Supporting Information for:

Kinetic Resolution of Racemic Allylic Alcohols via Iridium-Catalyzed Asymmetric Hydrogenation: Scope, Synthetic Applications and Insight into the Origin of Selectivity.

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Contents

1. General methods

All reactions were conducted under nitrogen atmosphere using magnetic stirring.

CH_2Cl_2 was freshly distilled using CaH_2 under nitrogen atmosphere. THF was freshly distilled using sodium-benzophenone under nitrogen.

All reagents were used as supplied commercially without further purification. Chromatographic separations were performed on Kiesel gel 60 H silica gel (particle size: 0.063-0.100 mm) or Brockmann I, activated, basic Al_2O_3 (particle size: ~150 mesh). Thin layer chromatography (TLC) was performed on aluminium plates coated with Kieselgel 60 (0.20 mm, UV254) and visualized under ultraviolet light (ν = 254 nm), or by staining with ethanolic phosphomolybdic acid and heating.

^{1}H NMR spectra were recorded on a Bruker 400 MHz or 500 MHz at 400/500 MHz in $CDCl_3$ and referenced internally to the residual $CDCl_3$ peak (7.26 ppm). ^{13}C NMR spectra were recorded at 100/125 MHz in $CDCl_3$ and referenced to the central peak of $CDCl_3$ (77.0 ppm). Chemical shifts are reported in ppm (δ scale).

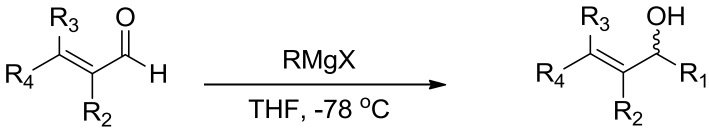
Enantiomeric excesses were determined by either using SFC on chiral stationary phases with a diode array detector at 210 nm, 230 nm and 254 nm or using GC on chiral stationary phases with a MS detector. (Refer to the individual compounds for specific chromatographic details.) Racemic compounds were used for comparison.

HRMS data were obtained using a Bruker MicroTOF-Q II instrument operation at ambient temperature.

Optical rotations were recorded on an Autopol IV polarimeter from Rudolp Research Analytical, equipped with a sodium lamp (589 nm) and a 10 cm cell.

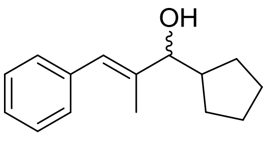
2. General procedure for the synthesis of racemic allylic alcohols

General Procedure A: The corresponding Grignard reagent (1.5 eq.) was slowly added to a solution of α-methyl-cinnamaldehyde (1.0 eq.) in dry THF at -78 ℃. The reaction was stirred and monitored by TLC. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution, extracted with Et_2O. The combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude product, which was then purified by column chromatography on silica gel (Pentane/Et_2O 80/20) to give the corresponding product in good to excellent yield.



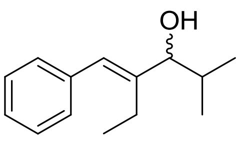
(±)**1a-1j, 1af-1ak**

Substrate	R_1	R_2	R_3	R_4	Ref.
(±)-**1a**	Me	Me	H	Ph	(1)
(±)-**1b**	Et	Me	H	Ph	(2)
(±)-**1c**	*n*-Bu	Me	H	Ph	(3)
(±)-**1d**	*i*-Pr	Me	H	Ph	(3)
(±)-**1e**	*t*-Bu	Me	H	Ph	(4)
(±)-**1f**	Ph	Me	H	Ph	(3)
(±)-**1g**	Cp	Me	H	Ph	New
(±)-**1h**	Cy	Me	H	Ph	(3)
(±)-**1i**	Bn	Me	H	Ph	(2)
(±)-**1k**	CH_2TMS	Me	H	Ph	(5)
(±)-**1af**	*i*-Pr	Et	H	Ph	New
(±)-**1ag**	Et	H	Me	Ph	(19)
(±)-**1ah**	Cy	H	Me	Ph	New
(±)-**1ai**	*i*-Pr	H	Me	Me	(20)
(±)-**1aj**	*t*-Bu	H	Me	Me	(20)
(±)-**1ak**	Cy	H	Me	Cy	New



(±)-**1g**

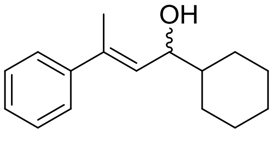
(*E*)-1-cyclopentyl-2-methyl-3-phenylprop-2-en-1-one. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.18 (m, 1H), 6.45 (s, 5H), 3.90 (d, *J* = 8.8 Hz, 1H), 2.16 (dd, *J* = 16.2, 8.3 Hz, 1H), 1.93 – 1.82 (m, 4H), 1.74 – 1.42 (m, 7H), 1.30 – 1.17 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.23, 137.74, 129.14, 128.24, 126.95, 126.57, 83.54, 43.79, 29.60 (d, *J* = 30.4 Hz), 25.76 (d, *J* = 11.0 Hz), 13.11. HRMS-ESI; *m/z* [M+Na$^+$] = 239.1401, calcd. For $C_{15}H_{20}NaO$: 239.1406.



(±)-**1af**

(*E*)-4-benzylidene-2-methylhexan-3-ol. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 4H), 7.22 (ddd, *J* = 6.4, 3.1, 1.5 Hz, 1H), 6.48 (s, 1H), 3.91 (d, *J* = 6.4 Hz, 1H), 2.44 – 2.14 (m, 2H), 1.93 (dq, *J* = 13.4, 6.7 Hz, 1H), 1.57 (s, 1H), 1.12 (t, *J* = 7.6 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.02, 137.88, 128.77, 128.35, 126.55, 126.26, 81.99, 31.95, 21.73, 20.11, 17.74, 14.12. HRMS-ESI; *m/z* [$M+Na^+$] = 227.3025, calcd. For $C_{14}H_{20}NaO$: 227.3027.

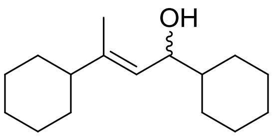


(±)-**1ah**

(*E*)-1-cyclohexyl-3-phenylbut-2-en-1-ol

Colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 5.78 (dd, J = 9.0, 1.3 Hz, 1H), 4.27 (dd, J = 8.9, 7.1 Hz, 1H), 2.10 (s, 3H), 2.03 – 1.95 (m, 1H), 1.83 – 1.65 (m, 3H), 1.56 – 1.44 (m, 2H), 1.34 – 1.13 (m, 3H), 1.12 – 0.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.30, 137.77, 129.76, 128.38, 127.35, 125.98, 73.39, 44.66, 29.06, 28.78, 26.70, 26.30, 26.17, 16.68. HRMS-ESI; *m/z* [$M+Na^+$] = 253.1563, calcd. For $C_{16}H_{22}NaO$: 253.1567.



(±)-**1ak**

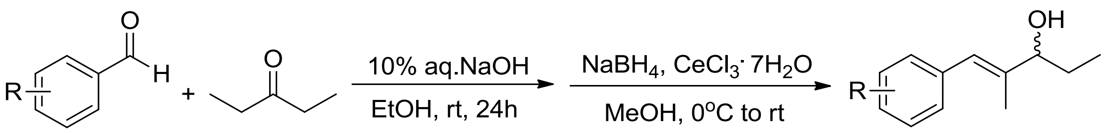
(*E*)-1,3-dicyclohexylbut-2-en-1-ol

Colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 5.15 (d, J = 9.0 Hz, 1H), 4.07 (dd, J = 8.8, 7.4 Hz, 1H), 1.97 – 1.88 (m, 1H), 1.88 – 1.64 (m, 9H), 1.63 (s, 3H), 1.40 – 1.07 (m, 11H), 1.03 – 0.82 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.40, 124.69, 72.91, 47.55, 44.55, 32.07, 31.99, 29.16, 28.71, 26.82, 26.75, 26.48, 26.34, 26.20, 15.31. HRMS-ESI; *m/z* [$M+Na^+$] = 259.2032, calcd. For $C_{16}H_{28}NaO$: 259.2036.

General Procedure B: The suitable aromatic aldehyde (40 mmol) and aliphatic ketone (160 mmol) were dissolved in EtOH (20 mL) under magnetic stirring and aq. NaOH (5 mL, 10%) was added dropwise to the solution. The mixture was stirred at r.t. for 24 h, and then it was poured in ice water (100 mL), neutralized with aq. HCl (1 M) and extracted with EtOAc (3 × 100 mL). The combined organic phase was washed with aq. $NaHCO_3$ (100 mL) and brine (100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography (Pentane/Et_2O, 90/10), affording the pure unsaturated ketone (59-90% yield).

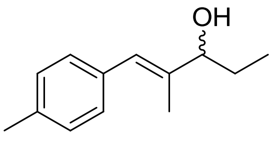
To a solution of enone (10 mmol) in MeOH, $CeCl_3 \cdot 7H_2O$ (10 mmol, 1 equiv.) was added and cooled in an ice bath. When the $CeCl_3 \cdot 7H_2O$ was completely dissolved, $NaBH_4$ (11 mmol, 1.1 equiv.) was added to the reaction mixture in small portions over 10 minutes. The reaction was allowed to warm up to room temperature. Upon completion (approximately 1 h), the solvent was removed under vacuum. Water was added to the crude reaction mixture and stirred for 20 minutes then extracted with Et_2O. The organic phase was washed with brine and dried over Na_2SO_4 and concentrated under vacuum to give the resulting crude which was purified by column chromatography (Pentane/Et_2O, 80/20) to give the corresponding product in good to excellent yield.



(±)**1k-1s**

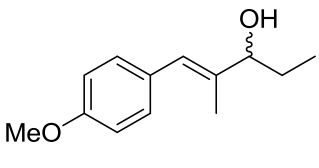
Substrate	R	Ref.
(±)-**1l**	*p*-Me	New

(±)-**1m**	*p*-OMe	New
(±)-**1n**	*p*-F	New
(±)-**1o**	*p*-Cl	New
(±)-**1p**	*p*-Br	New
(±)-**1q**	*m*-Me	New
(±)-**1r**	*p*-NO_2	New
(±)-**1s**	3-thiophene	New
(±)-**1t**	2-thiophene	New



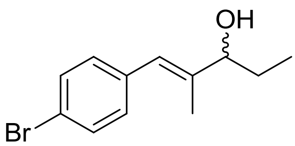
(±)-**1l**

(*E*)-2-methyl-1-(p-tolyl)pent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 4H), 6.45 (s, 1H), 4.09 (t, *J* = 6.2 Hz, 1H), 2.35 (s, 3H), 1.86 (d, *J* = 1.4 Hz, 3H), 1.73 – 1.62 (m, 2H), 1.59 (d, *J* = 3.4 Hz, 1H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.41, 136.24, 134.84, 129.03, 128.96, 126.08, 79.83, 28.08, 21.30, 13.21, 10.25. HRMS-ESI; *m*/*z* [M+Na$^+$] = 213.1244, calcd. For $C_{13}H_{18}NaO$: 213.1250.



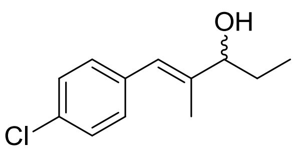
(±)-**1m**

(*E*)-1-(4-methoxyphenyl)-2-methylpent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.91 – 6.84 (m, 2H), 6.42 (s, 1H), 4.08 (td, *J* = 6.6, 2.9 Hz, 1H), 3.81 (s, 3H), 1.85 (d, *J* = 1.3 Hz, 3H), 1.73 – 1.61 (m, 2H), 1.58 (d, *J* = 3.6 Hz, 1H), 0.93 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.27, 138.52, 130.33, 130.29, 125.72, 113.70, 79.91, 55.40, 28.09, 13.16, 10.27.HRMS-ESI; *m*/*z* [M+Na$^+$] = 229.1194, calcd. For $C_{13}H_{18}NaO_2$: 229.1199.



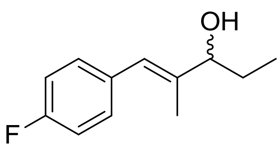
(±)-**1p**

(*E*)-1-(4-bromophenyl)-2-methylpent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.19 – 7.09 (m, 2H), 6.42 (s, 1H), 4.09 (dd, *J* = 6.4, 4.9 Hz, 1H), 1.83 (d, *J* = 1.4 Hz, 3H), 1.73 – 1.56 (m, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.14, 136.66, 131.36, 130.72, 124.87, 120.37, 79.44, 28.12, 13.38, 10.18. HRMS-ESI; *m*/*z* [M+Na$^+$] = 277.0200, calcd. For $C_{12}H_{15}BrNaO$: 277.0198.



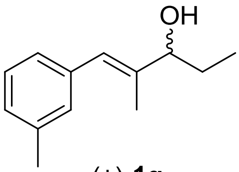
(±)-**1o**

(*E*)-1-(4-chlorophenyl)-2-methylpent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.23 – 7.17 (m, 2H), 6.44 (s, 1H), 4.09 (t, *J* = 6.1 Hz, 1H), 1.82 (t, *J* = 5.4 Hz, 3H), 1.71 – 1.56 (m, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.00, 136.20, 132.24, 130.38, 128.41, 124.86, 79.46, 28.13, 13.35, 10.19. HRMS-ESI; *m*/*z* [M+Na$^+$] = 233.0713, calcd. For $C_{12}H_{15}ClNaO$: 233.0704.



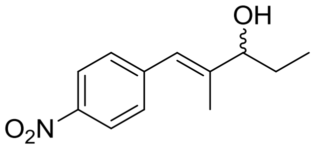
(±)-**1n**

(*E*)-1-(4-fluorophenyl)-2-methylpent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.06 – 6.97 (m, 2H), 6.44 (s, 1H), 4.13 – 4.04 (m, 1H), 1.83 (d, *J* = 1.3 Hz, 3H), 1.72 – 1.57 (m, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.86. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.52 (d, *J* = 245.8 Hz), 140.13, 133.75 (d, *J* = 3.4 Hz), 133.75 (d, *J* = 3.4 Hz), 130.62 (d, *J* = 7.8 Hz), 125.01, 115.12 (d, *J* = 21.3 Hz), 79.55, 28.12, 13.20, 10.21. HRMS-ESI; *m*/*z* [M+Na$^+$] = 217.1010, calcd. For $C_{12}H_{15}FNaO$: 217.0999.



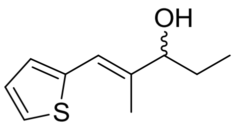
(±)-**1q**

(*E*)-2-methyl-1-(m-tolyl)pent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 1H), 7.12 – 7.01 (m, 3H), 6.46 (s, 1H), 4.10 (td, *J* = 6.6, 2.9 Hz, 1H), 2.36 (s, 3H), 1.86 (d, *J* = 1.4 Hz, 3H), 1.72 – 1.63 (m, 2H), 1.59 (d, *J* = 3.3 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 139.99, 137.78, 137.70, 129.87, 128.15, 127.33, 126.24, 126.16, 79.76, 28.08, 21.60, 13.24, 10.23.HRMS-ESI; *m/z* [M+Na$^+$] = 213.1240, calcd. For $C_{13}H_{18}NaO$: 213.1250.



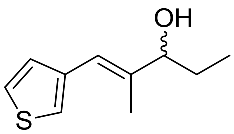
(±)-**1r**

(*E*)-2-methyl-1-(4-nitrophenyl)pent-1-en-3-ol.
Pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.14 (m, 2H), 7.42 (dd, *J* = 8.9, 2.0 Hz, 2H), 6.56 (s, 1H), 4.14 (dd, *J* = 9.7, 6.3 Hz, 1H), 1.89 (d, *J* = 1.4 Hz, 3H), 1.78 – 1.60 (m, 3H), 0.97 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 146.22, 144.70, 144.65, 129.70, 123.94, 123.64, 79.01, 28.26, 13.98, 10.11. HRMS-ESI; *m/z* [M+Na$^+$] = 244.0927, calcd. For $C_{12}H_{15}NNaO_3$: 244.0950.



(±)-**1t**

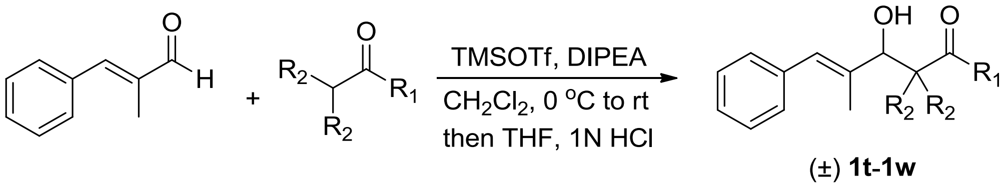
(*E*)-2-methyl-1-(p-tolyl)pent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.25 (m, 1H), 7.05 – 6.99 (m, 2H), 6.64 (s, 1H), 4.10 (t, *J* = 6.5 Hz, 1H), 1.97 (d, *J* = 1.2 Hz, 3H), 1.70 – 1.60 (m, 2H), 1.58 (d, *J* = 7.4 Hz, 1H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.86, 138.53, 127.20, 126.96, 125.06, 119.33, 79.65, 28.19, 14.10, 10.21.HRMS-ESI; *m/z* [M+Na$^+$] = 205.0649, calcd. For $C_{10}H_{14}NaOS$: 205.0658.



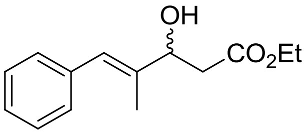
(±)-**1s**

(*E*)-2-methyl-1-(thiophen-3-yl)pent-1-en-3-ol.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.11 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.45 (s, 1H), 4.08 (td, *J* = 6.6, 3.3 Hz, 1H), 1.90 (d, *J* = 1.3 Hz, 3H), 1.70 – 1.61 (m, 2H), 1.58 (br, 1H), 0.96 – 0.89 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.40, 138.78, 128.94, 124.97, 122.76, 120.39, 79.73, 28.10, 13.78, 10.23. HRMS-ESI; *m/z* [M+Na$^+$] = 205.0656, calcd. For $C_{10}H_{14}NaOS$: 205.0658.

General Procedure C: To a dried round-bottomed flask was added CH_2Cl_2 (5 mL), enolate precursor (1.00 mmol, 1 equiv), *i*-Pr_2NEt (261 μL, 1.50 mmol, 1.5 equiv), aldehyde (1.40 mmol, 1.4 equiv), and TMSOTf (217 μL, 1.20 mmol, 1.2 equiv) at 0 ℃. The reaction was allowed to warm to room temperature and stirred for 24 h, then the mixture was filtered directly through a plug of silica gel (2.0 cm x 5.0 cm) and eluted with Et_2O. The eluent was concentrated in vacuo and the yellow residue analyzed by ^{1}H NMR spectroscopy to determine conversion. The unpurified mixture was dissolved in THF (6 mL) and treated with 1.0 N HCl (2 mL). After stirring 1 h, the mixture was diluted with Et_2O (20 mL) and water (20 mL). The layers were separated and the organic layer was washed sequentially with saturated $NaHCO_3$ (20 mL) and brine (20 mL). The organic layer was dried over Na_2SO_4 or $MgSO_4$, then filtered and concentrated in vacuo. Flash chromatography (5-20% EtOAc in pentane) afforded the pure product.



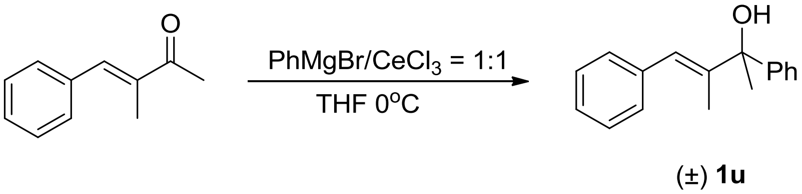
Substrate	R_1	R_2	Ref.
(±)-**1v**	OEt	H	New
(±)-**1w**	Ph	H	(6)
(±)-**1x**	Me	H	(7)
(±)-**1y**	OMe	Me	(8)

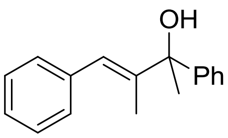


(±)-**1v**

(*E*)-ethyl 3-hydroxy-4-methyl-5-phenylpent-4-enoate. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.19 (m, 3H), 6.60 (s, 1H), 4.61 (td, *J* = 6.0, 3.7 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.02 – 2.94 (m, 1H), 2.69 – 2.61 (m, 2H), 1.89 (d, *J* = 1.3 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.72, 138.26, 137.46, 129.12, 128.26, 126.72, 126.15, 73.71, 61.03, 40.44, 14.36, 13.99. HRMS-ESI; *m/z* [M+Na^+] = 257.1149, calcd. For $C_{14}H_{18}NaO_3$: 257.1148.

General Procedure D: The Grignard reagent (1.5 mmol) was added to a suspension of cerium chloride anhydrous (1.5 mmol) in THF. The mixture was stirred at room temperature for 1 h and cooled to 0 ℃. The carbonyl compound (1 mmol) was added with vigorous stirring. After 30 min the reaction mixture was worked up by 10% aqueous AcOH (10 mL). The product was extracted into Et_2O, and the combined extracts were washed with brine, $NaHCO_3$ solution and brine and dried with MgSO4. The solvent was evaporated and the residue was purified by column chromatography to give the addition product.

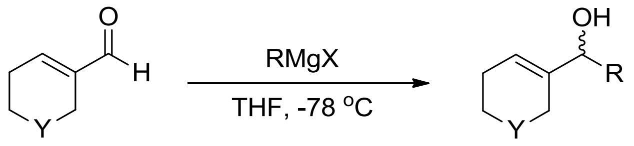




(±)-**1u**

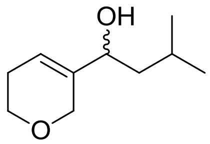
(*E*)-3-methyl-2,4-diphenylbut-3-en-2-ol. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.39 – 7.20 (m, 8H), 6.86 (s, 1H), 1.95 (d, *J* = 1.5 Hz, 1H), 1.81 (s, 3H), 1.72 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.29, 143.05, 138.17, 129.24, 128.39, 128.23, 127.15, 126.54, 125.62, 124.54, 28.78, 15.15. HRMS-ESI; *m/z* [M+Na^+] = 261.1257, calcd. For $C_{17}H_{18}NaO$: 261.1250.

General Procedure E: The corresponding Grignard reagent (1.5 eq.) was slowly added to a solution of cyclohex-1-enecarbaldehyde or 5,6-dihydro-2H-pyran-3-carbaldehyde (1.0 eq.) in dry THF at -78 ℃. The reaction was stirred and monitored by TLC. Upon completion, the reaction was quenched with a saturated aqueous NH_4Cl solution, extracted with Et_2O. The combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude product, which was then purified by column chromatography on silica gel (Pentane/Et_2O 80/20) to give the corresponding product in good to excellent yield.



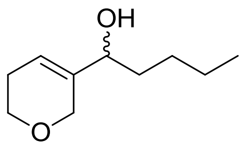
Y= CH_2 or O. (±)**1aa-1ae**

Substrate	Y	R	Ref.
(±)-**1aa**	O	*i*-Bu	New
(±)-**1ab**	O	*n*-Bu	New
(±)-**1ac**	CH_2	Et	(2)
(±)-**1ad**	CH_2	*n*-Bu	(16)
(±)-**1ae**	CH_2	Cy	(9)



(±)-**1aa**

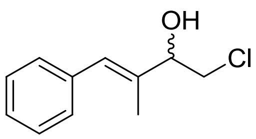
1-(5,6-dihydro-2H-pyran-3-yl)-3-methylbutan-1-ol. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (s, 1H), 4.26 – 4.05 (m, 3H), 3.80 (dt, *J* = 10.8, 5.3 Hz, 1H), 3.69 (ddd, *J* = 11.3, 6.8, 4.9 Hz, 1H), 2.26 – 2.04 (m, 2H), 1.78 – 1.62 (m, 1H), 1.53 – 1.41 (m, 2H), 1.32 (ddd, *J* = 13.6, 7.8, 5.6 Hz, 1H), 0.92 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.21, 119.99, 72.51, 64.82, 64.56, 44.38, 25.13, 24.89, 23.24, 22.38. HRMS-ESI; *m/z* [$M+Na^+$] = 193.1201, calcd. For $C_{10}H_{18}NaO_2$: 193.1204.



(±)-**1ab**

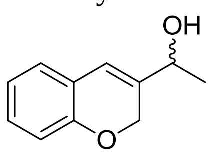
1-(5,6-dihydro-2H-pyran-3-yl)pentan-1-ol. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (s, 1H), 4.25 – 4.06 (m, 2H), 4.00 (dd, *J* = 10.1, 6.7 Hz, 1H), 3.79 (dt, *J* = 10.8, 5.3 Hz, 1H), 3.70 (ddd, *J* = 11.3, 6.6, 5.0 Hz, 1H), 2.26 – 2.05 (m, 2H), 1.57 – 1.45 (m, 3H), 1.41 – 1.19 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.88, 120.07, 74.33, 64.87, 64.57, 34.99, 28.08, 25.11, 22.72, 14.17. HRMS-ESI; *m/z* [$M+Na^+$] = 193.1197, calcd. For $C_{10}H_{18}NaO_2$: 193.1204.

Other Substrates:



(±) **1j**

(*E*)-1-chloro-3-methyl-4-phenylbut-3-en-2-ol (±) **1j** was prepared according to a reported procedure and has been previously characterized. [10]



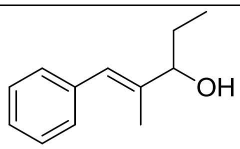
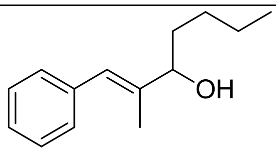
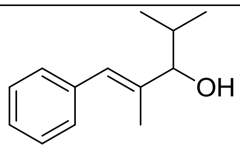
(±) **1z**

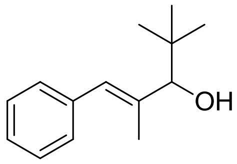
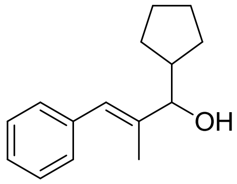
1-(2H-chromen-3-yl)ethanol (±) **1z** was prepared according to a reported procedure and has been previously characterized. [11]

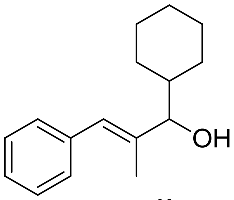
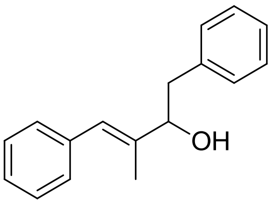
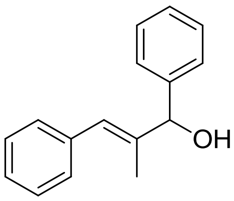
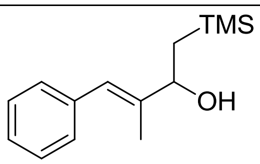
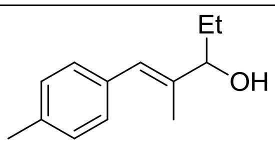
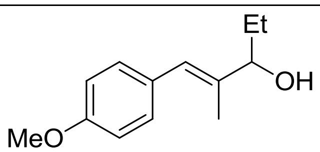
3. General procedure for kinetic resolution via asymmetric hydrogenation

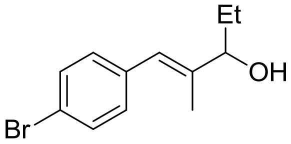
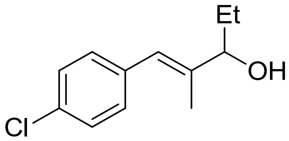
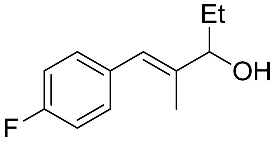
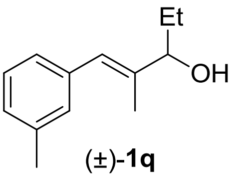
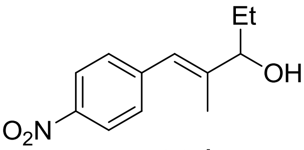
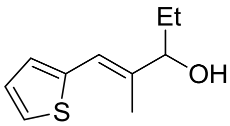
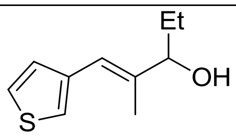
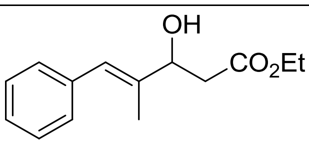
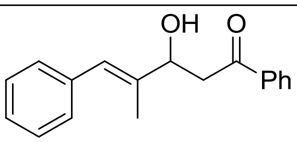
A glass vial was charged with 0.2 mmol substrate, K_2CO_3 and catalyst, 1 mL dry toluene was added. The vial was placed in a hydrogenation apparatus and flushed 3 times with nitrogen. The reactor was then purged 8 times using hydrogen, before filling to the required pressure. The reaction was stirred at room temperature for the required time before the hydrogen pressure was released and the solvent was removed under vacuum. Conversions were determined by ^{1}H NMR spectroscopy of crude product. The crude product was then purified by column chromatography on silica gel (Pentane/Acetone 25/1 to 15/1) to yield the corresponding resolved starting material and hydrogenated product. For substrates **1b**, **1c**, **1d**, **1f**, **1g**, **1h**, **1i**, **1j**, **1l**, **1m**, **1n**, **1o**, **1p**, **1q**, **1r**, **1s**, **1t**, **1v**, **1w**, **1x**, **1y**, **1ac**, **1ad**, **1ae**, **1af**, **1ag**, **1ah**, **1ai**, **1aj**, **1ak**, the resolved starting materials were isolated completely, and the purity of recovered starting material were confirmed by ^{1}H NMR (spectra attached below). The pure resolved starting materials were used for the determinations of optical rotation and ee values. For substrates **1e**, **1u**, **1z**, **1aa**, **1ab**, the separations were not complete. The yields are based on the ^{1}H NMR ratio of the amount of recovered starting material and hydrogenated product, and the mixtures were used for determinations of *ee* values. Few pure fractions were collected to obtain enantioenriched samples for the measurements of optical rotation. For substrate **1k**, the crude sample was passed through a plug of silica gel (Pentane/Diethyl ether 1/1), and then solvent was removed to obtain a mixture of resolved starting material and hydrogenated product, the mixture was used for the determination of ee value, no measurement of optical rotation was performed due to instability of the compound during purification. The *ee* values were determined using GC or SFC on chiral stationary phase.

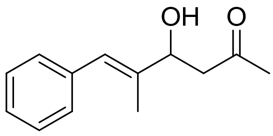
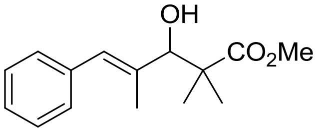
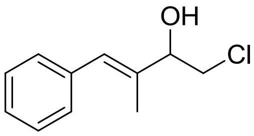
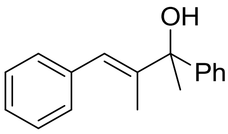
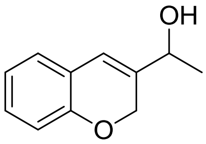
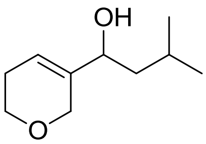
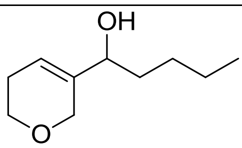
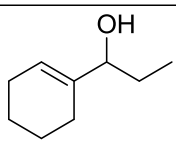
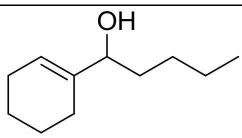
Table of Hydrogenation conditions

Allylic alcohol	Hydrogenation conditions				Conversion
	Cat. (mol %)	K_2CO_3 (mol %)	H_2 (Bar)	Time (min)	
 (±)-**1b**	0.2	10	1	10	55%
 (±)-**1c**	0.5	10	1	20	57%
 (±)-**1d**	1.0	10	3	60	54%

 (±)-**1e**	1.0	10	3	60	52%
 (±)-**1g**	1.0	10	3	60	49%

 (±)-**1h**	1.0	10	3	60	53%
 (±)-**1i**	0.5	10	3	60	52%
 (±)-**1f**	0.2	20	1	15	61%
 (±)-**1k**	1.0	10	3	60	49%
 (±)-**1l**	0.2	10	1	10	55%
 (±)-**1m**	0.2	10	1	10	55%

 (±)-**1p**	0.2	10	1	10	54%
 (±)-**1o**	0.2	10	1	10	53%
 (±)-**1n**	0.2	10	1	10	57%
 (±)-**1q**	0.2	10	1	10	54%
 (±)-**1r**	0.2	10	1	10	54%
 (±)-**1t**	0.2	10	1	10	52%
 (±)-**1s**	0.2	10	1	10	54%
 (±)-**1v**	1.0	10	3	60	56%
 (±)-**1w**	1.0	10	3	60	54%

 (±)-**1x**	1.0	10	3	60	51%
 (±)-**1y**	1.0	10	3	60	51%
 (±)-**1j**	0.2	10	1	15	56%
 (±)-**1u**	0.5	10	3	60	63%
 (±)-**1z**	0.2	10	1	30	56%
 (±)-**1aa**	1.0	10	3	15	53%
 (±)-**1ab**	1.0	10	3	15	53%
 (±)-**1ac**	1.0	10	3	30	55%
 (±)-**1ad**	1.0	10	3	30	58%

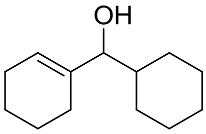
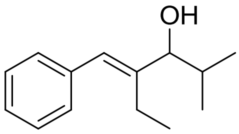
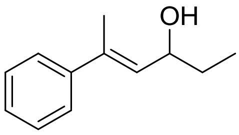
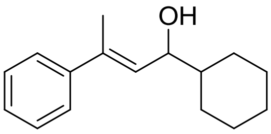
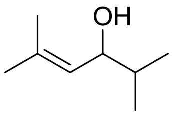
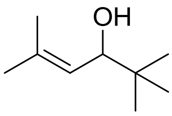
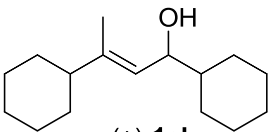
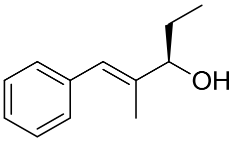
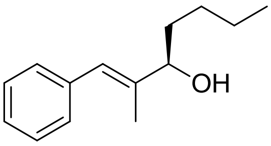
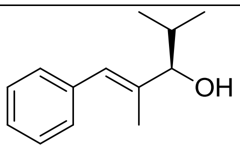
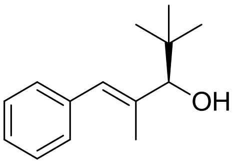
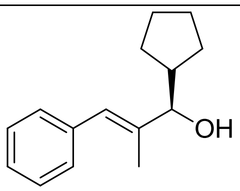
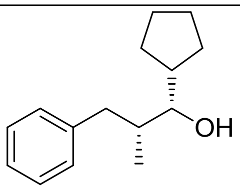
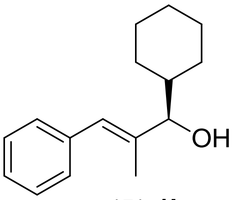
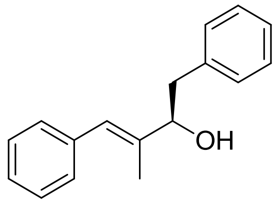
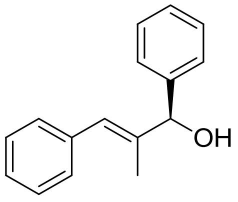
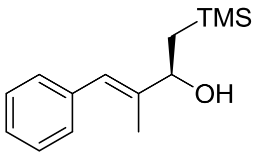
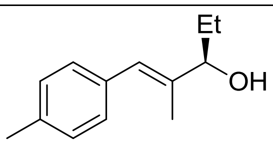
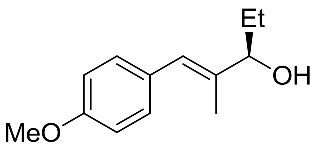
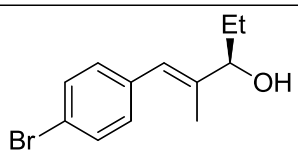
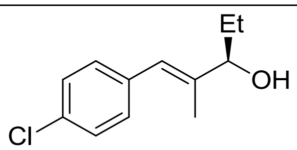
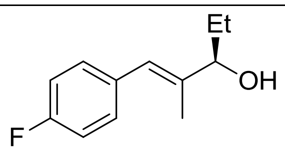
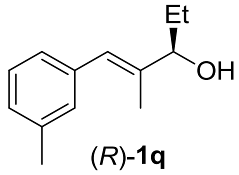
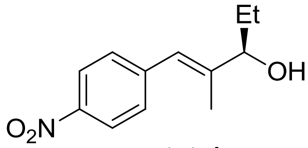
 (±)-**1ae**	1.0	10	3	30	58%
 (±)-**1af**	1.0	10	5	60	61%
 (±)-**1ag**	0.5	10	3	30	57%
 (±)-**1ah**	0.5	10	3	30	64%
 (±)-**1ai**	0.5	10	3	30	53%
 (±)-**1aj**	0.5	10	3	30	50%
 (±)-**1ak**	0.5	10	3	20	58%

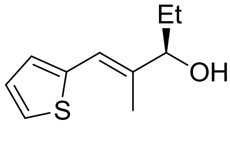
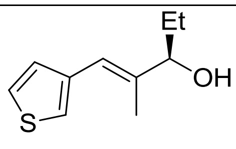
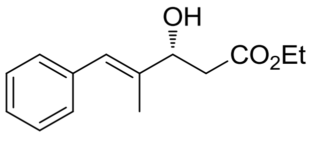
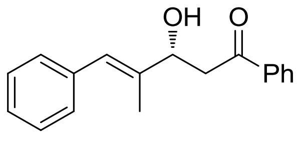
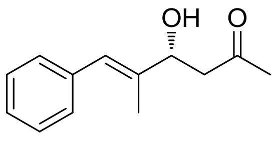
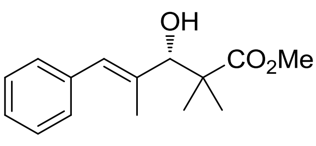
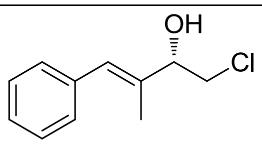
Table of Kinetic Resolution Results

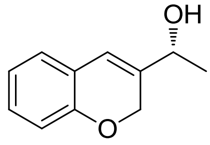
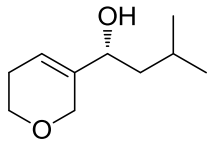
Recovered Allylic Alcohol	Yield	Separation Method	*ee* & Optical Rotation
 (*R*)-**1b**	41%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 7.6 min (major)/8.2 (minor)	99% $[\alpha]_D^{25.0}$ = -39.5 (c = 0.2 in $CHCl_3$) Lit. [12] (90% *ee* for *R*) $[\alpha]_D^{20.0}$ = -40.3 (c = 1.0 in $CHCl_3$)
 (*R*)-**1c**	40%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 7.6 min (major)/8.2 (minor)	99% $[\alpha]_D^{25.0}$ = -46.5 (c = 0.2 in $CHCl_3$) Lit. [13] (94% *ee* for *S*) $[\alpha]_D^{25.0}$ = +18.0 (c = 1.0 in $CHCl_3$)
 (*R*)-**1d**	41%	**SFC**, IC column, 5% MeOH, 2 ml/min, 230nm, t_R = 6.2 min (major)/6.5 (minor)	99% $[\alpha]_D^{25.0}$ = -49.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1e**	47% (mixture)	**SFC**, OJH column, 5% MeOH, 2 ml/min, 254nm, t_R = 6.2 min (minor)/7.2 (major)	99% $[\alpha]_D^{25.0}$ = -105.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1g**	47%	**SFC**, OJH column, 10% MeOH, 2 ml/min, 254nm, t_R = 6.3 min (minor)/6.7 (major)	89% $[\alpha]_D^{25.0}$ = -80.5 (c = 0.2 in $CHCl_3$)
 (1*R*,2*R*)-**2g**	46%	**SFC**, OZH column, 10% MeOH, 2 ml/min, 210nm, t_R = 11.5 min (minor)/12.5 (major)	98% *ee* 99:1 *d.r.* $[\alpha]_D^{22.0}$ = +2.6 (c = 0.3 in $CHCl_3$)
 (*R*)-**1h**	45%	**SFC**, ID column, 5% MeOH, 2 ml/min, 230nm, t_R = 13.7 min (major)/15.2 (minor)	99% $[\alpha]_D^{25.0}$ = -48.5 (c = 0.2 in $CHCl_3$)

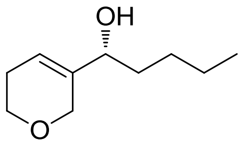
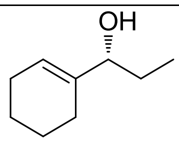
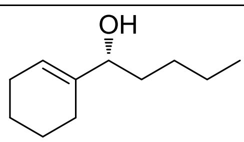
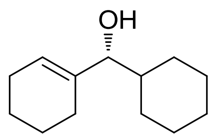
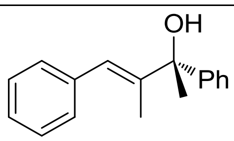
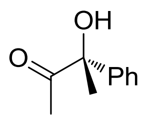
 (*R*)-**1i**	46%	**SFC**, OZH column, 10% MeOH, 2 ml/min, 254nm, t_R = 7.0 min (minor)/7.4 (major)	99% $[\alpha]_D^{25.0}$ = -49.5 (c = 0.2 in $CHCl_3$)

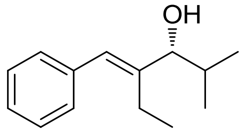
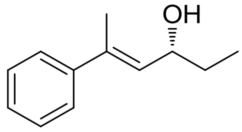
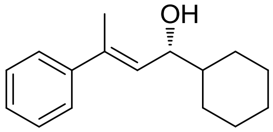
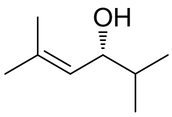
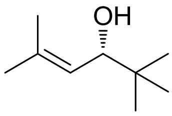
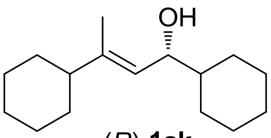
 (*R*)-**1f**	37%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R =16.8 min (major)/20.3 (minor)	99% $[\alpha]_D^{25.0}$ = -5.5 (c = 0.2 in $CHCl_3$) Lit. [12] (73% *ee* for *R*) $[\alpha]_D^{25.0}$ = -15.5 (c = 1.2 in $CHCl_3$)
 (*S*)-**1k**	45% (mixture)	**SFC**, IC column, 5% MeOH, 2 ml/min, 230nm, t_R = 4.8 min (major)/5.1 (minor)	87% — —
 (*R*)-**1l**	40%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 9.2 min (major)/10.0 (minor)	99% $[\alpha]_D^{25.0}$ = -29.0 (c = 0.2 in $CHCl_3$)
 (*R*)-**1m**	39%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 15.3 min (major)/16.1 (minor)	99% $[\alpha]_D^{25.0}$ = -26.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1p**	44%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 11.2 min (minor)/12.1 (major)	99% $[\alpha]_D^{25.0}$ = -27.0 (c = 0.2 in $CHCl_3$)
 (*R*)-**1o**	44%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 7.9 min (major)/7.1 (minor)	99% $[\alpha]_D^{25.0}$ = -34.0 (c = 0.2 in $CHCl_3$)
 (*R*)-**1n**	40%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 5.9min (minor)/6.2 (major)	99% $[\alpha]_D^{25.0}$ = -30.0 (c = 0.2 in $CHCl_3$)

 (*R*)-**1q**	43%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 8.6 min (major)/9.5 (minor)	99% $[\alpha]_D^{25.0}$ = -41.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1r**	40%	**SFC**, OJH column, 5% MeOH, 2 ml/min, 254nm, t_R = 6.2 min (minor)/6.7 (major)	95% $[\alpha]_D^{25.0}$ = -41.5 (c = 0.2 in $CHCl_3$)

