified by silica-gel column chromatography to give *cis*-**6** in 80% overall yield with > 20:1 dr.



cis-**6**

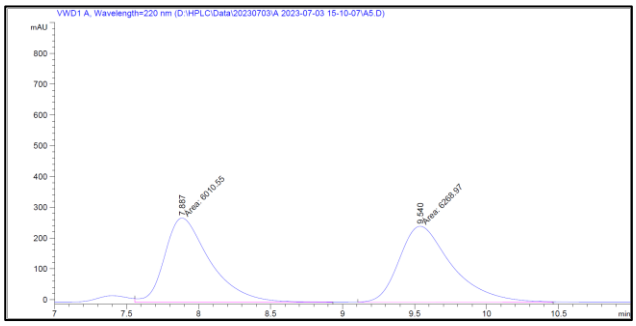
***tert*-butyl (2*R*,7*R*,*E*)-2-((diphenylmethylene)amino)-7-phenyl-7-(4-phenyl-1*H*-1,2,3-triazol-1-yl)hept-4-enoate (*cis*-6)**: yield (92 mg, 80%); sticky liquid; > 20:1 dr; $[\alpha]^{20}_D$ = +38.7 (*c* 0.72, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralcel AD-H, *i*-propanol/hexane = 25/75, flow rate 1.0 mL/min, λ = 220 nm); t_r = 7.89 and 9.54 min.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.66 (m, 2H), 7.55 – 7.51 (m, 3H), 7.35 – 7.28 (m, 6H), 7.27 – 7.19 (m, 8H), 7.05 – 7.00 (m, 2H), 5.52 – 5.43 (m, 2H), 5.35 – 5.26 (m, 1H), 3.85 (dd, *J* = 7.0, 5.8 Hz, 1H), 3.21 – 3.08 (m, 1H), 2.98 – 2.83 (m, 1H), 2.51 – 2.38 (m, 2H), 1.32 (s, 9H).

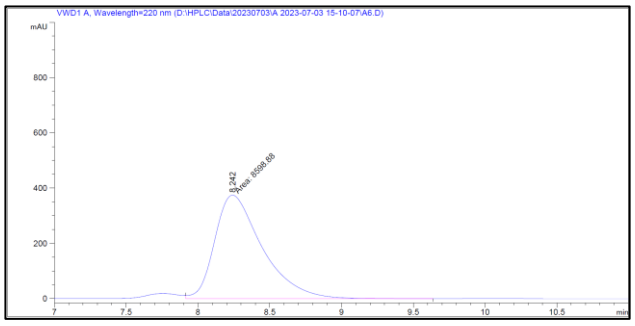
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 170.2, 147.6, 139.5, 138.5, 136.5, 130.8, 130.6, 130.2, 129.0, 128.8, 128.7, 128.6, 128.4, 128.01, 127.99, 127.8, 127.1, 127.0, 125.7, 118.9, 81.0, 65.7, 65.3, 38.3, 36.8, 28.

HRMS (ESI+) calcd. For $C_{38}H_{39}N_4O_2$ ($[M+H]^+$): 583.7580, found: 583.7588.

HPLC chromatogram of compound *cis*-6



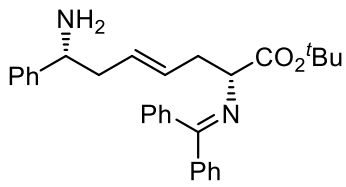
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.887	FM	0.3661	6010.55420	273.62256	48.9478
2	9.540	MM	0.4234	6268.96875	246.75447	51.0522



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.242	FM	0.3830	8598.88281	374.22989	100.0000

(2*R*,7*S*,*E*)-**3a** (76 mg, 0.2 mmol) and PPh_3 (105 mg, 0.4 mmol) were dissolved in dry THF (5 mL) under an argon atmosphere, DIAD (81 mg, 0.4 mmol) was added dropwise under 0 ℃ and stirred for 10 min. Then DPPA (111 mg, 0.4 mmol) was added dropwise at the same time. The reaction mixture was stirred at room temperature for 16 h. Then the solution was concentrated under reduced pressure. The crude product was obtained by silica-gel column chromatography.

A flame-dried Schlenk tube was cooled to room temperature and evacuated and backfilled with argon for three times. To this Schlenk tube were added the crude product (96 mg, 0.2 mmol), PPh_3 (105 mg, 0.4 mmol), H_2O (0.2 mL) and THF (2 mL). The mixture was stirred overnight at 40 ℃. And then the mixture was concentrated in vacuo and purified by silica-gel column chromatography to give *cis*-**7** in 76% overall yield with > 20:1 dr.



cis-**7**

***tert*-butyl (2*R*,7*R*,*E*)-7-amino-2-((diphenylmethylene)amino)-7-phenylhept-4-enoate (*cis*-7)**: yield (68 mg, 76%); colorless oil; > 20:1 dr, $[\alpha]^{20}_D$ = +74.0 (c 0.27, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralpak IC, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm); t_r = 15.50 and 19.13 min.

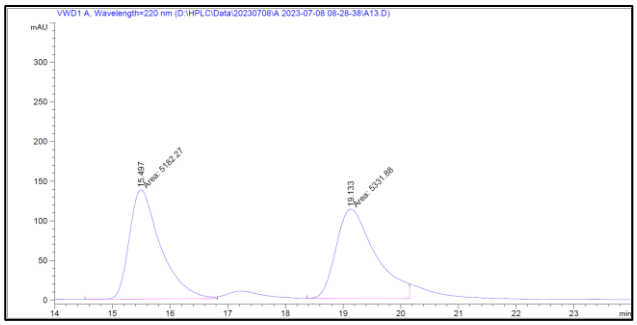
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.54 (m, 2H), 7.38 – 7.33 (m, 3H), 7.31 – 7.19 (m, 7H),

7.16 – 7.06 (m, 3H), 5.43 – 5.30 (m, 2H), 3.90 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.81 (dd, *J* = 8.2, 5.0 Hz, 1H), 2.57 – 2.46 (m, 2H), 2.34 – 2.26 (m, 1H), 2.22 – 2.13 (m, 1H), 1.36 (s, 9H).

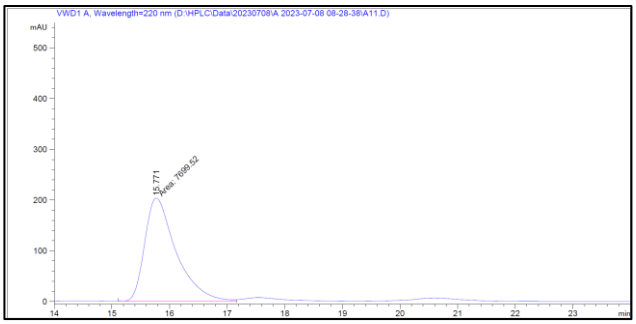
^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.0, 170.1, 145.8, 139.6, 136.6, 130.2, 129.63, 129.56, 128.7, 128.5, 128.4, 128.3, 128.0, 127.8, 126.9, 126.3, 81.0, 66.0, 55.4, 43.0, 37.0, 28.0.

HRMS (ESI+) calcd. For $C_{30}H_{35}N_2O_2$ ($[M+H]^+$): 455.2693, found: 455.2695.

HPLC chromatogram of compound *cis*-7

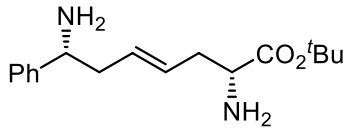


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.497	MF	0.6272	5182.27393	137.71826	49.2885
2	19.133	MF	0.7893	5331.88281	112.58241	50.7115



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.771	MF	0.6305	7699.51904	203.53770	100.0000

The compound *cis*-**7** was dissolved in THF (2 mL) and 15% citric acid (1 mL) was added. The tube was sealed, and the mixture was stirred for 2 h. The mixture was then neutralized by adding sat. aq. $NaHCO_3$. The resulting solution was extracted with EtOAc (3 × 2 mL). The organic phases were collected and dried over Na_2SO_4. After filtration, the solvent was removed under reduce pressure, and the crude product was purified by silica gel chromatography to give *cis*-**8** in 83% yield with > 20:1 dr.



cis-**8**

***tert*-butyl (2*R*,7*R*,*E*)-2,7-diamino-7-phenylhept-4-enoate (*cis*-8)**: yield (48 mg, 83%); colorless oil; > 20:1 dr; $[\alpha]^{20}_D$ = +64.2 (*c* 0.27, CH_2Cl_2).

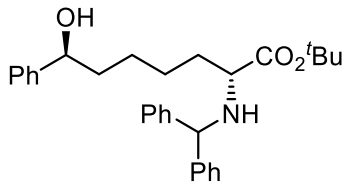
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.21 (m, 5H), 5.56 – 5.42 (m, 2H), 4.08 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.36 (dd, *J* = 8.2, 5.0 Hz, 1H), 2.56 – 2.40 (m, 3H), 2.31 – 2.23 (m, 1H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 141.3, 130.1, 129.4, 128.8, 127.9, 126.7, 81.8, 55.3,

53.7, 40.7, 36.9, 28.0.

HRMS (ESI+) calcd. For $C_{17}H_{27}N_2O_2$ ($[M+H]^+$): 291.2067, found: 291.2061.

A flame-dried Schlenk tube was cooled to room temperature and evacuated and backfilled with hydrogen for three times. To this Schlenk tube were added (2*R*,7*S*,*E*)-**3a** (91 mg, 0.2 mmol), Pd/C (3 mg, 10 wt%), EtOAc (2 mL) and the reaction mixture was stirred under 1 atm hydrogen gas pressure at room temperature overnight. Then the resulting mixture was concentrated and purified by flash column chromatography to afford the desired product *trans*-**9** in 80% overall yield with > 20:1 dr.



trans-**9**

***tert*-butyl (2*R*,7*S*)-2-(benzhydrylamino)-7-hydroxy-7-phenylheptanoate (*trans*-9)**: yield (74 mg, 80%); colorless oil; > 20:1 dr; $[\alpha]^{20}_D$ = -0.9 (*c* 0.45, CH_2Cl_2).

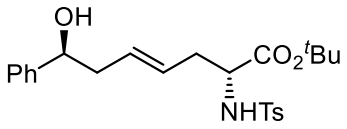
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.33 (m, 2H), 7.30 – 7.25 (m, 4H), 7.25 – 7.07 (m, 9H), 4.70 (s, 1H), 4.56 (dd, *J* = 7.4, 5.8 Hz, 1H), 2.95 (dd, *J* = 7.4, 5.8 Hz, 1H), 1.86 – 1.58 (m, 5H), 1.54 – 1.45 (m, 2H), 1.39 (s, 9H), 1.34 – 1.28 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.1, 144.8, 144.5, 142.9, 128.5, 128.44, 128.39, 127.7, 127.5, 127.3, 127.1, 125.8, 80.9, 74.5, 65.5, 59.7, 38.9, 33.7, 28.2, 25.7, 25.6.

HRMS (ESI+) calcd. For $C_{30}H_{38}NO_3$ ($[M+H]^+$): 460.2846, found: 460.2842.

To a solution of (2*R*,7*S*,*E*)-**3a** (0.2 mmol) in THF (0.1 mL) was added 15% citric acid (1 mL). The mixture was stirred at room temperature for 1 h, quenched with sat. aq. $NaHCO_3$ and extracted with EtOAc (3 × 2 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was removed and the crude product amine was obtained. To a solution of crude product in DCM (2 mL) was added triethylamine (61 mg, 0.6 mmol) and TsCl (114 mg, 0.6 mmol) followed by DMAP (7.5 mg, 0.06 mmol). The mixture was stirred overnight and then the resulting mixture was concentrated and purified by flash column chromatography to afford the desired product *trans*-**10** in 78% overall

yield with > 20:1 dr.



trans-**10**

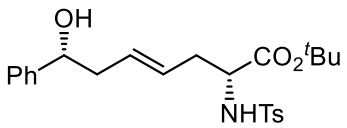
***tert*-butyl (2*R*,7*S*,*E*)-7-hydroxy-2-((4-methylphenyl)sulfonamido)-7-phenylhept-4-enoate (*trans*-10)**: yield (63 mg, 78%); white solid; m.p. 88-90 °C; > 20:1 dr; $[\alpha]^{10}_D$ = -53.9 (*c* 0.53, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.25 – 7.14 (m, 4H), 5.48 – 5.31 (m, 2H), 5.19 (d, *J* = 9.2 Hz, 1H), 4.63 (dd, *J* = 8.0, 4.8 Hz, 1H), 3.83 – 3.74 (m, 1H), 2.41 – 2.33 (m, 3H), 2.32 (s, 3H), 2.31 – 2.25 (m, 1H), 1.19 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.0, 143.9, 143.5, 137.0, 131.3, 129.6, 128.4, 127.5, 127.3, 127.0, 125.7, 82.6, 73.2, 55.8, 42.5, 36.7, 27.7, 21.4.

HRMS (ESI+) calcd. For $C_{24}H_{32}NO_5S$ ($[M+H]^+$): 446.1996, found: 446.1990.

To a solution of (2*R*,7*R*,*E*)-**3a** (0.2 mmol) in THF (0.1 mL) was added 15% citric acid (1 mL). The mixture was stirred at room temperature for 1 h, quenched with sat. aq. $NaHCO_3$ and extracted with EtOAc (3 × 2 mL). The organic layers were combined and dried over Na_2SO_4. The solvent was removed and the crude product amine was obtained. To a solution of crude product in DCM (2 mL) was added triethylamine (61 mg, 0.6 mmol) and TsCl (114 mg, 0.6 mmol) followed by DMAP (7.5 mg, 0.06 mmol). The mixture was stirred overnight and then the resulting mixture was concentrated and purified by flash column chromatography to afford the desired product *cis*-**10** in 77% overall yield with > 20:1 dr.



cis-**10**

***tert*-butyl (2*R*,7*R*,*E*)-7-hydroxy-2-((4-methylphenyl)sulfonamido)-7-phenylhept-4-enoate (*cis*-10)**: yield (62 mg, 77%); white solid; m.p. 100-102 °C; > 20:1 dr; $[\alpha]^{10}_D$ = +17.8 (*c* 0.47, CH_2Cl_2).

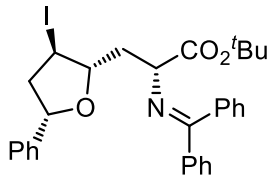
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.27 (m, 4H), 7.23 – 7.19 (m,

3H), 5.48 – 5.31 (m, 2H), 5.09 (d, *J* = 9.2 Hz, 1H), 4.61 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.82 – 3.75 (m, 1H), 2.44 – 2.33 (m, 3H), 2.32 (s, 3H), 2.31 – 2.26 (m, 1H), 1.18 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 143.8, 143.5, 136.9, 131.3, 129.6, 128.4, 127.5, 127.3, 127.1, 125.7, 82.6, 73.0, 55.8, 42.8, 36.7, 27.7, 21.4.

HRMS (ESI+) calcd. For $C_{24}H_{32}NO_5S$ ($[M+H]^+$): 446.1996, found: 446.1997.

To a solution of (2*R*,7*S*,*E*)-**3a** (137 mg, 0.3 mmol) and $NaHCO_3$ (51 mg, 0.6 mmol) in MeCN (3 mL)was added I_2 (229 mg, 0.9 mmol) at -20 ºC. The mixture was stirred for 12 h before quenched by addition of sat. aq. Na_2SO_3. The aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were concentrated, and purified using flash chromatography to give the desired product **11** in 45% yield with > 20:1 dr and **11'** in 27% yield with > 20:1 dr.



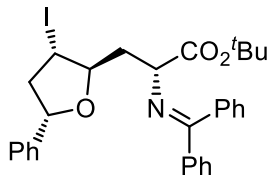
11

***tert*-butyl (*R*)-2-((diphenylmethylene)amino)-3-((2*S*,3*R*,5*S*)-3-iodo-5-phenyltetrahydrofuran-2-yl)propanoate (11)**: yield (79 mg, 45%); white solid; m.p. 140-142 ºC; > 20:1 dr; $[\alpha]^{15}_D$ = -18.0 (*c* 0.56, CH_2Cl_2).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.27 (m, 10H), 7.18 – 7.11 (m, 3H), 5.07 (dd, *J* = 12.6, 2.6 Hz, 1H), 4.30 – 4.23 (m, 2H), 3.98 (dd, *J* = 9.0, 6.6 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.41 – 2.30 (m, 1H), 1.89 – 1.78 (m, 1H), 1.71 – 1.64 (m, 1H), 1.20 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.7, 147.6, 142.4, 142.0, 129.0, 128.4, 128.2, 128.0, 127.6, 127.5, 127.3, 126.6, 92.1, 80.6, 71.6, 65.8, 63.2, 42.9, 32.1, 27.8, 23.9.

HRMS (ESI+) calcd. For $C_{30}H_{33}INO_3$ ($[M+H]^+$): 582.1500, found: 582.1492.



11'

***tert*-butyl (*R*)-2-((diphenylmethylene)amino)-3-((2*R*,3*S*,5*S*)-3-iodo-5-phenyltetrahydrofuran-2-yl)propanoate (11')**: yield (47 mg, 27%); white solid; m.p. 68-70 °C; > 20:1 dr; $[\alpha]^{20}_{D}$ = +132.9 (*c* 0.44, CH_2Cl_2).

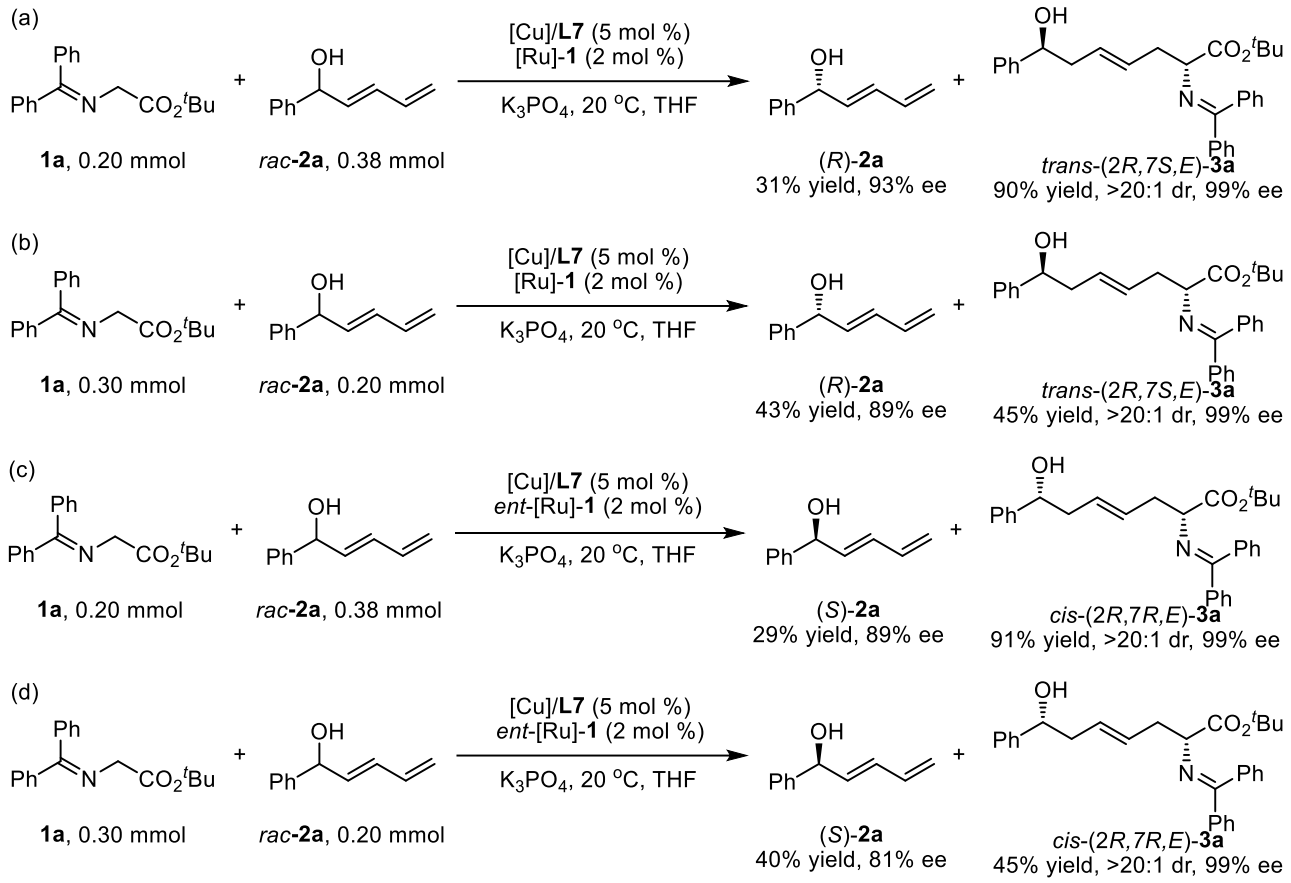
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.45 (m, 4H), 7.44 – 7.26 (m, 8H), 7.24 – 7.16 (m, 3H), 4.60 (dd, *J* = 11.6, 2.4 Hz, 1H), 4.14 – 4.06 (m, 1H), 3.93 (d, *J* = 8.8 Hz, 1H), 3.90 – 3.84 (m, 1H), 2.72 – 2.62 (m, 1H), 2.40 – 2.32 (m, 1H), 2.14 – 2.07 (m, 1H), 1.96 – 1.86 (m, 1H), 1.19 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 143.0, 142.8, 142.1, 128.3, 128.2, 127.8, 127.7, 127.6, 127.4, 126.1, 92.5, 80.3, 72.7, 65.4, 62.6, 42.3, 37.7, 27.7, 23.2.

HRMS (ESI+) calcd. For $C_{30}H_{33}INO_3$ ($[M+H]^+$): 582.1500, found: 582.1502.

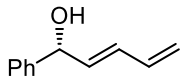
7. Kinetic resolution studies

Scheme S3. **Kinetic resolution studies.**



Under argon, to a flame dried Schlenk tube were added $Cu(MeCN)_4BF_4$ (0.01 mmol) and **L7** (0.01 mmol) and degassed THF (1 mL). The reaction mixture was stirred at 20 ºC for about 30 min. Then, [Ru]-**1** (0.004 mmol), imino ester **1a** (0.2 mmol), dienyl carbinol **2a** (0.38 mmol), K_3PO_4 (0.2 mmol) and THF (1 mL) were added into the Schlenk tube under argon. The reaction mixture was continuously stirred at 20 ºC. Once starting material was consumed (monitored by TLC), the organic solvent was removed by rotary evaporation. The whole residue was further purified by column chromatography to give the desired product **3a**, which was analyzed by HPLC to determine the dr value and enantiomeric excess. The recovered **2a** was analyzed by HPLC to determine the enantiomeric excess. We can get the *trans*-(2*R*,7*S*,*E*)-**3a** in 90% yield (> 20:1 dr, 99% ee) and (*R*)-**2a** in 31% yield (93% ee) (Scheme S3a). By the same operation, but using 0.2 mmol **2a** and 0.3 mmol **1a**, we can only get the *trans*-(2*R*,7*S*,*E*)-**3a** in 45% yield with > 20:1 dr and 99% ee, and (*R*)-**2a** in 43% yield with 89% ee (Scheme S3b). By the same operation, but using *ent*-[Ru]-**1** instead of [Ru]-

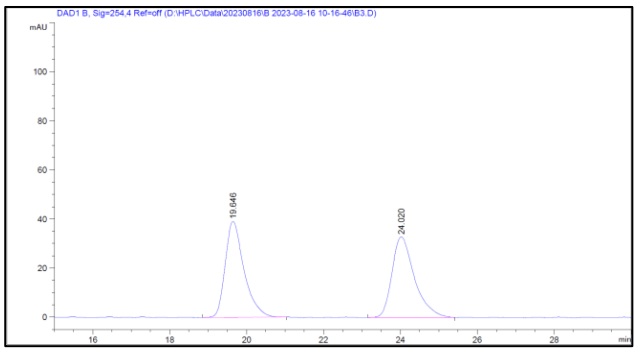
1, we can get the *cis*-(2*R*,7*R*,*E*)-**3a** in 91% yield with > 20:1 dr and 99% ee, and (*S*)-**2a** in 29% yield with 89% ee (Scheme S3c). When we use 0.20 mmol **2a** and 0.30 mmol **1a** with *ent*-[Ru]-**1**, the *cis*-(2*R*,7*R*,*E*)-**3a** in 45% yield with > 20:1 dr and 99% ee, and (*S*)-**2a** in 40% yield with 81% ee will be obtained. Thus, the bimetallic copper/ruthenium relay catalysis undergoes kinetic resolution process.

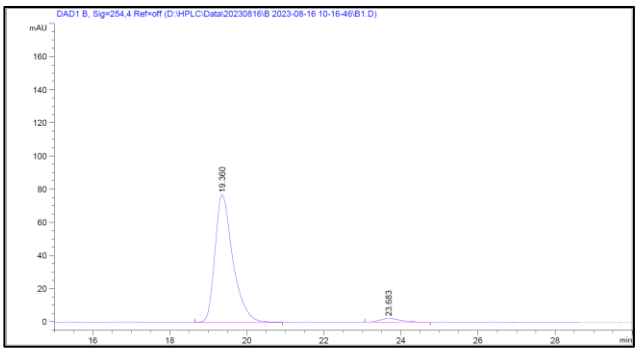


(*R*)-**2a**

(*R*,*E*)-1-phenylpenta-2,4-dien-1-ol ((*R*)-2a): yield (30 mg, 31%); colorless oil; $[\alpha]^{20}_{D}$ = -35.8 (*c* 0.51, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralpak OD-H, *i*-propanol/hexane = 3/97, flow rate 1 mL/min, λ = 254 nm); t_r = 19.65 and 24.02 min.

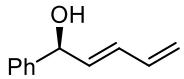
HPLC chromatogram of compound (*R*)-2a





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.646	BB	0.5101	1328.04858	39.12090	49.8424
2	24.020	BB	0.6084	1336.44556	32.86478	50.1576

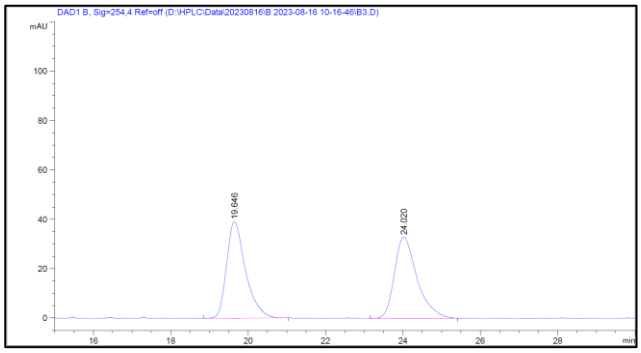
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.360	BB	0.4830	2467.29248	76.75365	96.7882
2	23.683	BB	0.4526	81.87313	2.22864	3.2118

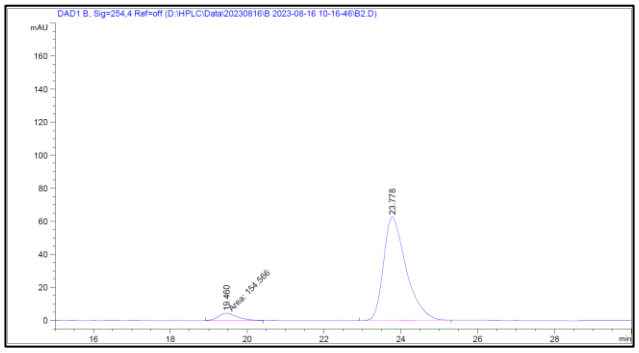


(*S*)-**2a**

(*S*,*E*)-1-phenylpenta-2,4-dien-1-ol ((*S*)-2a): yield (28 mg, 29%); colorless oil; $[\alpha]^{20}_{D}$ = +31.1 (*c* 0.67, CH_2Cl_2); The product was analyzed by HPLC to determine the enantiomeric excess: 89% ee (Chiralpak OD-H, *i*-propanol/hexane = 3/97, flow rate 1 mL/min, λ = 254 nm); t_r = 19.65 and 24.02 min.

HPLC chromatogram of compound (*S*)-2a





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.646	BB	0.5101	1328.04858	39.12090	49.8424
2	24.020	BB	0.6084	1336.44556	32.86478	50.1576

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.460	FM	0.5754	154.56577	4.47691	5.7026
2	23.778	BB	0.6268	2555.87793	62.54356	94.2974

8. X-ray structures of (2*R*,7*S*,*E*)-*trans*-10 and (2*R*,7*R*,*E*)-*cis*-10

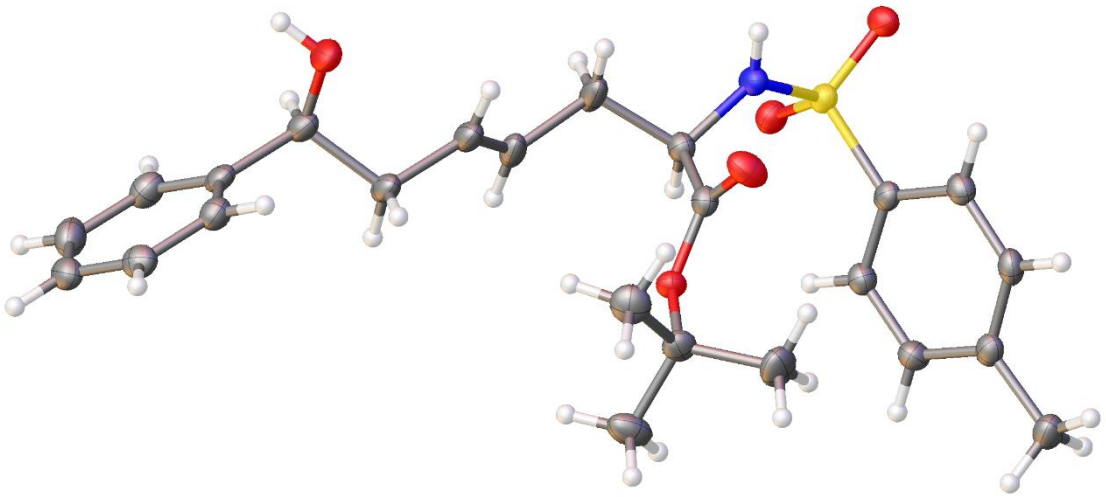


Figure S1. X-ray structure of (2*R*,7*S*,*E*)-*trans*-**10**.

Crystal data for (2*R*,7*S*,*E*)-*trans*-**10**: 2($C_{24}H_{31}NO_5S$), M_r = 891.11, T = 100 K, monoclinic, space group P 1 21 1, a = 18.8686(2), b = 5.43670(10), c = 22.9849(2) Å, α = 90, β = 94.9320(10), γ = 90, V = 2349.13(5) Å3, Z = 2, 8325 unique reflections, final R_1 = 0.0362 and wR_2 = 0.0991 for 8532 observed [I>2σ(I)] reflections, Flack χ = 0.023(13). CCDC 2328948 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

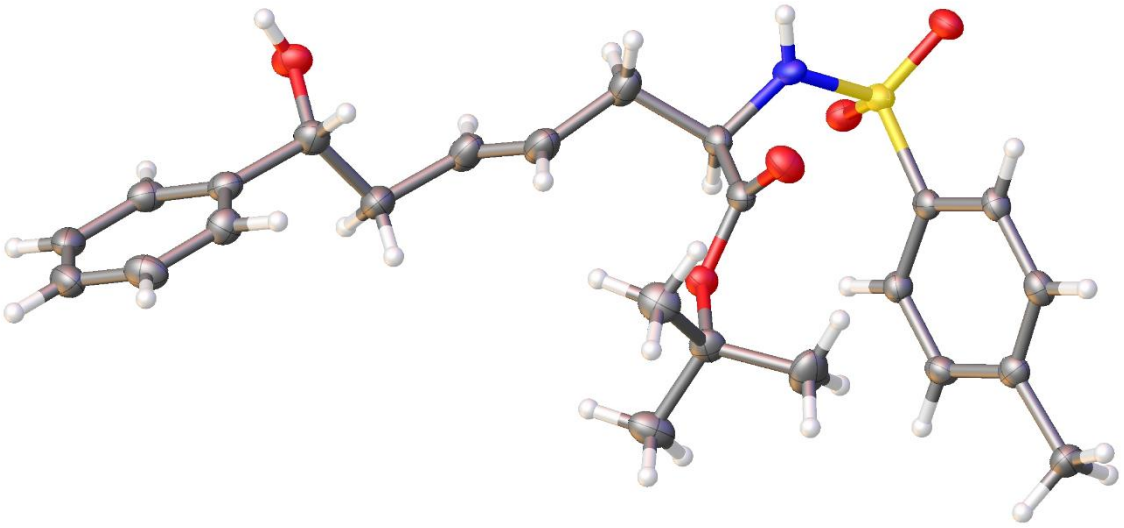


Figure S2. X-ray structure of (2*R*,7*R*,*E*)-*cis*-**10**.

Crystal data for (2*R*,7*R*,*E*)-*cis*-**10**: $C_{24}H_{31}NO_5S$, M_r = 445.56, T = 100 K, monoclinic, space group P 1 21 1, a = 12.6662(4), b = 5.60080(10), c = 36.6350(11) Å, α = 90, β = 116.175(4), γ = 90, V = 2332.40(13) Å3, Z = 4, 5635 unique reflections, final R_1 = 0.0615 and wR_2 = 0.1710 for 7349 observed [I>2σ(I)] reflections, Flack χ = 0.042(15). CCDC 2328949 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

9. References

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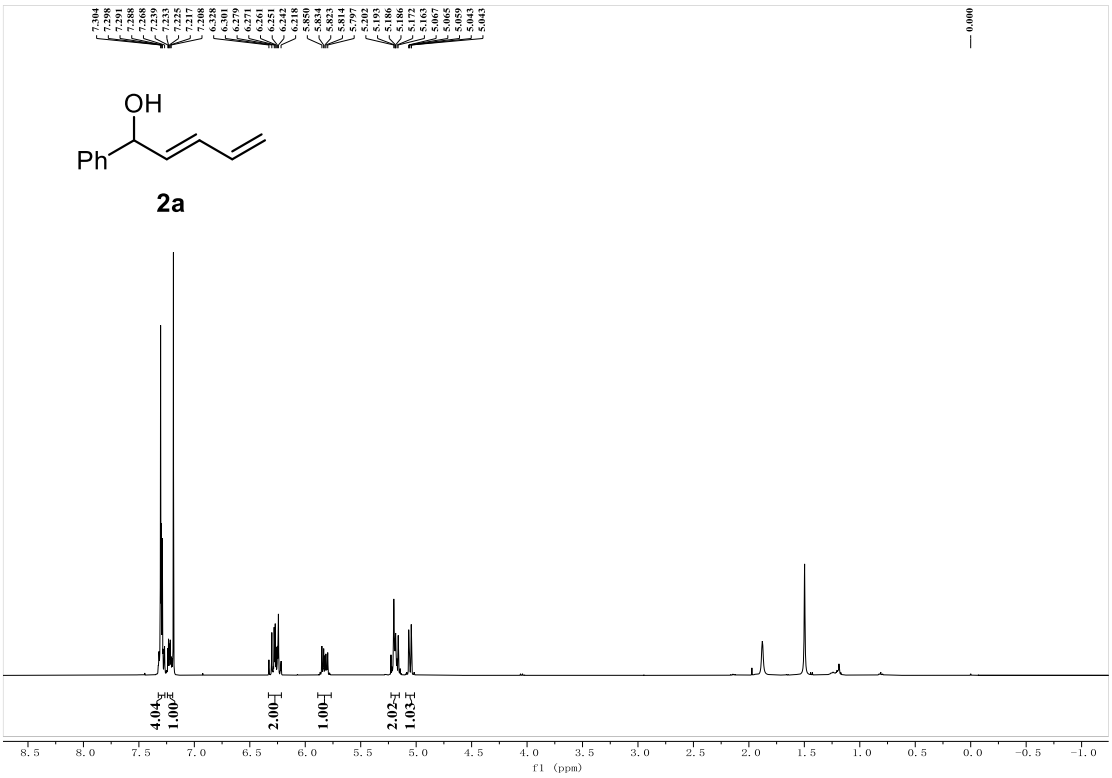
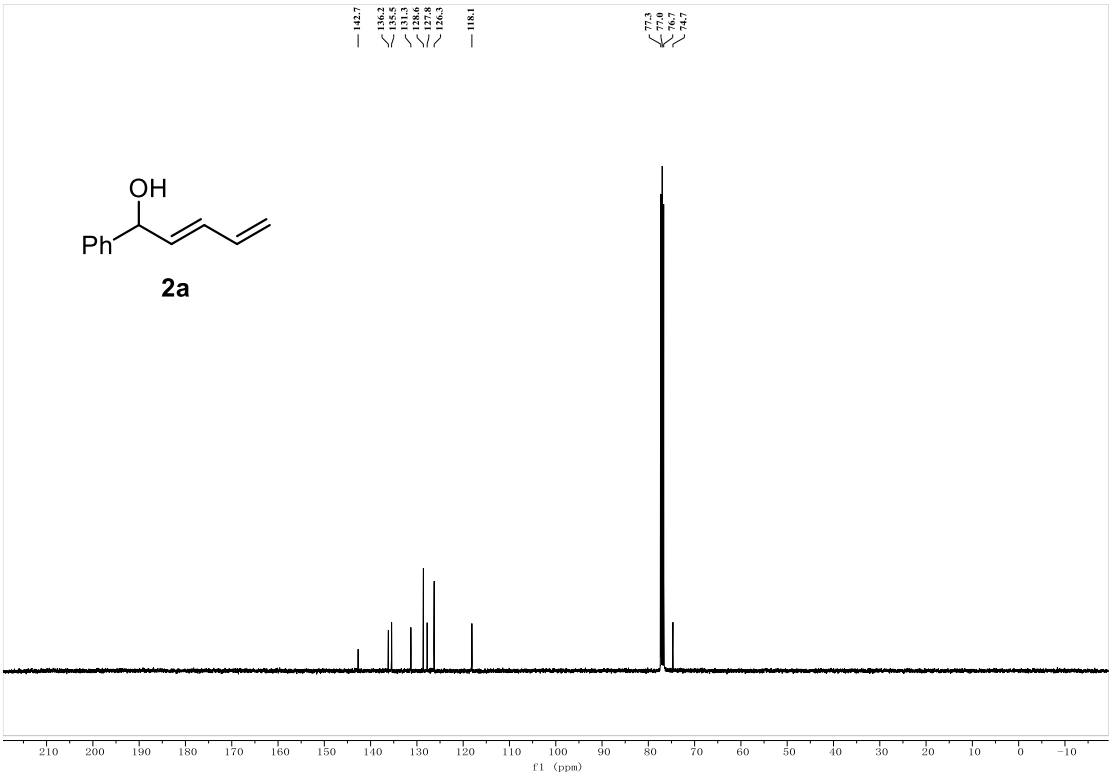
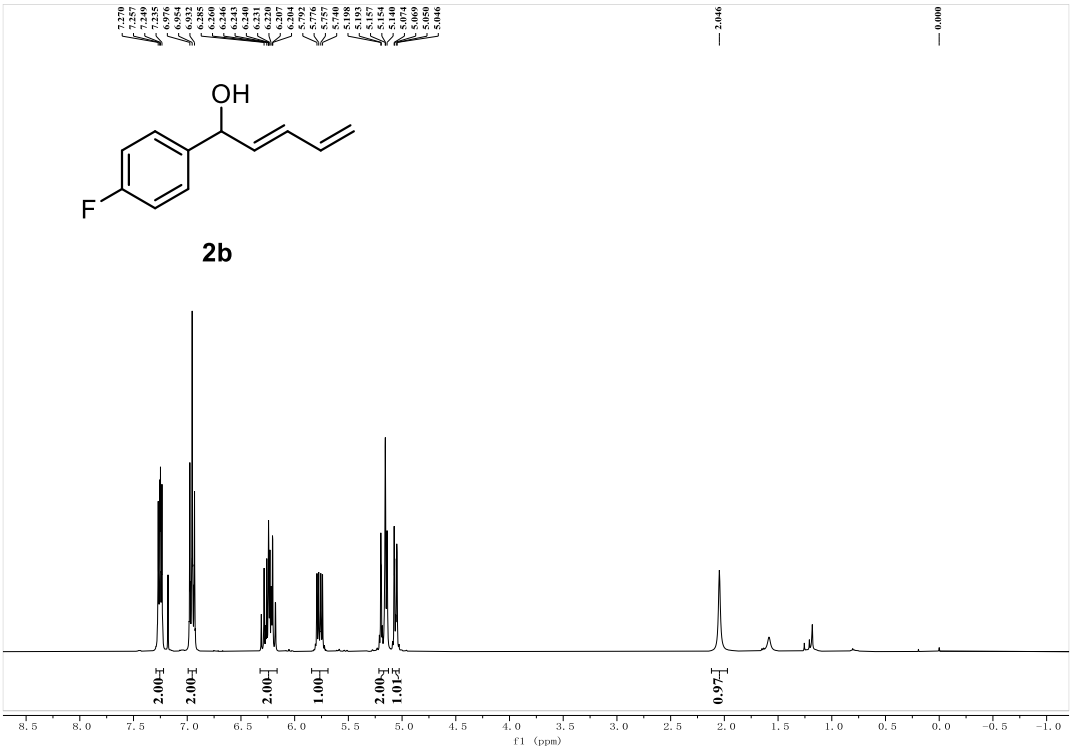
10. NMR spectra



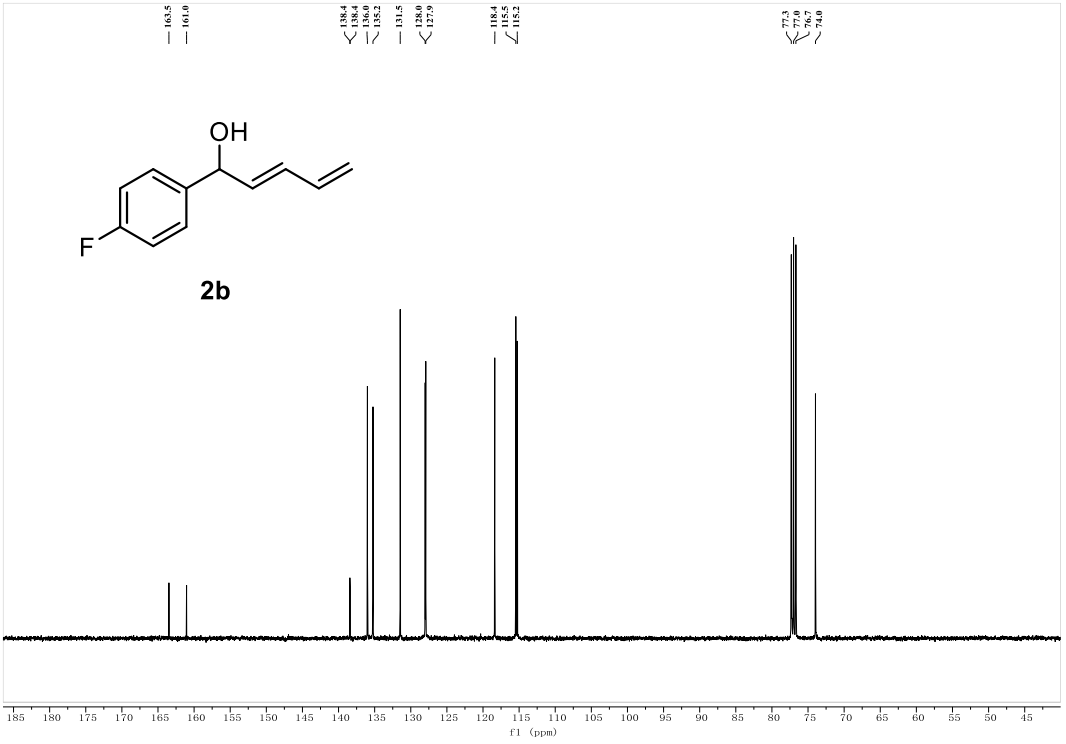
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



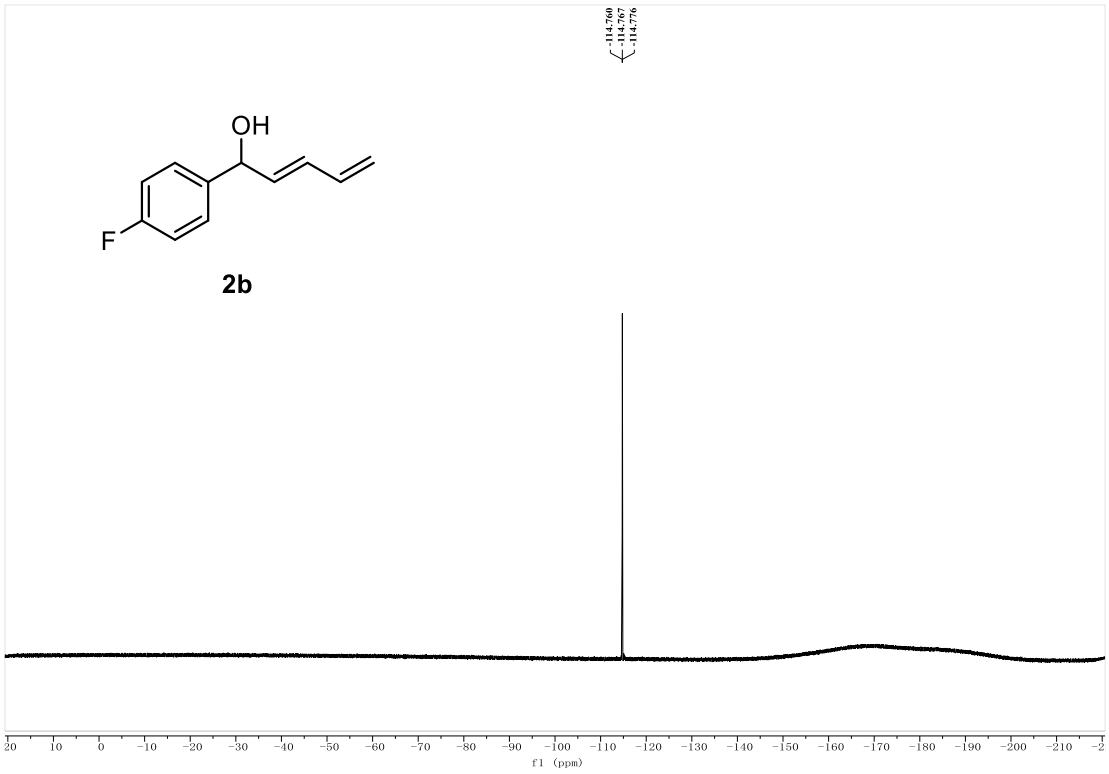
^{13}C NMR (101 MHz, $CDCl_3$) of **2a**



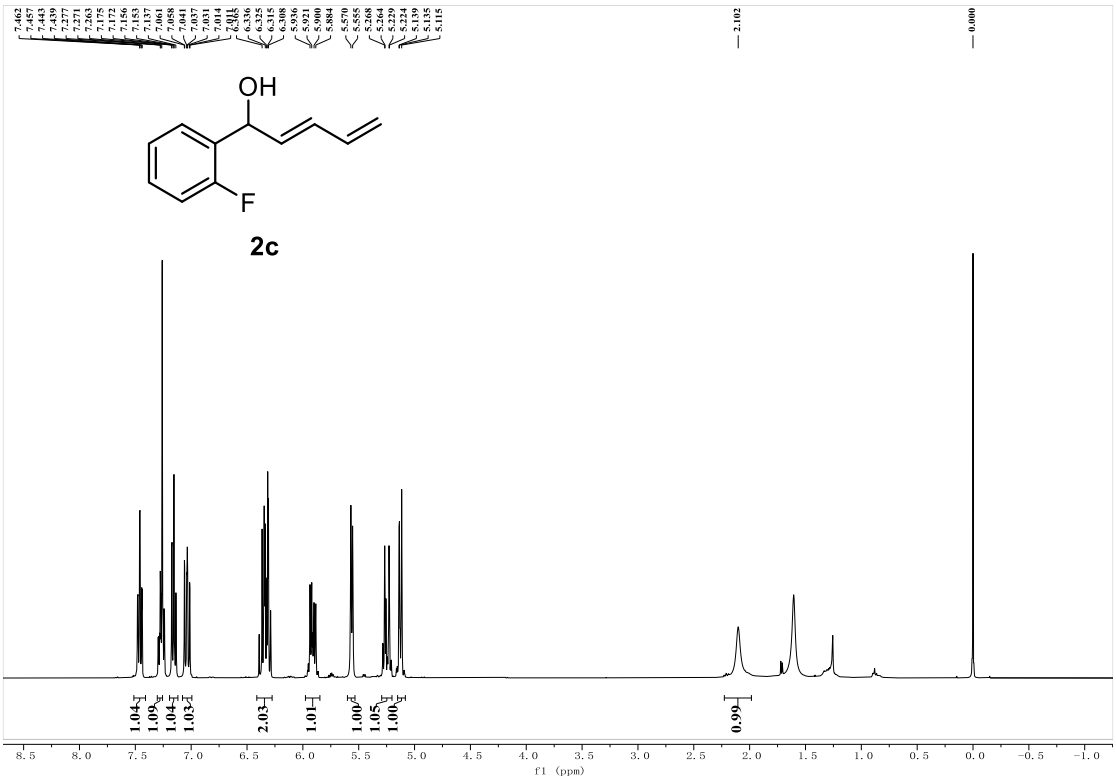
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



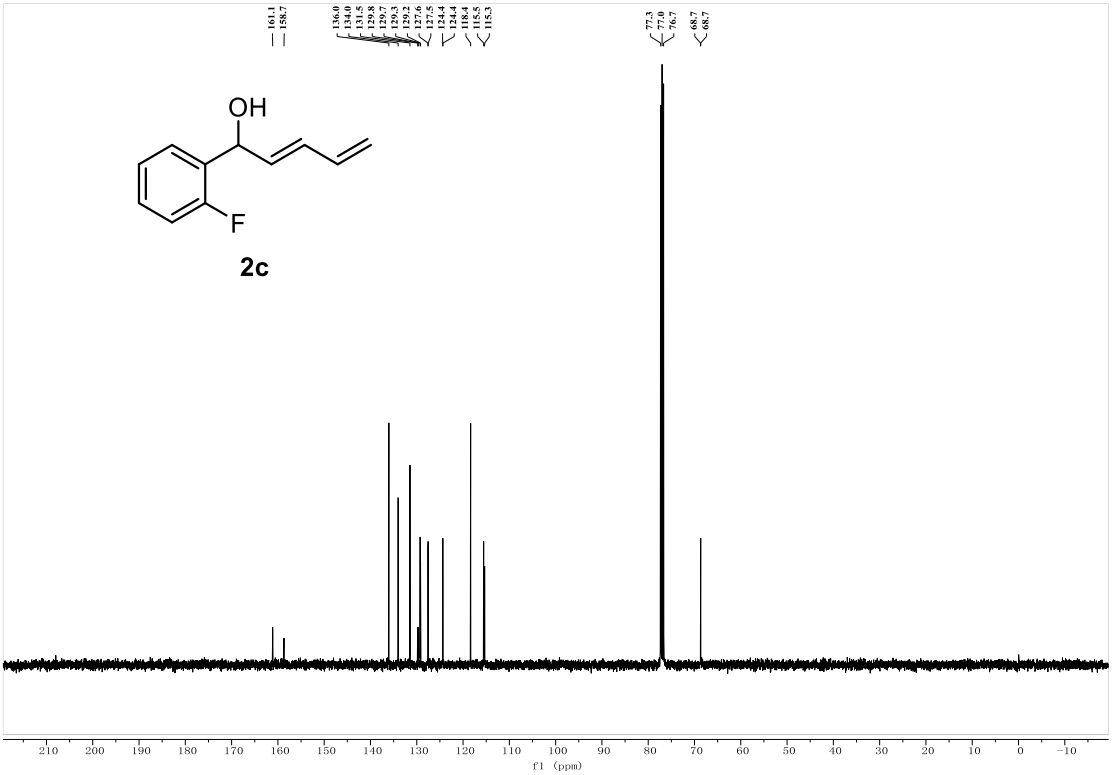
^{13}C NMR (101 MHz, $CDCl_3$) of **2b**



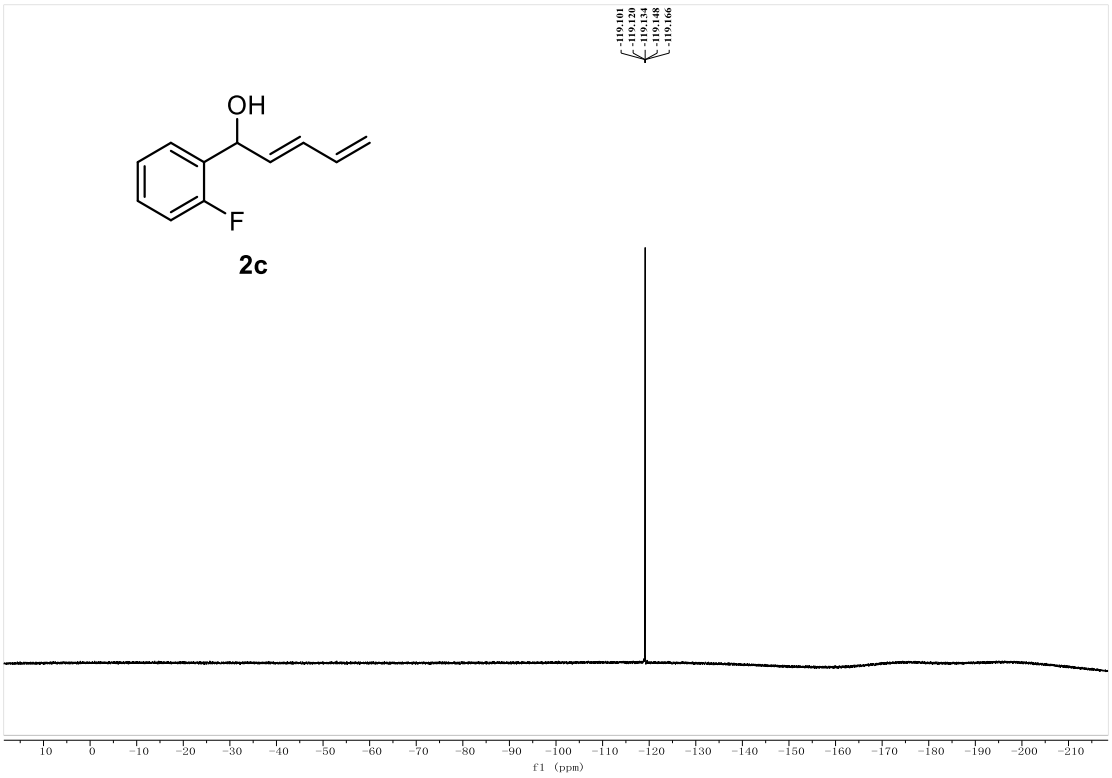
^{19}F NMR (376 MHz, $CDCl_3$) of **2b**



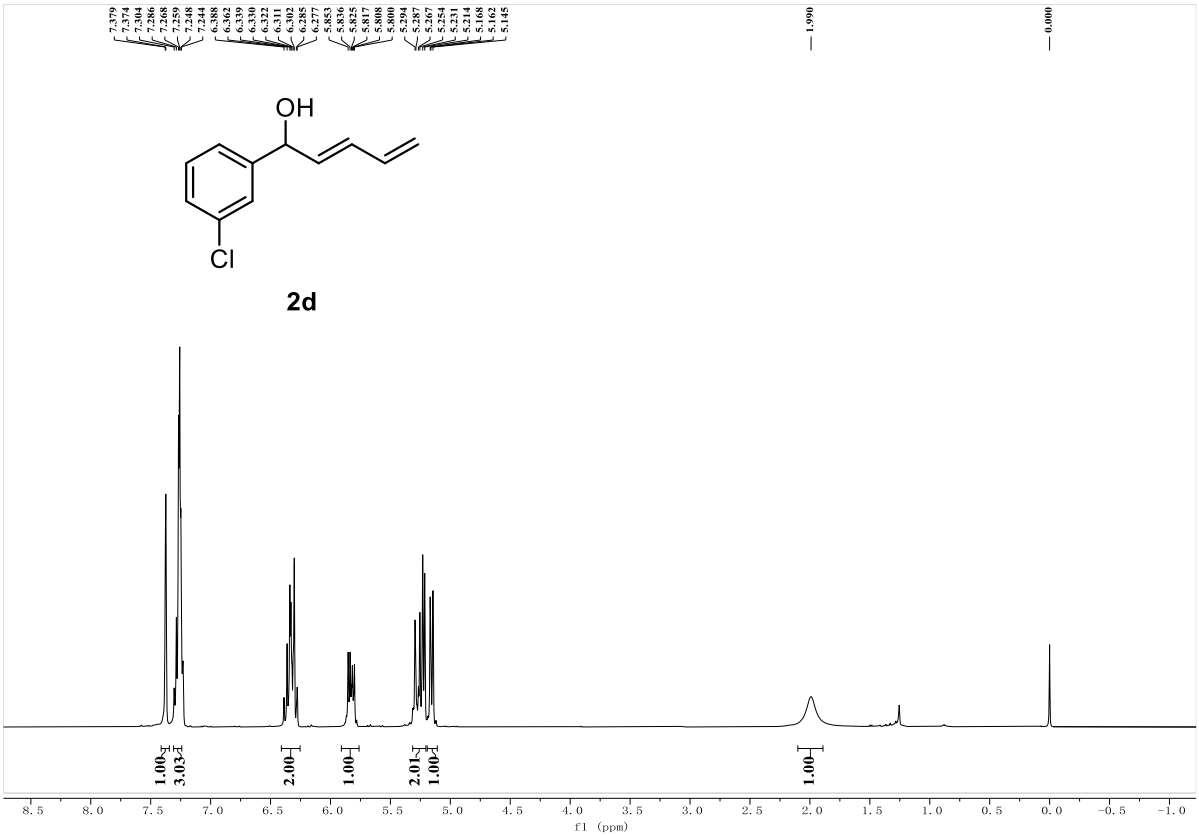
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



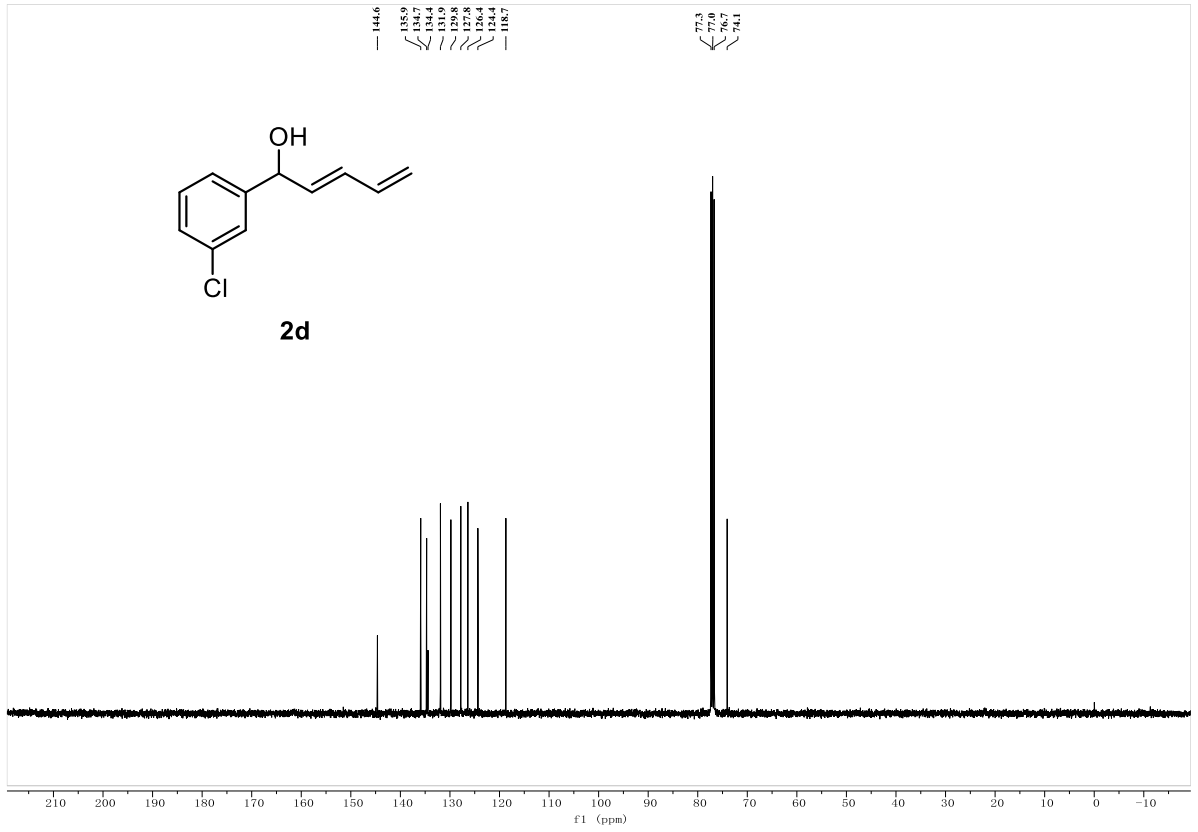
^{13}C NMR (101 MHz, $CDCl_3$) of **2c**



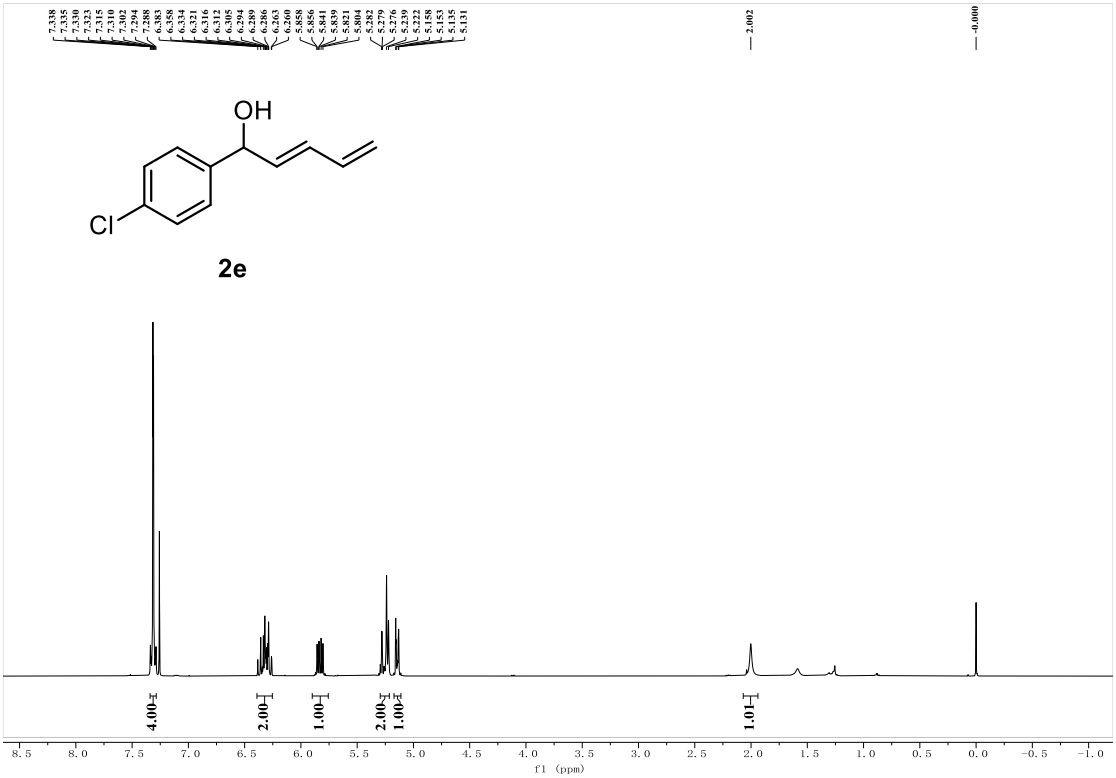
^{19}F NMR (376 MHz, $CDCl_3$) of **2c**



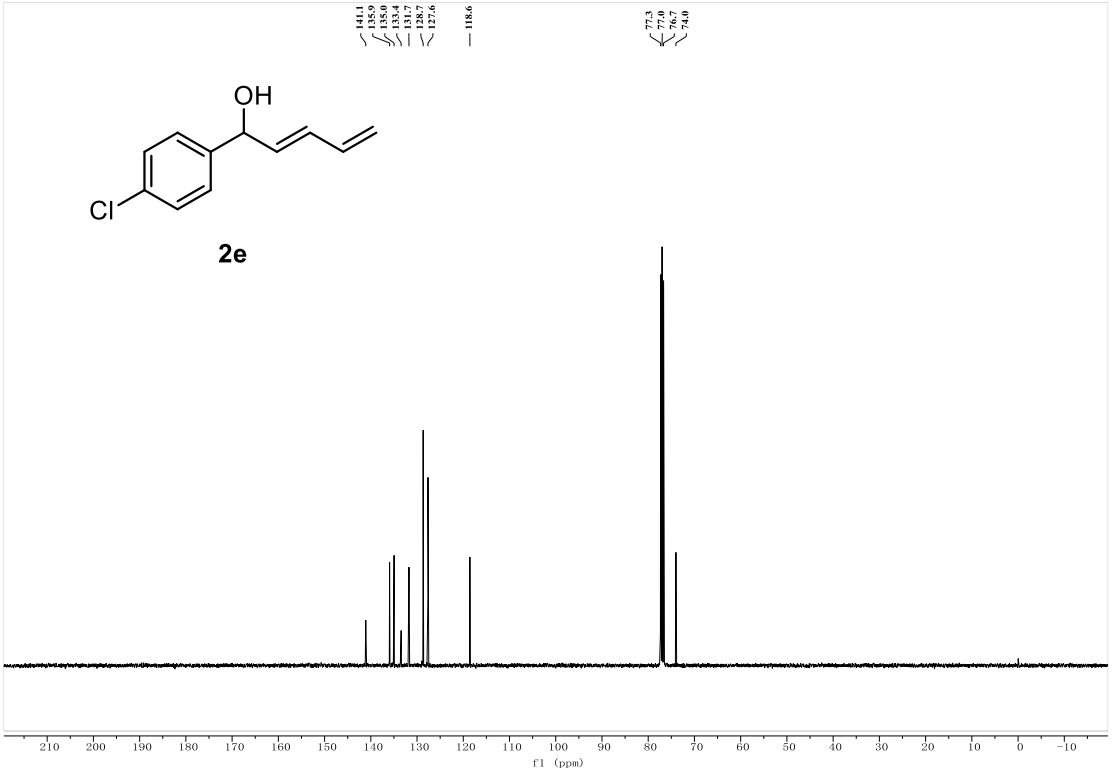
^{1}H NMR (400 MHz, $CDCl_3$) of **2d**



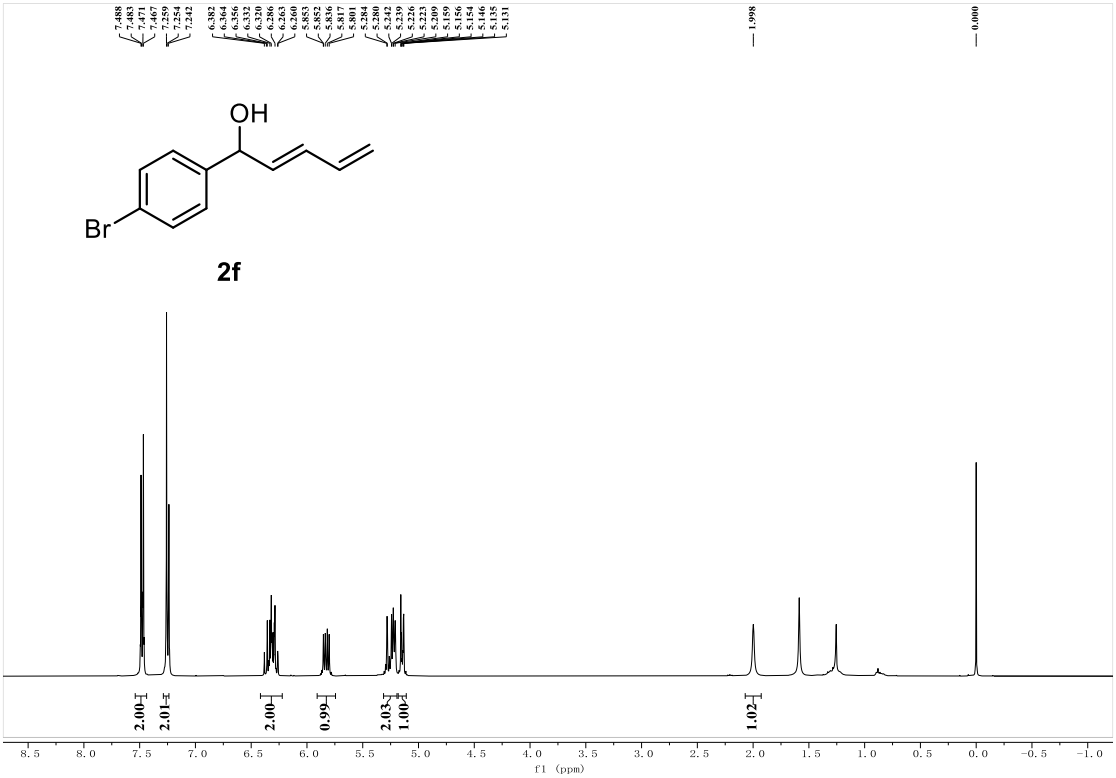
^{13}C NMR (101 MHz, $CDCl_3$) of **2d**



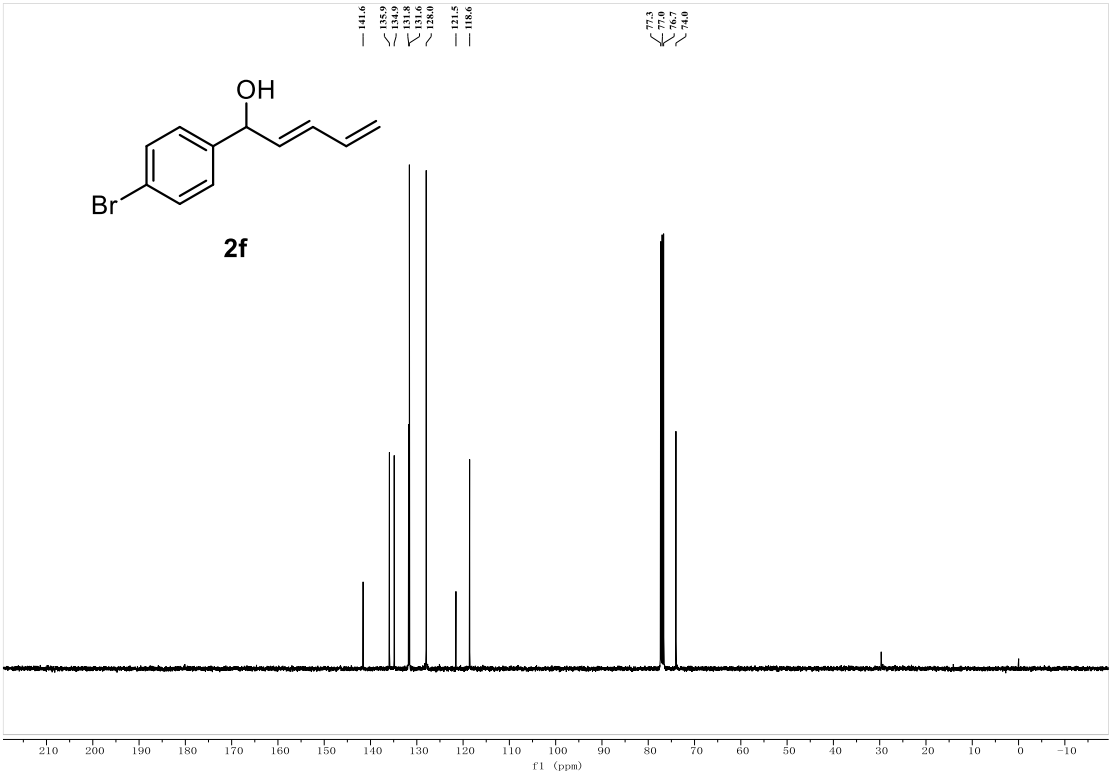
^{1}H NMR (400 MHz, $CDCl_3$) of **2e**



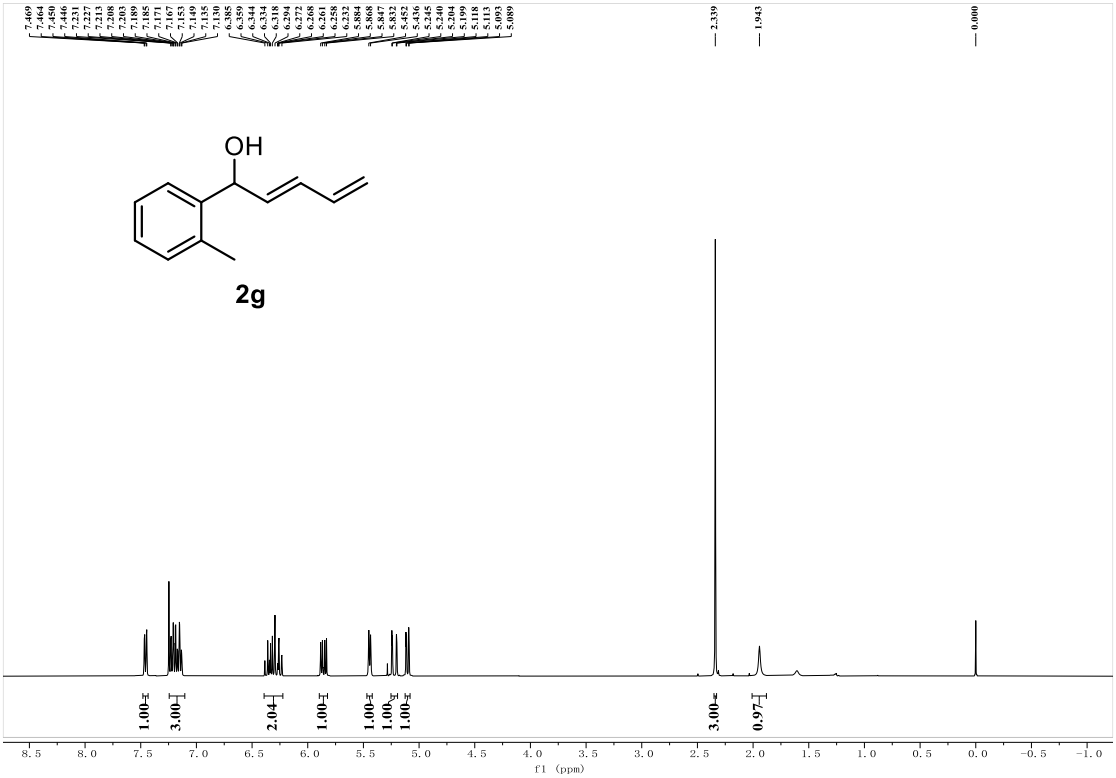
^{13}C NMR (101 MHz, $CDCl_3$) of **2e**



^{1}H NMR (400 MHz, $CDCl_3$) of **2f**

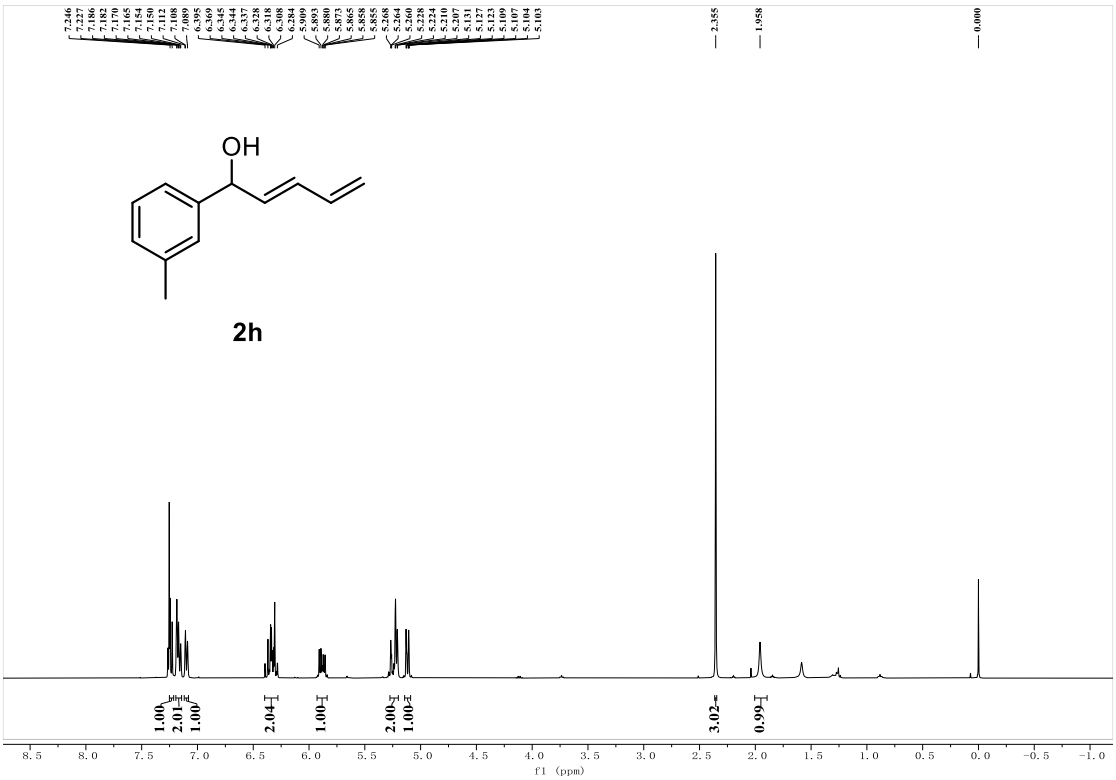


^{13}C NMR (101 MHz, $CDCl_3$) of **2f**

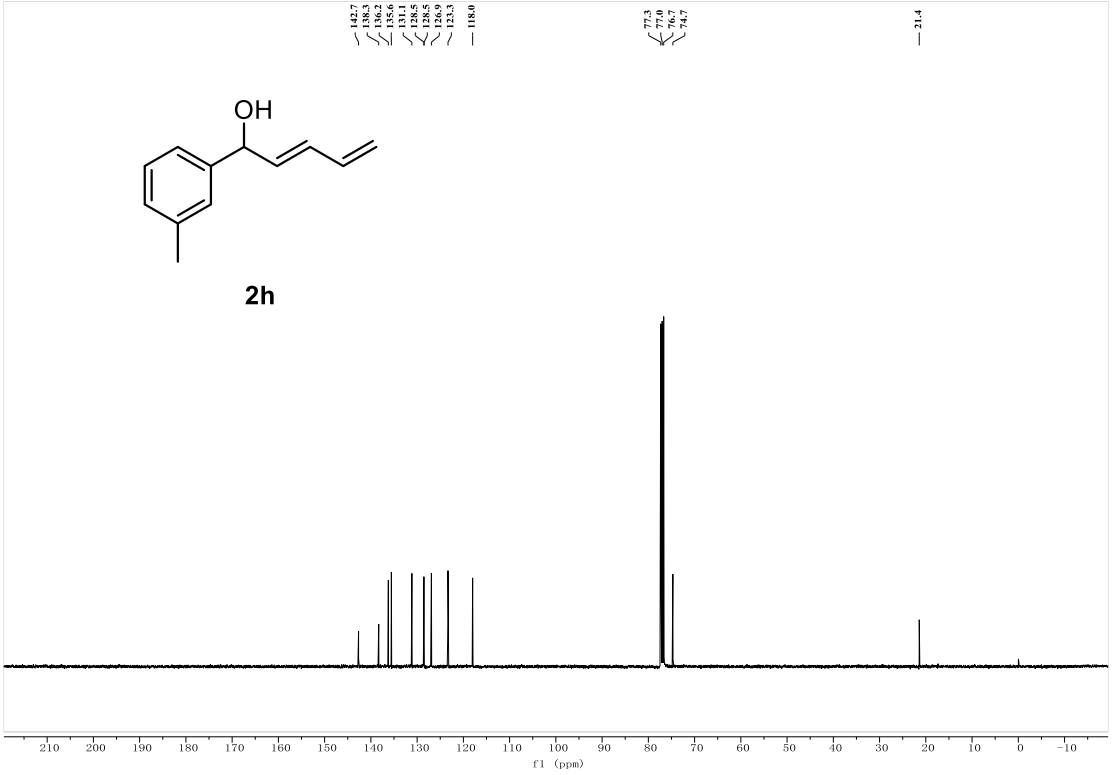


^{1}H NMR (400 MHz, $CDCl_3$) of **2g**

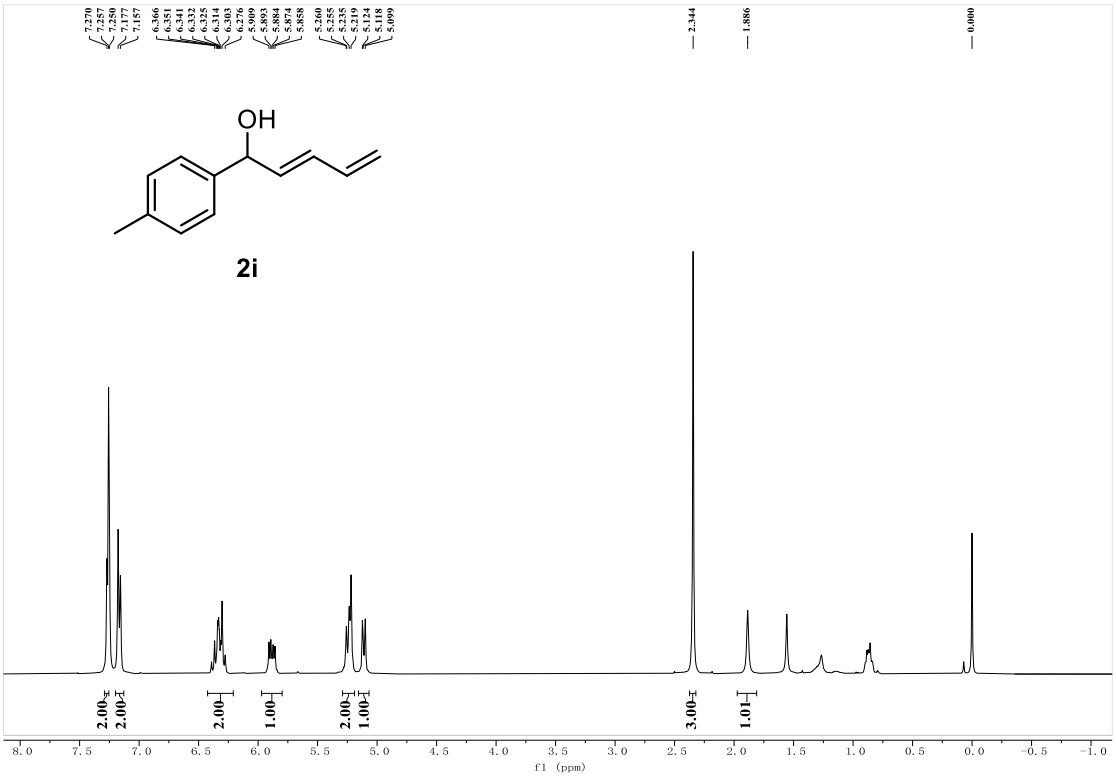
^{13}C NMR (101 MHz, $CDCl_3$) of **2g**



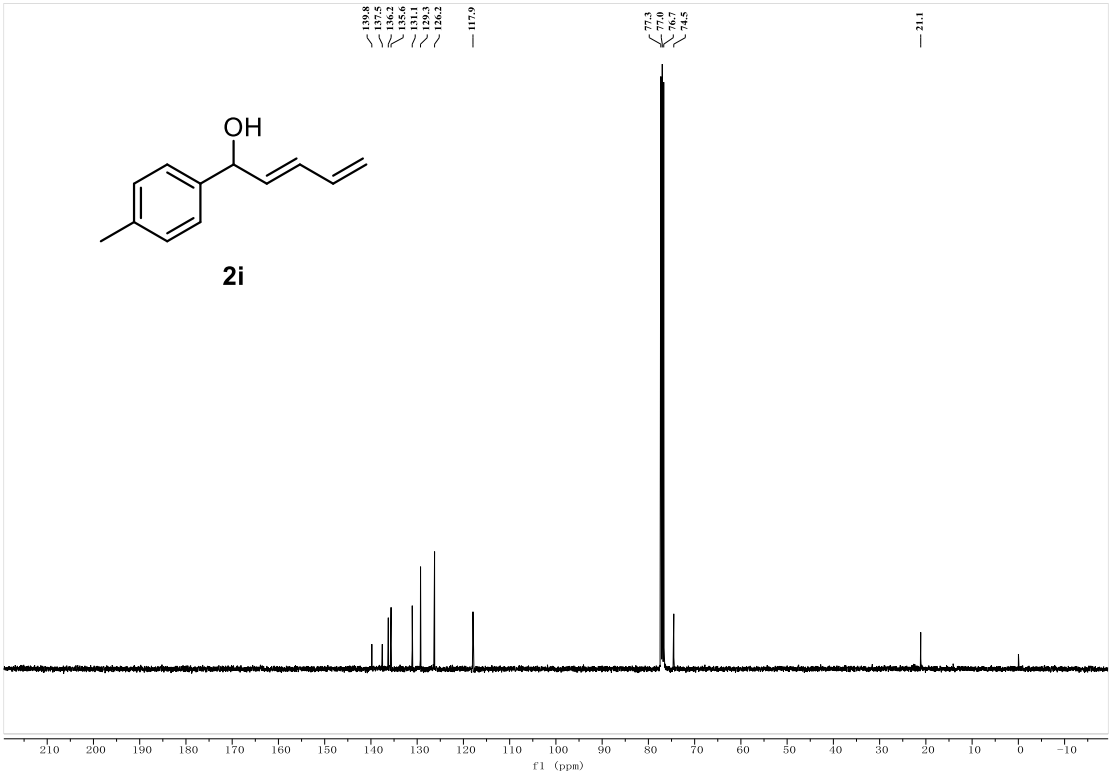
^{1}H NMR (400 MHz, $CDCl_3$) of **2h**



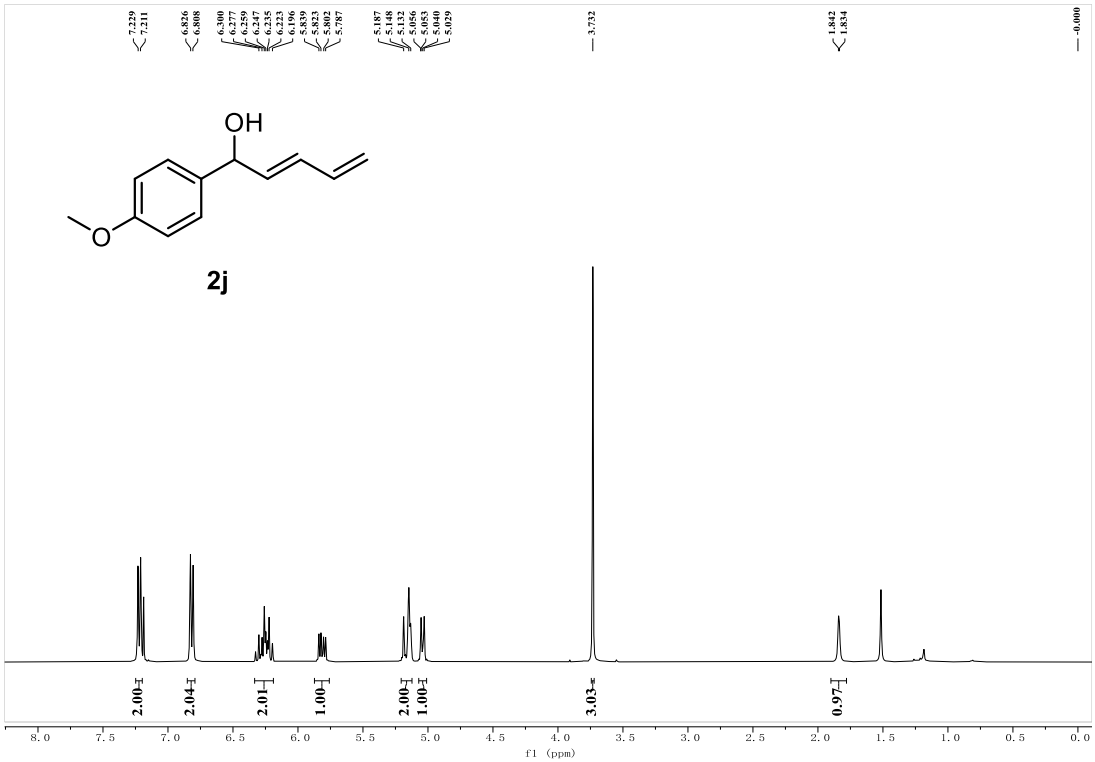
^{13}C NMR (101 MHz, $CDCl_3$) of **2h**



^{1}H NMR (400 MHz, $CDCl_3$) of **2i**



^{13}C NMR (101 MHz, $CDCl_3$) of **2i**



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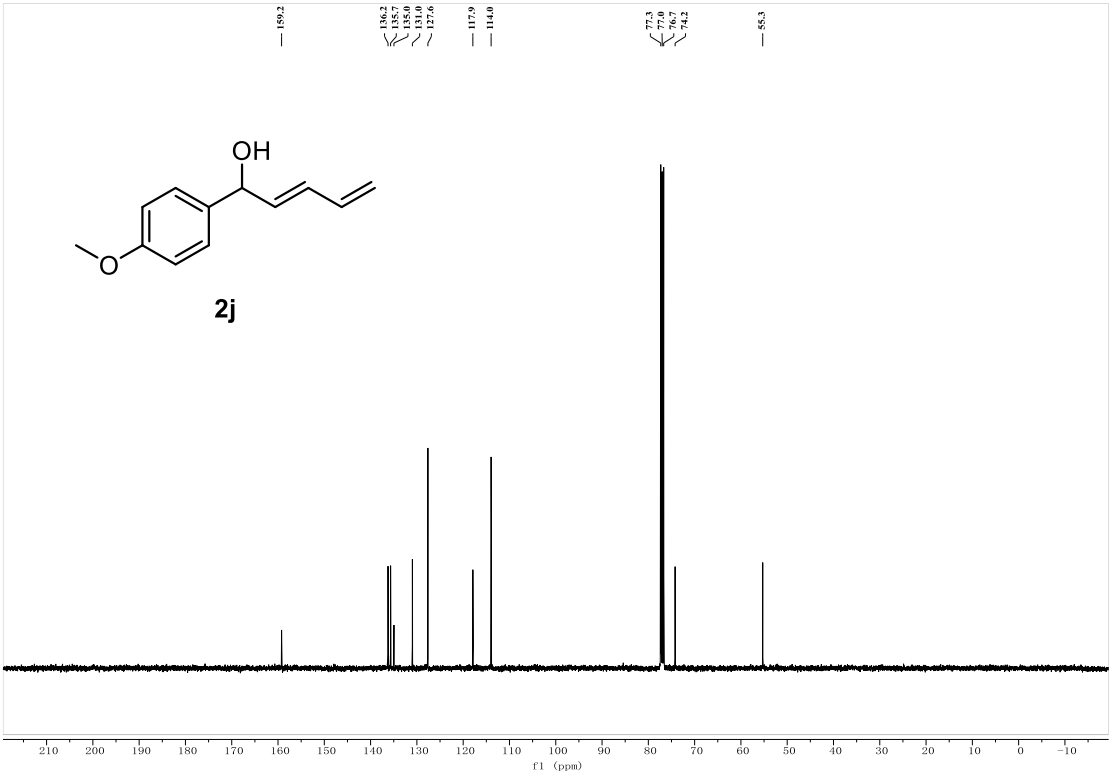
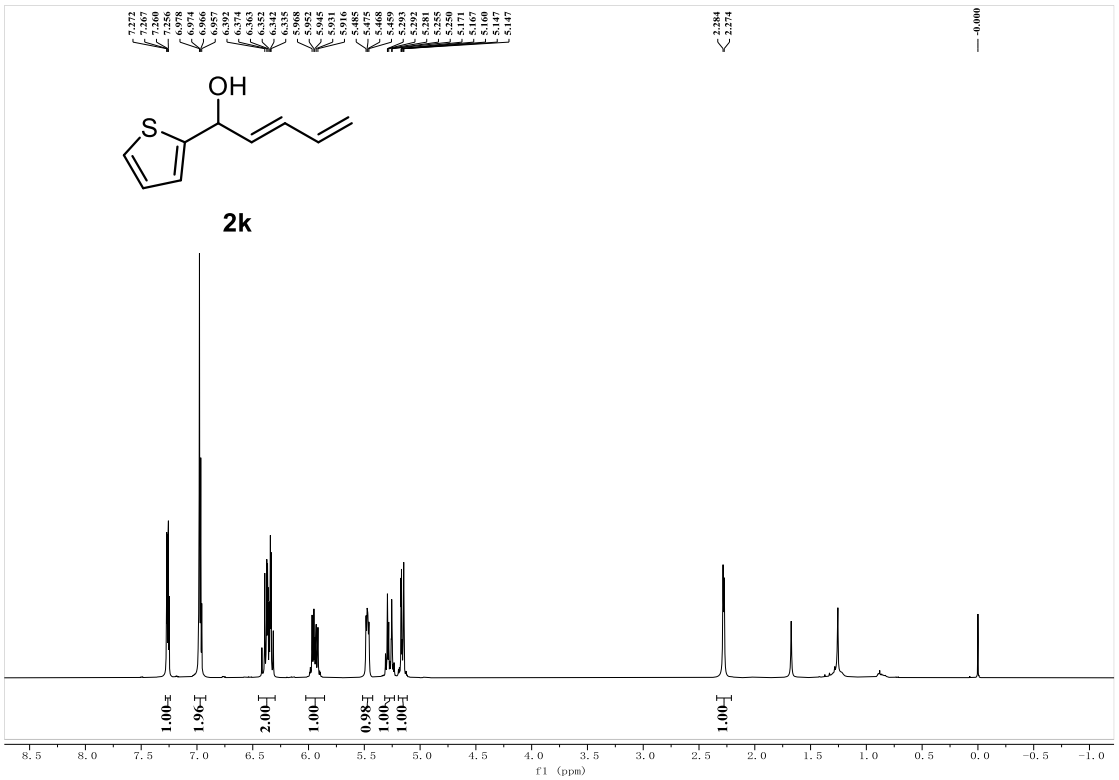
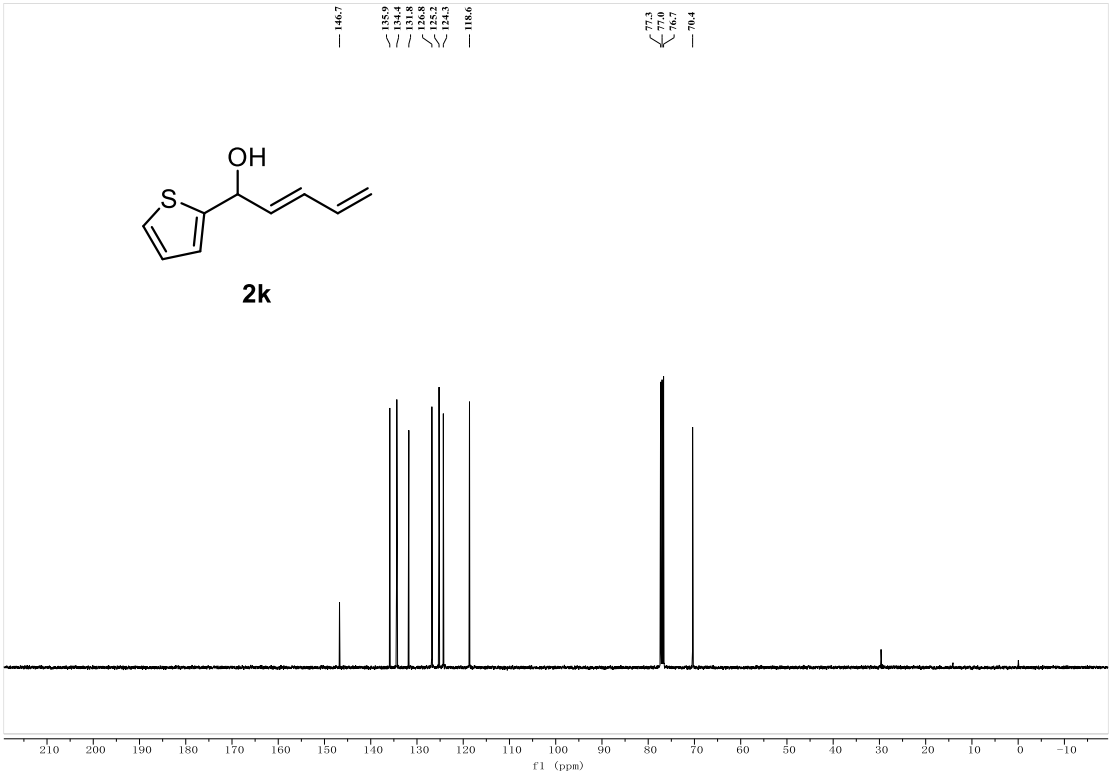


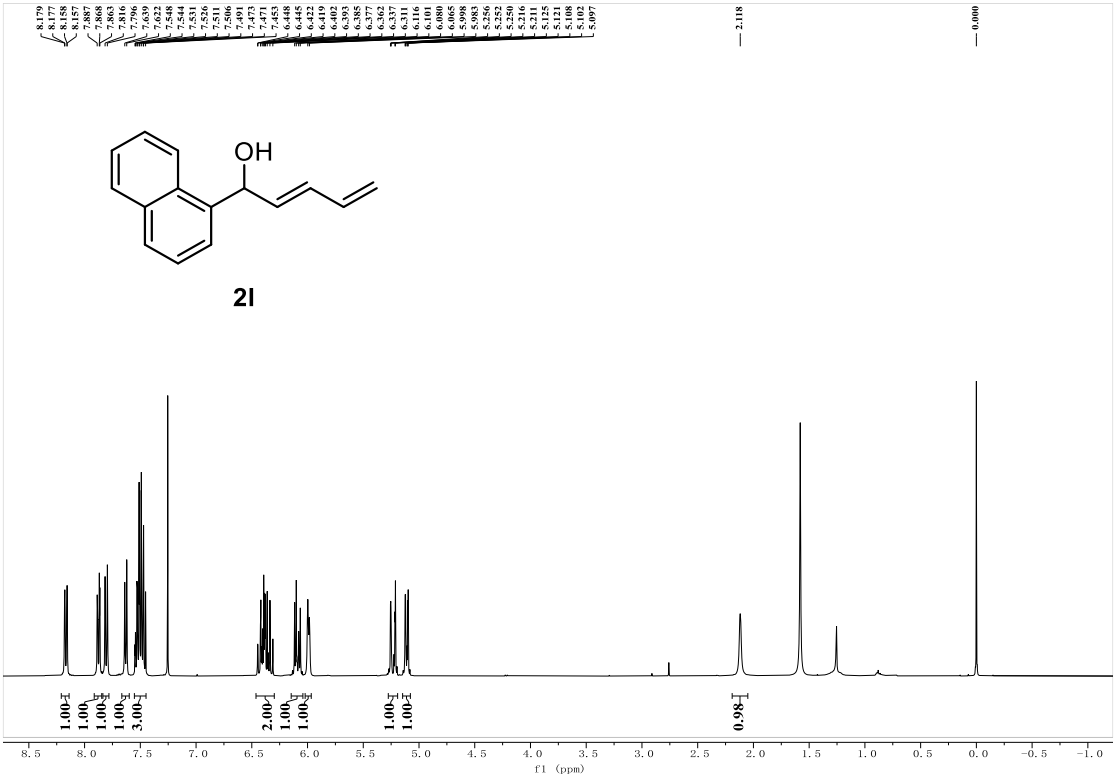
^{13}C NMR (101 MHz, $CDCl_3$) of **2j**



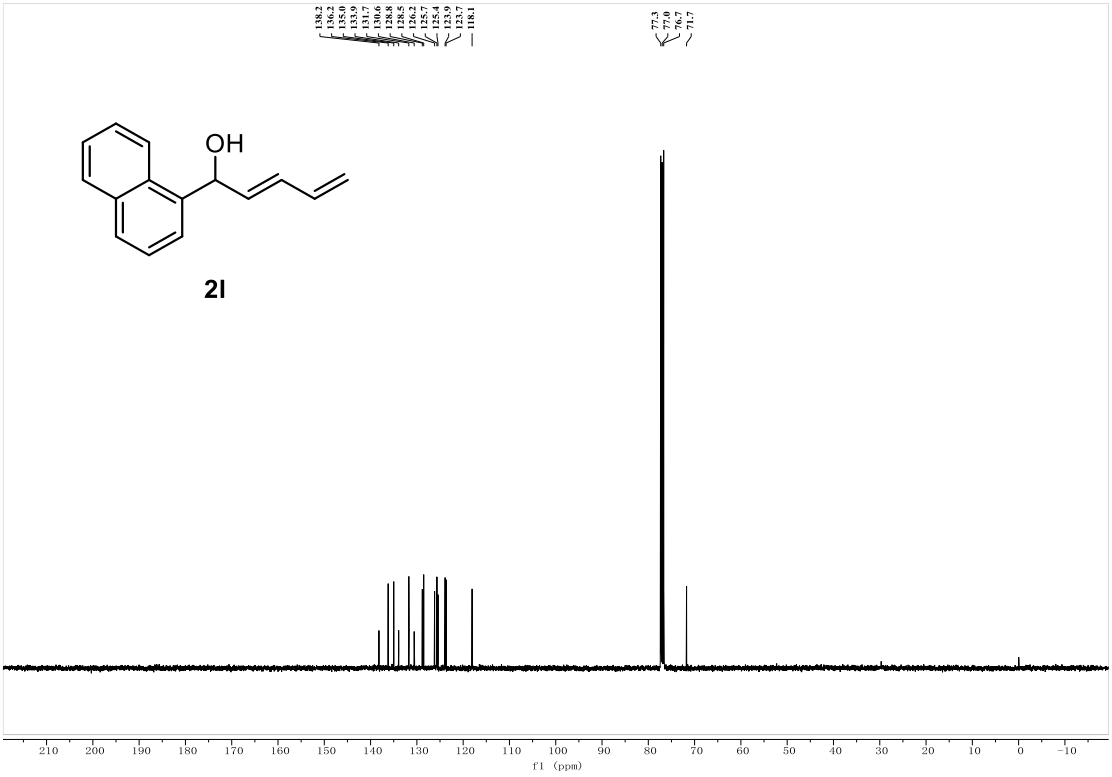
^{1}H NMR (400 MHz, $CDCl_3$) of **2k**



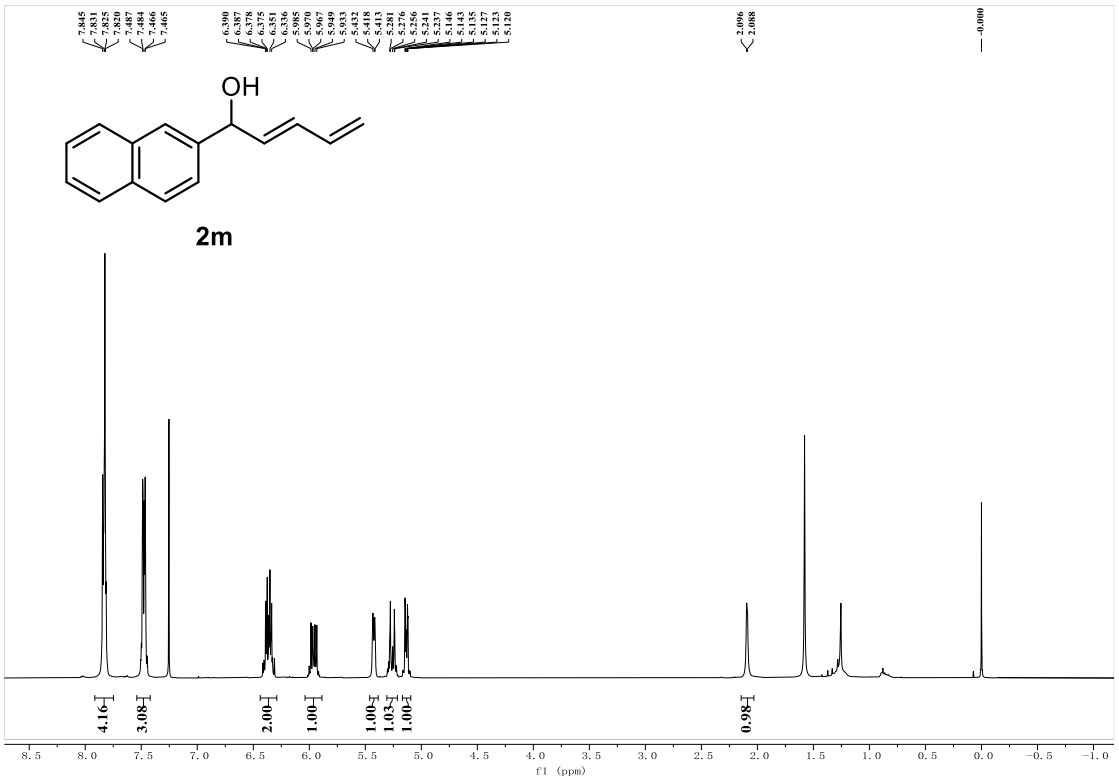
^{13}C NMR (101 MHz, $CDCl_3$) of **2k**



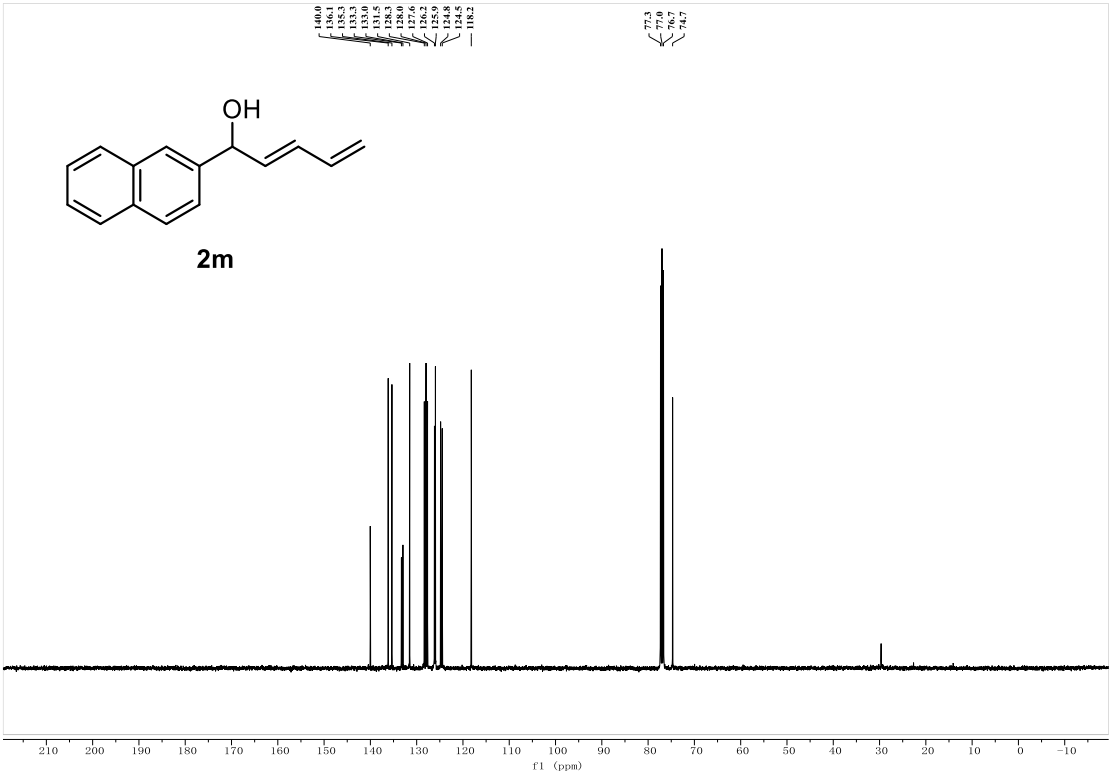
^{1}H NMR (400 MHz, $CDCl_3$) of **2l**



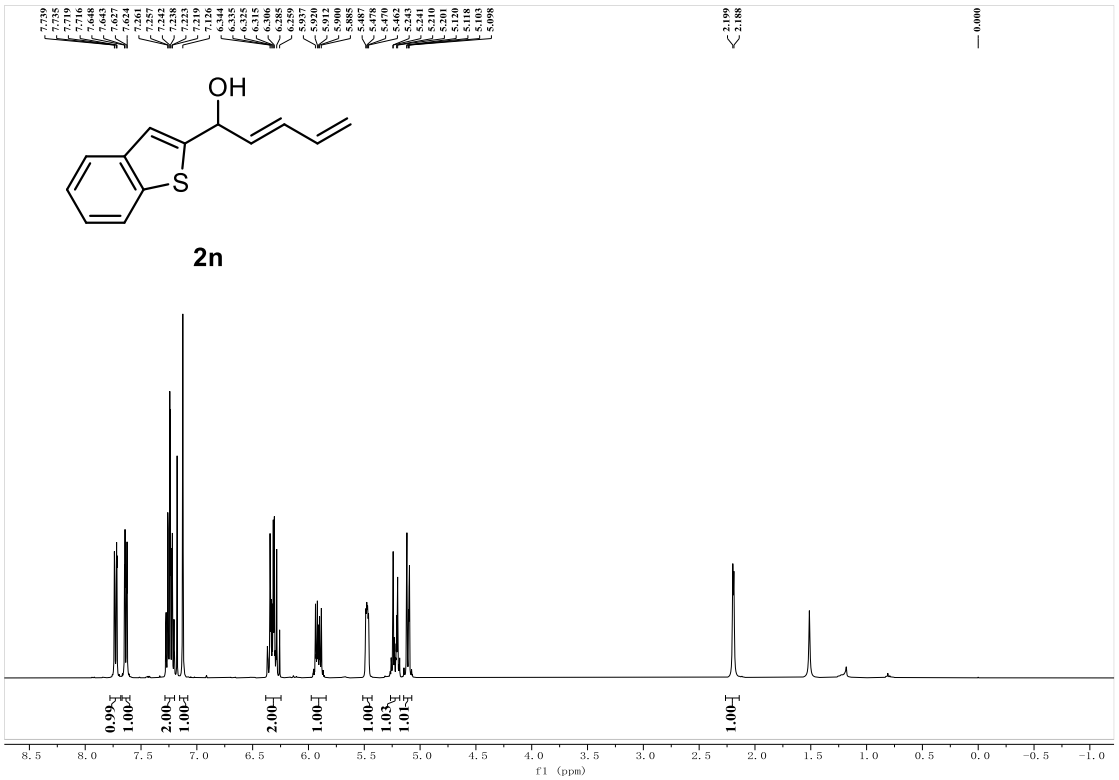
^{13}C NMR (101 MHz, $CDCl_3$) of **2l**



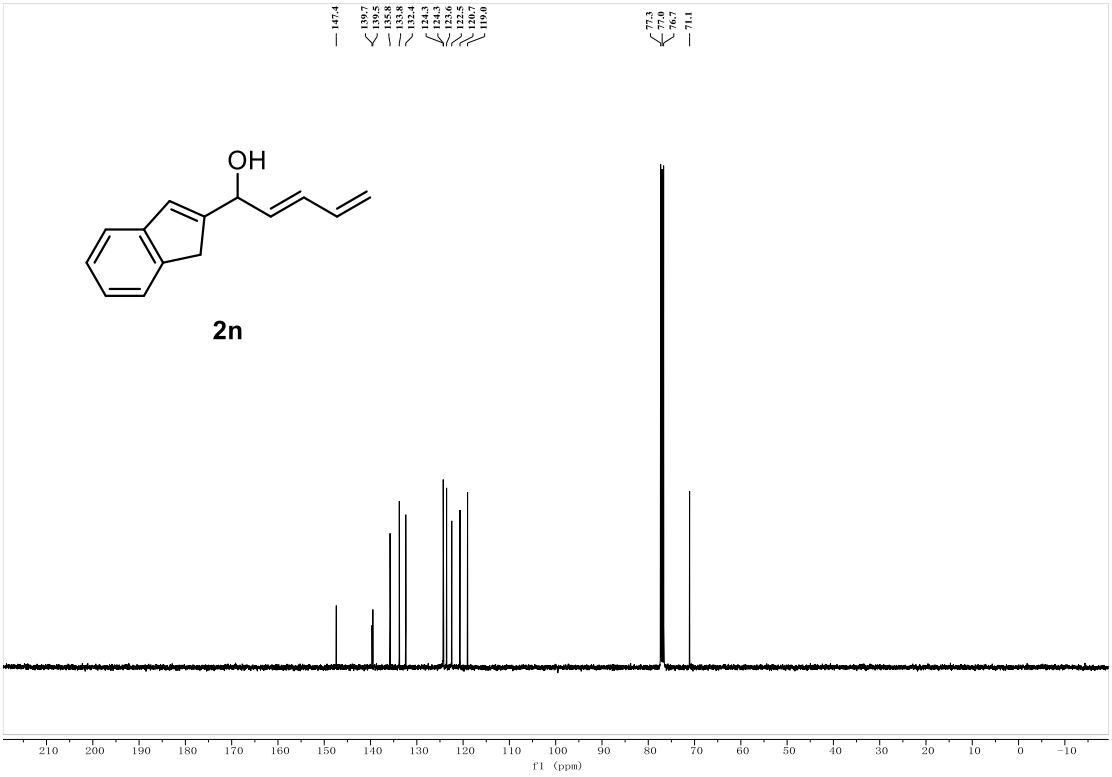
^{1}H NMR (400 MHz, $CDCl_3$) of **2m**



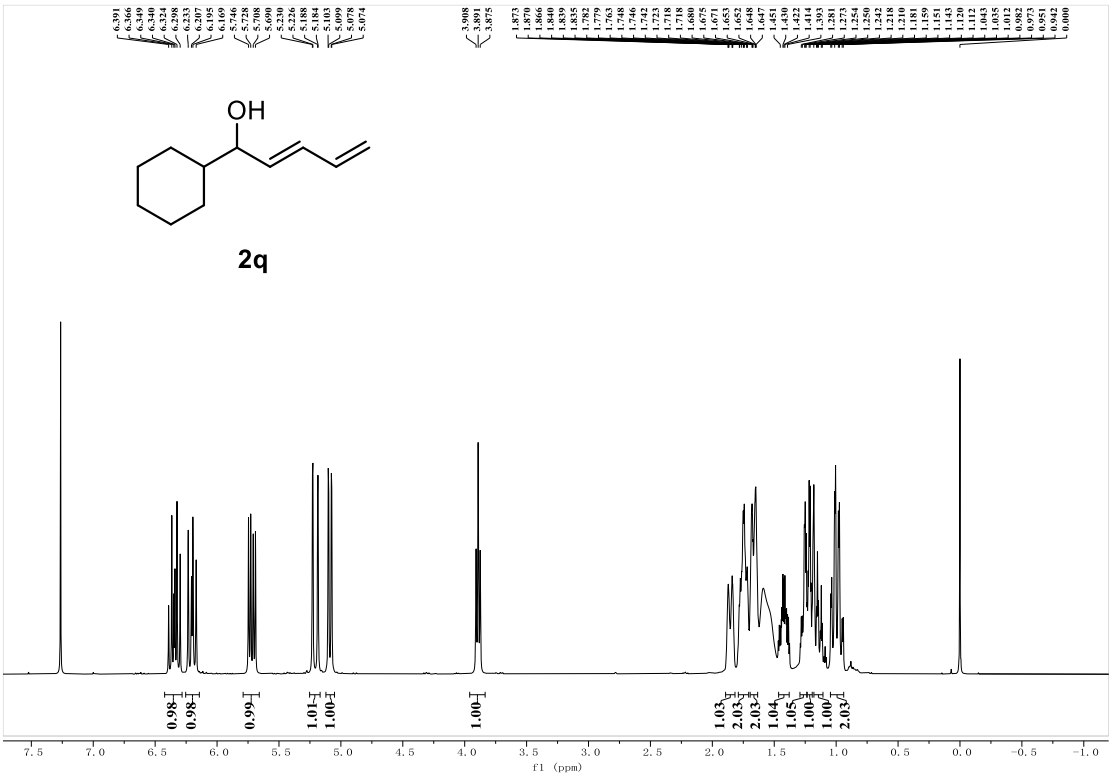
^{13}C NMR (101 MHz, $CDCl_3$) of **2m**



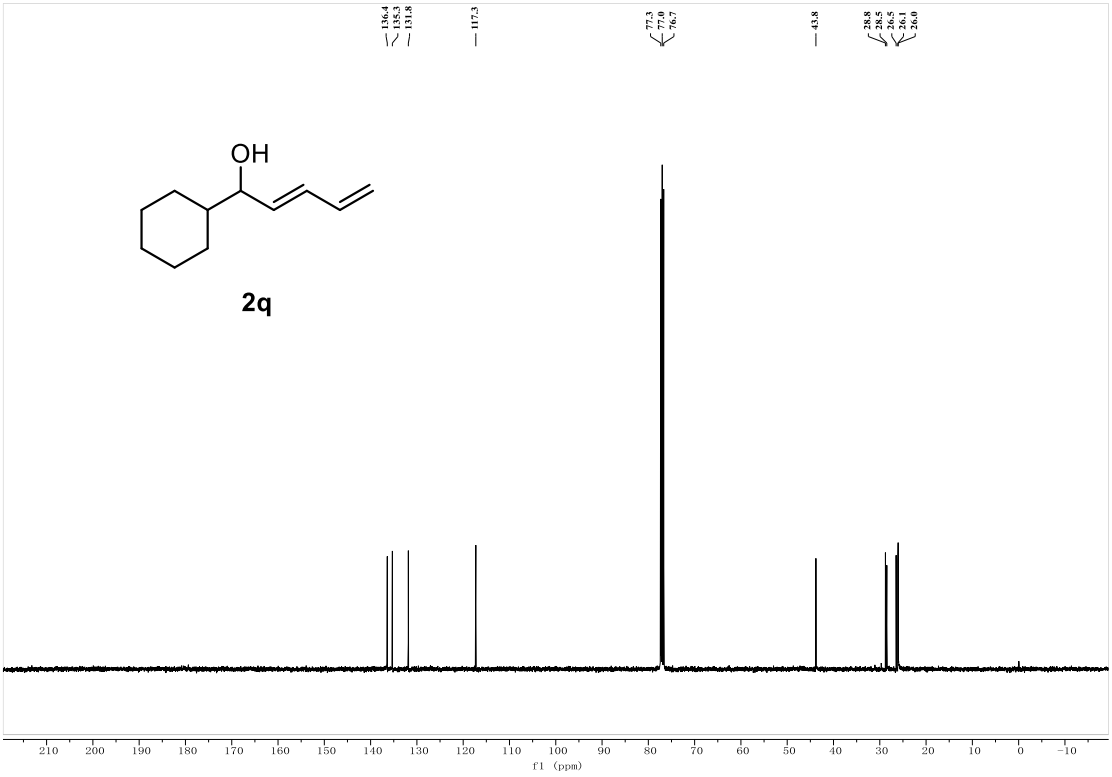
^{1}H NMR (400 MHz, $CDCl_3$) of **2n**



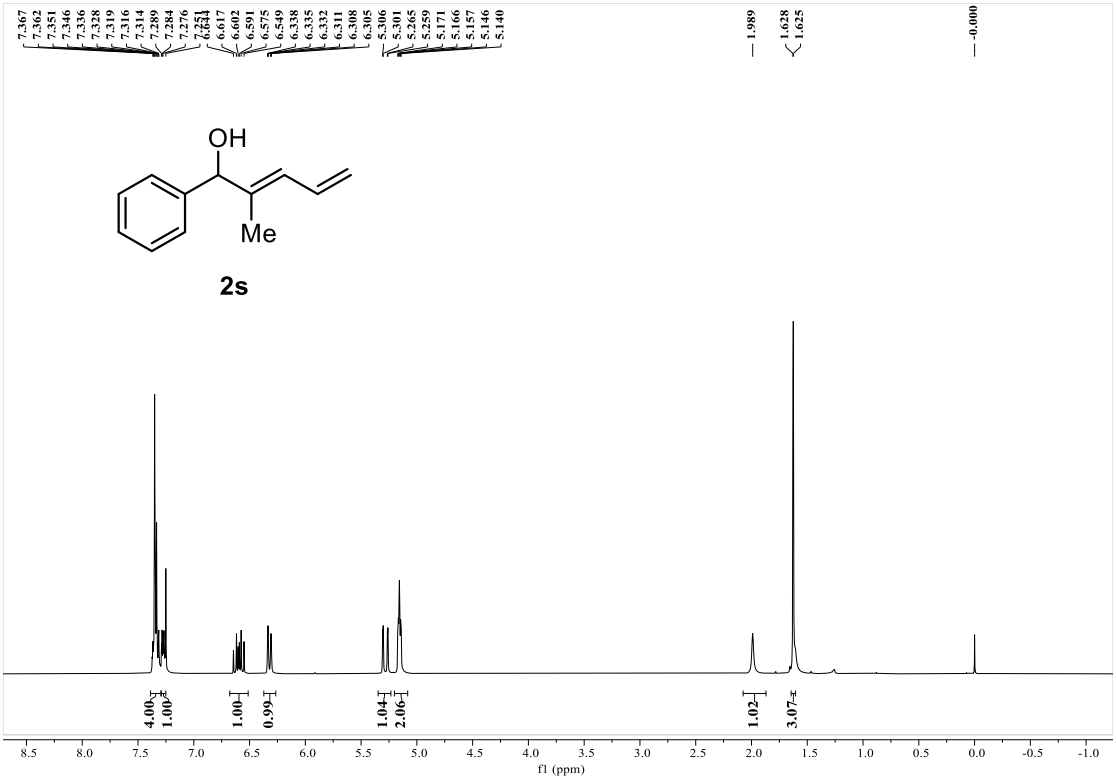
^{13}C NMR (101 MHz, $CDCl_3$) of **2n**



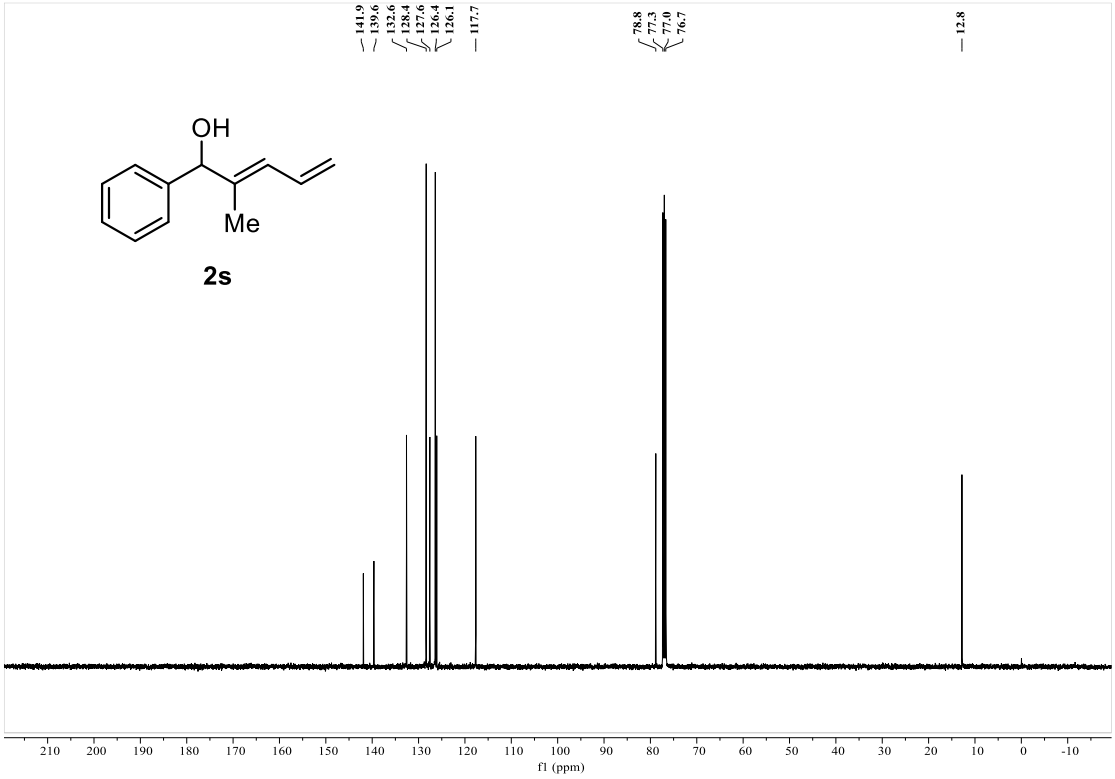
^{1}H NMR (400 MHz, $CDCl_3$) of **2q**



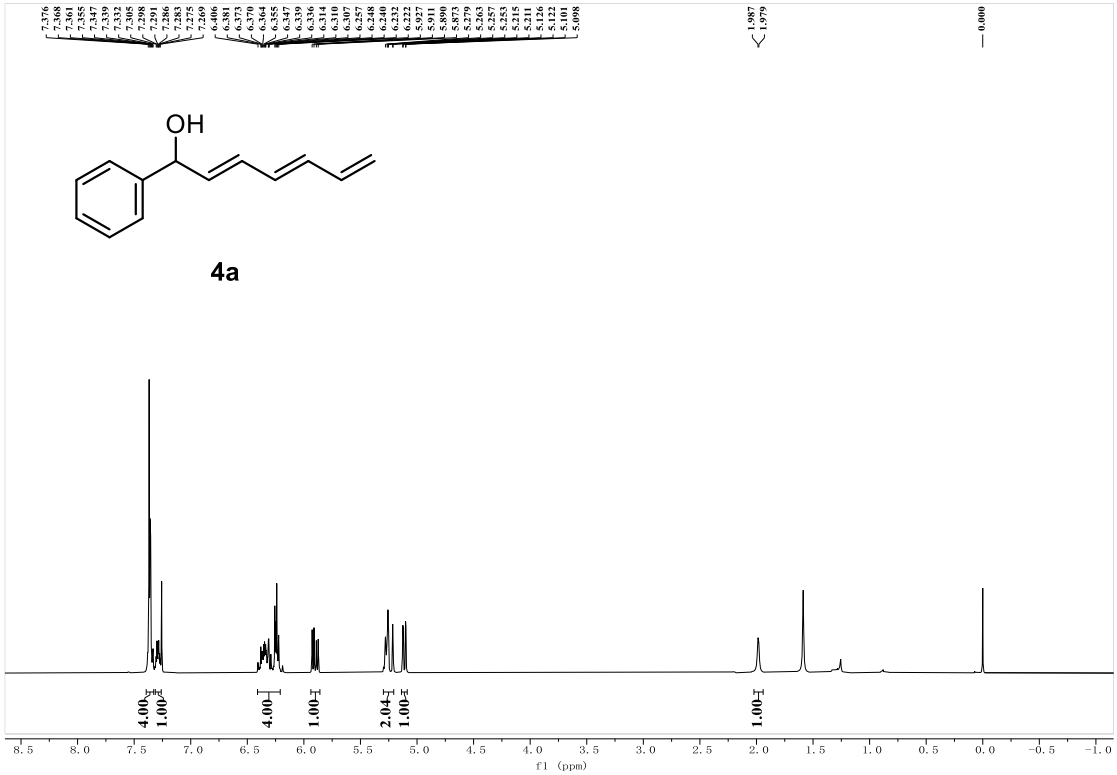
^{13}C NMR (101 MHz, $CDCl_3$) of **2q**