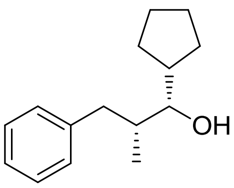
 (*R*)-**1t**	45%	**SFC**, OJH column, 5% MeOH, 2 ml/min, 254nm, t_R = 12.1 min (minor)/14.5 (major)	94% $[\alpha]_D^{25.0}$ = -17.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1s**	44%	**SFC**, OJH column, 5% MeOH, 2 ml/min, 254nm, t_R = 12.5 min (minor)/13.8 (major)	99% $[\alpha]_D^{25.0}$ = -30.0 (c = 0.2 in $CHCl_3$)
 (*R*)-**1v**	40%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 12.6 min (minor)/14.1 (major)	99% $[\alpha]_D^{25.0}$ = +3.0 (c = 0.2 in $CHCl_3$)
 (*R*)-**1w**	42%	**SFC**, OJH column, 15% MeOH, 2 ml/min, 254nm, t_R = 15.0 min (major)/16.5 (minor)	93% $[\alpha]_D^{25.0}$ = +29.0 (c = 0.2 in $CHCl_3$)
 (*R*)-**1x**	45%	**SFC**, OJH column, 10% MeOH, 2 ml/min, 254nm, t_R = 5.4 min (major)/6.0 (minor)	89% $[\alpha]_D^{25.0}$ = +13.0 (c = 0.2 in $CHCl_3$)
 (*S*)-**1y**	47%	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 9.9 min (minor)/10.3 (major)	99% $[\alpha]_D^{25.0}$ = -49.5 (c = 0.2 in $CHCl_3$) Lit. [8] (86% *ee* for *R*) $[\alpha]_D^{25.0}$ = +67.0 (c = 1.0 in $CHCl_3$)
 (*R*)-**1j**	40%	**SFC**, OJH column, 5% MeOH, 2 ml/min, 254nm, t_R = 11.5 min (minor)/12.5 (major)	99% $[\alpha]_D^{25.0}$ = +6.0 (c = 0.2 in $CHCl_3$)

 (*R*)-**1z**	42% (mixture)	**SFC**, OJH column, 10% MeOH, 2 ml/min, 254nm, t_R = 7.4 min (minor)/8.2 (major)	89% $[\alpha]_D^{25.0}$ = +20.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1aa**	45% (mixture)	**SFC**, IA column, 5% MeOH, 2 ml/min, 210nm, t_R = 7.9 min (major)/9.2 (minor)	89% $[\alpha]_D^{25.0}$ = +5.0 (c = 0.1 in $CHCl_3$)

 (*R*)-**1ab**	44% (mixtur e)	**SFC**, IA column, 5% MeOH, 2 ml/min, 210nm, t_R = 6.2 min (minor)/6.7 (major)	90% $[\alpha]_D^{25.0}$ = -1.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1ac**	41%	**GC-MS**: column Chiraldex β-DM, 50˚C to 175°C at 1°C/min. t_R = 55.7 min(minor) /58.0(major)	96% $[\alpha]_D^{25.0}$ = -6.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1ad**	40%	**GC-MS**: column Chiraldex β-DM, 50˚C to 175°C at 1°C/min. t_R = 70.5 min(minor)/74.2(major)	99% $[\alpha]_D^{25.0}$ = -0.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1ae**	39%	**SFC**, OJH column, 5% MeOH, 2 ml/min, 210nm, t_R = 3.4 min (minor)/3.6 (major)	99% $[\alpha]_D^{25.0}$ = -4.0 (c = 0.2 in $CHCl_3$) Lit.[9](98% *ee* for *S*) $[\alpha]_D^{20.0}$ = +2.8 (c = 1.0 in $CHCl_3$)
 (*S*)-**1u**	35% (below)	**SFC**, IC column, 5% MeOH, 2 ml/min, 254nm, t_R = 13.1 min (major)/14.2 (minor)	98% $[\alpha]_D^{25.0}$ = -14.0 (c = 0.1 in $CHCl_3$)
 (*R*)-**pu**	91%	--	98% $[\alpha]_D^{25.0}$ = +103.0 (c = 0.5 in EtOH) Lit. [14] (99% *ee* for *R*) $[\alpha]_D^{20.0}$ = +152.1 (c = 2.0 in EtOH)

 (*S*)-**1af**	35%	**SFC**, IC column, 5% MeOH, 2 ml/min, 230nm, t_R = 9.1 min (major)/10.1 (minor)	96% $[\alpha]_D^{25.0}$ = -6.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1ag**	40%	**SFC**, IC column, 5% MeOH, 2 ml/min, 230nm, t_R = 16.7 min (minor)/21.2 (major)	92% $[\alpha]_D^{25.0}$ = +5.6 (c = 0.3 in $CHCl_3$) Lit. [21] (91% *ee* for *R*) $[\alpha]_D^{22.0}$ = +2.2 (c = 0.9 in $CHCl_3$)
 (*R*)-**1ah**	30%	**SFC**, IC column, 10% MeOH, 2 ml/min, 230nm, t_R = 15.5min (minor)/19.7 (major)	99% $[\alpha]_D^{25.0}$ = +58.5 (c = 0.2 in $CHCl_3$)
 (*R*)-**1ai**	42%	**GC-MS**: column Chiraldex β-DM, 50˚C to 140°C at 1°C/min. t_R = 17.2 min(minor) /22.4(major)	91% $[\alpha]_D^{25.0}$ = +7.5 (c = 0.2 in $CHCl_3$) Lit. [22] (--% *ee* for *R*) $[\alpha]_D^{22.0}$ = +8.8 (c = 1.0 in $CHCl_3$)
 (*R*)-**1aj**	43%	**GC-MS**: column Chiraldex β-DM, 50˚C to 140°C at 1°C/min. t_R = 20.5 min(minor) /22.2(major)	96% $[\alpha]_D^{25.0}$ = +8.5 (c = 0.3 in $CHCl_3$)
 (*R*)-**1ak**	36%	**SFC**, ODH column, 5% MeOH, 2 ml/min, 210nm, t_R = 9.5min (major)/10.5 (minor)	96% $[\alpha]_D^{25.0}$ = +19.0 (c = 0.3 in $CHCl_3$)

Hydrogenated product 2g



(1*R*,2*R*)-**2g**

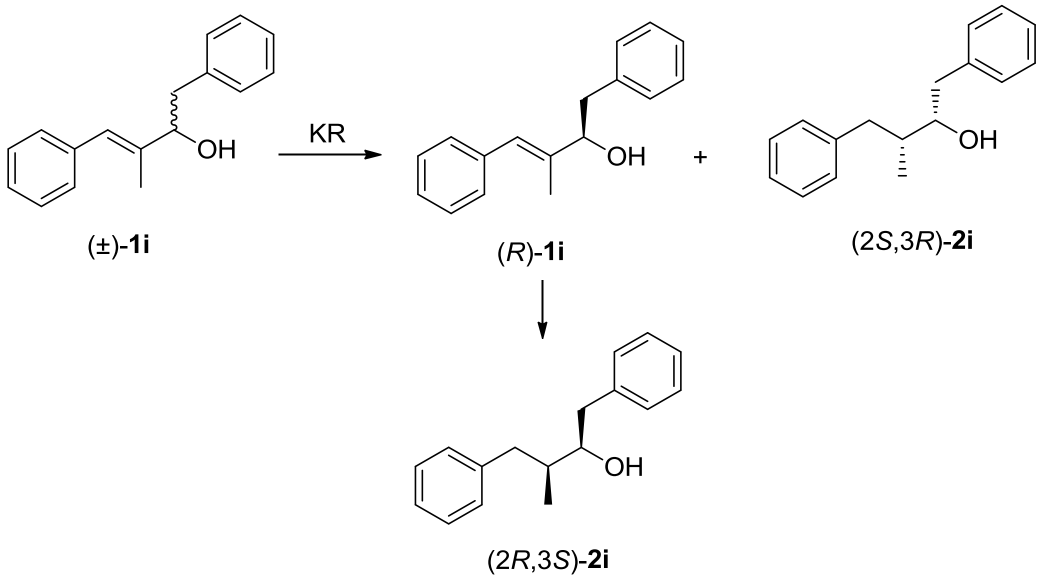
(1R, 2R) -1-cyclopentyl-2-methyl-3-phenylpropan-1-ol.

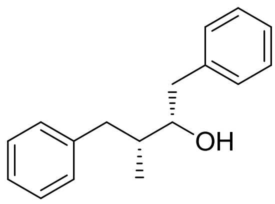
Colorless oil. 98% *ee*, 99:1 *d.r.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 2H), 7.22 – 7.15 (m, 3H), 3.42 – 3.28 (m, 1H), 2.99 (dd, *J* = 13.3, 3.6 Hz, 1H), 2.32 (dd, *J* = 13.3, 10.5 Hz, 1H), 2.20 – 2.06 (m, 1H), 1.92 – 1.70 (m, 3H), 1.70 – 1.49 (m, 4H), 1.48 – 1.18 (m, 2H), 0.87 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.71, 129.39, 128.32, 125.81, 80.24, 43.46, 39.49, 37.11, 29.45, 28.68, 25.83, 25.73, 16.82. HRMS-ESI; m/z [M+Na$^+$] = 241.1565, calcd. For $C_{17}H_{20}NaO$: 241.1568. $[\alpha]_D^{25.0}$ = +2.6 (c = 0.3 in $CHCl_3$)

4.Double stereodifferentiation and synthesis of ketone 3

Double stereodifferentiation: A vial was charged with the resolved allylic alcohol (*R*)-**1h** (22 mg) and Ir-complex (0.4 mg). Dry toluene (1 ml) was added and the vial was placed in a hydrogenation apparatus. The reactor was purged 3 times with N_2, and then filled with H_2 (3 bar). The reaction was stirred at room temperature for 10 min before the H_2 pressure was released and the solvent was removed *in vacuo*. The crude product was purified through silica column chromatography to give the hydrogenated product 22 mg (quantitative yield).



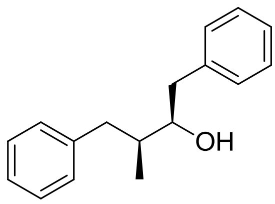


(2*S*,3*R*)-**2i**

(2S,3R)-3-methyl-1,4-diphenylbutan-2-ol.

Colorless oil. 96% *ee*, 96:4 *d.r.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 10H), 3.70 (tt, *J* = 5.6, 3.4 Hz, 1H), 3.06 – 2.89 (m, 2H), 2.65 (dd, *J* = 13.6, 9.8 Hz, 1H), 2.46 (dd, *J* = 13.4, 9.4 Hz, 1H), 2.05 – 1.90 (m, 1H), 1.57 – 1.51 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.10, 139.06, 129.55, 129.40, 128.82, 128.39, 126.66, 125.97, 76.30, 40.61, 40.51, 38.78, 15.54. HRMS-ESI; m/z [M+Na$^+$] = 263.1409, calcd. For $C_{17}H_{20}NaO$: 263.1406. $[\alpha]_D^{25.0}$ = -15.0 (c = 0.2 in $CHCl_3$)



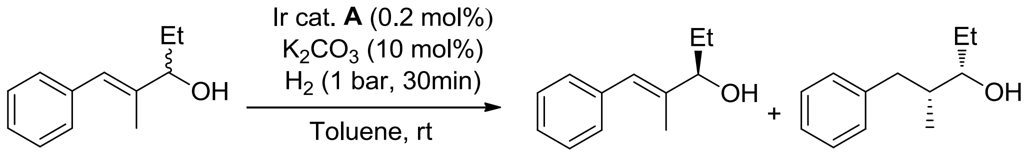
(2*R*,3*S*)-**2i**

(2R,3S)-3-methyl-1,4-diphenylbutan-2-ol.

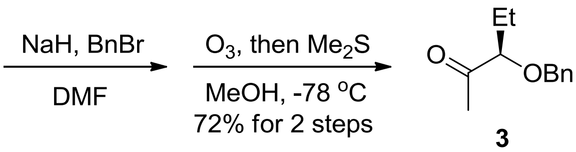
Colorless oil. 99% *ee*, >99:1 *d.r.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 10H), 3.70 (tt, *J* = 5.6, 3.4 Hz, 1H), 3.06 – 2.89 (m, 2H), 2.65 (dd, *J* = 13.6, 9.8 Hz, 1H), 2.46 (dd, *J* = 13.4, 9.4 Hz, 1H), 2.05 – 1.90 (m, 1H), 1.57 – 1.51 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 141.10, 139.06, 129.55, 129.40, 128.82, 128.39, 126.66, 125.97, 76.30, 40.61, 40.51, 38.78, 15.54.HRMS-ESI; m/z [M+Na$^+$] = 263.1409, calcd. For $C_{17}H_{20}NaO$: 263.1406. $[\alpha]_D^{25.0}$ =+16.0 (c = 0.2 in $CHCl_3$)

Ketone **3** was synthesized according to the following scheme**:**



(±)-**1b** (1.0 g) (*R*)-**1b** **2b**

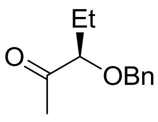


3

Step 1, gram scale kinetic resolution: A glass vial was charged with 1.0g (5.67mmol) racemic substrate (±**1b**), 78mg K_2CO_3 (0.56 mmol) and 20 mg (0.011mol) catalyst, 8 ml dry toluene was added. The vial was placed in a hydrogenation apparatus and flushed 3 times with nitrogen. The reactor was then purged 8 times using hydrogen, before filling to the 1 bar. The reaction was stirred at room temperature for the 60 min before the hydrogen pressure was released and the solvent was removed under vacuum. The crude product was passed through a short silica gel layer, eluted with a mixture of Et_2O: Pentane (1:1) and remove the solvent to give the mixture of resolved alcohol and hydrogenated product (992 mg, 99% yield, 46% NMR yield for *R*-**1b**).

Step 2, benzylation: the obtained mixture was used without further purification. To a solution of mixture (200mg) in 5ml THF/DMF(4:1) was added 60mg(1.5 eq) NaH slowly at 0 °C. The mixture was stirred 30 min and then 0.71 ml(3.0 eq) BnBr was added. The reaction was further stirred at room temperature overnight, and then was quenched with water and extracted with Et_20. After evaporation of the solvent, the crude extract was purified by column chromatography to afford a mixture of protected alcohols as a colorless oil (277 mg, 91%).

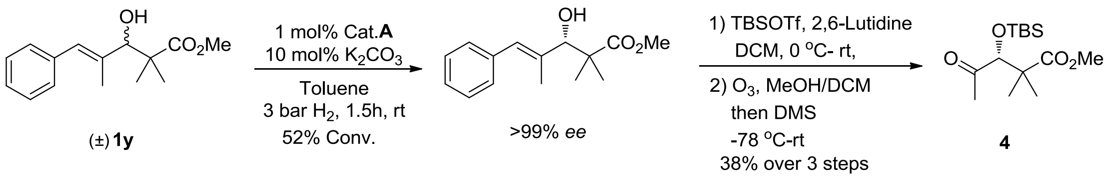
Step 3, ozonolysis: To a stirred solution of the mixture of protected alcohols (277mg) in MeOH at -78°C was bubbled through freshly generated ozone. After the color of the reaction mixture changed to light blue (ca.10min), it was quenched with dimethyl sulfide (0.3 ml, 4eq) and allowed to worm to room temperature. After 1 h, the solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography to afford pure methyl ketone **3** (71 mg 79%).



3

(R)-3-(benzyloxy)pentan-2-one.
Colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 3.71 (dd, *J* = 7.0, 5.7 Hz, 1H), 2.18 (s, 3H), 1.79 – 1.66 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.61, 137.73, 128.62, 128.05, 127.96, 86.48, 72.47, 25.61, 25.29, 9.71. $[\alpha]_D^{25.0}$ = +58.0 (c = 0.5 in $CHCl_3$) Lit.[15](*S*) $[\alpha]_D^{25.0}$ = -113 (c = 2.6 in $CHCl_3$)

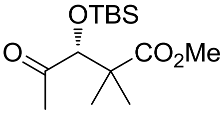
5. Asymmetric formal synthesis of inthomycin A and B.



(*R*)-methyl-3-((tert-butyldimethylsilyl)oxy)-2,2-dimethyl-4-oxopentanoate (4): kinetic resolution: A glass vial was charged with 248 mg (1.0 mmol) racemic substrate (**±1y**), 13.8mg K_2CO_3 (0.1 mmol) and 16.3 mg (0.01mmol) catalyst, 3 ml dry toluene was added. The vial was placed in a hydrogenation apparatus and flushed 3 times with nitrogen. The reactor was then purged 8 times using hydrogen, before filling to the 3 bar. The reaction was stirred at room temperature for the 1.5h before the hydrogen pressure was released and the solvent was removed under vacuum. The crude product was passed through a short silica gel layer, eluted with a mixture of Et_2O: Pentane (1:1) and remove the solvent to give the mixture of resolved alcohol and hydrogenated product. (4 separated reactions were set parallel in the same reactor)

To a solution of the resolved mixture (4.0 mmol) in CH_2Cl_2 were added 2,6-lutidine (1.8 ml, 16 mmol) and TBSOTf (2.3 ml, 10 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued for 0.5 h. The raction was quenched with saturated NH_4Cl at 0°C and extracted with Et_2O. The extract was washed with brine, dried over Na_2SO_4, and concentrated to give crude product. The crude product was passed through a short silica gel layer, eluted with a mixture of Et_2O: Pentane (5:95) and remove the solvent to give the mixture of the protected products.

To a stirred solution of the mixture of protected alcohols in a mixture of MeOH:CH_2Cl_2(1:4) 20 ml at -78°C was bubbled through freshly generated ozone. After the color of the reaction mixture changed to light blue (ca.25min), it was quenched with dimethyl sulfide (1.2 ml, 4eq) and allowed to worm to room temperature. After 1 h, the solvent was removed under reduced pressure, and the obtained residue was purified by flash column chromatography to afford pure methyl ketone **4** (438 mg 38%).



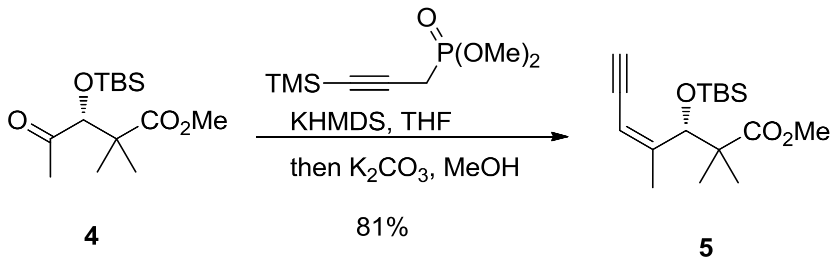
4

(*R*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2,2-dimethyl-4-oxopentanoate

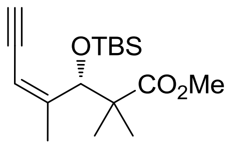
Colorless oil. R_f=0.3 (Et_2O: Pentane= 1:4)

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 (s, 1H), 3.68 (s, 3H), 2.15 (s, 3H), 1.21 (s, 3H), 1.13 (s, 3H), 0.94 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 211.45, 175.81, 82.80, 52.11, 47.66, 27.58, 25.84, 22.06, 20.81, 18.13, -4.55, -5.05. HRMS-ESI; m/z [M+Na$^+$] = 311.1660, calcd. For $C_{14}H_{28}NaO_4Si$: 311.1649. $[\alpha]_D^{26.6}$ =+34.6 (c = 0.5 in $CHCl_3$)



(*S*,*Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2,2,4-trimethylhept-4-en-6-ynoate (5): To a solution of phosphonate (881mg, 4.0 mmol) in THF (10 mL) was added KHMDS (4.2 mL of 1M solution in THF, 4.2 mmol) at 0 ℃ and the mixture was stirred at 0 ℃ for 30 min. Then the mixture was then cooled to –78 ℃ and a solution of methylketone **4** (577 mg, 2.0 mmol) in THF (3ml) was added to the mixture at-78 ℃. The mixture was stirred at -78 ℃ for 1 h and slowly warm to 0 °C over 2h, and then quenched by the addition of H_2O. The mixture was extracted with Et_2O, dried over Na_2SO_4 and evaporated to give a mixture of TMS protected and deprotected enyl. The residue was dissolved in MeOH (10ml) and was added K_2CO_3 (828 mg, 6 mmol) and stirred at room temperature overnight. The reaction mixture was filtered and concentrated to give the crude product. Flash chromatography (10: 90 Et_2O/Pentane) to afford the enyne **5** (503 mg, 81%) with exclusive stereoselectivity.



5

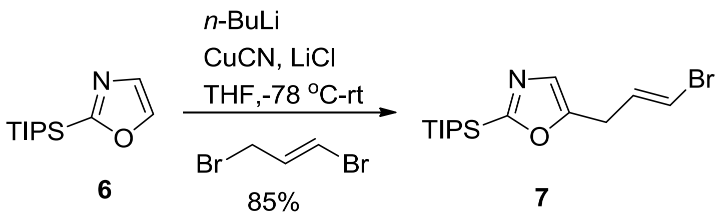
(*S,Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2,2,4-trimethylhept-4-en-6-ynoate

Colorless oil. R_f=0.4 (Et_2O: Pentane= 1:10)

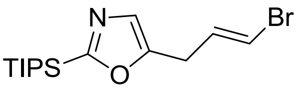
^1H NMR (400 MHz, CDCl3) δ 5.45 – 5.41 (m, 1H), 5.15 (s, 1H), 3.66 (s, 3H), 3.13 (s, 1H), 1.80 (d, J = 1.1 Hz, 3H), 1.21 (s, 3H), 1.18 (s, 3H), 0.87 (s, 9H), 0.05 (s, 3H), -0.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.01, 152.99, 108.65, 82.00, 80.78, 76.51, 51.88, 49.28, 25.83, 22.70, 20.84, 18.79, 18.16, -4.81, -5.47.

HRMS-ESI; m/z [M+Na$^+$] = 333.1854, calcd. For $C_{17}H_{30}NaO_3Si$: 333.1856. $[\alpha]_D^{27.0}$ =-127.2 (c = 0.5 in $CHCl_3$)

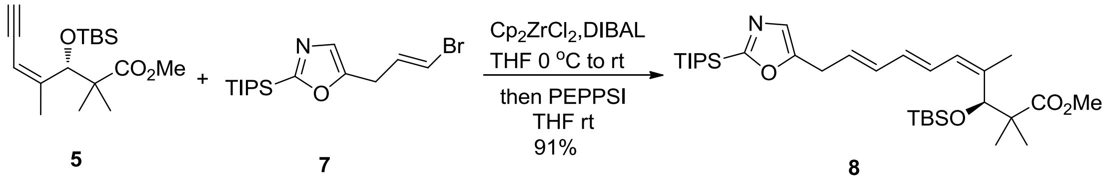


(*E*)-5-(3-bromoallyl)-2-(triisopropylsilyl)oxazole (7): To a solution a TIPS oxzole **6** (902mg, 4mmol) in THF (20 ml) was added *n*-BuLi (2.2 mL, 1.9 M in hexanes, 4.2 mmol) dropwise at –78 ℃. The reaction mixture was stirred for 30 min at –78 ℃ and a solution of LiCl (144 mg, 3.4 mmol) and CuCN (154 mg, 1.7 mmol) in THF (6 mL) was added dropwise. After a further 2 h, *trans* 1,3-dibromoprop-1-ene (1.2 g, 6 mmol) was added dropwise and the reaction stirred at room temperature for 2 h. The reaction was quenched with saturated NH_4Cl and extracted with Et_2O. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated to give the crude product. Flash chromatography (5:95 to 10:90 Et_2O/Pentane) to afford the vinyl bromide **7** (1.170g , 85%).



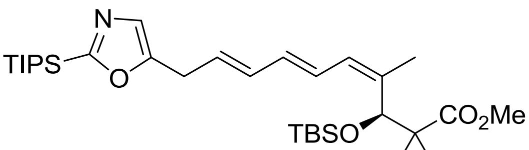
7

(*E*)-5-(3-bromoallyl)-2-(triisopropylsilyl)oxazole
Colorless oil. R_f=0.3 (Et_2O: Pentane= 1:8)
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.37 – 6.12 (m, 2H), 3.45 (d, *J* = 6.7 Hz, 2H), 1.37 (dt, *J* = 14.4, 7.3 Hz, 3H), 1.12 (d, *J* = 7.4 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.42, 150.73, 132.15, 123.39, 107.82, 29.38, 18.50, 11.11.HRMS-ESI; m/z [M+H$^+$] =344.1038, calcd. For $C_{15}H_{27}BrNOSi$: 344.1040.



5 **7** **8**

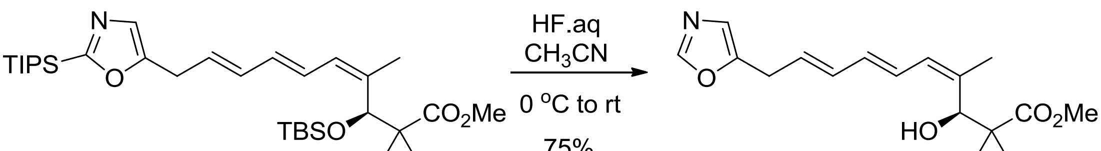
(*S,4Z,6E,8E*)-methyl-3-((tert-butyldimethylsilyl)oxy)-2,2,4-trimethyl-10-(2-(triisopropylsilyl)oxazol-5-yl)deca-4,6,8-trienoate (8): To a solution of $ZrCp_2Cl_2$ (584 mg, 2.0 mmol) in THF (4.5 mL) was added dropwise a solution of DIBAL (2.0 mL, 1.0 M solution in hexane, 2.0 mmol) at 0 ℃ in dark under argon atmosphere, and the resulting suspension was stirred at 0 ℃ for 30 min followed by the addition of a solution of enyl **5** (415 mg, 1.3 mmol) in THF (2 mL). The reaction mixture was warmed to room temperature and stirred for further 30 min. To a solution of vinyl bromide (344 mg, 1.0 mmol) and PEPPSI (34 mg, 0.05 mmol) in THF (3 mL) was added the above reaction mixture, and the resulting reaction mixture was stirred at room temperature 24h. The reaction mixture was quenched with water and extracted with Et_2O. The extract was dried over Na_2SO_4 and concentrated to give crude product. Flash chromatography (5:95 to 10:90 Et_2O/Pentane) to afford the triene **8** (524 mg, 91%).



8

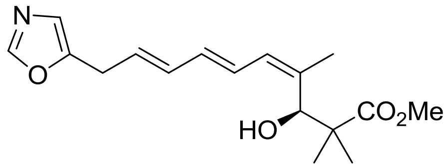
(*S,Z*)-methyl 3-((tert-butyldimethylsilyl)oxy)-2,2,4-trimethylhept-4-en-6-ynoate
Pale yellow oil. R_f=0.4 (Et_2O: Pentane= 1:10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.41 (t, *J* = 12.5 Hz, 1H), 6.26 – 6.04 (m, 2H), 5.98 (d, *J* = 11.4 Hz, 1H), 5.82 – 5.68 (m, 1H), 4.93 (s, 1H), 3.61 (s, 3H), 3.50 (d, *J* = 6.6 Hz, 2H), 1.78 (s, 3H), 1.45 – 1.24 (m, 6H), 1.21 (s, 3H), 1.13 (d, *J* = 7.4 Hz, 18H), 1.09 (s, 3H), 0.91 – 0.84 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.14, 167.99, 152.56, 138.12, 133.22, 131.87, 129.75, 127.91, 127.64, 123.08, 74.32, 51.83, 49.60, 34.27, 29.11, 25.85, 22.48, 22.37, 21.47, 19.94, 18.53, 18.20, 14.19, 11.14, -4.72, -5.40. HRMS-ESI; m/z [M+Na$^+$] = 578.3713, calcd. For $C_{17}H_{20}NaO$: 578.3718. $[\alpha]_D^{27.0}$ =-97.6 (c = 0.5 in $CHCl_3$)



8 **9**

***(S,4Z,6E,8E)*-methyl-3-hydroxy-2,2,4-trimethyl-10-(oxazol-5-yl)deca-4,6,8-trienoate (9):** To a solution of **8** (175mg, 0.3 mmol) in CH_3CN (4 ml) was added HF-pyridine (0.4 ml) at 0 ℃. The reaction mixture was stirred at room temperature for 10 h and the basified with saturated $NaHCO_3$ at 0 ℃ and extracted with CH_2Cl_2 and dried over Na_2SO_4 and concentrated to give crude product. Flash chromatography (20:80 to 40:60 EtOAc/Pentane) to afford the alcohol **8** (68 mg, 75%), *ee* >99% determined by chiral SFC, OJH column, 10% MeOH, 2 ml/min, 254nm, t_R = 4.3 min (minor)/4.7 (major).



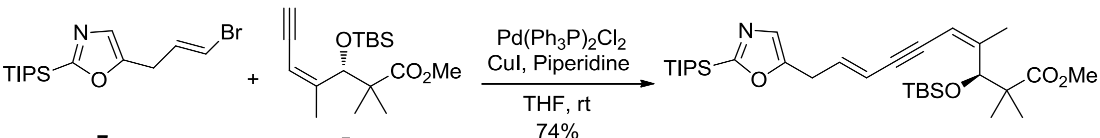
9

(*S,4Z,6E,8E*)-methyl 3-hydroxy-2,2,4-trimethyl-10-(oxazol-5-yl)deca-4,6,8-trienoate

Pale yellow oil.

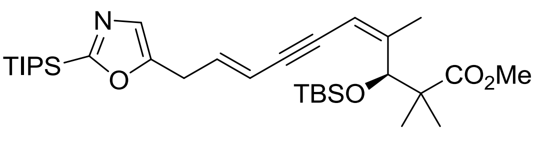
R_f=0.3 (EtOAc/Pentane = 1:2)

^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 6.79 (s, 1H), 6.43 (dd, *J* = 13.8, 11.5 Hz, 1H), 6.24 – 6.08 (m, 2H), 6.03 (d, *J* = 11.4 Hz, 1H), 5.78 – 5.68 (m, 1H), 4.72 (d, *J* = 6.1 Hz, 1H), 3.71 (s, 3H), 3.48 (d, *J* = 6.8 Hz, 2H), 3.26 (d, *J* = 6.4 Hz, 1H), 1.75 (s, 3H), 1.27 (s, 3H), 1.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.51, 150.95, 150.55, 136.99, 133.53, 131.91, 130.32, 128.04, 127.38, 122.71, 75.26, 52.35, 47.00, 28.99, 24.51, 21.18, 19.66. HRMS-ESI; *m/z* [M+Na$^+$] =328.1526, calcd. For $C_{17}H_{23}NNaO_4$: 328.1519. $[\alpha]_D^{27.0}$ =-87.0 (c = 0.5 in $CHCl_3$) Lit.[17](*R*) $[\alpha]_D^{27.0}$ =+81.9 (c = 0.99 in $CHCl_3$)



7 **5** **10**

***(S,4Z,8E)*-methyl-3-((tert-butyldimethylsilyl)oxy)-2,2,4-trimethyl-10-(2-(triisopropylsilyl)oxazol-5-yl)deca-4,8-dien-6-ynoate (10):** To a mixture of $Pd(Ph_3P)_2Cl_2$ (35 mg, 0.05mmol) and CuI (19 mg, 0.1 mmol) in THF (3ml) under argon, piperidine (0.3ml 3mmol) and vinyl bromide **7** (344mg, 1.0mmol) were added, followed by the addition of enyl 5 (341mg 1.1mmol). The reaction mixture was allowed to stired for 30 mins at room temperature. The resulting mixture was diluted with Et_2O then filter through short pad of silica gel using Et_2O as eluent. The solution was washed with saturated NH_4Cl, dried over Na_2SO_4 and concentrated to give the crude product. Flash chromatography (5:95 to 10:90 Et_2O/Pentane) to afford the product **10** (424mg, 74%).



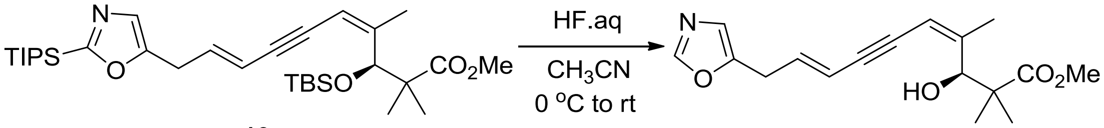
10

***(S,4Z,8E)*-methyl-3-((tert-butyl dimethylsilyl)oxy)-2,2,4-trimethyl-10-(2-(triisopropylsilyl)oxazol-5-yl)deca-4,8-dien-6-ynoate**

Pale yellow oil.

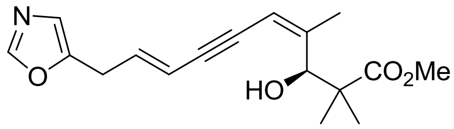
R_f=0.4 (Et_2O: Pentane= 1:10)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.19 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.74 (dd, *J* = 15.8, 1.9 Hz, 1H), 5.53 (s, 1H), 5.14 (s, 1H), 3.63 (s, 3H), 3.55 (d, *J* = 6.7 Hz, 2H), 1.81 (d, *J* = 1.3 Hz, 3H), 1.58 (s, 1H), 1.45 – 1.22 (m, 6H), 1.20 (s, 3H), 1.16 (s, 3H), 1.13 (d, *J* = 7.4 Hz, 18H), 0.90 – 0.84 (m, 12H), 0.04 (s, 3H), -0.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.04, 168.27, 151.52, 151.02, 136.98, 123.35, 112.92, 109.62, 92.18, 86.92, 76.62, 51.83, 49.19, 29.45, 25.81, 22.67, 20.82, 18.87, 18.51, 18.15, 11.11, -4.77, -5.54. HRMS-ESI; m/z [M+Na$^+$] = 596.3562, calcd. For $C_{32}H_{55}NNaO_4Si_2$: 596.3561. $[\alpha]_D^{27.0}$ =-124.4 (c = 0.5 in $CHCl_3$)



10 11

***(S,4Z,8E)*-methyl-3-hydroxy-2,2,4-trimethyl-10-(oxazol-5-yl)deca-4,8-dien-6-ynoate (11):** To a solution of **10** (143mg, 0.25 mmol) in CH_3CN (10 ml) was added 47% HF (2.0 ml) at 0 ℃. The reaction mixture was stirred at room temperature overnight and the basified with saturated $NaHCO_3$ at 0 ℃ and extracted with CH_2Cl_2 and dried over Na_2SO_4 and concentrated to give crude product. Flash chromatography (20:80 to 40:60 EtOAc/Pentane) to afford the alcohol **11** (62 mg, 82%), *ee* >99% determined by chiral SFC, OJH column, 10% MeOH, 2 ml/min, 254nm, t_R = 3.7 min (major)/4.0 (minor)



11

(*S,4Z,8E*)-methyl-3-hydroxy-2,2,4-trimethyl-10-(oxazol-5-yl)deca-4,8-dien-6-ynoate
Pale yellow oil.
R_f=0.3 (EtOAc/Pentane = 1:2)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 6.82 (s, 1H), 6.11 (dt, *J* = 15.7, 6.8 Hz, 1H), 5.73 (dd, *J* = 15.8, 1.7 Hz, 1H), 5.57 (s, 1H), 4.83 (d, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 3.57 (d, *J* = 7.2 Hz, 1H), 3.50 (d, *J* = 6.8 Hz, 2H), 1.75 (d, *J* = 1.3 Hz, 3H), 1.32 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.41, 150.72, 149.84, 149.68, 136.53, 123.07, 113.25, 109.75, 91.78, 86.98, 77.30, 52.32, 46.78, 29.15, 24.64, 20.84, 18.51. HRMS-ESI; m/z [M+Na$^+$] = 326.1368, calcd. For $C_{17}H_{21}NNaO_4$: 326.1363. $[\alpha]_D^{27.0}$ =+34.0 (c = 0.5 in $CHCl_3$) Lit.[18](*R*) $[\alpha]_D^{25.0}$ =-26.1 (c = 0.6 in $CHCl_3$)

6. DFT calculation

Computational Details

All calculations were performed with Jaguar [1] (version 10.1) using the B3LYP-D3 [2, 3] functional in combination with the LACVP** basis set.[4] First, all the structures were optimized in the gas phase. The solvent energies for the optimized structures were then calculated using the Poisson-Boltzmann solver with toluene as the solvent. The energies that are shown, with the XYZ coordinates, were obtained from the optimized in the gas phase calculations. All the transition states were characterized by one negative vibrational frequency. The XYZ coordinates of the calculated structures are listed below. All computations were carried out using the computational cluster resources at the National Supercomputer Centre based at Linkoping University, Sweden.

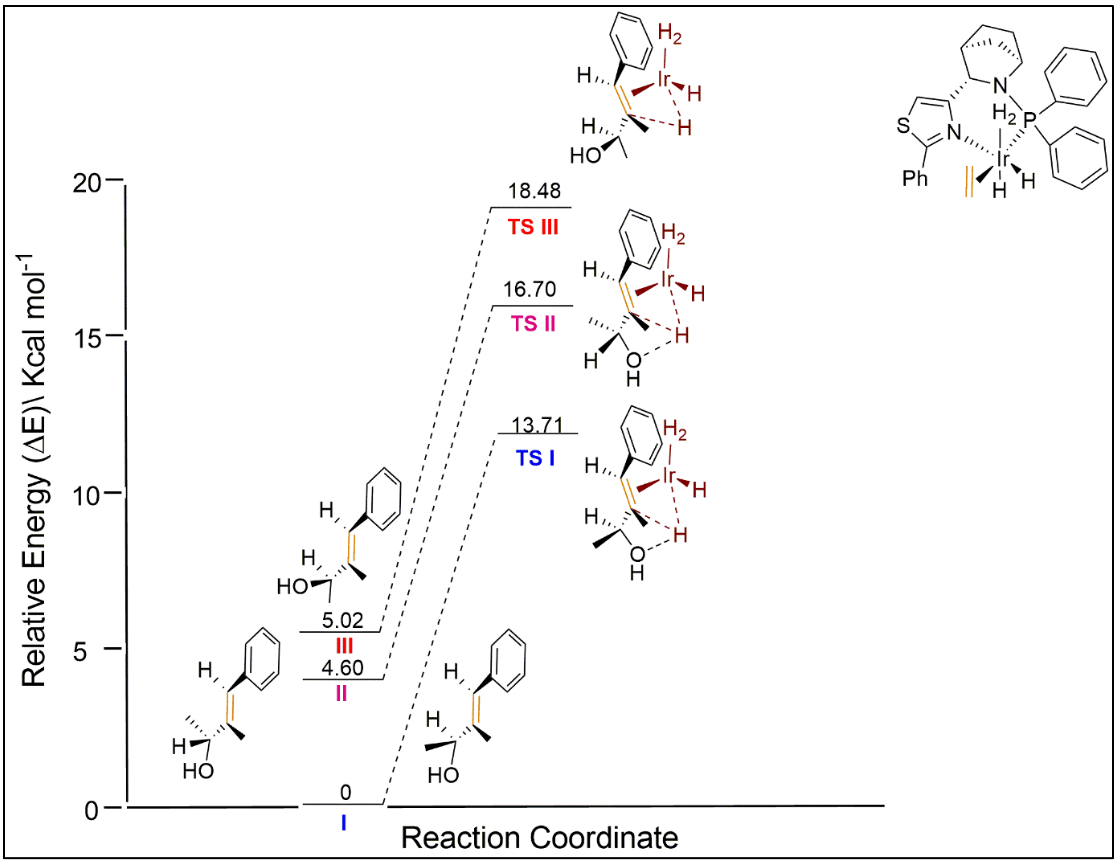


Figure 1: Energy profile depicting the transition state of the 3 diastereomers

XYZ coordinates of structures calculated

Start struc I (Energy = -2502.917707 Hartrees, 0 Kcal mol^{-1})

N1 1.6720290000000 1.4404950000000 -0.2942120000000
C2 3.9801810000000 1.6695860000000 -1.1074260000000
C3 2.1869590000000 3.2231680000000 -1.7120120000000
C4 3.4006230000000 2.4700650000000 -2.3229730000000
C5 1.0786770000000 2.1737280000000 -1.4403950000000
C6 2.9923860000000 2.0494030000000 0.0165270000000
H7 4.9962490000000 1.9912990000000 -0.8568660000000
H8 3.1036650000000 1.8228190000000 -3.1536850000000
H9 0.9236690000000 1.5337460000000 -2.3160650000000
H10 3.3037020000000 1.8051640000000 1.0332690000000
H11 3.9985960000000 0.5903830000000 -1.2725050000000
H12 1.8485130000000 4.0716450000000 -2.3112790000000
H13 4.1270240000000 3.1893200000000 -2.7109250000000
C14 2.6954180000000 3.5269910000000 -0.2850220000000
H15 1.9417340000000 3.9609590000000 0.3780940000000
H16 3.5906870000000 4.1546590000000 -0.2774930000000
C17 -0.2800390000000 2.7142960000000 -1.0495710000000
N18 -1.2105070000000 1.9733800000000 -0.4812780000000
C19 -2.3279110000000 2.7254150000000 -0.1120280000000
C20 -2.2540290000000 4.0367340000000 -0.4809580000000
H21 -2.9778070000000 4.8142270000000 -0.2821080000000
P22 1.0557060000000 0.0131220000000 0.3470710000000
Ir23 -0.9932580000000 -0.3160540000000 -0.6029700000000
H24 -1.9625620000000 -0.3009560000000 0.9900940000000
C25 0.9285620000000 0.3081900000000 2.1449060000000
C26 0.4388730000000 0.7493730000000 4.8662030000000
C27 0.7176440000000 1.6093850000000 2.6224940000000
C28 0.8853460000000 -0.7725790000000 3.0393390000000
C29 0.6422960000000 -0.5495980000000 4.3939000000000
C30 0.4777470000000 1.8274220000000 3.9797420000000
H31 1.0494500000000 -1.7851310000000 2.6808400000000
H32 0.6166320000000 -1.3895210000000 5.0821210000000
H33 0.3236960000000 2.8386970000000 4.3452770000000
H34 0.2535140000000 0.9203400000000 5.9226610000000
S35 -0.7404450000000 4.3710340000000 -1.2486050000000
C36 -3.4289490000000 2.1513100000000 0.6881530000000
C37 -3.1467700000000 1.5840740000000 1.9414520000000
C38 -4.7568040000000 2.2214880000000 0.2444610000000
C39 -4.1784100000000 1.0748720000000 2.7277500000000
H40 -2.1222470000000 1.5685160000000 2.3042380000000
C41 -5.7877890000000 1.7142980000000 1.0380910000000
H42 -4.9764230000000 2.6663690000000 -0.7221340000000
C43 -5.4998540000000 1.1372120000000 2.2765040000000
H44 -3.9527760000000 0.6405500000000 3.6973960000000
H45 -6.8145790000000 1.7670760000000 0.6885980000000
H46 -6.3032160000000 0.7433080000000 2.8922700000000
C47 2.3244760000000 -1.2827590000000 0.1597770000000

C48 3.4257560000000 -1.3354010000000 1.0305450000000
C49 2.2589970000000 -2.1663090000000 -0.9273020000000
C50 4.4441000000000 -2.2616800000000 0.8151970000000
H51 3.4838120000000 -0.6632900000000 1.8815530000000
C52 3.2814910000000 -3.0906950000000 -1.1379160000000
C53 4.3727520000000 -3.1396870000000 -0.2685580000000
H54 5.2906750000000 -2.3000340000000 1.4943630000000
H55 3.2234870000000 -3.7763250000000 -1.9781430000000
H56 5.1661650000000 -3.8628010000000 -0.4332020000000
H65 -1.6618500000000 -1.0541720000000 0.9323220000000
C66 -3.7070540000000 -4.5395010000000 -0.6263150000000
C67 -3.2352100000000 -3.3820510000000 -1.2416530000000
C68 -3.6596490000000 -2.1152160000000 -0.8024190000000
C69 -4.5723960000000 -2.0552410000000 0.2673360000000
C70 -5.0432620000000 -3.2129390000000 0.8797820000000
C71 -4.6093120000000 -4.4632400000000 0.4363660000000
H72 -3.3655360000000 -5.5084370000000 -0.9793440000000
H73 -2.5292570000000 -3.4762330000000 -2.0535720000000
H74 -4.9065640000000 -1.0850670000000 0.6266320000000
H75 -5.7470610000000 -3.1397300000000 1.7042150000000
H76 -4.9703060000000 -5.3699490000000 0.9131400000000
C77 -3.2162740000000 -0.8156700000000 -1.3544130000000
H78 -3.7634640000000 0.0178270000000 -0.9189920000000
C79 -2.4995470000000 -0.4968520000000 -2.5054950000000
C80 -1.9599260000000 -1.4891080000000 -3.5158250000000
H81 -1.3682520000000 -0.9574990000000 -4.2629270000000
H82 -1.3235820000000 -2.2451470000000 -3.0615660000000
H83 -2.7926250000000 -1.9965430000000 -4.0177140000000
C84 -2.7151000000000 0.9092280000000 -3.0645230000000
H85 -3.0492200000000 1.5619560000000 -2.2493250000000
C86 -3.8112700000000 0.8865360000000 -4.1382250000000
H87 -4.7470300000000 0.4998010000000 -3.7246160000000
H88 -4.0023240000000 1.9026970000000 -4.5029210000000
H89 -3.5202900000000 0.2642530000000 -4.9886200000000
O90 -1.4807080000000 1.3979830000000 -3.5953900000000
H91 -1.6854360000000 2.0793480000000 -4.2480920000000
H92 -0.1994060000000 -0.1448480000000 -1.9523550000000
H93 -0.7308290000000 -1.8535970000000 -0.8051150000000
H86 0.7385610000000 2.4451560000000 1.9300400000000
H90 1.4082480000000 -2.1280370000000 -1.5997950000000

Start str II (Energy = -2502.910380 Hartrees, 4.60 Kcal mol^{-1})

N1 1.6567600000000 1.4181230000000 -0.4252410000000
C2 3.8824230000000 1.6294990000000 -1.4249110000000
C3 2.0860380000000 3.2509940000000 -1.8083090000000
C4 3.2215490000000 2.4942780000000 -2.5529950000000
C5 0.9829960000000 2.2124460000000 -1.4864510000000
C6 3.0106900000000 1.9893220000000 -0.2027100000000
H7 4.9267880000000 1.9114470000000 -1.2567660000000
H8 2.8355020000000 1.8891720000000 -3.3788010000000

H9 0.7428480000000 1.6117080000000 -2.3692490000000
H10 3.4062460000000 1.6953100000000 0.7705630000000
H11 3.8490650000000 0.5570660000000 -1.6296600000000
H12 1.7156460000000 4.1300080000000 -2.3413040000000
H13 3.9320600000000 3.2105740000000 -2.9744720000000
C14 2.7304770000000 3.4851240000000 -0.4234130000000
H15 2.0562200000000 3.9176620000000 0.3205190000000
H16 3.6413720000000 4.0876440000000 -0.4775530000000
C17 -0.3299320000000 2.7376320000000 -0.9483010000000
N18 -1.2378030000000 1.9422340000000 -0.4137170000000
C19 -2.2793760000000 2.6574570000000 0.1820470000000
C20 -2.1768480000000 4.0087100000000 0.0166620000000
H21 -2.8493310000000 4.7669020000000 0.3906180000000
P22 1.0105420000000 0.0361360000000 0.2815320000000
Ir23 -1.0053380000000 -0.3312730000000 -0.7176350000000
H24 -2.0350940000000 -0.4046790000000 0.8379400000000
C25 0.8003410000000 0.4116240000000 2.0612850000000
C26 0.1404700000000 0.9879630000000 4.7253460000000
C27 0.7575860000000 1.7385860000000 2.5082620000000
C28 0.5117090000000 -0.6275970000000 2.9604910000000
C29 0.1835300000000 -0.3387350000000 4.2841510000000
C30 0.4331850000000 2.0236010000000 3.8365270000000
H31 0.5432190000000 -1.6618740000000 2.6267690000000
H32 -0.0371150000000 -1.1486920000000 4.9734360000000
H33 0.4031860000000 3.0557130000000 4.1739040000000
H34 -0.1167490000000 1.2109010000000 5.7565850000000
S35 -0.7328980000000 4.4165500000000 -0.8414080000000
C36 -3.3440900000000 2.0089400000000 0.9802310000000
C37 -3.0082180000000 1.3071520000000 2.1499110000000
C38 -4.6937060000000 2.1656190000000 0.6380190000000
C39 -4.0085810000000 0.7495740000000 2.9449170000000
H40 -1.9674250000000 1.2266930000000 2.4480720000000
C41 -5.6933040000000 1.6162240000000 1.4445690000000
H42 -4.9576040000000 2.7168790000000 -0.2601600000000
C43 -5.3534400000000 0.9011240000000 2.5950390000000
H44 -3.7361920000000 0.2096850000000 3.8470910000000
H45 -6.7364820000000 1.7436900000000 1.1706870000000
H46 -6.1316380000000 0.4731560000000 3.2199770000000
C47 2.2865260000000 -1.2585810000000 0.2011920000000
C48 3.2865850000000 -1.3523020000000 1.1821610000000
C49 2.3190040000000 -2.1206200000000 -0.9059820000000
C50 4.3053940000000 -2.2961820000000 1.0539120000000
H51 3.2651910000000 -0.6993540000000 2.0497330000000
C52 3.3415170000000 -3.0601970000000 -1.0289950000000
C53 4.3353870000000 -3.1500070000000 -0.0506630000000
H54 5.0730880000000 -2.3663320000000 1.8188540000000
H55 3.3585850000000 -3.7280820000000 -1.8852040000000
H56 5.1275050000000 -3.8865220000000 -0.1463880000000
H65 -1.6945090000000 -1.1381340000000 0.7675450000000
C66 -3.9993950000000 -4.3872990000000 -0.6307170000000

C67 -3.4353280000000 -3.3156370000000 -1.3213380000000
C68 -3.7366100000000 -1.9921940000000 -0.9551470000000
C69 -4.6231650000000 -1.7893870000000 0.1190480000000
C70 -5.1833420000000 -2.8593880000000 0.8082860000000
C71 -4.8708050000000 -4.1685270000000 0.4371660000000
H72 -3.7560090000000 -5.4019420000000 -0.9328330000000
H73 -2.7682430000000 -3.5261390000000 -2.1435860000000
H74 -4.8644430000000 -0.7756490000000 0.4230910000000
H75 -5.8634810000000 -2.6704520000000 1.6342930000000
H76 -5.3044800000000 -5.0091820000000 0.9709350000000
C77 -3.2056080000000 -0.7630390000000 -1.5940540000000
H78 -3.7345010000000 0.1223690000000 -1.2527080000000
C79 -2.4255110000000 -0.5837050000000 -2.7329660000000
C80 -1.8331110000000 -1.6932060000000 -3.5823820000000
H81 -1.0906290000000 -1.2679310000000 -4.2609280000000
H82 -1.3475330000000 -2.4709560000000 -2.9993650000000
H83 -2.6296350000000 -2.1510120000000 -4.1838610000000
C84 -2.5357560000000 0.7136860000000 -3.5480310000000
O85 -1.2143620000000 1.2054020000000 -3.8123850000000
H86 -1.2668350000000 1.7828310000000 -4.5851860000000
H87 -0.1776070000000 -0.1137740000000 -2.0373510000000
H88 -0.7038860000000 -1.8542280000000 -0.9637390000000
H89 -2.9739270000000 0.3607390000000 -4.4986110000000
C90 -3.4405170000000 1.8248730000000 -3.0264770000000
H91 -4.4711700000000 1.4786770000000 -2.9080980000000
H92 -3.0852050000000 2.2248180000000 -2.0792360000000
H93 -3.4521950000000 2.6437860000000 -3.7532680000000
H90 1.5412810000000 -2.0546890000000 -1.6604700000000
H94 0.9633670000000 2.5469430000000 1.8145180000000

Start str III (Energy = -2502,909701 Hartrees, 5.02 Kcal mol^{-1})

N1 1.6811690000000 1.4357110000000 -0.3236960000000
C2 4.0126200000000 1.5789630000000 -1.0893700000000
C3 2.2894960000000 3.1956740000000 -1.7333780000000
C4 3.4901300000000 2.4005160000000 -2.3167680000000
C5 1.1422690000000 2.1829630000000 -1.4833840000000
C6 3.0166500000000 1.9967680000000 0.0135590000000
H7 5.0348500000000 1.8610630000000 -0.8175610000000
H8 3.1924090000000 1.7652090000000 -3.1565920000000
H9 1.0086800000000 1.5353760000000 -2.3579640000000
H10 3.2967050000000 1.7431600000000 1.0370770000000
H11 3.9928380000000 0.4996650000000 -1.2539900000000
H12 1.9912430000000 4.0535290000000 -2.3405300000000
H13 4.2497010000000 3.0947940000000 -2.6858170000000
C14 2.7780320000000 3.4832620000000 -0.2958700000000
H15 2.0272500000000 3.9447640000000 0.3515470000000
H16 3.6944270000000 4.0790310000000 -0.2714690000000
C17 -0.2118600000000 2.7656850000000 -1.1261470000000
N18 -1.1875590000000 2.0422990000000 -0.6096610000000
C19 -2.2789040000000 2.8232290000000 -0.2260330000000

C20 -2.1429500000000 4.1443050000000 -0.5402070000000
H21 -2.8401430000000 4.9427960000000 -0.3291580000000
P22 1.0014250000000 0.0264660000000 0.2938920000000
Ir23 -1.0396320000000 -0.2616640000000 -0.6867800000000
H24 -1.9908950000000 -0.1607960000000 0.9002490000000
C25 0.8330420000000 0.3294930000000 2.0870570000000
C26 0.2554350000000 0.7942630000000 4.7868320000000
C27 0.6561080000000 1.6387650000000 2.5558990000000
C28 0.7135840000000 -0.7475050000000 2.9792130000000
C29 0.4263600000000 -0.5126590000000 4.3231270000000
C30 0.3728730000000 1.8685750000000 3.9028520000000
H31 0.8496240000000 -1.7665390000000 2.6270860000000
H32 0.3396890000000 -1.3497080000000 5.0098480000000
H33 0.2443830000000 2.8857630000000 4.2617920000000
H34 0.0341940000000 0.9740750000000 5.8348930000000
S35 -0.6033580000000 4.4466310000000 -1.2672380000000
C36 -3.3997560000000 2.2613720000000 0.5599270000000
C37 -3.1356630000000 1.7373390000000 1.8361200000000
C38 -4.7167760000000 2.2920800000000 0.0859150000000
C39 -4.1751670000000 1.2307270000000 2.6146550000000
H40 -2.1193460000000 1.7475070000000 2.2210990000000
C41 -5.7551600000000 1.7831460000000 0.8683630000000
H42 -4.9252190000000 2.6987220000000 -0.8994580000000
C43 -5.4862550000000 1.2496000000000 2.1298310000000
H44 -3.9627010000000 0.8306800000000 3.6021070000000
H45 -6.7727650000000 1.7993980000000 0.4903110000000
H46 -6.2961680000000 0.8545930000000 2.7362850000000
C47 2.2251730000000 -1.3141230000000 0.1425790000000
C48 3.2979850000000 -1.4051160000000 1.0459910000000
C49 2.1488000000000 -2.2113000000000 -0.9330770000000
C50 4.2769110000000 -2.3814620000000 0.8736300000000
H51 3.3620270000000 -0.7252250000000 1.8905160000000
C52 3.1320890000000 -3.1857630000000 -1.1002310000000
C53 4.1945640000000 -3.2723990000000 -0.1988770000000
H54 5.1000620000000 -2.4499340000000 1.5787500000000
H55 3.0642150000000 -3.8825720000000 -1.9303160000000
H56 4.9559460000000 -4.0359020000000 -0.3283970000000
H65 -1.7096210000000 -0.9256210000000 0.8716240000000
C66 -3.8231020000000 -4.6044830000000 -0.6361930000000
C67 -3.4529860000000 -3.4429500000000 -1.3125680000000
C68 -3.6533650000000 -2.1803350000000 -0.7279990000000
C69 -4.2601770000000 -2.1281300000000 0.5422810000000
C70 -4.6251020000000 -3.2878040000000 1.2176370000000
C71 -4.3998730000000 -4.5359730000000 0.6322730000000
H72 -3.6654950000000 -5.5697220000000 -1.1089300000000
H73 -3.0352620000000 -3.5342760000000 -2.3045120000000
H74 -4.4398300000000 -1.1602100000000 1.0041360000000
H75 -5.0890400000000 -3.2197870000000 2.1978260000000
H76 -4.6827160000000 -5.4453110000000 1.1548390000000
C77 -3.3076190000000 -0.8760450000000 -1.3406290000000

H78 -3.8696260000000 -0.0561280000000 -0.8980860000000
C79 -2.6464890000000 -0.5465930000000 -2.5200800000000
C80 -2.0905940000000 -1.5431230000000 -3.5115530000000
H81 -1.3410320000000 -1.0800340000000 -4.1551940000000
H82 -1.6175660000000 -2.3920260000000 -3.0232890000000
H83 -2.9078950000000 -1.8997950000000 -4.1493580000000
C84 -3.0116230000000 0.8259510000000 -3.1030750000000
O85 -4.2138720000000 0.5587940000000 -3.8341790000000
H86 -4.3739520000000 1.2923040000000 -4.4426550000000
H87 -0.2467450000000 -0.1559620000000 -2.0480340000000
H88 -0.8074960000000 -1.8085900000000 -0.8423160000000
H89 -3.2299400000000 1.5018670000000 -2.2664040000000
C90 -1.9615590000000 1.4834390000000 -3.9959340000000
H91 -1.0056050000000 1.5792800000000 -3.4785540000000
H92 -1.8085610000000 0.9094610000000 -4.9136530000000
H93 -2.2939840000000 2.4889610000000 -4.2788300000000
H90 1.3180910000000 -2.1477270000000 -1.6280820000000
H94 0.7345570000000 2.4719830000000 1.8645330000000

TSI (Energy = -2502.895853 Hartrees, 13.71 Kcal mol^{-1})

N1 1.6347230000000 1.5455950000000 -0.2709460000000
C2 3.8664670000000 1.8096280000000 -1.2935230000000
C3 1.9645650000000 3.2455700000000 -1.8416950000000
C4 3.1578270000000 2.5053500000000 -2.5036890000000
C5 0.9294490000000 2.1715490000000 -1.4150560000000
C6 2.9530280000000 2.2170370000000 -0.1161730000000
H7 4.8814290000000 2.1916040000000 -1.1433290000000
H8 2.8251870000000 1.7940400000000 -3.2658270000000
H9 0.7487230000000 1.4701150000000 -2.2368300000000
H10 3.3549990000000 2.0488080000000 0.8840620000000
H11 3.9284630000000 0.7254400000000 -1.3996610000000
H12 1.5439740000000 4.0395390000000 -2.4628610000000
H13 3.8179570000000 3.2262700000000 -2.9935430000000
C14 2.5666120000000 3.6594440000000 -0.4800880000000
H15 1.8452110000000 4.0991150000000 0.2146470000000
H16 3.4293130000000 4.3234710000000 -0.5803920000000
C17 -0.4290140000000 2.6968860000000 -0.9882120000000
N18 -1.3339890000000 1.9739410000000 -0.3548170000000
C19 -2.4935350000000 2.7006350000000 -0.0730290000000
C20 -2.4678880000000 3.9784490000000 -0.5520350000000
H21 -3.2302130000000 4.7356730000000 -0.4369740000000
P22 1.1595840000000 0.0761070000000 0.4008860000000
Ir23 -1.0806630000000 -0.3056600000000 -0.1987550000000
H24 -2.0843740000000 -0.4389740000000 1.1439700000000
C25 1.3593830000000 0.3241060000000 2.2012840000000
C26 1.3120040000000 0.6840750000000 4.9832730000000
C27 1.1295960000000 1.5959200000000 2.7476280000000
C28 1.5572740000000 -0.7678290000000 3.0605710000000
C29 1.5340320000000 -0.5849630000000 4.4438770000000
C30 1.1112440000000 1.7733710000000 4.1315770000000

H31 1.7314020000000 -1.7594250000000 2.6530650000000
H32 1.6913980000000 -1.4360490000000 5.1001430000000
H33 0.9399130000000 2.7632430000000 4.5449440000000
H34 1.2942880000000 0.8228350000000 6.0600090000000
S35 -0.9622290000000 4.3098140000000 -1.3313780000000
C36 -3.6104120000000 2.1196540000000 0.6984440000000
C37 -3.3906060000000 1.6026670000000 1.9838100000000
C38 -4.9063710000000 2.1110100000000 0.1655000000000
C39 -4.4473700000000 1.0560670000000 2.7088840000000
H40 -2.3938320000000 1.6469610000000 2.4139530000000
C41 -5.9632830000000 1.5675620000000 0.8962240000000
H42 -5.0779680000000 2.5161180000000 -0.8282970000000
C43 -5.7333330000000 1.0312080000000 2.1633760000000
H44 -4.2707190000000 0.6582190000000 3.7037750000000
H45 -6.9635780000000 1.5587790000000 0.4735910000000
H46 -6.5545360000000 0.6015380000000 2.7288250000000
C47 2.3741950000000 -1.2130720000000 -0.0480370000000
C48 3.6325390000000 -1.2767180000000 0.5733440000000
C49 2.0782440000000 -2.0961370000000 -1.0955760000000
C50 4.5749090000000 -2.2116160000000 0.1508970000000
H51 3.8718810000000 -0.6047520000000 1.3922950000000
C52 3.0255600000000 -3.0283250000000 -1.5175750000000
C53 4.2728250000000 -3.0874360000000 -0.8946940000000
H54 5.5437200000000 -2.2595700000000 0.6392480000000
H55 2.7874790000000 -3.7121840000000 -2.3270560000000
H56 5.0082040000000 -3.8175160000000 -1.2195820000000
H65 -1.2315410000000 -0.3844860000000 1.4809700000000
C66 -3.9837500000000 -4.3677140000000 -0.5919960000000
C67 -3.1677500000000 -3.2681580000000 -0.8478490000000
C68 -3.7111740000000 -1.9768900000000 -0.9632420000000
C69 -5.0975410000000 -1.8306710000000 -0.7836790000000
C70 -5.9139410000000 -2.9305300000000 -0.5223430000000
C71 -5.3618390000000 -4.2081480000000 -0.4324580000000
H72 -3.5378630000000 -5.3548040000000 -0.5086730000000
H73 -2.0974550000000 -3.4150320000000 -0.9296790000000
H74 -5.5380760000000 -0.8381610000000 -0.8421590000000
H75 -6.9826210000000 -2.7868670000000 -0.3896710000000
H76 -5.9939760000000 -5.0674870000000 -0.2311510000000
C77 -2.9334220000000 -0.7414390000000 -1.2723200000000
H78 -3.5649910000000 0.1403560000000 -1.1754600000000
C79 -1.9712640000000 -0.6156220000000 -2.3770650000000
C80 -1.5663880000000 -1.8368050000000 -3.2014430000000
H81 -0.8934650000000 -1.5327150000000 -4.0060130000000
H82 -1.0697590000000 -2.5897250000000 -2.5930330000000
H83 -2.4631430000000 -2.2946000000000 -3.6290420000000
C84 -2.1810470000000 0.6573430000000 -3.2177870000000
H85 -2.4883800000000 1.4636750000000 -2.5401610000000
C86 -3.2801970000000 0.4427860000000 -4.2607220000000
H87 -4.2111500000000 0.1214280000000 -3.7841360000000
H88 -3.4808460000000 1.3810280000000 -4.7894670000000

H89 -2.9845780000000 -0.3090300000000 -4.9964200000000
O90 -0.9295590000000 0.9838410000000 -3.8223250000000
H91 -1.0828030000000 1.6256990000000 -4.5271450000000
H92 -0.7336250000000 -0.3133770000000 -1.8849940000000
H93 -0.8386750000000 -1.8540570000000 -0.1266520000000
H86 0.9598010000000 2.4406800000000 2.0862840000000
H90 1.1039980000000 -2.0555700000000 -1.5727940000000

TSII (Energy = -2502.89109 Hartrees, 16.70 Kcal mol^{-1})

N1 1.6093260000000 1.5855550000000 -0.3250610000000
C2 3.7532660000000 1.8228080000000 -1.5202360000000
C3 1.8623520000000 3.3406110000000 -1.8488330000000
C4 2.9724680000000 2.5939210000000 -2.6374470000000
C5 0.8334370000000 2.2787370000000 -1.3849460000000
C6 2.9564880000000 2.2096800000000 -0.2540420000000
H7 4.7911690000000 2.1623050000000 -1.4422730000000
H8 2.5541340000000 1.9262140000000 -3.3969810000000
H9 0.5709170000000 1.6094620000000 -2.2136060000000
H10 3.4340940000000 1.9880650000000 0.7016450000000
H11 3.7640720000000 0.7425340000000 -1.6738960000000
H12 1.4153800000000 4.1724100000000 -2.3979980000000
H13 3.6148690000000 3.3149350000000 -3.1502620000000
C14 2.5918880000000 3.6772660000000 -0.5277180000000
H15 1.9509360000000 4.1110400000000 0.2448110000000
H16 3.4663120000000 4.3164660000000 -0.6768320000000
C17 -0.4722240000000 2.8021090000000 -0.8240430000000
N18 -1.3986380000000 2.0150890000000 -0.3072590000000
C19 -2.5123570000000 2.7289580000000 0.1418420000000
C20 -2.4211740000000 4.0728600000000 -0.0721320000000
H21 -3.1475570000000 4.8279270000000 0.1929300000000
P22 1.1378890000000 0.1083420000000 0.3299670000000
Ir23 -1.1165700000000 -0.2558560000000 -0.2287770000000
H24 -2.1336900000000 -0.3348910000000 1.1091090000000
C25 1.4029110000000 0.3014160000000 2.1260240000000
C26 1.4670440000000 0.5787630000000 4.9117800000000
C27 1.2500920000000 1.5652950000000 2.7140060000000
C28 1.5815030000000 -0.8246970000000 2.9446000000000
C29 1.6137660000000 -0.6829250000000 4.3315070000000
C30 1.2870010000000 1.7014930000000 4.1017410000000
H31 1.6987010000000 -1.8093650000000 2.5008550000000
H32 1.7553050000000 -1.5583580000000 4.9583940000000
H33 1.1755980000000 2.6842330000000 4.5506400000000
H34 1.4925000000000 0.6857130000000 5.9921120000000
S35 -0.9163830000000 4.4757400000000 -0.8206540000000
C36 -3.6679220000000 2.0582040000000 0.7817780000000
C37 -3.5558530000000 1.5324170000000 2.0767510000000
C38 -4.8863520000000 1.9520910000000 0.0993620000000
C39 -4.6363140000000 0.8737470000000 2.6617750000000
H40 -2.6224790000000 1.6455790000000 2.6224350000000
C41 -5.9660900000000 1.2919710000000 0.6870190000000

H42 -4.9786430000000 2.3751070000000 -0.8974760000000
C43 -5.8391460000000 0.7439530000000 1.9633230000000
H44 -4.5420520000000 0.4660380000000 3.6639550000000
H45 -6.9037410000000 1.2017150000000 0.1466280000000
H46 -6.6767140000000 0.2221240000000 2.4163300000000
C47 2.3326610000000 -1.1731760000000 -0.1870860000000
C48 3.6090550000000 -1.2465610000000 0.3958820000000
C49 2.0089060000000 -2.0370160000000 -1.2422960000000
C50 4.5428850000000 -2.1668140000000 -0.0751730000000
H51 3.8694060000000 -0.5938940000000 1.2240990000000
C52 2.9471380000000 -2.9555380000000 -1.7122970000000
C53 4.2141590000000 -3.0204120000000 -1.1310890000000
H54 5.5259940000000 -2.2203270000000 0.3832320000000
H55 2.6864890000000 -3.6236550000000 -2.5280660000000
H56 4.9431080000000 -3.7386300000000 -1.4949540000000
H65 -1.2851450000000 -0.2136640000000 1.4506260000000
C66 -4.3123360000000 -4.0619740000000 -0.0424000000000
C67 -3.4090660000000 -3.0407030000000 -0.3316030000000
C68 -3.8379090000000 -1.8498680000000 -0.9377890000000
C69 -5.2069760000000 -1.7119450000000 -1.2209340000000
C70 -6.1130710000000 -2.7303600000000 -0.9287890000000
C71 -5.6674880000000 -3.9141960000000 -0.3411940000000
H72 -3.9553820000000 -4.9750560000000 0.4255100000000
H73 -2.3662740000000 -3.1617020000000 -0.0625200000000
H74 -5.5655290000000 -0.7916380000000 -1.6757130000000
H75 -7.1663930000000 -2.5981640000000 -1.1604690000000
H76 -6.3692790000000 -4.7107230000000 -0.1118340000000
C77 -2.9499280000000 -0.7076550000000 -1.3268310000000
H78 -3.5194700000000 0.2149940000000 -1.3703060000000
C79 -1.9342150000000 -0.8167680000000 -2.3823050000000
C80 -1.5450980000000 -2.2054750000000 -2.8886390000000
H81 -0.6875930000000 -2.1343430000000 -3.5618700000000
H82 -1.3114710000000 -2.8892940000000 -2.0767150000000
H83 -2.3953150000000 -2.6192280000000 -3.4416950000000
C84 -1.9575580000000 0.1914930000000 -3.5573660000000
O85 -0.5871740000000 0.4374980000000 -3.8947810000000
H86 -0.5524040000000 0.8661940000000 -4.7595730000000
H87 -0.7137910000000 -0.3902760000000 -1.8863820000000
H88 -0.8492510000000 -1.7954660000000 -0.0825430000000
H89 -2.4379880000000 -0.3737920000000 -4.3722410000000
C90 -2.7296310000000 1.4923510000000 -3.3716880000000
H91 -3.7986720000000 1.3040610000000 -3.2401540000000
H92 -2.3636380000000 2.0621070000000 -2.5196750000000
H93 -2.6155610000000 2.1066710000000 -4.2709250000000
H90 1.0219410000000 -1.9942170000000 -1.6897130000000
H94 1.0992130000000 2.4356310000000 2.0823280000000

TSIII (Energy = -2502.88825 Hartrees) 18.48 Kcal mol^{-1})
N1 1.7501570000000 1.6705870000000 -0.2037080000000
C2 3.9921490000000 1.9701990000000 -1.2002700000000
C3 2.0708350000000 3.3601380000000 -1.7933630000000

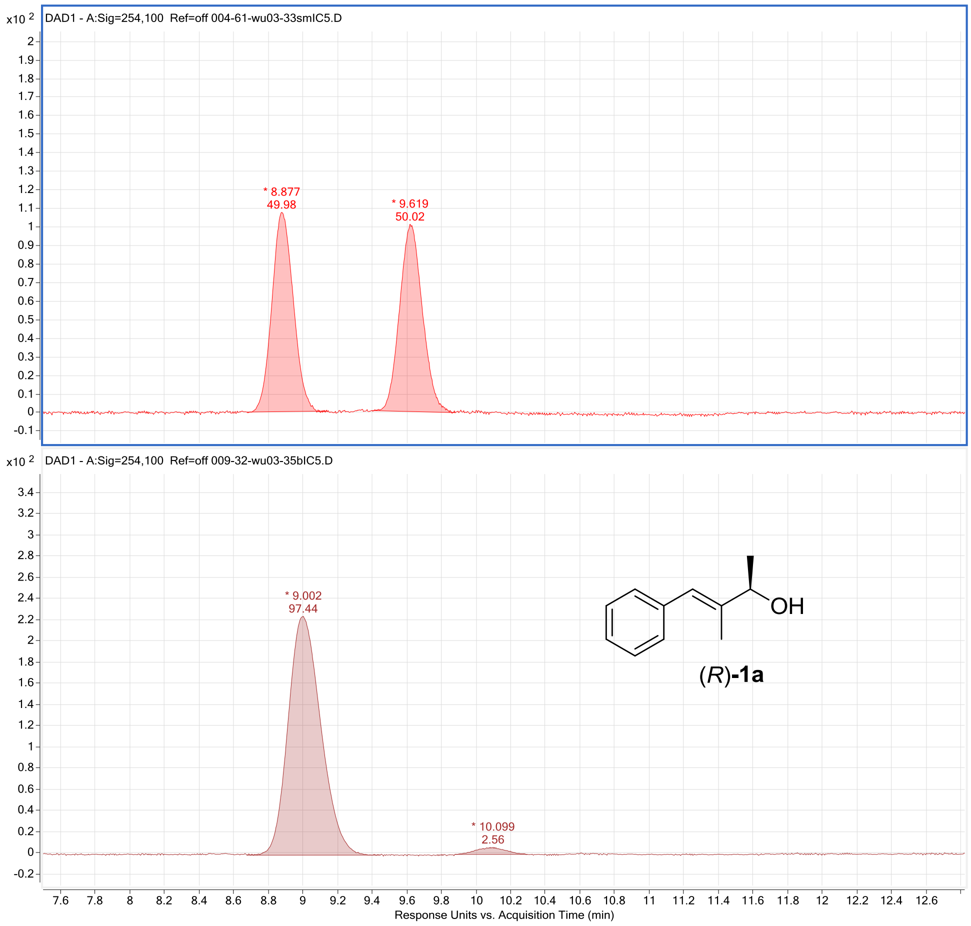
C4 3.2903820000000 2.6406240000000 -2.4281470000000
C5 1.0541980000000 2.2695690000000 -1.3674380000000
C6 3.0527210000000 2.3713780000000 -0.0403230000000
H7 4.9972580000000 2.3729810000000 -1.0385690000000
H8 2.9874150000000 1.9161280000000 -3.1911170000000
H9 0.9187440000000 1.5414790000000 -2.1763520000000
H10 3.4434830000000 2.2243110000000 0.9676810000000
H11 4.0771890000000 0.8867040000000 -1.2954060000000
H12 1.6391170000000 4.1369820000000 -2.4285020000000
H13 3.9424240000000 3.3713230000000 -2.9142870000000
C14 2.6429280000000 3.8010660000000 -0.4269300000000
H15 1.9031840000000 4.2337930000000 0.2522030000000
H16 3.4930850000000 4.4817010000000 -0.5237600000000
C17 -0.3264380000000 2.7635730000000 -0.9813210000000
N18 -1.2385180000000 1.9913220000000 -0.4226750000000
C19 -2.4138630000000 2.6856580000000 -0.1228380000000
C20 -2.3873090000000 3.9926130000000 -0.5134720000000
H21 -3.1647770000000 4.7314730000000 -0.3793590000000
P22 1.2973790000000 0.1953360000000 0.4858330000000
Ir23 -0.9032860000000 -0.2569320000000 -0.1919010000000
H24 -1.9874870000000 -0.2502860000000 1.1097570000000
C25 1.4557870000000 0.4819590000000 2.2849660000000
C26 1.3526240000000 0.8801910000000 5.0574980000000
C27 1.1551940000000 1.7489560000000 2.8066890000000
C28 1.6971270000000 -0.5863090000000 3.1618490000000
C29 1.6460530000000 -0.3842060000000 4.5416340000000
C30 1.1087640000000 1.9457000000000 4.1870130000000
H31 1.9275310000000 -1.5732590000000 2.7711710000000
H32 1.8380010000000 -1.2158810000000 5.2133540000000
H33 0.8835450000000 2.9315800000000 4.5836500000000
H34 1.3141960000000 1.0342620000000 6.1317180000000
S35 -0.8661770000000 4.3907010000000 -1.2313330000000
C36 -3.5371440000000 2.0449100000000 0.5985340000000
C37 -3.3708230000000 1.6510860000000 1.9347190000000
C38 -4.7642770000000 1.8226450000000 -0.0374490000000
C39 -4.4078840000000 1.0117310000000 2.6114260000000
H40 -2.4290270000000 1.8522650000000 2.4390790000000
C41 -5.7990720000000 1.1773140000000 0.6406900000000
H42 -4.8976040000000 2.1336100000000 -1.0701620000000
C43 -5.6193140000000 0.7641390000000 1.9609620000000
H44 -4.2729440000000 0.7095500000000 3.6460250000000
H45 -6.7409110000000 0.9894560000000 0.1343220000000
H46 -6.4227740000000 0.2548380000000 2.4848050000000
C47 2.5654460000000 -1.0597270000000 0.0867400000000
C48 3.8303610000000 -1.0303640000000 0.6984130000000
C49 2.3030040000000 -2.0155390000000 -0.9043380000000
C50 4.8142320000000 -1.9393230000000 0.3162240000000
H51 4.0431840000000 -0.3045070000000 1.4780230000000
C52 3.2914350000000 -2.9223810000000 -1.2859030000000
C53 4.5463130000000 -2.8850300000000 -0.6772220000000

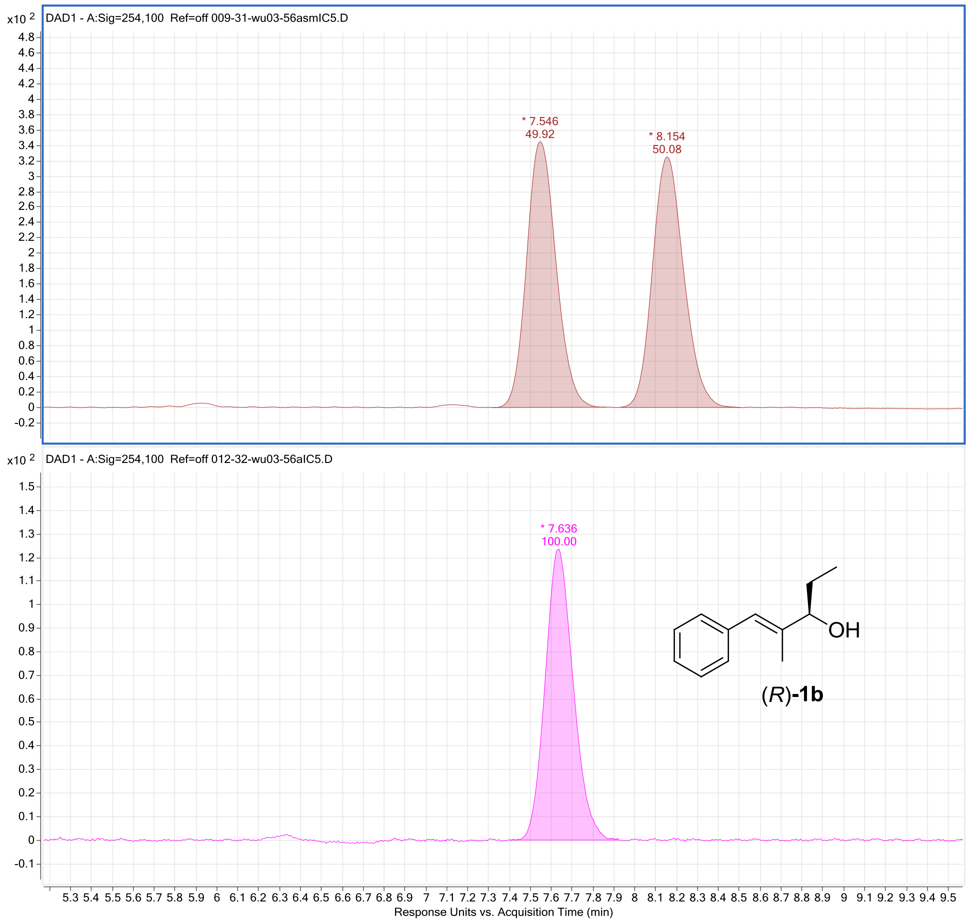
H54 5.7885970000000 -1.9134150000000 0.7953020000000
H55 3.0780770000000 -3.6637960000000 -2.0505170000000
H56 5.3140120000000 -3.5950020000000 -0.9709070000000
H65 -1.1630330000000 -0.2001910000000 1.4846150000000
C66 -5.5179910000000 -3.1747850000000 -1.7179250000000
C67 -4.5982890000000 -2.1555620000000 -1.9535030000000
C68 -3.6194780000000 -1.8353800000000 -0.9966120000000
C69 -3.5928710000000 -2.5545270000000 0.2018670000000
C70 -4.5169170000000 -3.5748520000000 0.4396830000000
C71 -5.4801880000000 -3.8889970000000 -0.5180090000000
H72 -6.2653840000000 -3.4121960000000 -2.4702630000000
H73 -4.6237070000000 -1.5955920000000 -2.8851740000000
H74 -2.8415530000000 -2.3258410000000 0.9496140000000
H75 -4.4796330000000 -4.1258040000000 1.3755820000000
H76 -6.1961490000000 -4.6849100000000 -0.3328220000000
C77 -2.7052450000000 -0.6921480000000 -1.3344660000000
H78 -3.2539750000000 0.2424700000000 -1.4336080000000
C79 -1.6734580000000 -0.8505010000000 -2.3531080000000
C80 -1.3375200000000 -2.2528810000000 -2.8331250000000
H81 -0.3241540000000 -2.3221360000000 -3.2362250000000
H82 -1.4514760000000 -2.9760910000000 -2.0260480000000
H83 -2.0462380000000 -2.5054380000000 -3.6277540000000
C84 -1.6756450000000 0.2413990000000 -3.4441950000000
O85 -2.8943810000000 -0.0026720000000 -4.1429500000000
H86 -2.8871760000000 0.4993930000000 -4.9684600000000
H87 -0.4012150000000 -0.4607620000000 -1.7891330000000
H88 -0.6696430000000 -1.8011110000000 0.0041450000000
H89 -1.7171890000000 1.2168230000000 -2.9366090000000
C90 -0.4747720000000 0.2051220000000 -4.3888990000000
H91 0.4756360000000 0.2385420000000 -3.8452400000000
H92 -0.4900620000000 -0.7045010000000 -4.9951820000000
H93 -0.4984580000000 1.0666470000000 -5.0652350000000
H90 1.3208220000000 -2.0577250000000 -1.3636700000000
H94 0.9565160000000 2.5747690000000 2.1297390000000

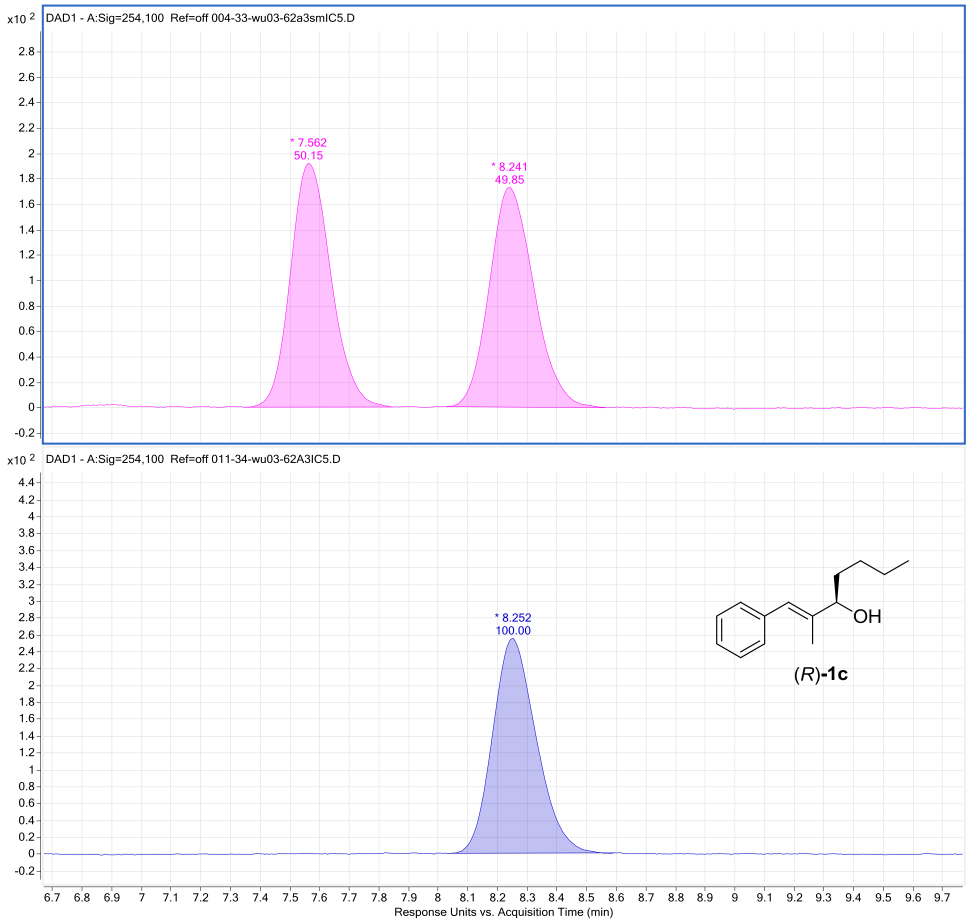
References

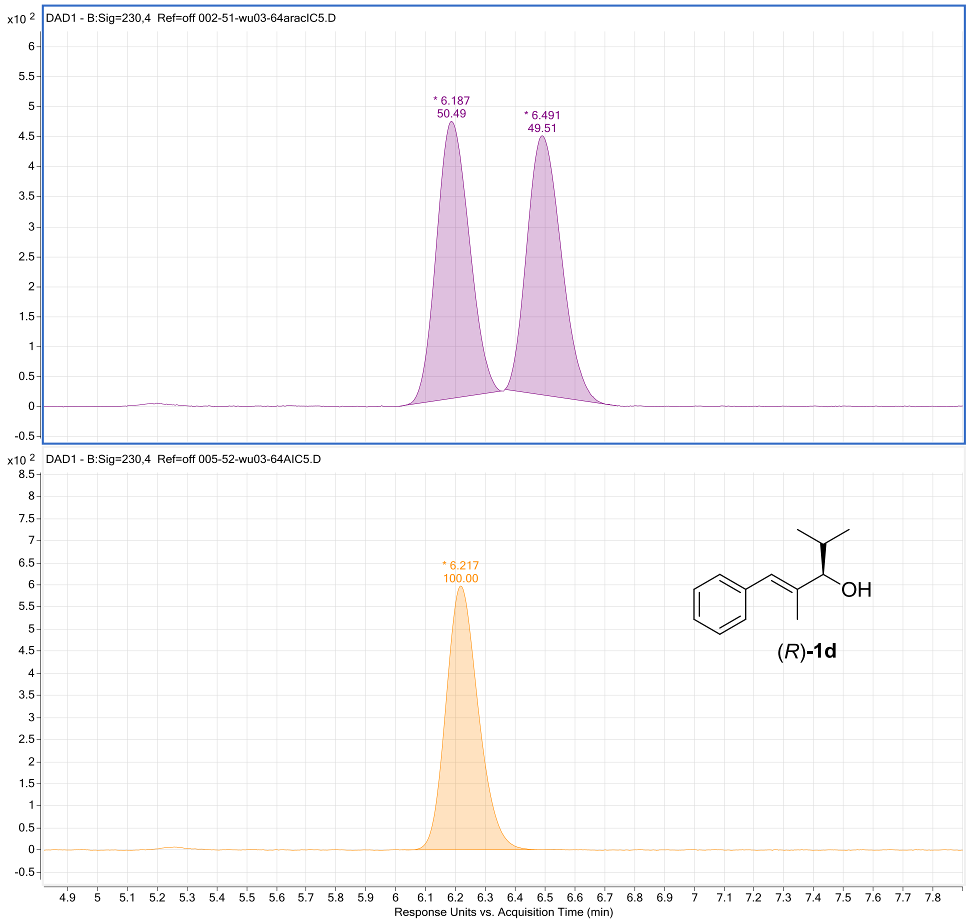
[1]Jaguar, version 7.9, Schrodinger, LLC, New York, NY, 2011.
[2] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785–789.
[3] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
[4] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270–283.