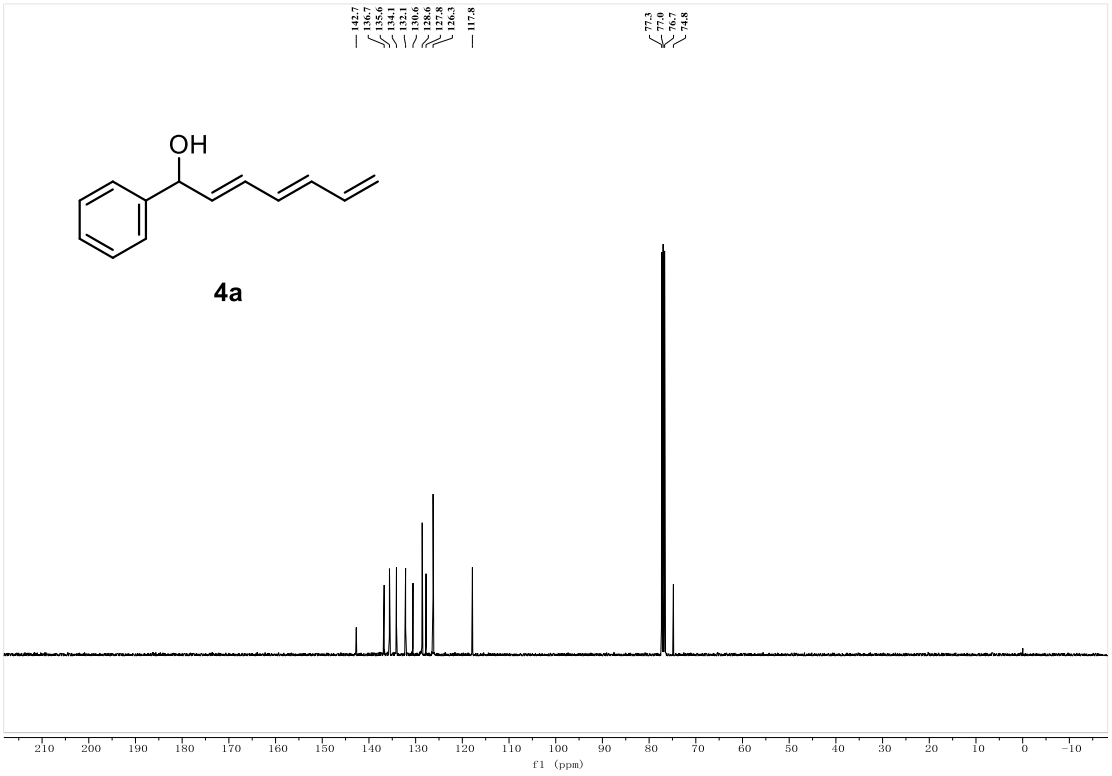
^{1}H NMR (400 MHz, $CDCl_3$) of **2s**



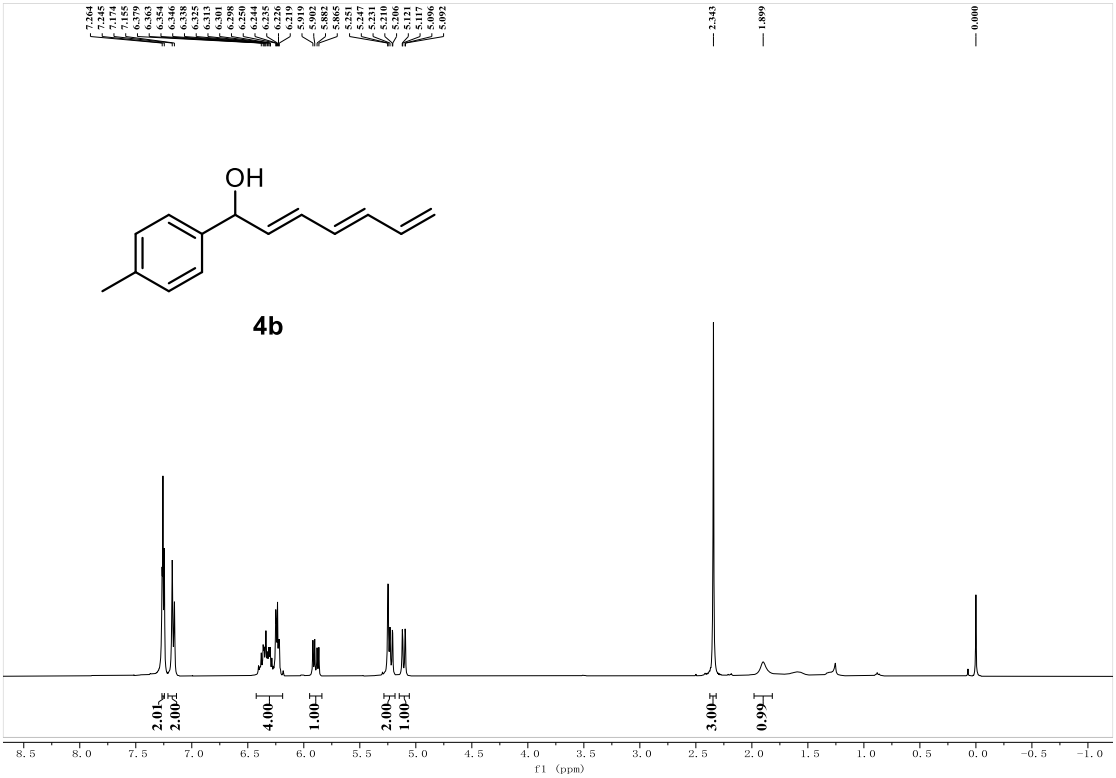
^{13}C NMR (101 MHz, $CDCl_3$) of **2s**



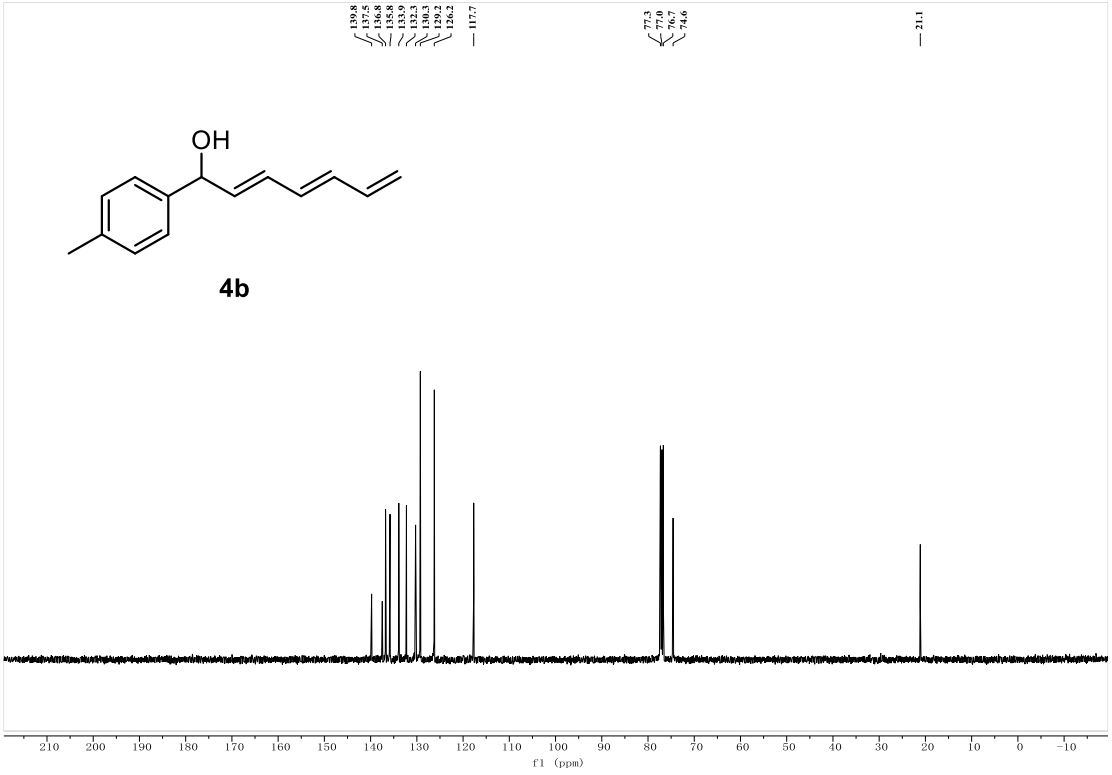
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



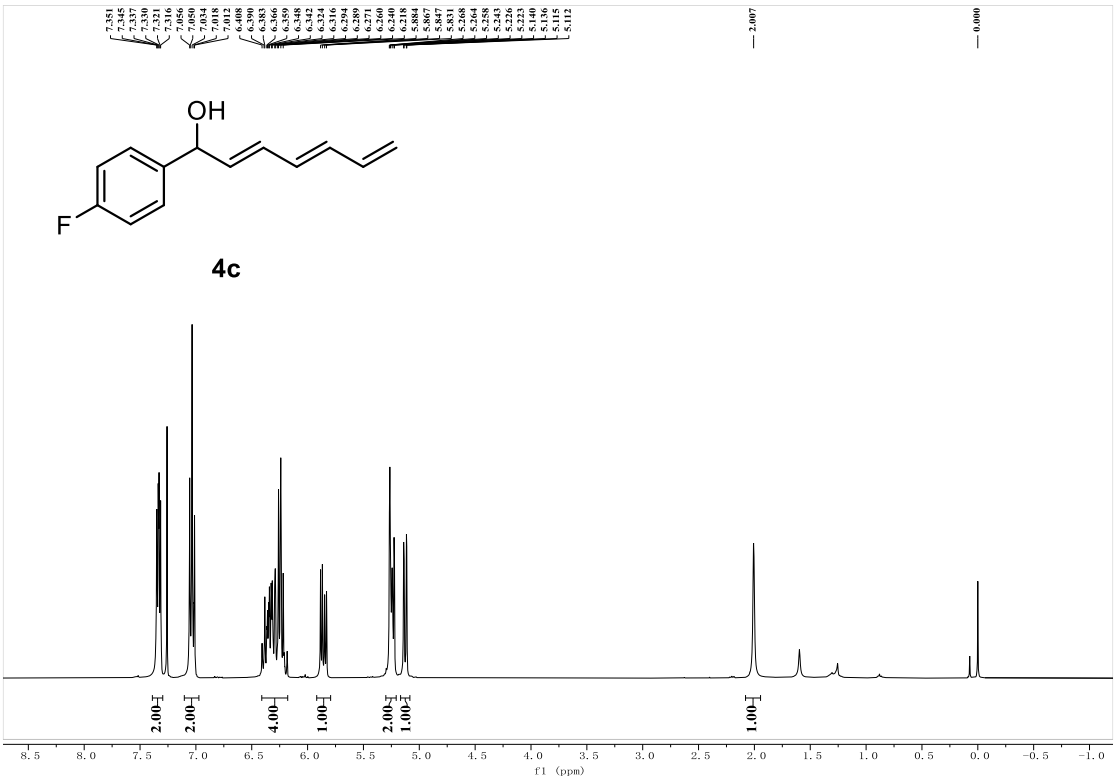
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



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



^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



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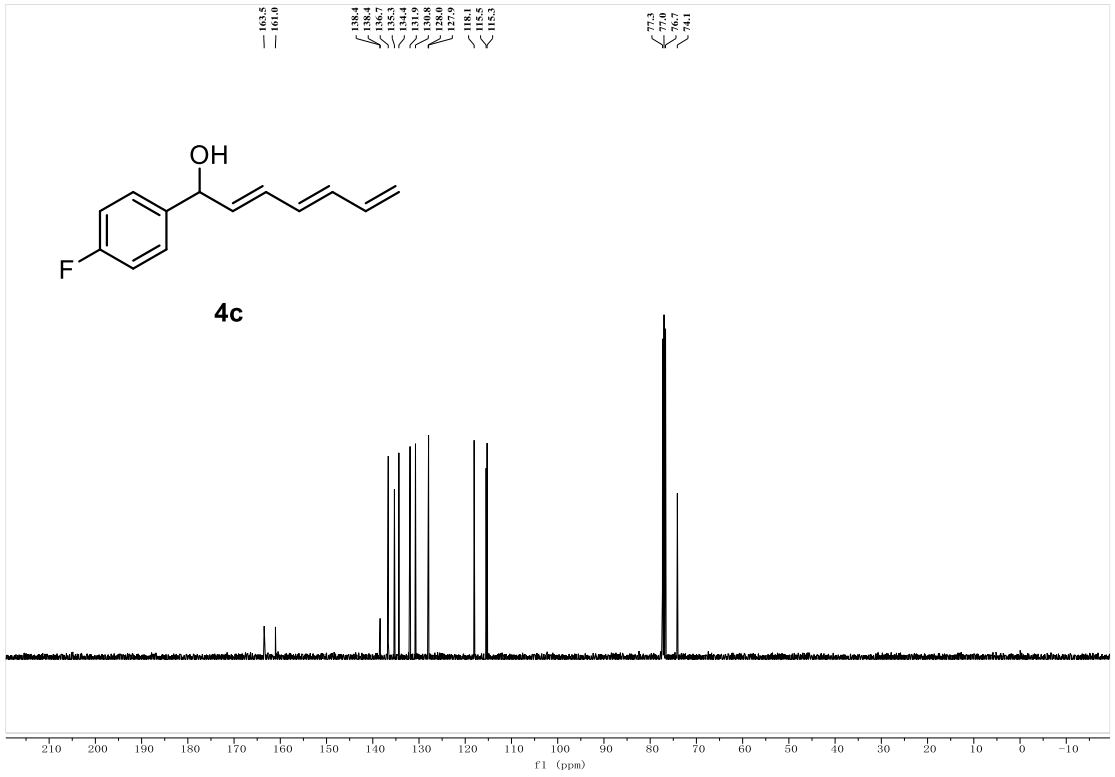
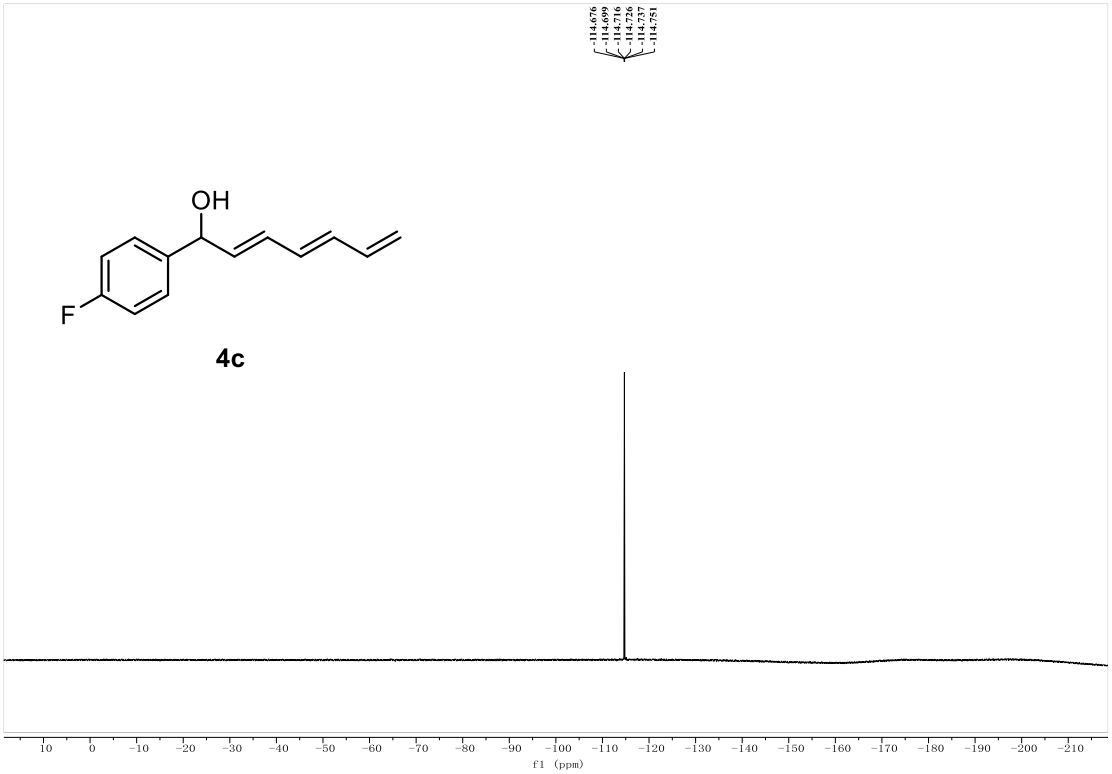
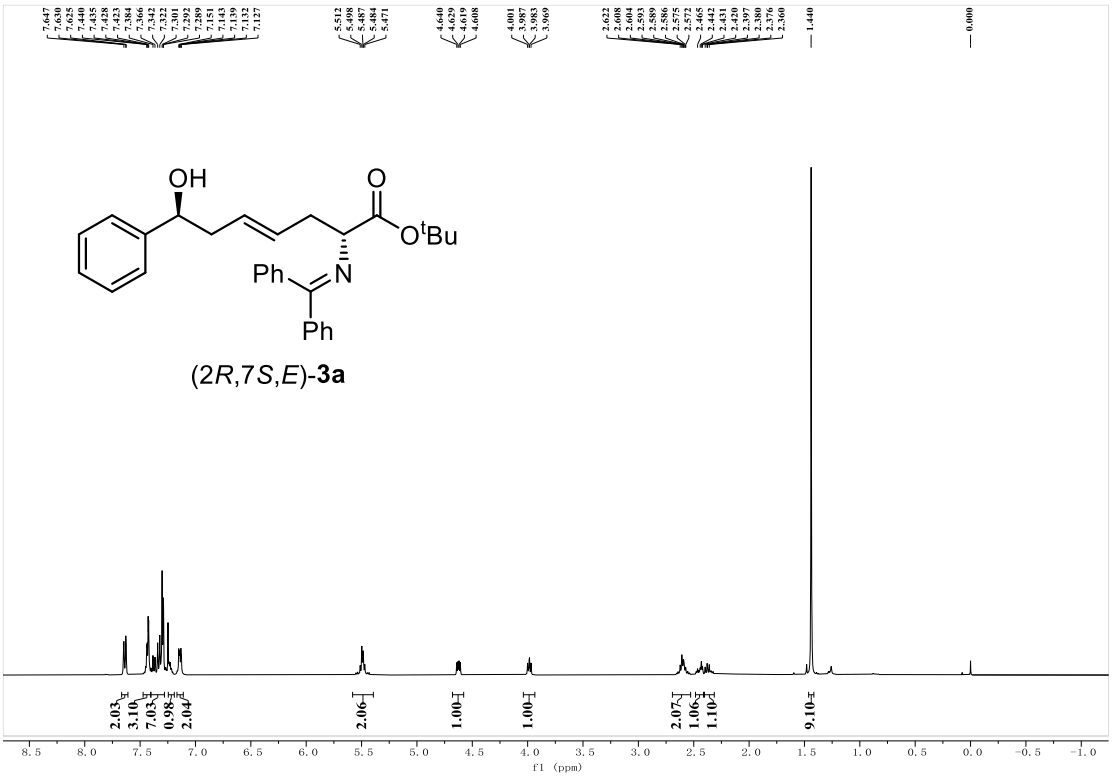


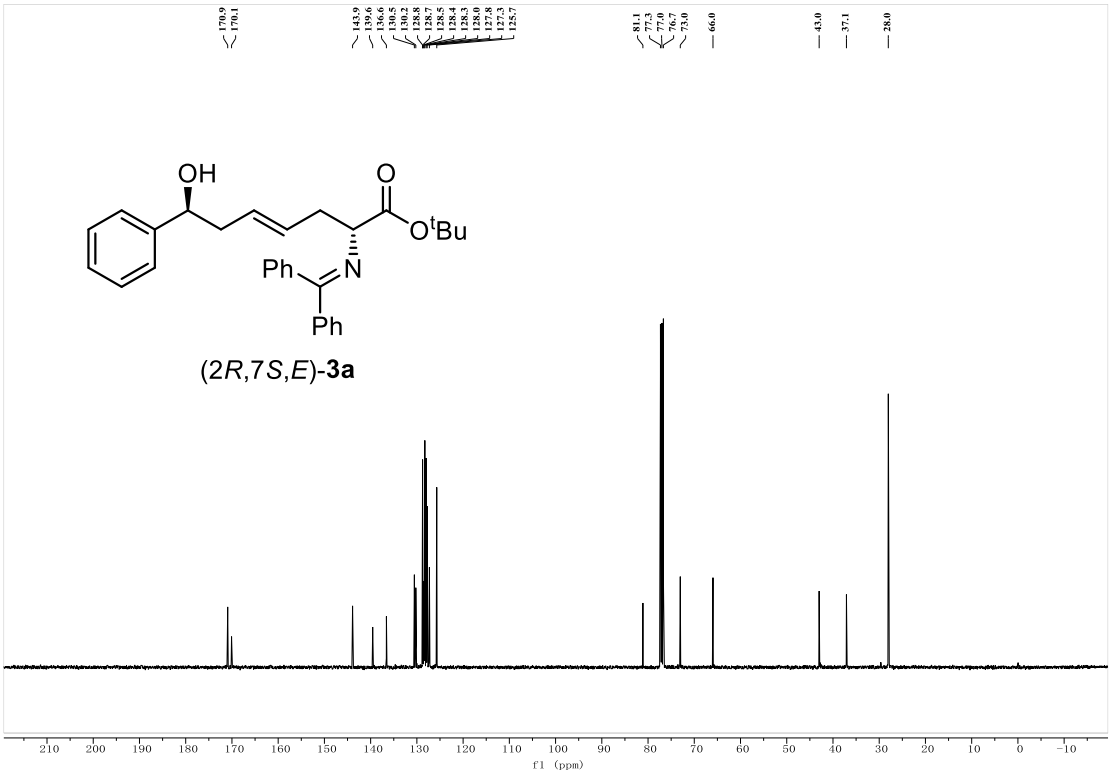
^{13}C NMR (101 MHz, $CDCl_3$) of **4c**



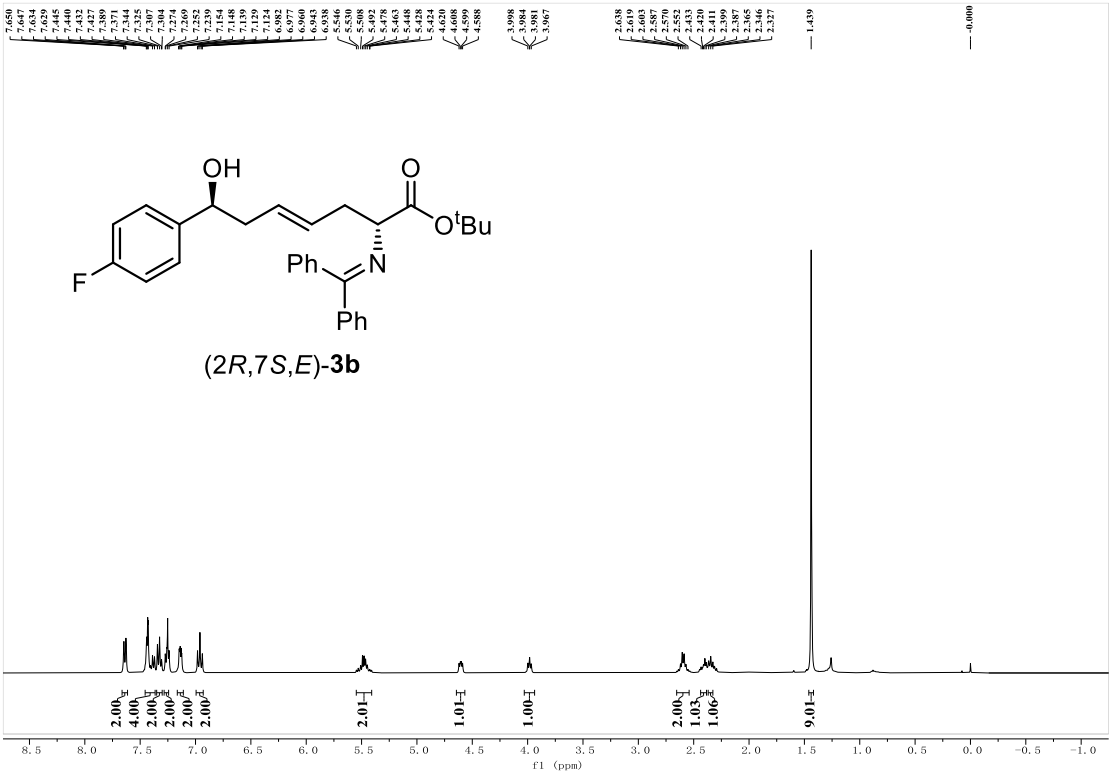
^{19}F NMR (376 MHz, $CDCl_3$) of **4c**



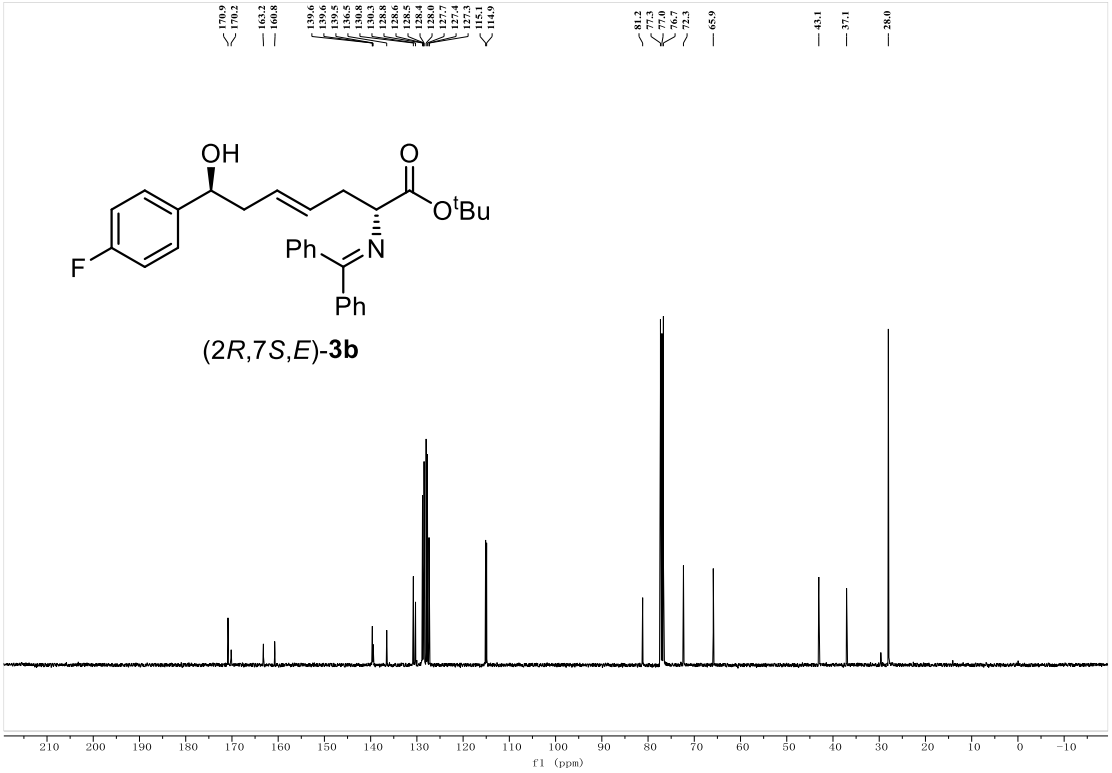
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3a**



^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3a**



^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3b**



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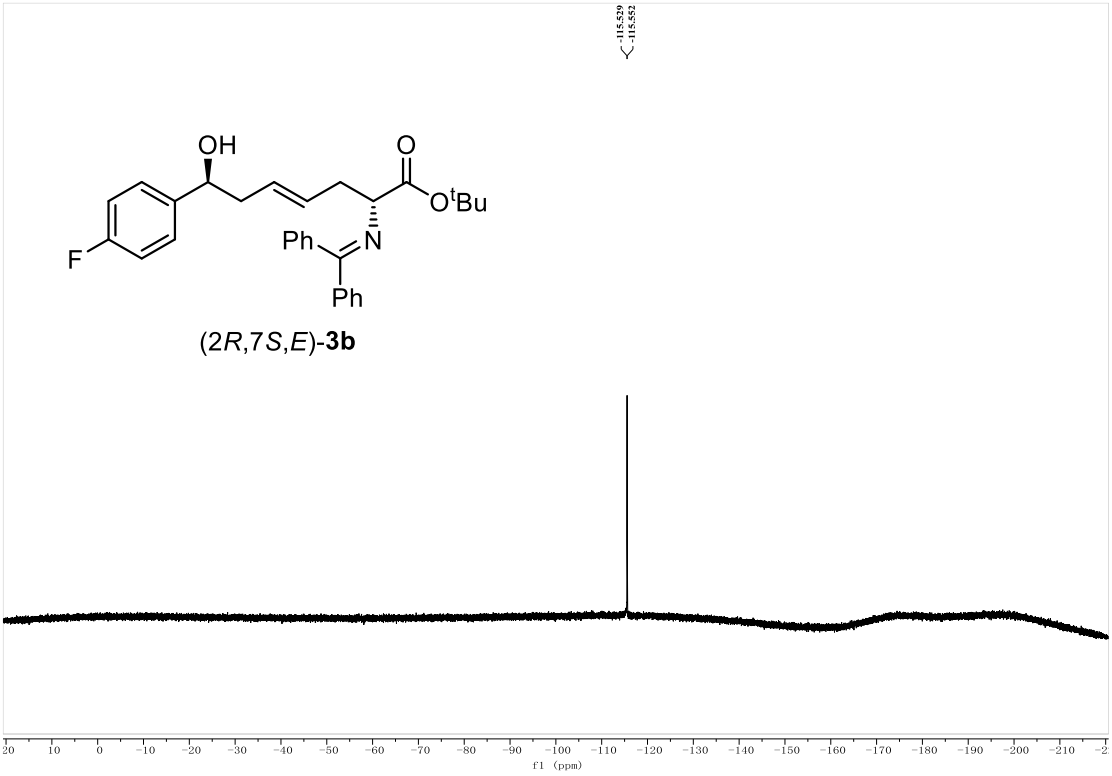
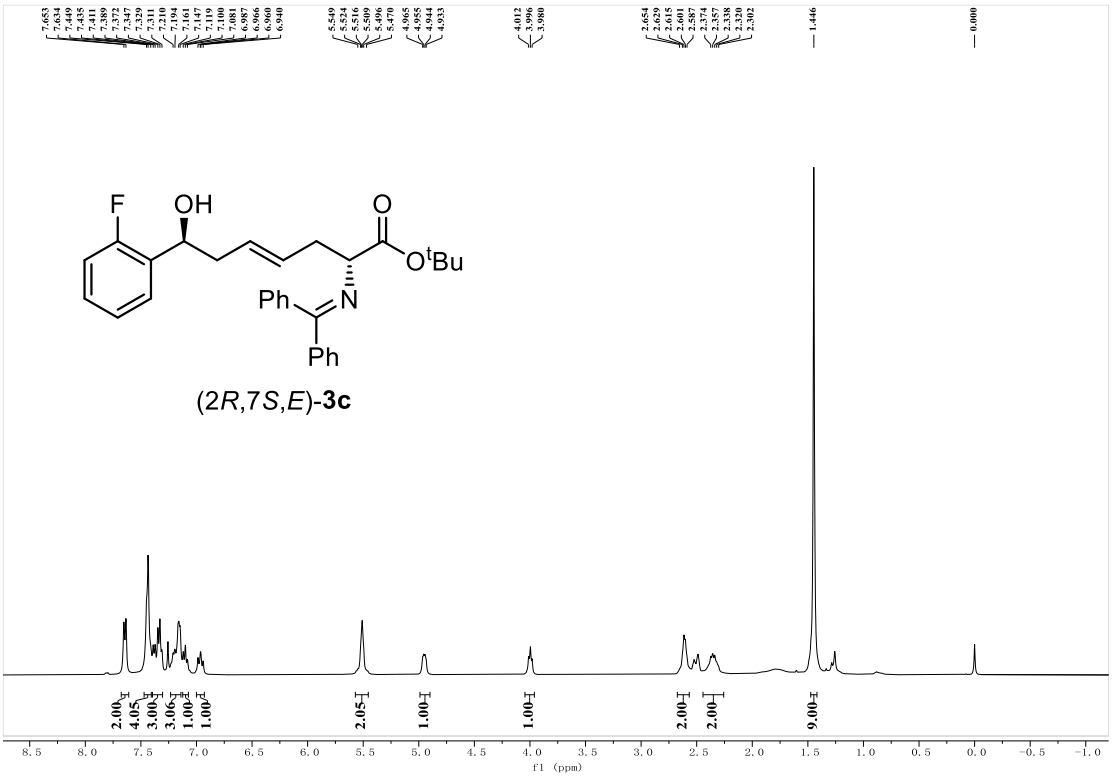
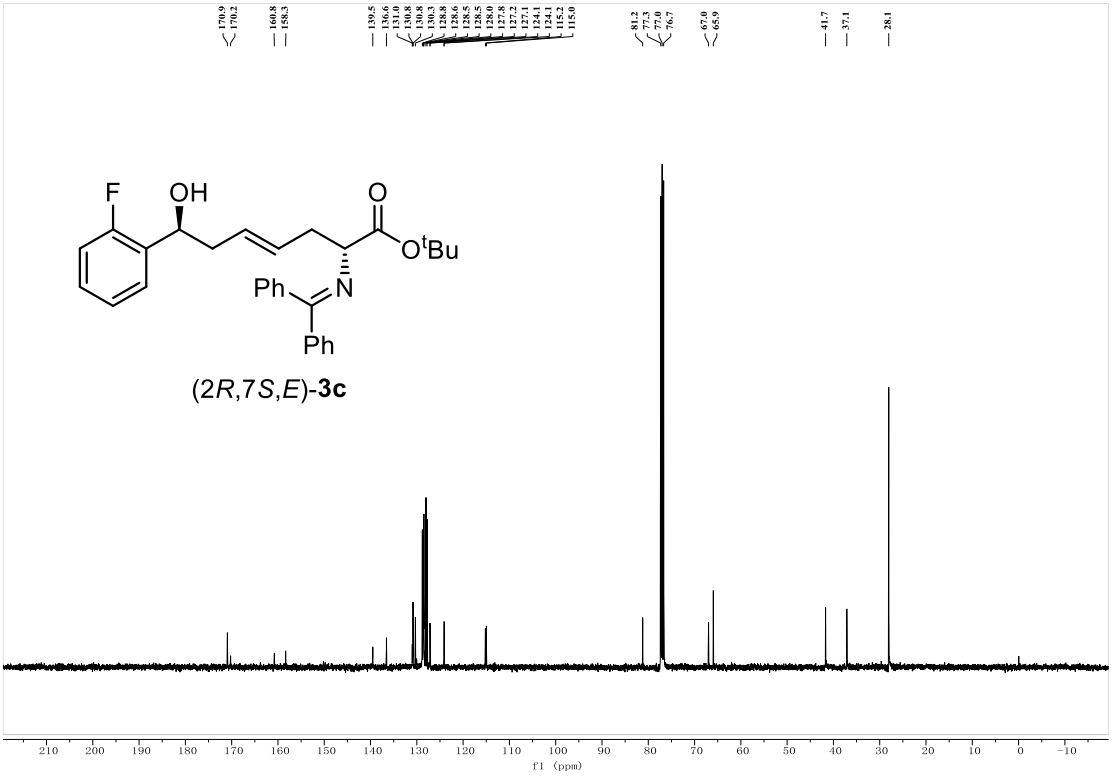


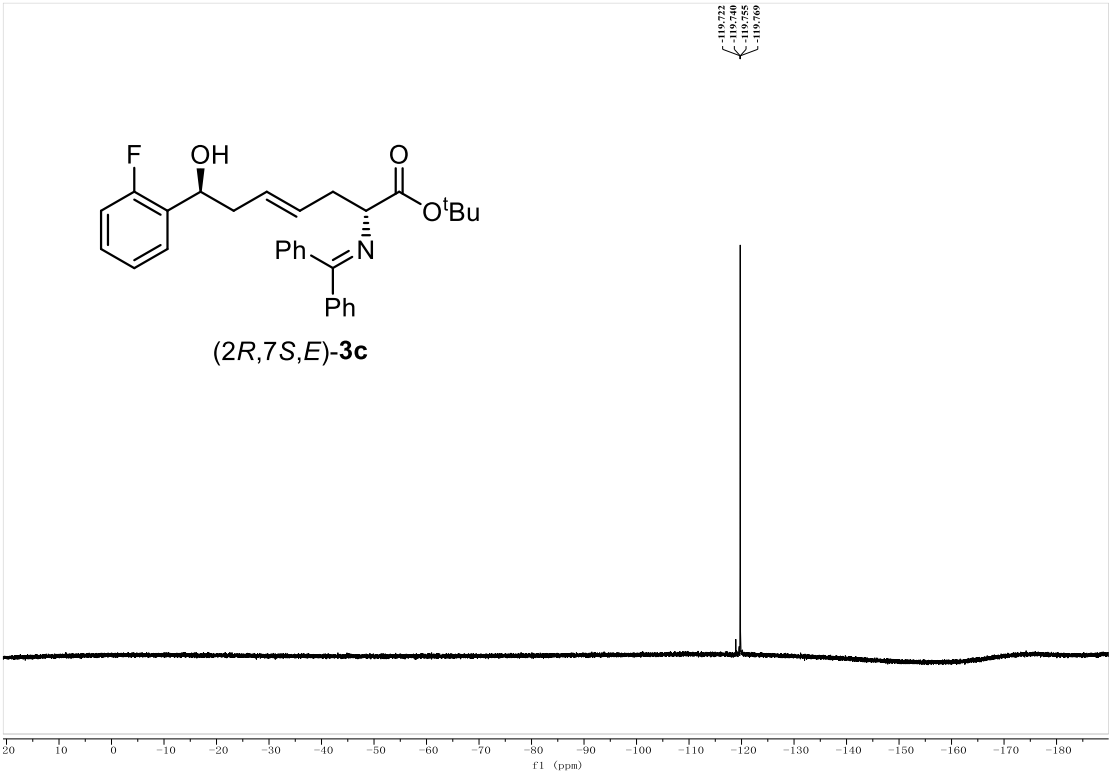
^{19}F NMR (376 MHz, $CDCl_3$) of **3b**



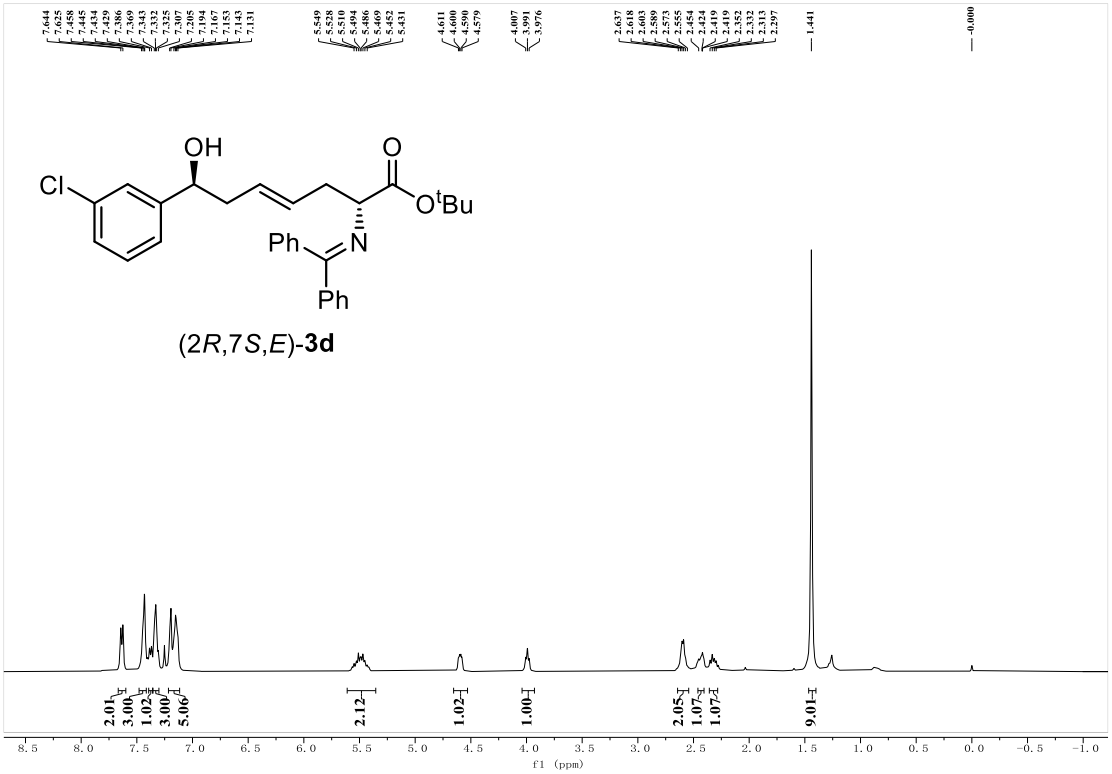
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3c**



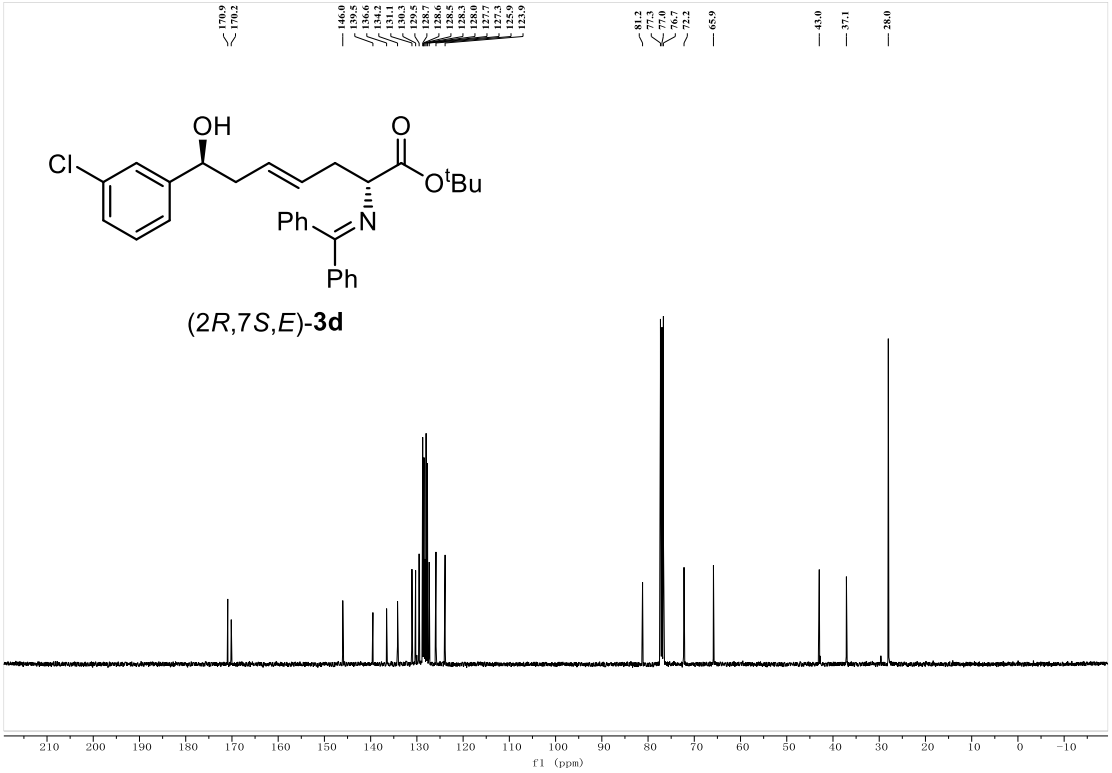
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3c**



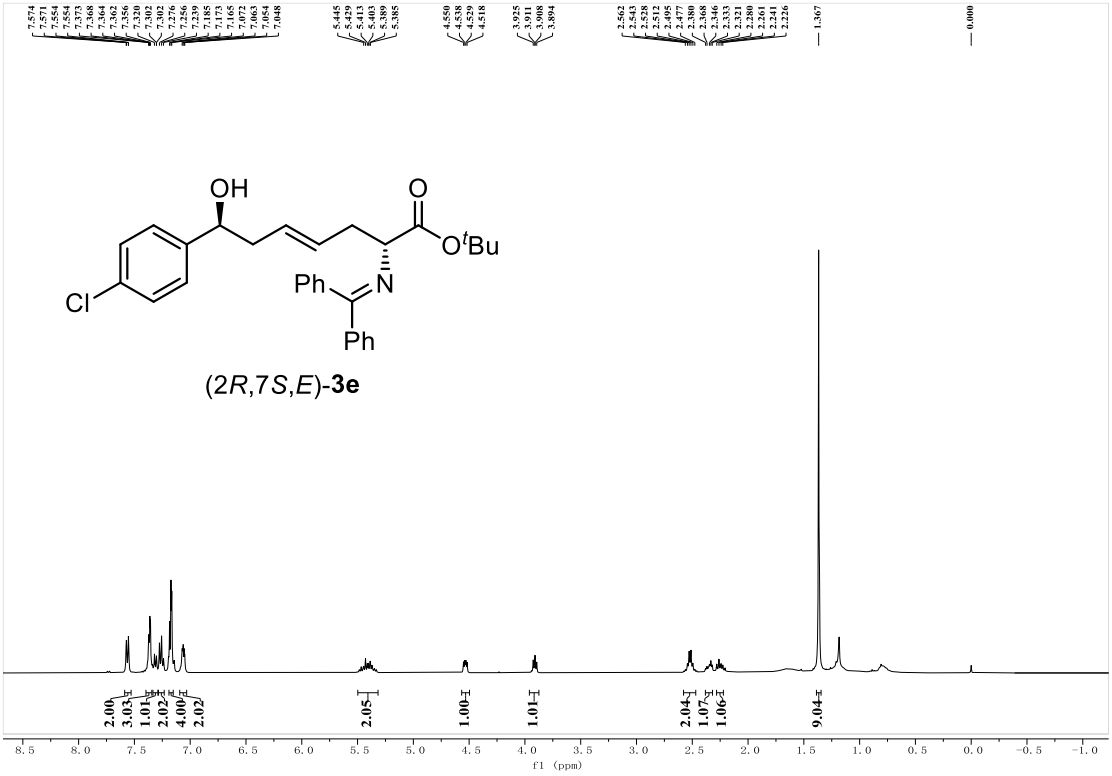
^{19}F NMR (376 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3c**



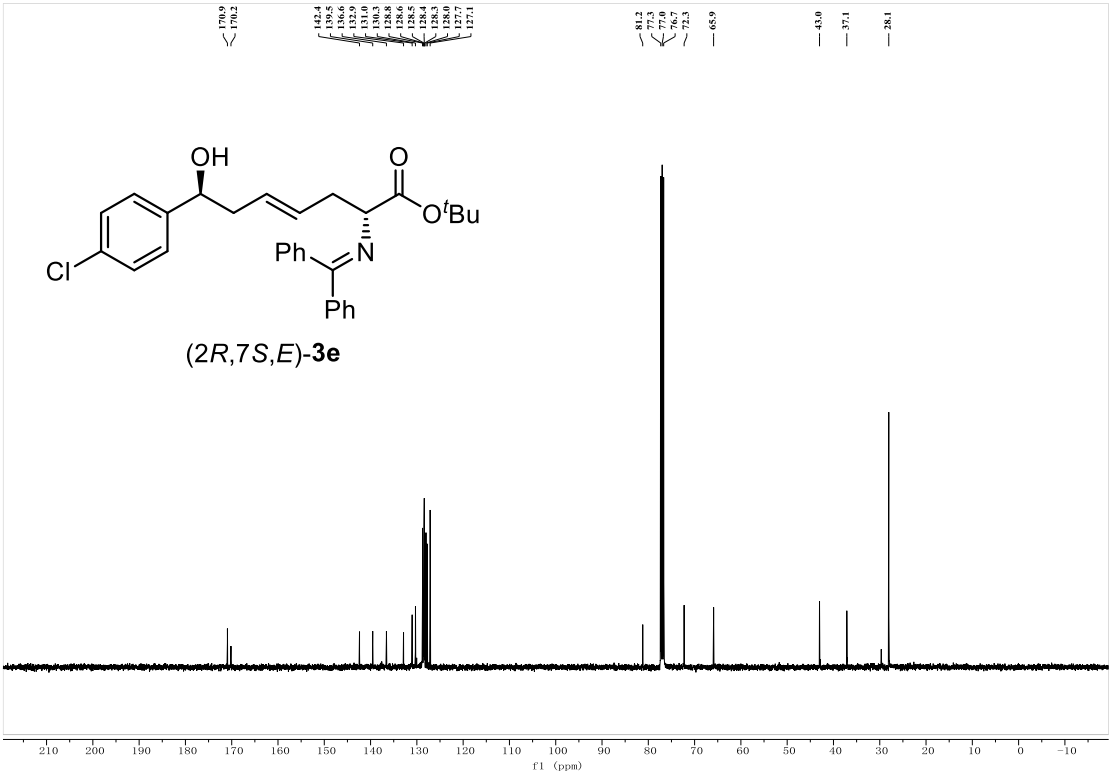
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3d**



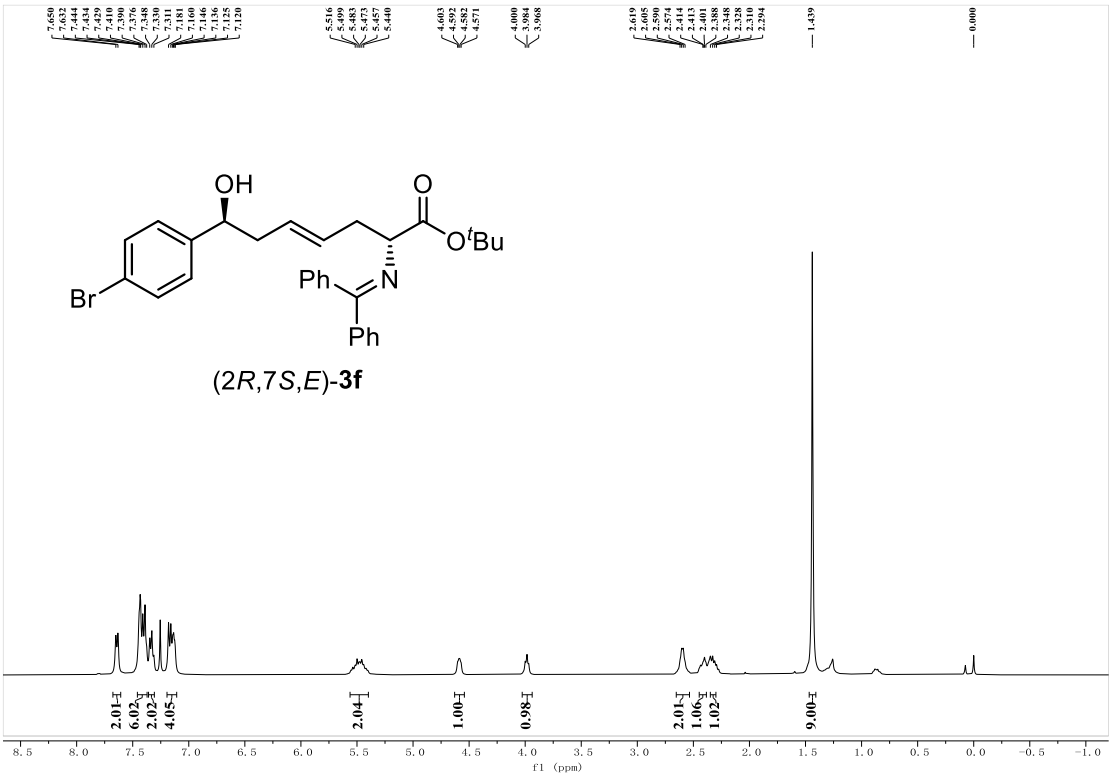
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3d**



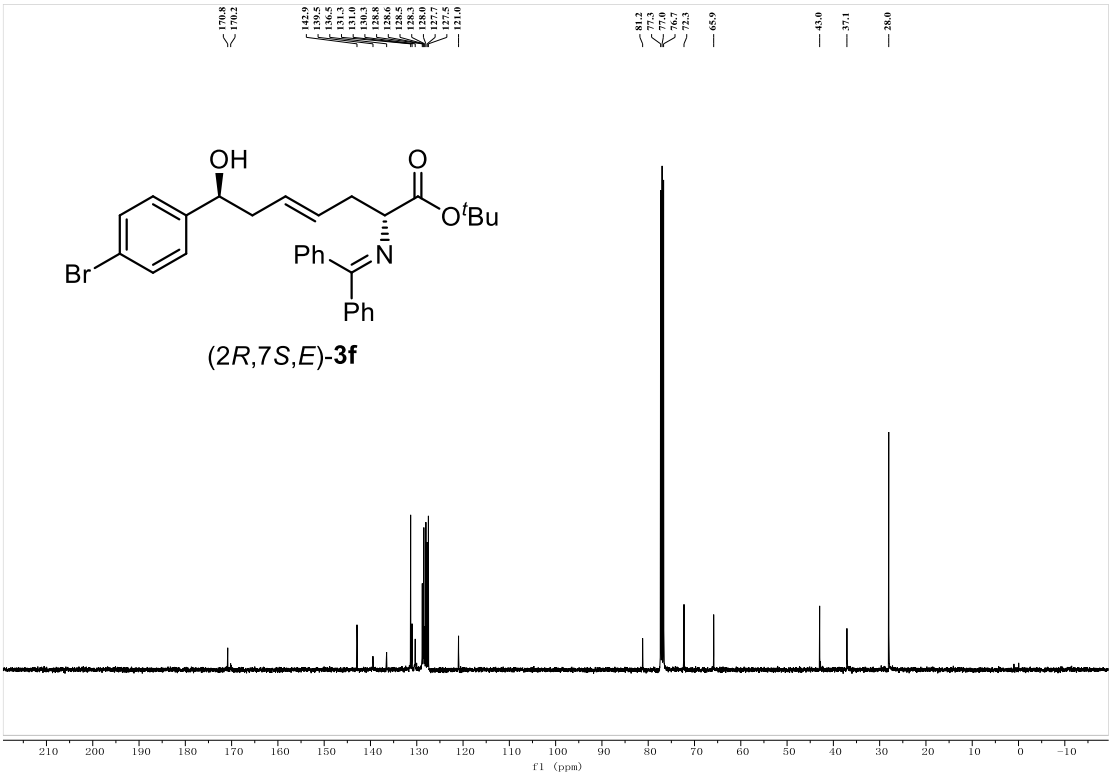
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3e**



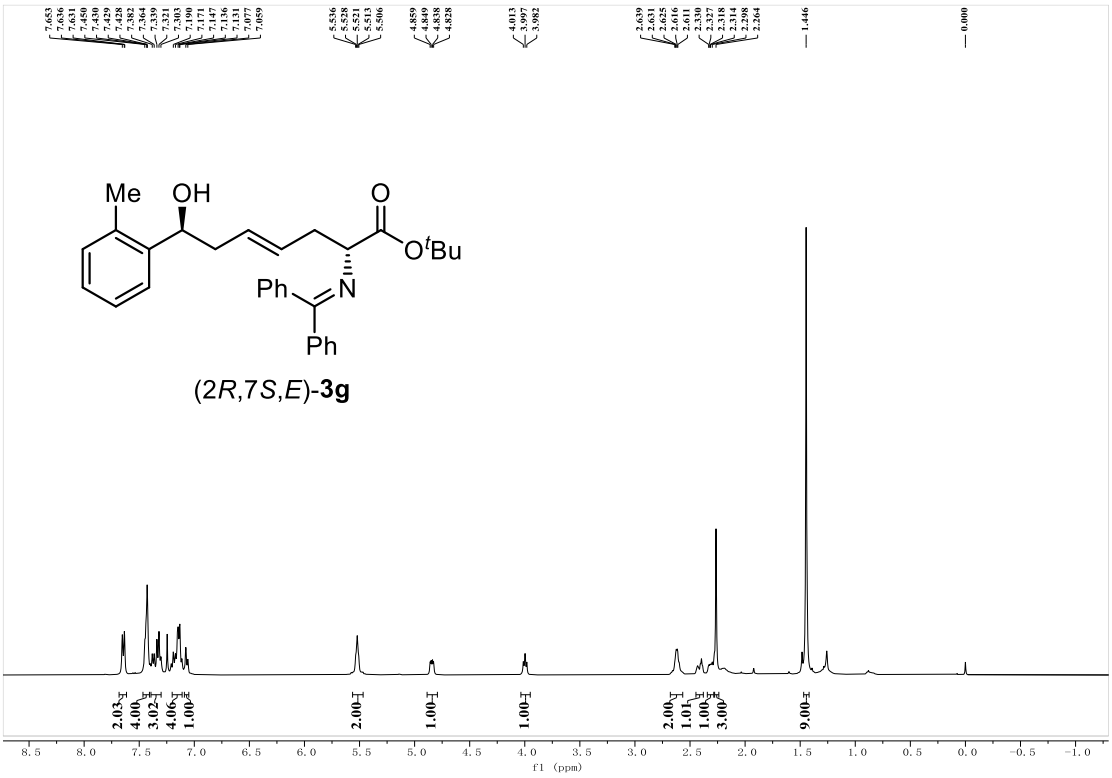
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3e**



^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3f**



^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3f**



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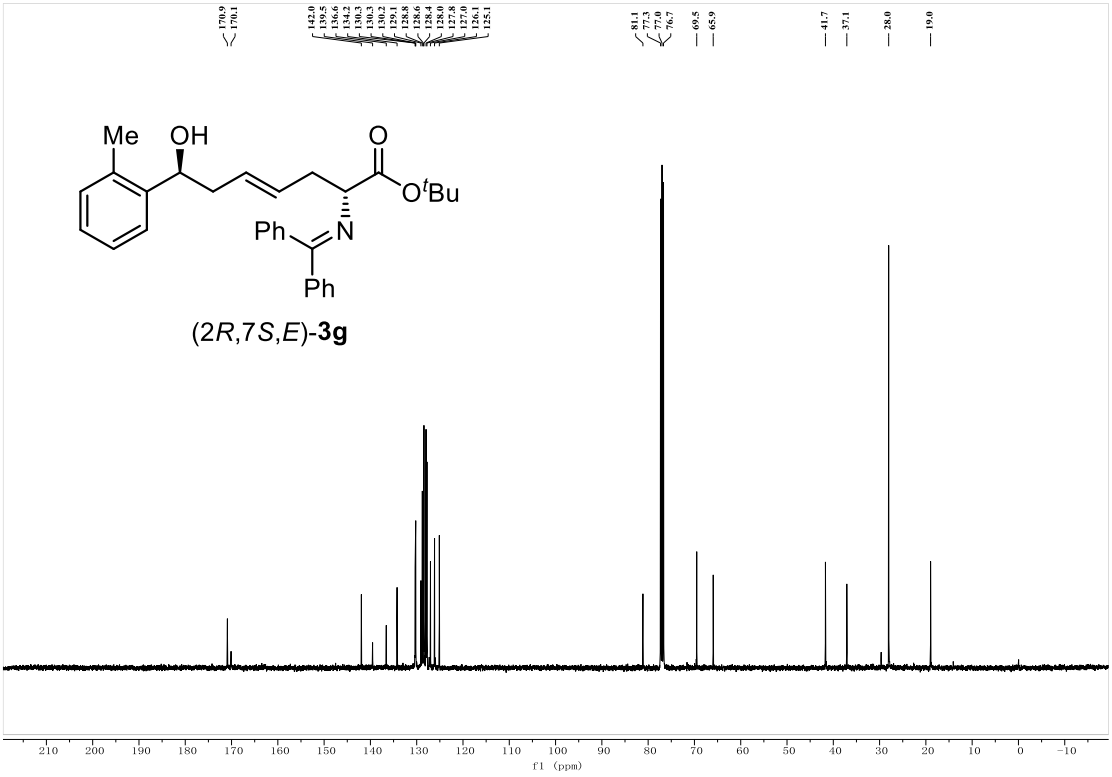
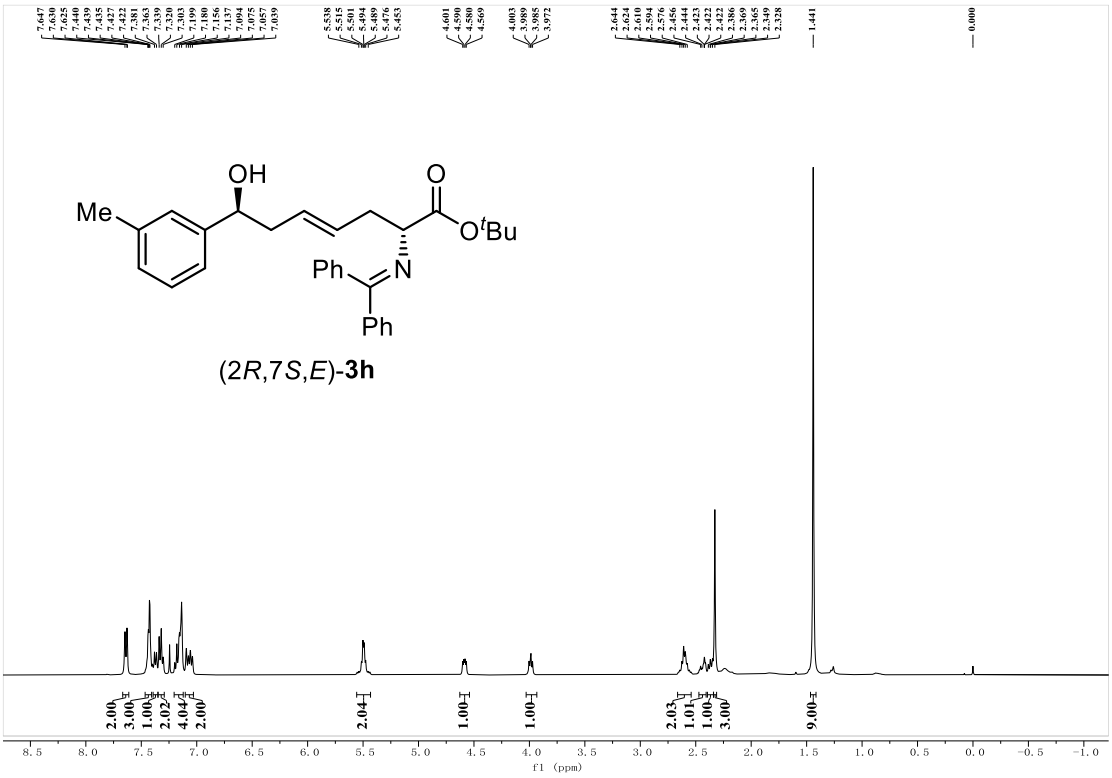


^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3g**



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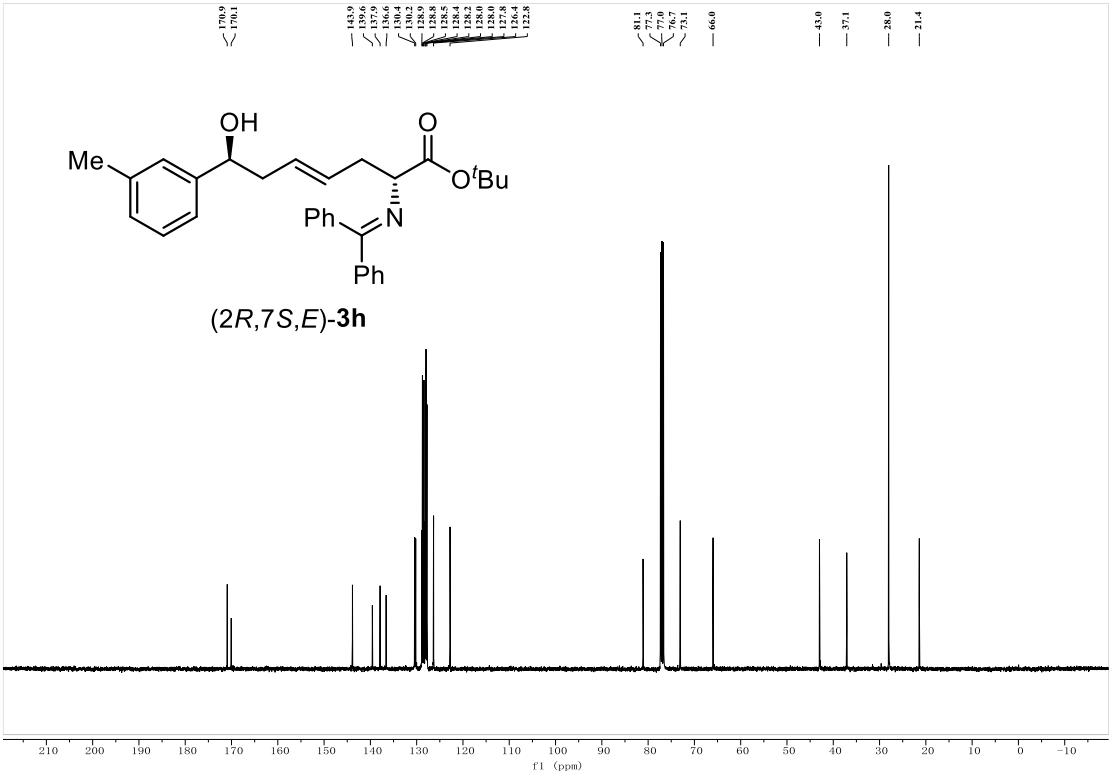
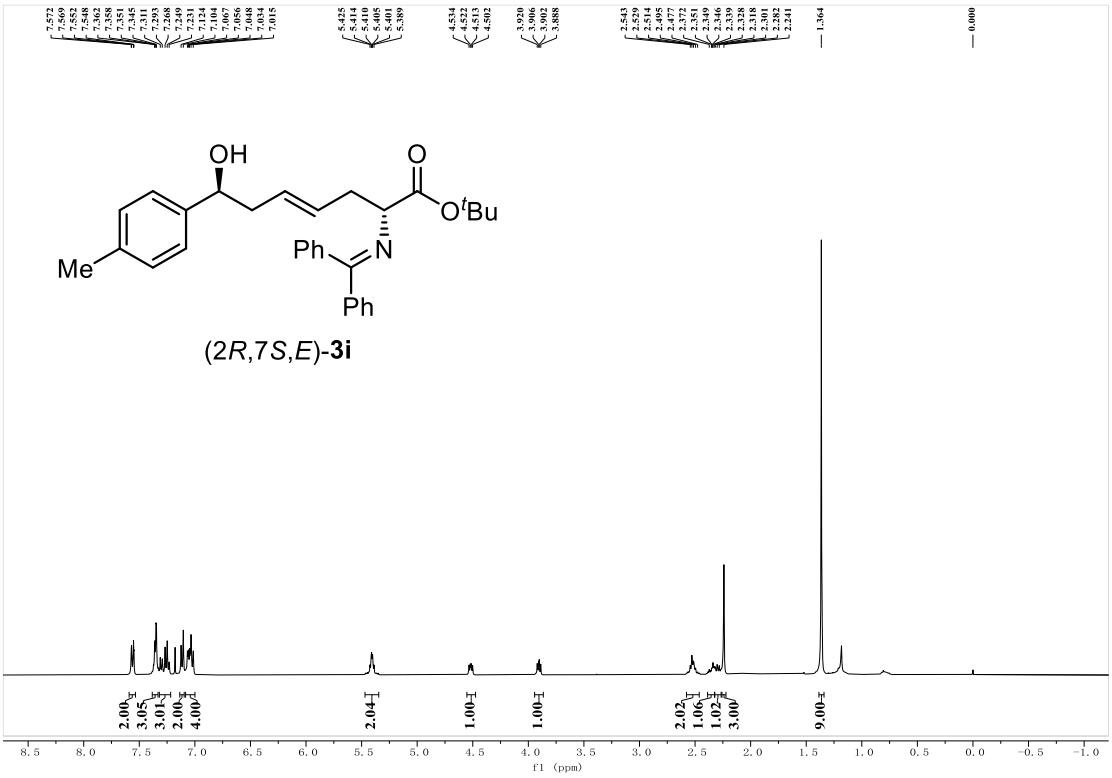
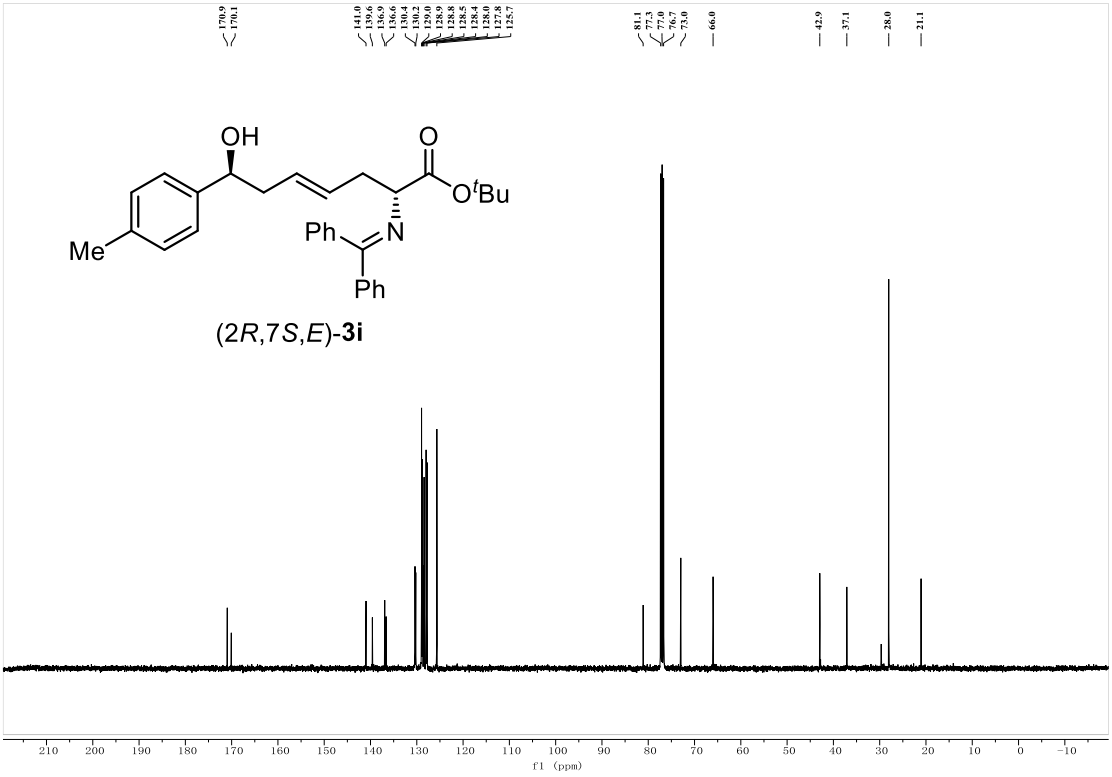


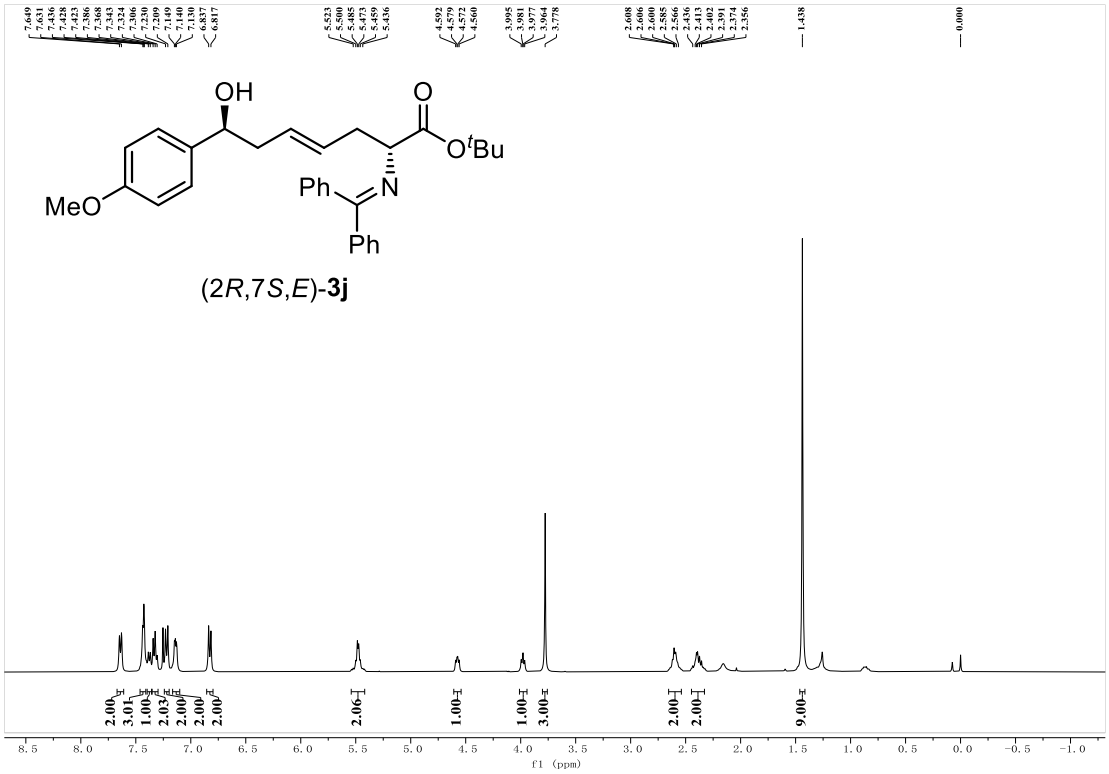
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3h**



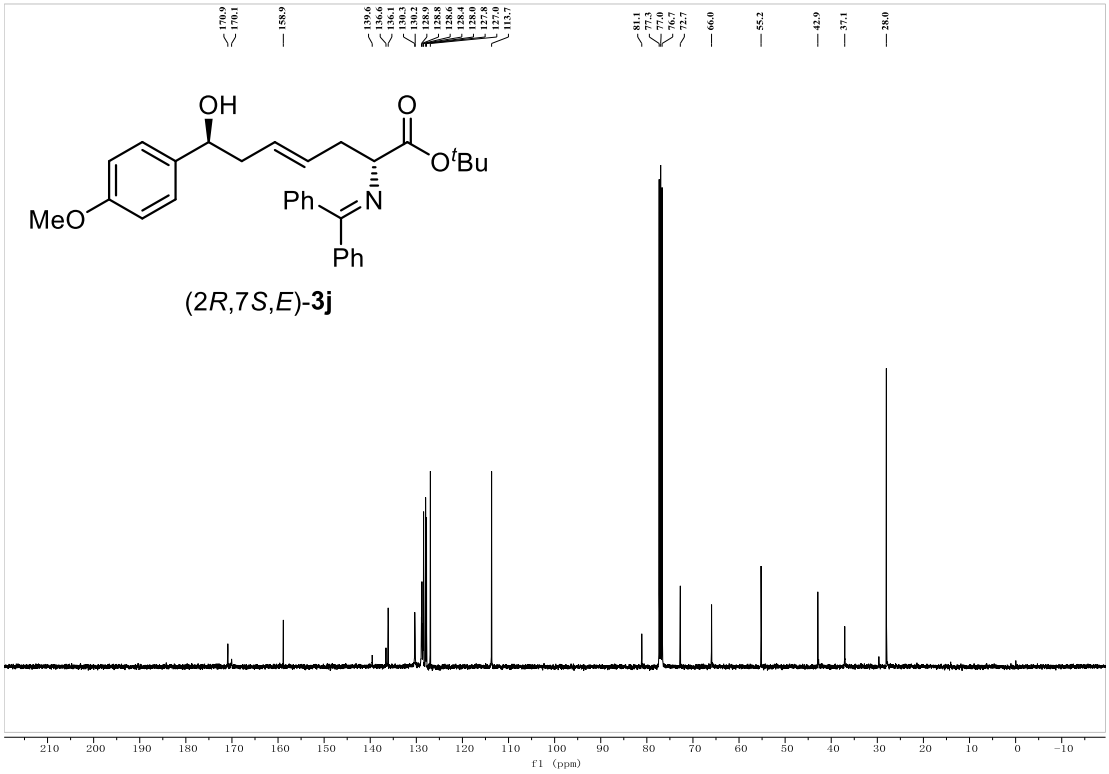
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3i**



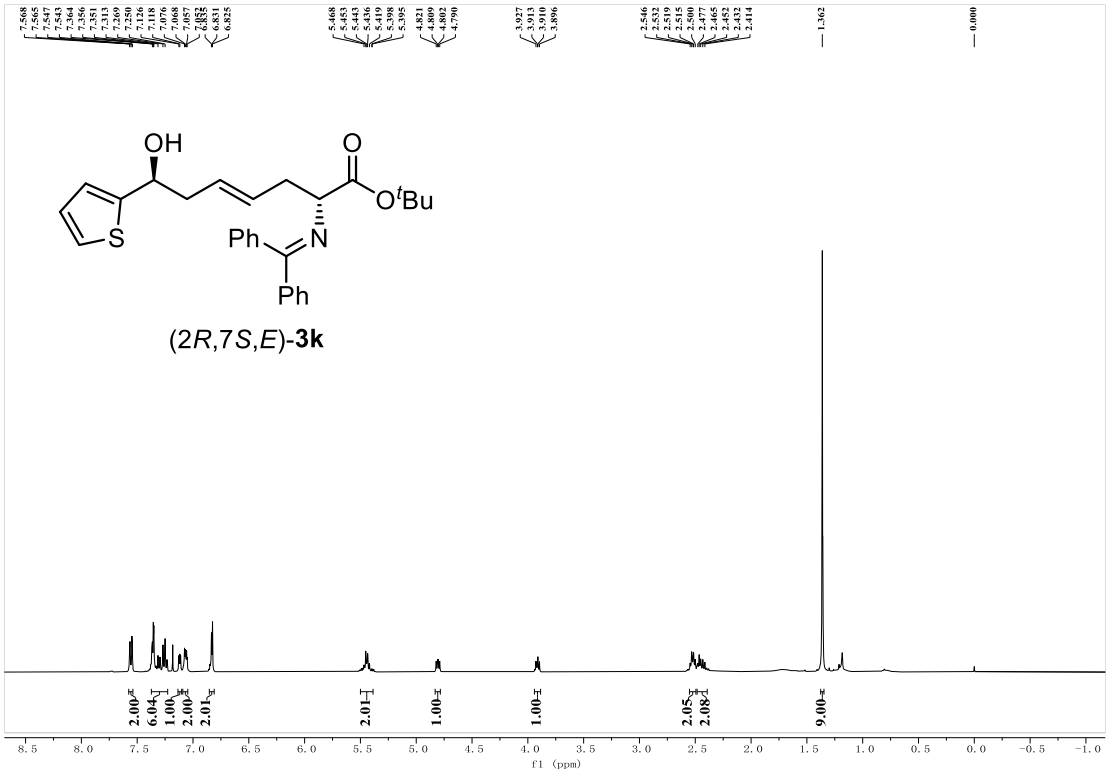
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3i**



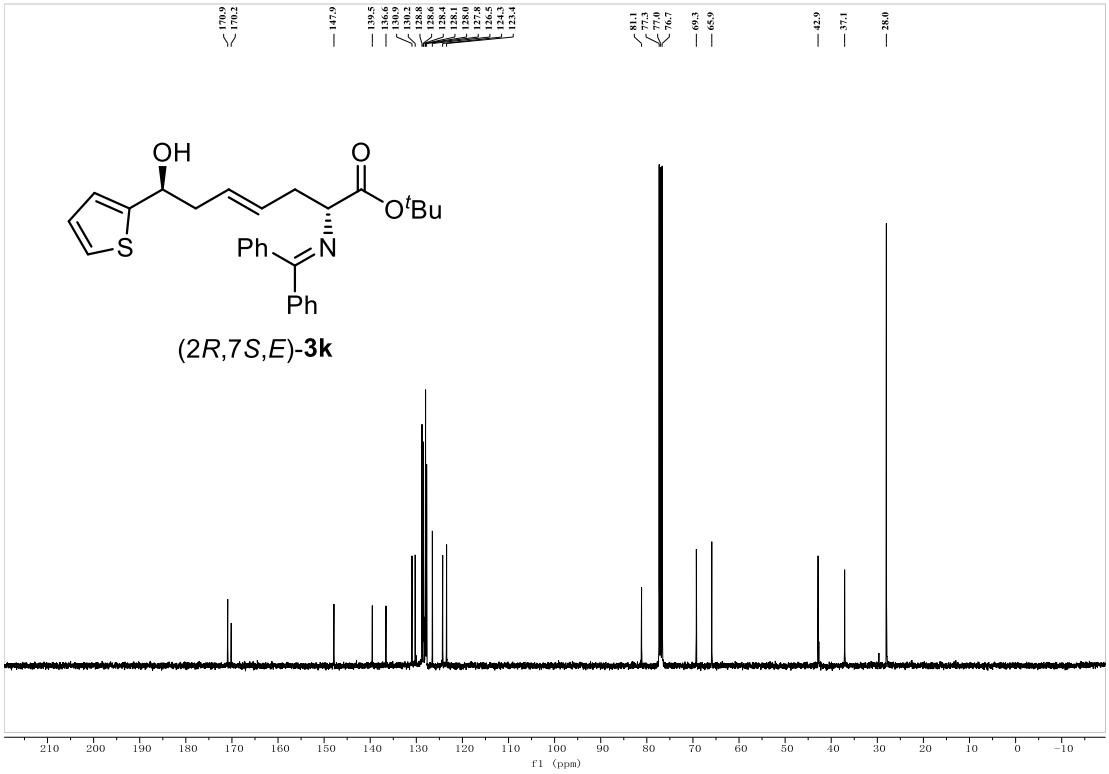
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3j**



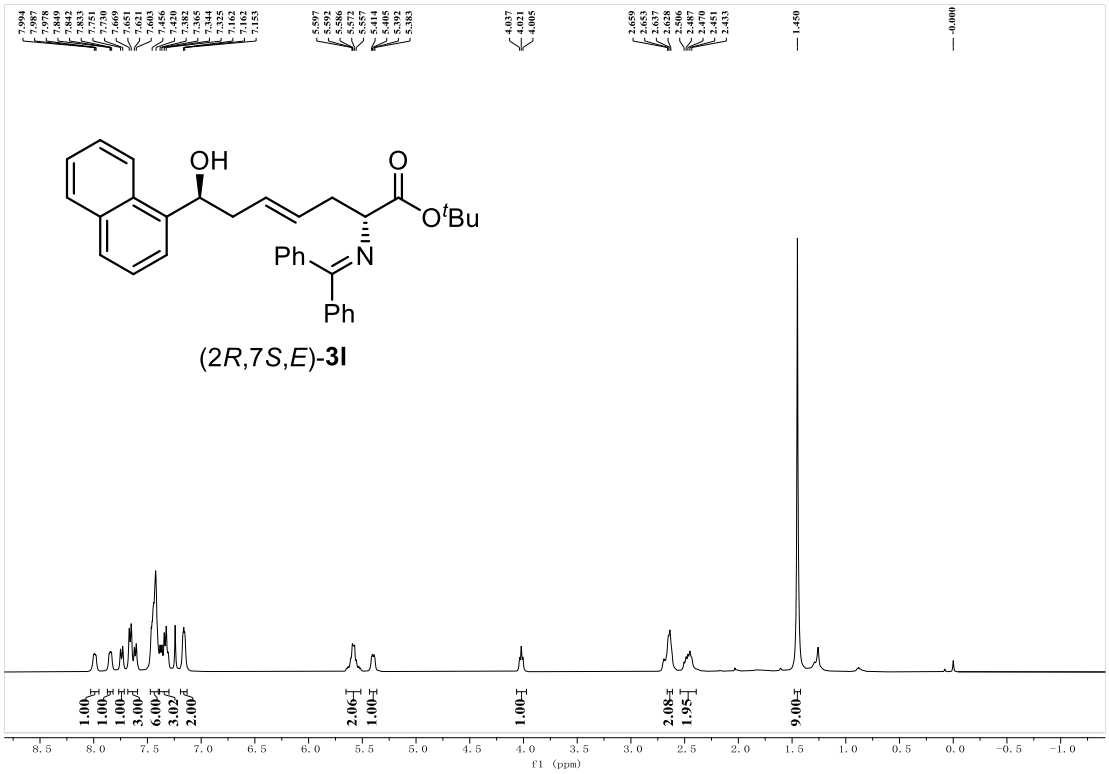
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3j**



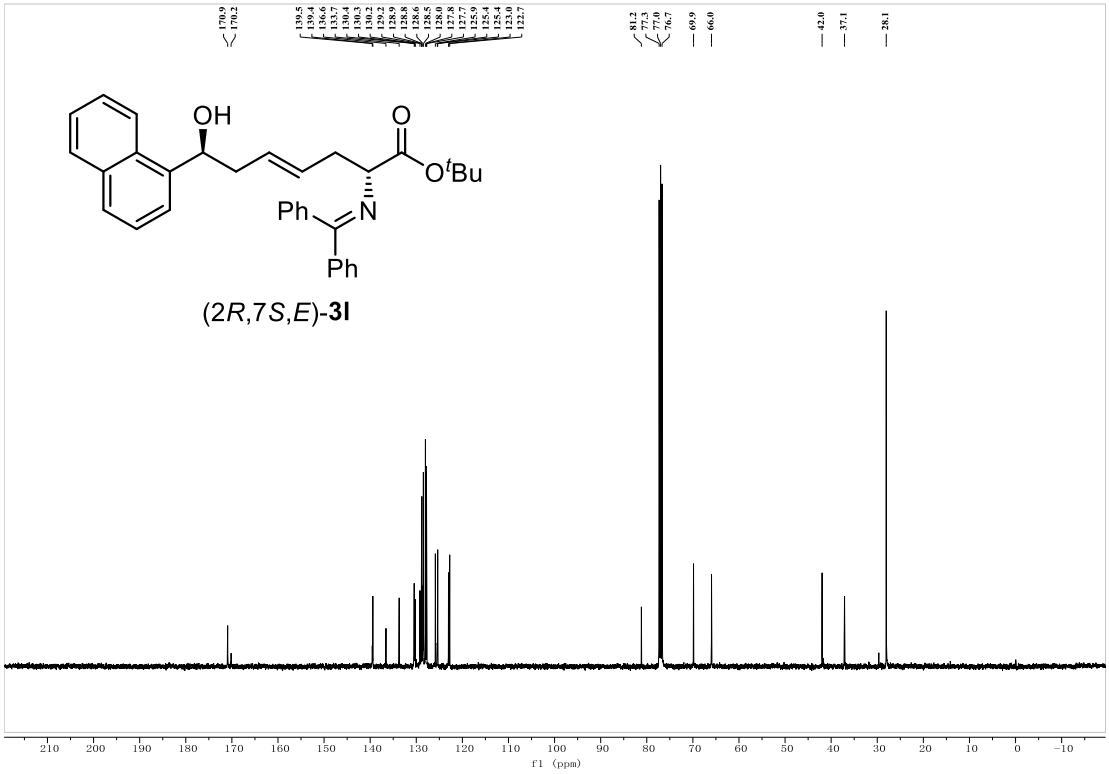
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3k**



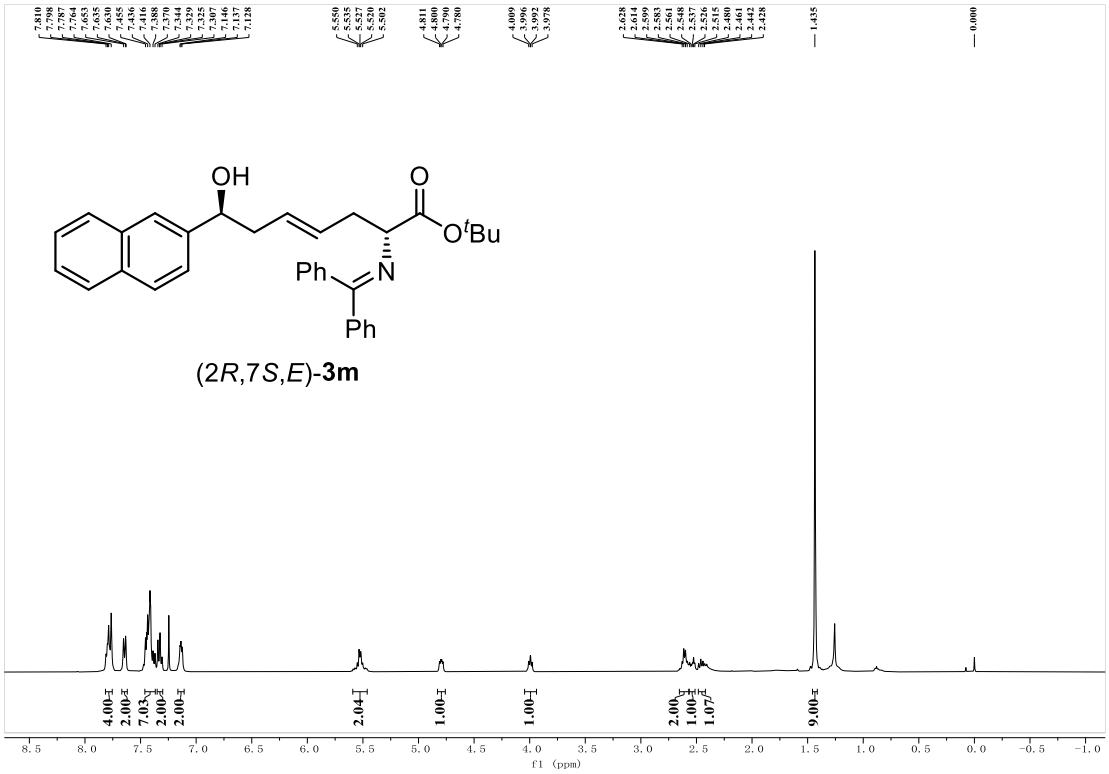
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3k**



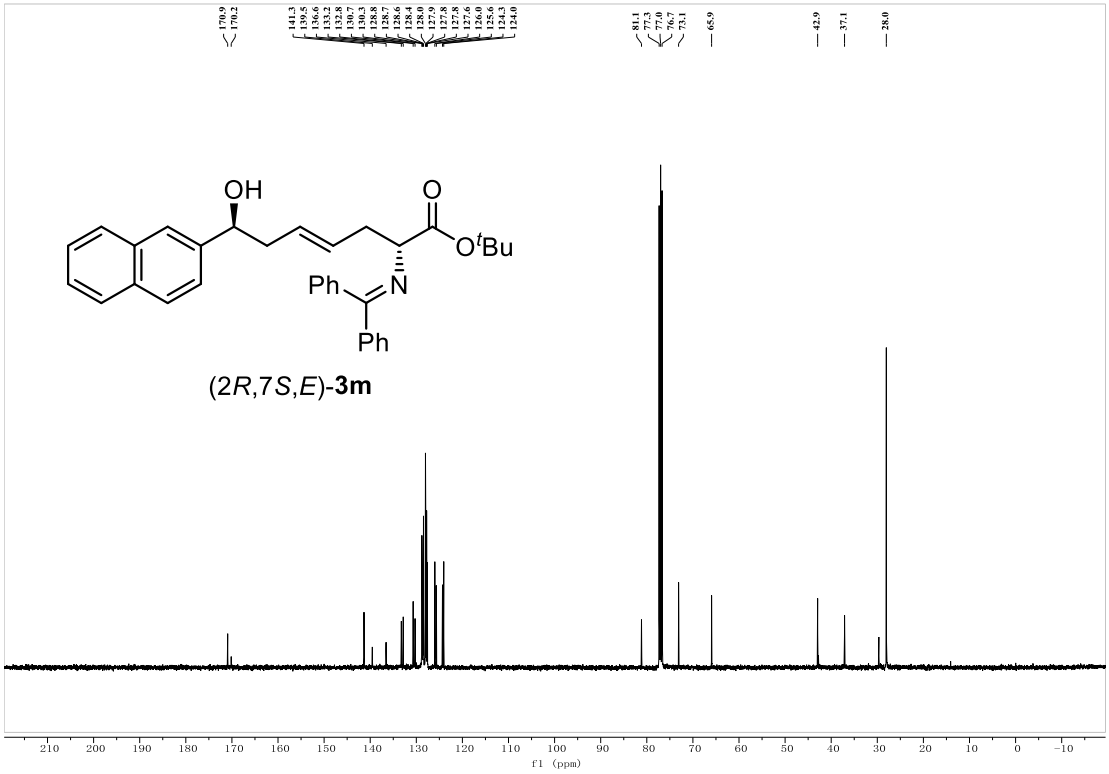
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3l**



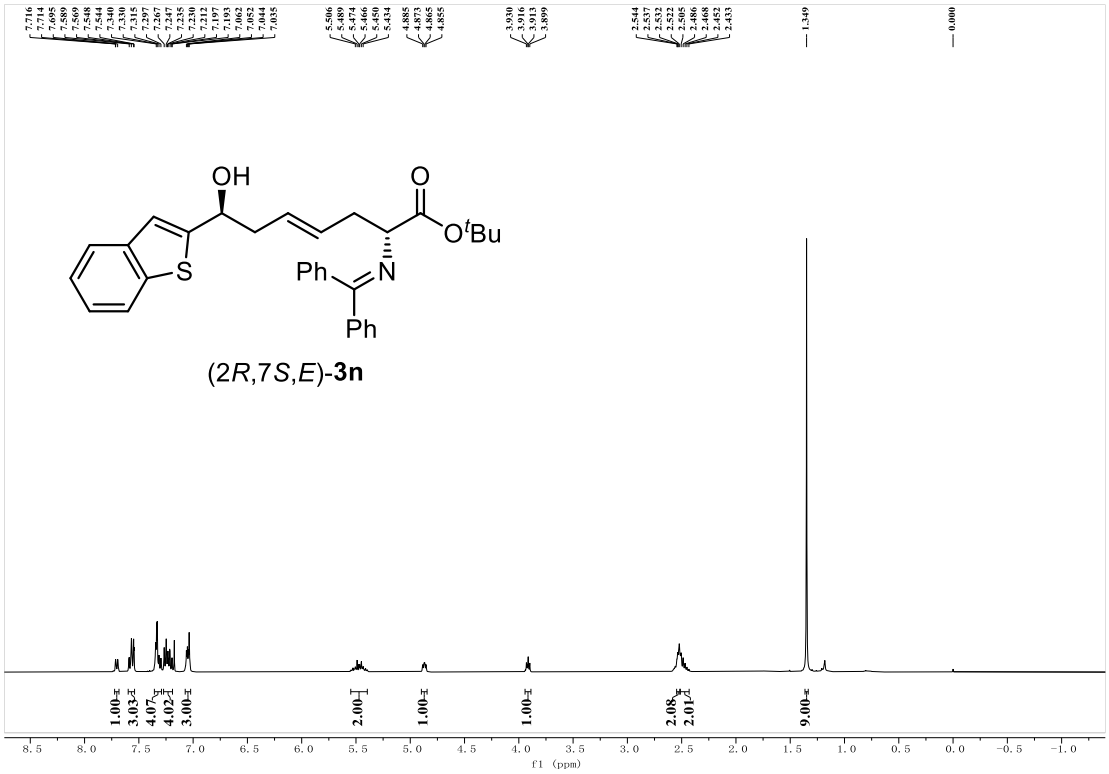
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3l**



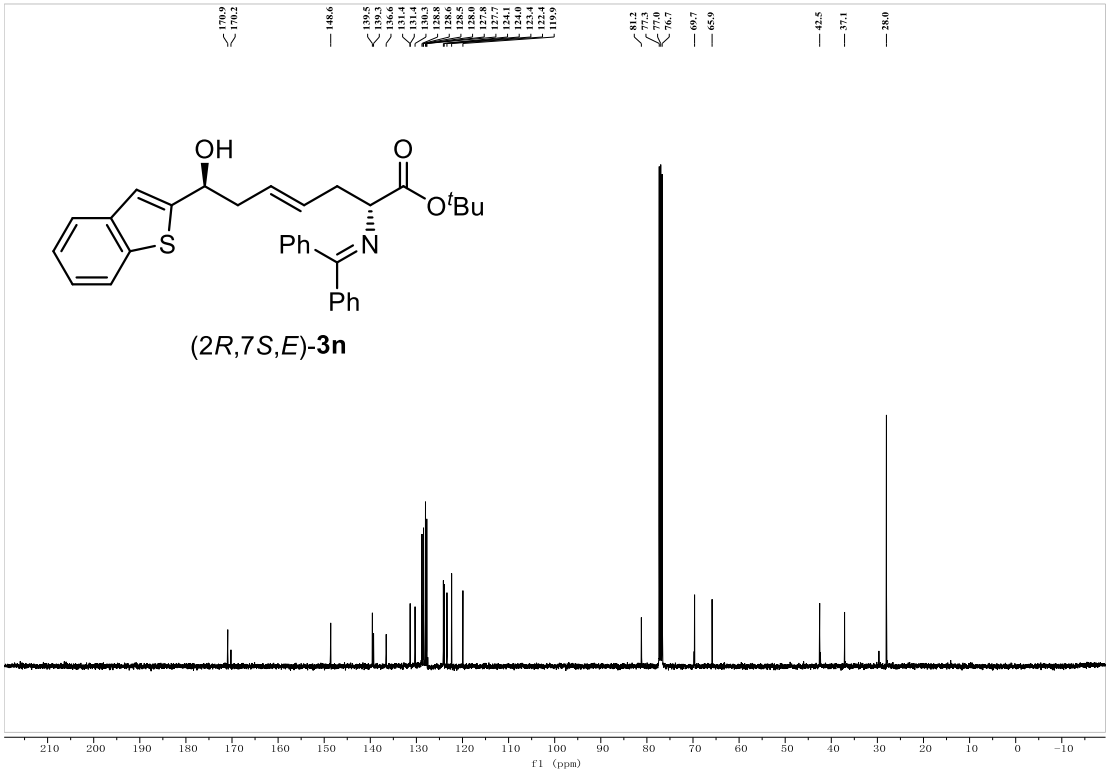
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3m**



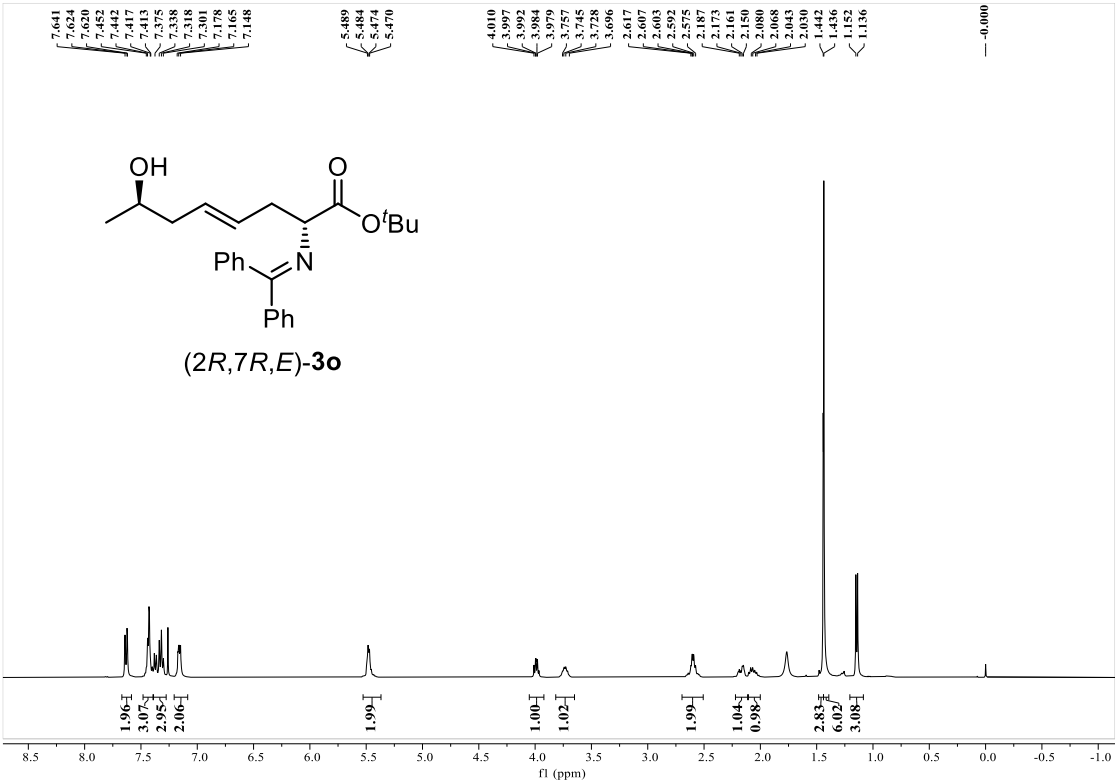
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3m**



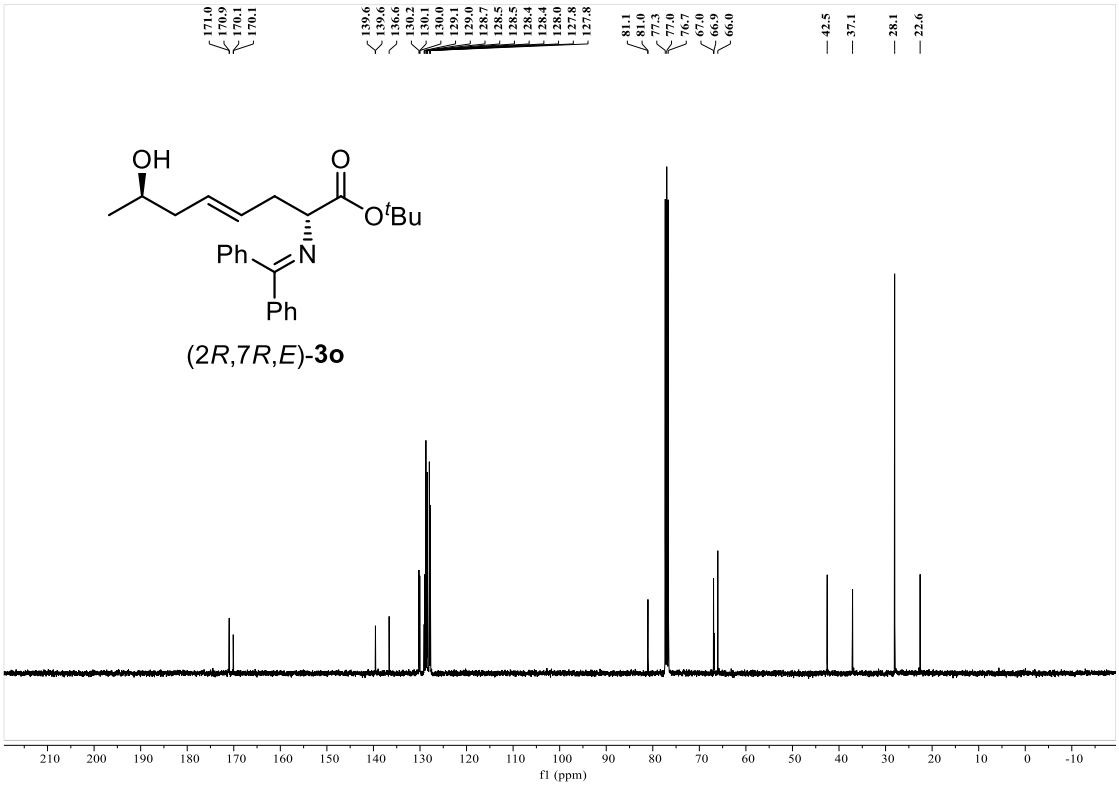
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3n**



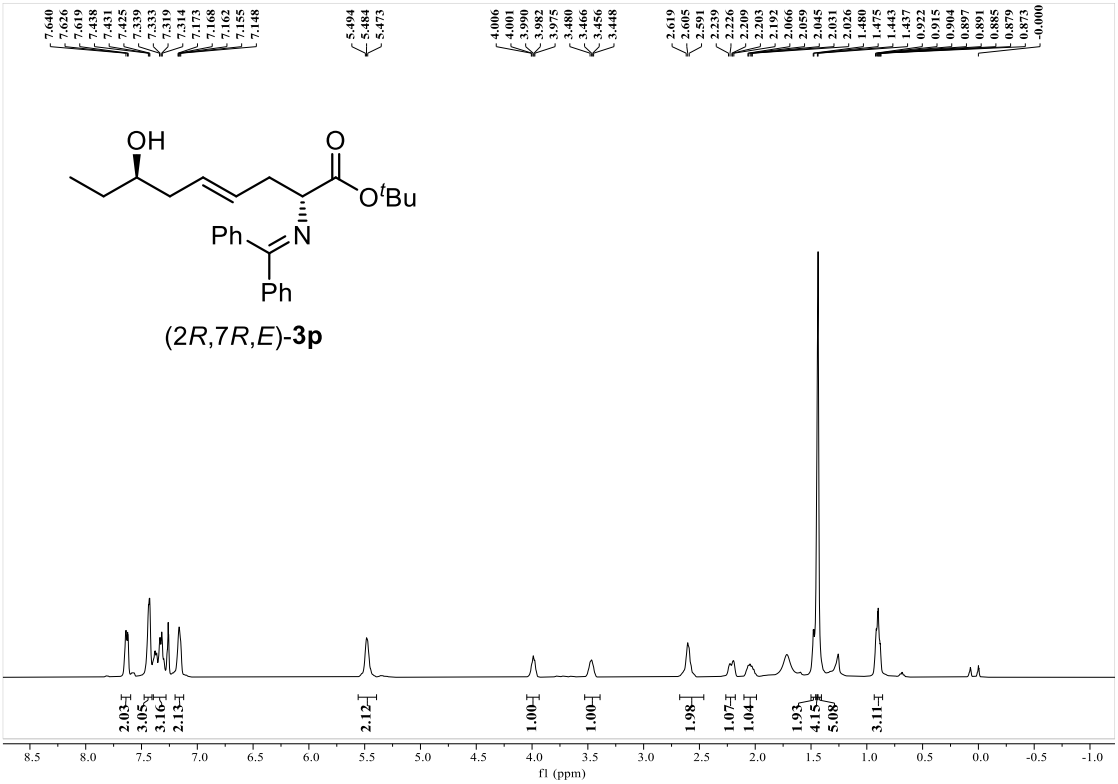
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3n**



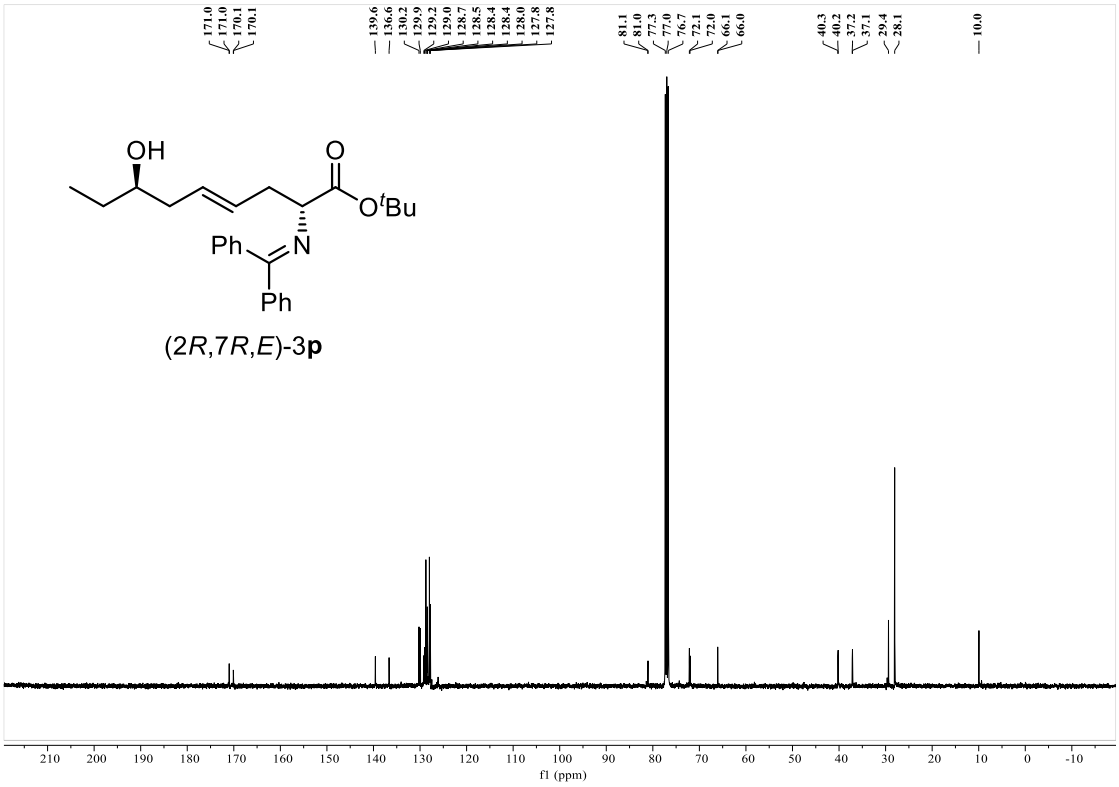
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3o**



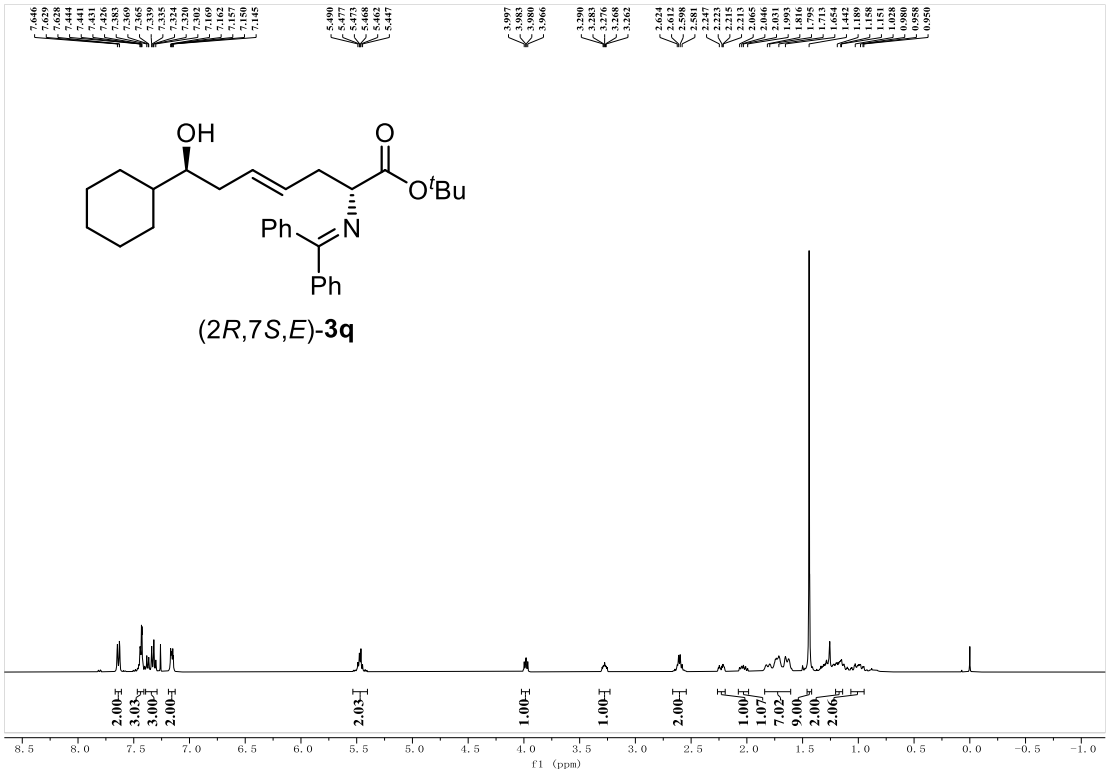
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3o**



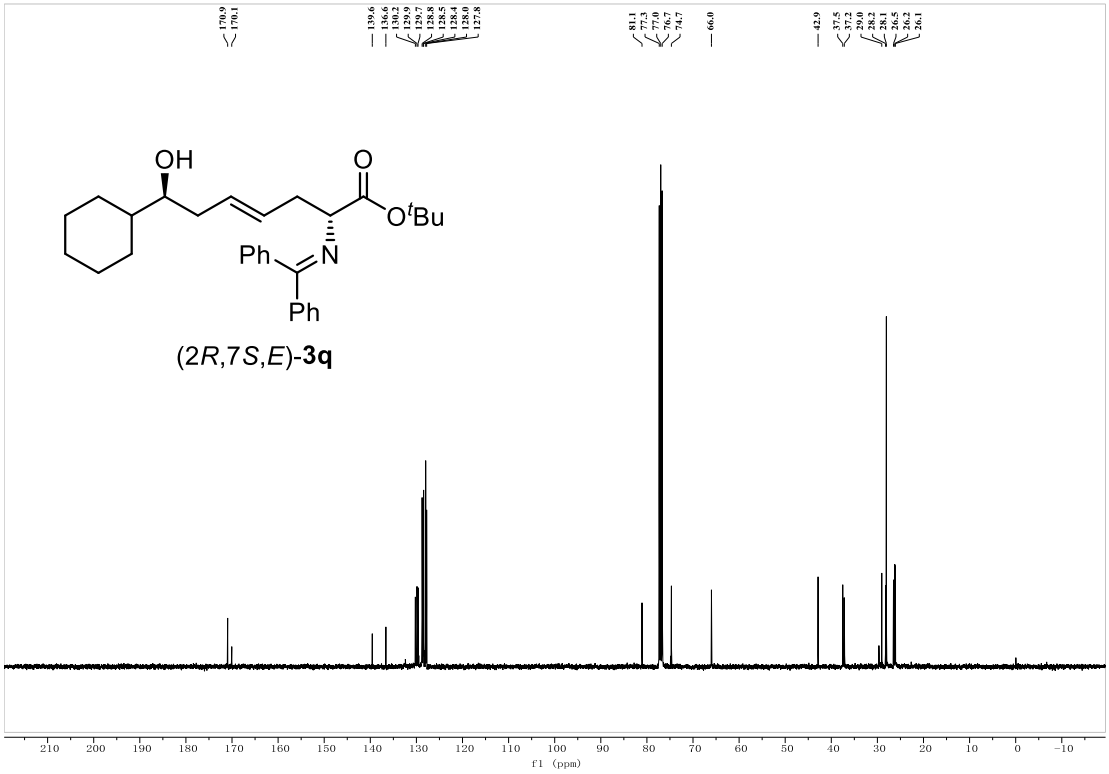
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3p**



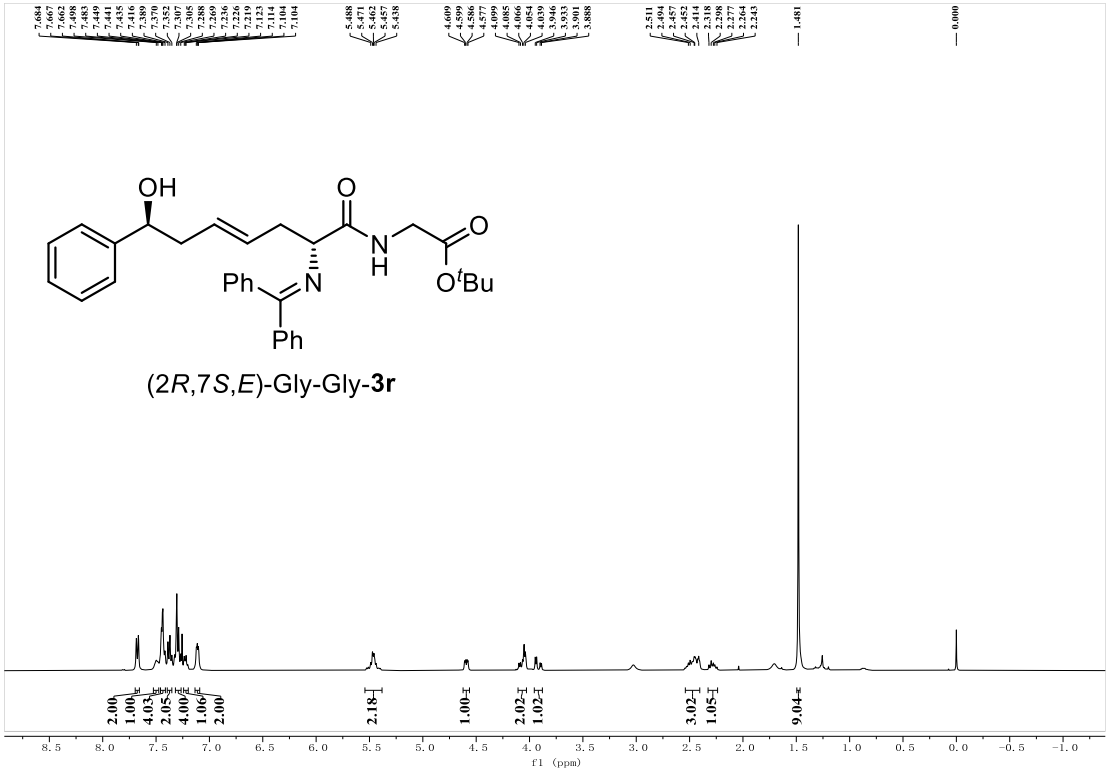
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3p**



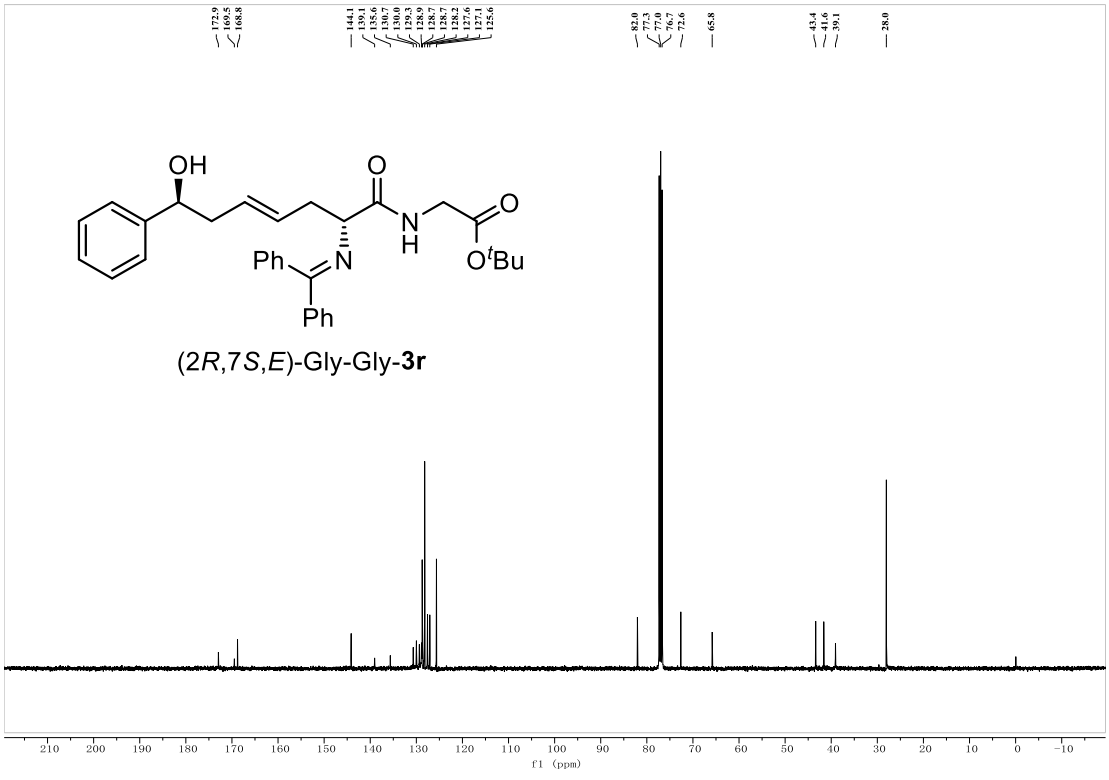
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3q**



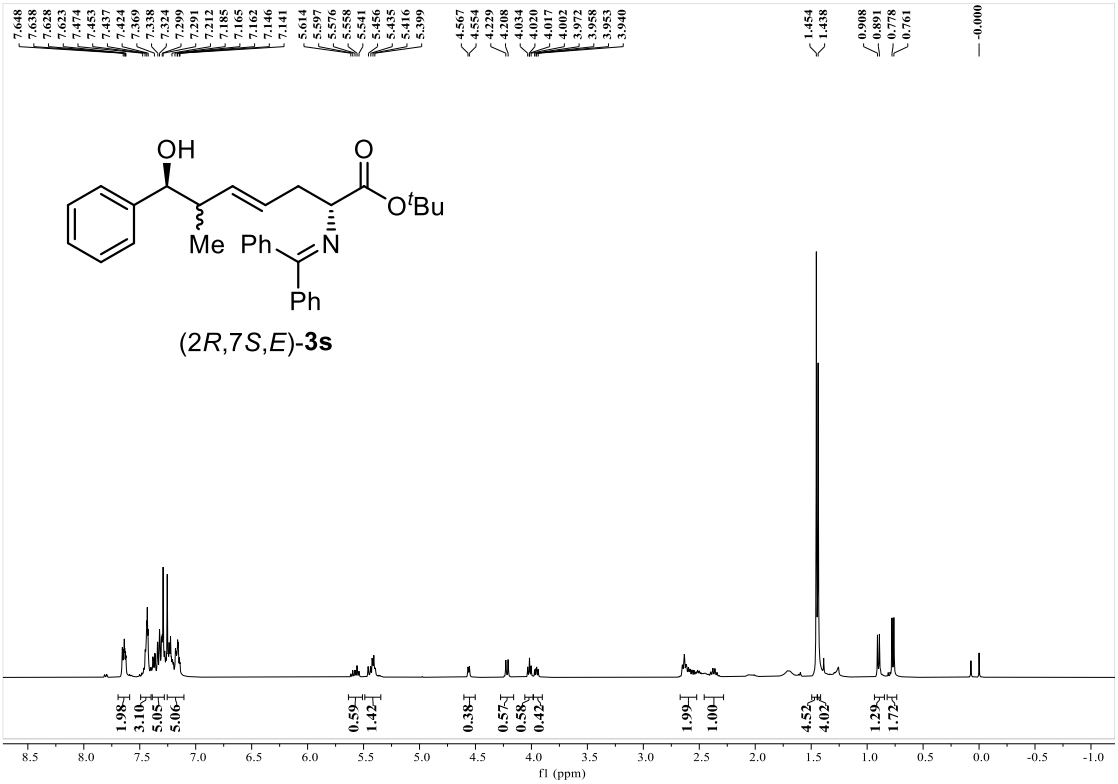
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3q**



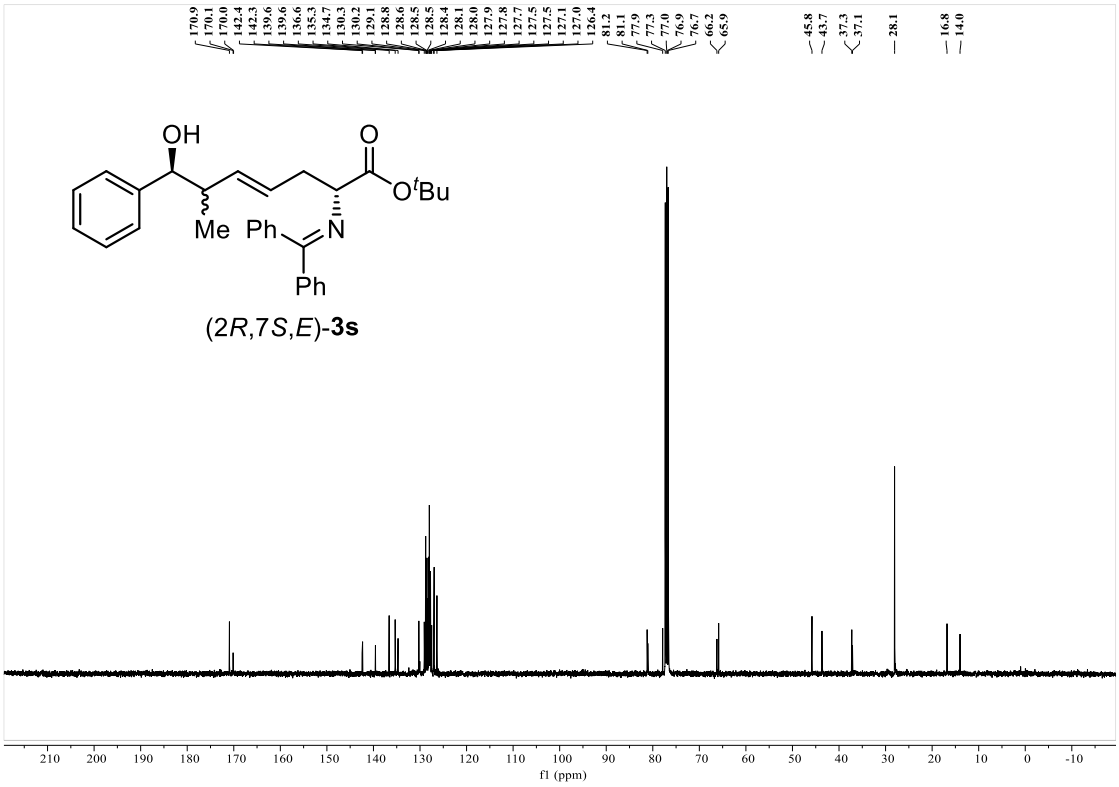
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-Gly-Gly-**3r**



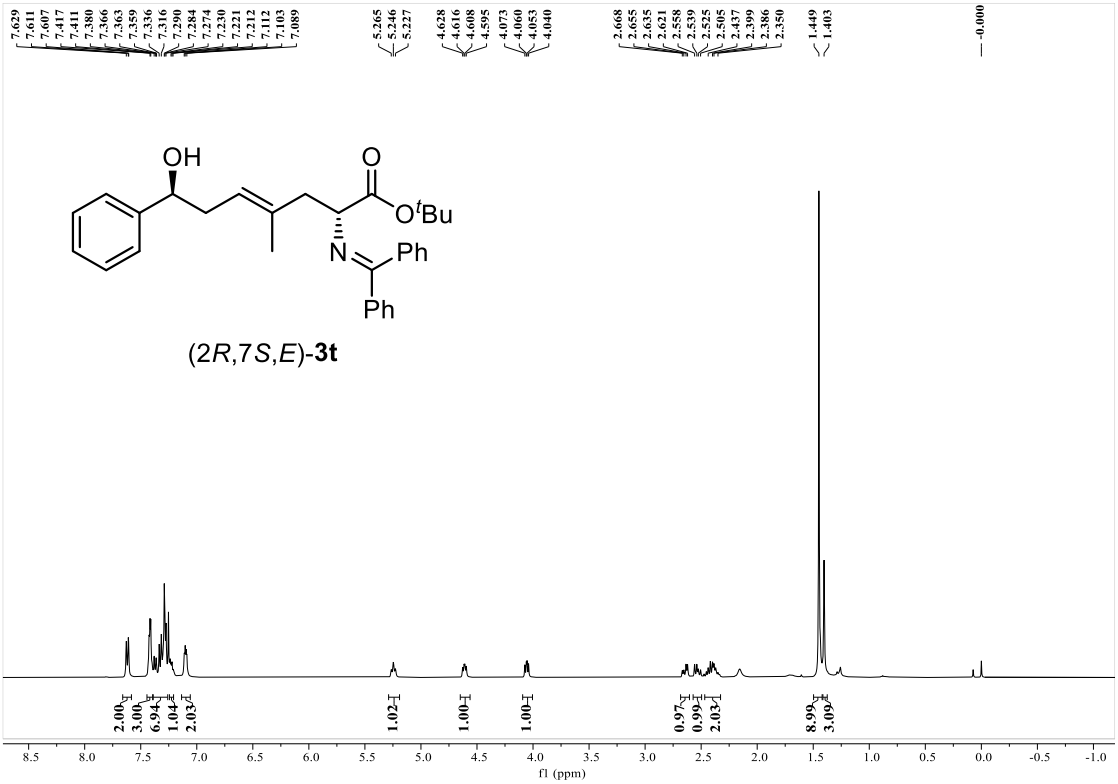
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-Gly-Gly-**3r**



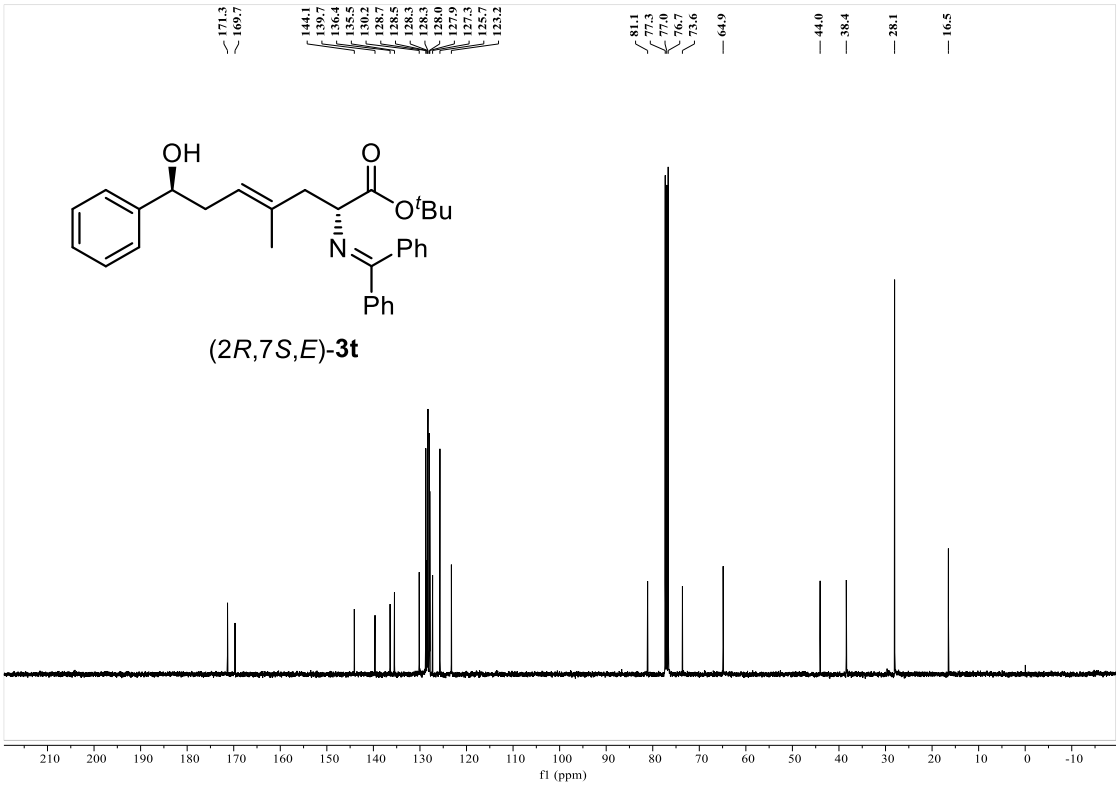
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3s**