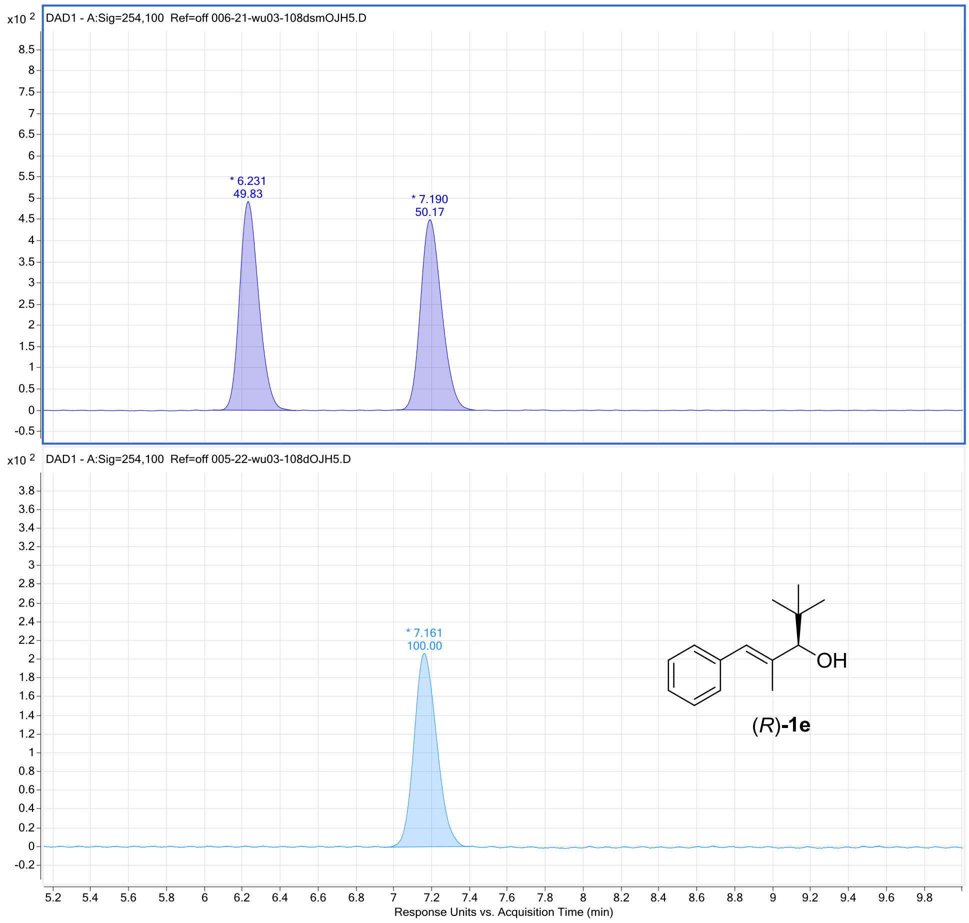
7. SFC and GC Chromatograms

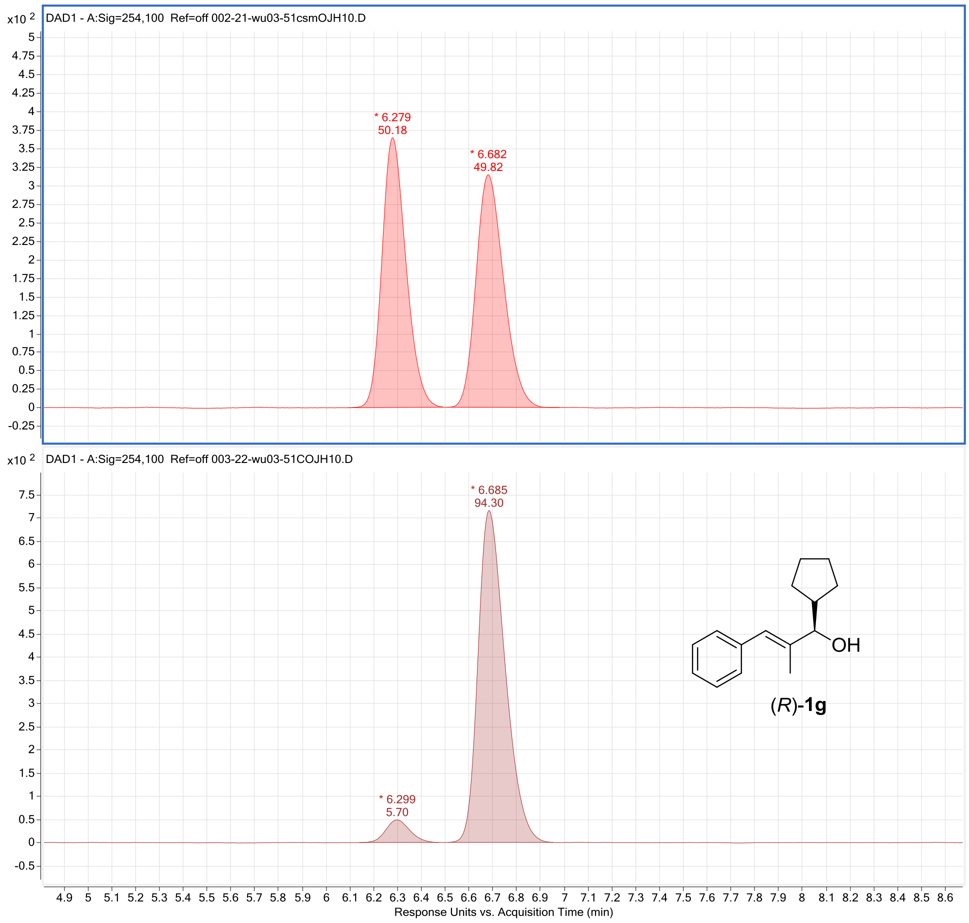


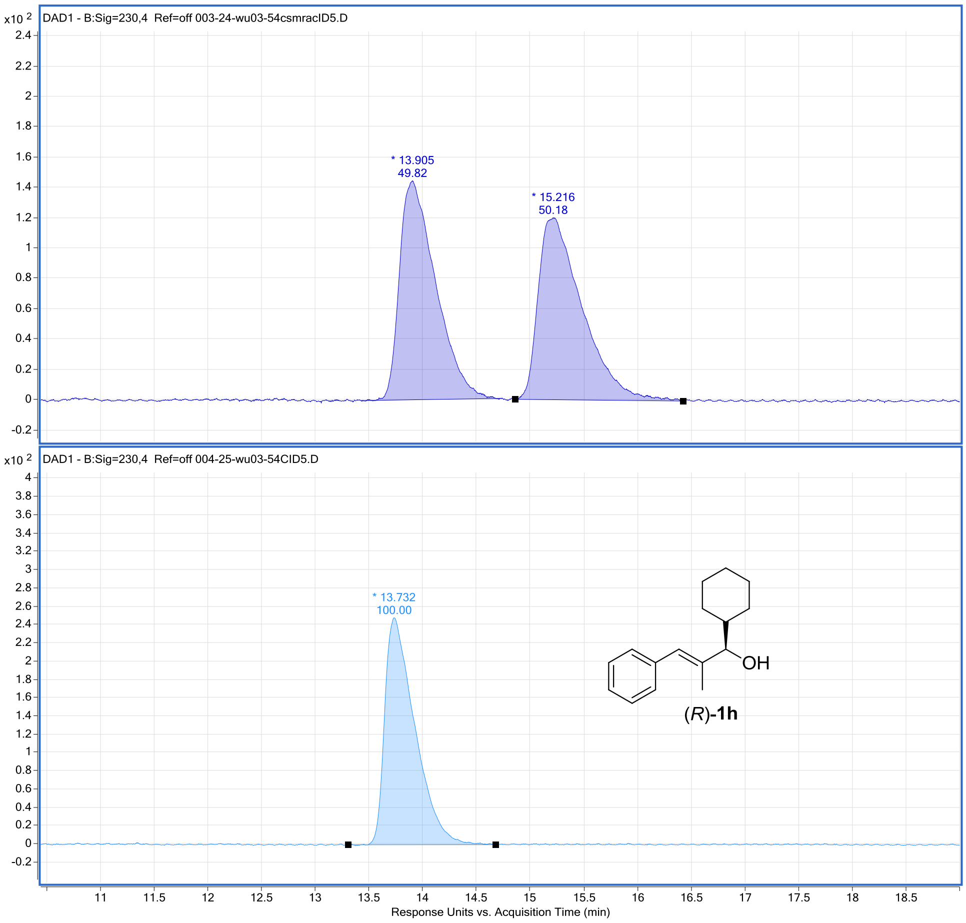

DAD1 - A:Sig=254,100 Ref=off 009-31-wu03-56asmIC5.D
* 7.546
49.92
* 8.154
50.08
DAD1 - A:Sig=254,100 Ref=off 012-32-wu03-56aIC5.D
* 7.636
100.00
OH
(R)-1b
Response Units vs. Acquisition Time (min)

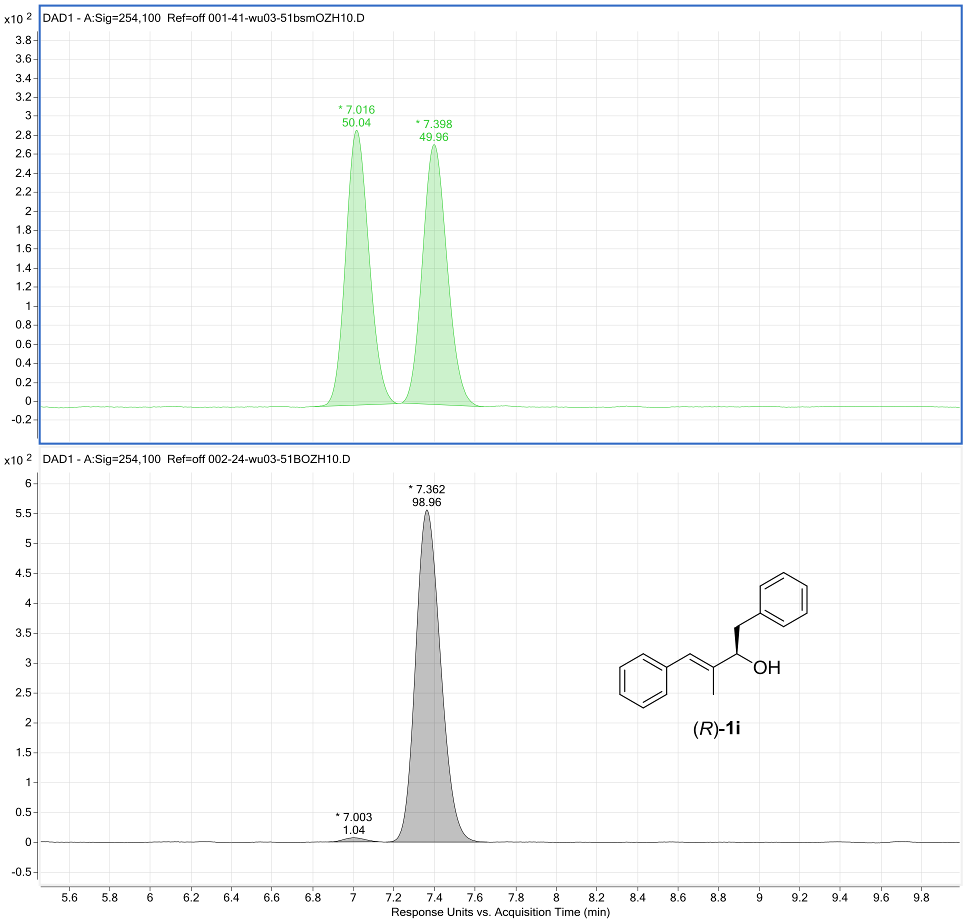

DAD1 - A:Sig=254,100 Ref=off 004-33-wu03-62a3smIC5.D
* 7.562
50.15
* 8.241
49.85
DAD1 - A:Sig=254,100 Ref=off 011-34-wu03-62A3IC5.D
* 8.252
100.00
OH
(R)-1c
Response Units vs. Acquisition Time (min)

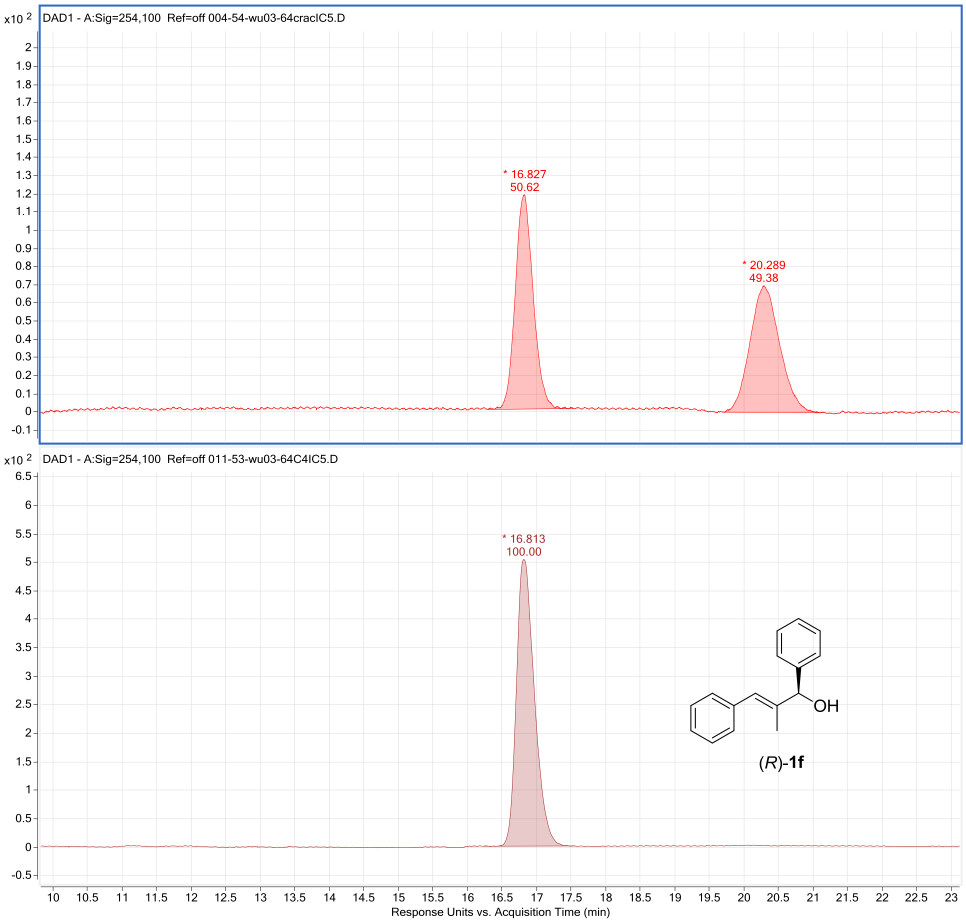

DAD1 - B:Sig=230,4 Ref=off 002-51-wu03-64aracIC5.D
* 6.187
50.49
* 6.491
49.51
DAD1 - B:Sig=230,4 Ref=off 005-52-wu03-64AIC5.D
* 6.217
100.00
OH
(R)-1d
Response Units vs. Acquisition Time (min)

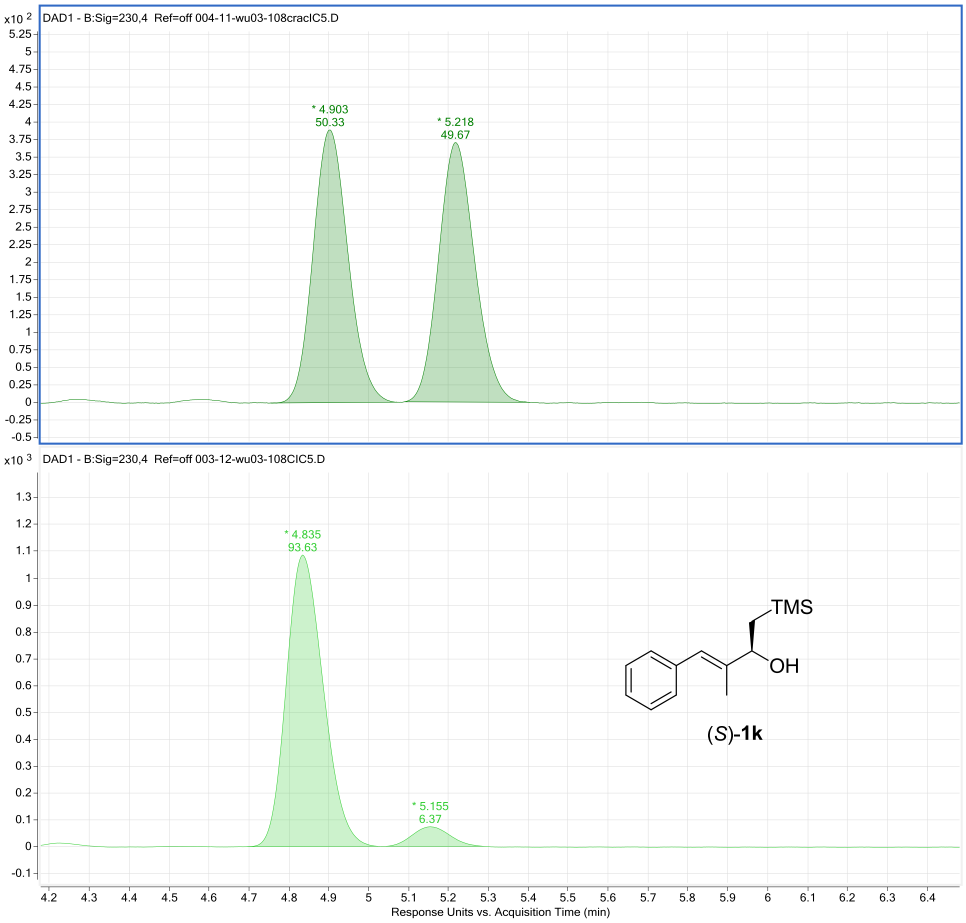

x10 2
DAD1 - A:Sig=254,100 Ref=off 006-21-wu03-108dsmOJH5.D
* 6.231
49.83
* 7.190
50.17
x10 2
DAD1 - A:Sig=254,100 Ref=off 005-22-wu03-108dOJH5.D
* 7.161
100.00
OH
(R)-1e
Response Units vs. Acquisition Time (min)

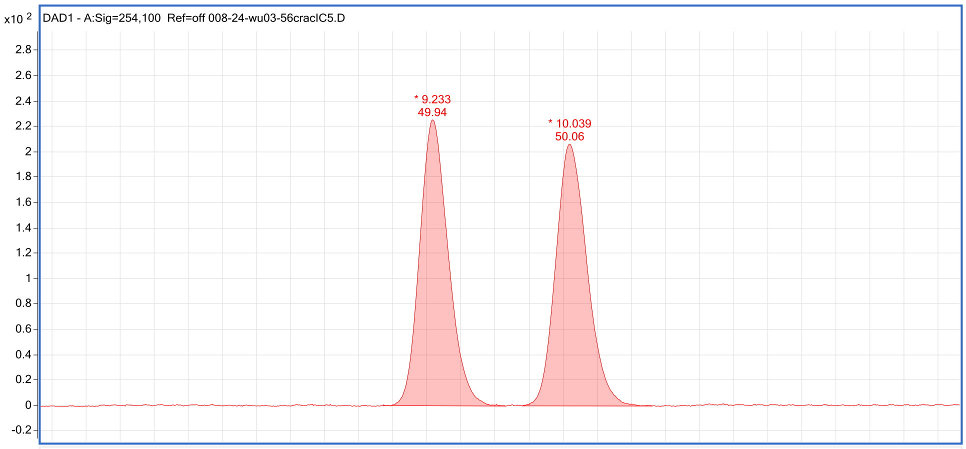

x10 2
DAD1 - A:Sig=254,100 Ref=off 002-21-wu03-51csmOJH10.D
* 6.279
50.18
* 6.682
49.82
x10 2
DAD1 - A:Sig=254,100 Ref=off 003-22-wu03-51COJH10.D
* 6.685
94.30
* 6.299
5.70
OH
(R)-1g
Response Units vs. Acquisition Time (min)

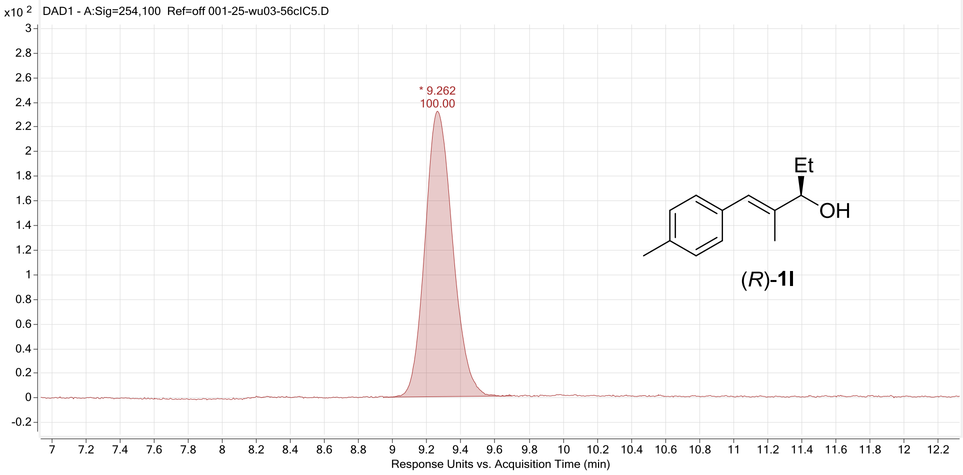

DAD1 - B:Sig=230,4 Ref=off 003-24-wu03-54csmracID5.D
* 13.905
49.82
* 15.216
50.18
DAD1 - B:Sig=230,4 Ref=off 004-25-wu03-54CID5.D
* 13.732
100.00
OH
(R)-1h
Response Units vs. Acquisition Time (min)

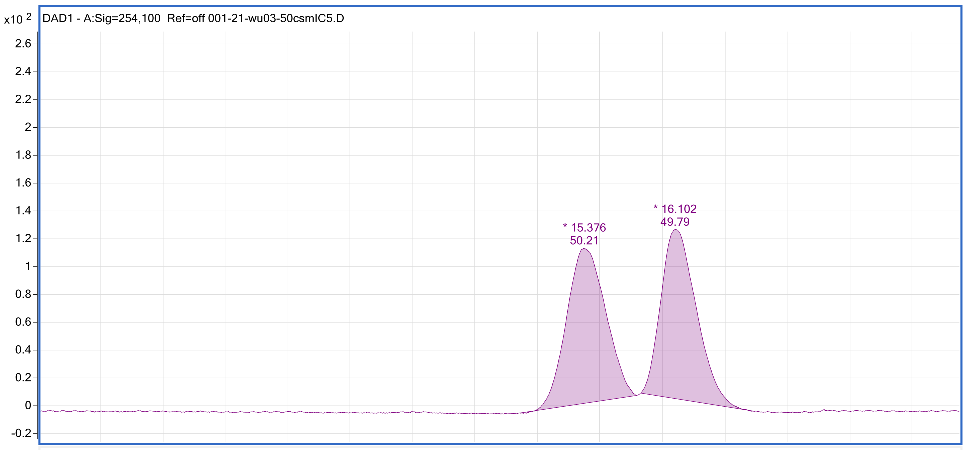

DAD1 - A:Sig=254,100 Ref=off 001-41-wu03-51bsmOZH10.D
* 7.016
50.04
* 7.398
49.96
DAD1 - A:Sig=254,100 Ref=off 002-24-wu03-51BOZH10.D
* 7.362
98.96
* 7.003
1.04
OH
(R)-1i
Response Units vs. Acquisition Time (min)

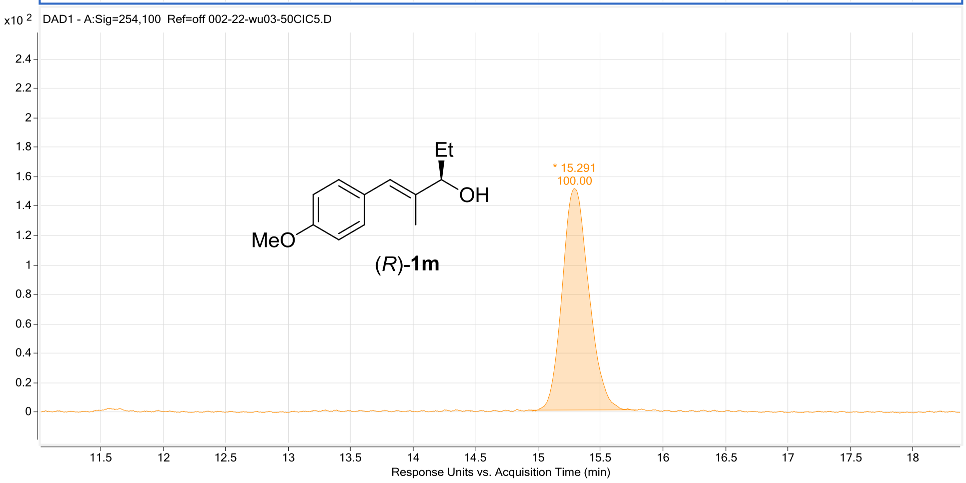

DAD1 - A:Sig=254,100 Ref=off 004-54-wu03-64cracIC5.D
* 16.827
50.62
* 20.289
49.38
DAD1 - A:Sig=254,100 Ref=off 011-53-wu03-64C4IC5.D
* 16.813
100.00
OH
(R)-1f
Response Units vs. Acquisition Time (min)

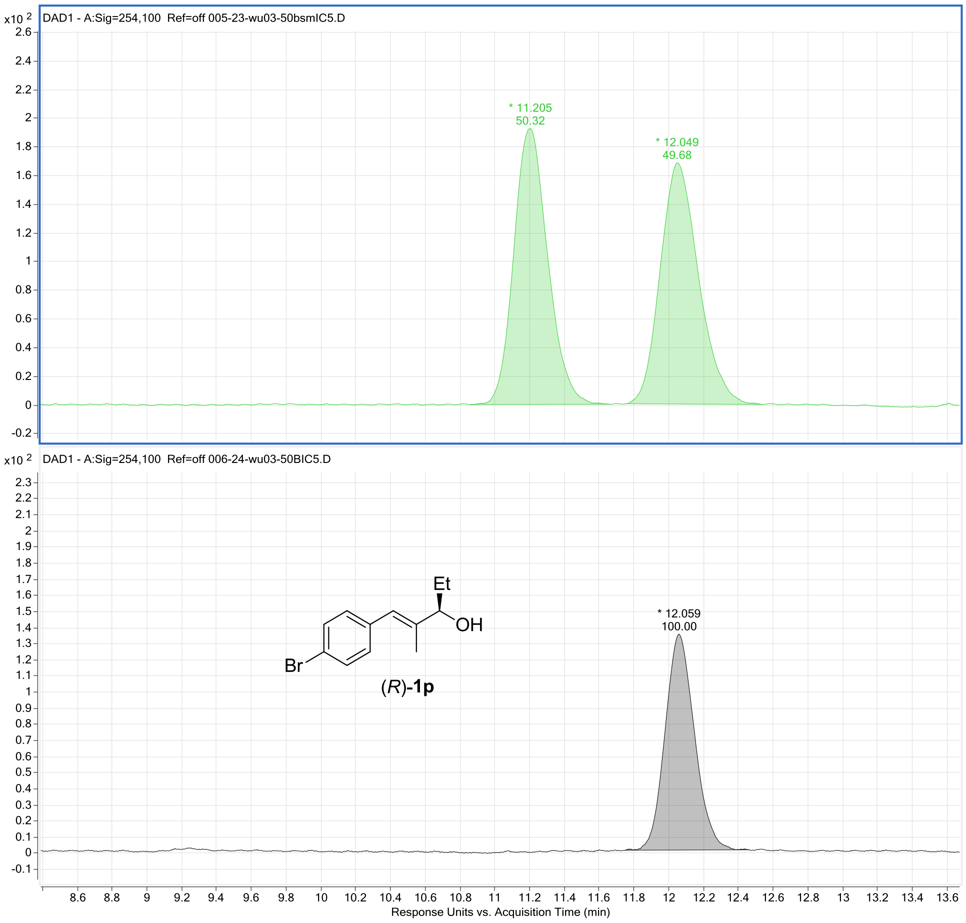

DAD1 - B:Sig=230,4 Ref=off 004-11-wu03-108cracIC5.D
* 4.903
50.33
* 5.218
49.67
DAD1 - B:Sig=230,4 Ref=off 003-12-wu03-108CIC5.D
* 4.835
93.63
* 5.155
6.37
TMS
OH
(S)-1k
Response Units vs. Acquisition Time (min)

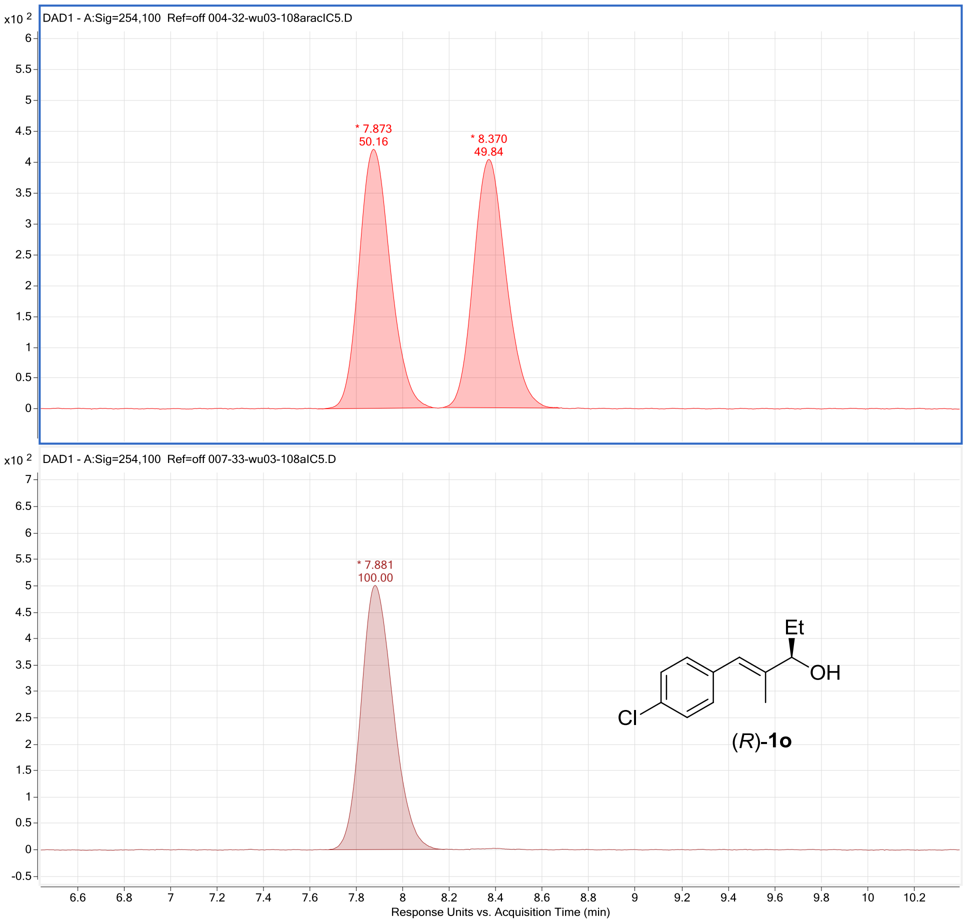

x10 2
DAD1 - A:Sig=254,100 Ref=off 008-24-wu03-56cracIC5.D
* 9.233
49.94
* 10.039
50.06

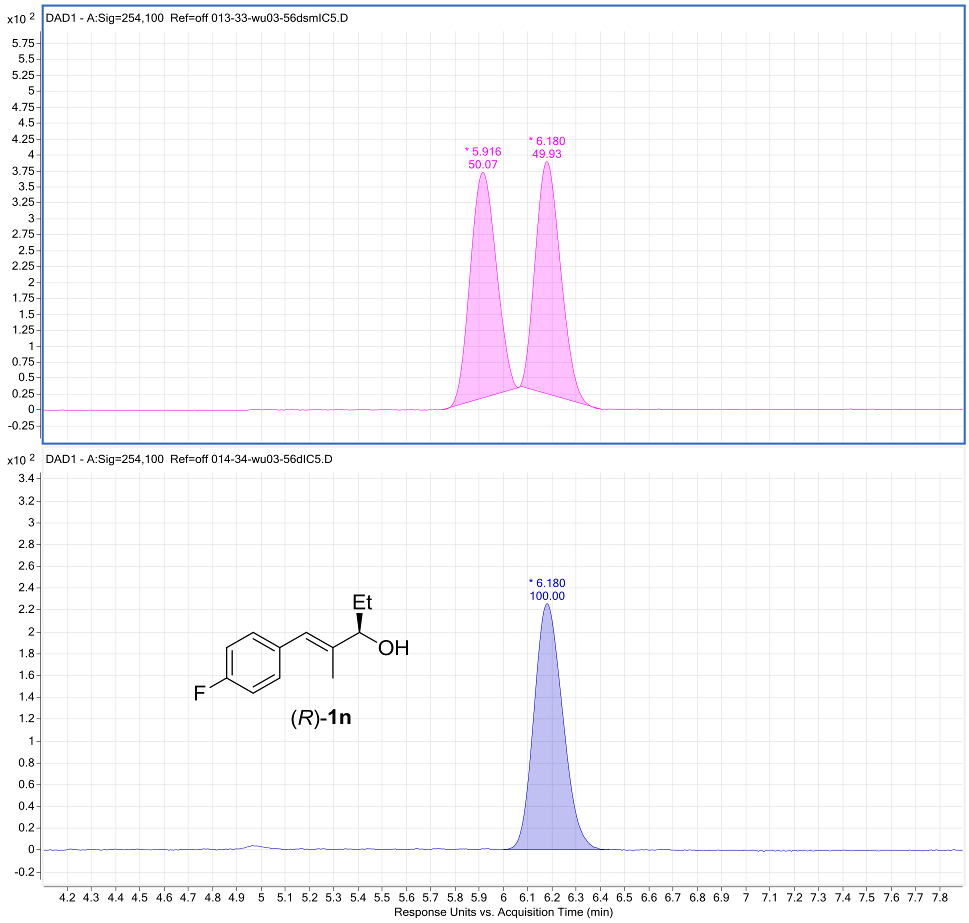

x10 2
DAD1 - A:Sig=254,100 Ref=off 001-25-wu03-56cIC5.D
* 9.262
100.00
Et
OH
(R)-1l
Response Units vs. Acquisition Time (min)

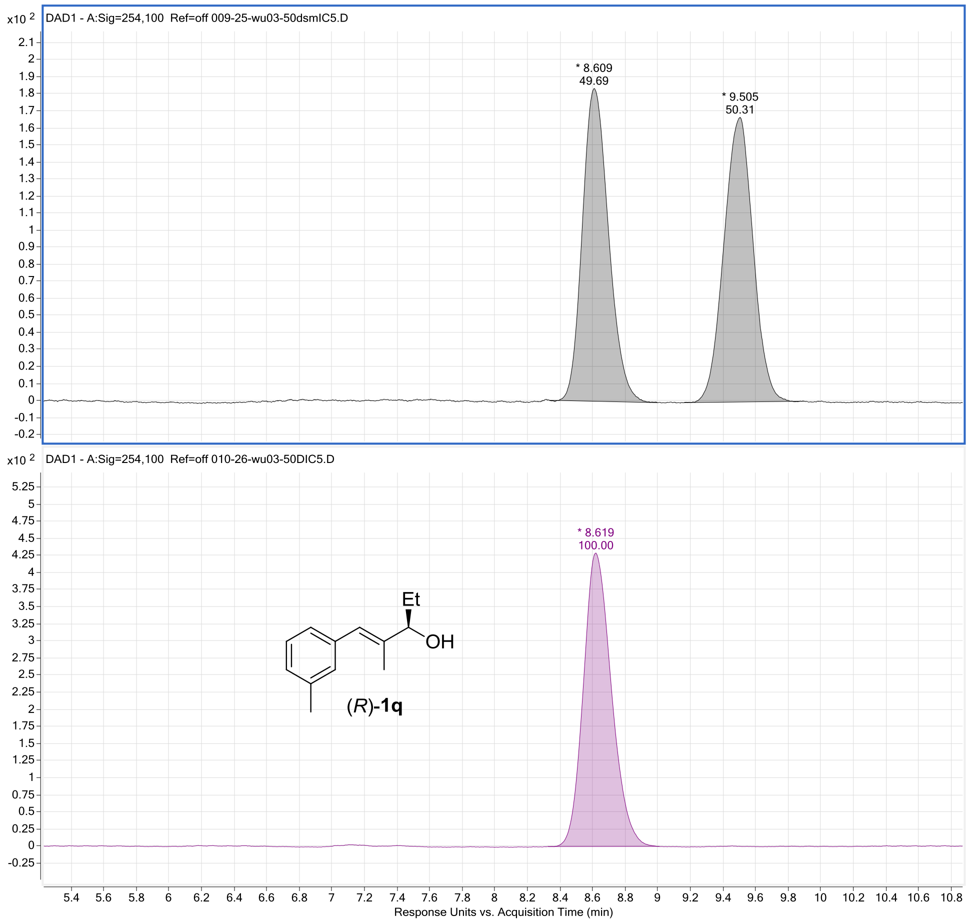

x10 2
DAD1 - A:Sig=254,100 Ref=off 001-21-wu03-50csmIC5.D
* 15.376
50.21
* 16.102
49.79

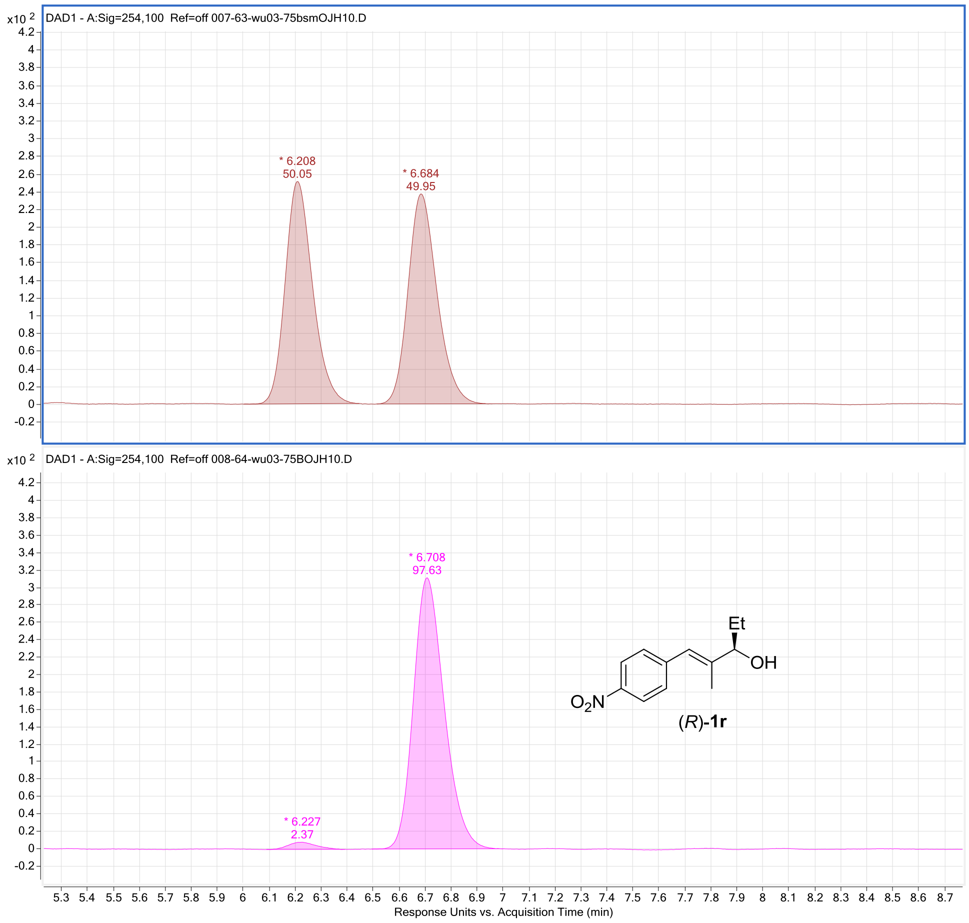

x10 2
DAD1 - A:Sig=254,100 Ref=off 002-22-wu03-50CIC5.D
Et
OH
MeO
(R)-1m
* 15.291
100.00
Response Units vs. Acquisition Time (min)

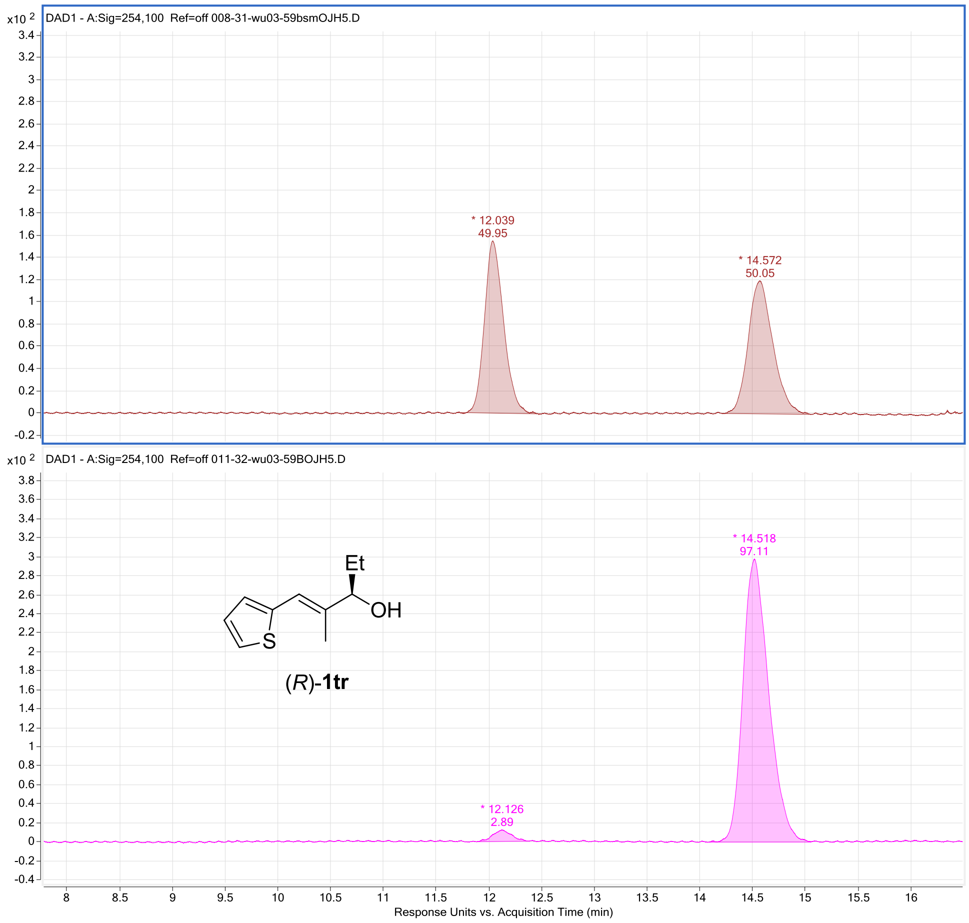

DAD1 - A:Sig=254,100 Ref=off 005-23-wu03-50bsmIC5.D
* 11.205
50.32
* 12.049
49.68
DAD1 - A:Sig=254,100 Ref=off 006-24-wu03-50BIC5.D
* 12.059
100.00
Et
OH
Br
(R)-1p
Response Units vs. Acquisition Time (min)