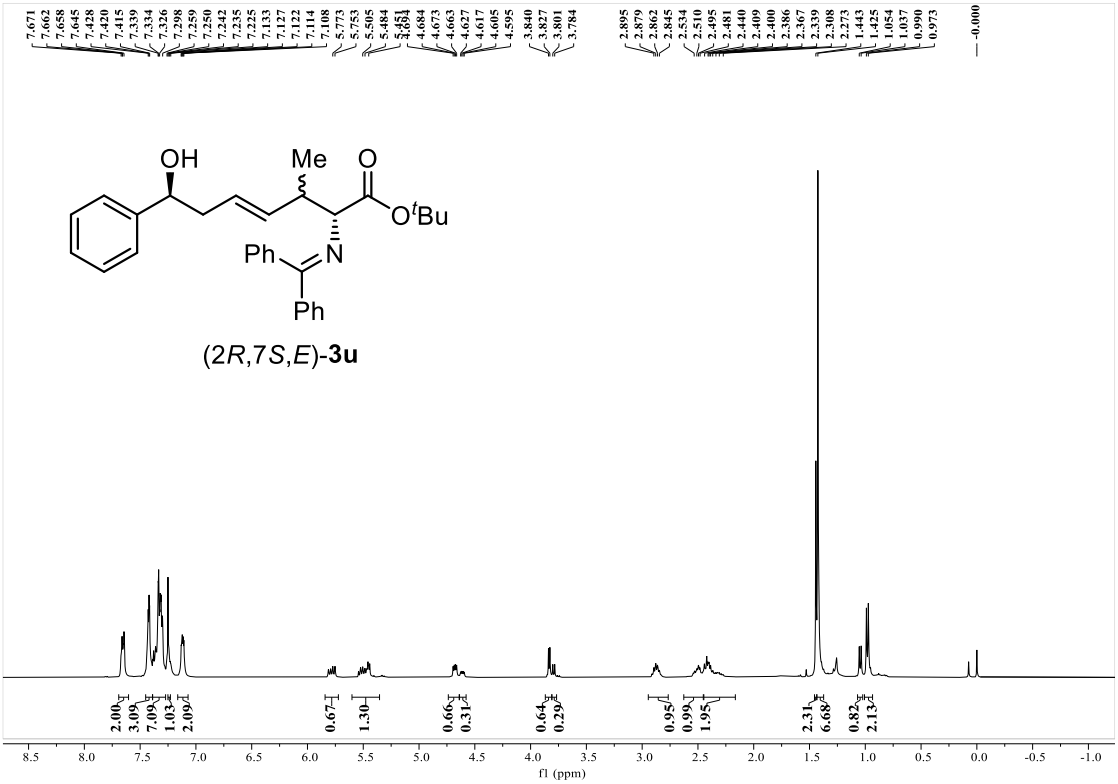
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3s**



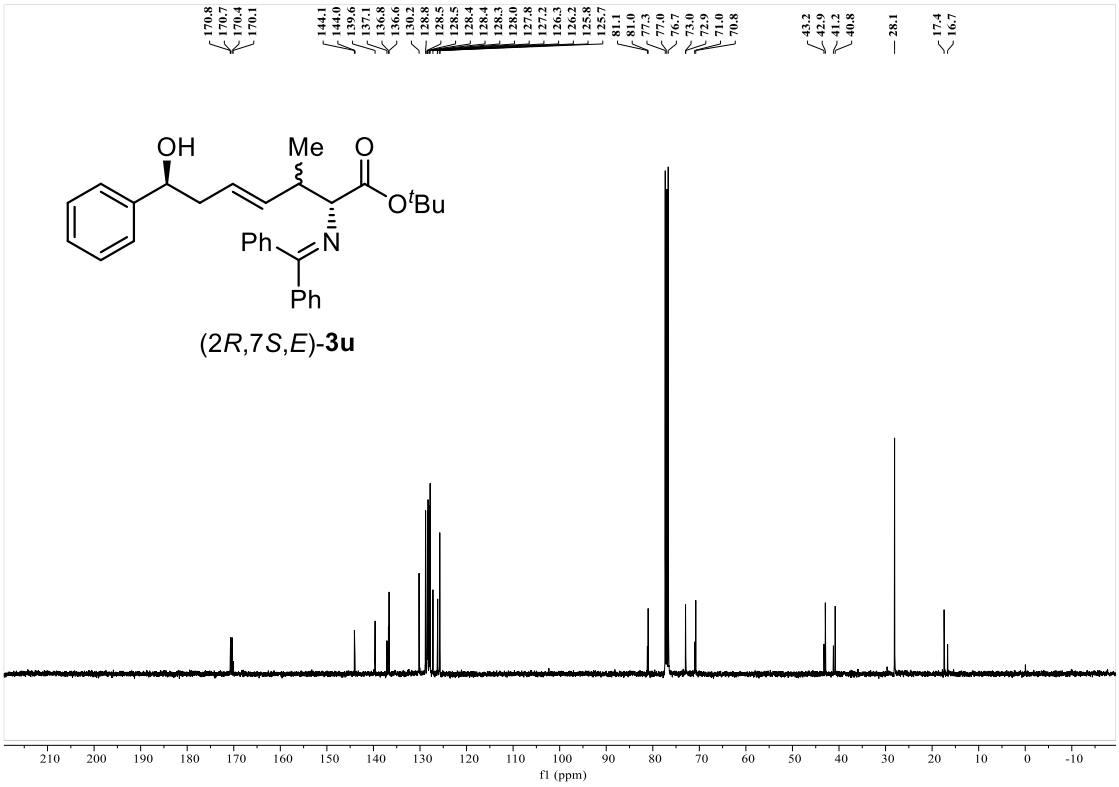
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3t**



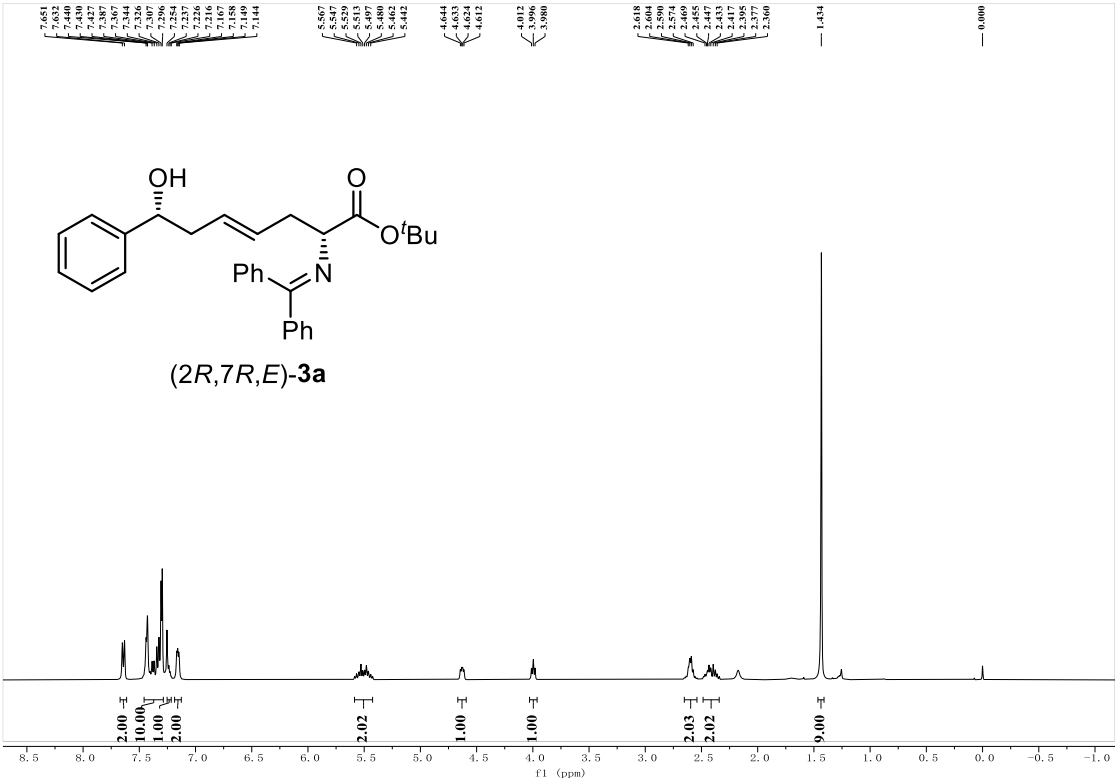
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3t**



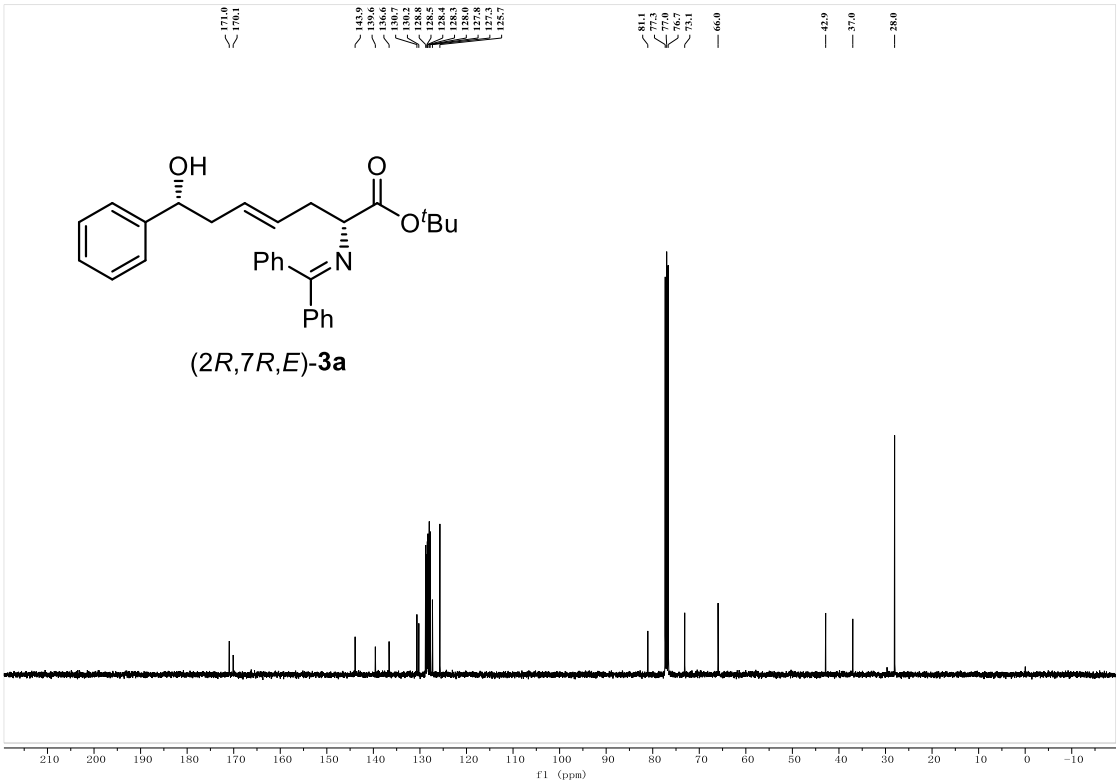
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3u**



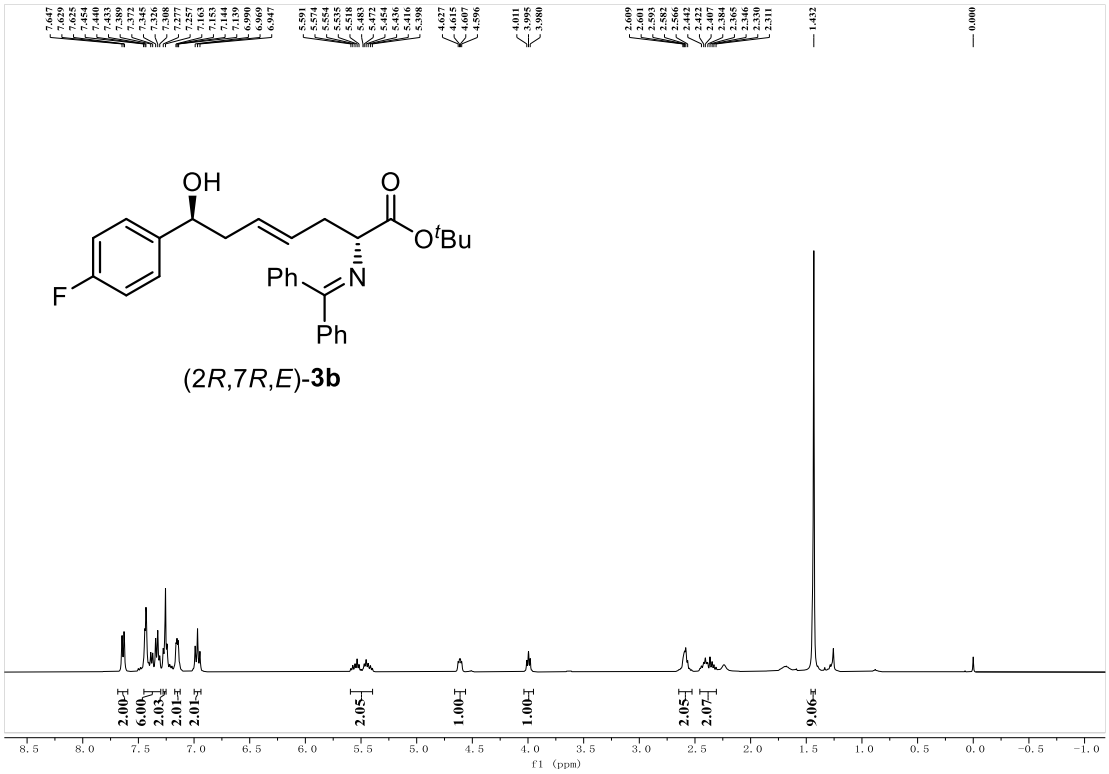
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3u**



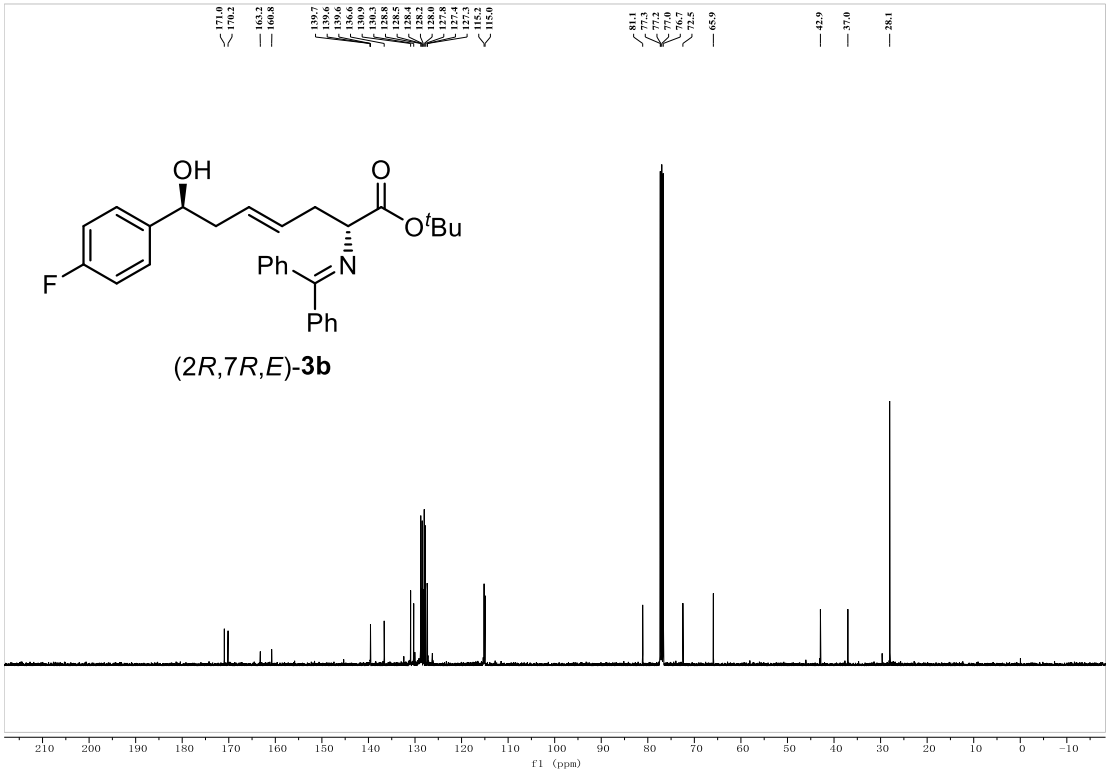
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3a**



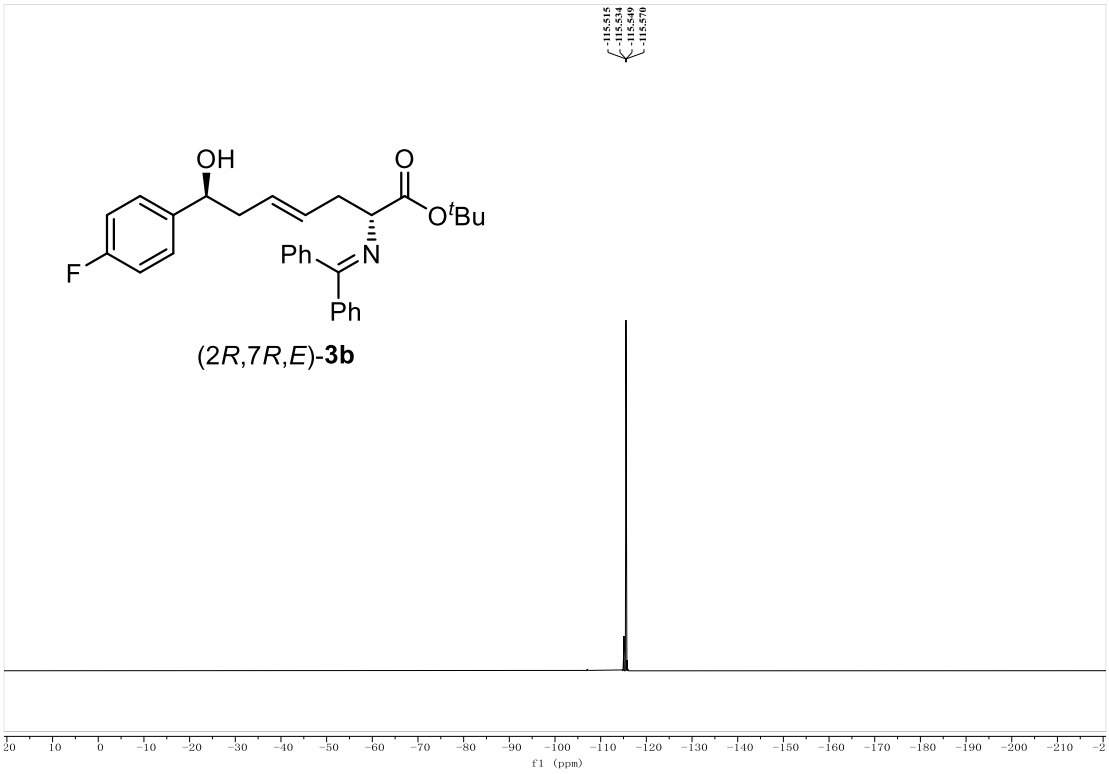
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3a**



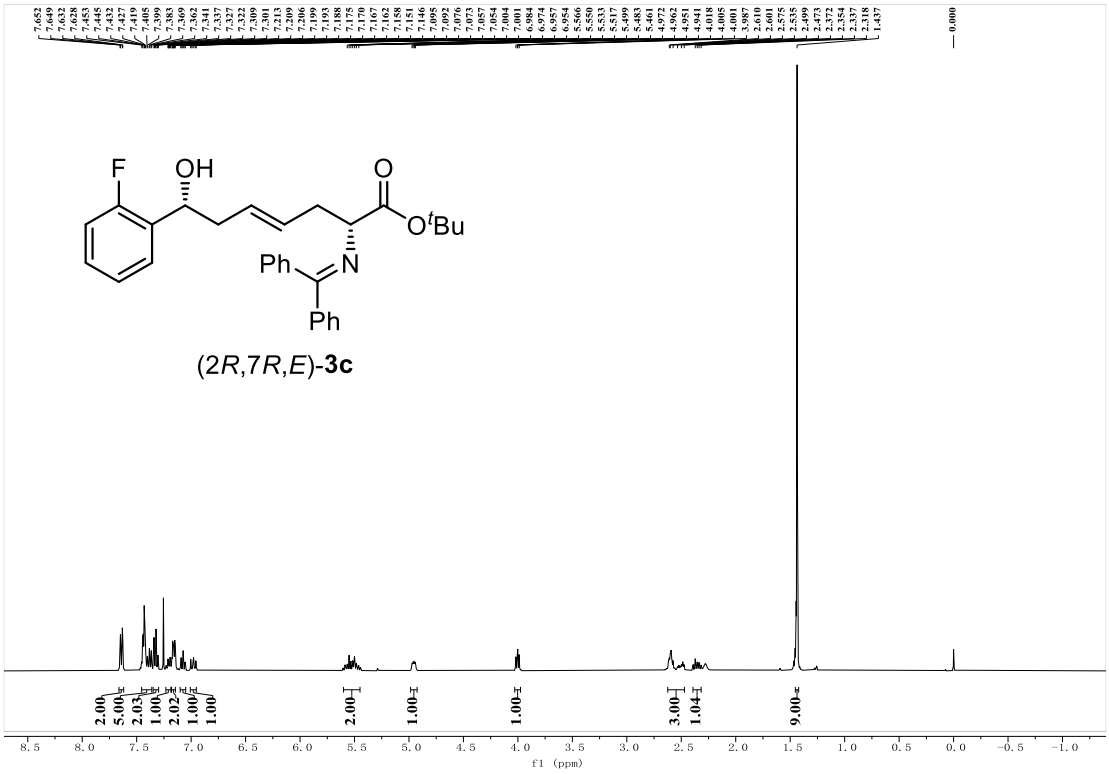
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3b**



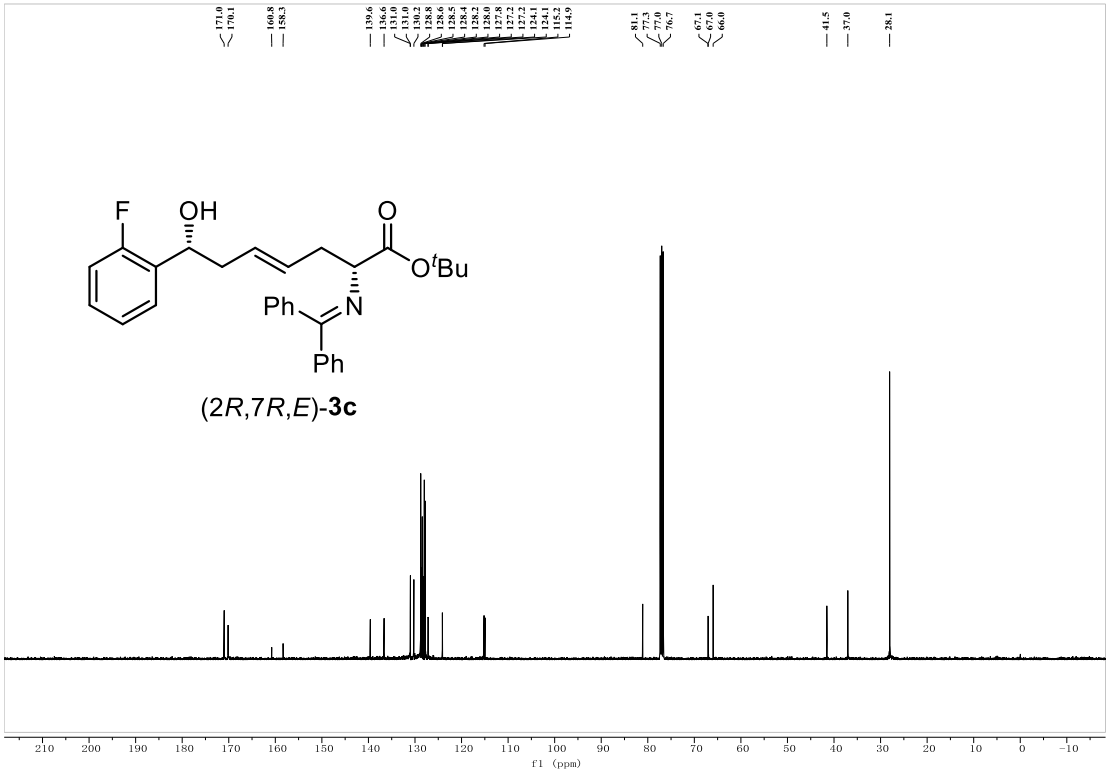
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3b**



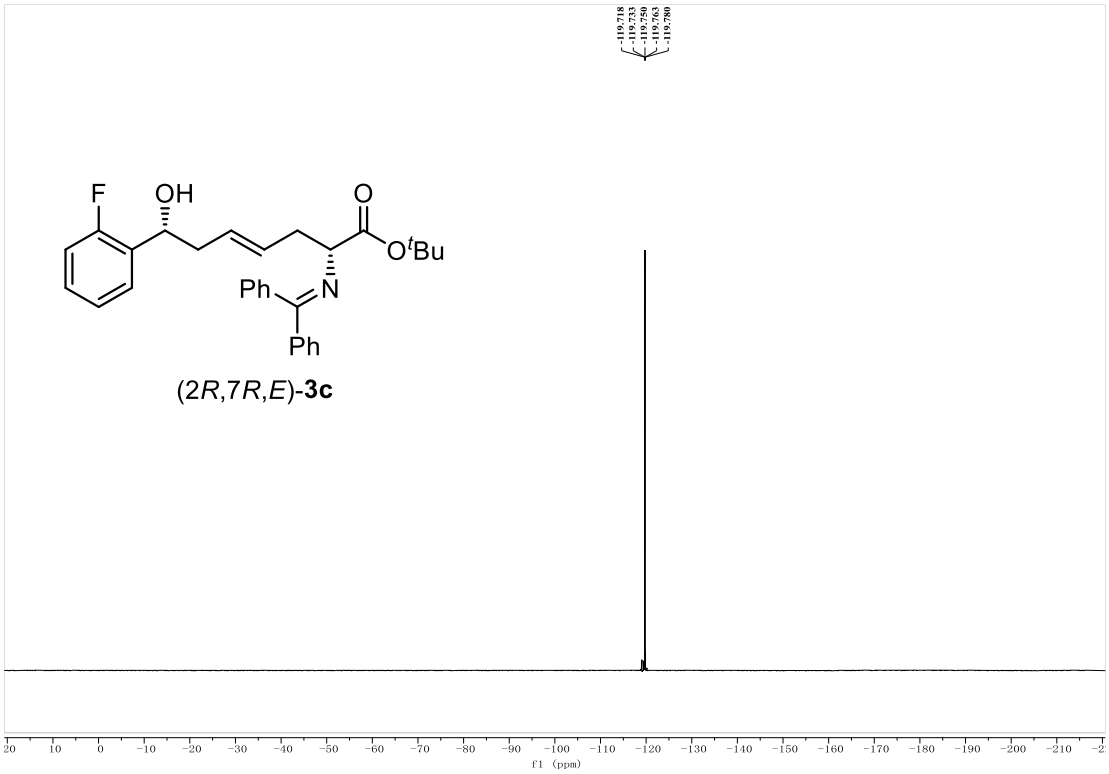
^{19}F NMR (376 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3b**



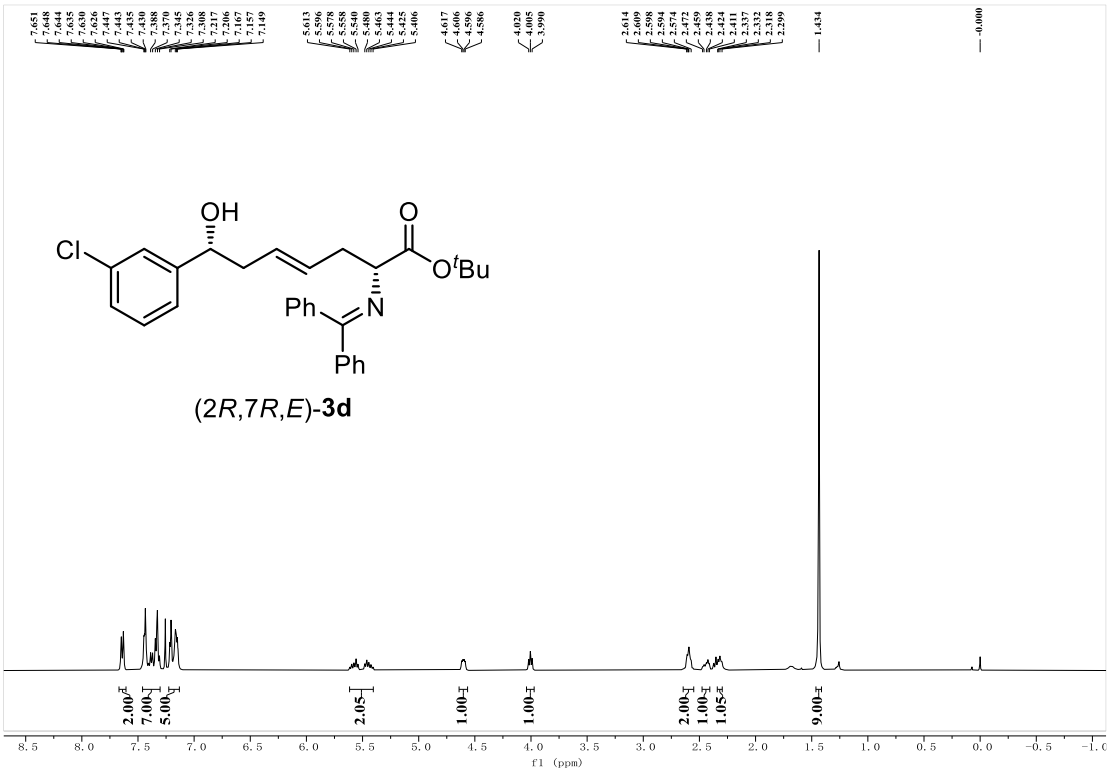
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3c**



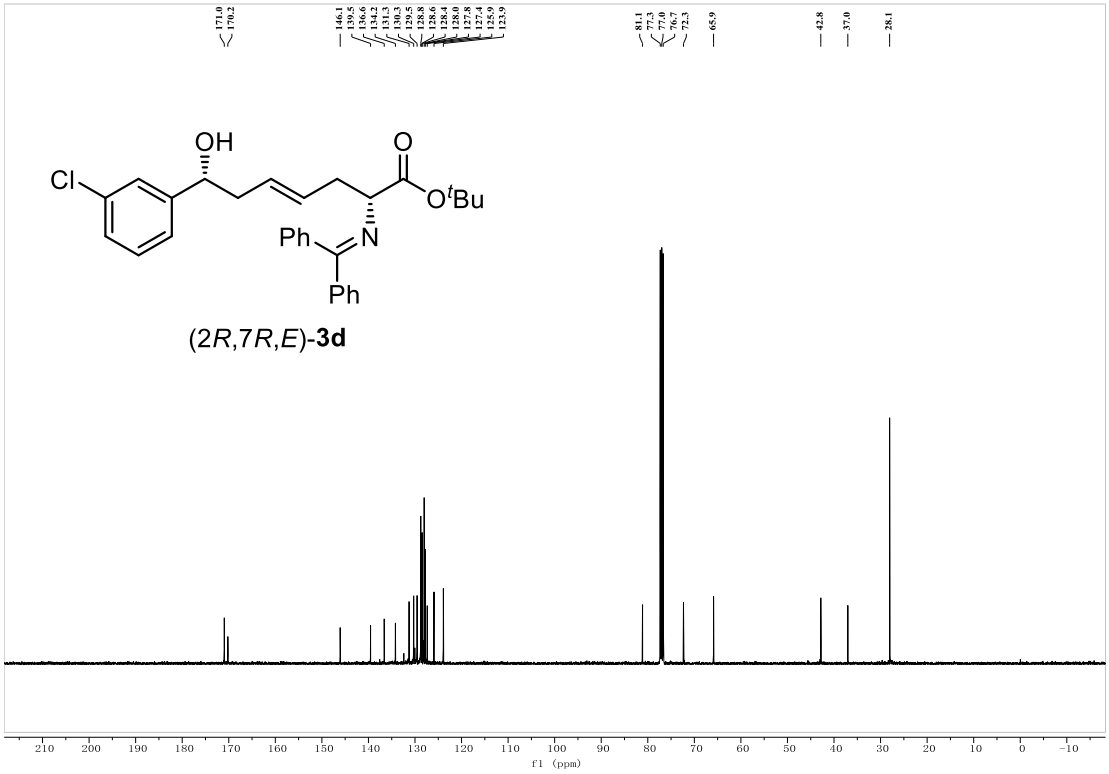
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3c**



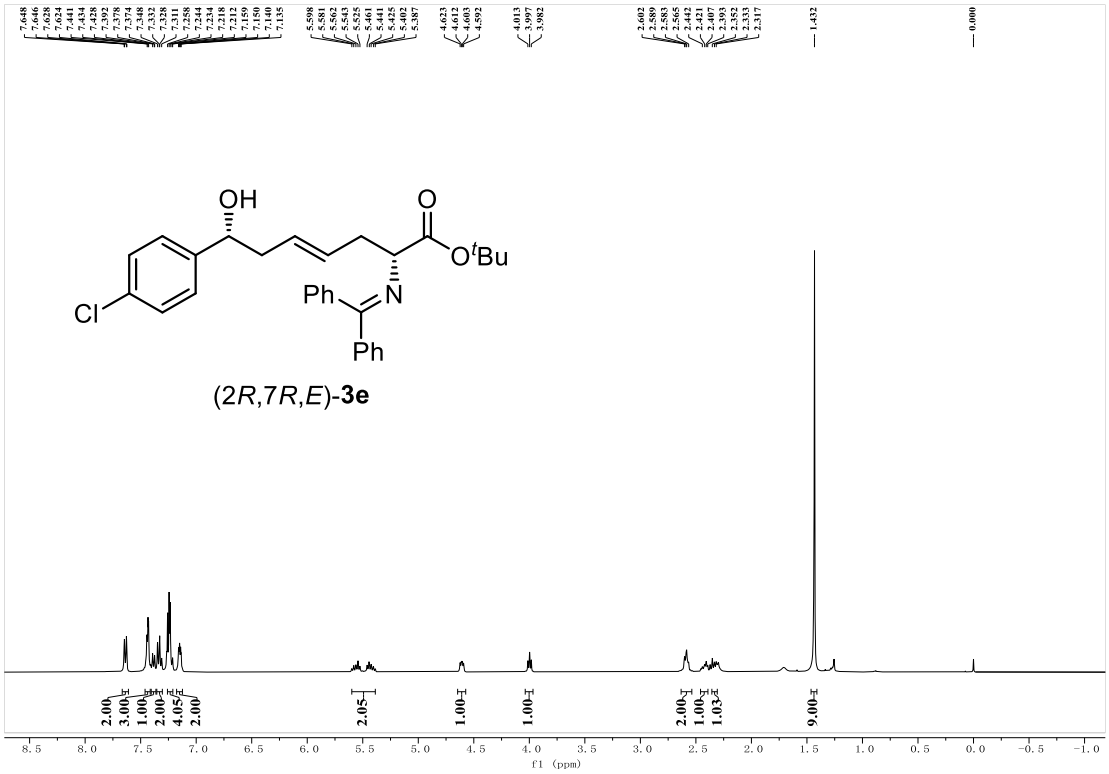
^{19}F NMR (376 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3c**



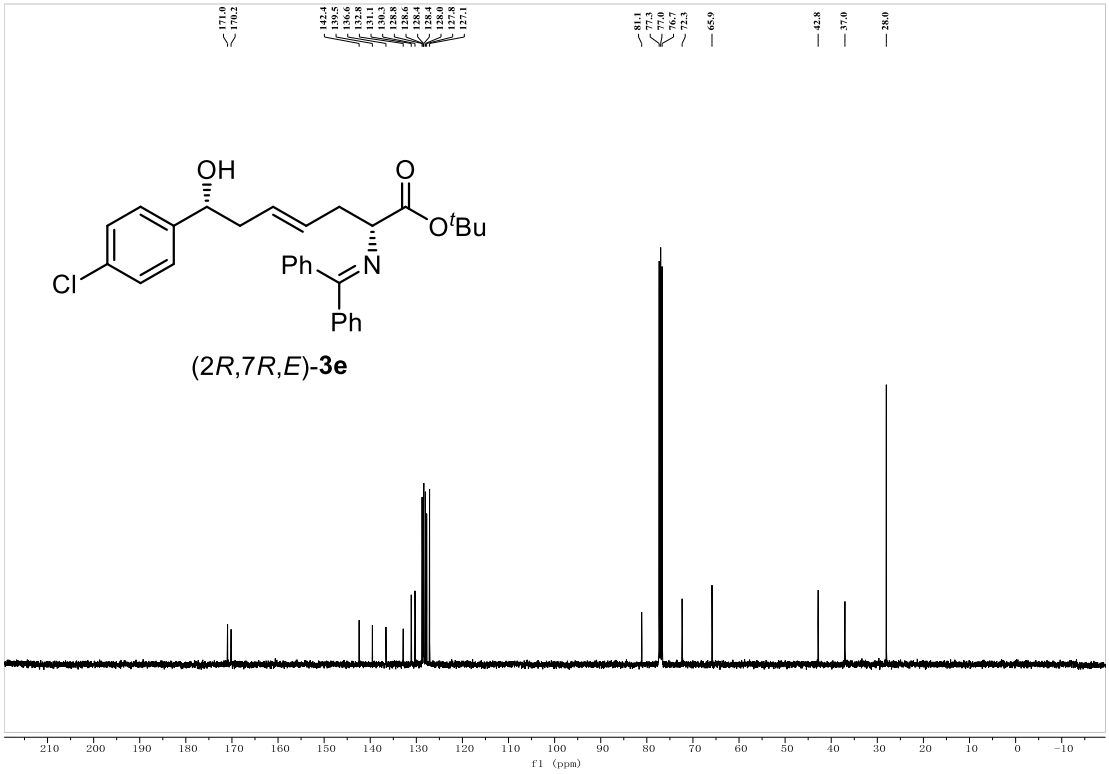
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3d**



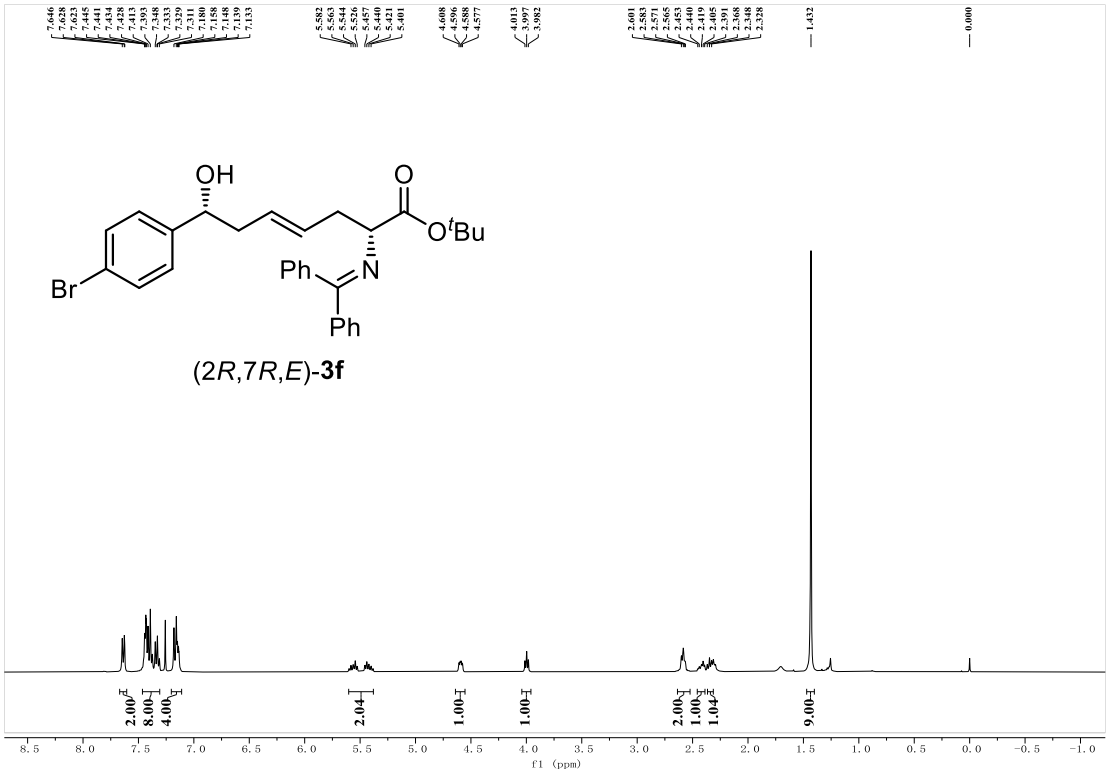
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3d**



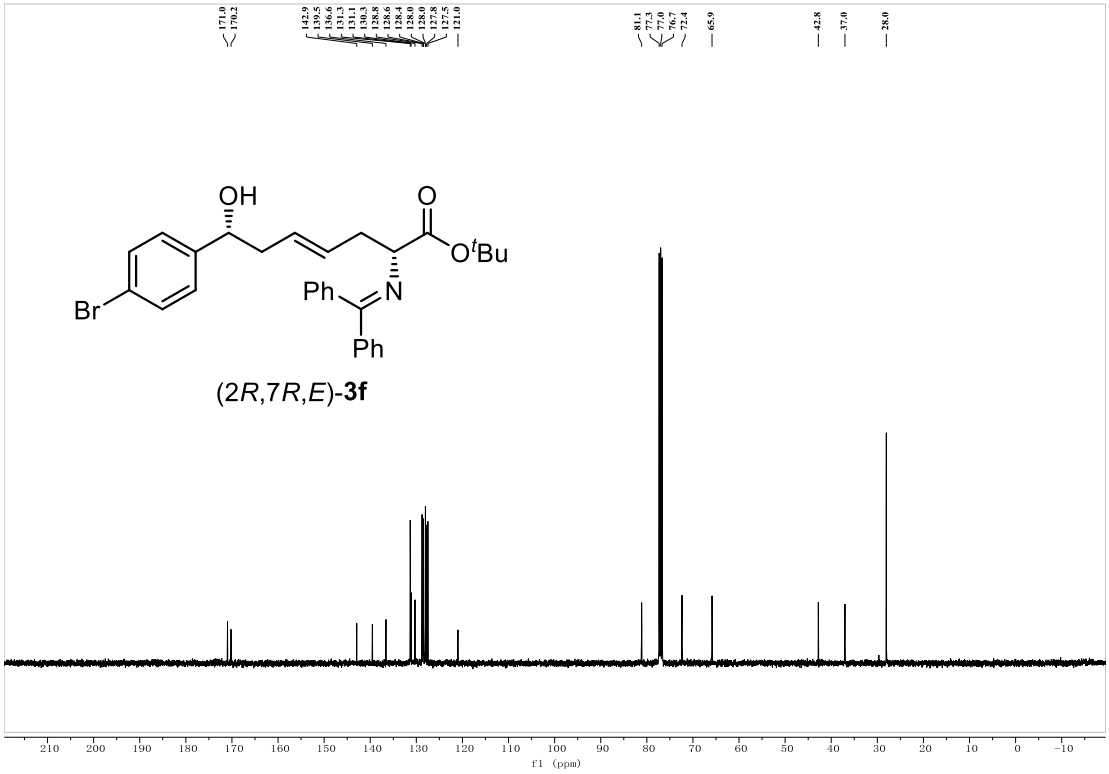
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3e**



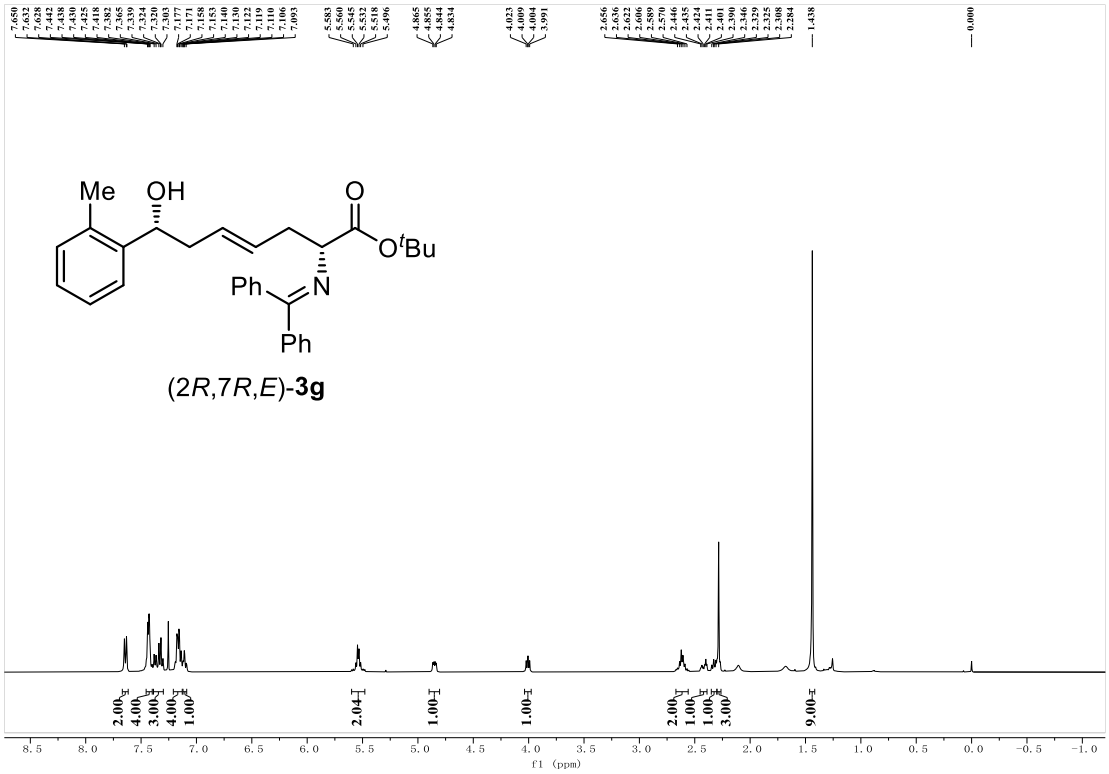
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3e**



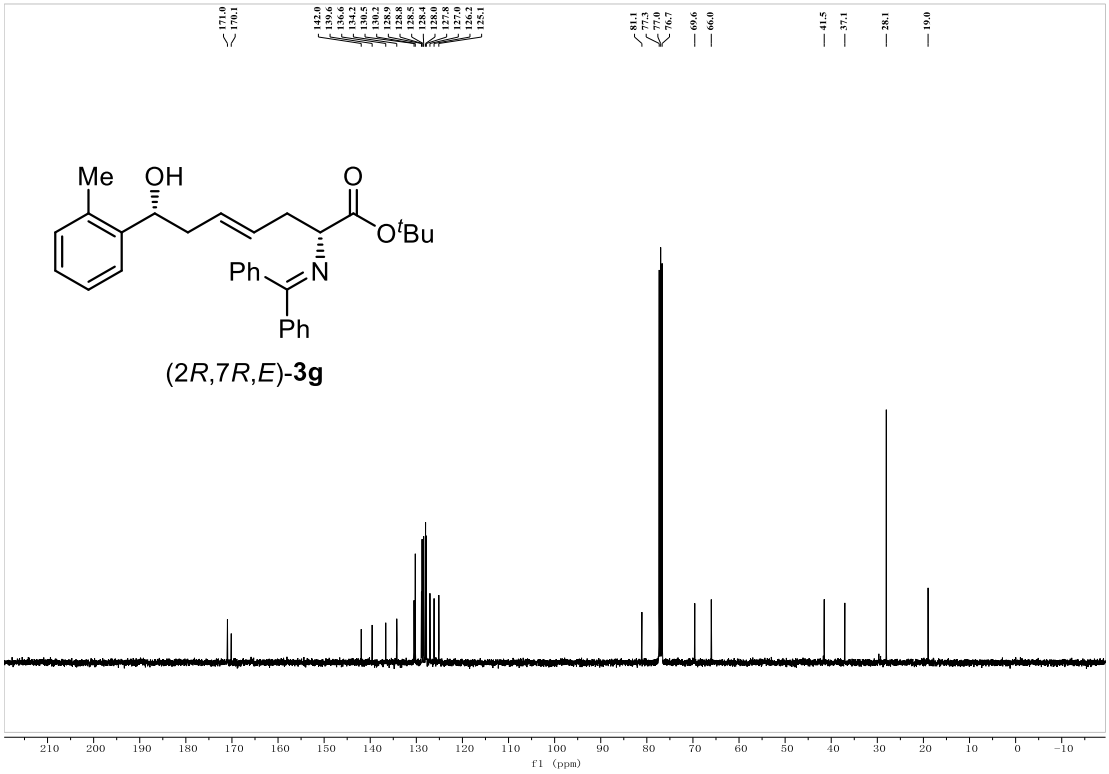
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3f**



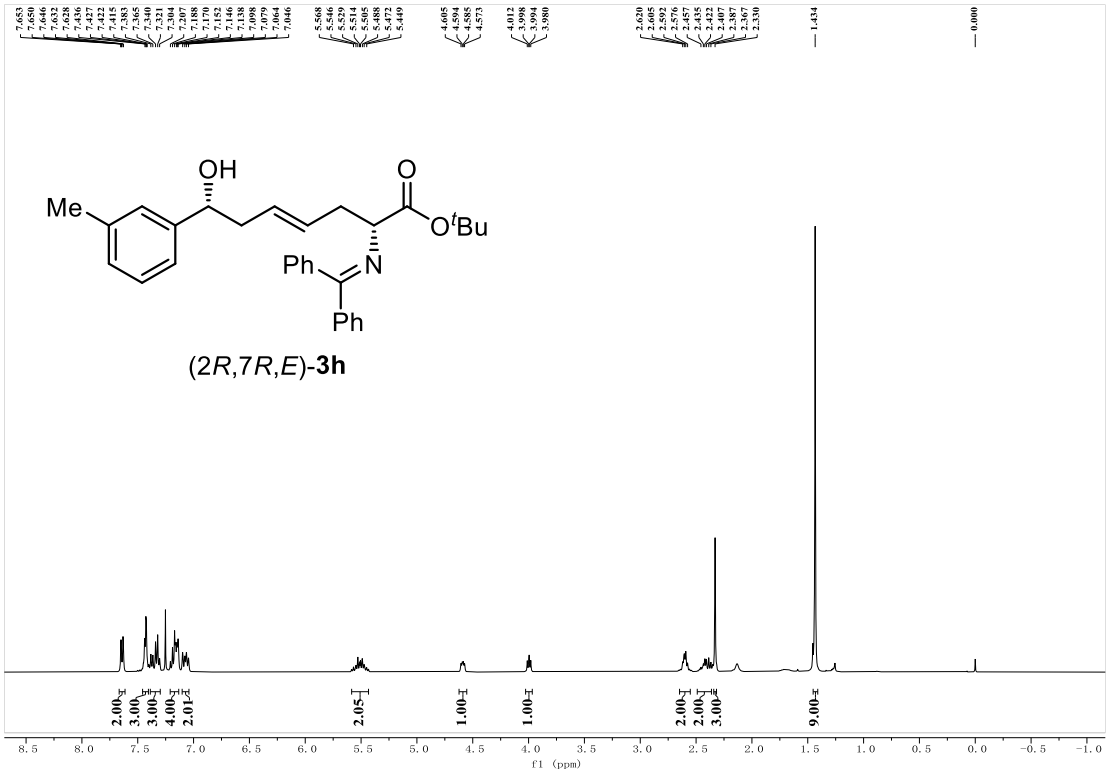
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3f**



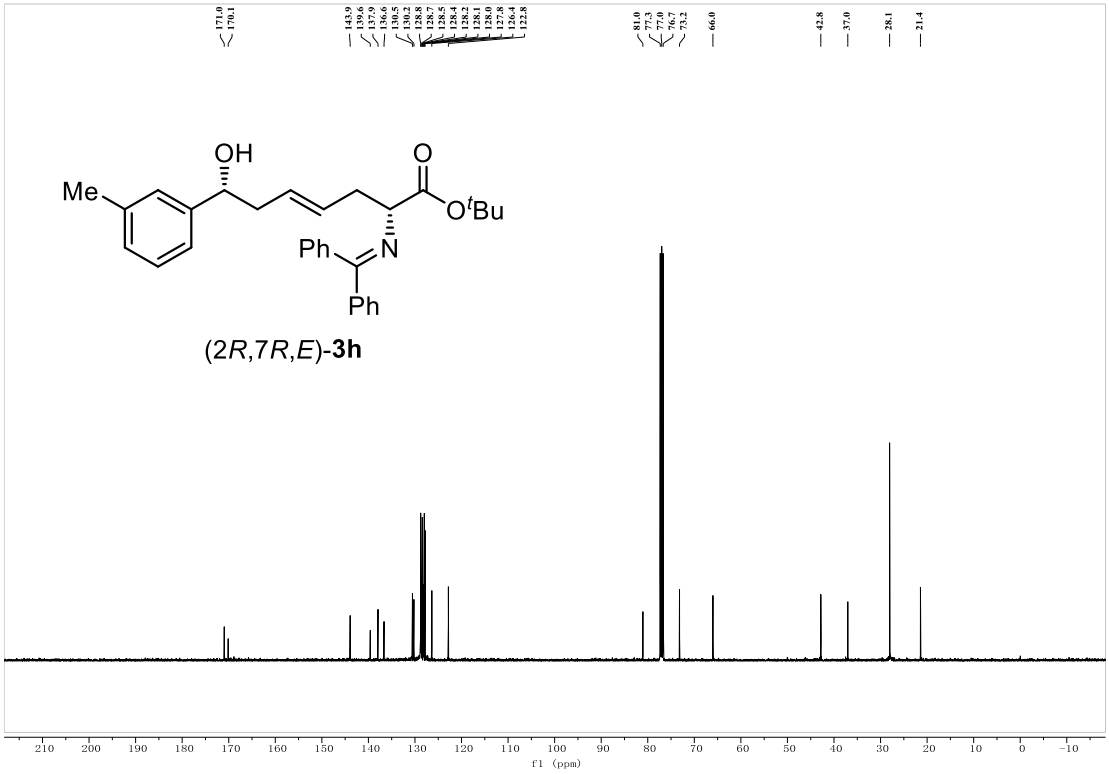
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3g**



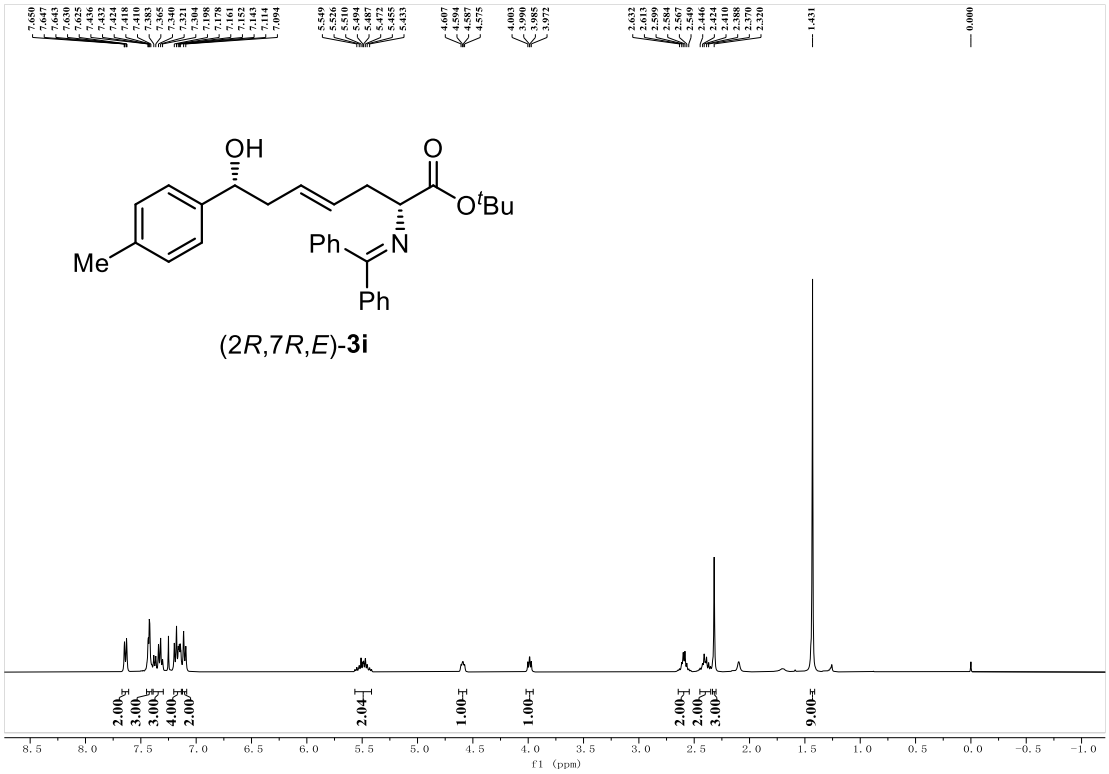
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3g**



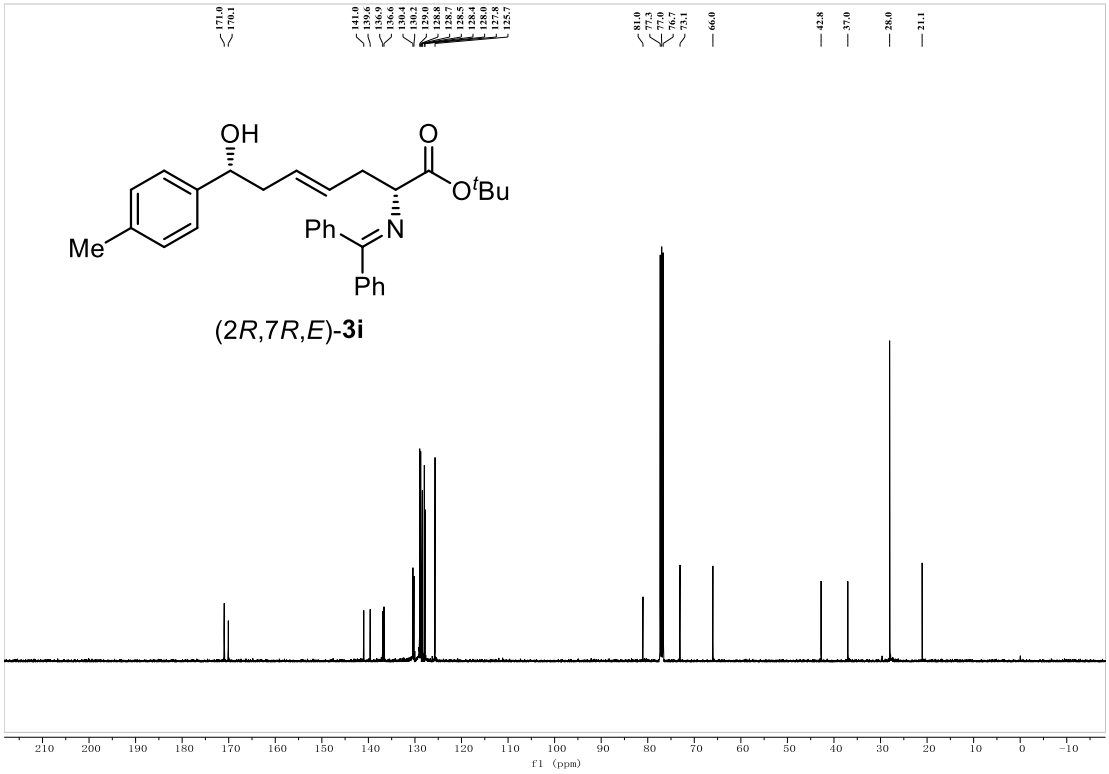
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3h**



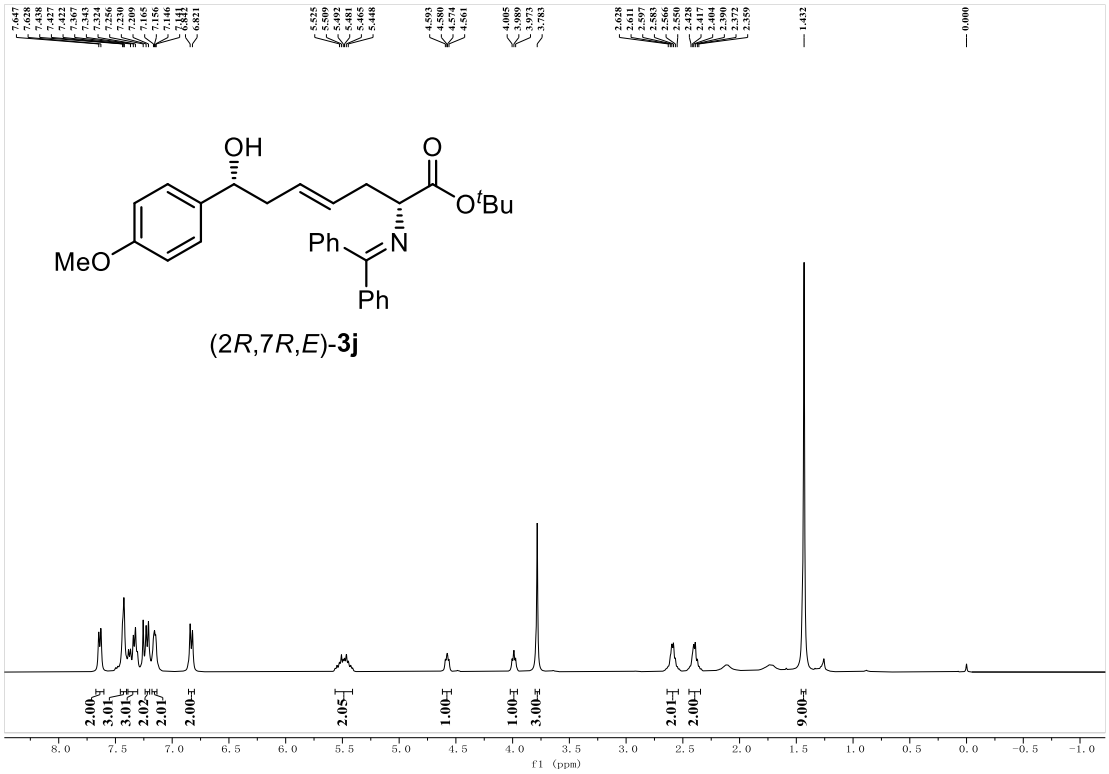
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3h**



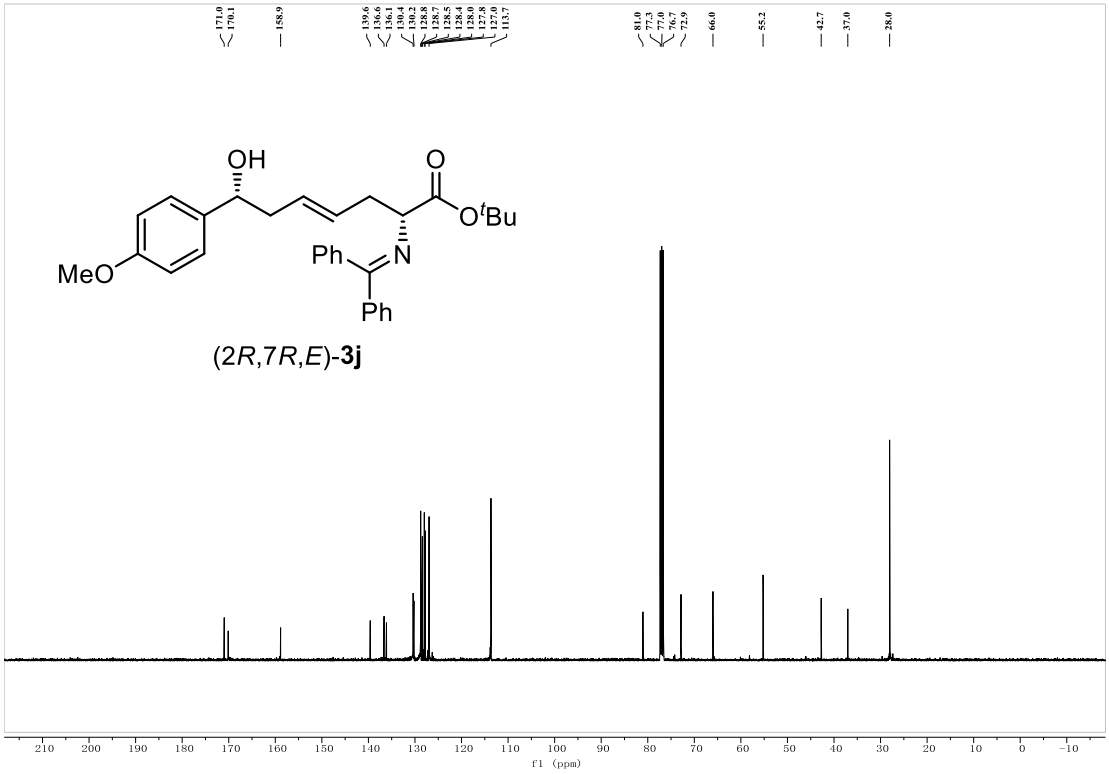
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3i**



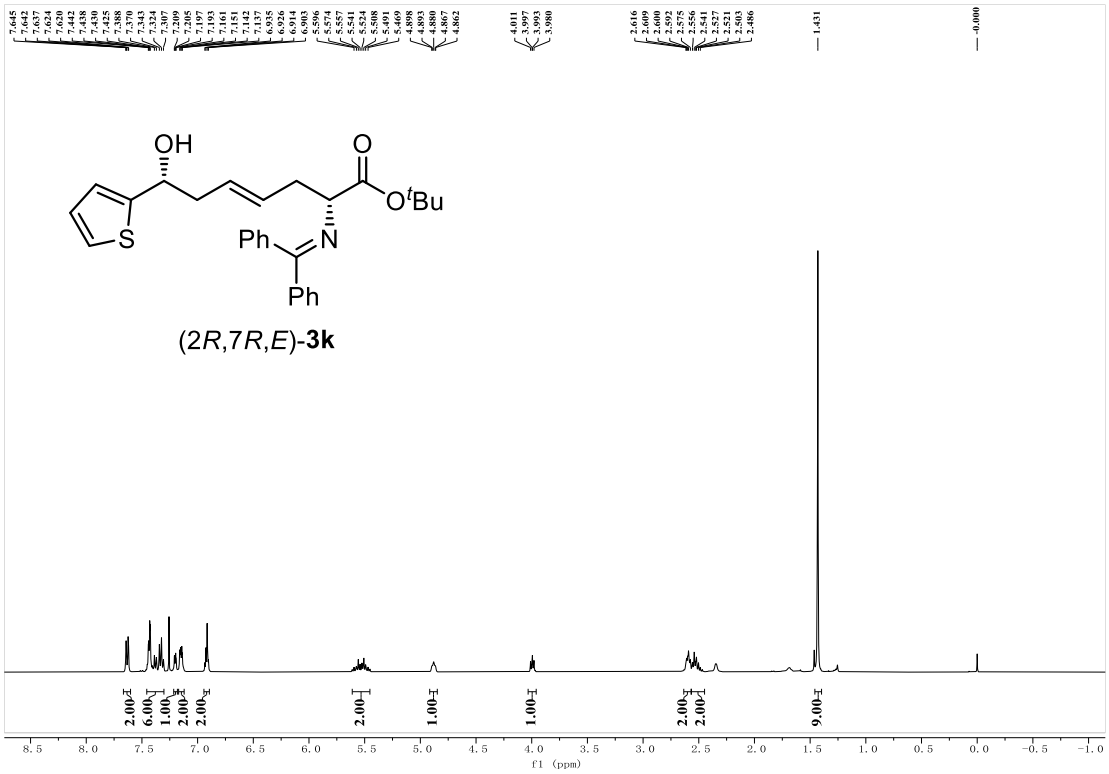
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3i**



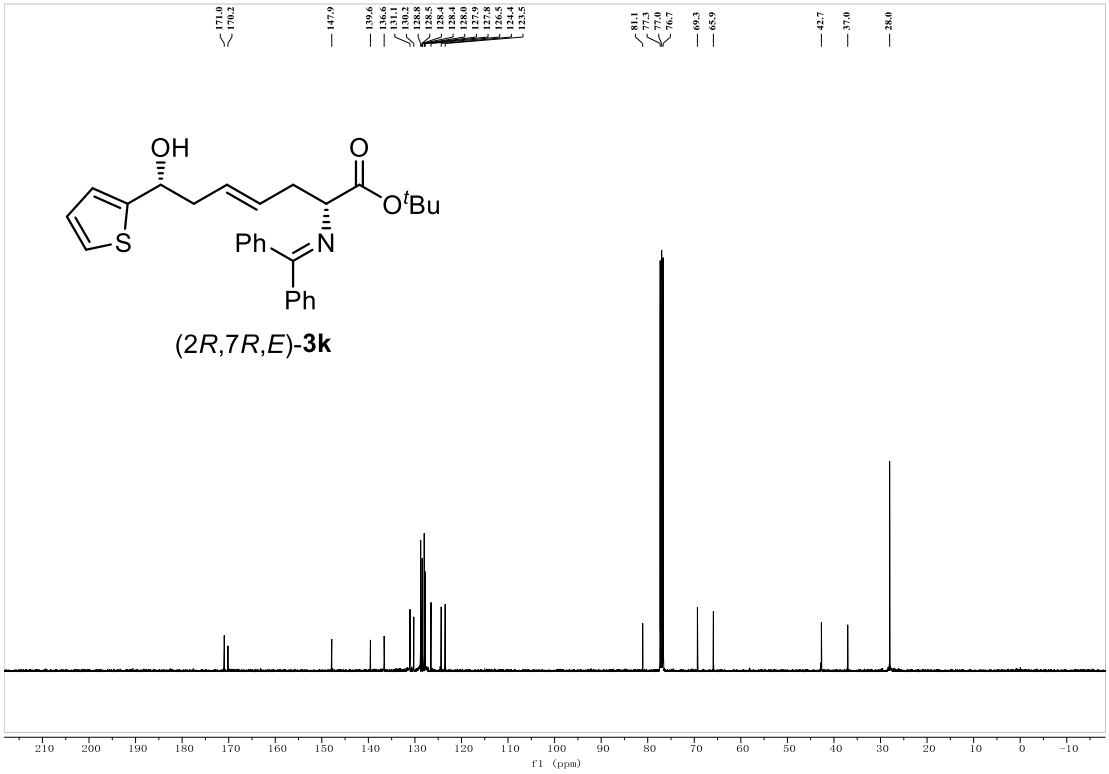
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3j**



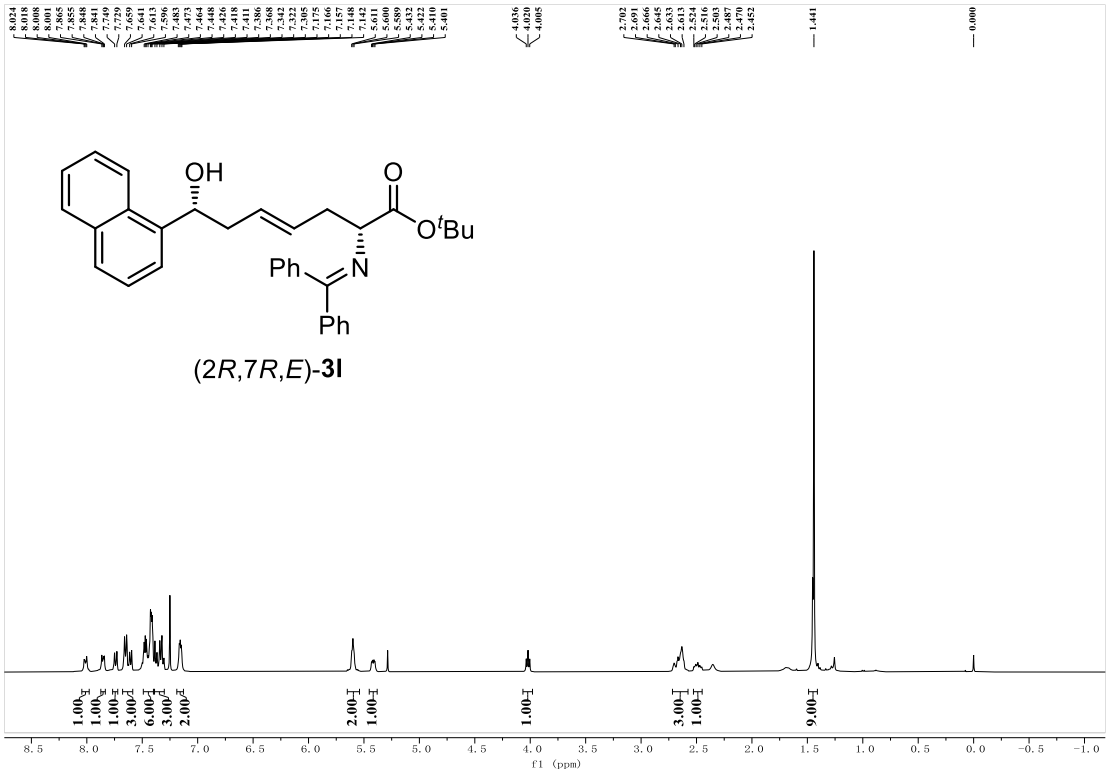
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3j**



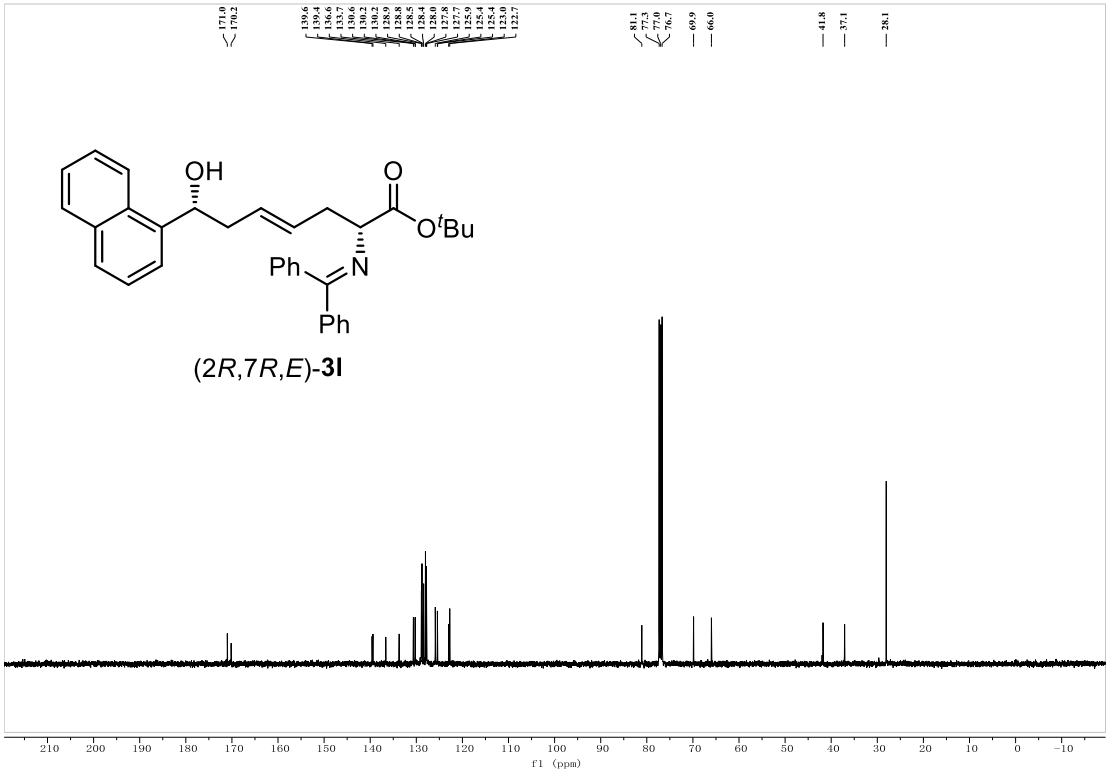
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3k**



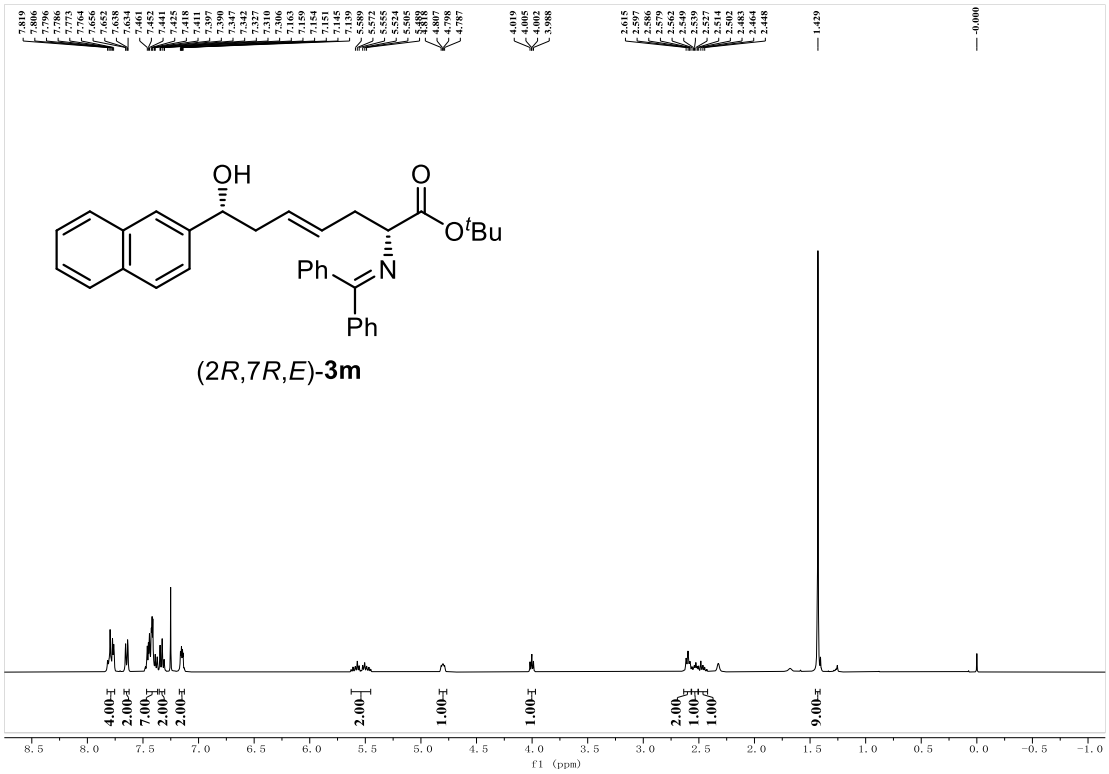
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3k**



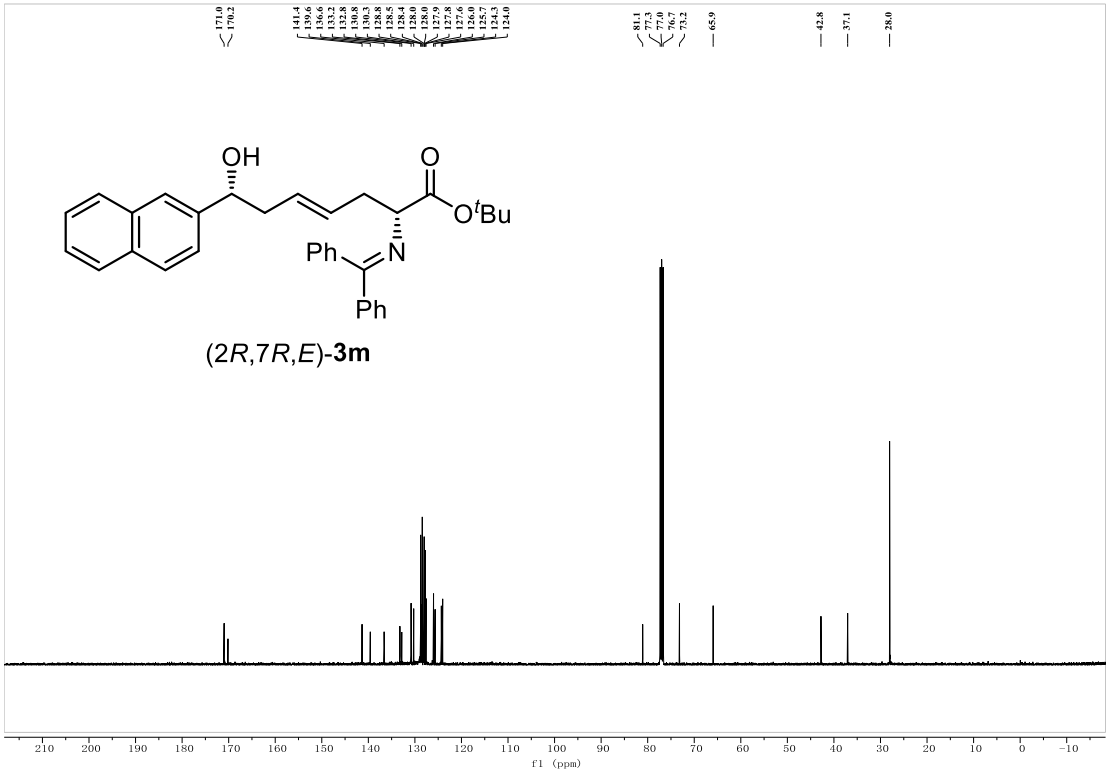
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3l**



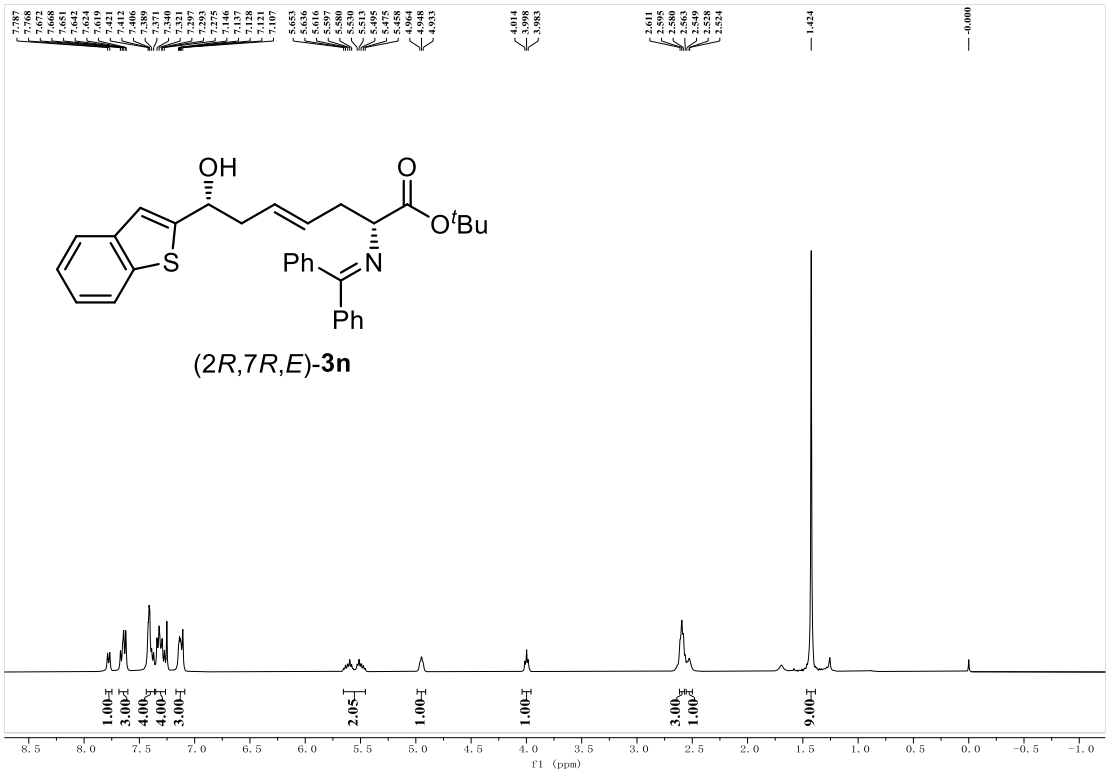
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3l**



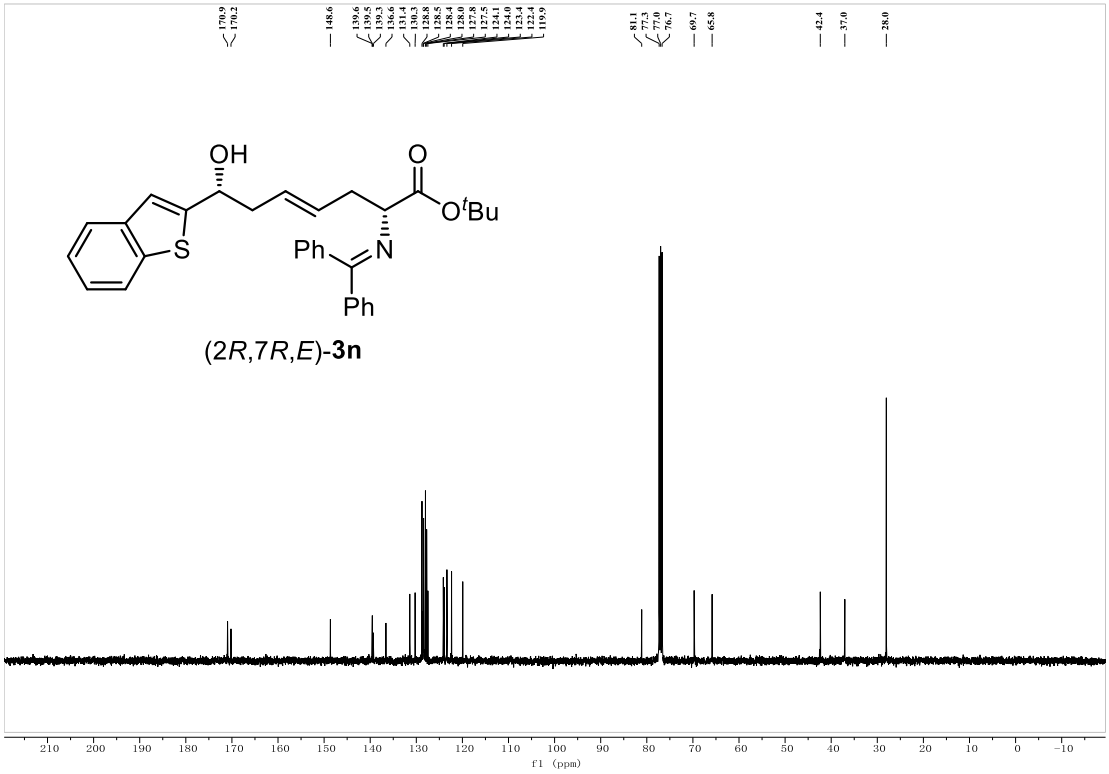
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3m**



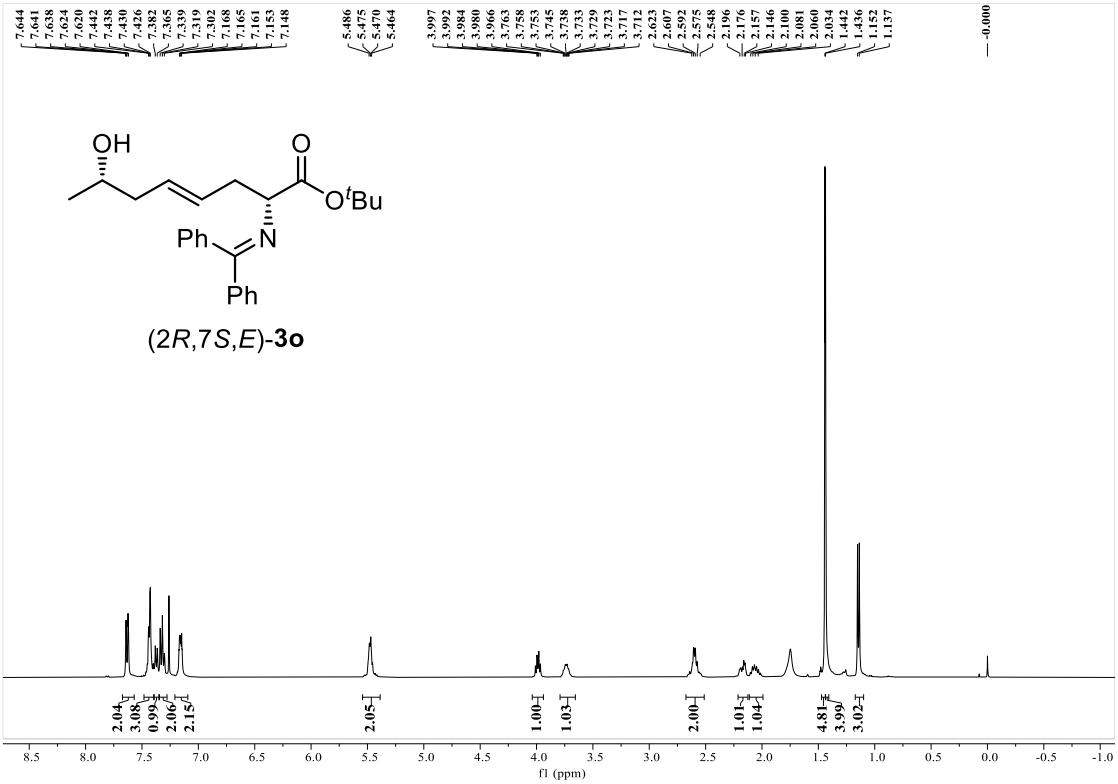
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3m**



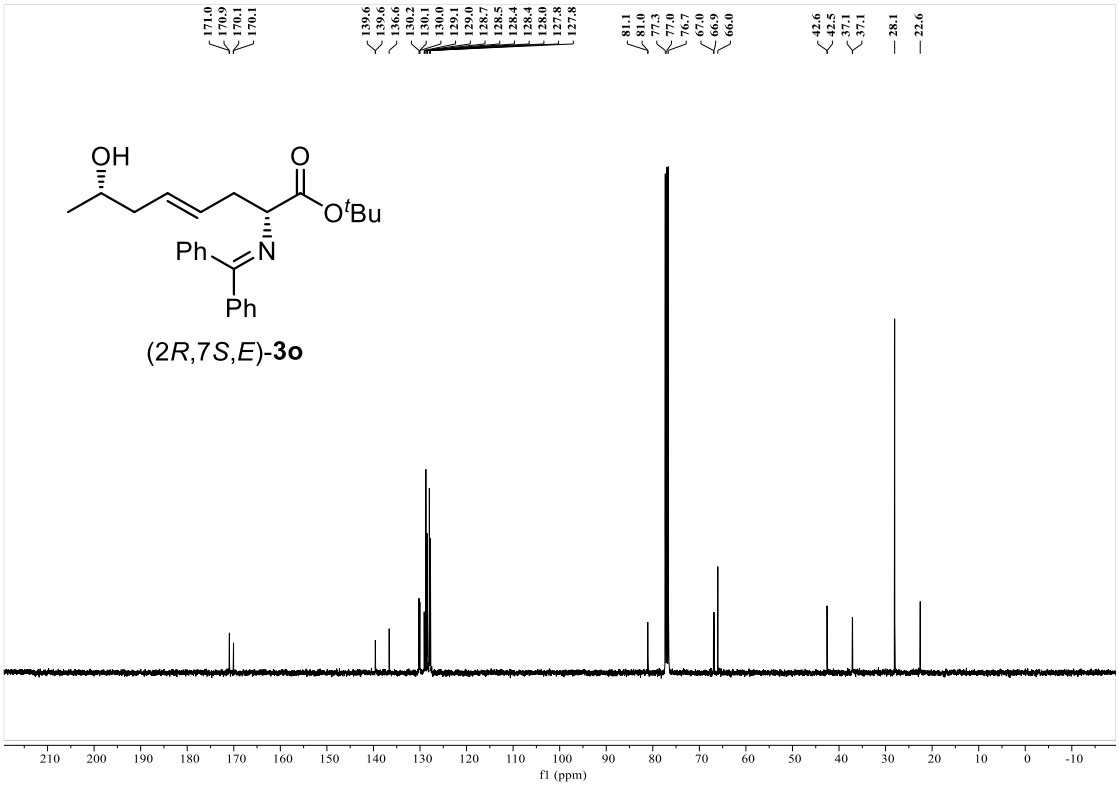
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3n**



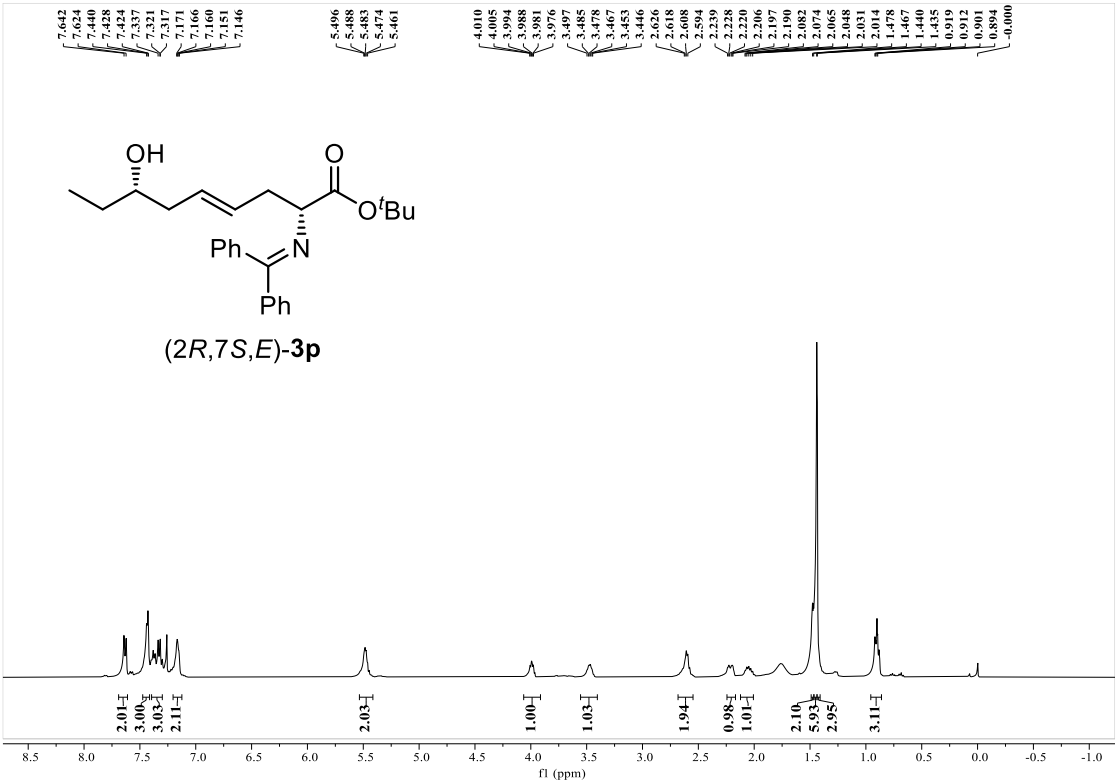
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3n**



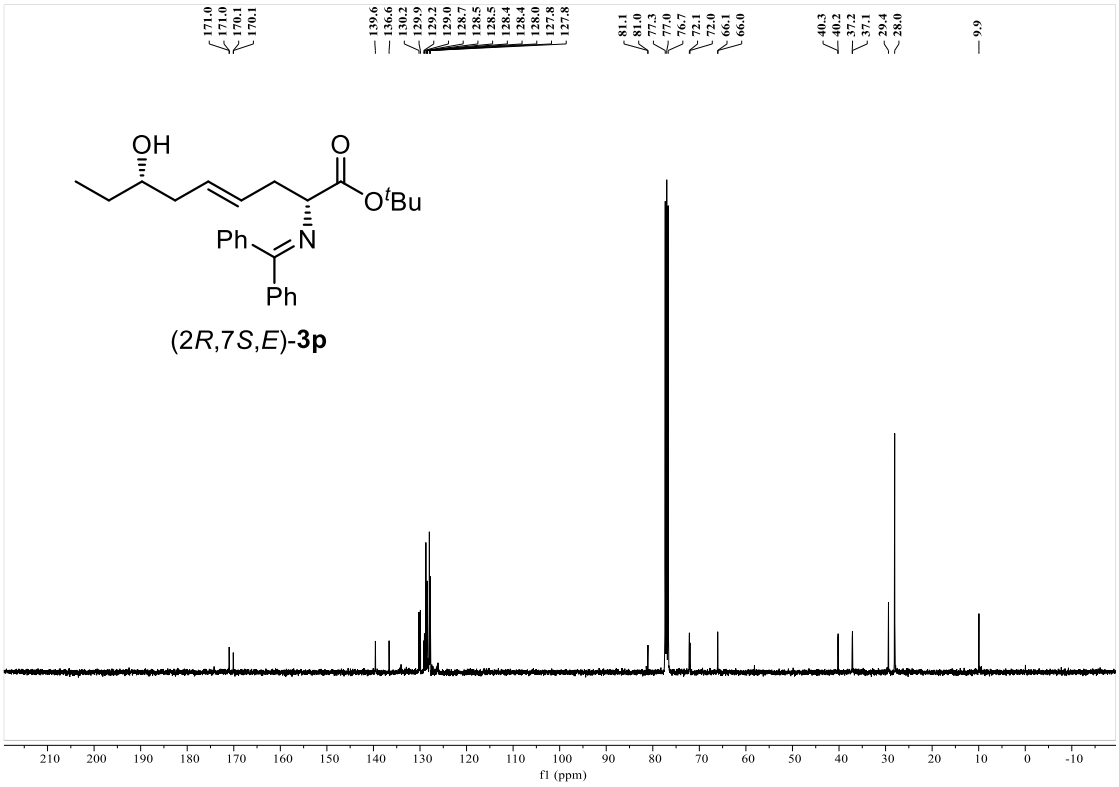
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3o**



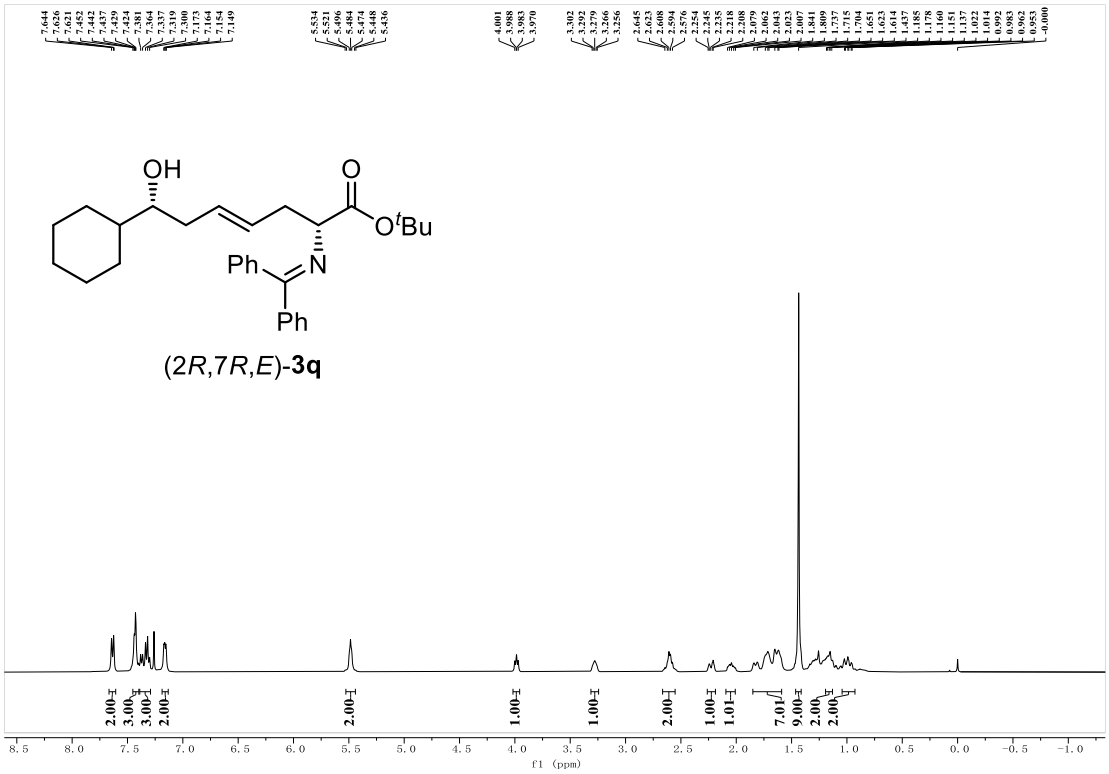
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3o**



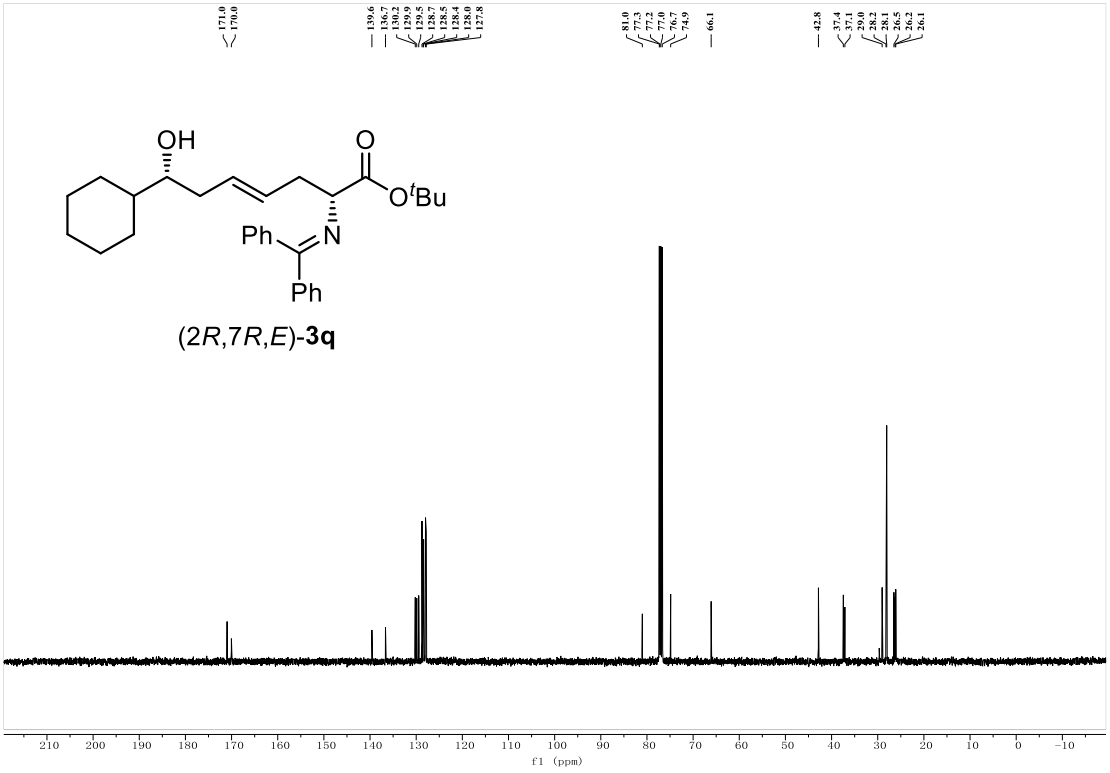
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3p**



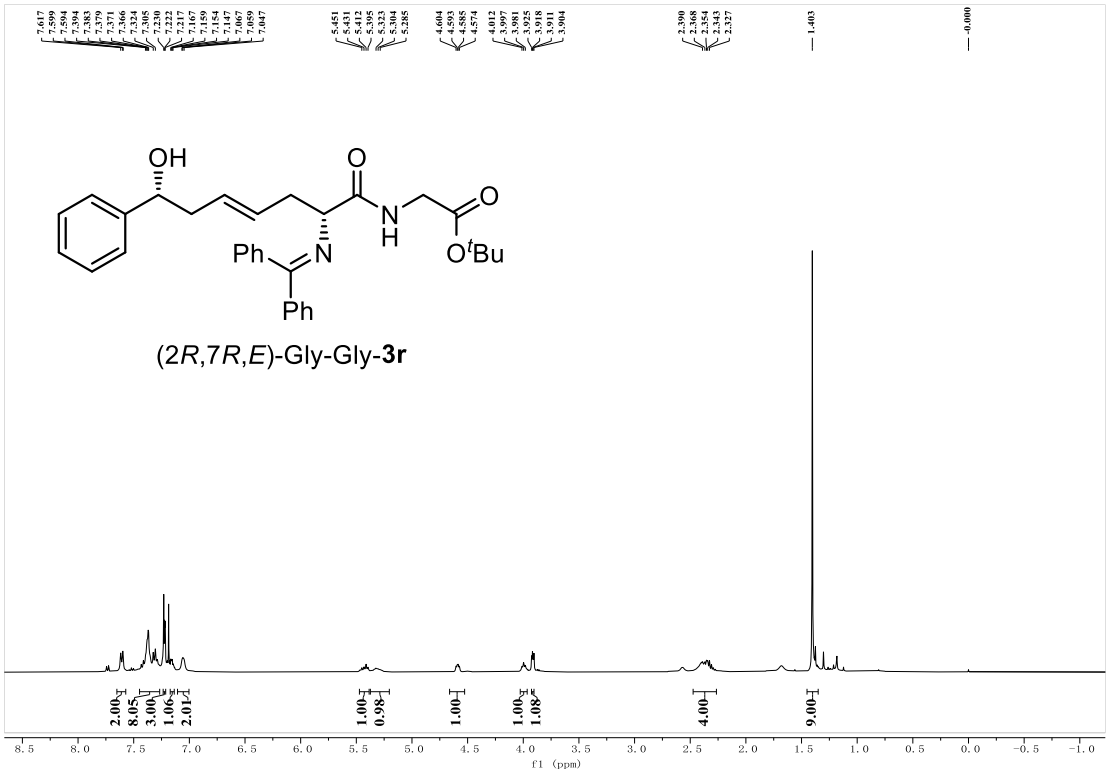
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-**3p**



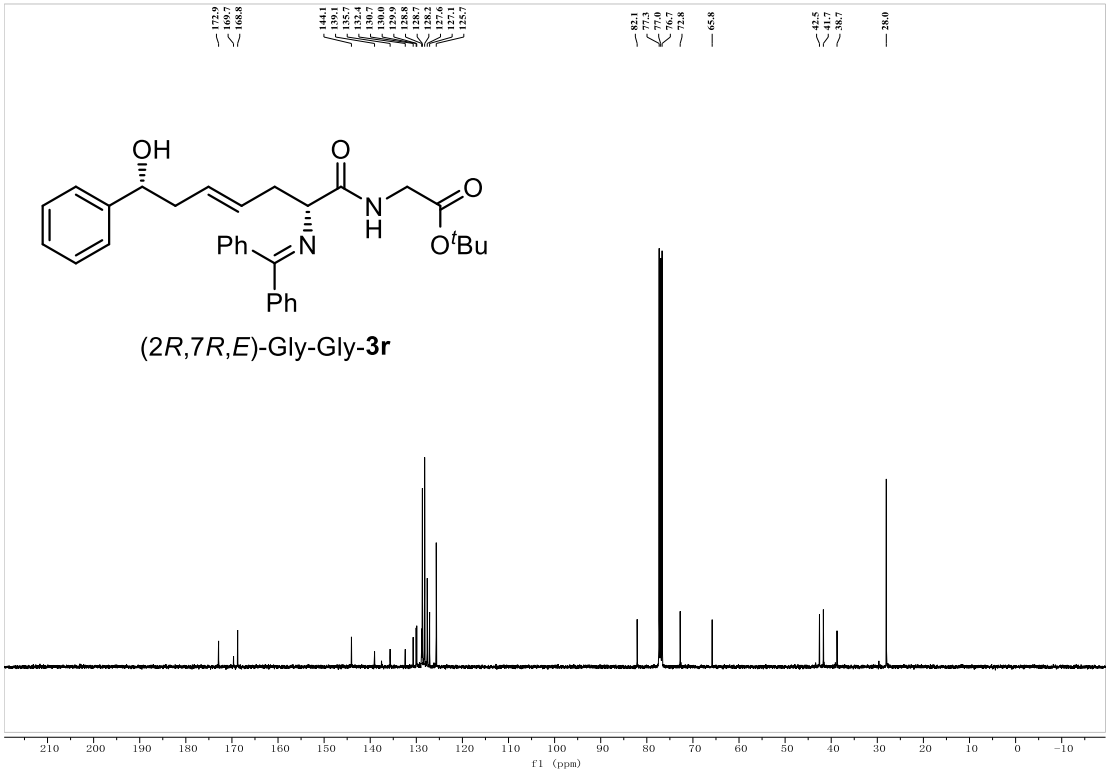
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3q**



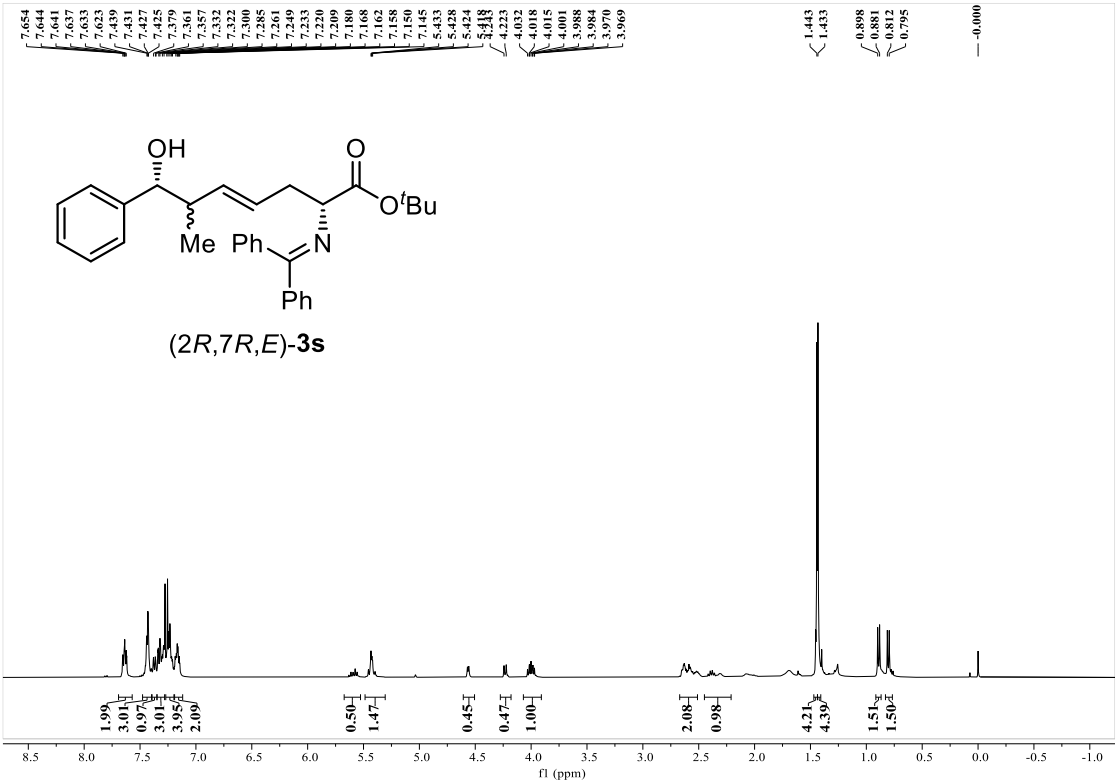
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3q**



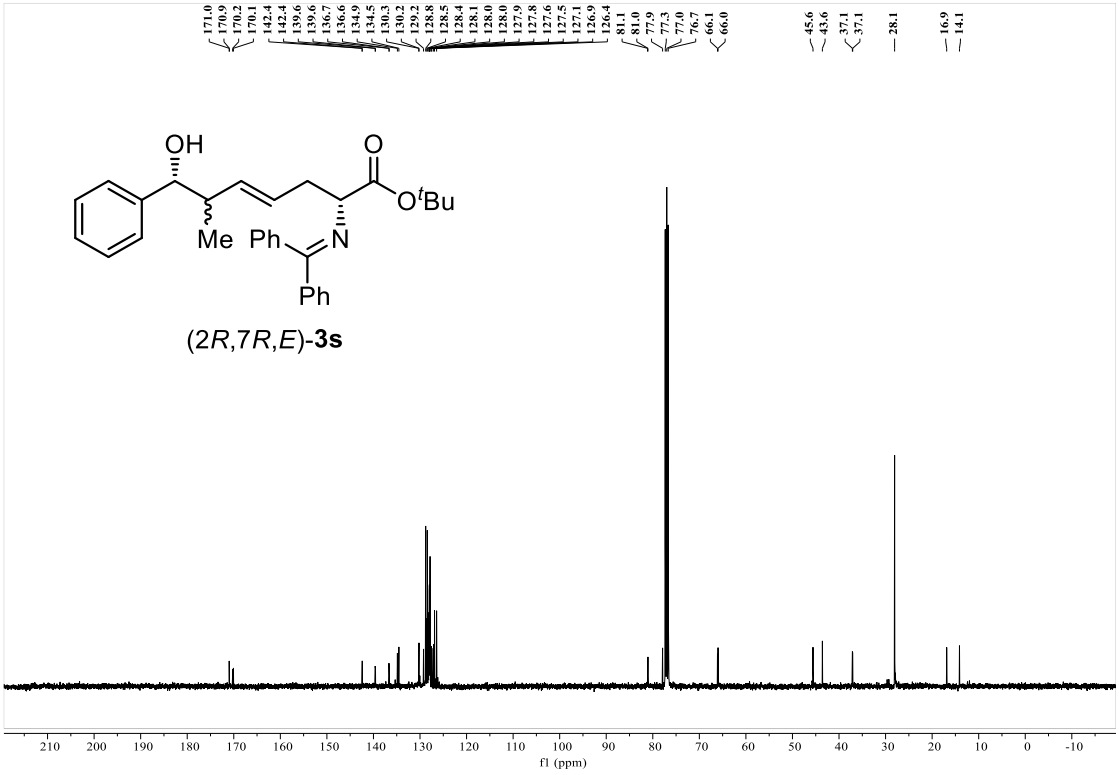
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3r**



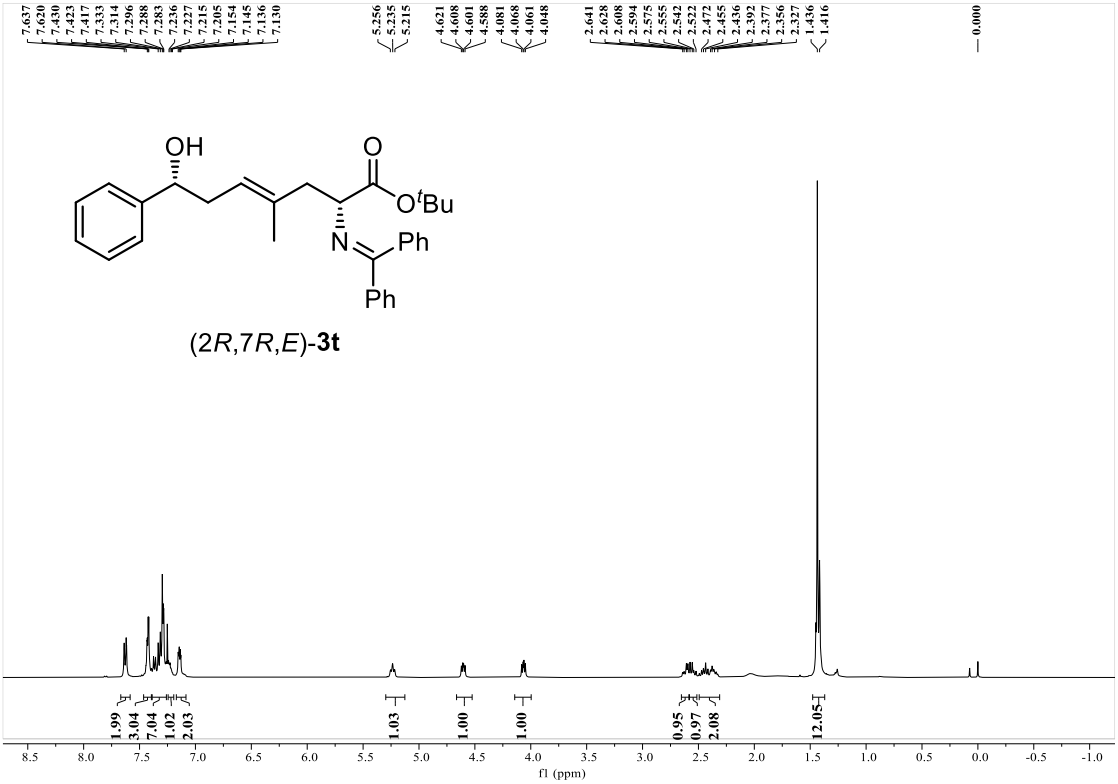
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3r**



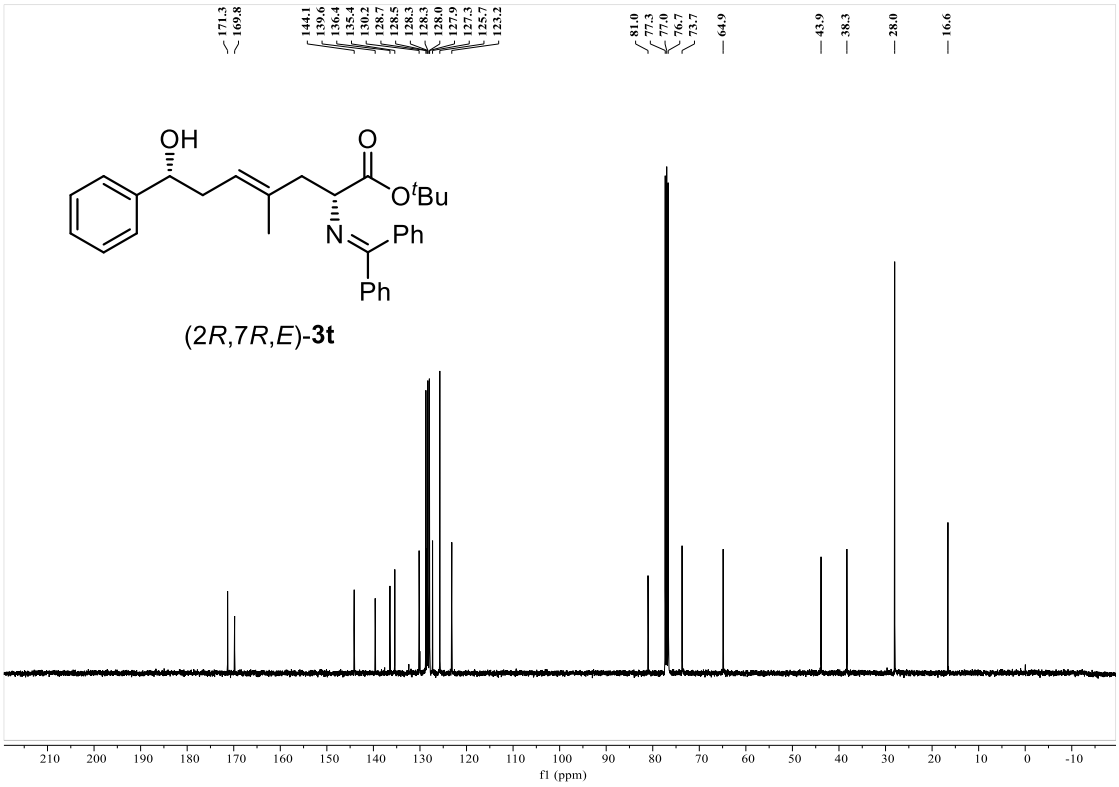
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3s**



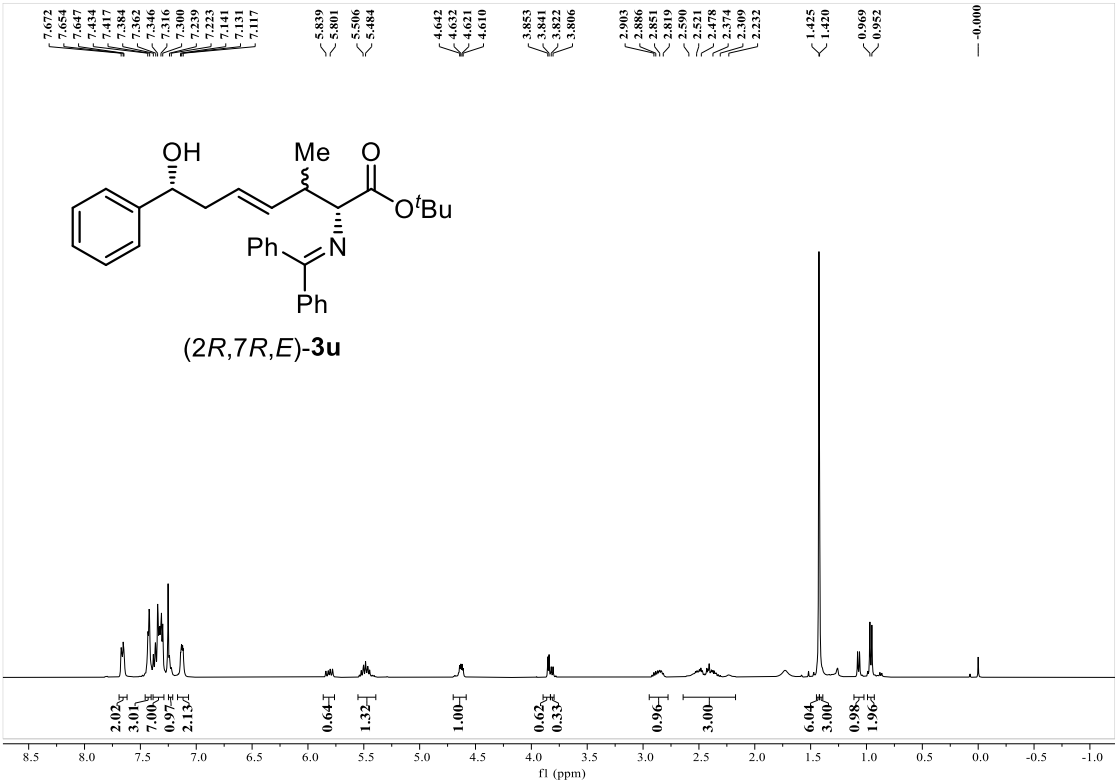
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3s**



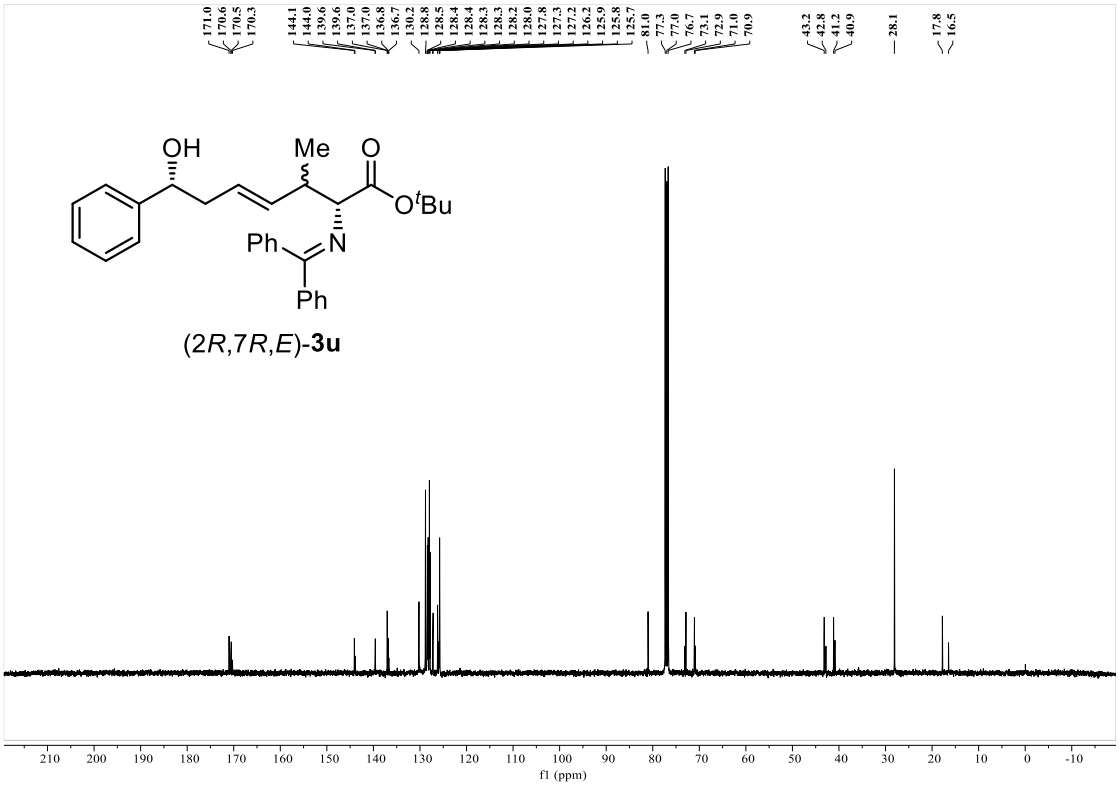
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3t**



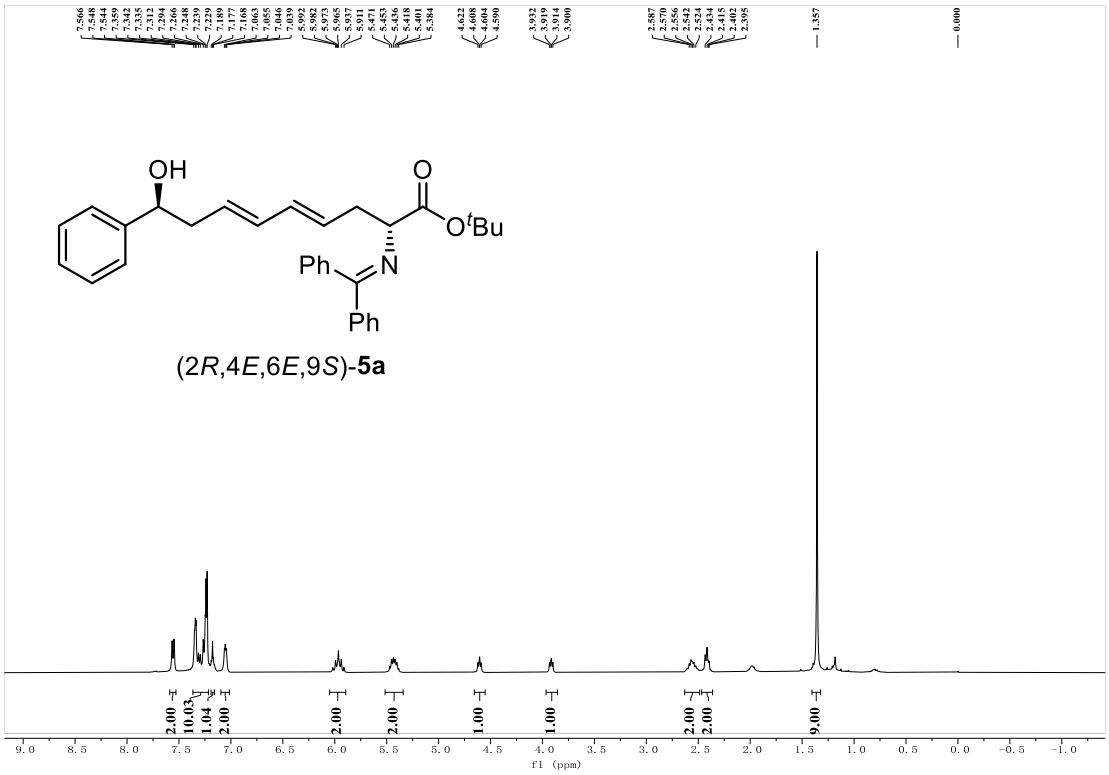
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3t**