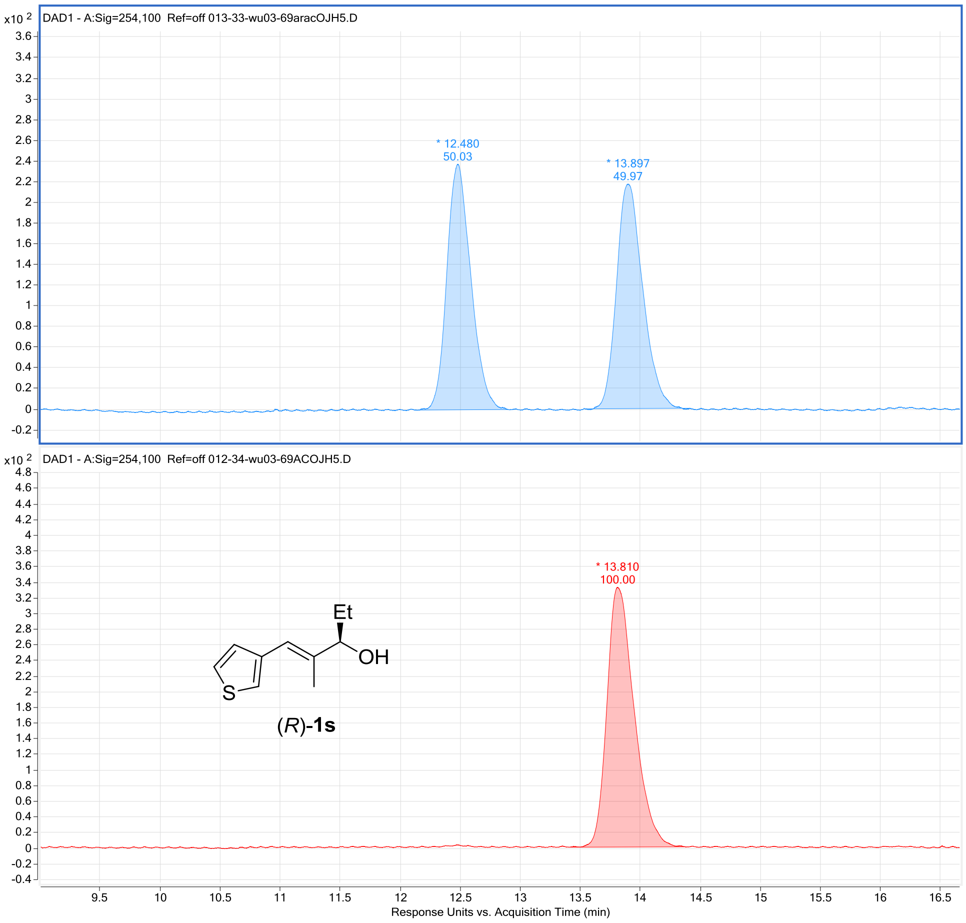

DAD1 - A:Sig=254,100 Ref=off 004-32-wu03-108aracIC5.D
* 7.873
50.16
* 8.370
49.84
DAD1 - A:Sig=254,100 Ref=off 007-33-wu03-108aIC5.D
* 7.881
100.00
Et
OH
Cl
(R)-1o
Response Units vs. Acquisition Time (min)

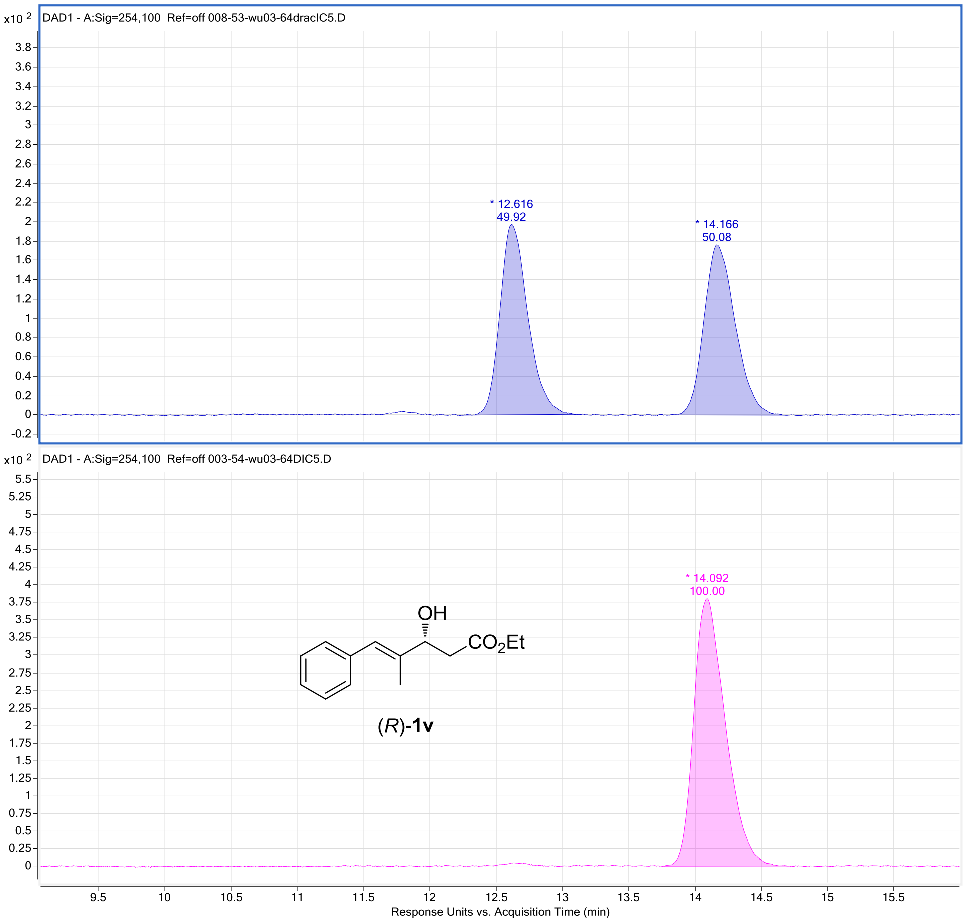

DAD1 - A:Sig=254,100 Ref=off 013-33-wu03-56dsmIC5.D
x10 2
* 5.916
50.07
* 6.180
49.93
DAD1 - A:Sig=254,100 Ref=off 014-34-wu03-56dIC5.D
* 6.180
100.00
Et
OH
F
(R)-1n
Response Units vs. Acquisition Time (min)

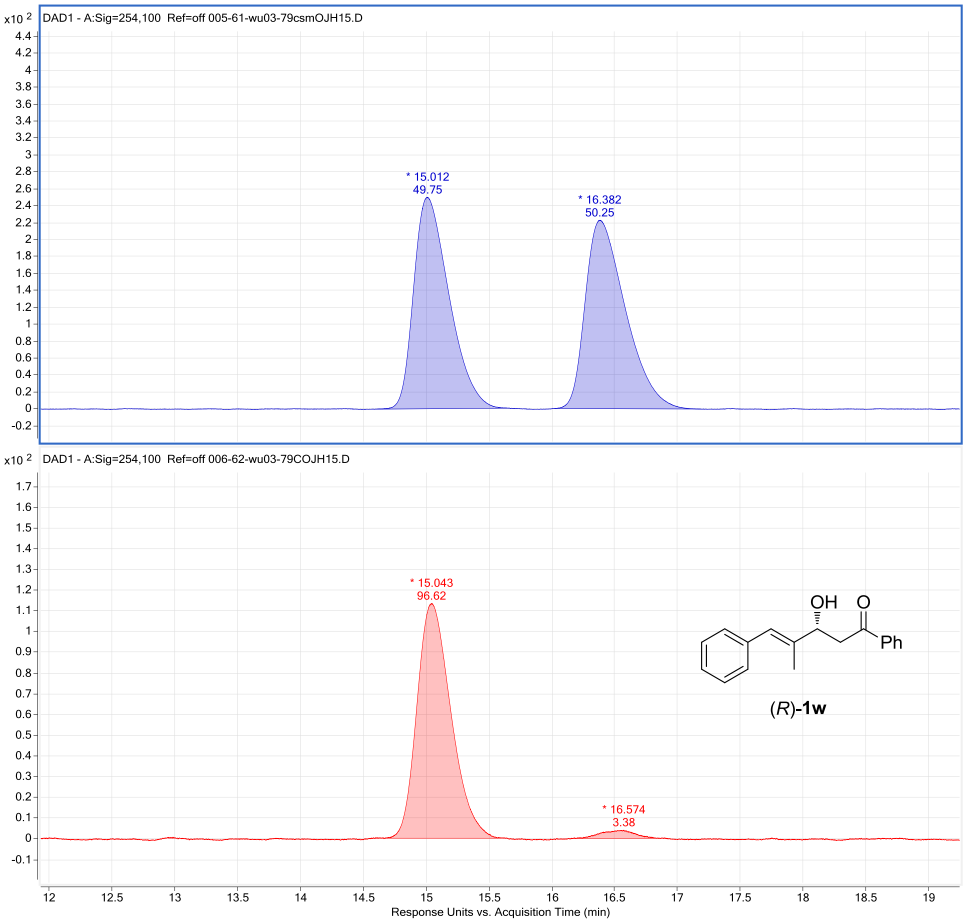

DAD1 - A:Sig=254,100 Ref=off 009-25-wu03-50dsmIC5.D
x10 2
* 8.609
49.69
* 9.505
50.31
DAD1 - A:Sig=254,100 Ref=off 010-26-wu03-50DIC5.D
* 8.619
100.00
Et
OH
(R)-1q
Response Units vs. Acquisition Time (min)

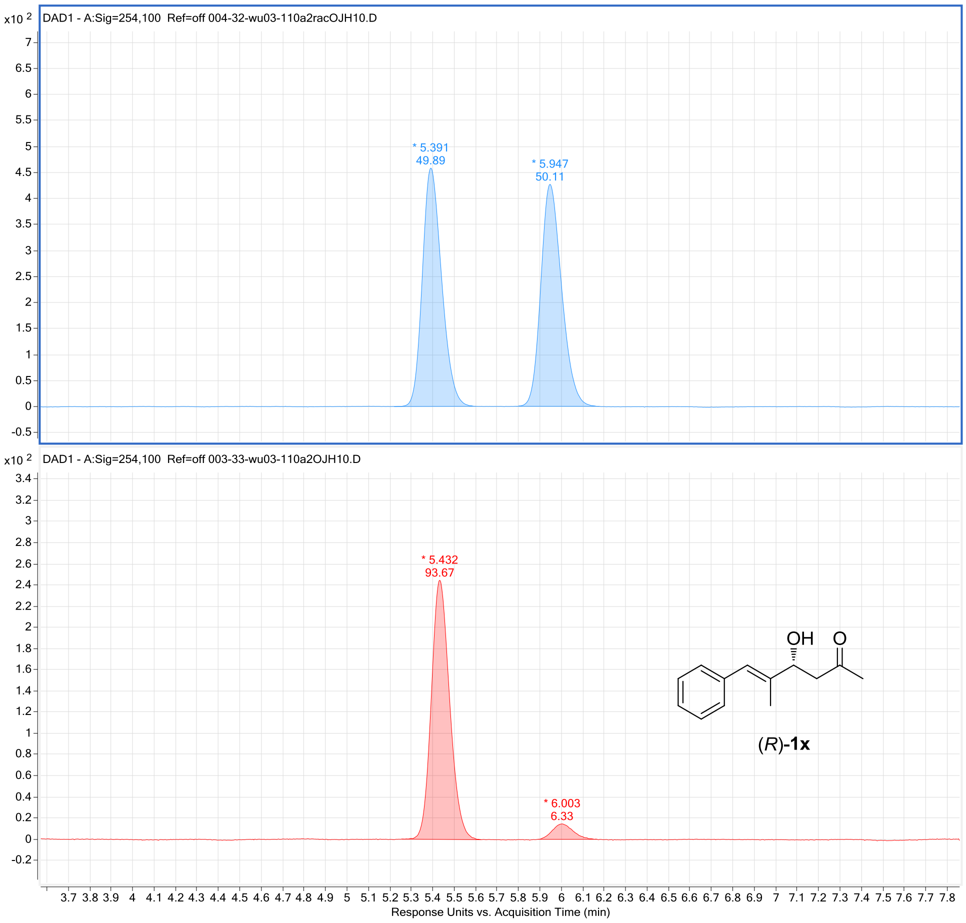

DAD1 - A:Sig=254,100 Ref=off 007-63-wu03-75bsmOJH10.D
* 6.208
50.05
* 6.684
49.95
DAD1 - A:Sig=254,100 Ref=off 008-64-wu03-75BOJH10.D
* 6.708
97.63
* 6.227
2.37
Et
OH
O_2N
(R)-1r
Response Units vs. Acquisition Time (min)

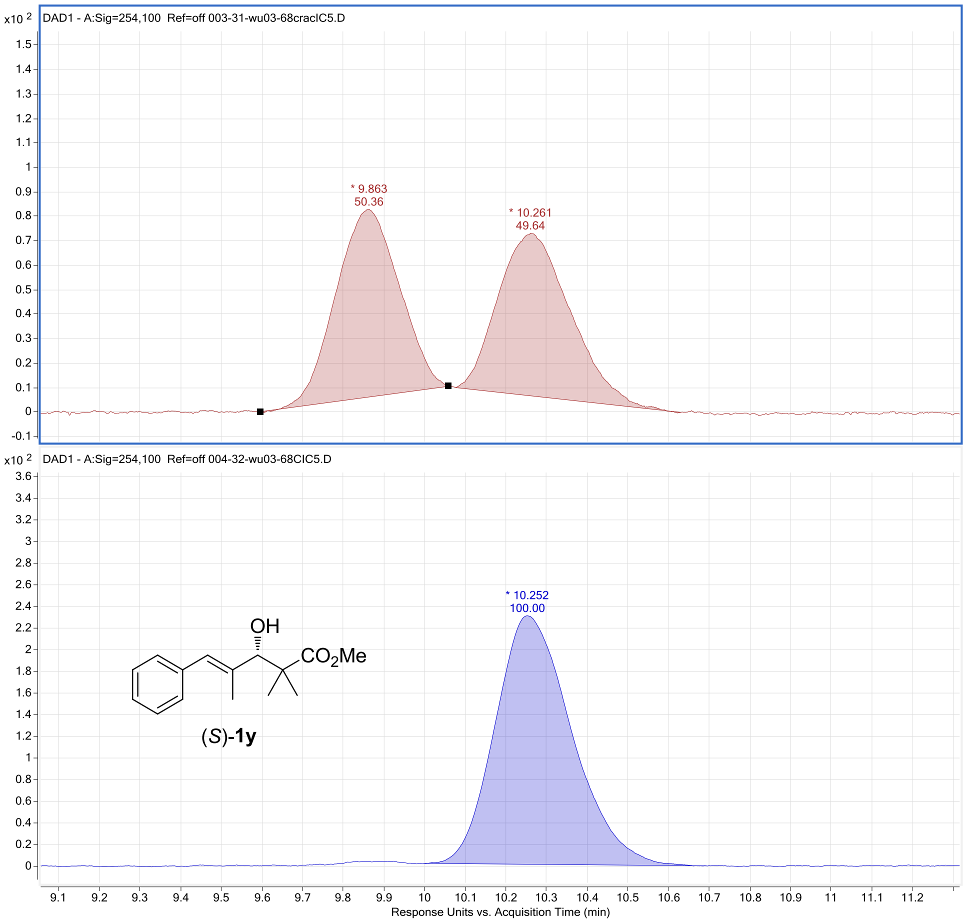

DAD1 - A:Sig=254,100 Ref=off 008-31-wu03-59bsmOJH5.D
* 12.039
49.95
* 14.572
50.05
DAD1 - A:Sig=254,100 Ref=off 011-32-wu03-59BOJH5.D
* 14.518
97.11
* 12.126
2.89
Et
OH
S
(R)-1tr
Response Units vs. Acquisition Time (min)

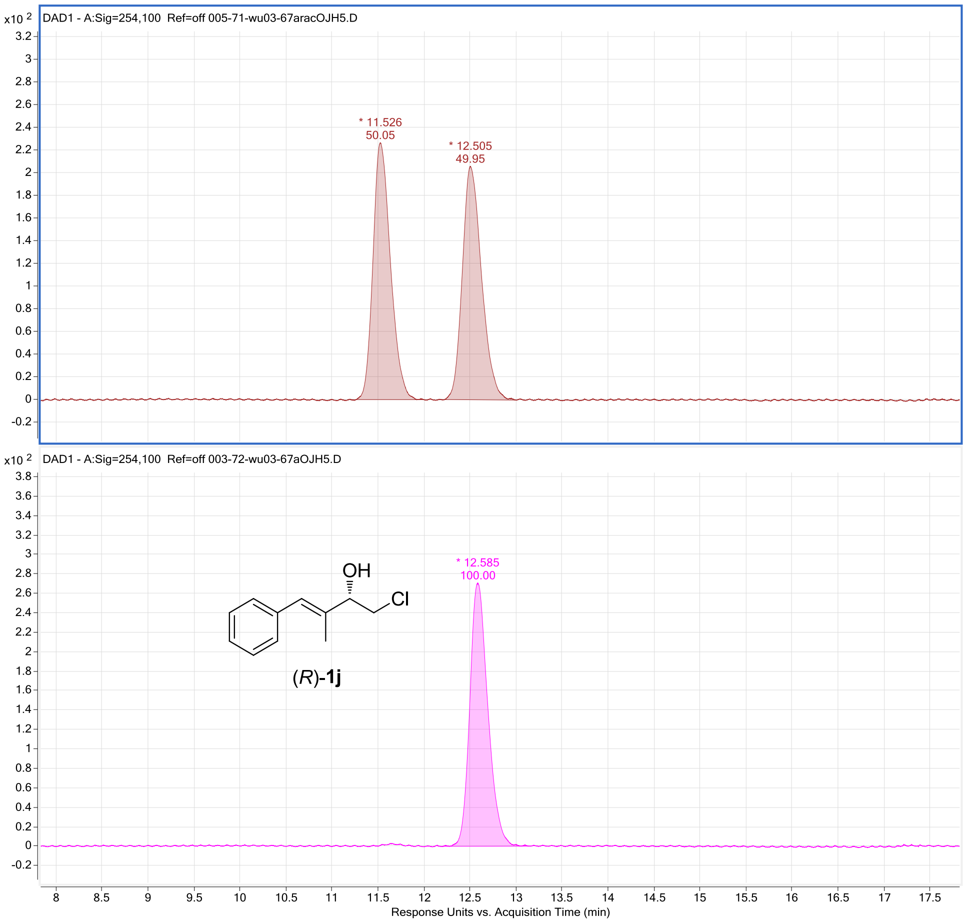

x10 2
DAD1 - A:Sig=254,100 Ref=off 013-33-wu03-69aracOJH5.D
* 12.480
50.03
* 13.897
49.97
DAD1 - A:Sig=254,100 Ref=off 012-34-wu03-69ACOJH5.D
* 13.810
100.00
Et
OH
S
(R)-1s
Response Units vs. Acquisition Time (min)

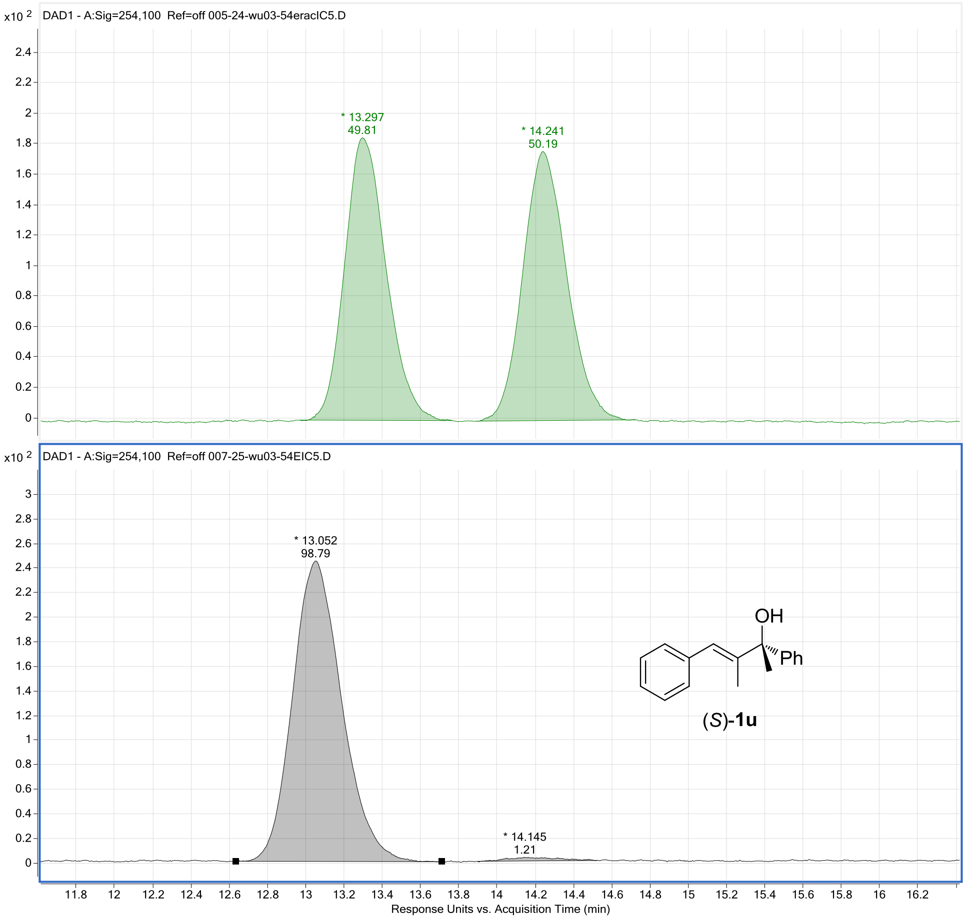

x10 2
DAD1 - A:Sig=254,100 Ref=off 008-53-wu03-64dracIC5.D
* 12.616
49.92
* 14.166
50.08
DAD1 - A:Sig=254,100 Ref=off 003-54-wu03-64DIC5.D
* 14.092
100.00
OH
CO2Et
(R)-1v
Response Units vs. Acquisition Time (min)

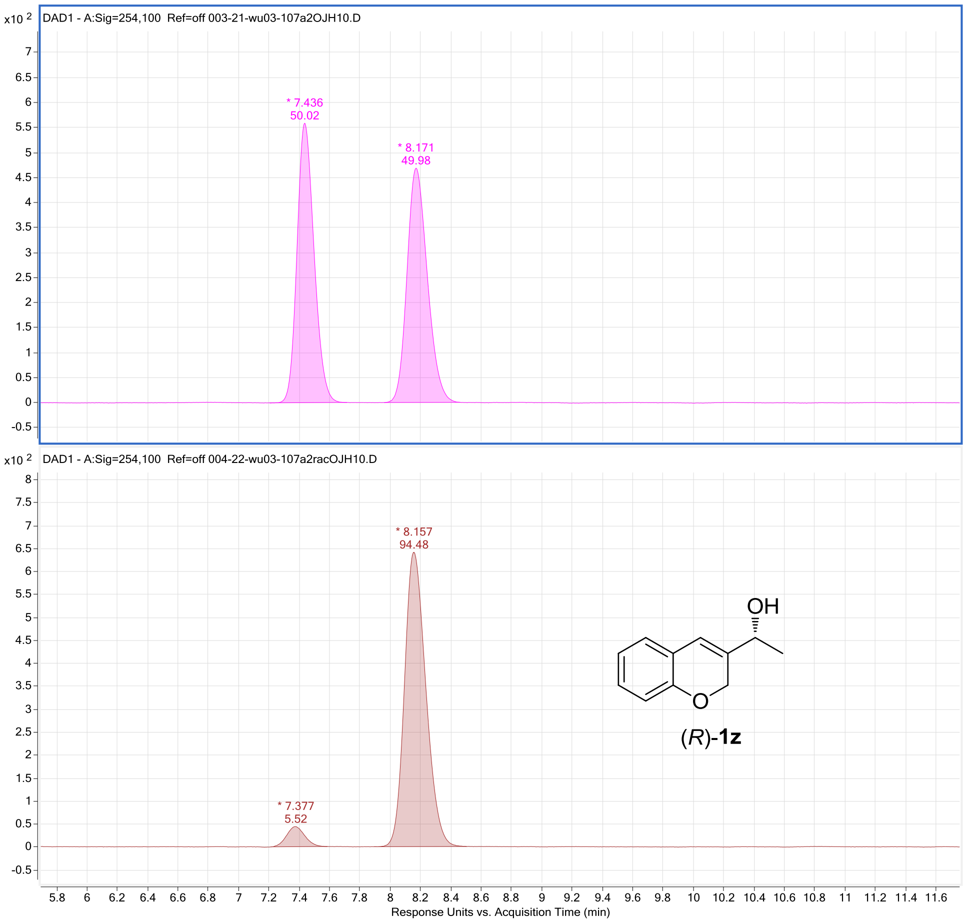

DAD1 - A:Sig=254,100 Ref=off 005-61-wu03-79csmOJH15.D
* 15.012
49.75
* 16.382
50.25
DAD1 - A:Sig=254,100 Ref=off 006-62-wu03-79COJH15.D
* 15.043
96.62
* 16.574
3.38
OH
O
Ph
(R)-1w
Response Units vs. Acquisition Time (min)

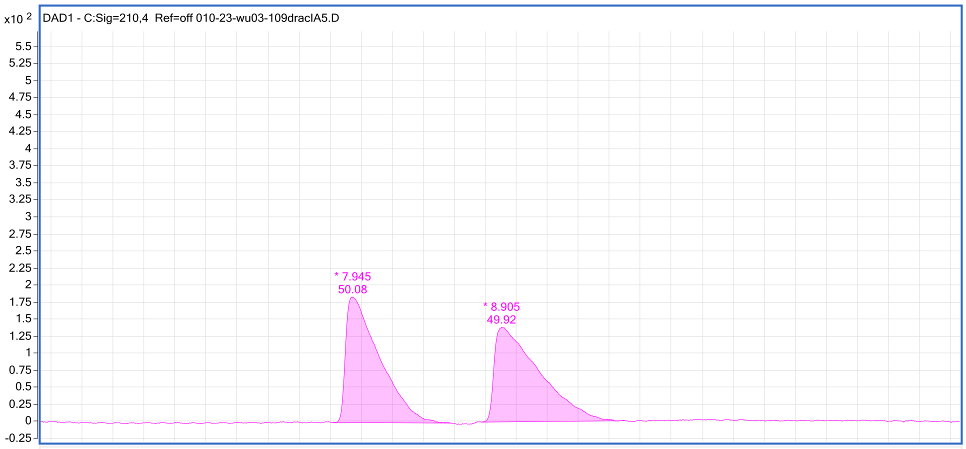

DAD1 - A:Sig=254,100 Ref=off 004-32-wu03-110a2racOJH10.D
* 5.391
49.89
* 5.947
50.11
DAD1 - A:Sig=254,100 Ref=off 003-33-wu03-110a2OJH10.D
* 5.432
93.67
* 6.003
6.33
OH
O
(R)-1x
Response Units vs. Acquisition Time (min)

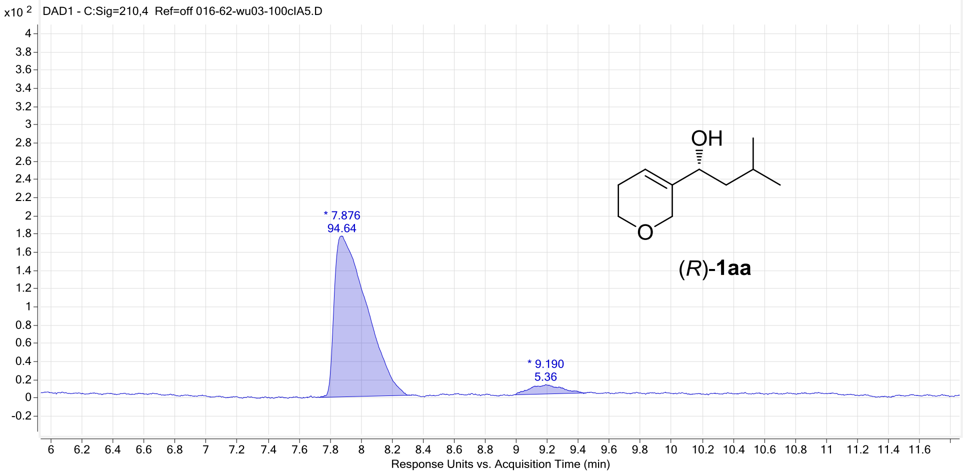

DAD1 - A:Sig=254,100 Ref=off 003-31-wu03-68cracIC5.D
* 9.863
50.36
* 10.261
49.64
DAD1 - A:Sig=254,100 Ref=off 004-32-wu03-68CIC5.D
* 10.252
100.00
OH
CO2Me
(S)-1y
Response Units vs. Acquisition Time (min)

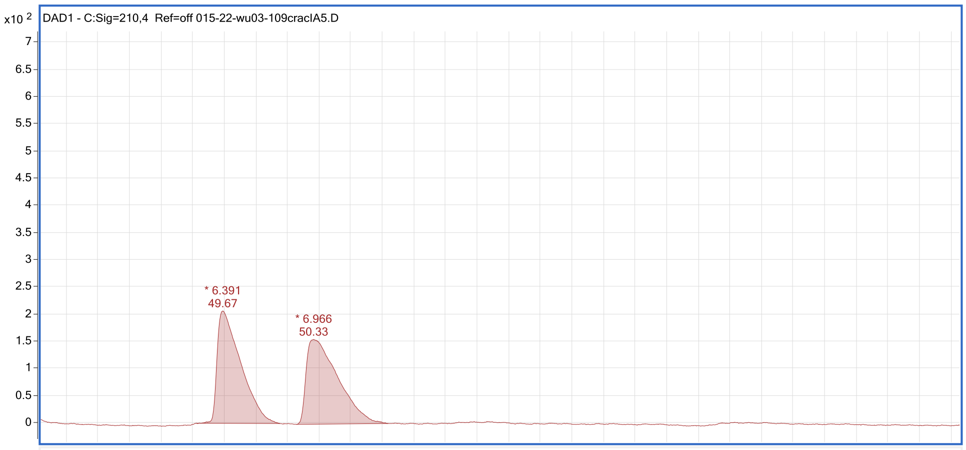

DAD1 - A:Sig=254,100 Ref=off 005-71-wu03-67aracOJH5.D
* 11.526
50.05
* 12.505
49.95
DAD1 - A:Sig=254,100 Ref=off 003-72-wu03-67aOJH5.D
* 12.585
100.00
OH
Cl
(R)-1j
Response Units vs. Acquisition Time (min)

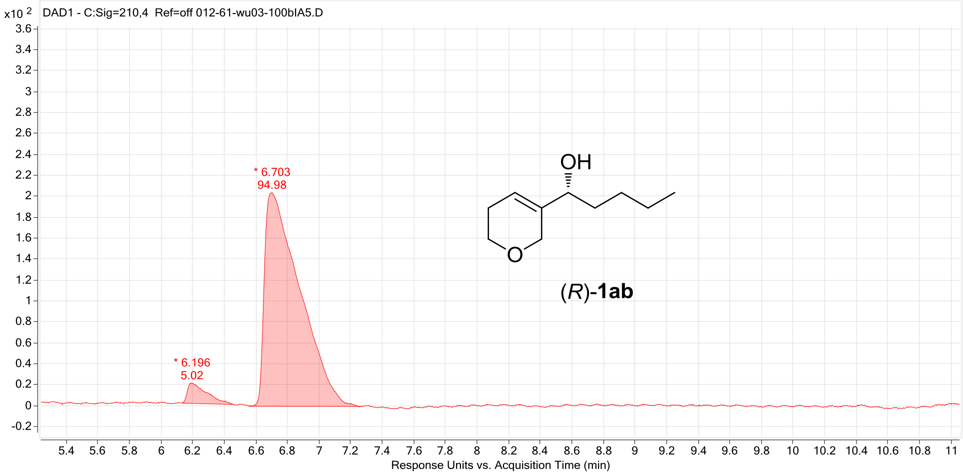

DAD1 - A:Sig=254,100 Ref=off 005-24-wu03-54eracIC5.D
* 13.297
49.81
* 14.241
50.19
DAD1 - A:Sig=254,100 Ref=off 007-25-wu03-54EIC5.D
* 13.052
98.79
* 14.145
1.21
OH
Ph
(S)-1u
Response Units vs. Acquisition Time (min)

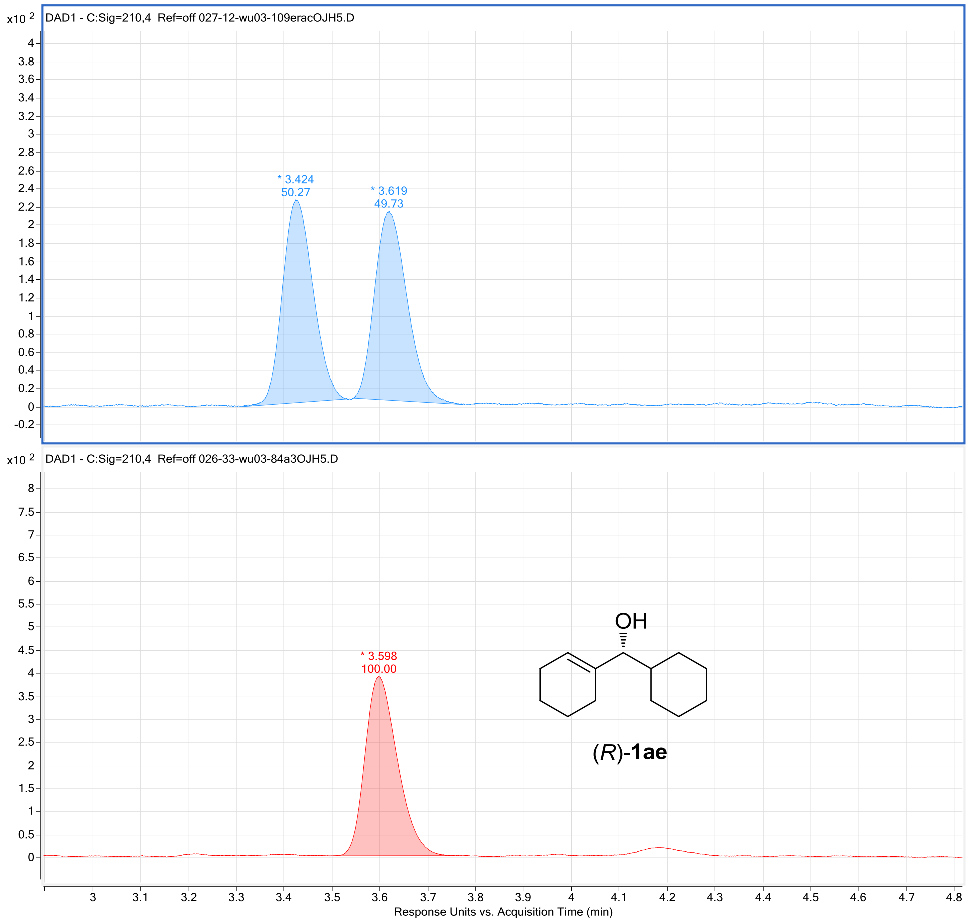

DAD1 - A:Sig=254,100 Ref=off 003-21-wu03-107a2OJH10.D
* 7.436
50.02
* 8.171
49.98
DAD1 - A:Sig=254,100 Ref=off 004-22-wu03-107a2racOJH10.D
* 8.157
94.48
* 7.377
5.52
OH
O
(R)-1z
Response Units vs. Acquisition Time (min)

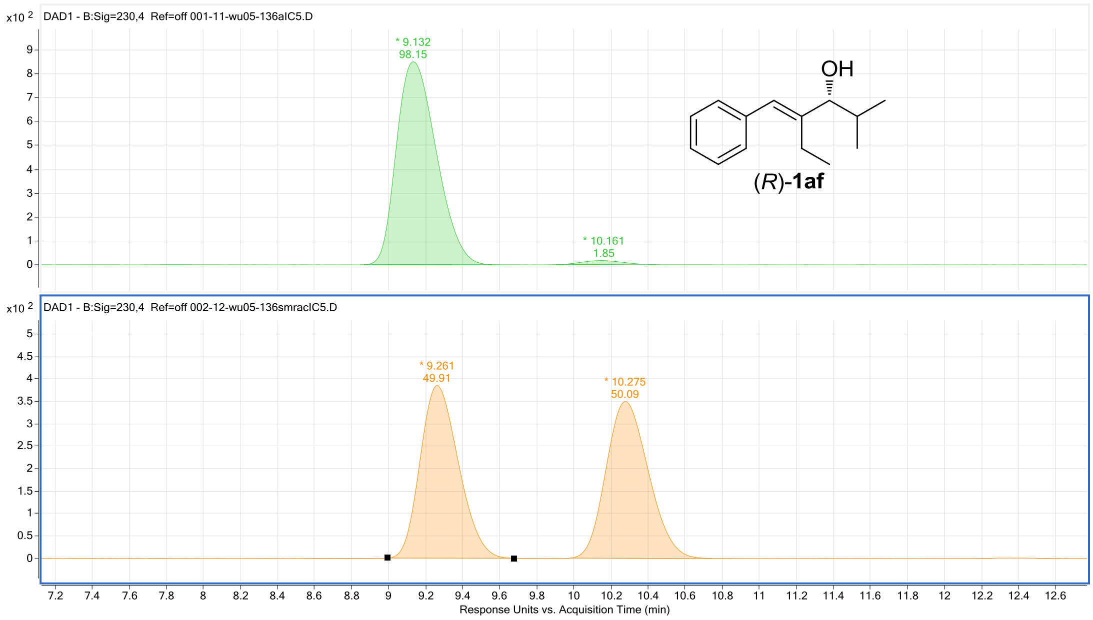

x10 2
DAD1 - C:Sig=210,4 Ref=off 010-23-wu03-109draclA5.D
* 7.945
50.08
* 8.905
49.92

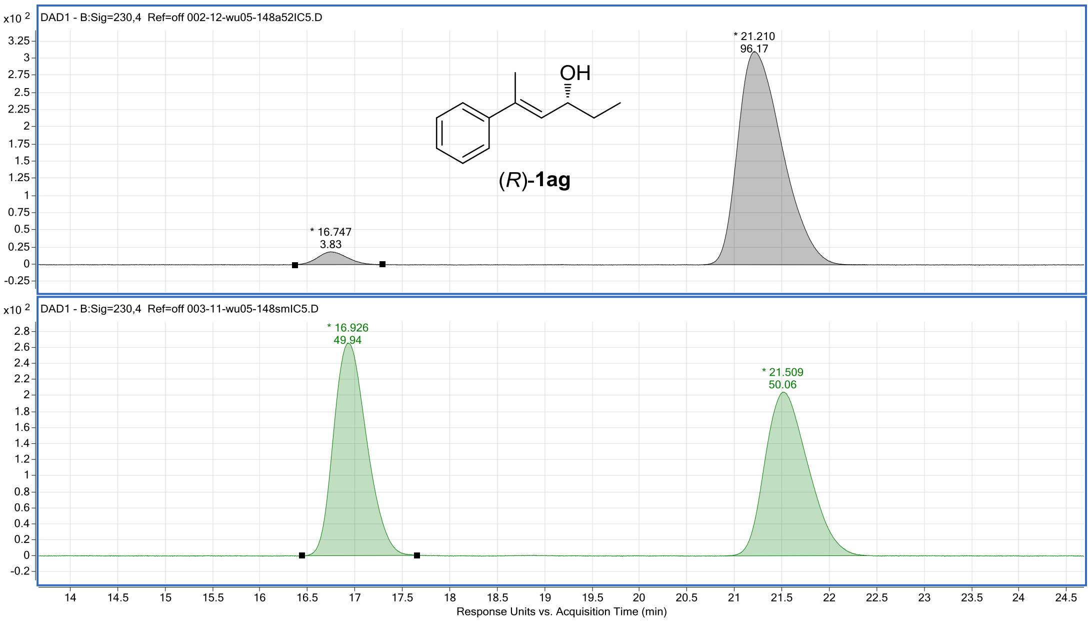

x10 2
DAD1 - C:Sig=210,4 Ref=off 016-62-wu03-100clA5.D
* 7.876
94.64
* 9.190
5.36
OH
O
(R)-1aa
Response Units vs. Acquisition Time (min)

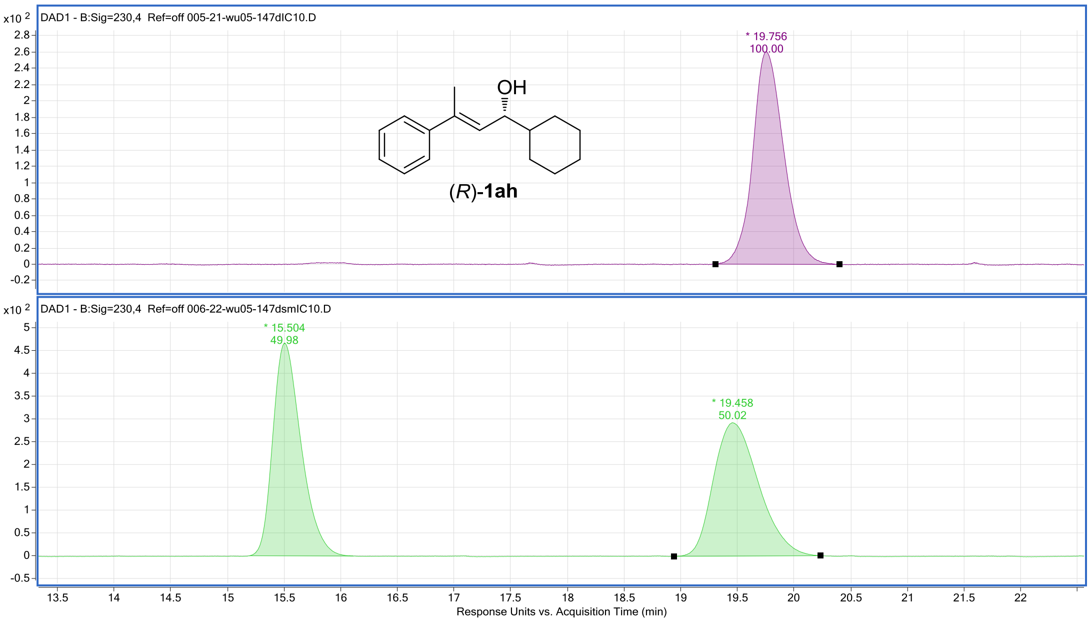

x10 2
DAD1 - C:Sig=210,4 Ref=off 015-22-wu03-109craclA5.D
* 6.391
49.67
* 6.966
50.33

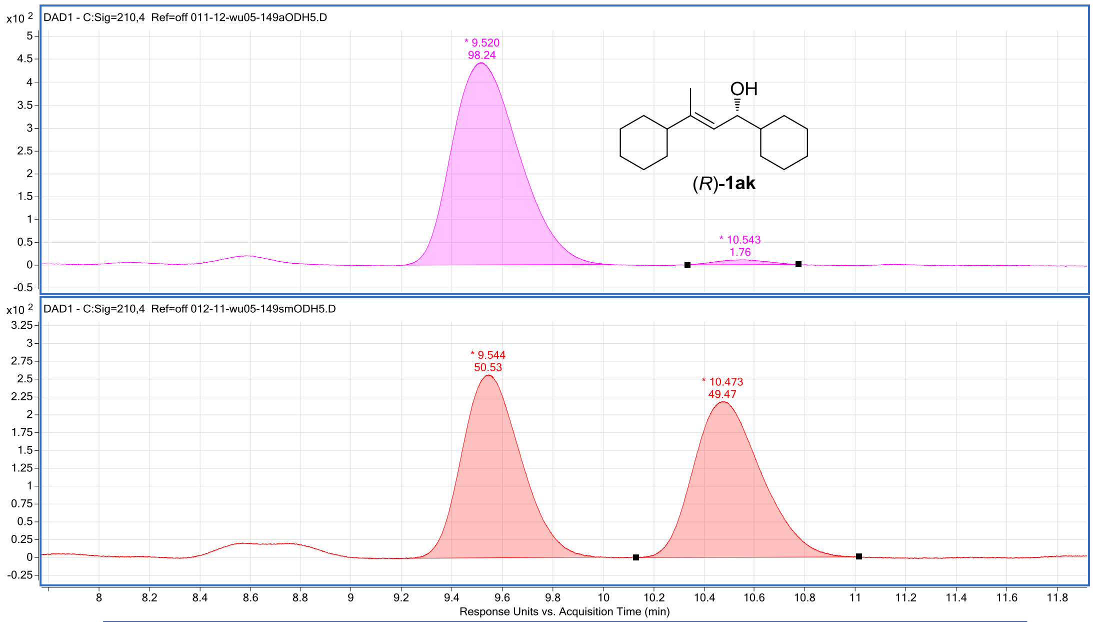

x10 2
DAD1 - C:Sig=210,4 Ref=off 012-61-wu03-100blA5.D
* 6.703
94.98
* 6.196
5.02
OH
O
(R)-1ab
Response Units vs. Acquisition Time (min)