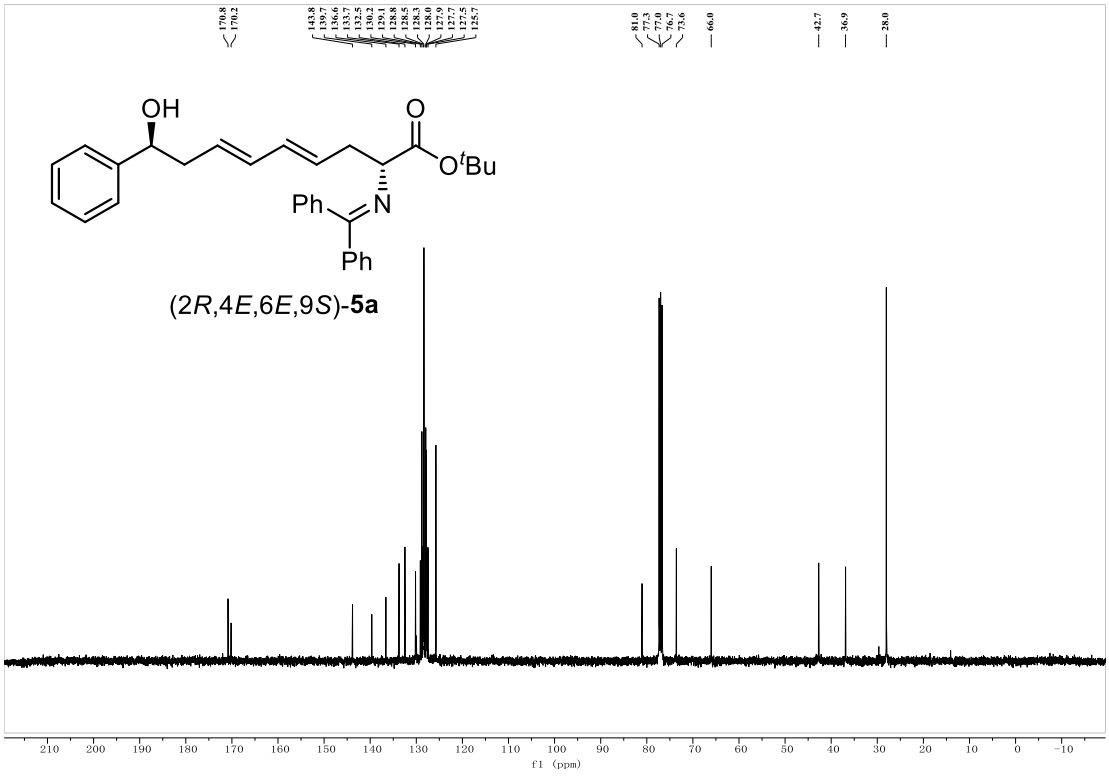
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-**3u**



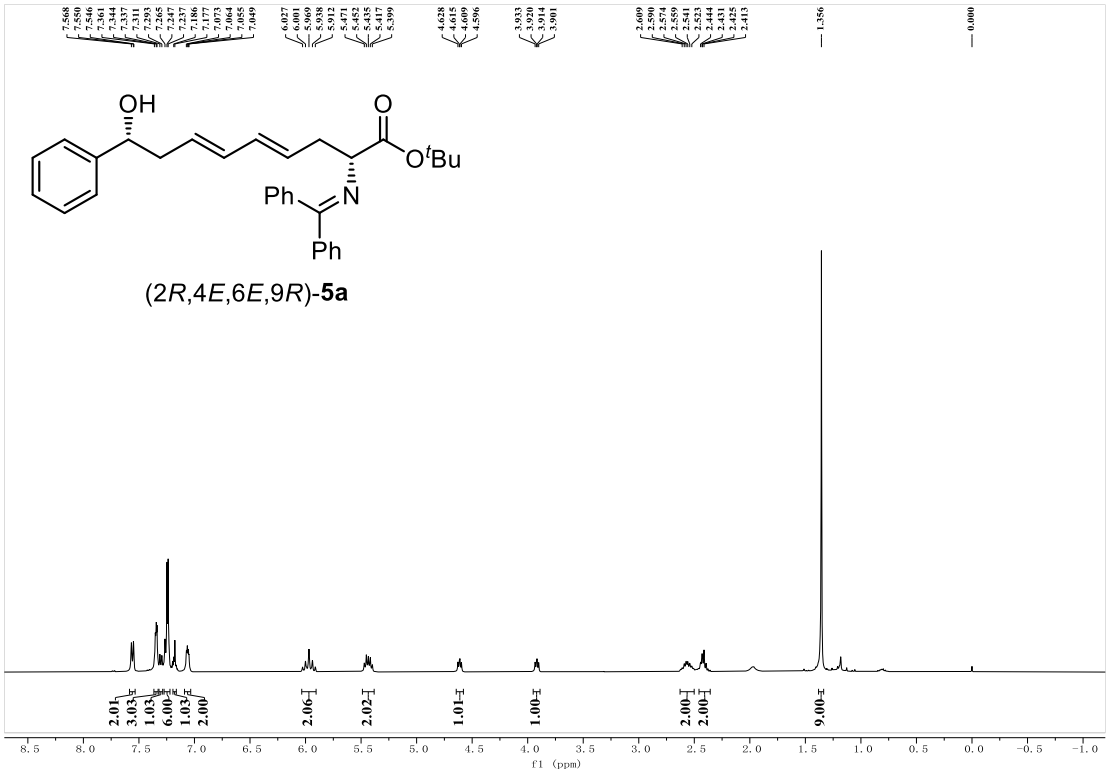
^{13}C NMR (101 MHz, $CDCl_3$) of 2*R*,7*R*,*E*)-**3u**



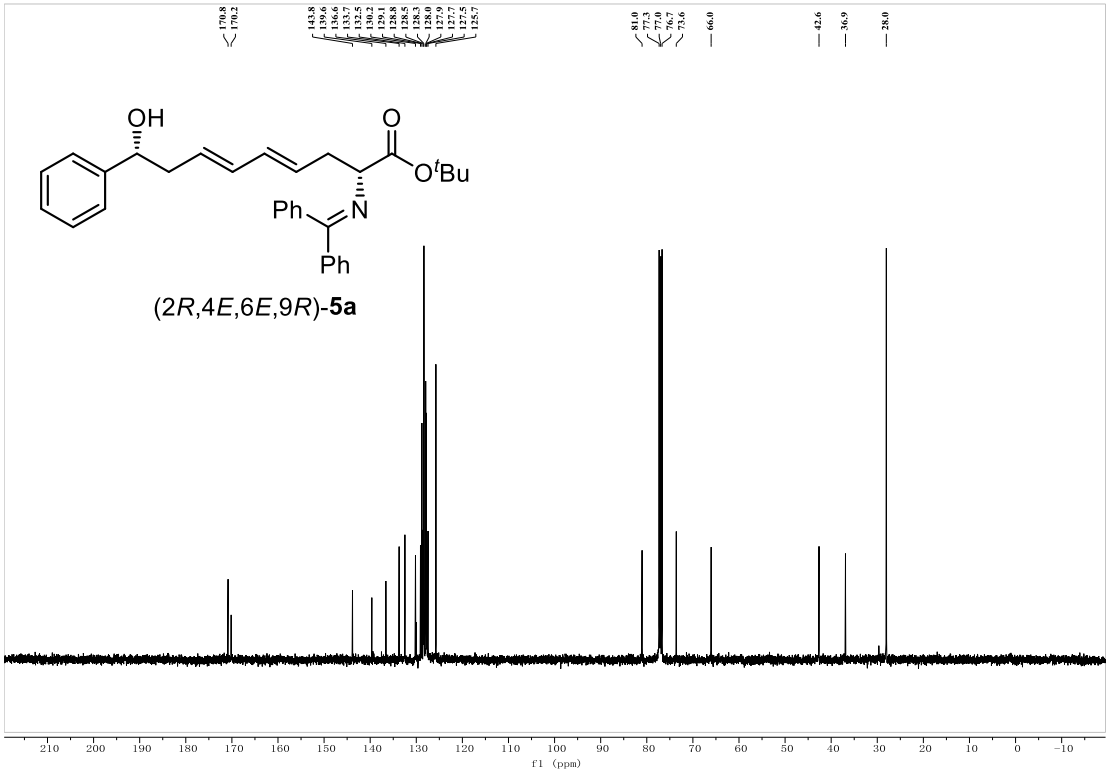
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-**5a**



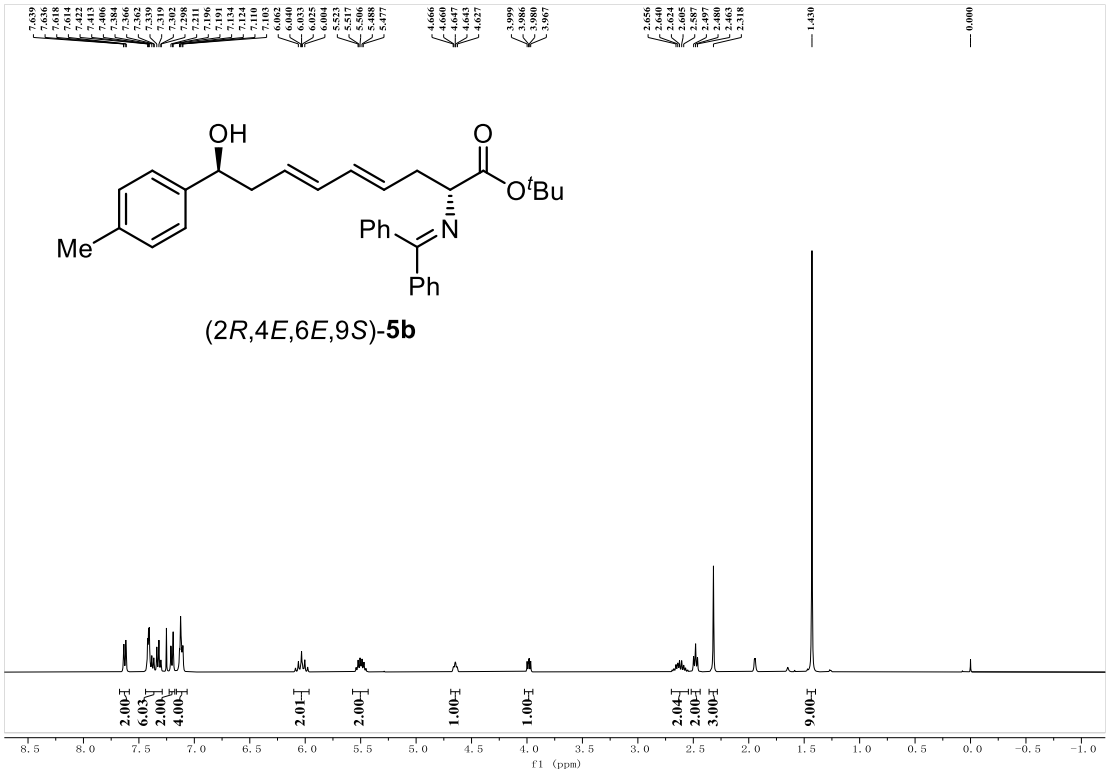
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-**5a**



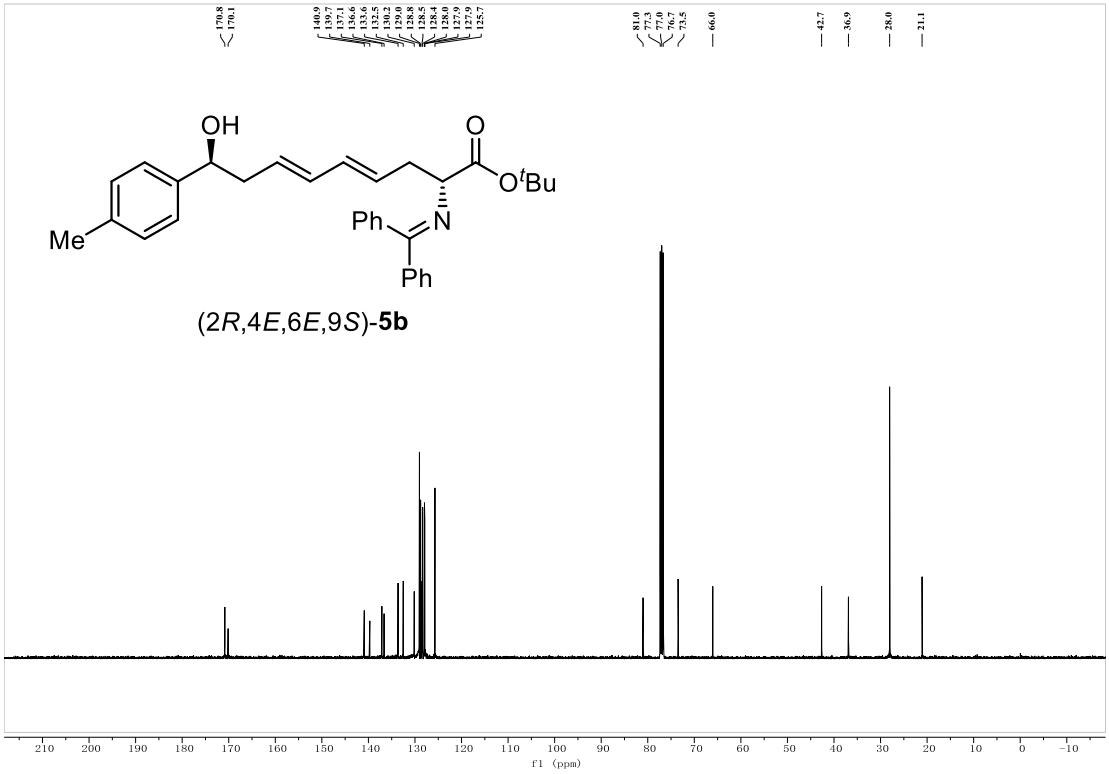
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-**5a**



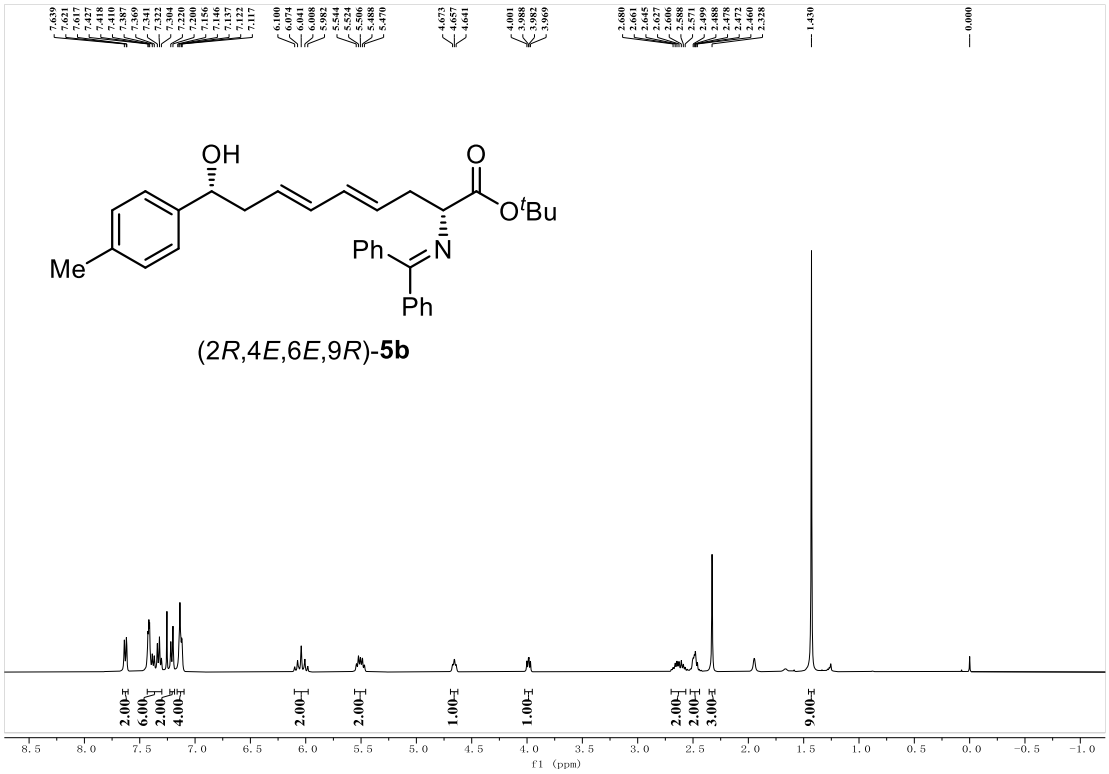
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-**5a**



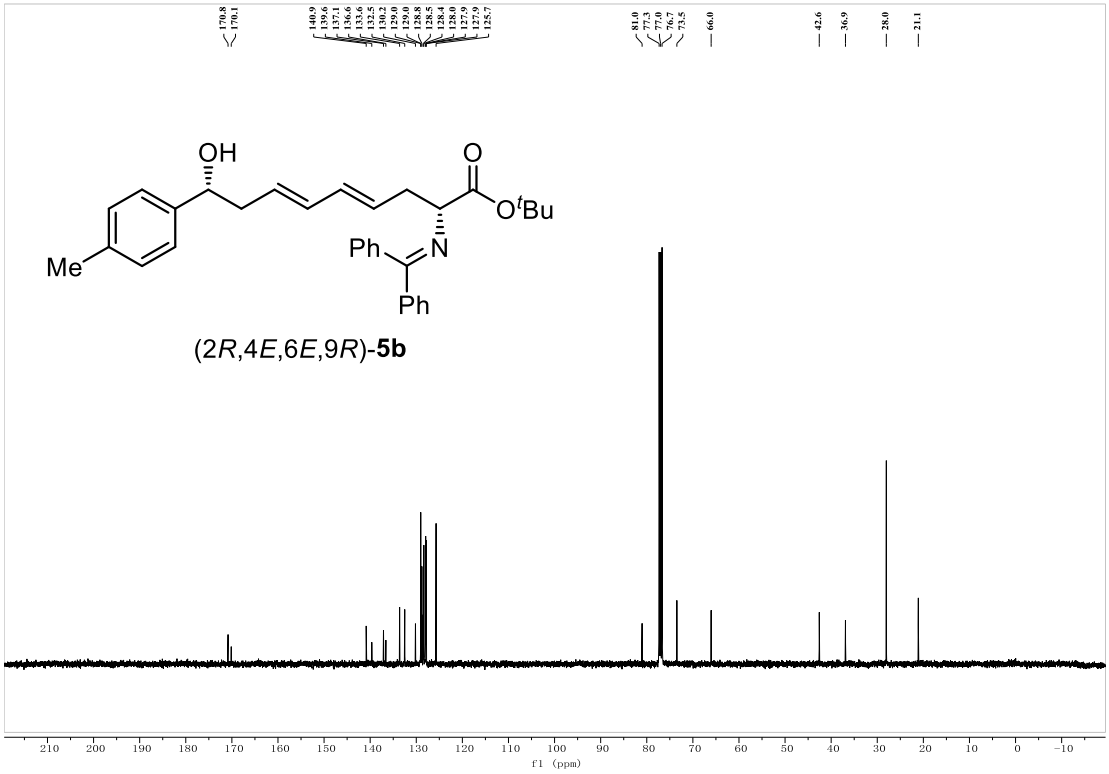
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-**5b**



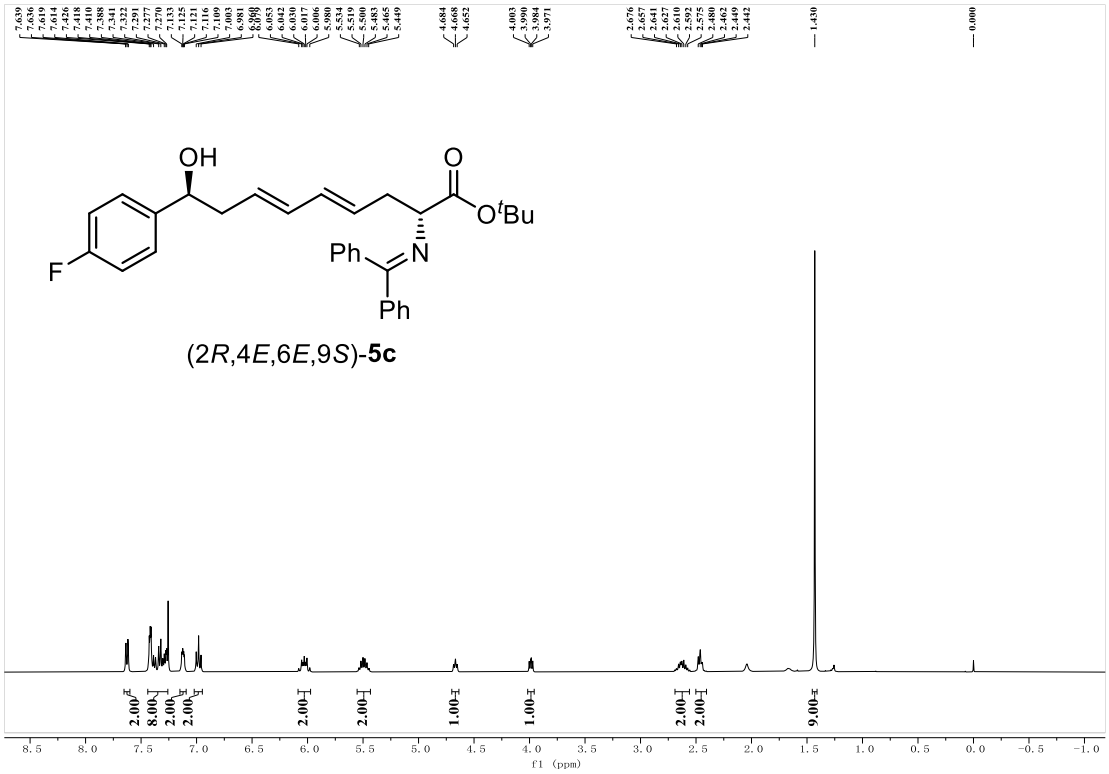
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-**5b**



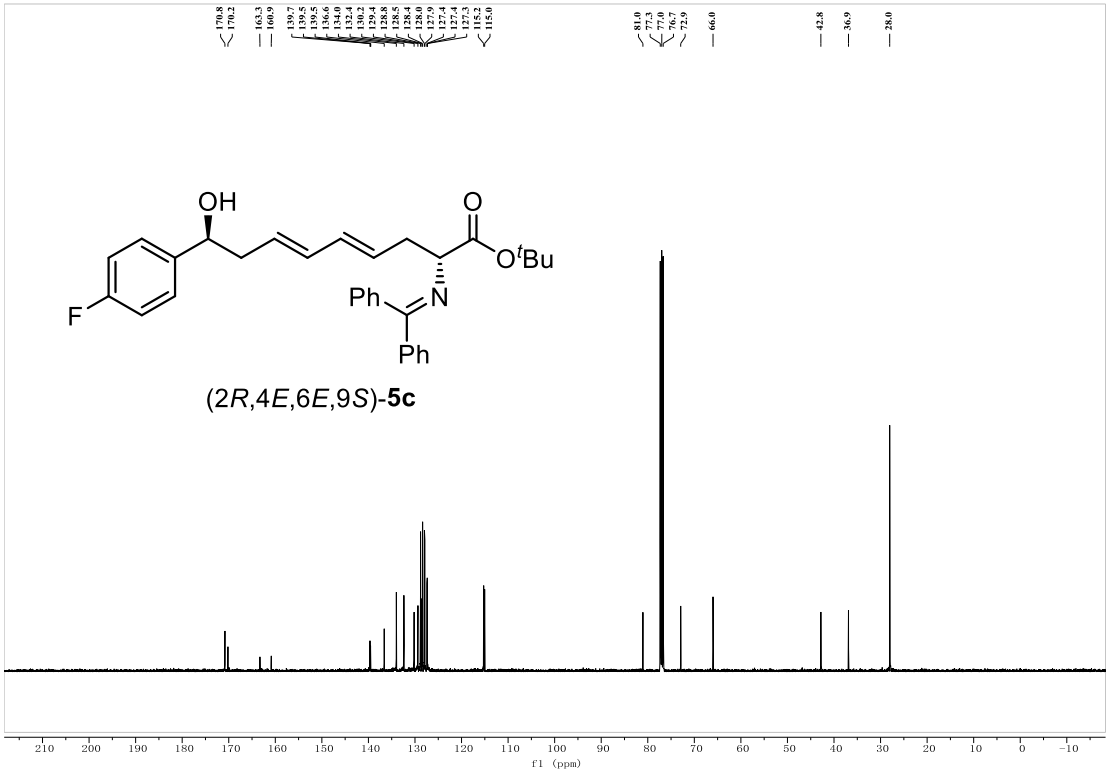
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-**5b**



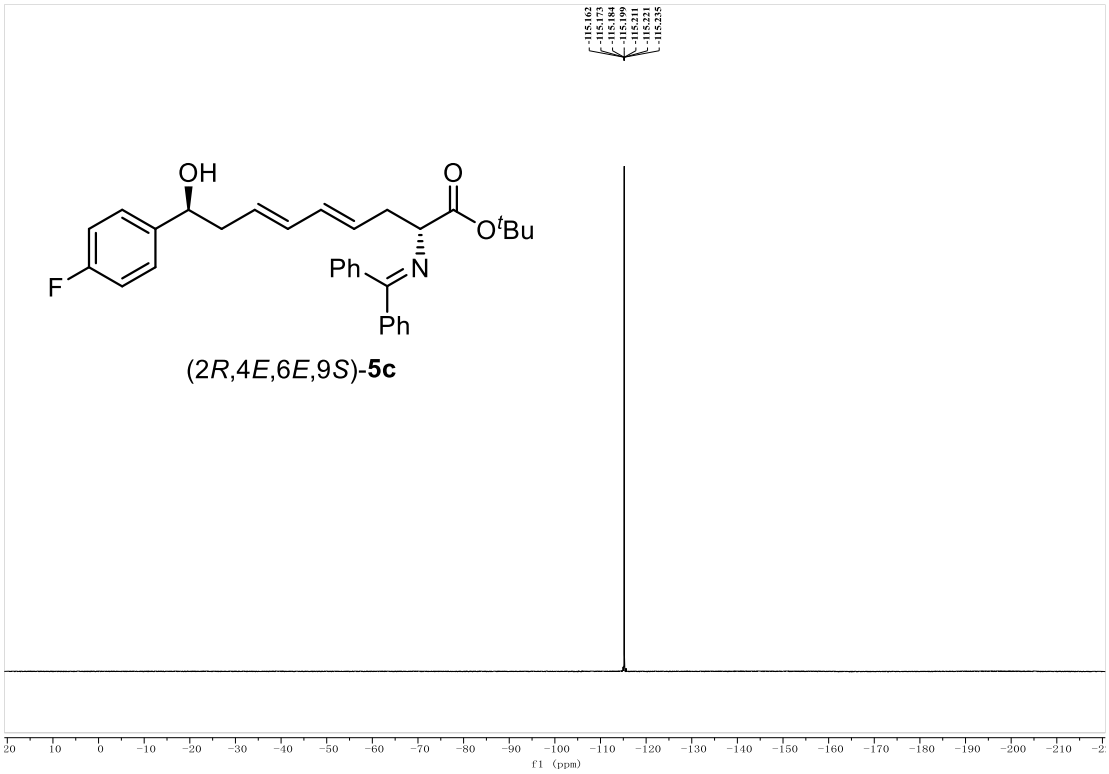
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-**5b**



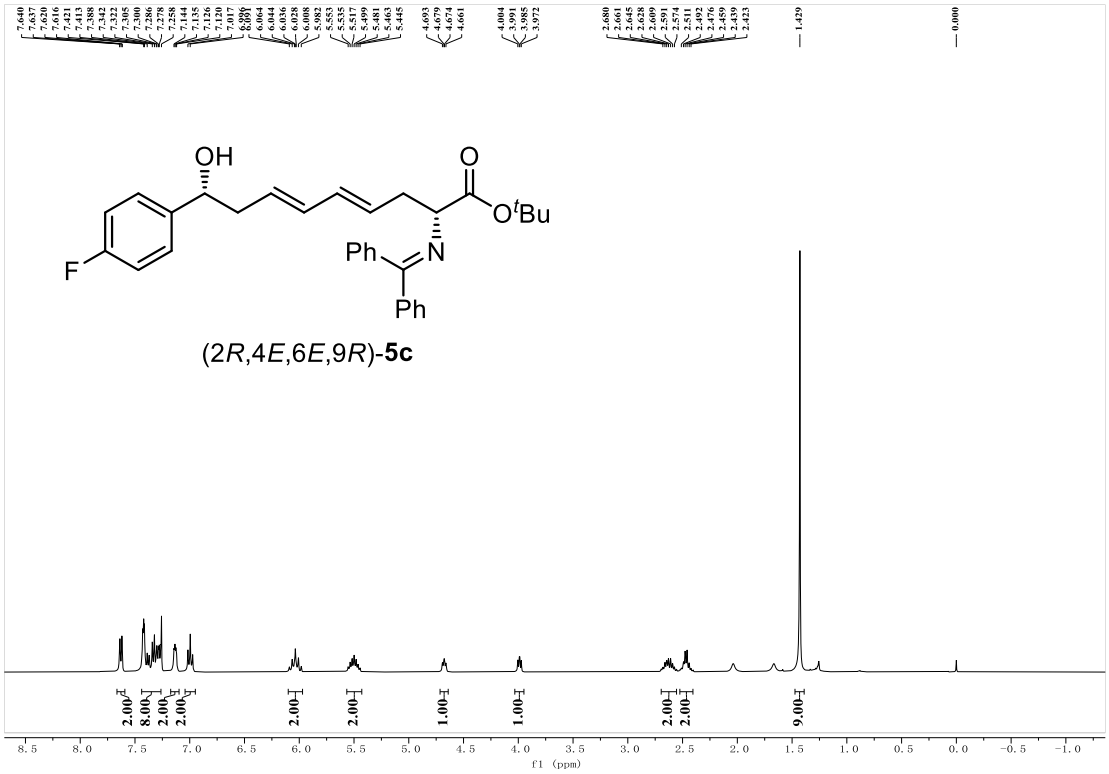
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-**5c**



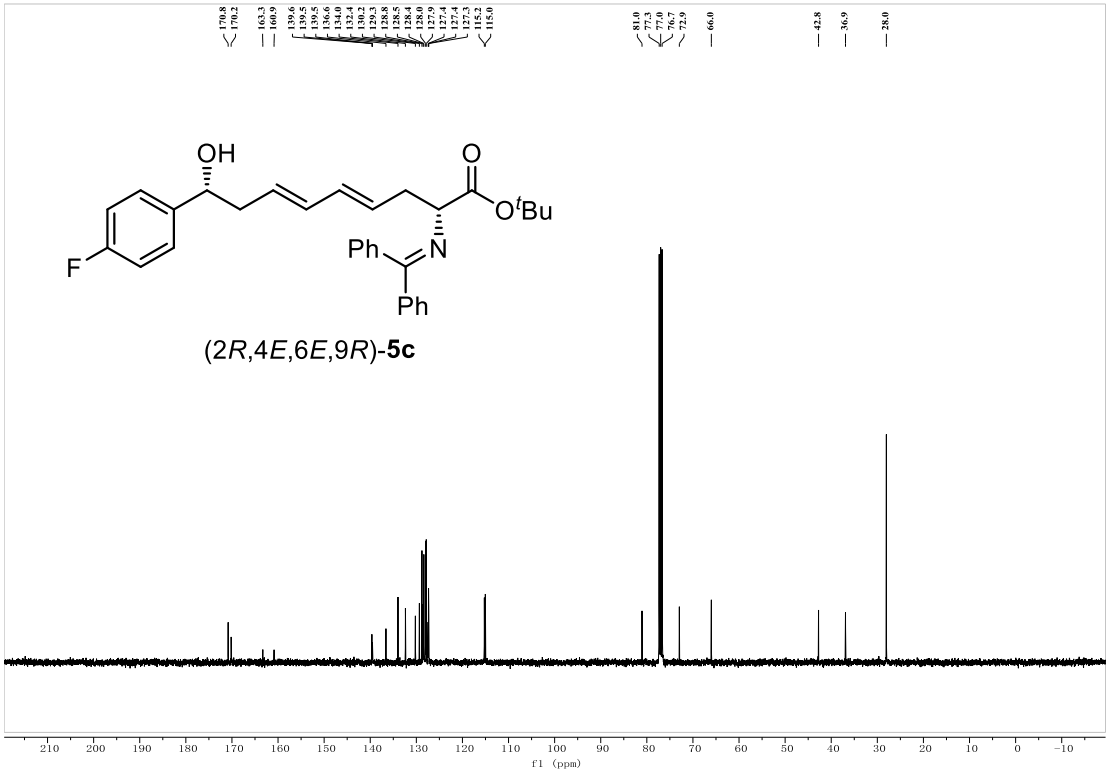
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-**5c**



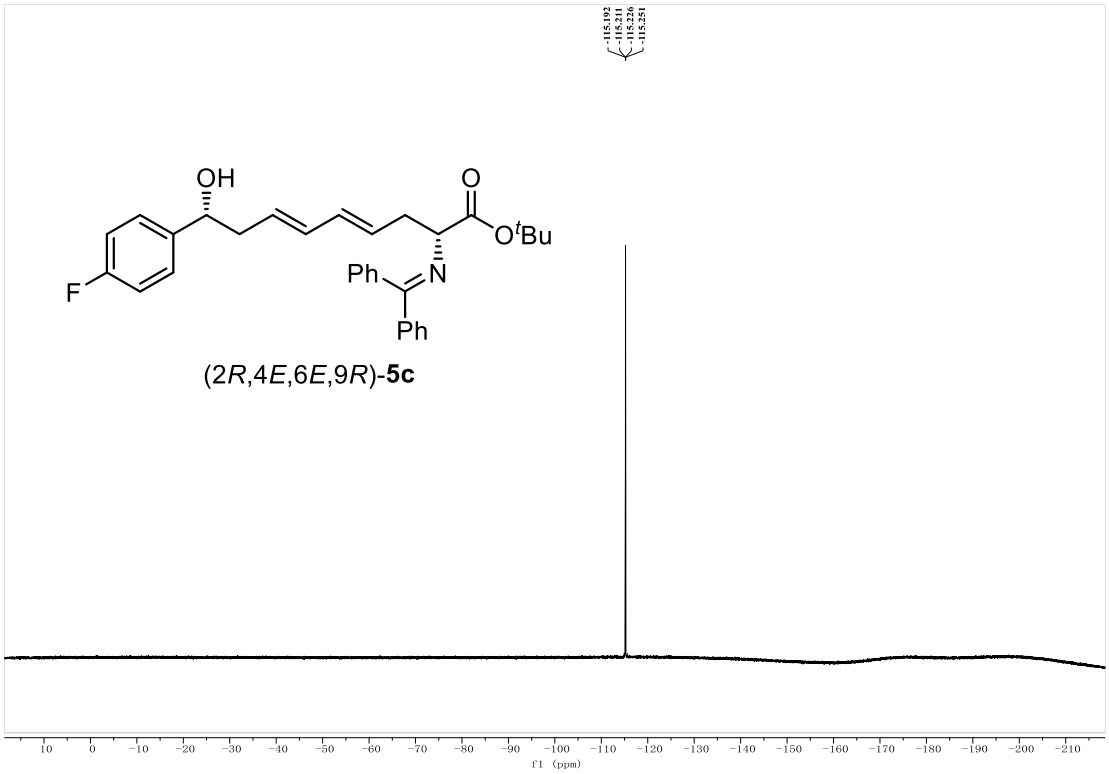
^{19}F NMR (376 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-**5c**



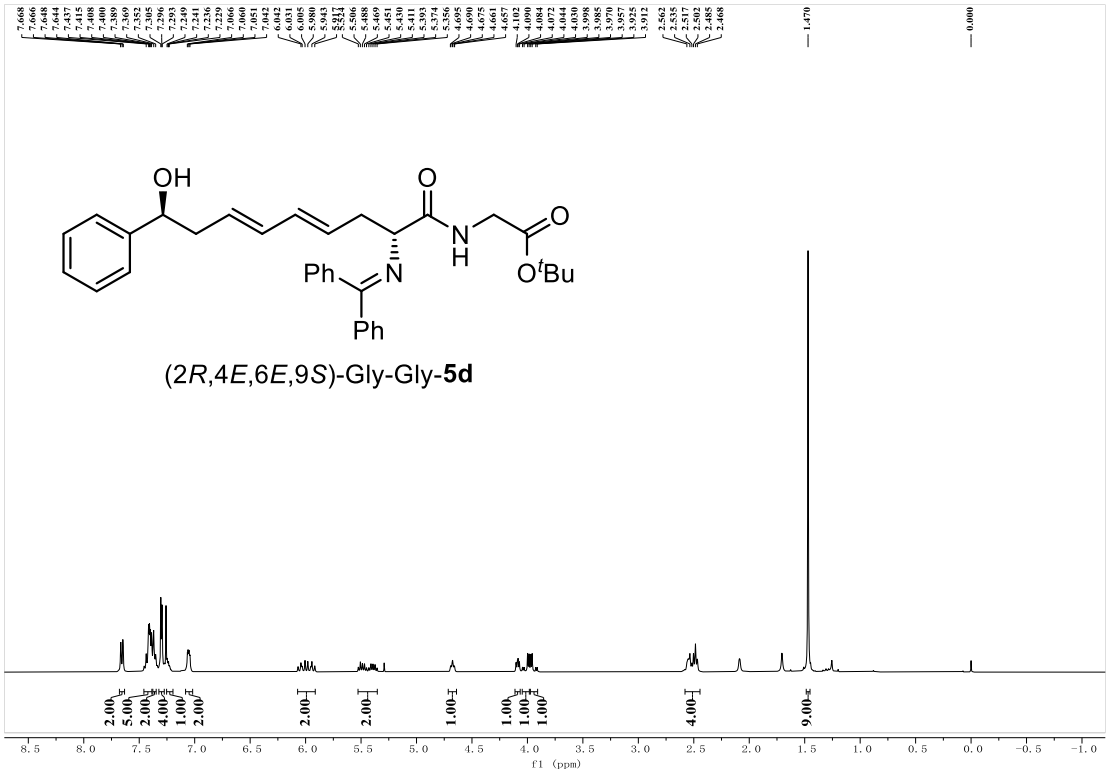
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-**5c**



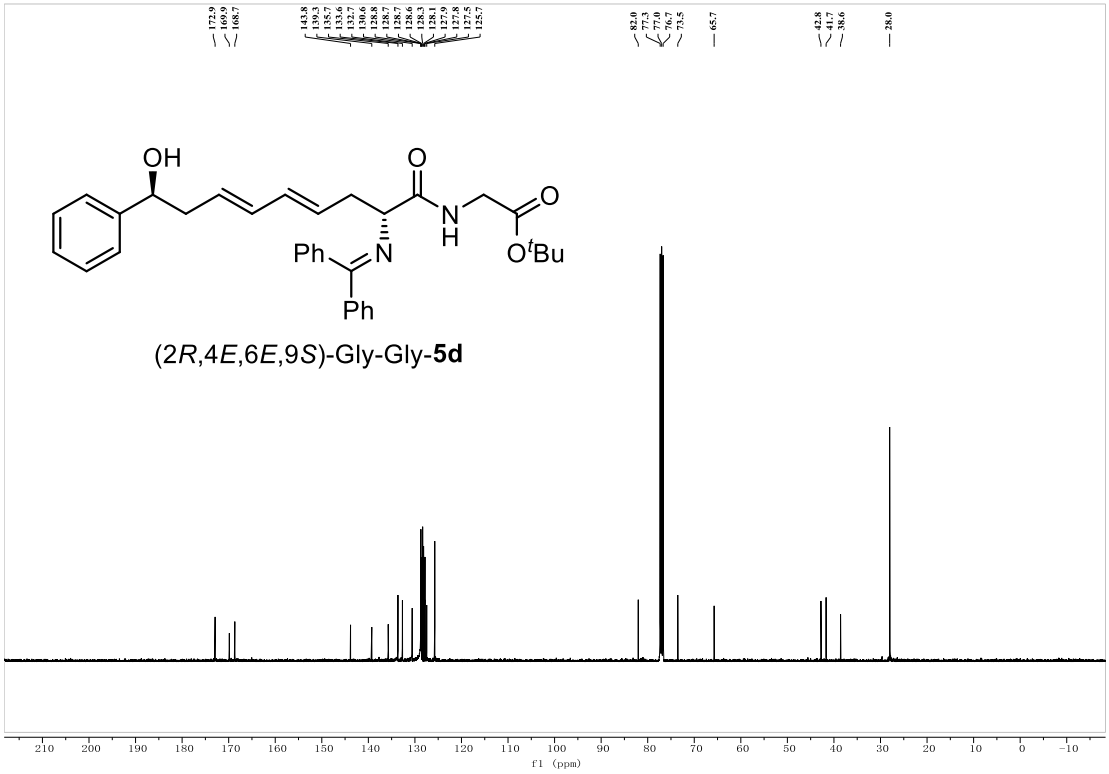
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-**5c**



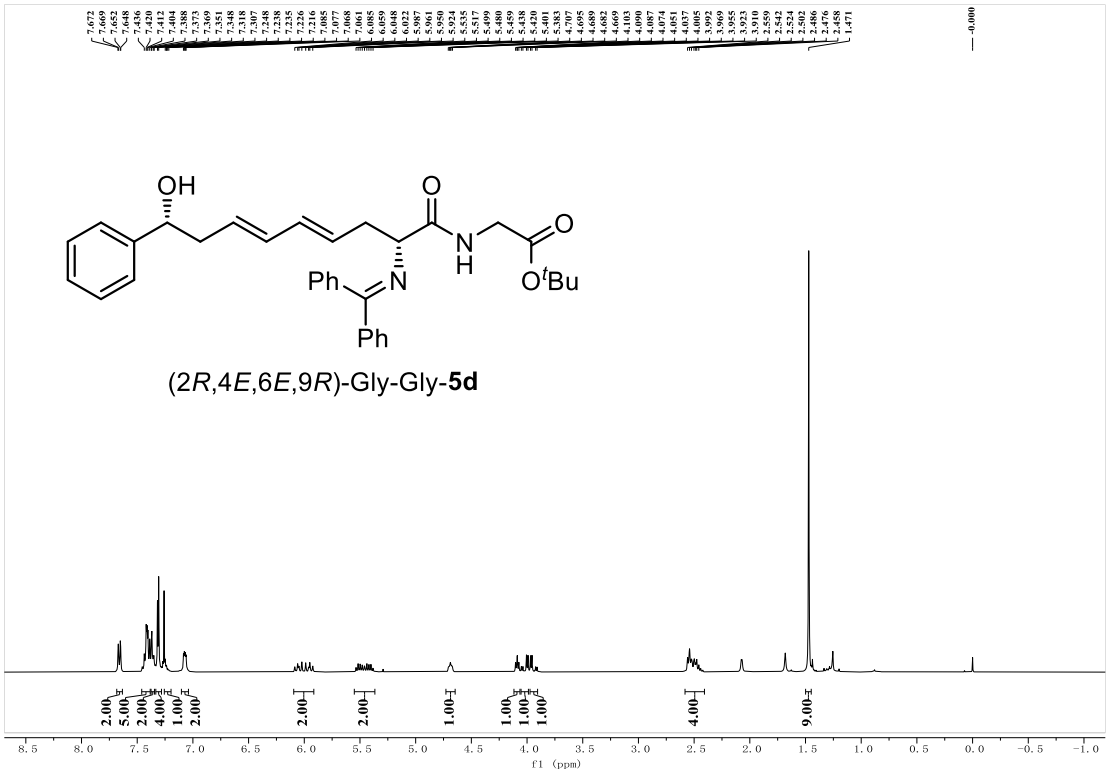
^{19}F NMR (376 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-**5c**



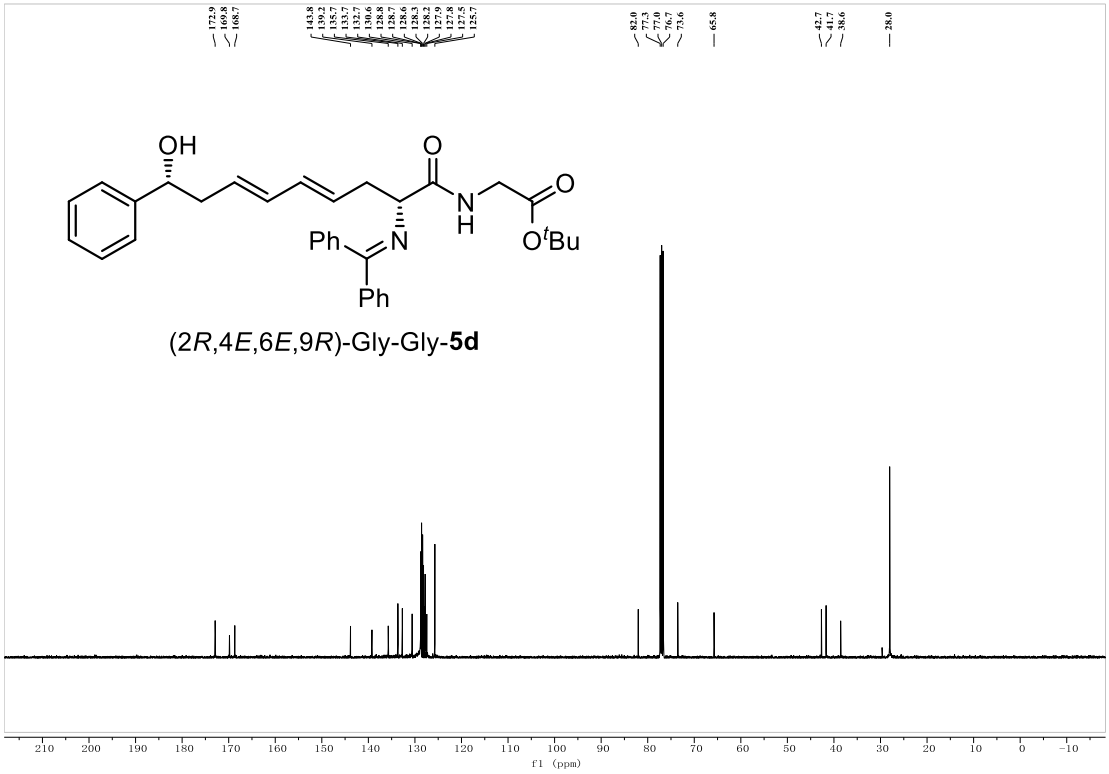
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-Gly-Gly-**5d**



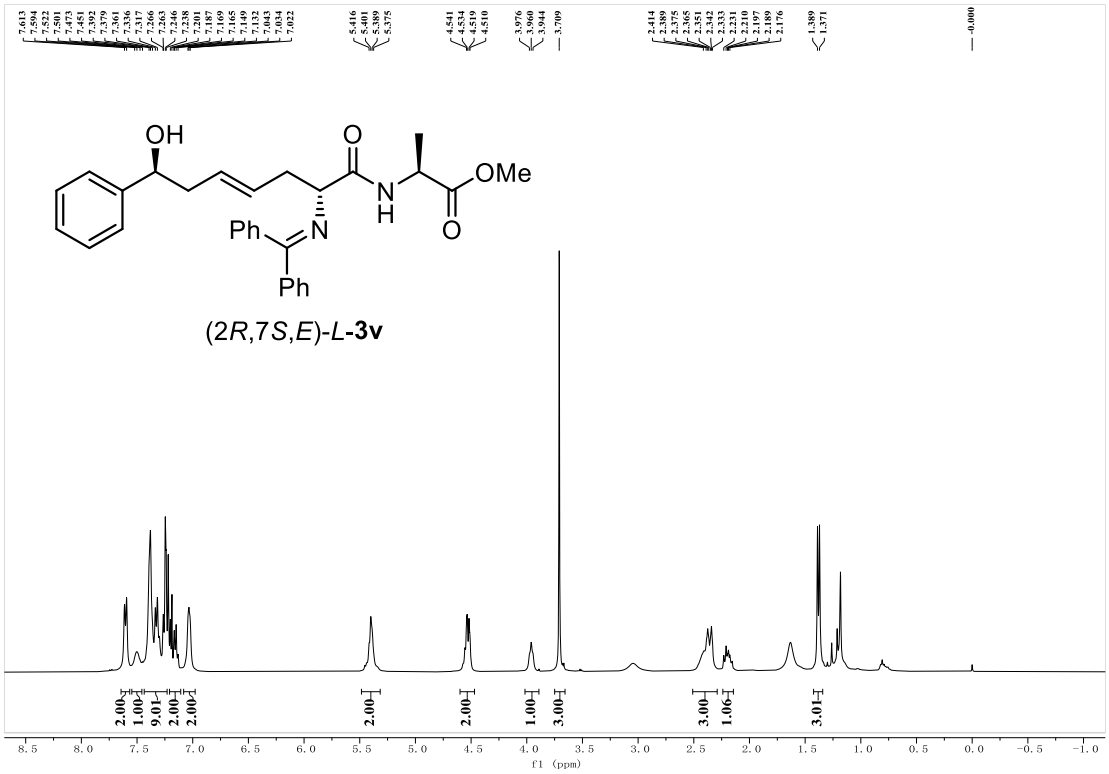
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*S*)-Gly-Gly-**5d**



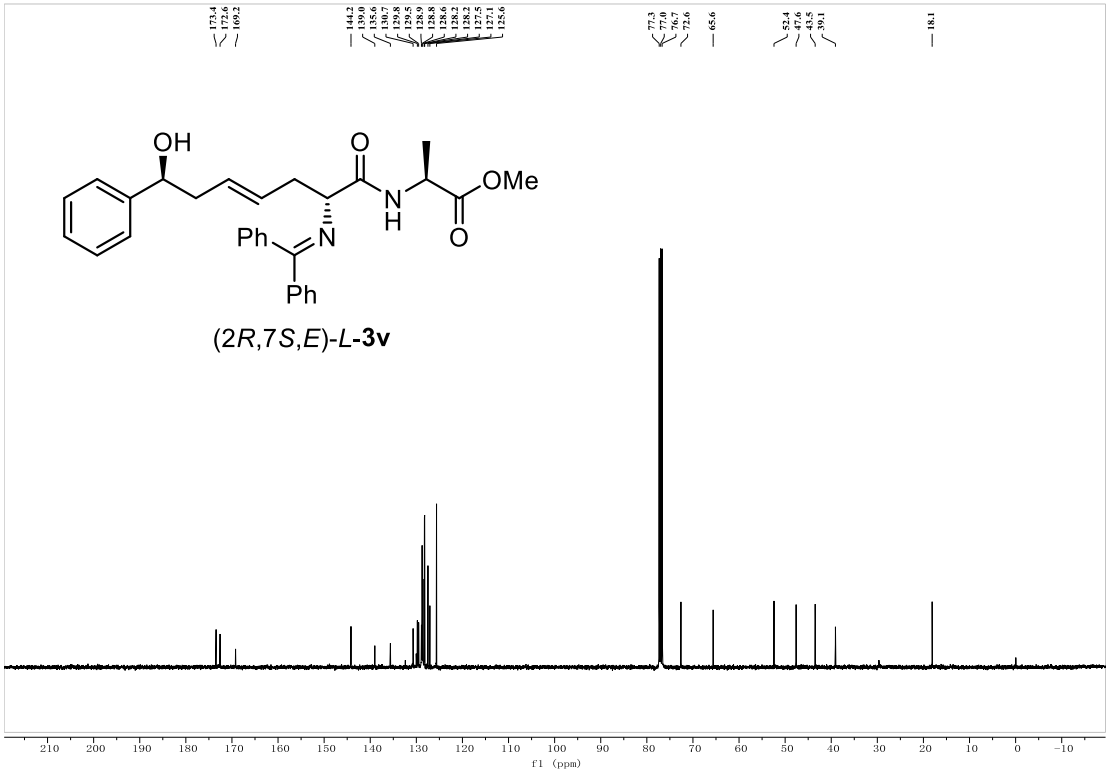
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-Gly-Gly-**5d**



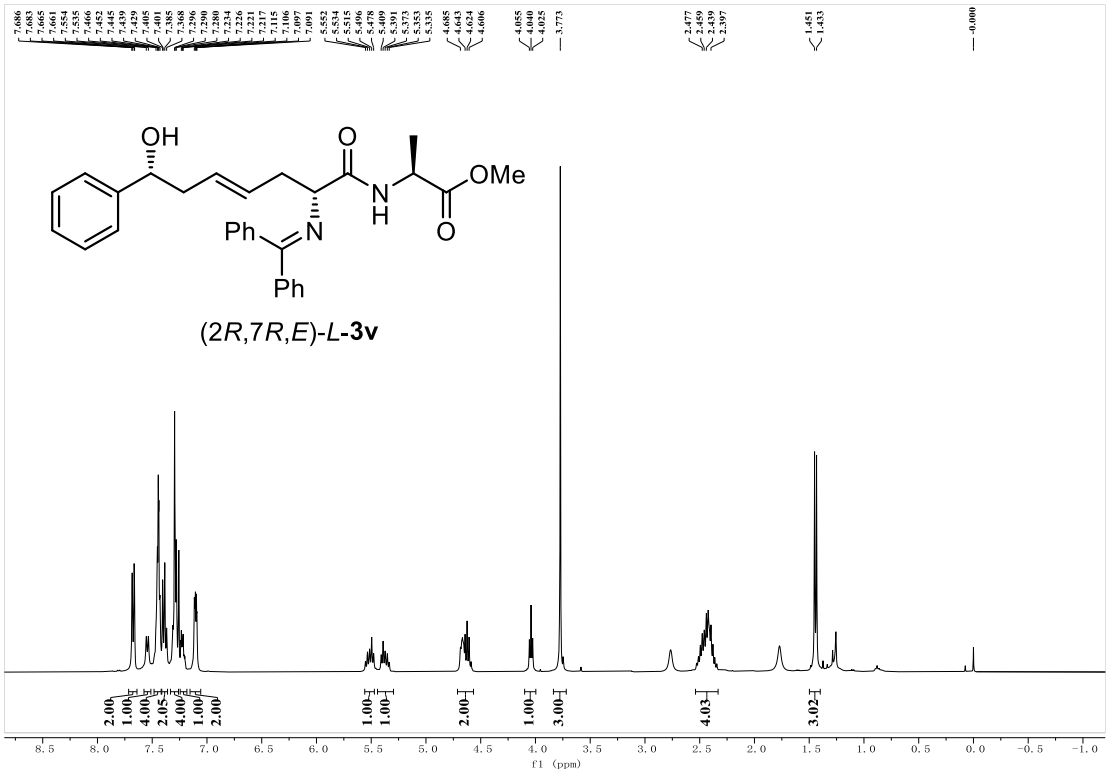
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,4*E*,6*E*,9*R*)-Gly-Gly-**5d**



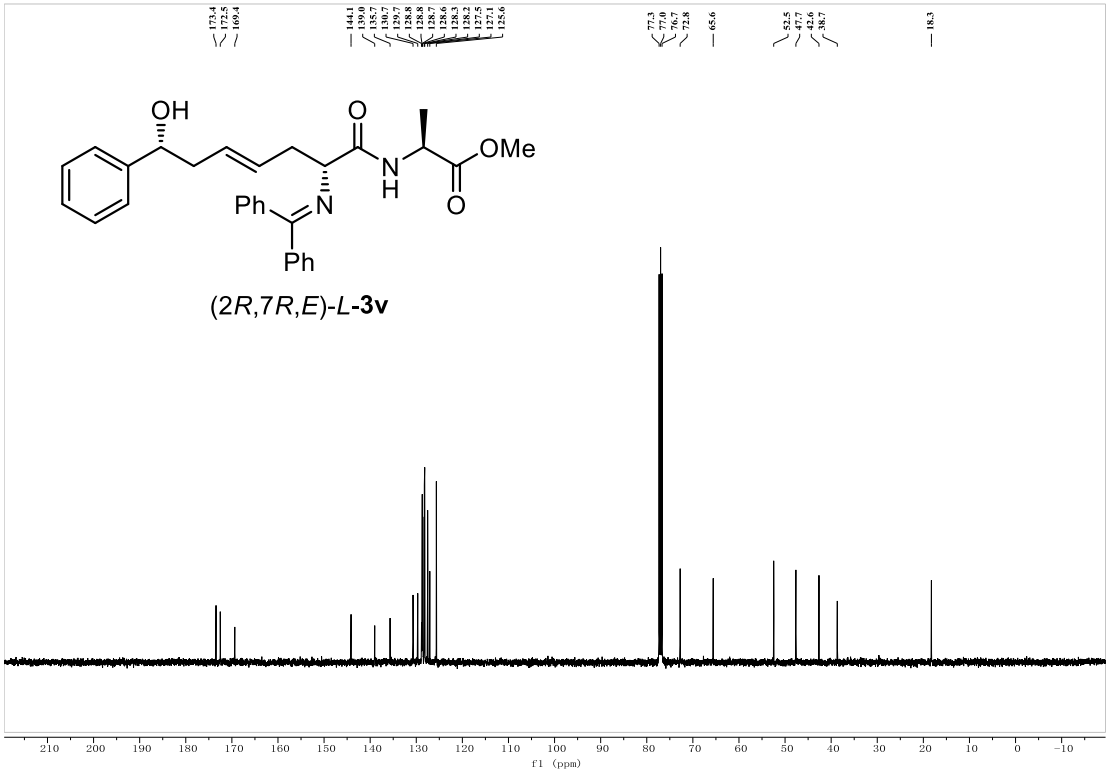
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-*L*-**3v**



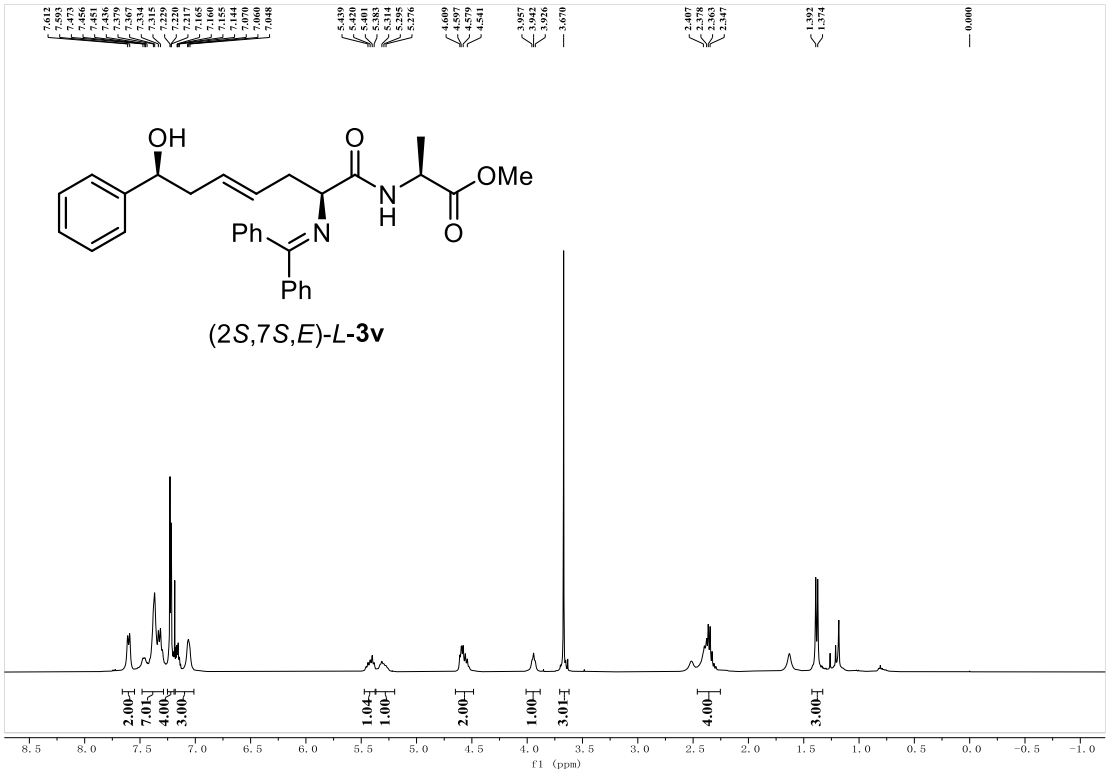
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*S*,*E*)-*L*-**3v**



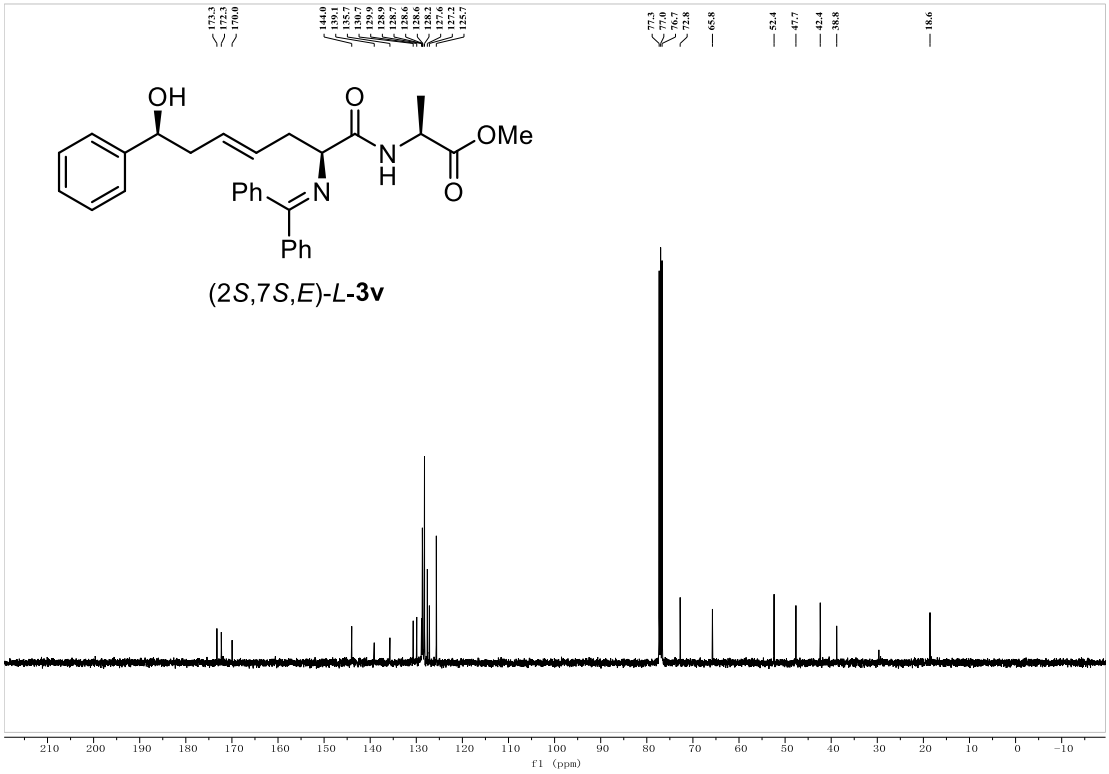
^{1}H NMR (400 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-*L*-**3v**



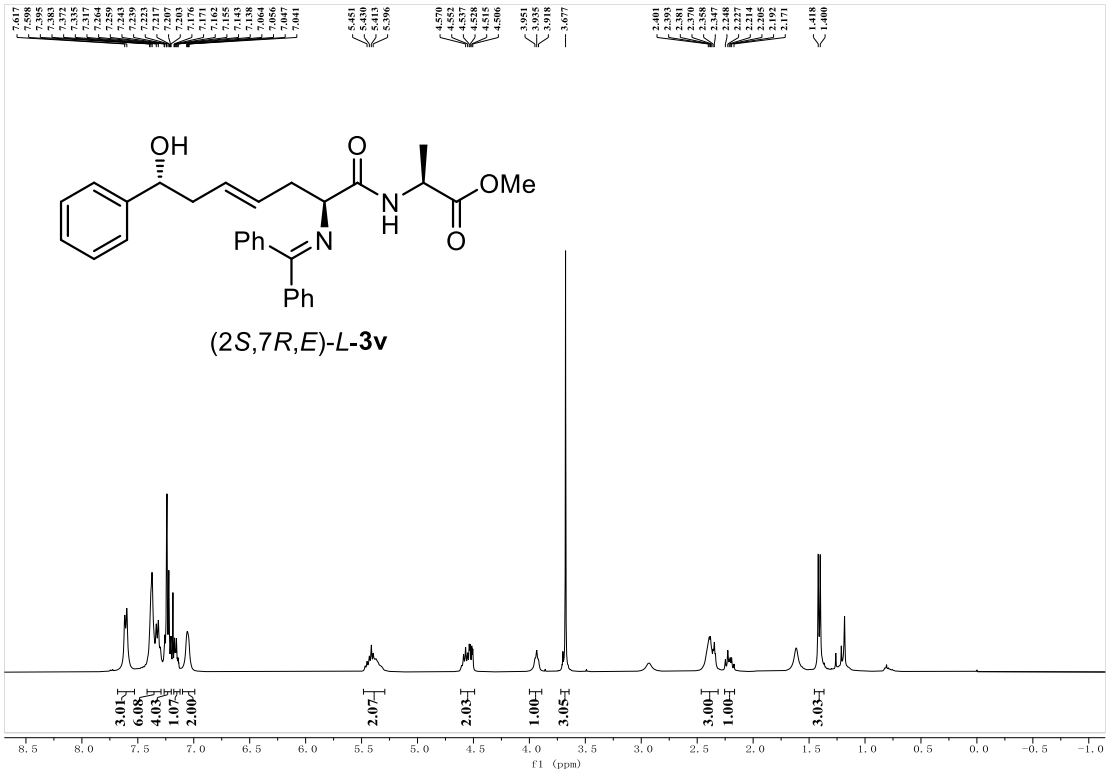
^{13}C NMR (101 MHz, $CDCl_3$) of (2*R*,7*R*,*E*)-*L*-**3v**