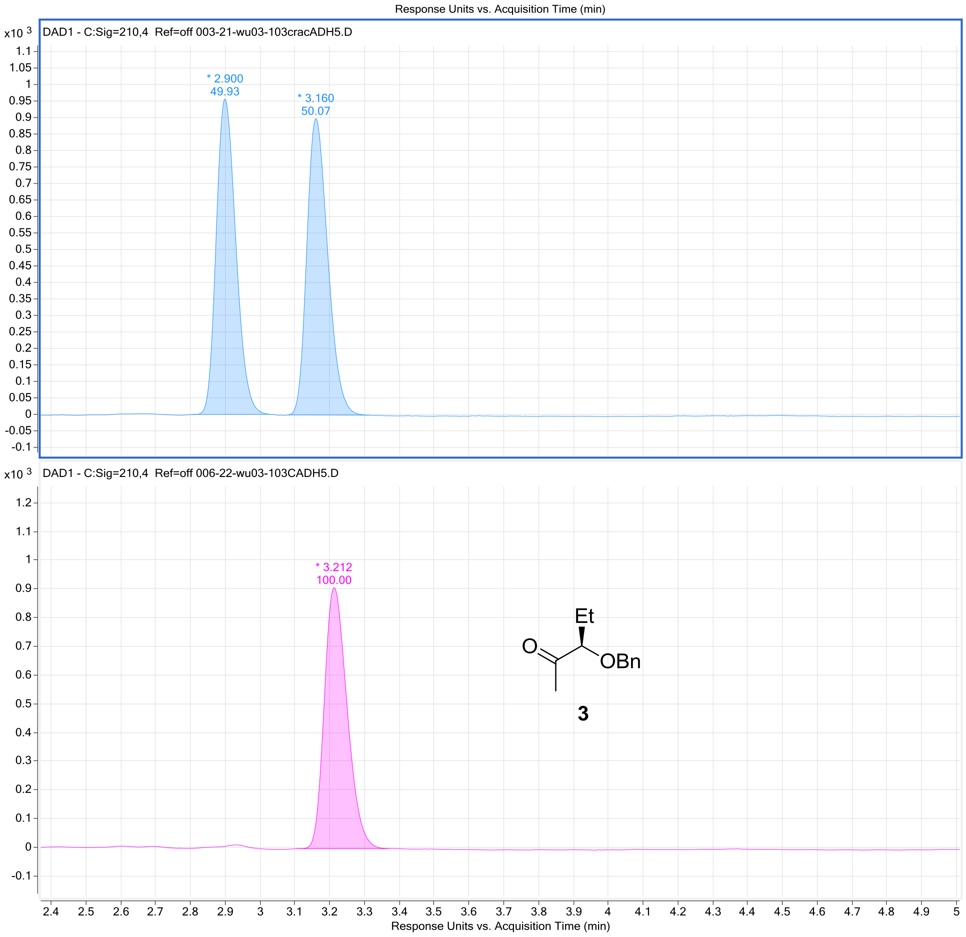

DAD1 - C:Sig=210,4 Ref=off 027-12-wu03-109eracOJH5.D
* 3.424
50.27
* 3.619
49.73
DAD1 - C:Sig=210,4 Ref=off 026-33-wu03-84a3OJH5.D
* 3.598
100.00
OH
(R)-1ae
Response Units vs. Acquisition Time (min)

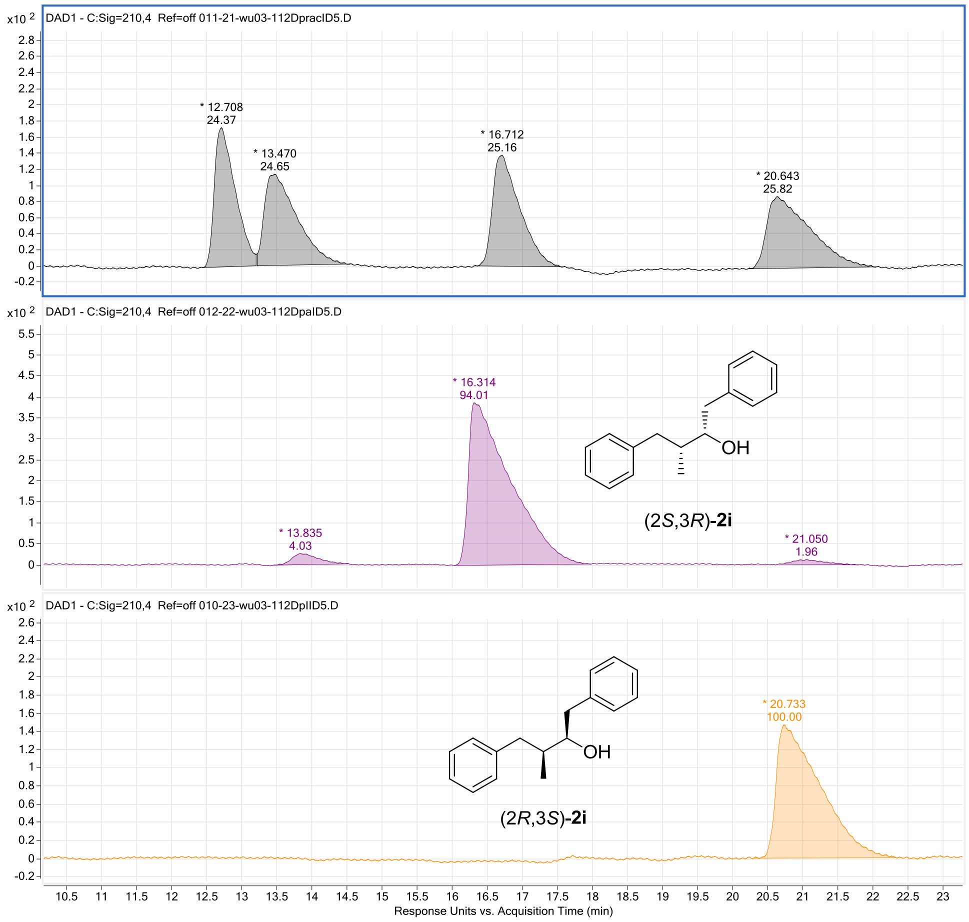

DAD1 - B:Sig=230,4 Ref=off 001-11-wu05-136alC5.D
* 9.132
98.15
* 10.161
1.85
OH
(R)-1af
DAD1 - B:Sig=230,4 Ref=off 002-12-wu05-136smraclC5.D
* 9.261
49.91
* 10.275
50.09
Response Units vs. Acquisition Time (min)


DAD1 - B:Sig=230,4 Ref=off 002-12-wu05-148a52IC5.D
* 16.747
3.83
* 21.210
96.17
OH
(R)-1ag
DAD1 - B:Sig=230,4 Ref=off 003-11-wu05-148smIC5.D
* 16.926
49.94
* 21.509
50.06
Response Units vs. Acquisition Time (min)

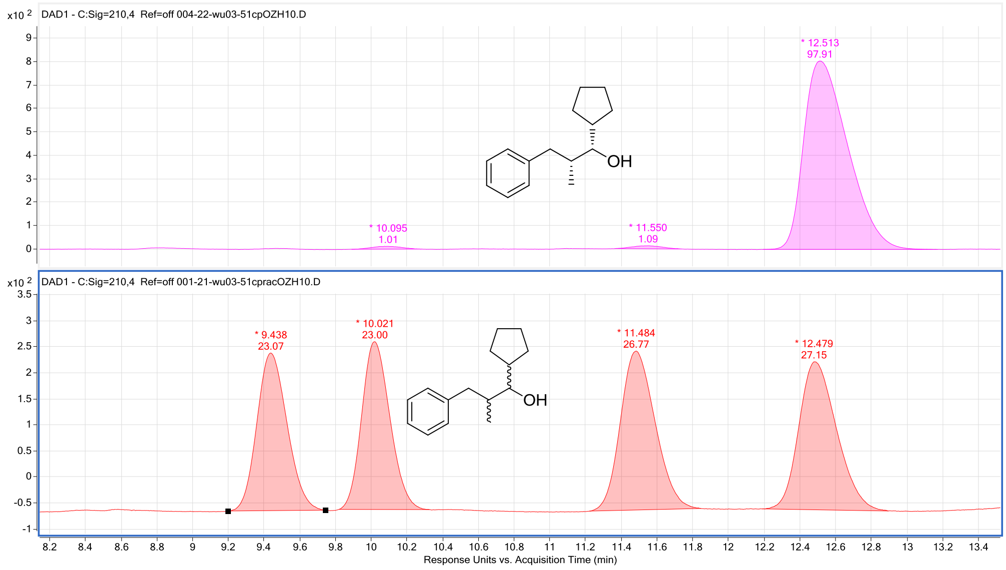

DAD1 - B:Sig=230,4 Ref=off 005-21-wu05-147dIC10.D
* 19.756
100.00
OH
(R)-1ah
DAD1 - B:Sig=230,4 Ref=off 006-22-wu05-147dsmIC10.D
* 15.504
49.98
* 19.458
50.02
Response Units vs. Acquisition Time (min)


DAD1 - C:Sig=210,4 Ref=off 011-12-wu05-149aODH5.D
* 9.520
98.24
* 10.543
1.76
OH
(R)-1ak
DAD1 - C:Sig=210,4 Ref=off 012-11-wu05-149smODH5.D
* 9.544
50.53
* 10.473
49.47
Response Units vs. Acquisition Time (min)

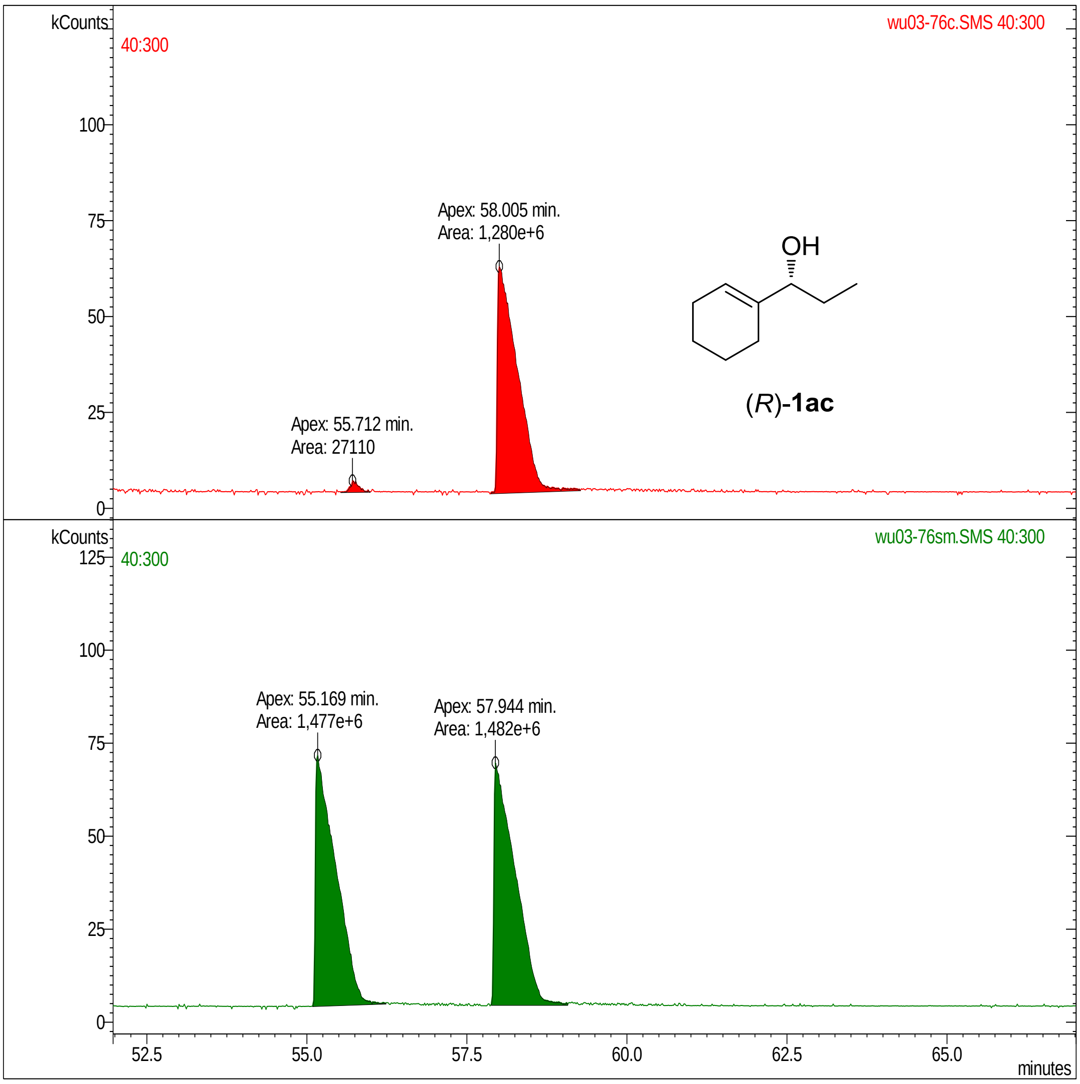

DAD1 - C:Sig=210,4 Ref=off 003-21-wu03-103cracADH5.D
* 2.900
49.93
* 3.160
50.07
DAD1 - C:Sig=210,4 Ref=off 006-22-wu03-103CADH5.D
* 3.212
100.00
Et
O
OBn
3
Response Units vs. Acquisition Time (min)

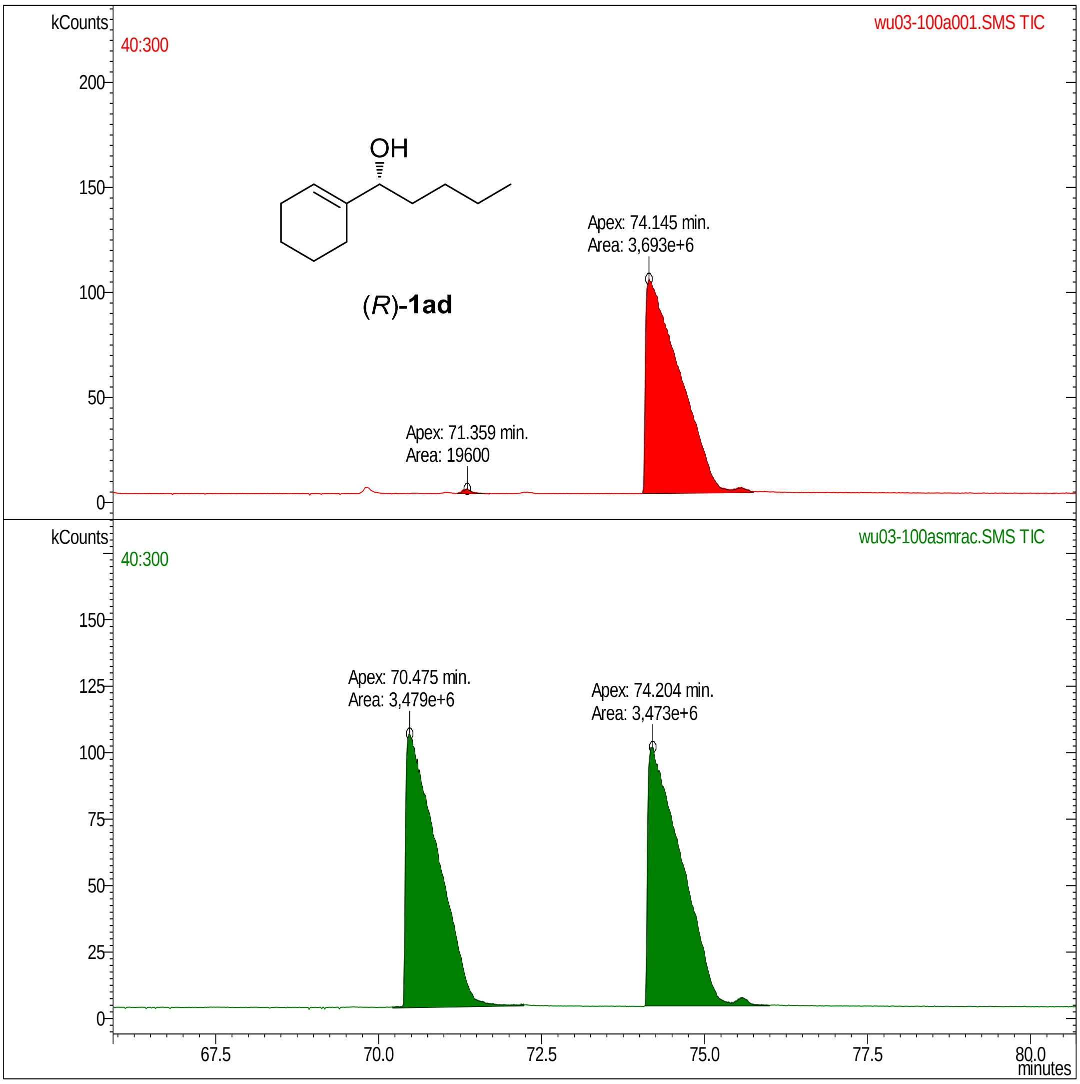


DAD1 - C:Sig=210,4 Ref=off 011-21-wu03-112DpracID5.D
* 12.708
24.37
* 13.470
24.65
* 16.712
25.16
* 20.643
25.82
DAD1 - C:Sig=210,4 Ref=off 012-22-wu03-112DpaID5.D
* 16.314
94.01
* 13.835
4.03
* 21.050
1.96
OH
(2S,3R)-2i
DAD1 - C:Sig=210,4 Ref=off 010-23-wu03-112DpIID5.D
* 20.733
100.00
OH
(2R,3S)-2i
Response Units vs. Acquisition Time (min)

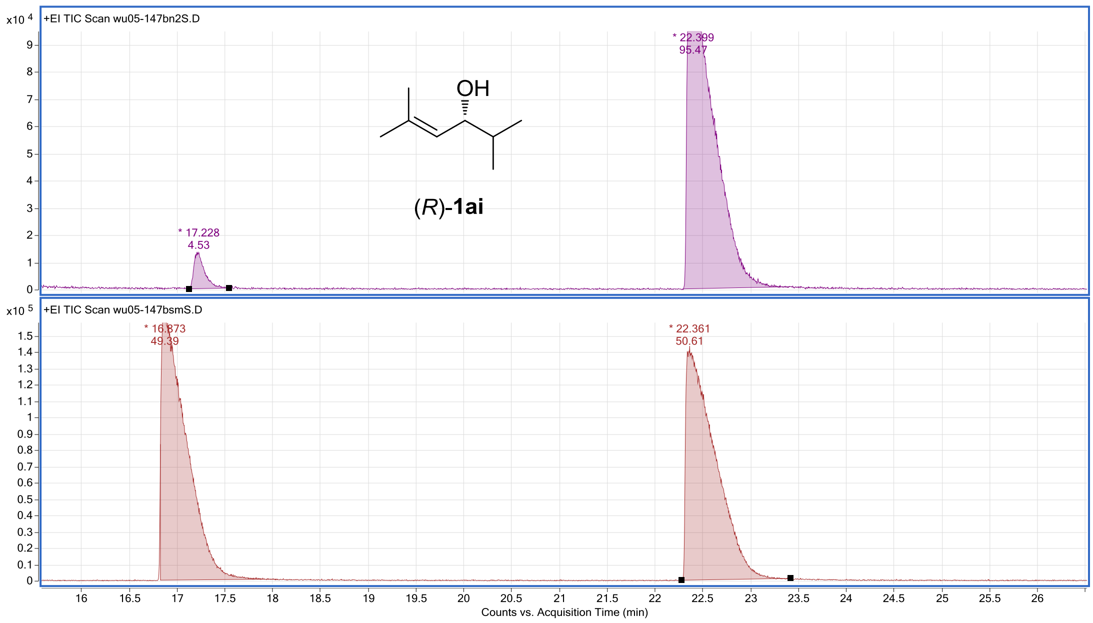


DAD1 - C:Sig=210,4 Ref=off 004-22-wu03-51cpOZH10.D
* 12.513
97.91
* 10.095
1.01
* 11.550
1.09
OH
DAD1 - C:Sig=210,4 Ref=off 001-21-wu03-51cpracOZH10.D
* 9.438
23.07
* 10.021
23.00
* 11.484
26.77
* 12.479
27.15
OH
Response Units vs. Acquisition Time (min)

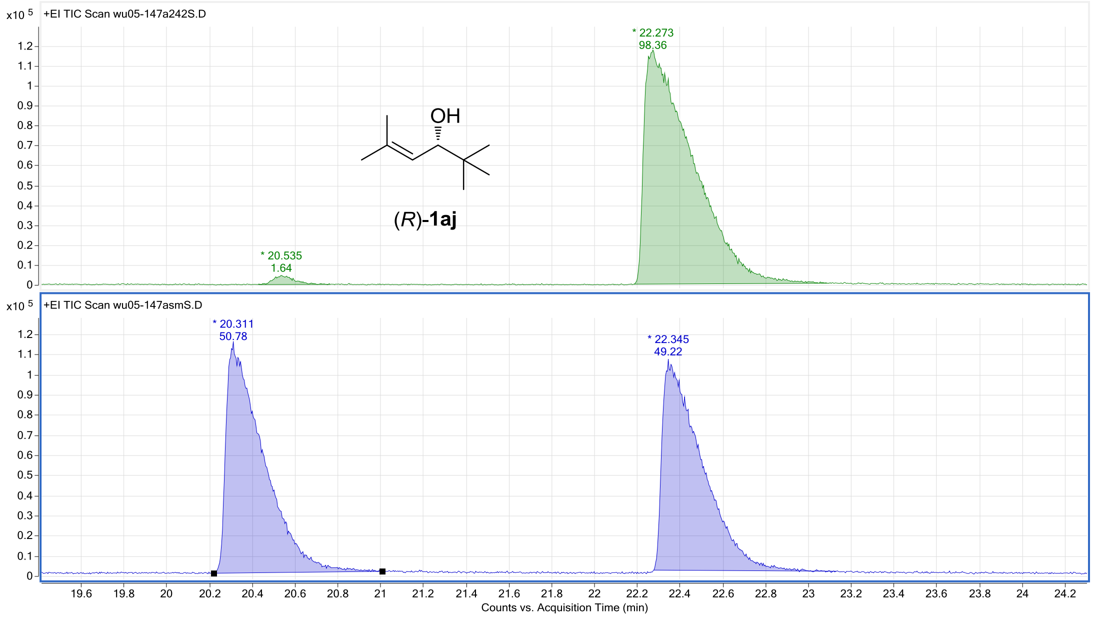

kCounts
40:300
wu03-76c.SMS 40:300
100
75
50
25
0
Apex: 58.005 min.
Area: 1,280e+6
Apex: 55.712 min.
Area: 27110
OH
(R)-1ac
kCounts
125
40:300
wu03-76sm.SMS 40:300
100
75
50
25
0
Apex: 55.169 min.
Area: 1,477e+6
Apex: 57.944 min.
Area: 1,482e+6
52.5
55.0
57.5
60.0
62.5
65.0
minutes

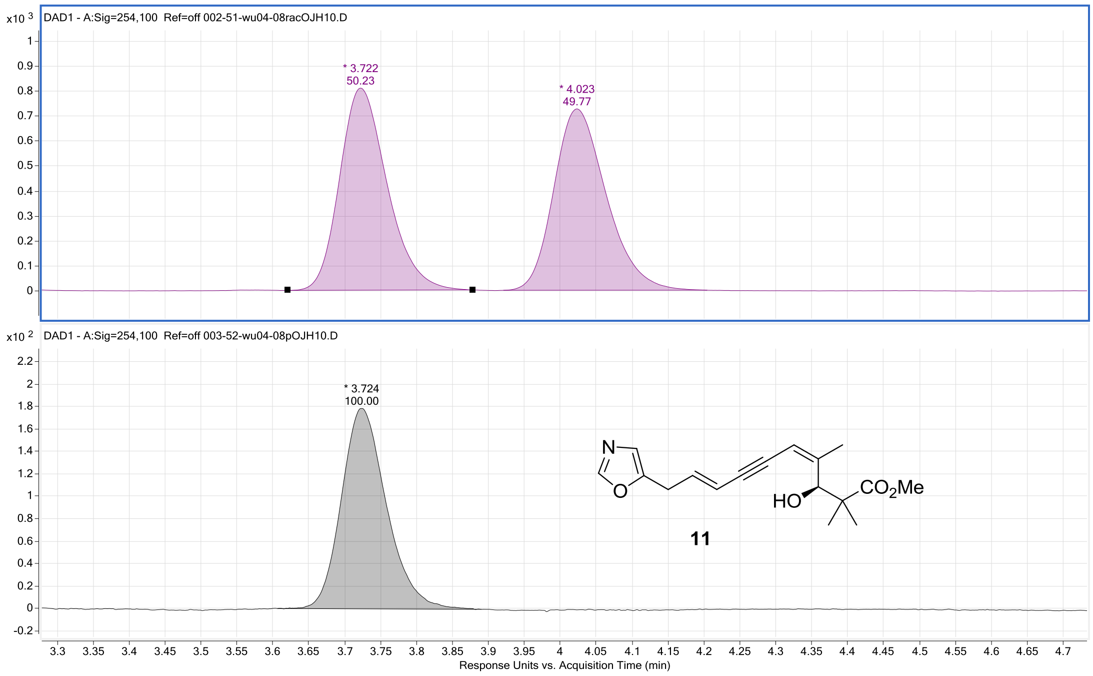


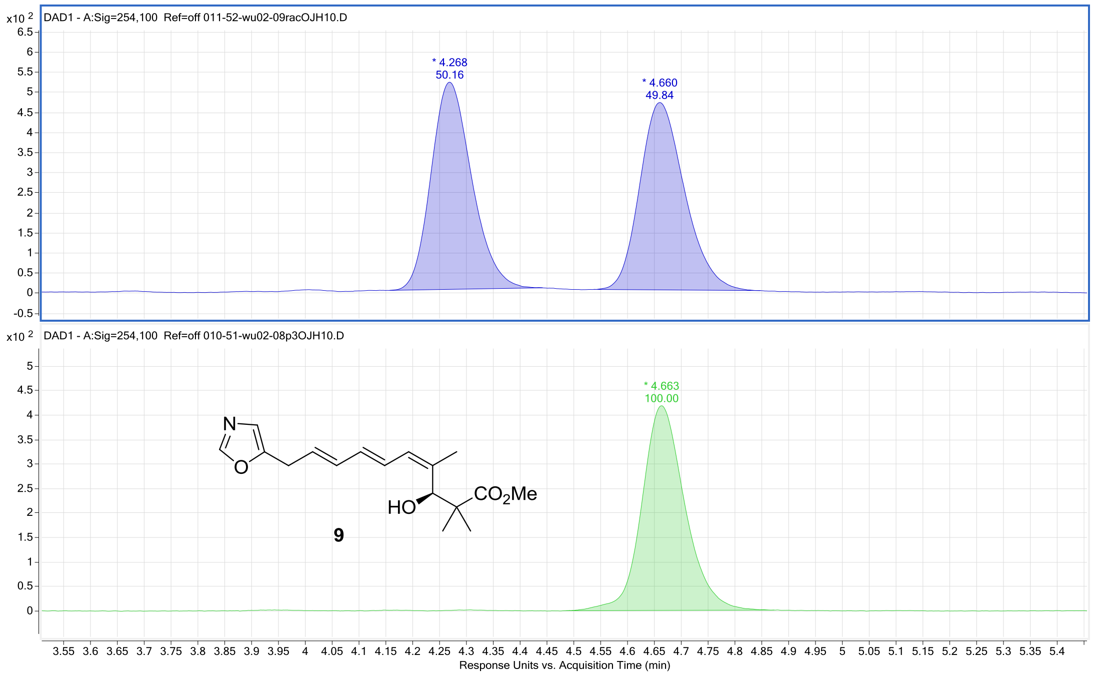
kCounts
40:300
wu03-100a001.SMS TIC
OH
(R)-1ad
Apex: 74.145 min.
Area: 3,693e+6
Apex: 71.359 min.
Area: 19600
kCounts
40:300
wu03-100asmrac.SMS TIC
Apex: 70.475 min.
Area: 3,479e+6
Apex: 74.204 min.
Area: 3,473e+6
minutes



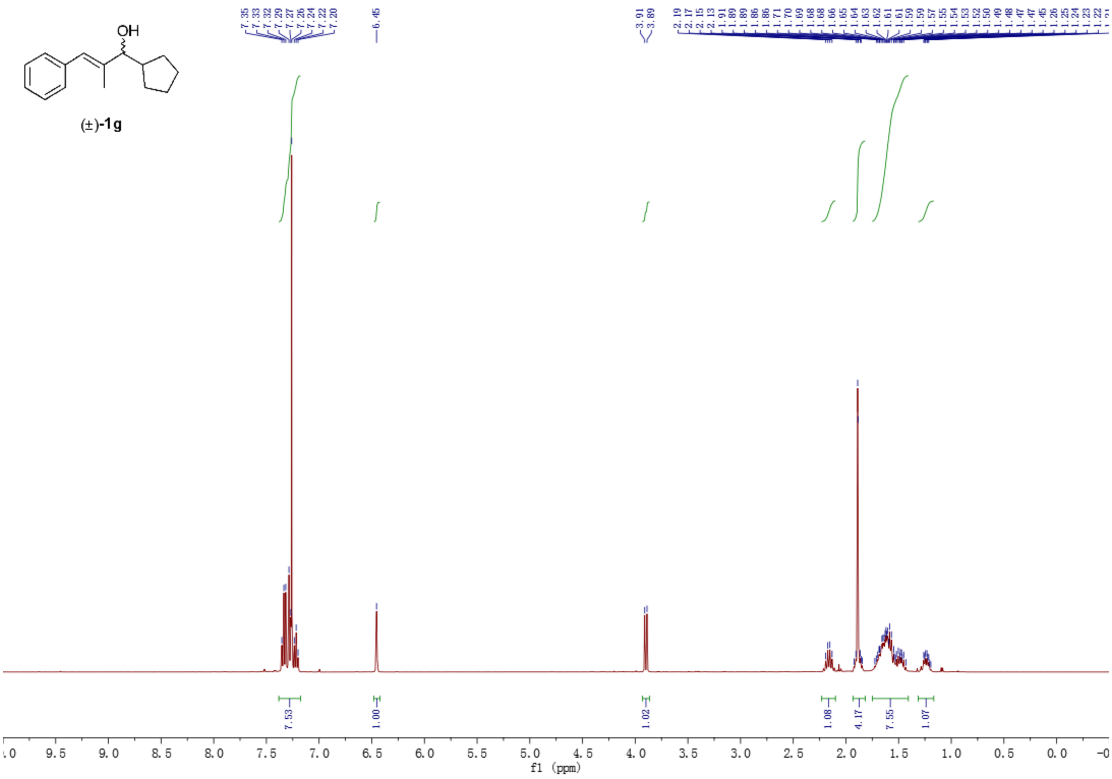
+EI TIC Scan wu05-147bn2S.D
OH
(R)-1ai
* 22.399
95.47
* 17.228
4.53
+EI TIC Scan wu05-147bsmS.D
* 16.873
49.39
* 22.361
50.61
Counts vs. Acquisition Time (min)

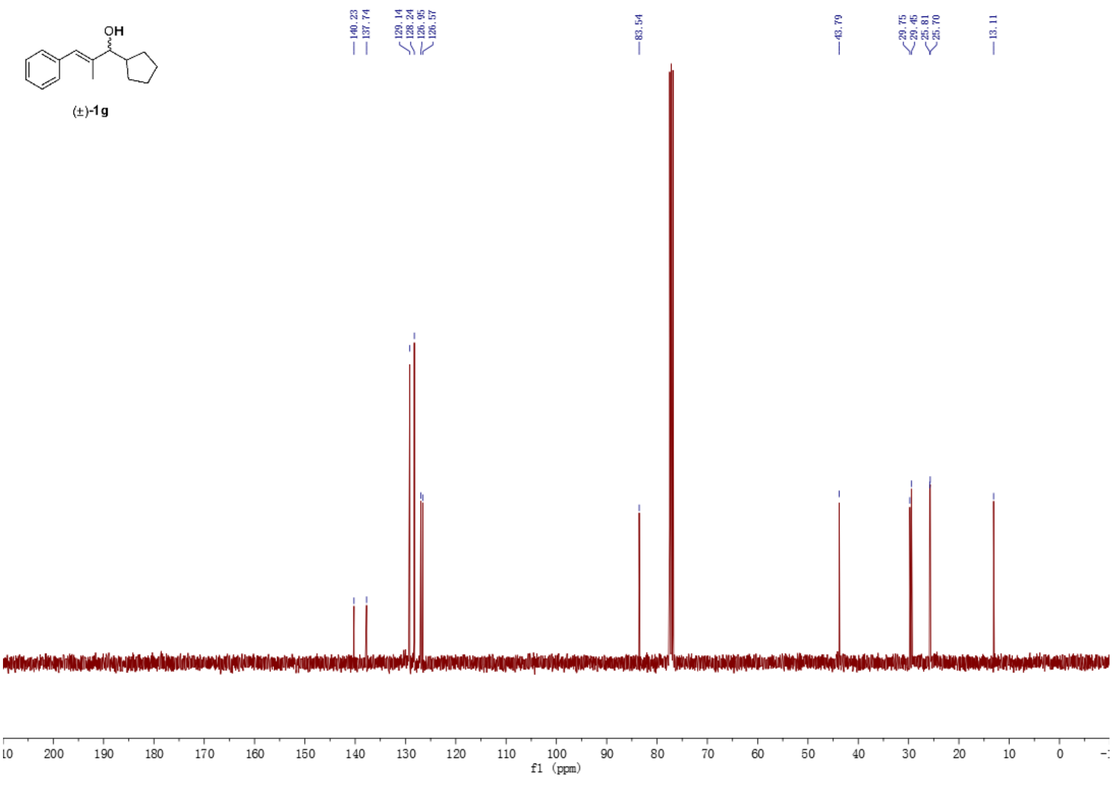

x10 5
+EI TIC Scan wu05-147a242S.D
* 22.273
98.36
* 20.535
1.64
OH
(R)-1aj
x10 5
+EI TIC Scan wu05-147asmS.D
* 20.311
50.78
* 22.345
49.22
Counts vs. Acquisition Time (min)

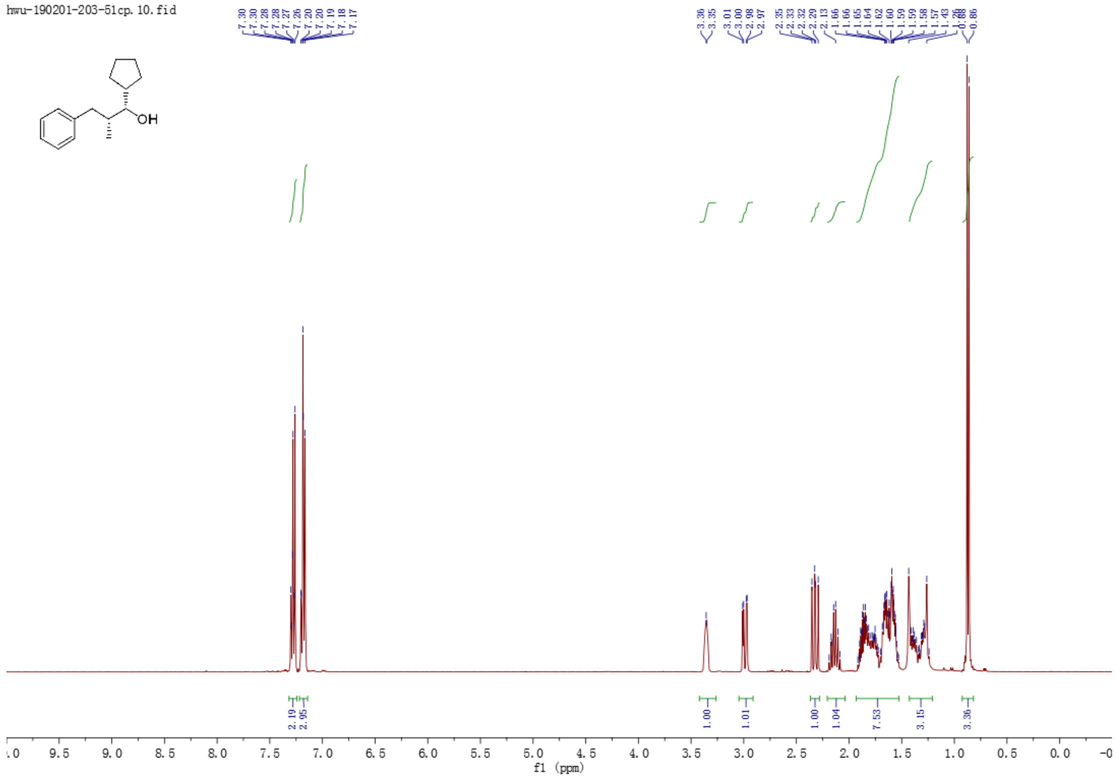

x10 3
DAD1 - A:Sig=254,100 Ref=off 002-51-wu04-08racOJH10.D
* 3.722
50.23
* 4.023
49.77
x10 2
DAD1 - A:Sig=254,100 Ref=off 003-52-wu04-08pOJH10.D
* 3.724
100.00
N
O
HO
CO2Me
11
Response Units vs. Acquisition Time (min)

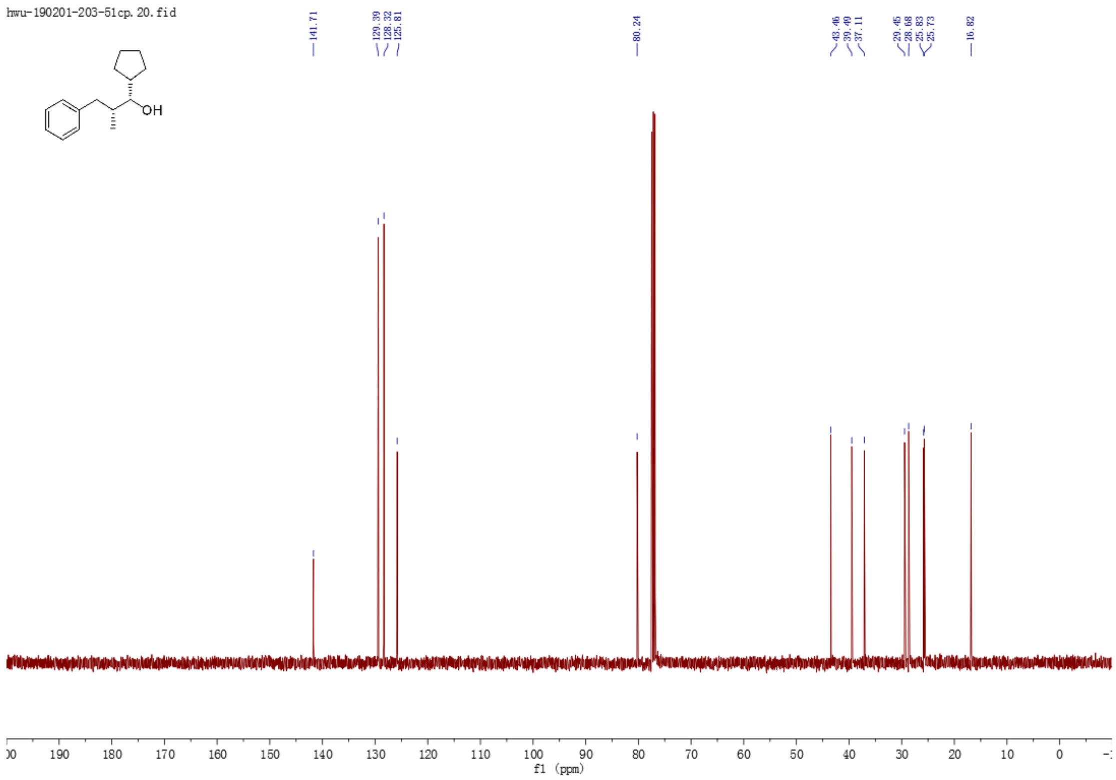

x10 2
DAD1 - A:Sig=254,100 Ref=off 011-52-wu02-09racOJH10.D
* 4.268
50.16
* 4.660
49.84
x10 2
DAD1 - A:Sig=254,100 Ref=off 010-51-wu02-08p3OJH10.D
* 4.663
100.00
9
Response Units vs. Acquisition Time (min)

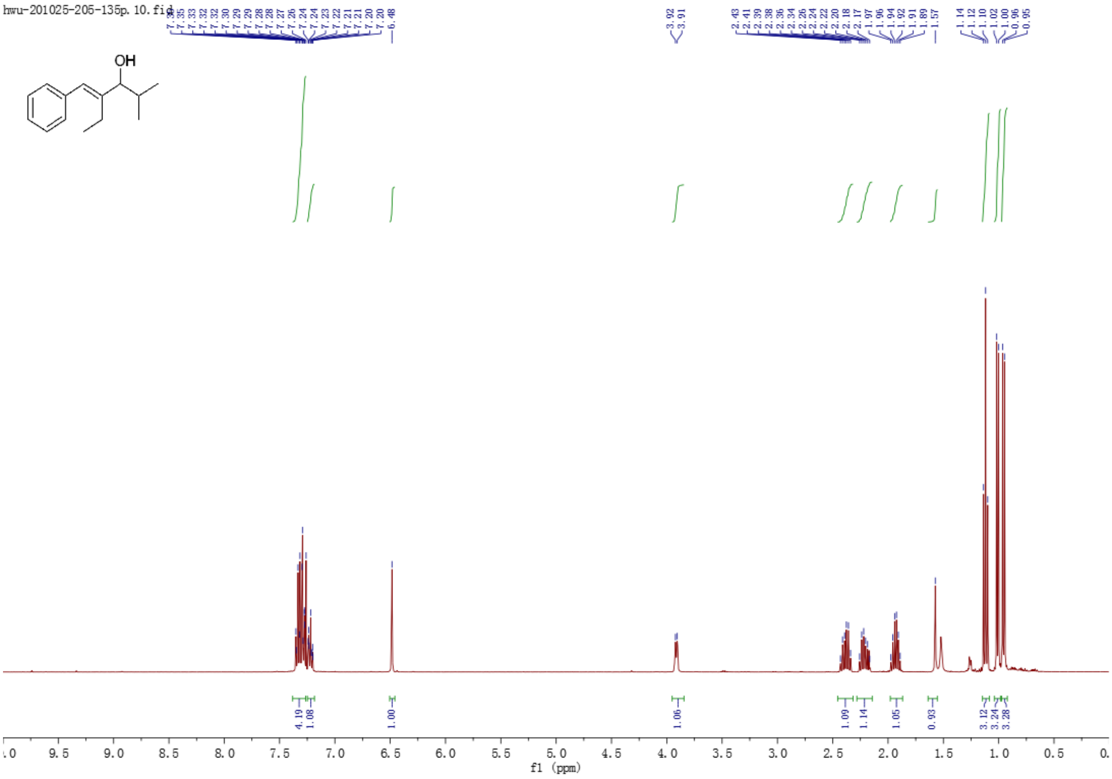
8. ^{1}H, ^{13}C and ^{19}F NMR spectroscopic data

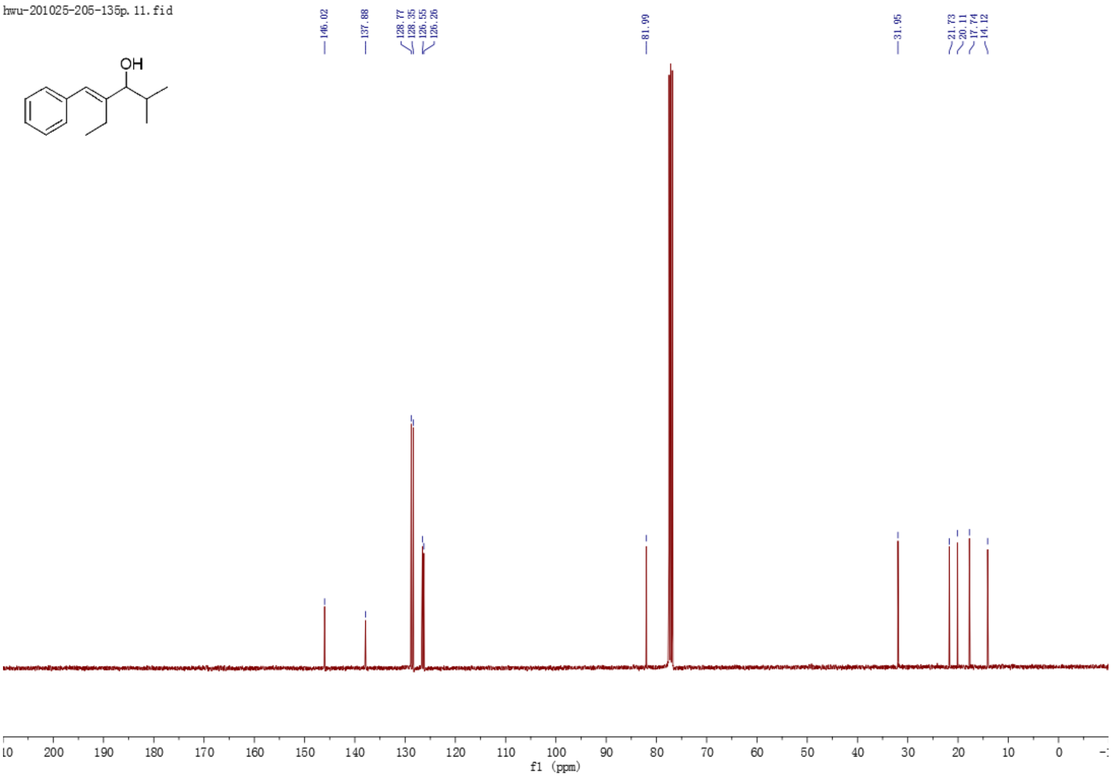


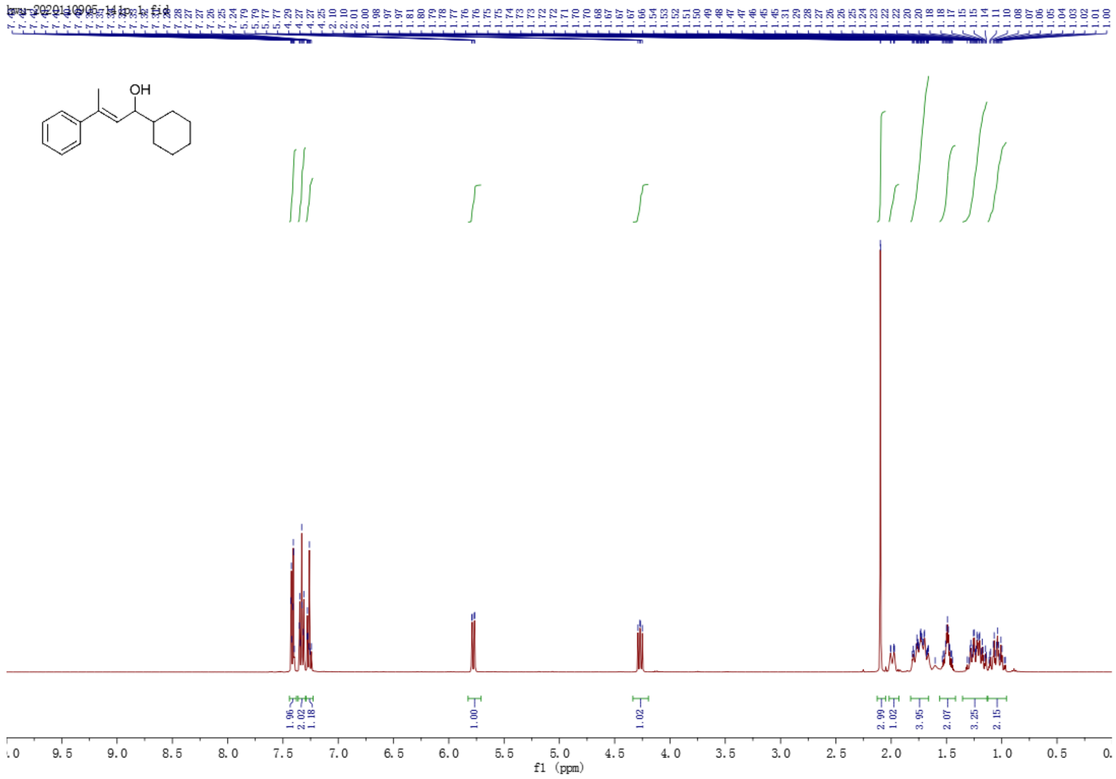


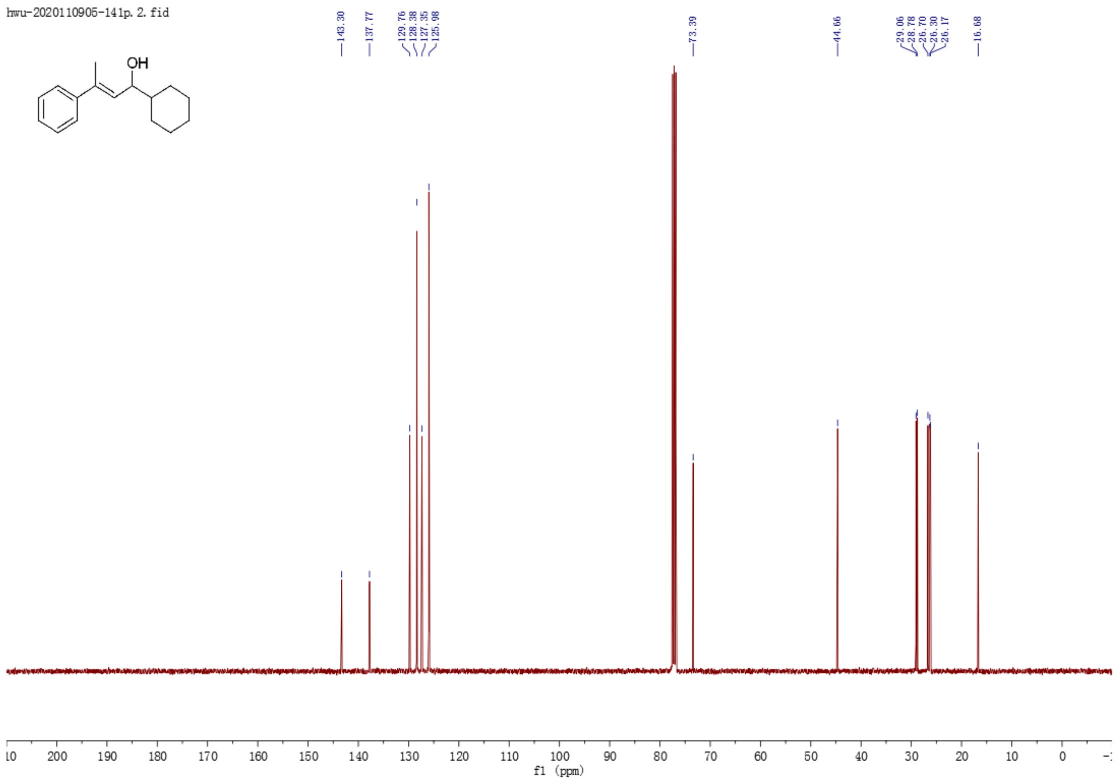

hwu-190201-203-51cp.10.fid
OH
7.30
7.30
7.28
7.28
7.27
7.26
7.20
7.20
7.19
7.18
7.17
3.36
3.35
3.01
3.00
2.98
2.97
2.35
2.33
2.32
2.29
2.13
1.66
1.66
1.65
1.64
1.62
1.60
1.59
1.59
1.58
1.57
1.43
0.88
0.86
2.19
2.95
1.00
1.01
1.00
1.04
7.53
3.15
3.36
f1 (ppm)

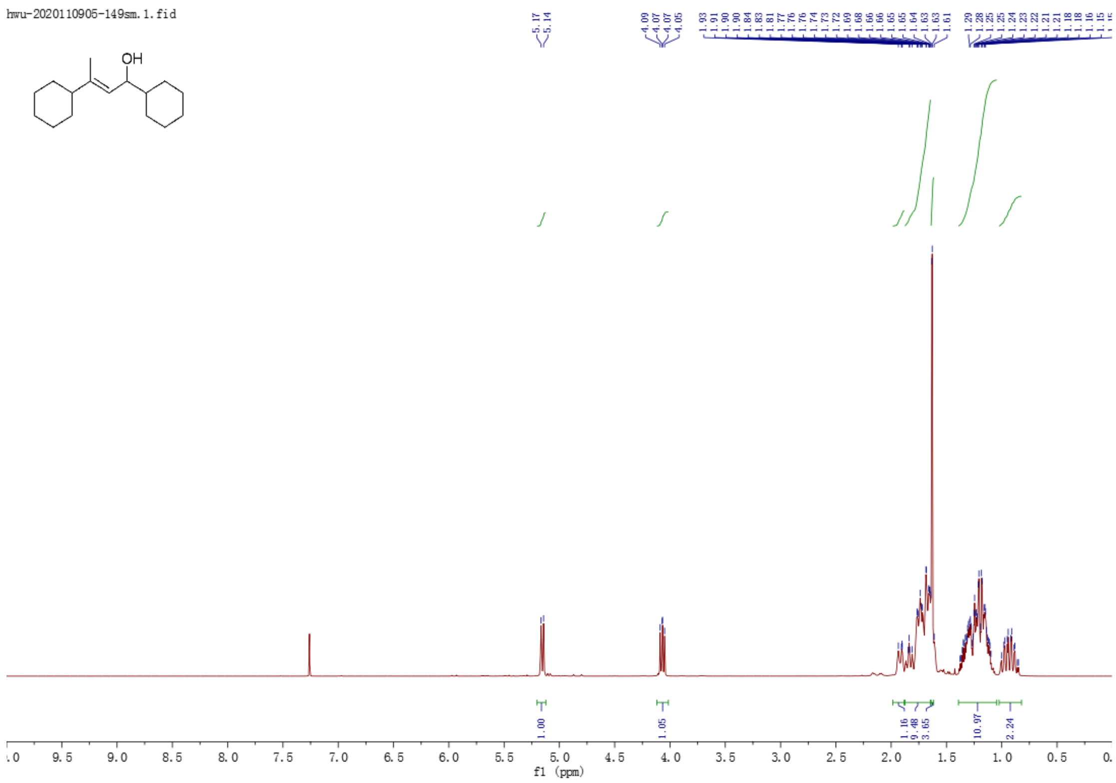

hwu-190201-203-51cp.20.fid
OH
141.71
129.39
128.32
125.81
80.24
43.46
39.49
37.11
29.45
28.68
25.83
25.73
16.82
f1 (ppm)


hwu-201025-205-135p.10.fid
OH
7.35
7.33
7.32
7.32
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.20
6.48
3.92
3.91
2.43
2.41
2.39
2.38
2.36
2.34
2.26
2.24
2.24
2.22
2.22
2.20
2.18
2.17
1.97
1.96
1.94
1.92
1.91
1.89
1.57
1.14
1.12
1.10
1.02
1.00
0.96
0.95
4.19
1.08
1.00
1.06
1.09
1.14
1.05
0.93
3.12
3.24
3.28
f1 (ppm)

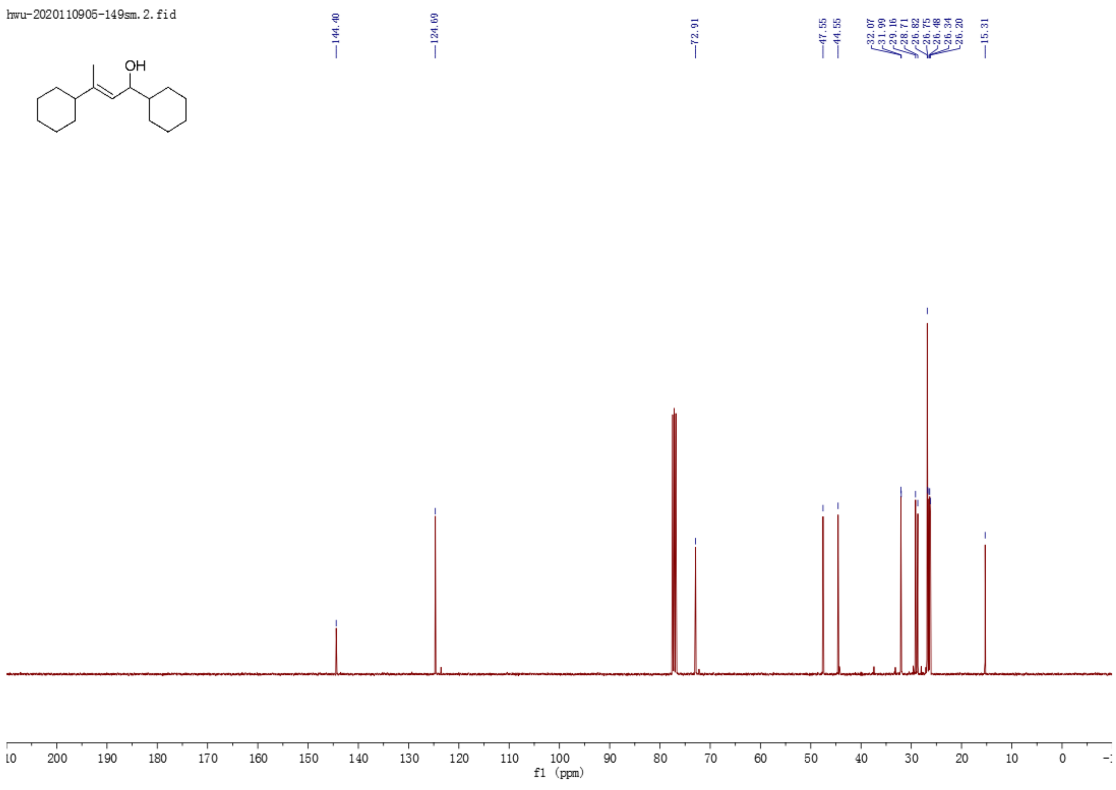

hwu-201025-205-135p.11.fid
OH
146.02
137.88
128.77
128.35
126.55
126.26
81.99
31.95
21.73
20.11
17.74
14.12
f1 (ppm)



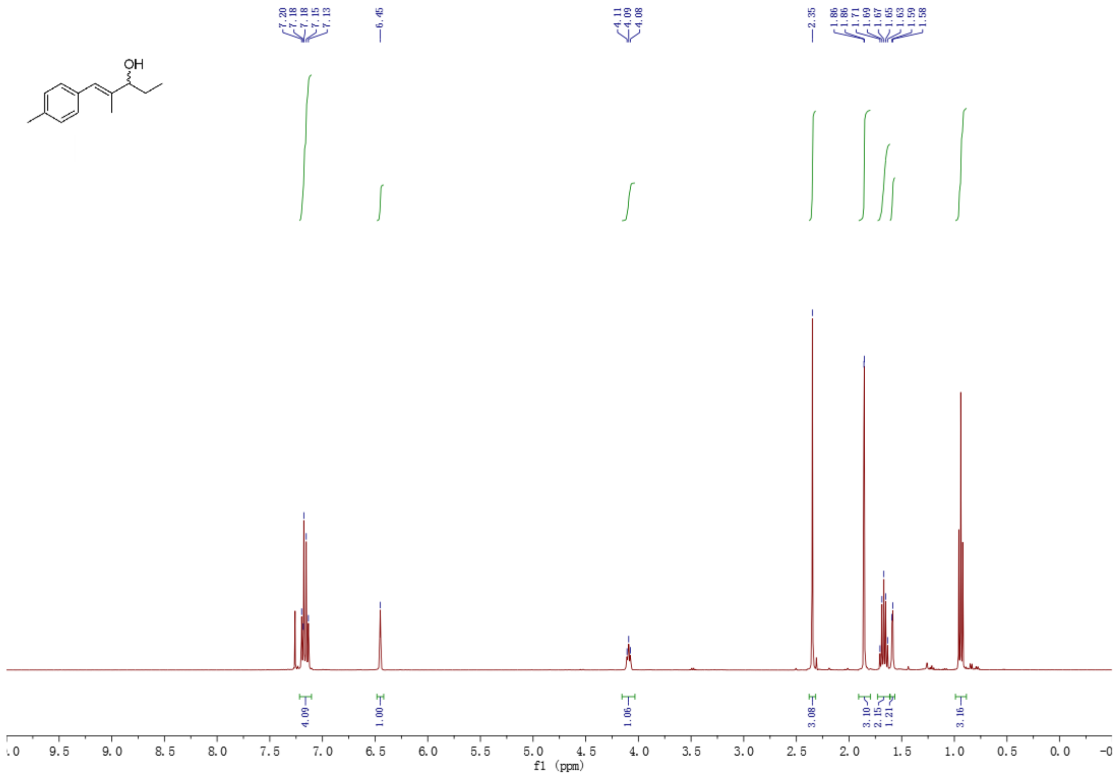


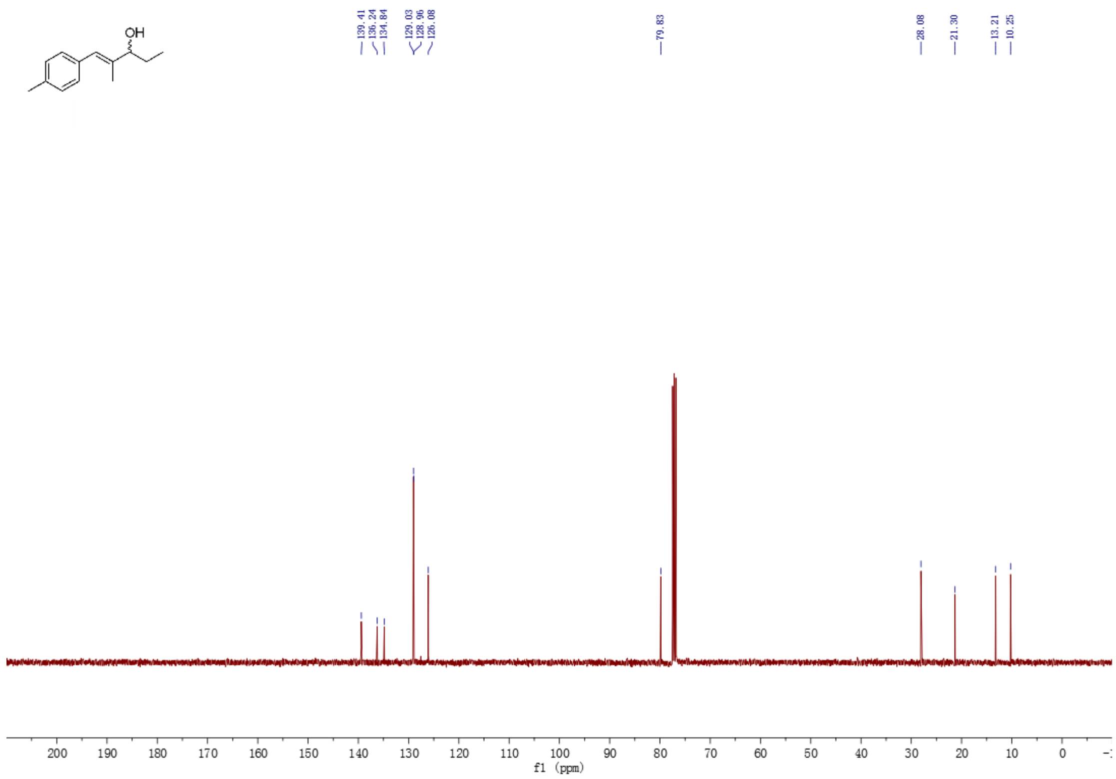


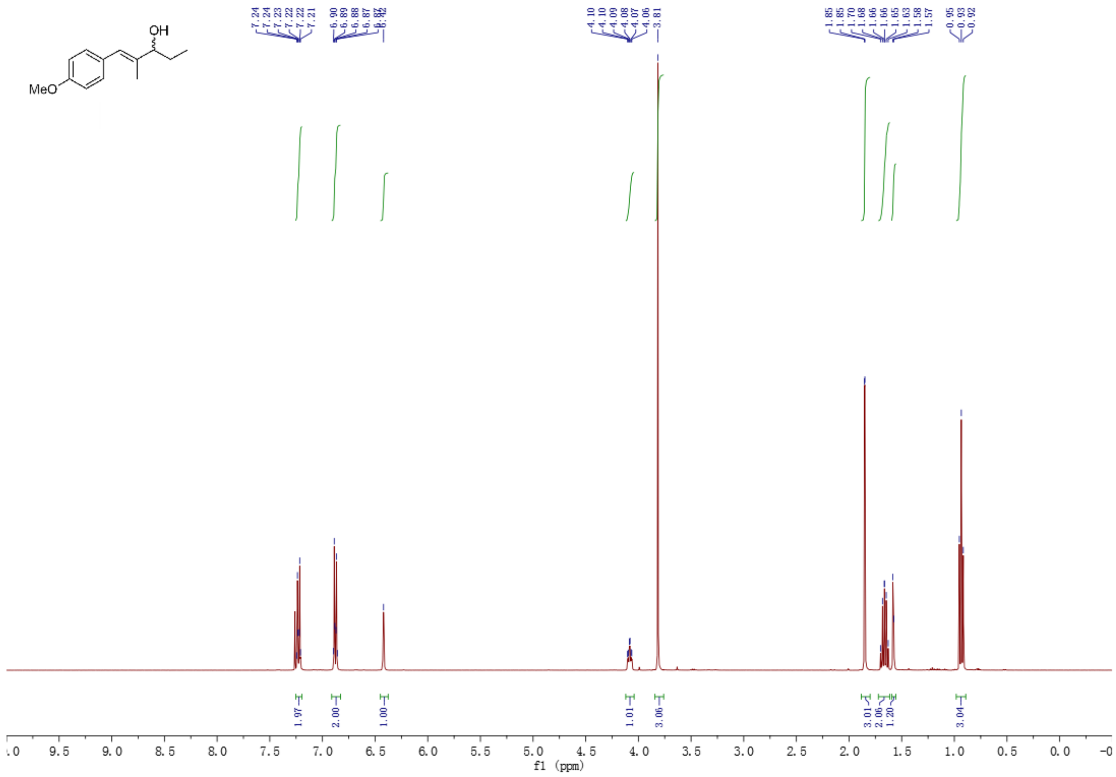
hwu-2020110905-149sm.1.fid
OH
5.17
5.14
4.09
4.07
4.07
4.05
1.93
1.91
1.90
1.88
1.84
1.83
1.81
1.77
1.76
1.74
1.73
1.72
1.69
1.68
1.66
1.66
1.65
1.65
1.64
1.63
1.63
1.61
1.29
1.28
1.25
1.25
1.24
1.23
1.22
1.21
1.18
1.16
1.15
1.00
1.05
1.16
9.48
3.65
10.97
2.24
f1 (ppm)

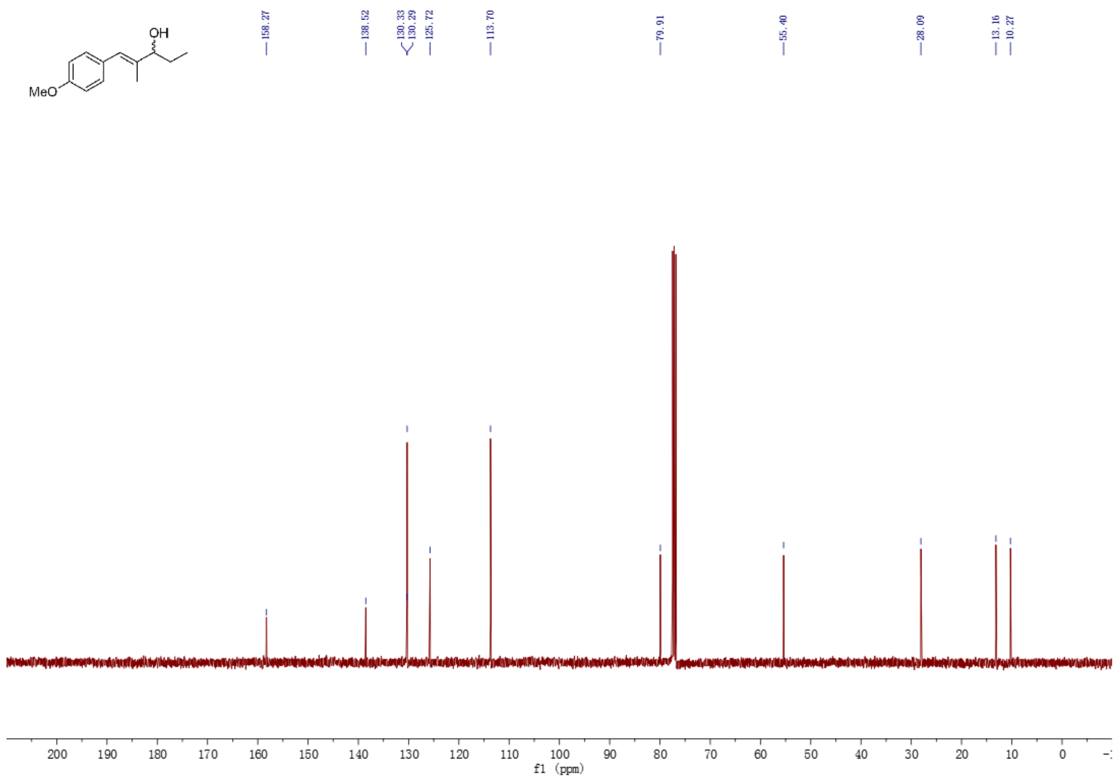


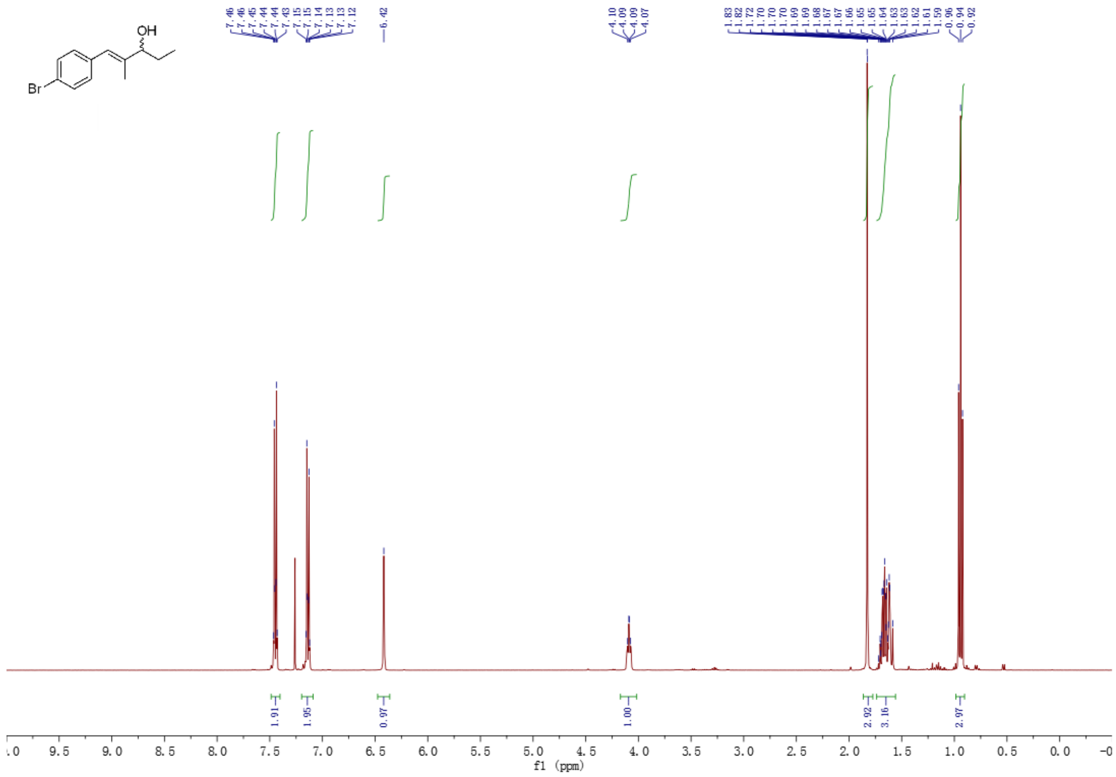
hwu-2020110905-149sm.2.fid
OH
144.40
124.69
72.91
47.55
44.55
32.07
31.99
29.16
28.71
26.82
26.75
26.48
26.34
26.20
15.31
f1 (ppm)