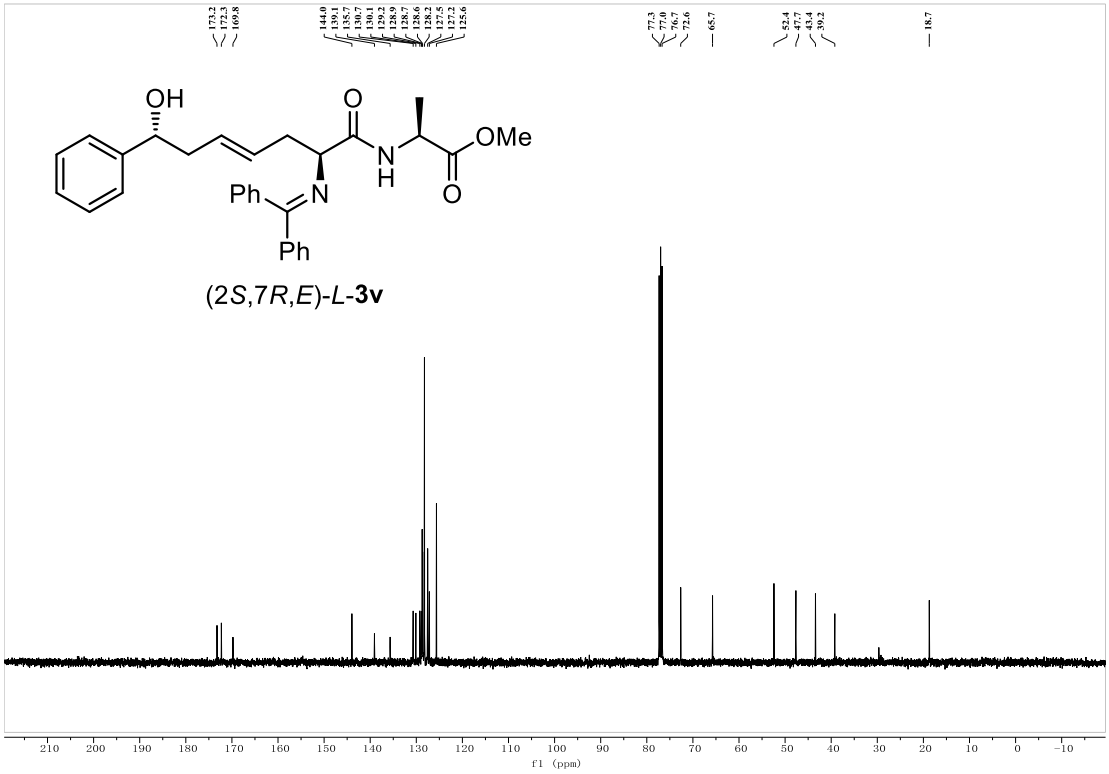
^{1}H NMR (400 MHz, $CDCl_3$) of (2*S*,7*S*,*E*)-*L*-**3v**



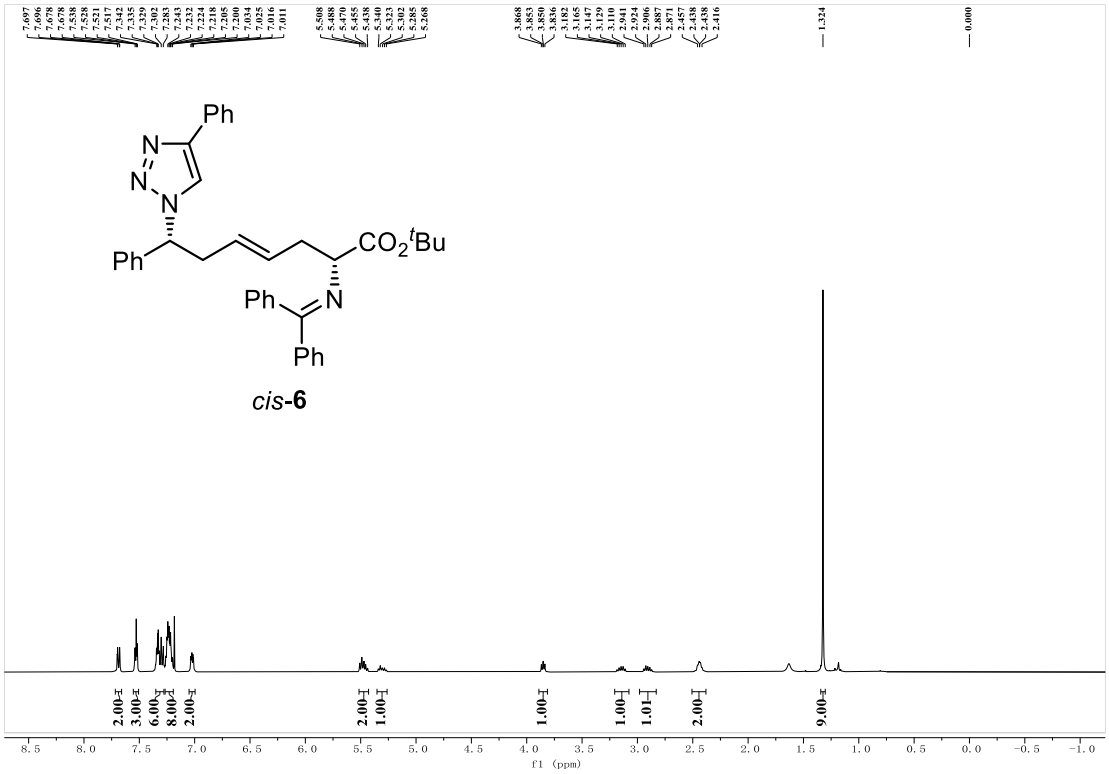
^{13}C NMR (101 MHz, $CDCl_3$) of (2*S*,7*S*,*E*)-*L*-**3v**



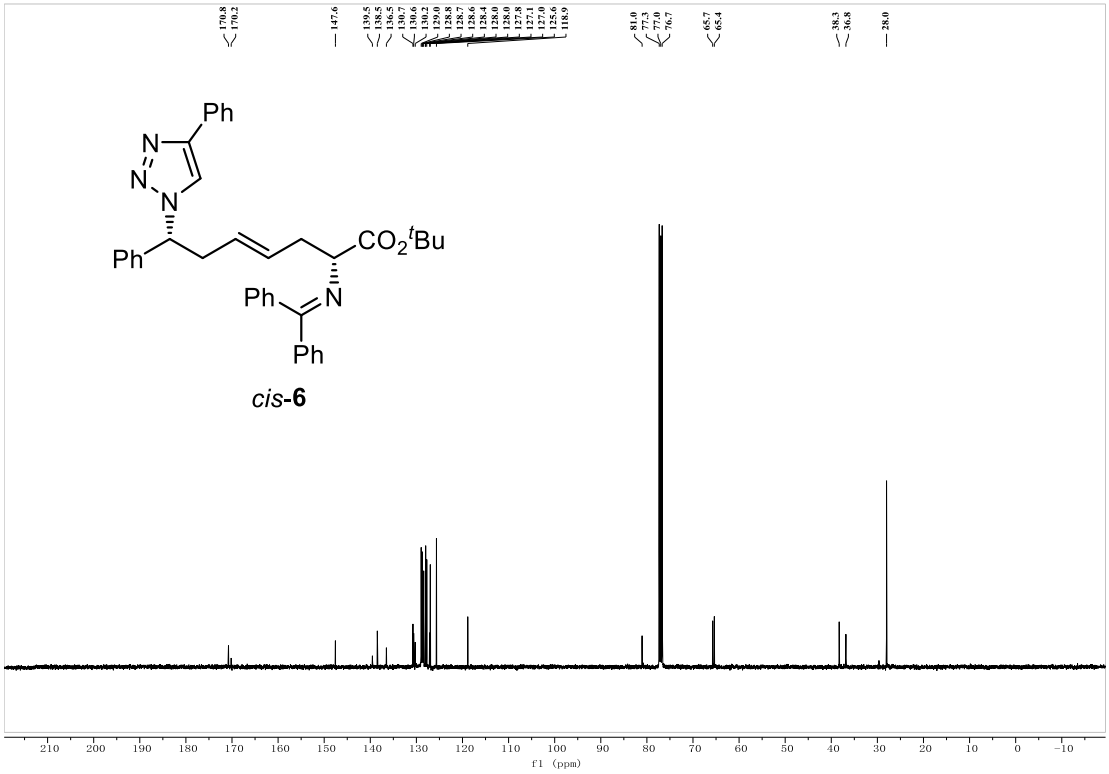
^{1}H NMR (400 MHz, $CDCl_3$) of (2*S*,7*R*,*E*)-*L*-**3v**



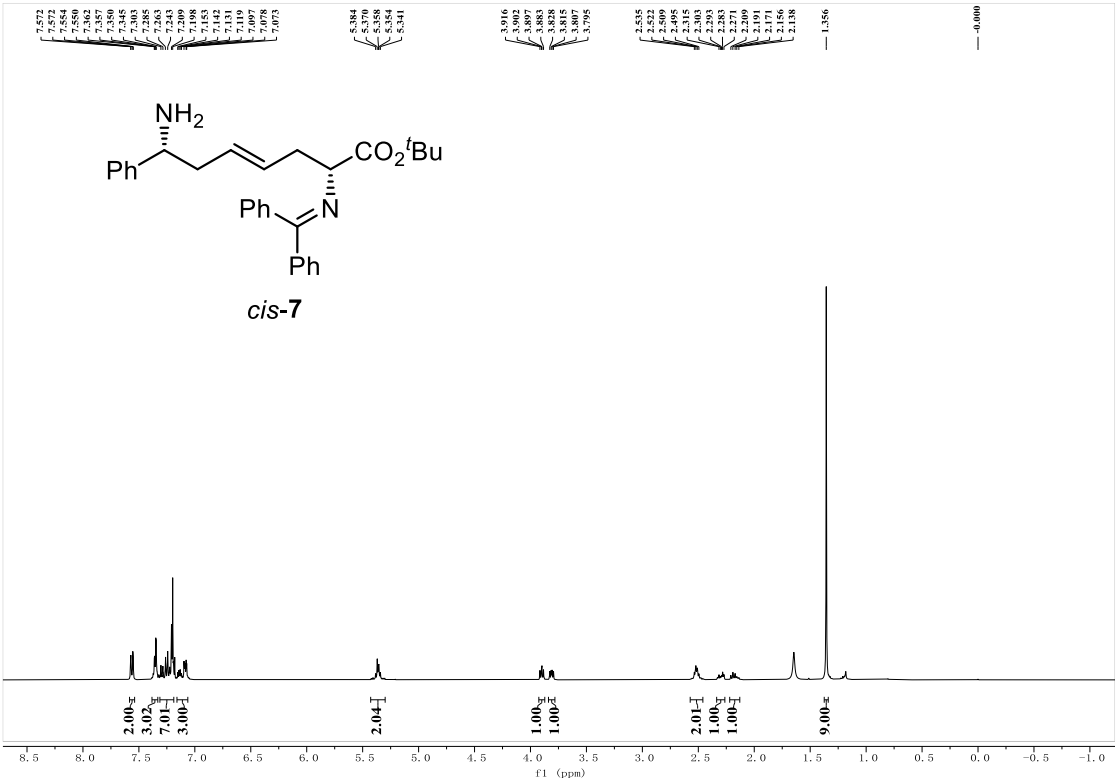
^{13}C NMR (101 MHz, $CDCl_3$) of (2*S*,7*R*,*E*)-*L*-**3v**



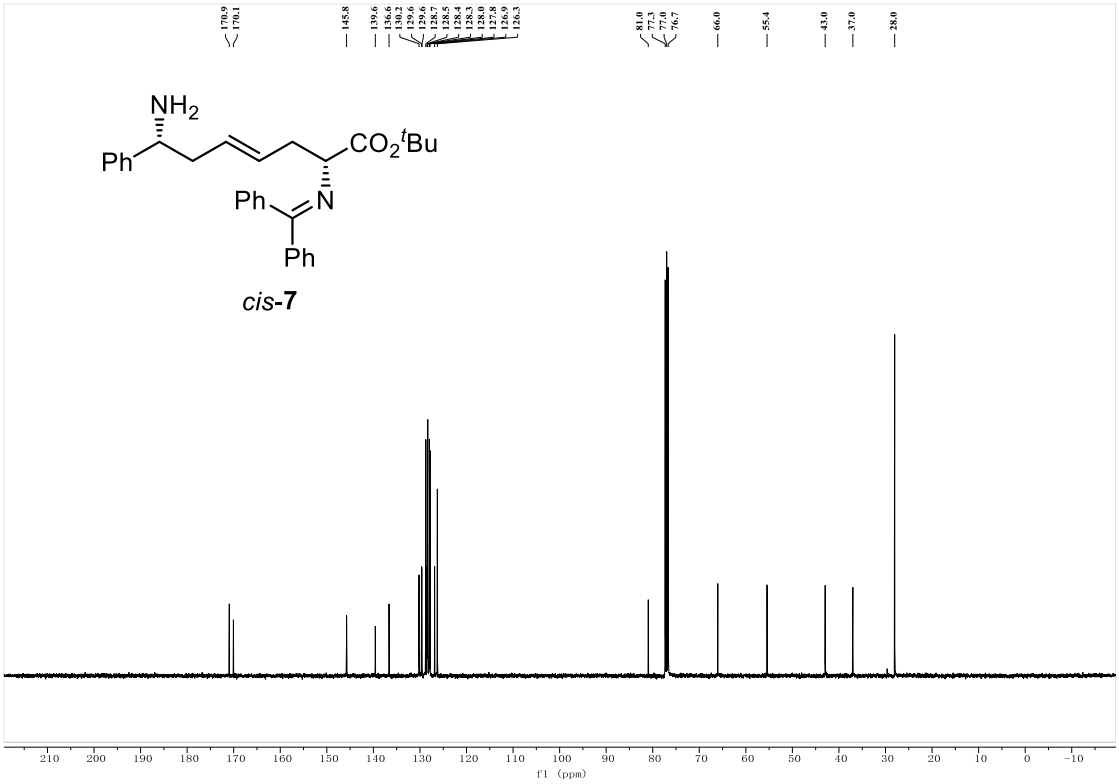
^{1}H NMR (400 MHz, $CDCl_3$) of *cis*-**6**



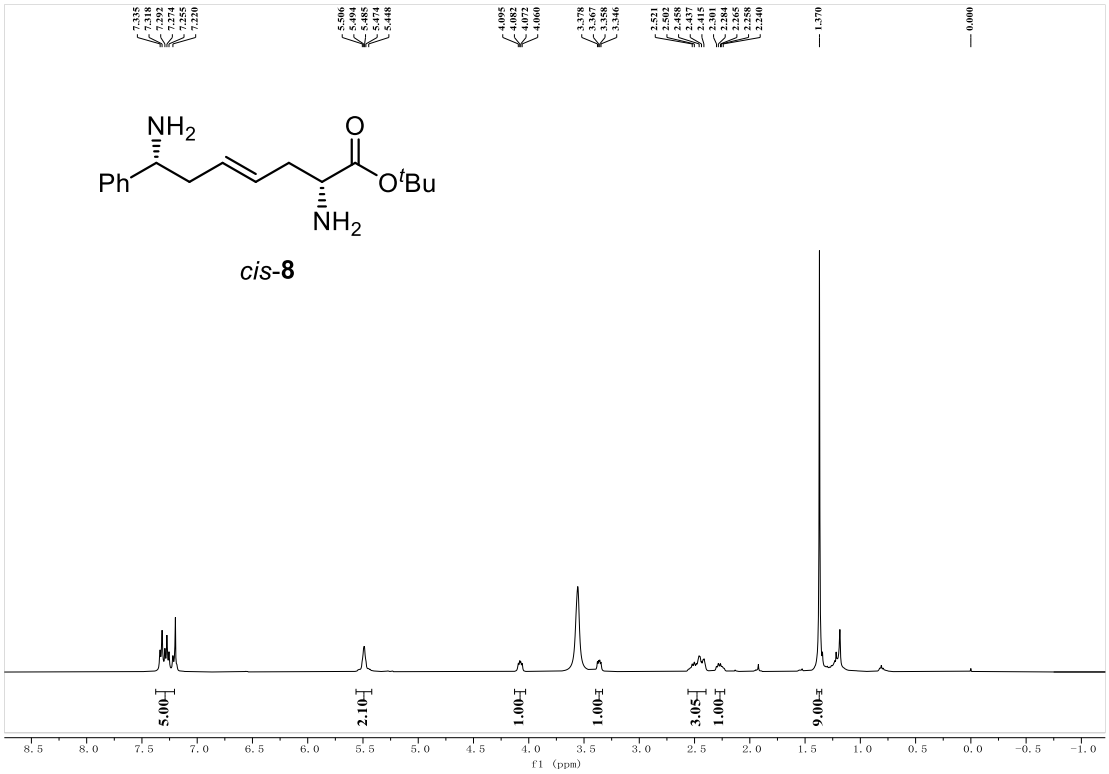
^{13}C NMR (101 MHz, $CDCl_3$) of *cis*-**6**



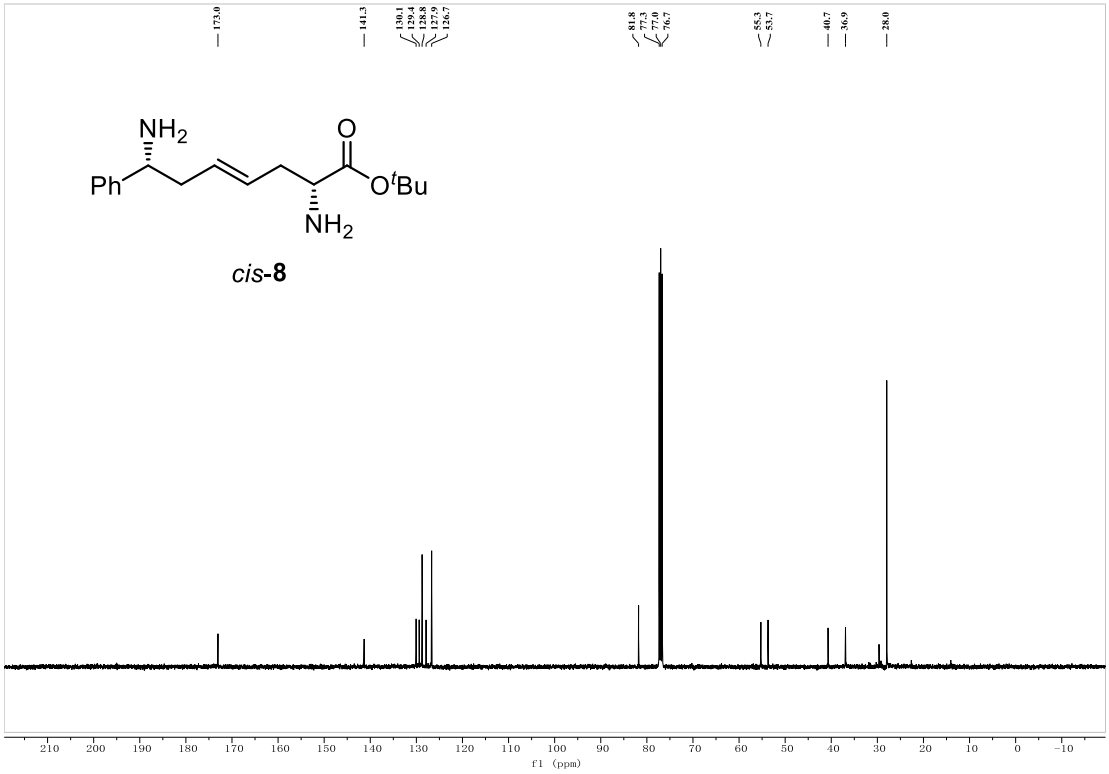
^{1}H NMR (400 MHz, $CDCl_3$) of *cis*-**7**



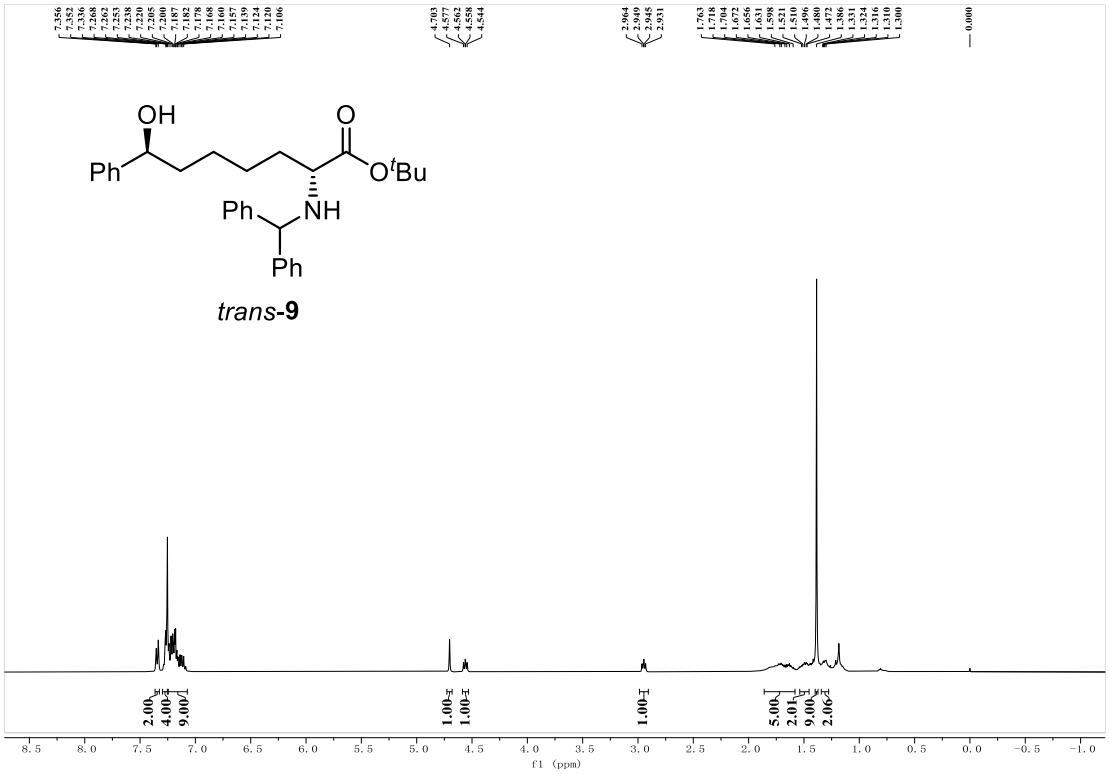
^{13}C NMR (101 MHz, $CDCl_3$) of *cis*-**7**



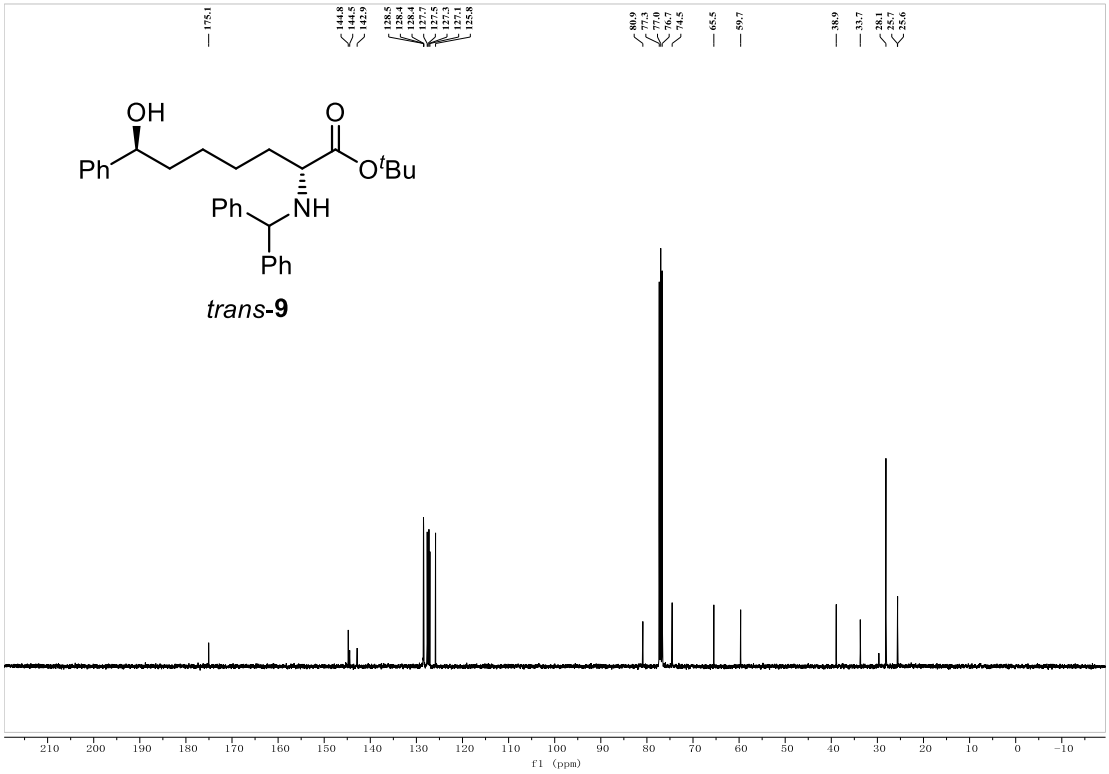
^{1}H NMR (400 MHz, $CDCl_3$) of *cis*-**8**



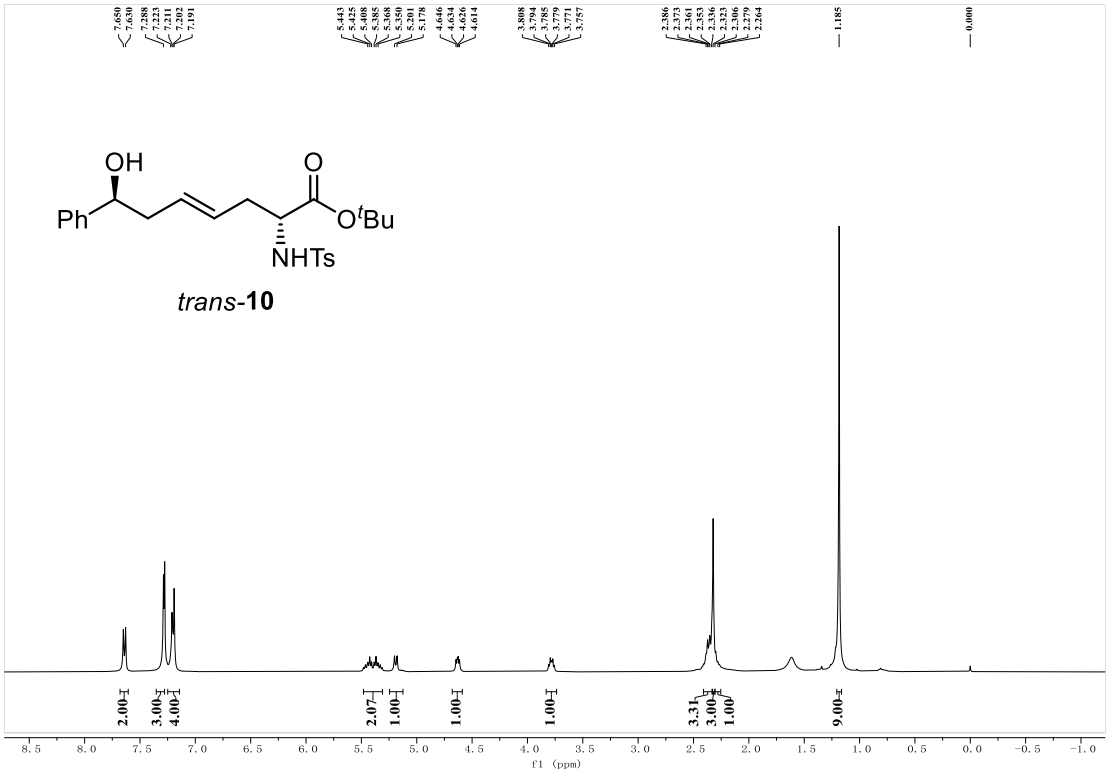
^{13}C NMR (101 MHz, $CDCl_3$) of *cis*-**8**



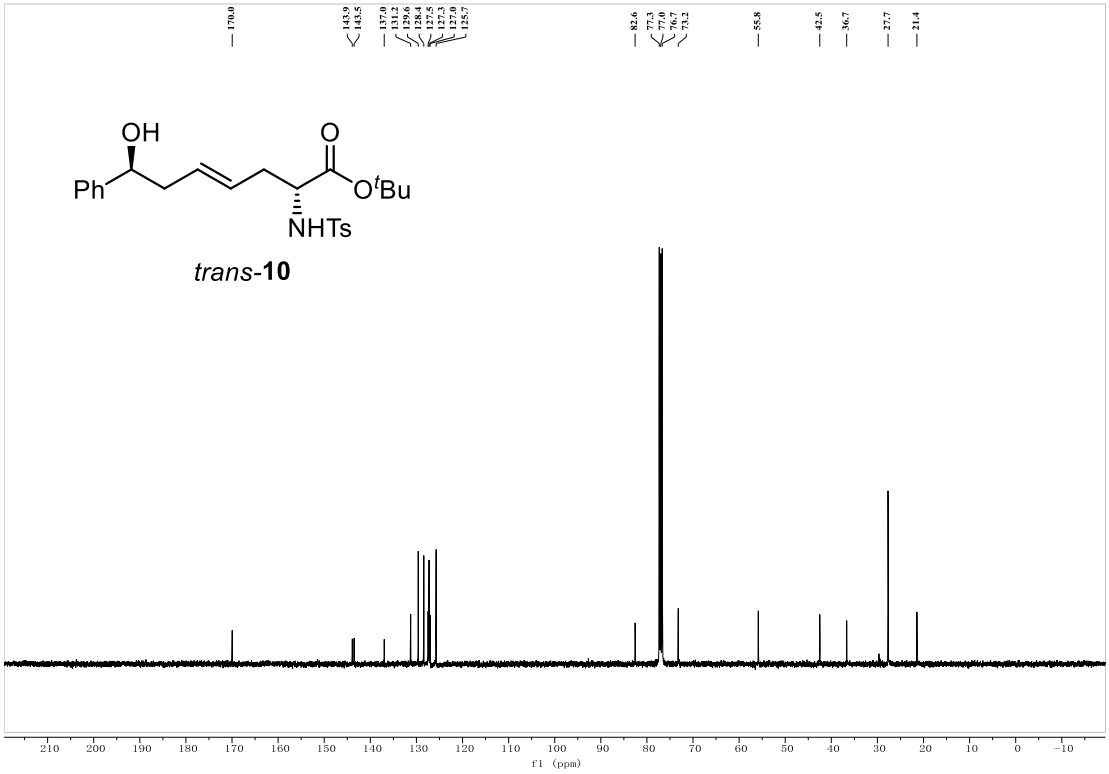
^{1}H NMR (400 MHz, $CDCl_3$) of *trans*-**9**



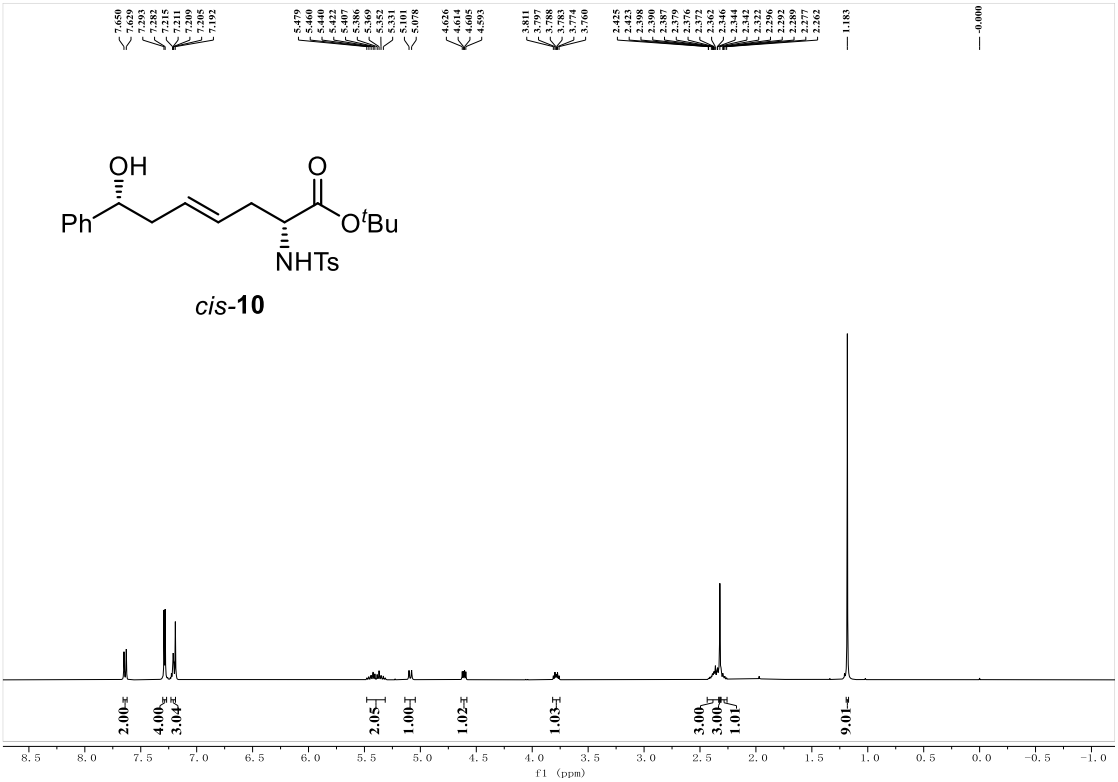
^{13}C NMR (101 MHz, $CDCl_3$) of *trans*-**9**



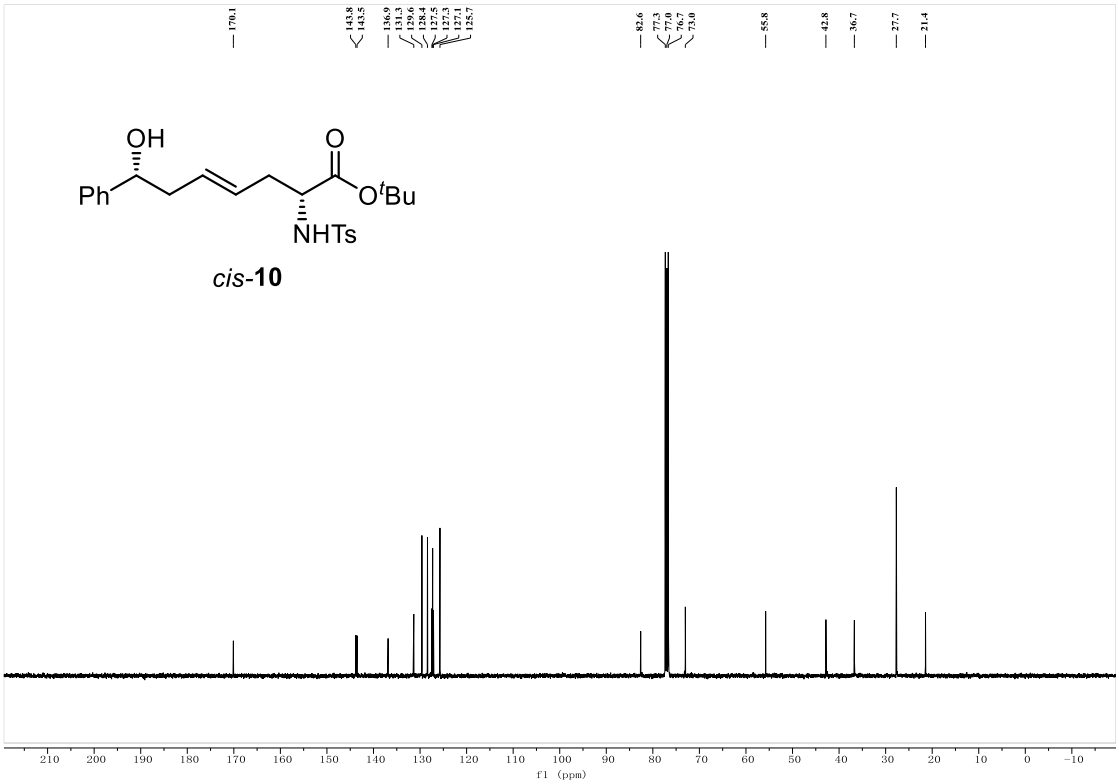
^{1}H NMR (400 MHz, $CDCl_3$) of *trans*-**10**



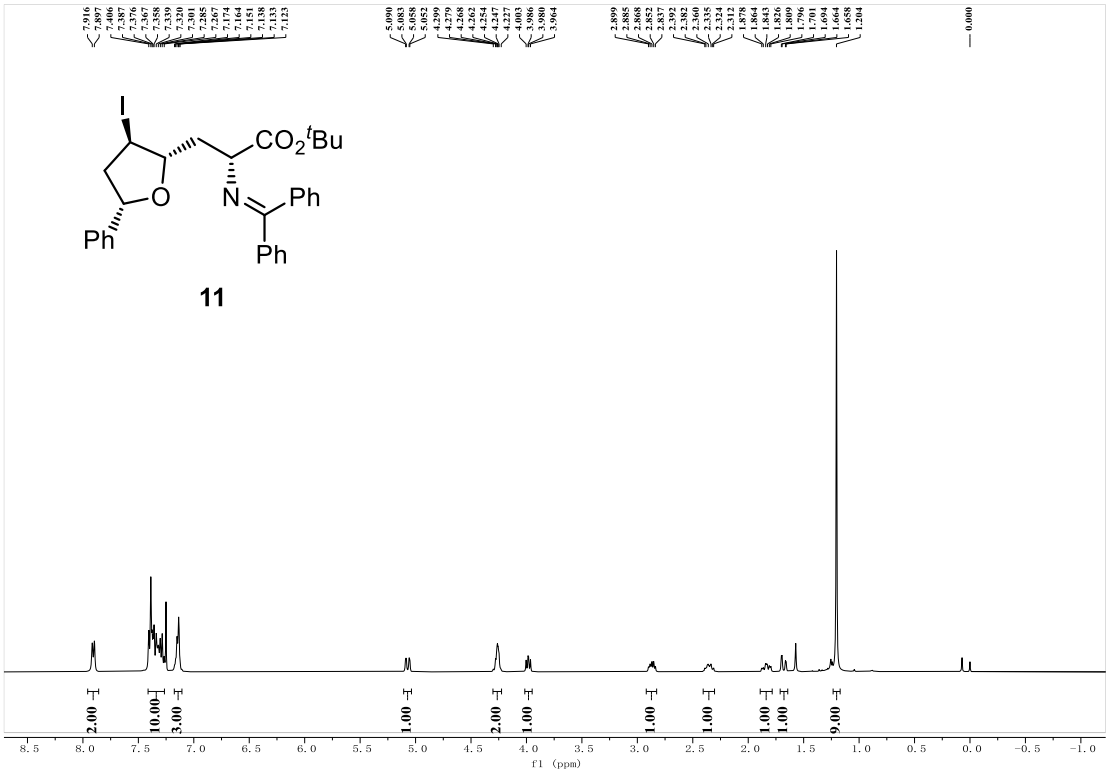
^{13}C NMR (101 MHz, $CDCl_3$) of *trans*-**10**



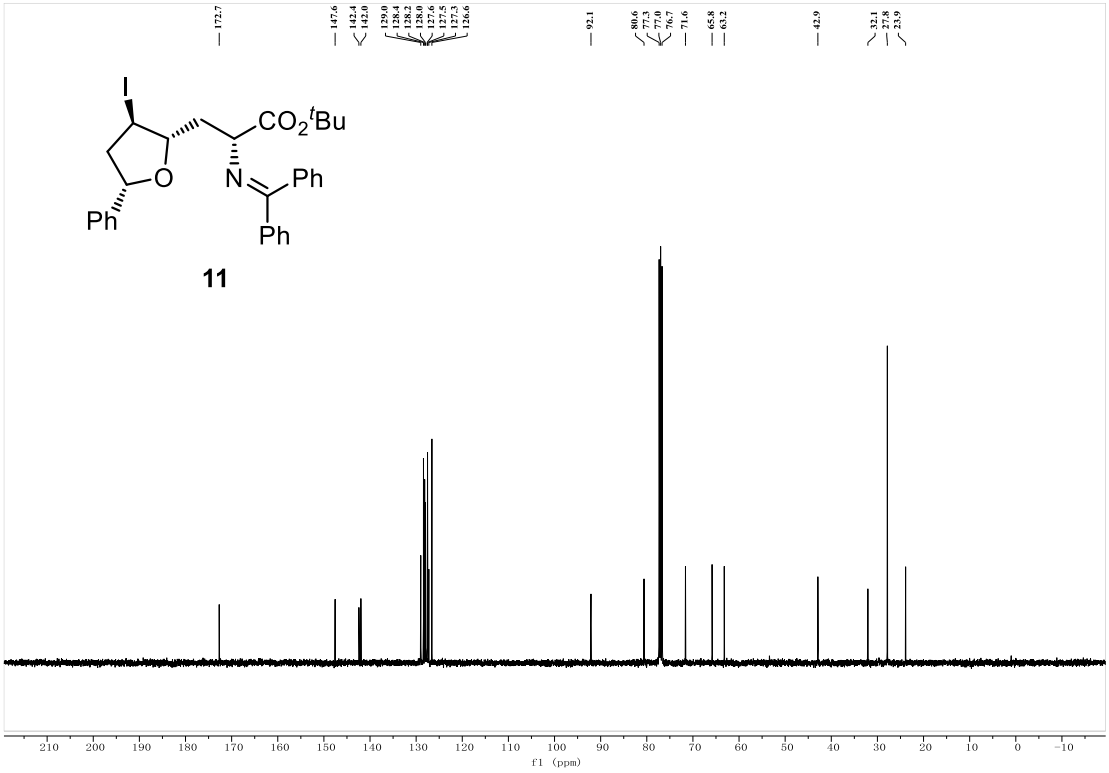
^{1}H NMR (400 MHz, $CDCl_3$) of *cis*-**10**



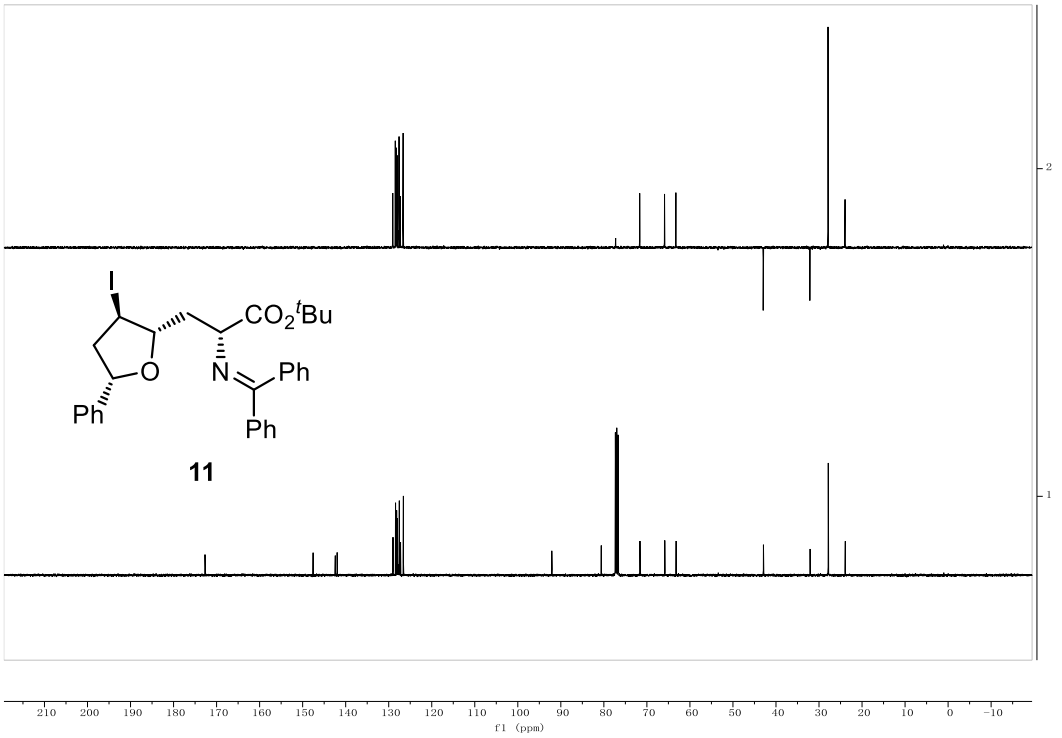
^{13}C NMR (101 MHz, $CDCl_3$) of *cis*-**10**



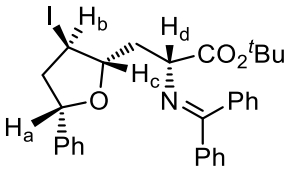
^{1}H NMR (400 MHz, $CDCl_3$) of **11**



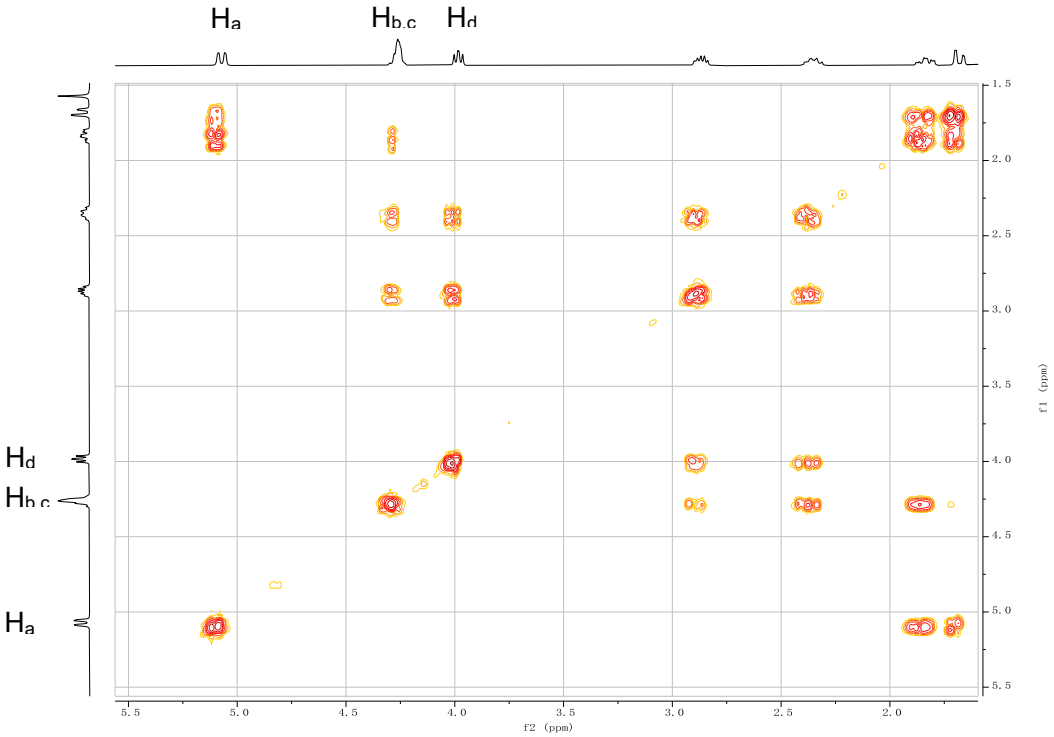
^{13}C NMR (101 MHz, $CDCl_3$) of **11**



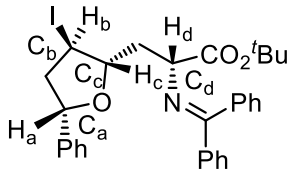
DEPT135 spectrum of **11**



11



COESY spectrum of **11**



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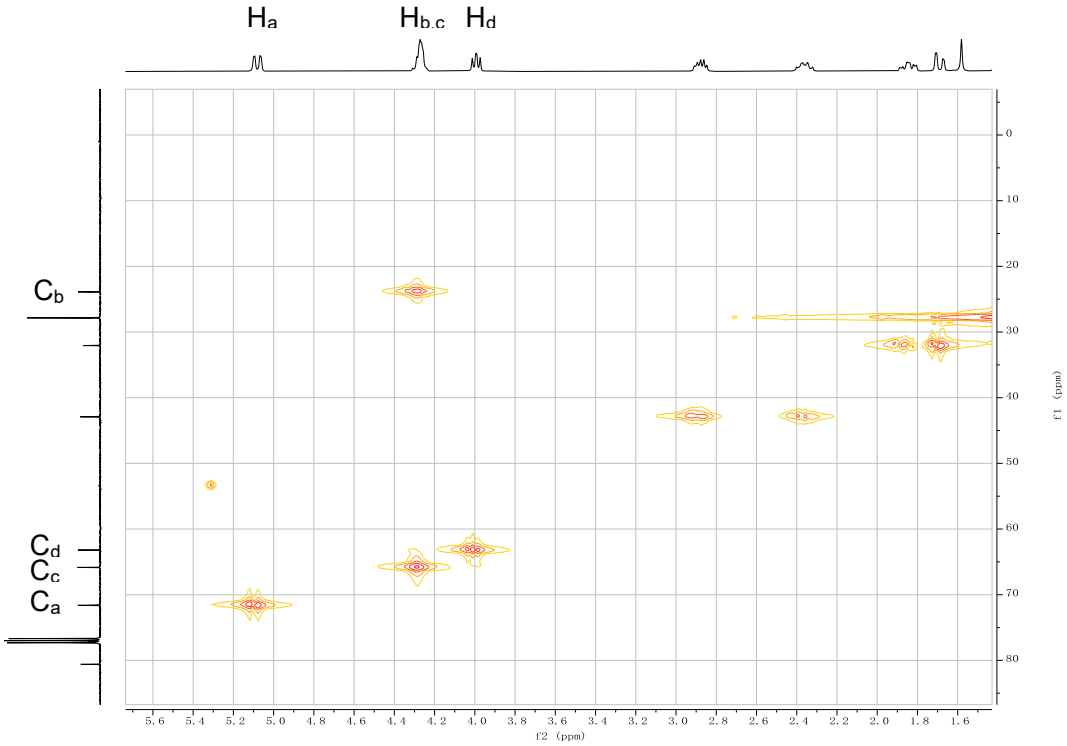
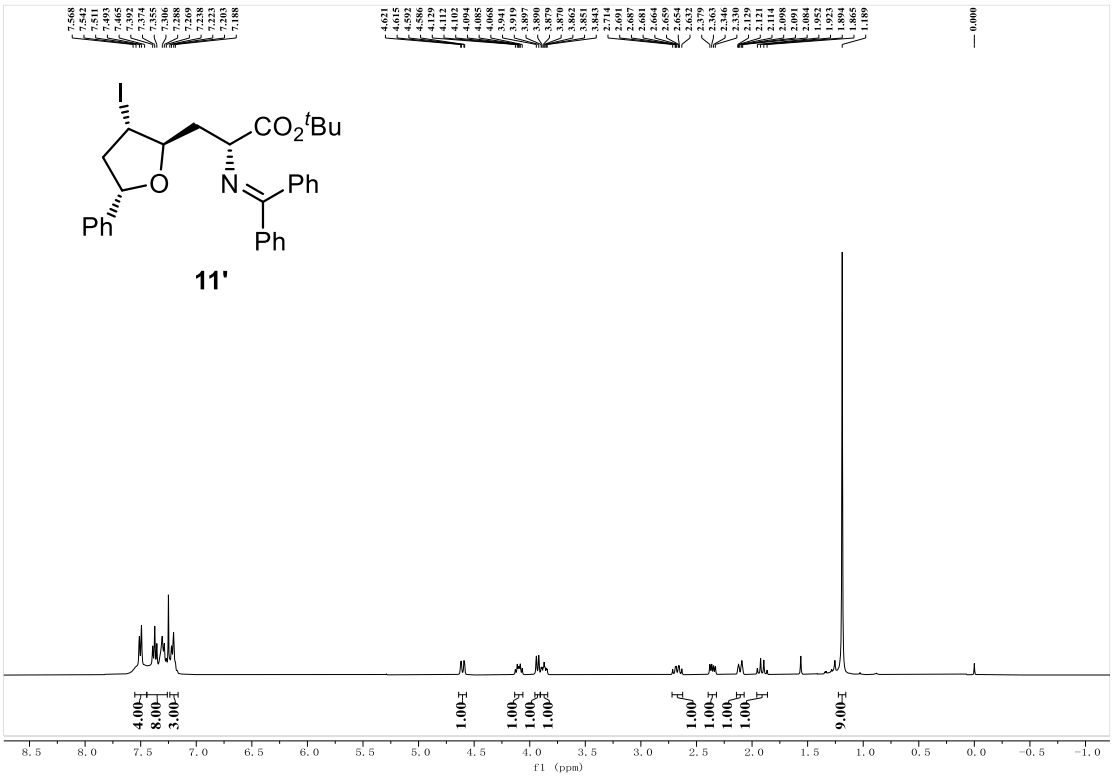
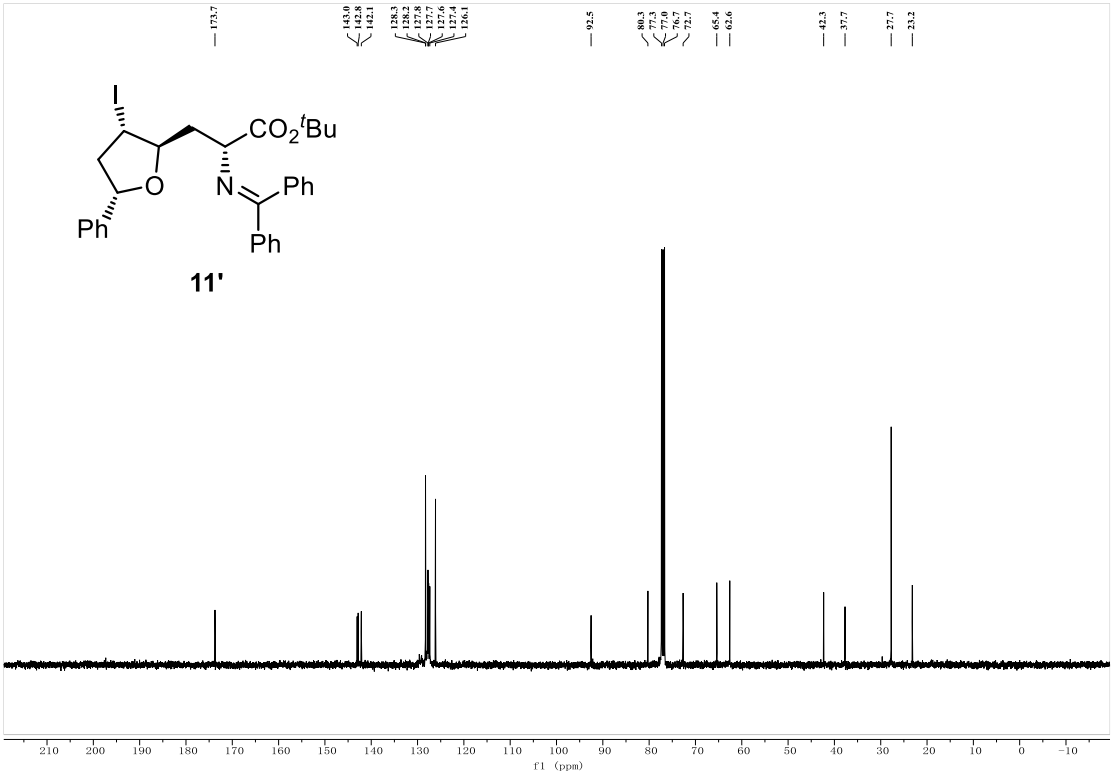


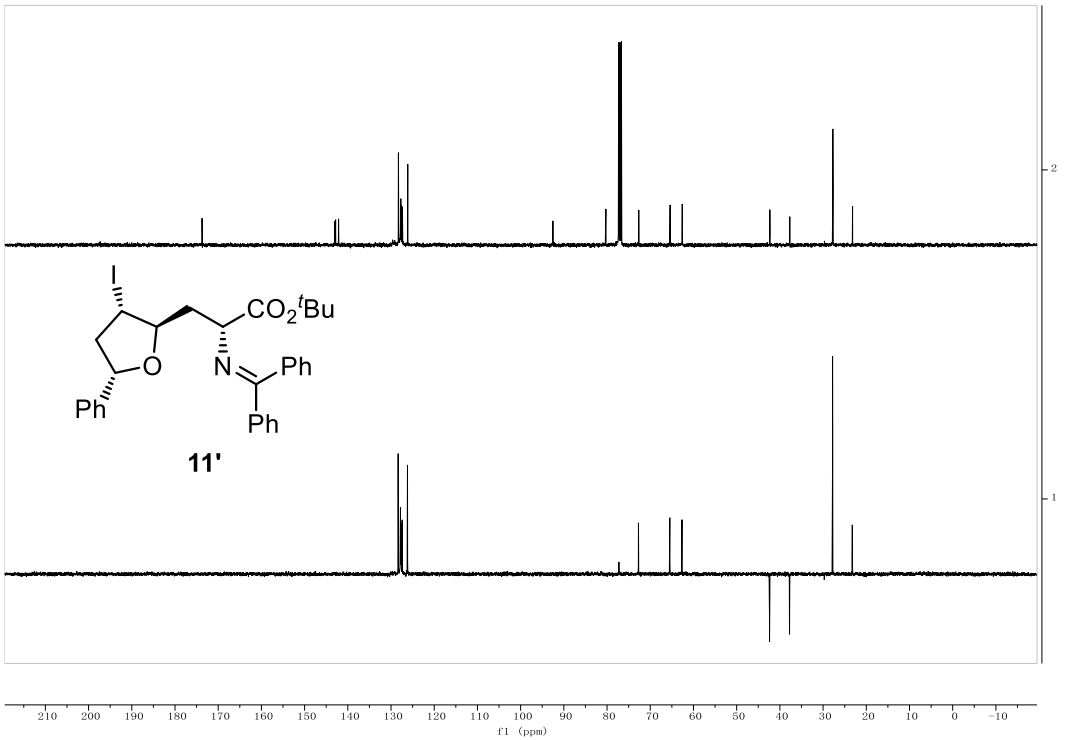
HMQC spectrum of **11**



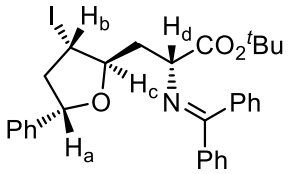
^{1}H NMR (400 MHz, $CDCl_3$) of **11'**



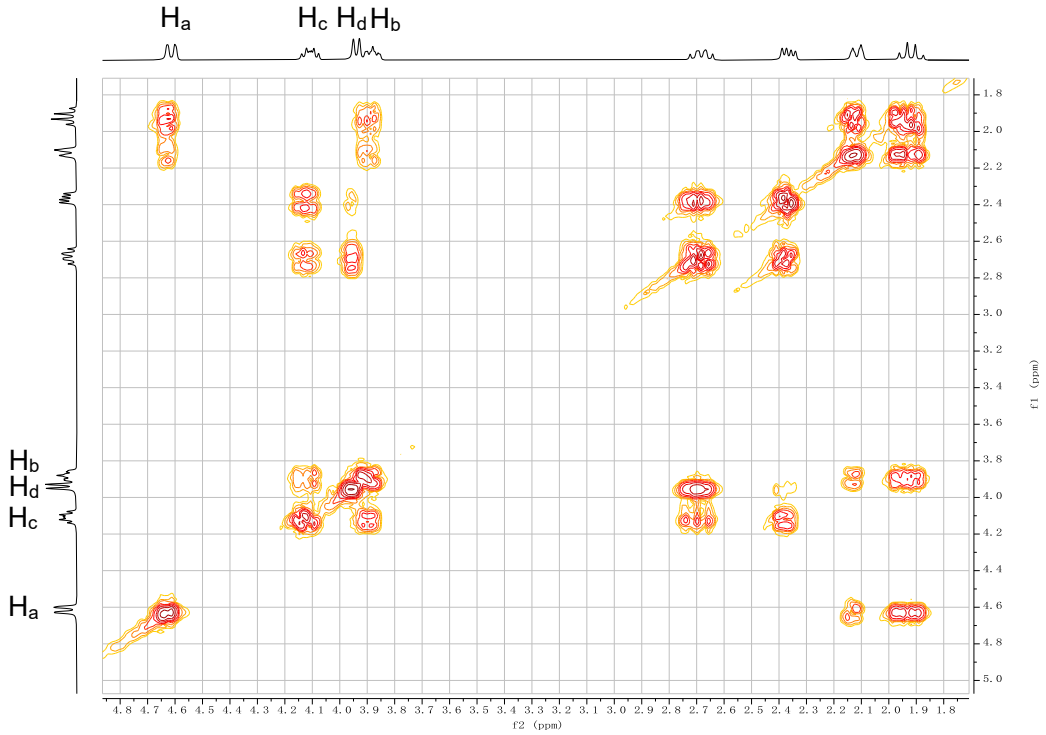
^{13}C NMR (101 MHz, $CDCl_3$) of **11'**



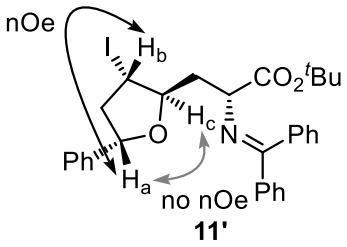
DEPT135 spectrum of **11'**



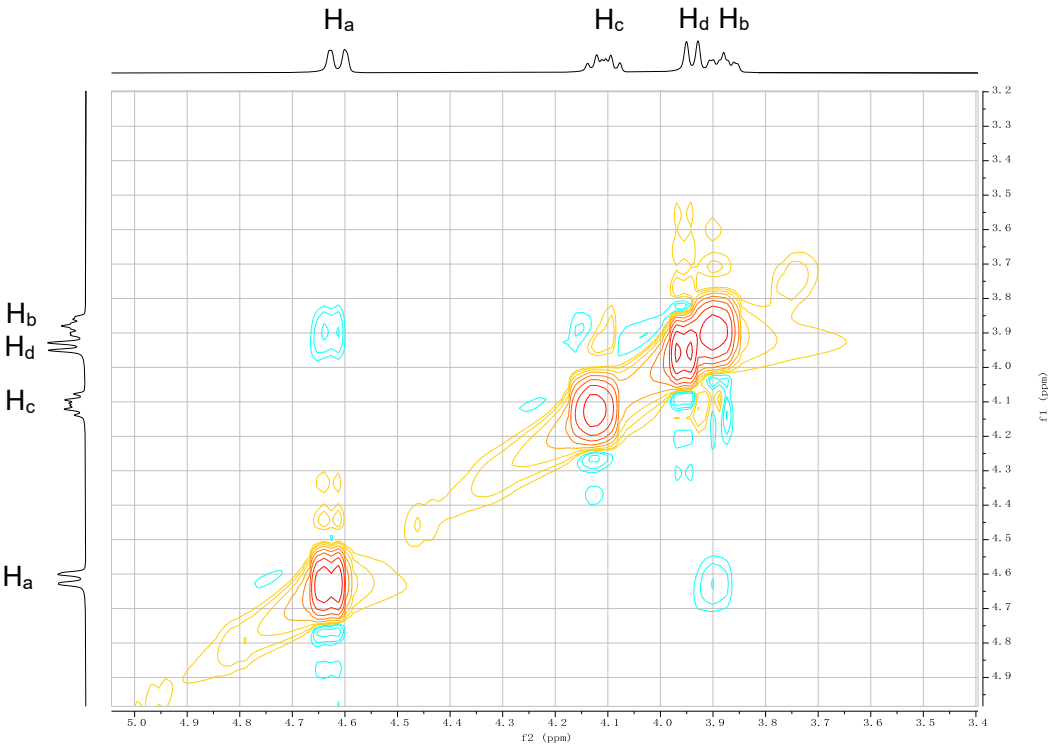
11'



COSY spectrum of **11'**



11'



NOESY spectrum of **11'**