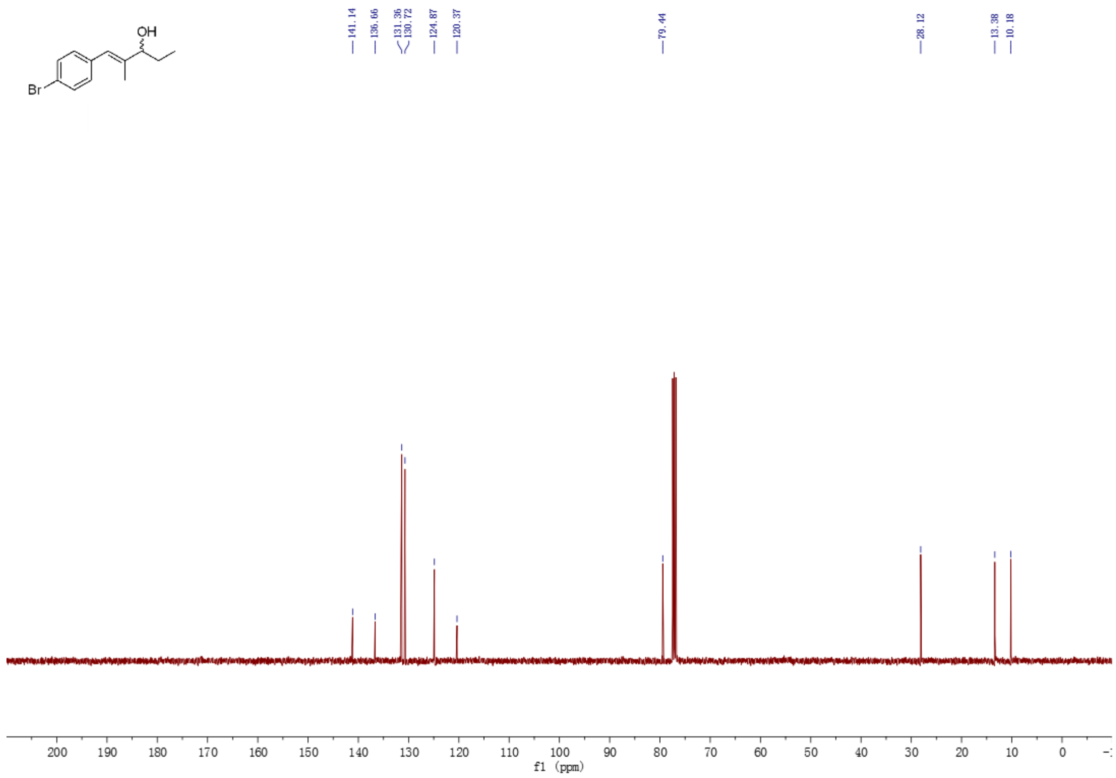


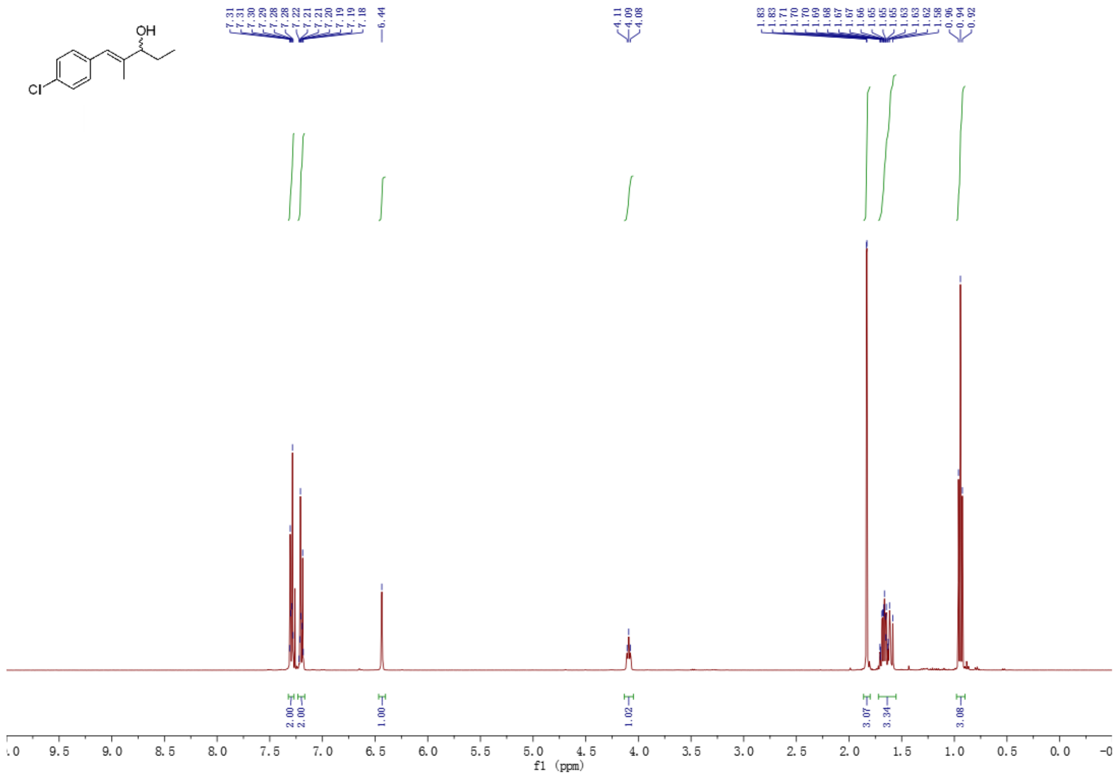


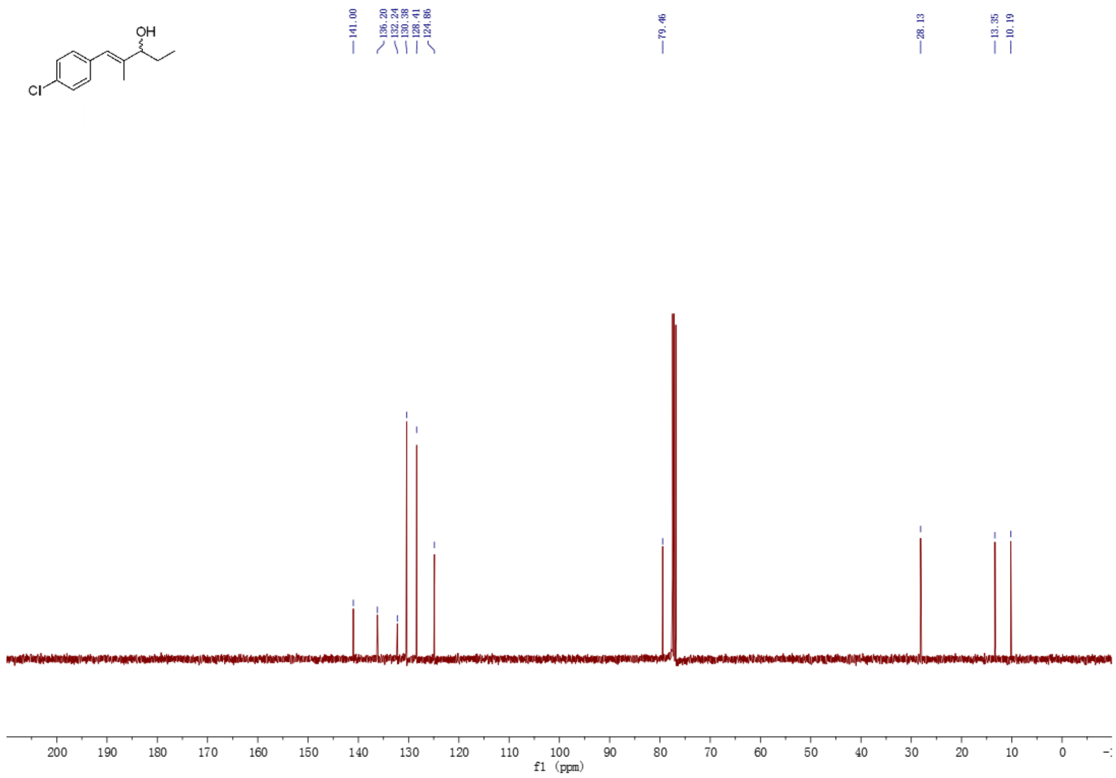


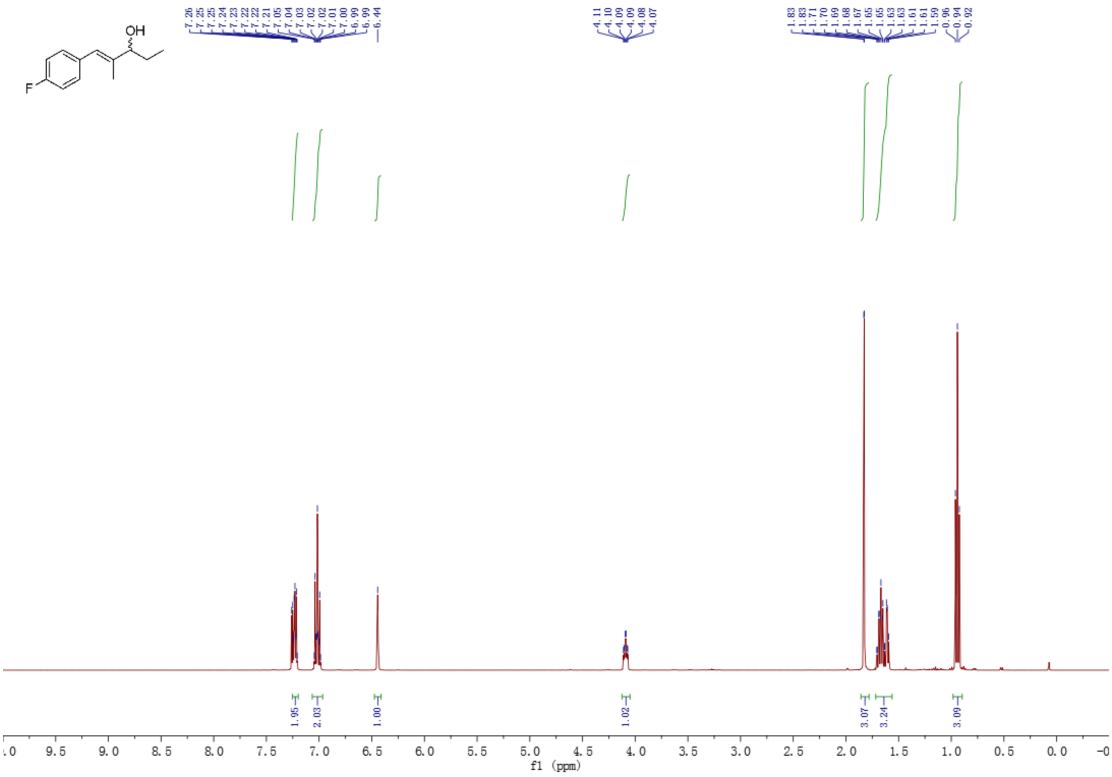


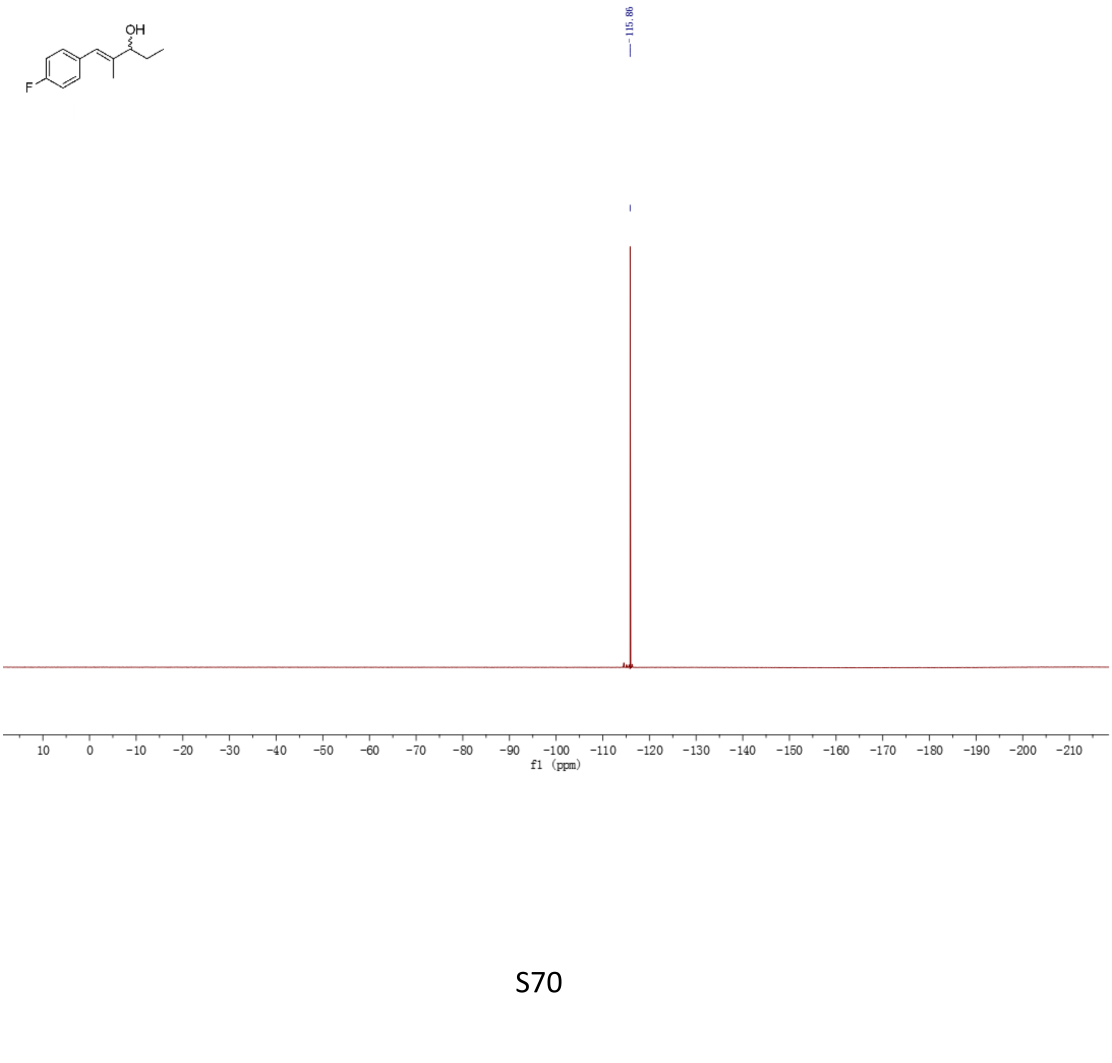


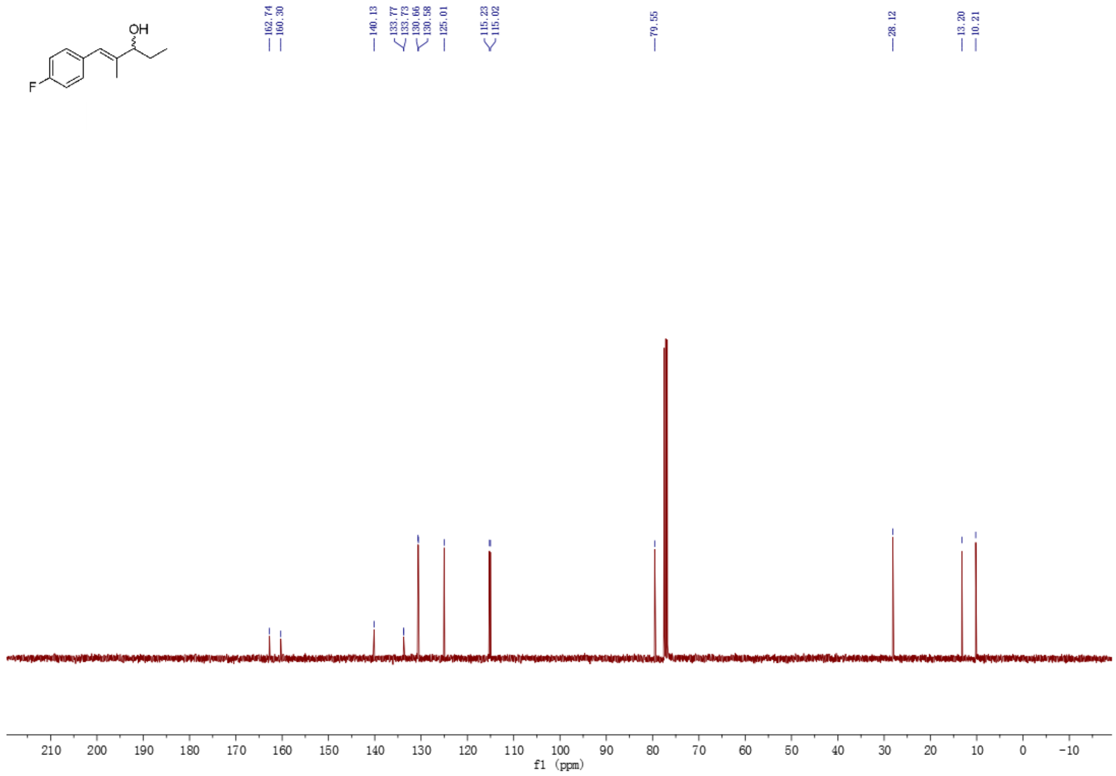


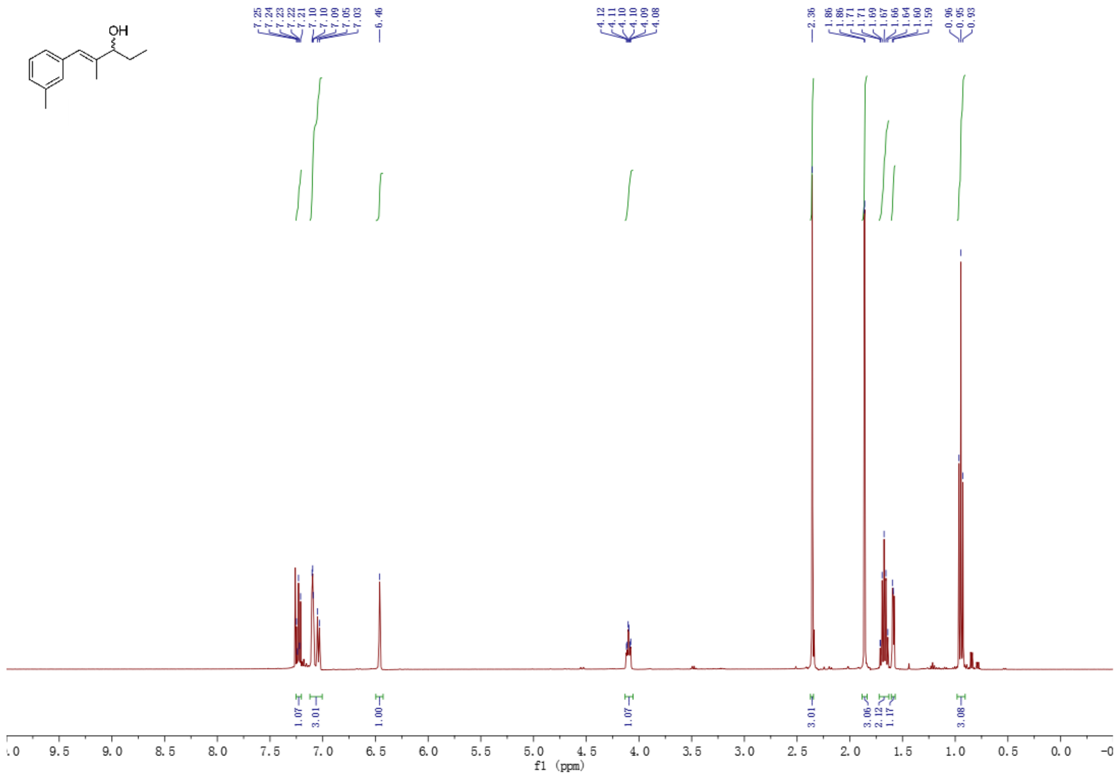


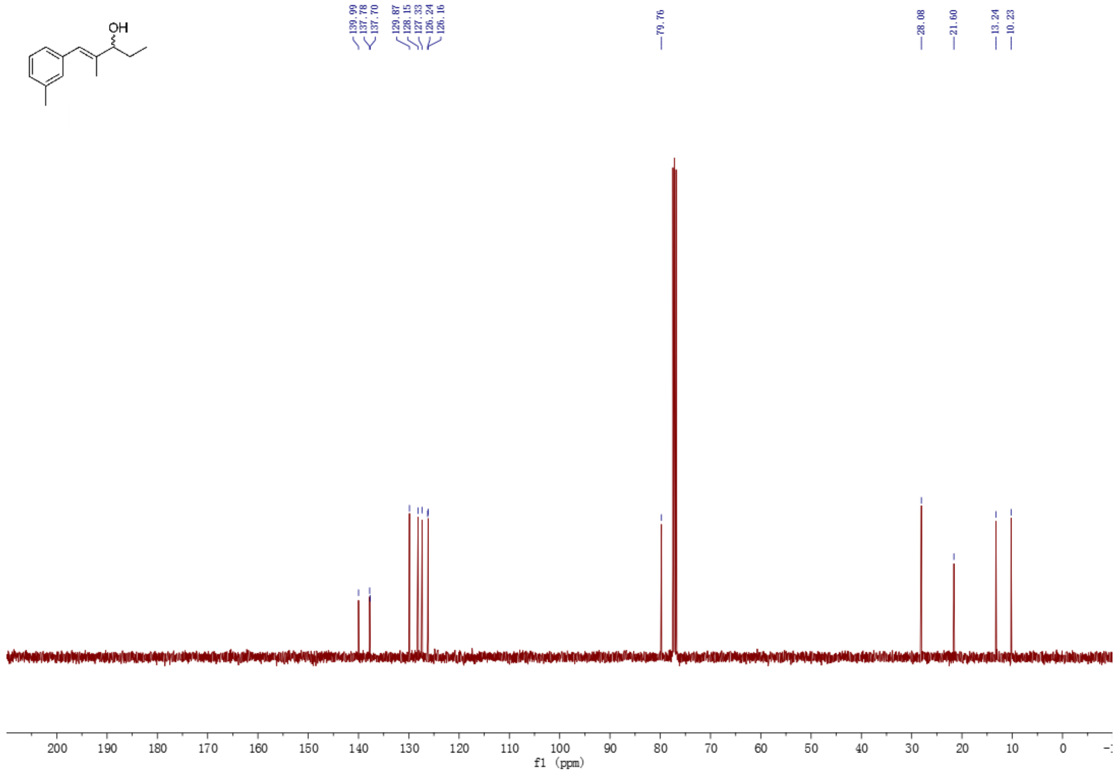


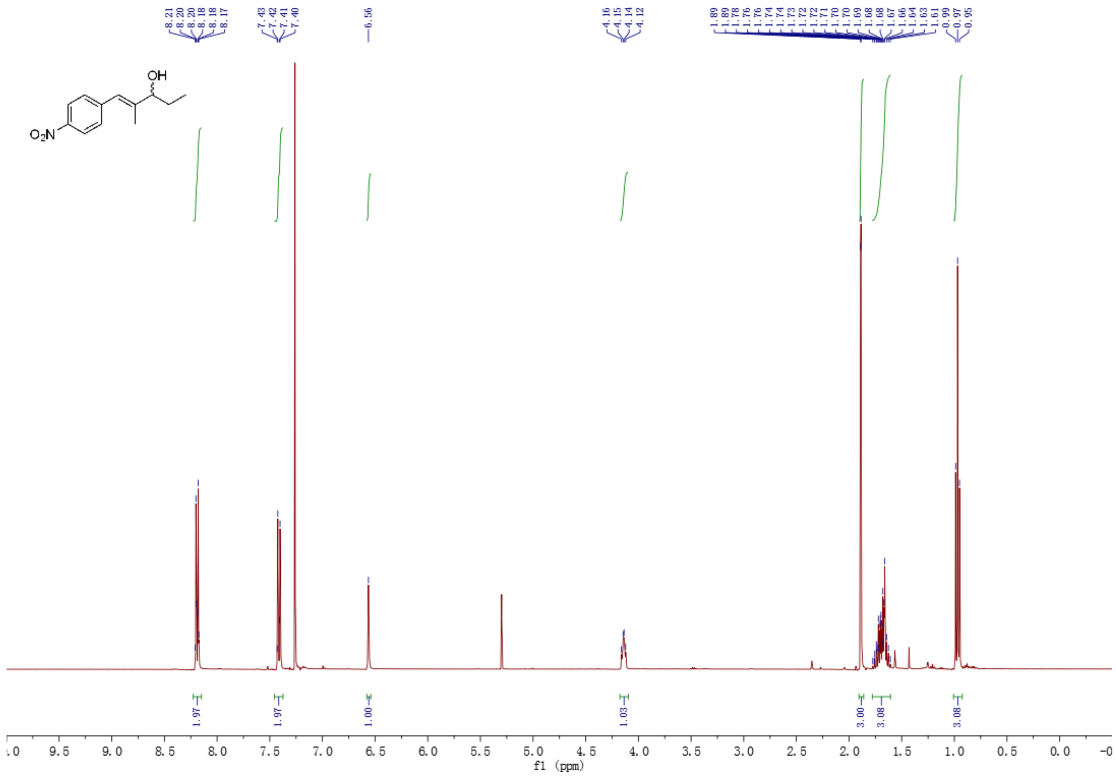


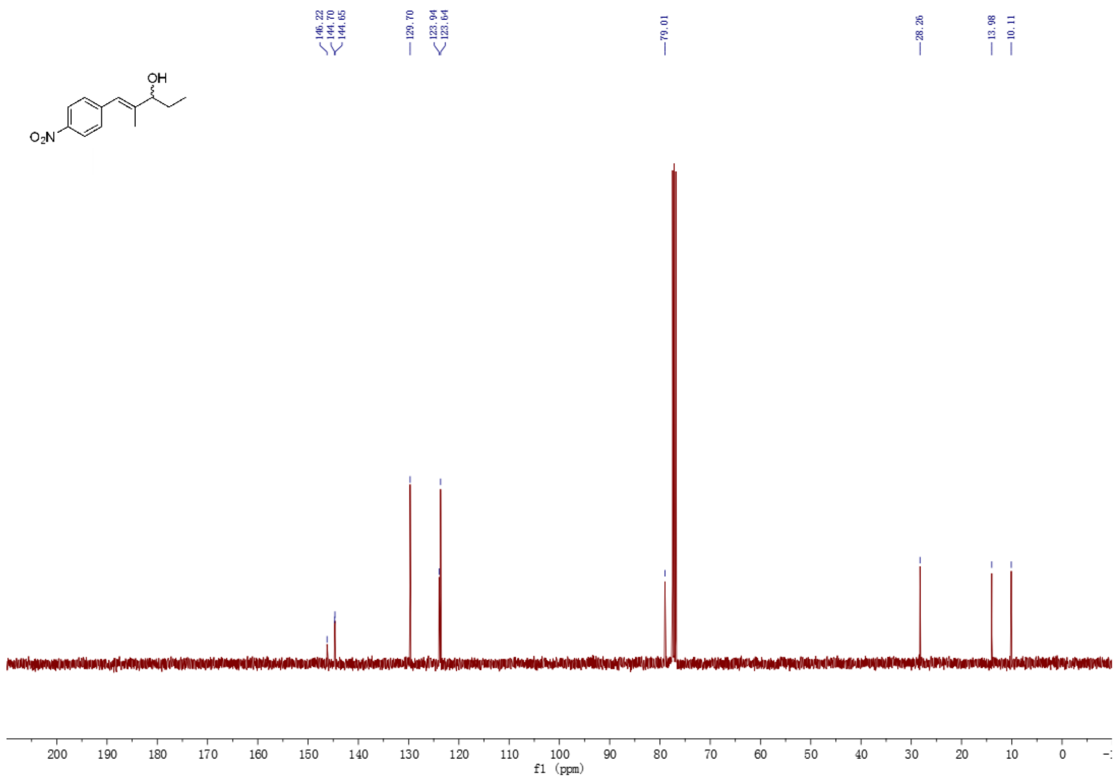


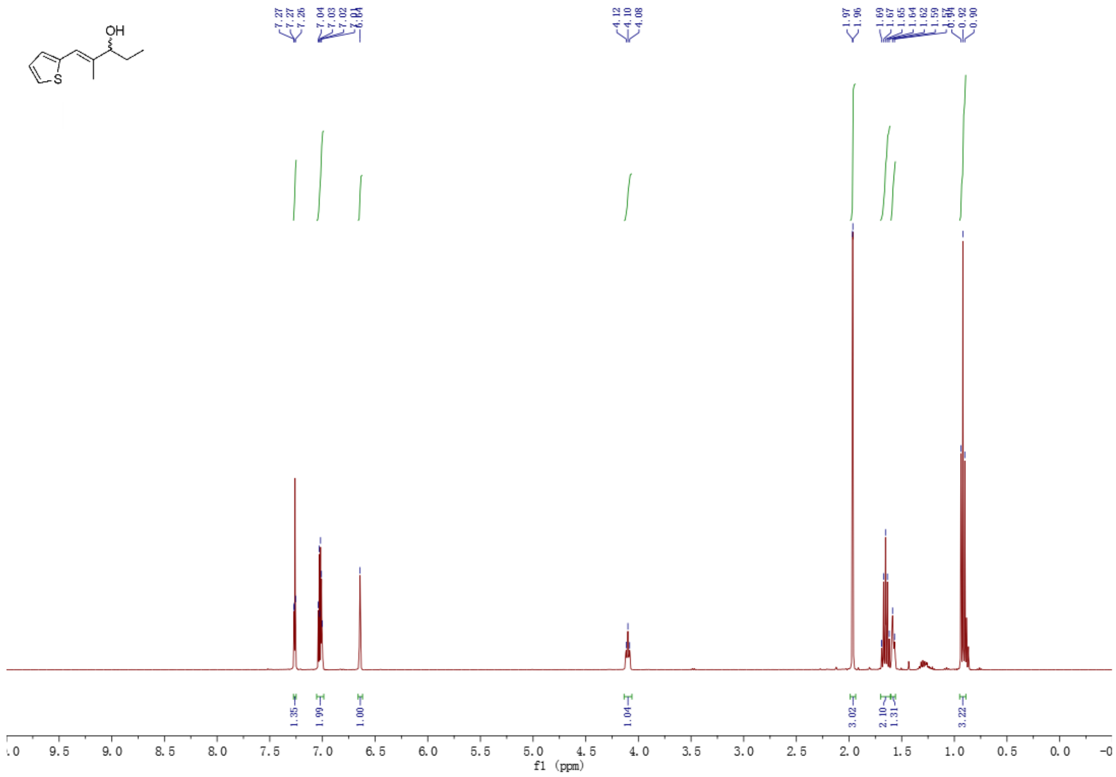

OH
F
162.74
160.30
140.13
133.77
133.73
130.66
130.58
125.01
115.23
115.02
79.55
28.12
13.20
10.21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

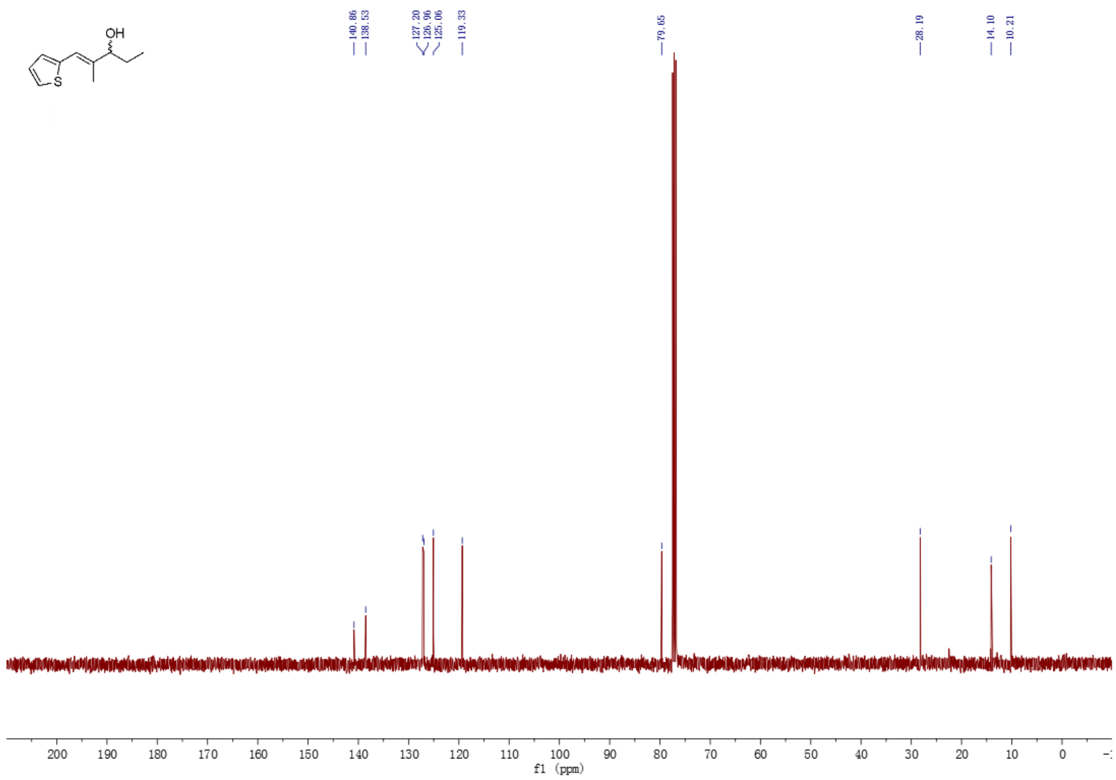

OH
7.25
7.24
7.23
7.22
7.21
7.10
7.10
7.09
7.05
7.03
6.46
4.12
4.11
4.10
4.10
4.09
4.08
2.36
1.86
1.86
1.71
1.71
1.69
1.67
1.66
1.64
1.60
1.59
0.96
0.95
0.93
1.07
3.01
1.00
1.07
3.01
3.06
2.12
1.17
3.08
f1 (ppm)

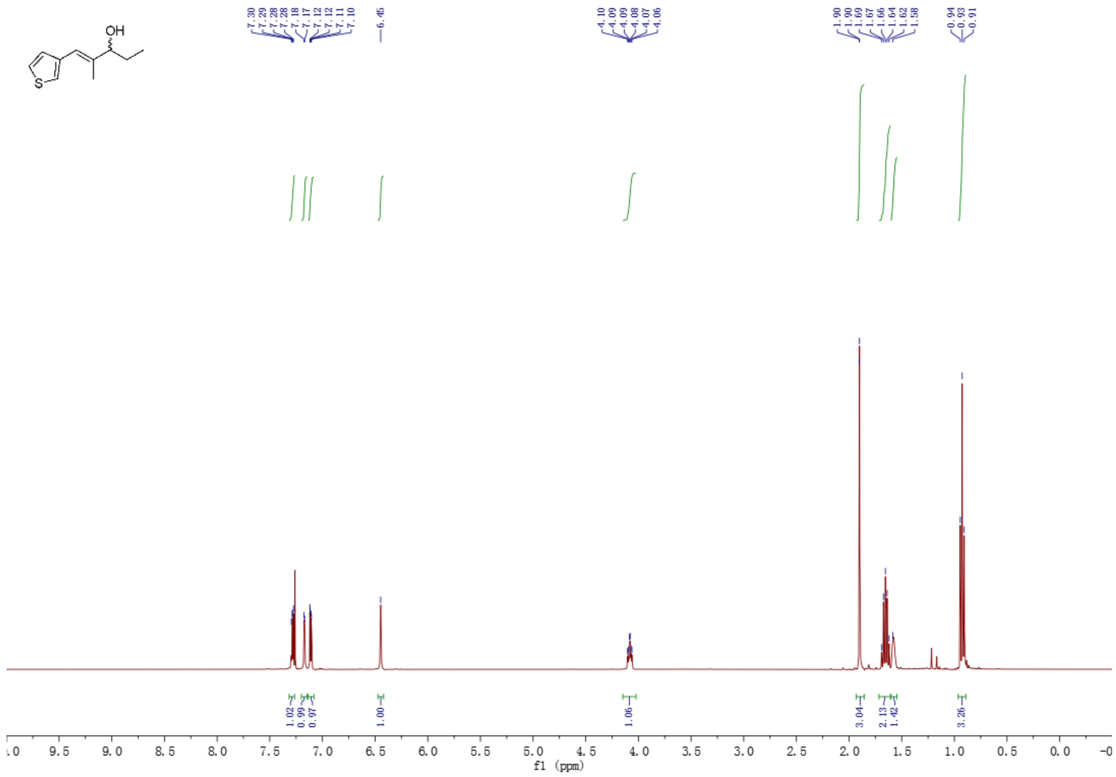

OH
139.99
137.78
137.70
129.87
128.15
127.33
126.24
126.16
79.76
28.08
21.60
13.24
10.23
f1 (ppm)



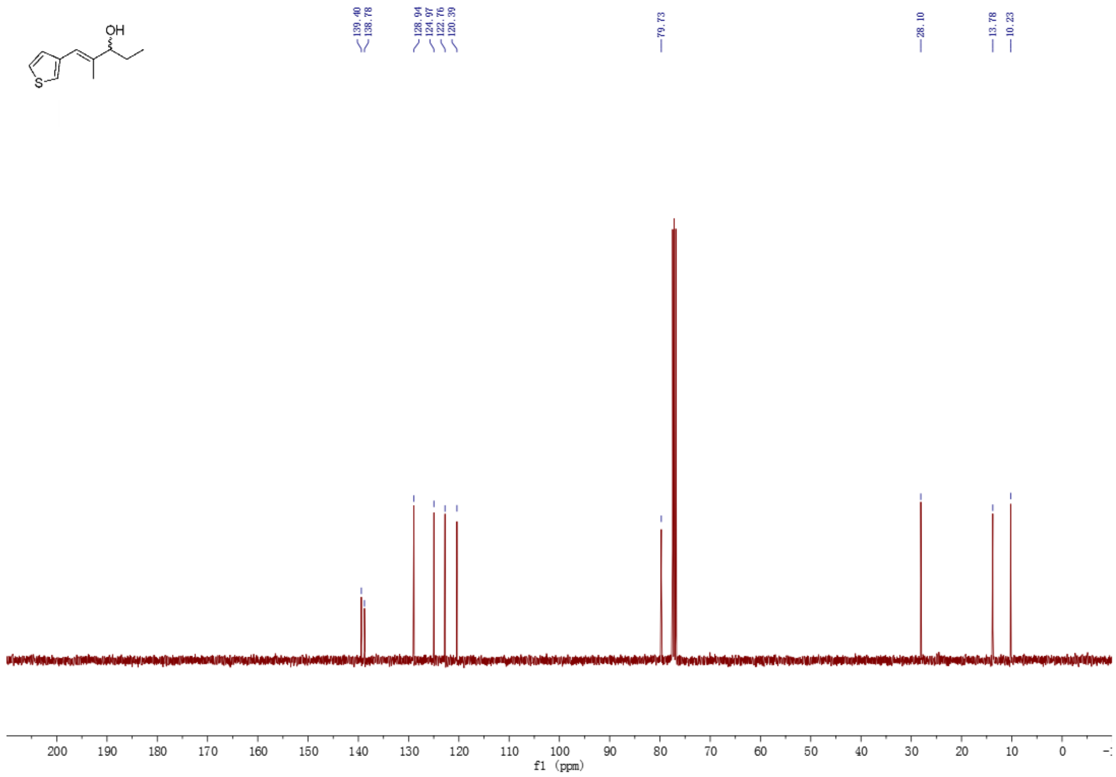




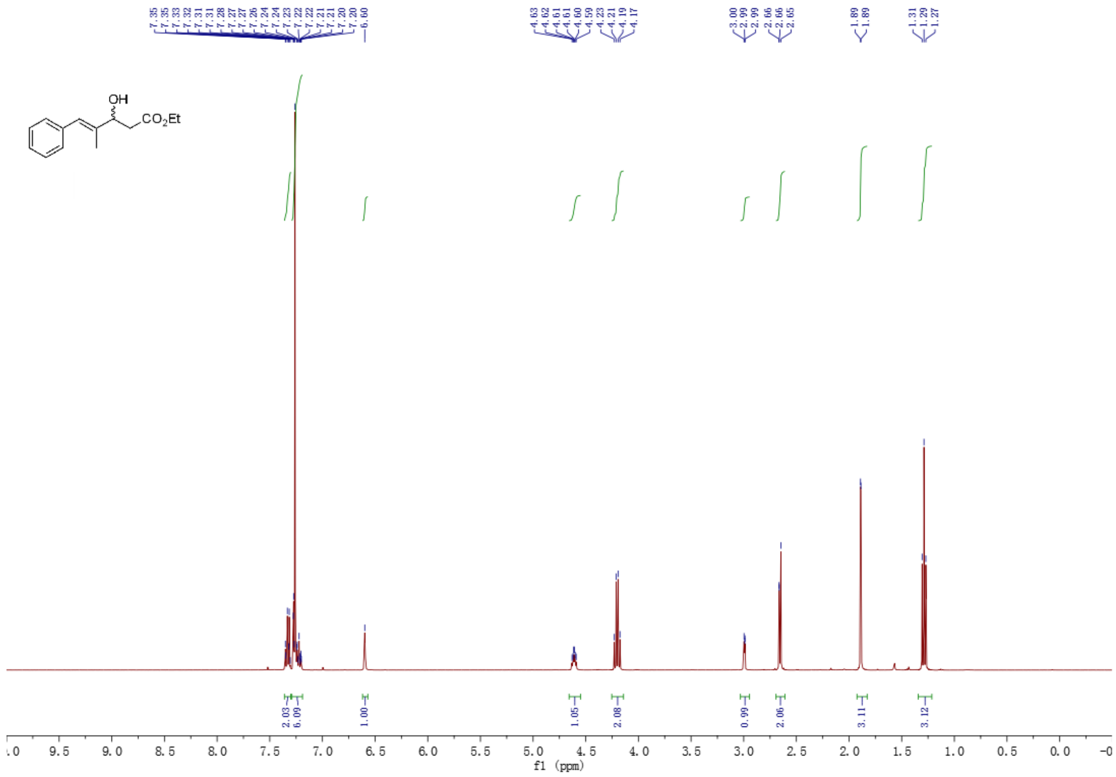


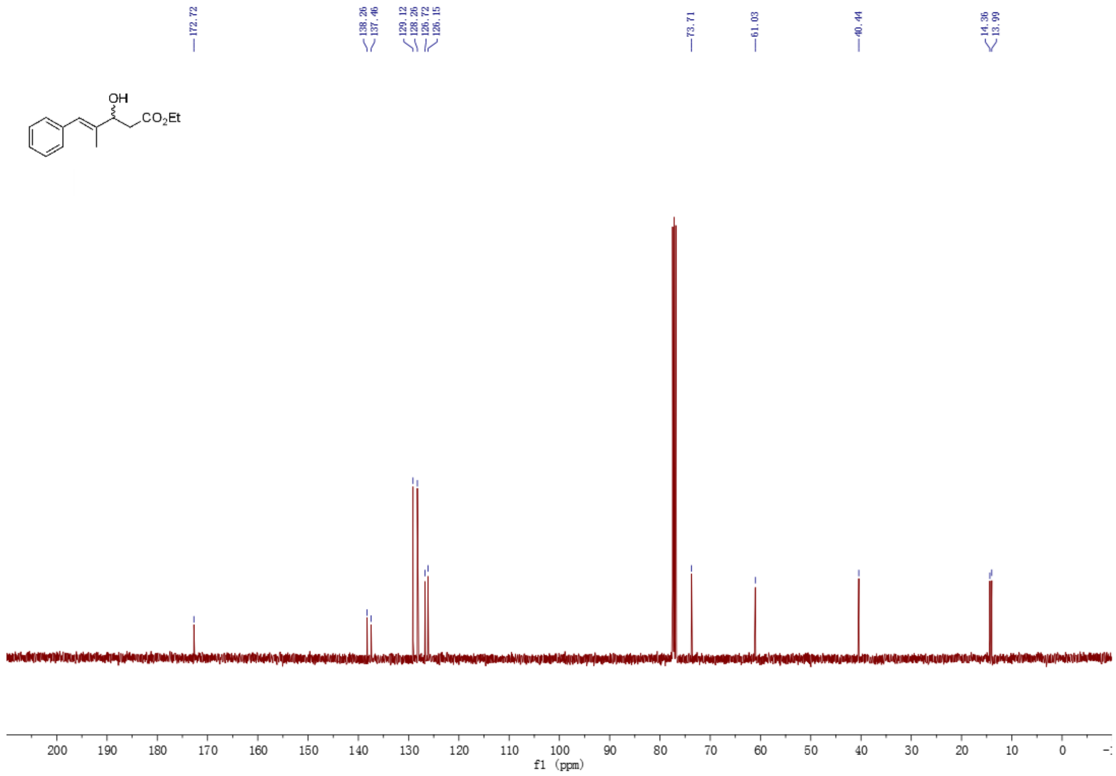


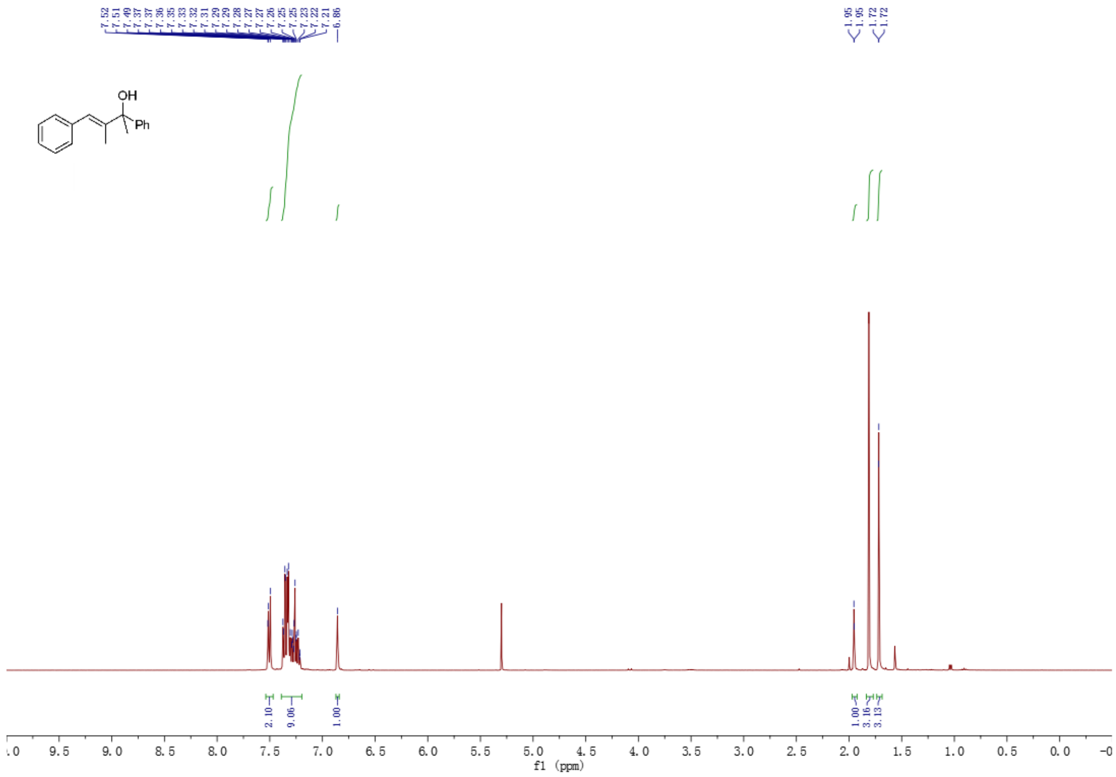
OH
S
7.30
7.29
7.28
7.28
7.18
7.17
7.12
7.12
7.11
7.10
6.45
4.10
4.09
4.09
4.08
4.07
4.06
1.90
1.90
1.69
1.67
1.66
1.64
1.62
1.58
0.94
0.93
0.91
1.02
0.99
0.97
1.00
1.06
3.04
2.13
1.42
3.26
f1 (ppm)

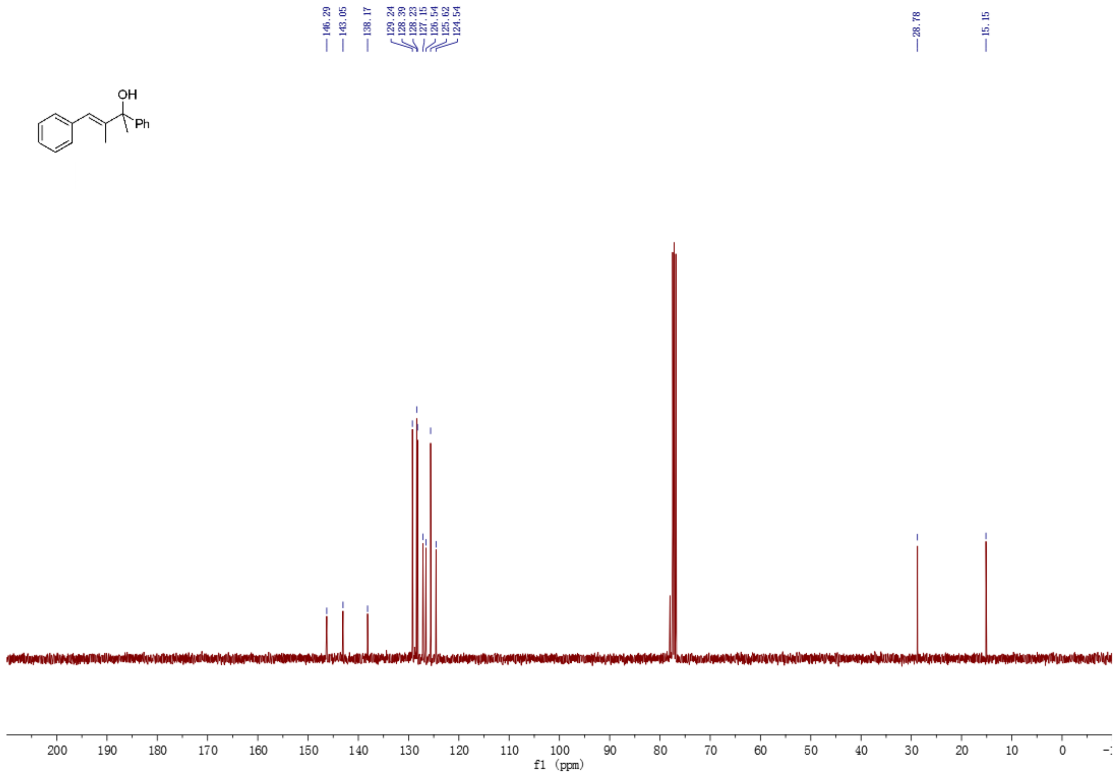


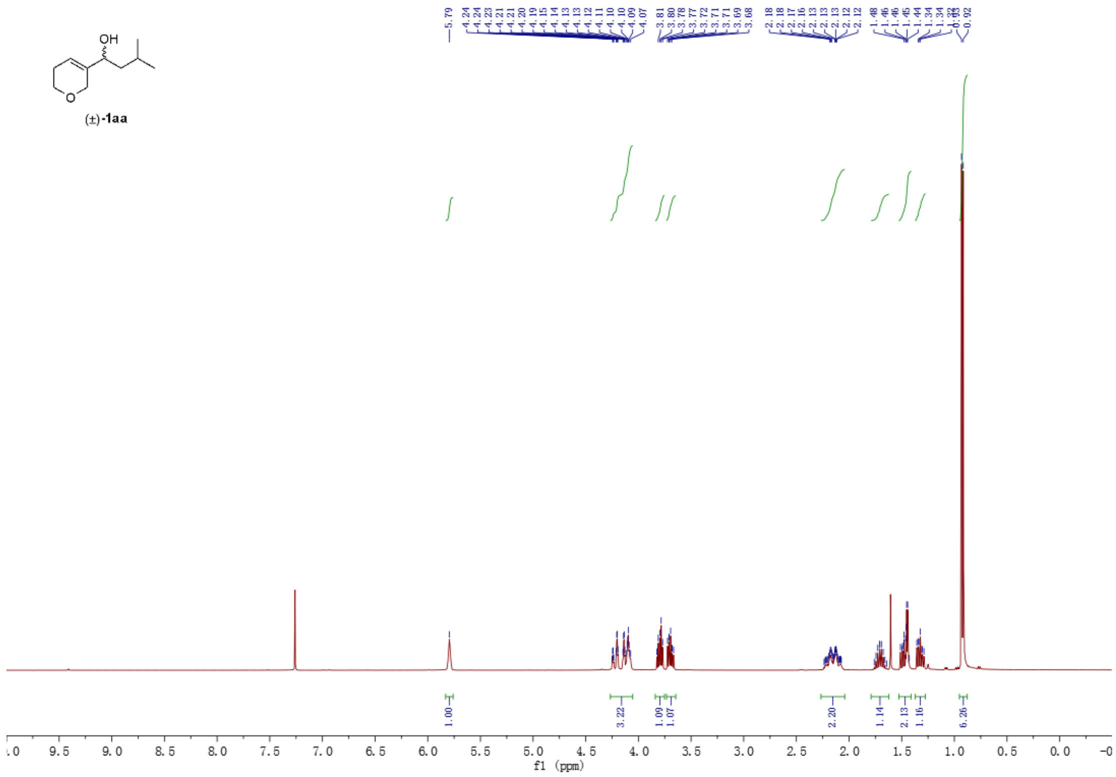
OH
S
139.40
138.78
128.94
124.97
122.76
120.39
79.73
28.10
13.78
10.23
f1 (ppm)

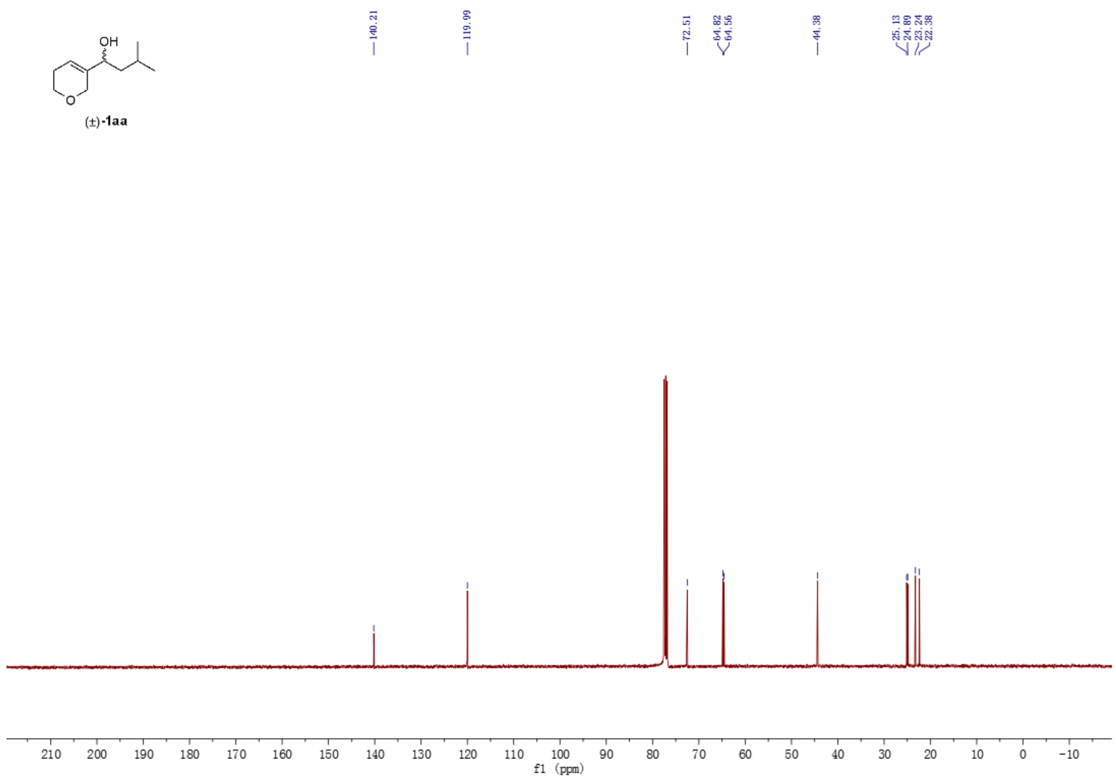


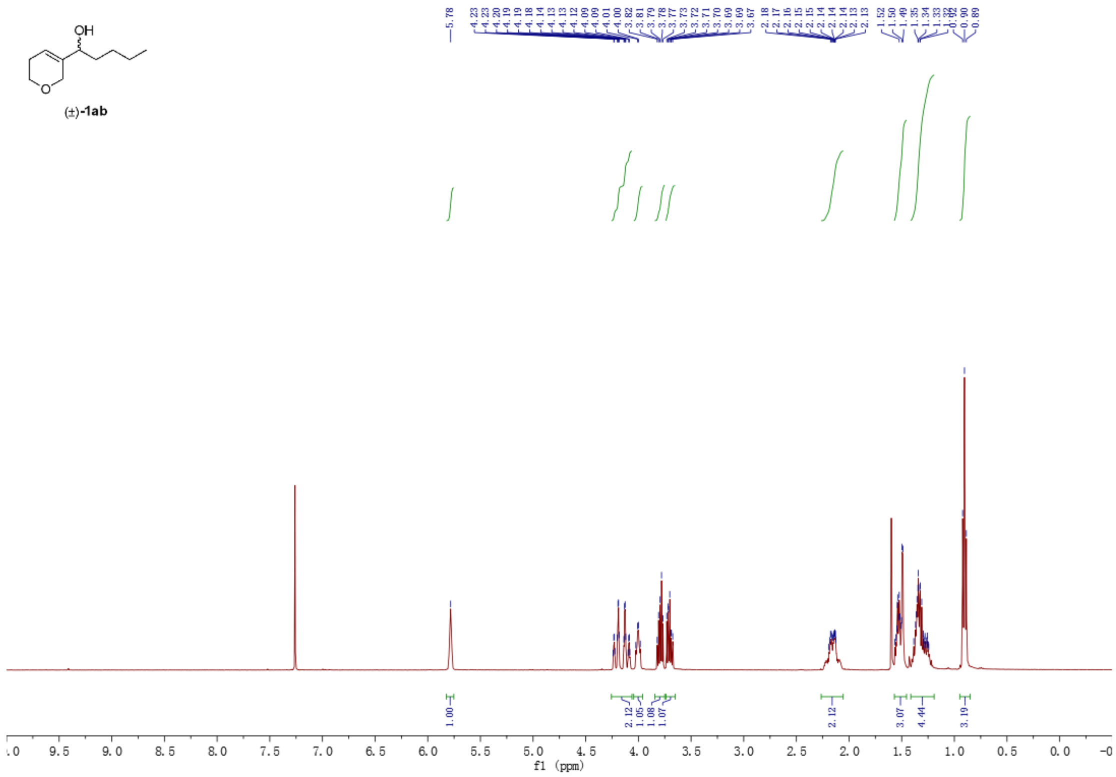




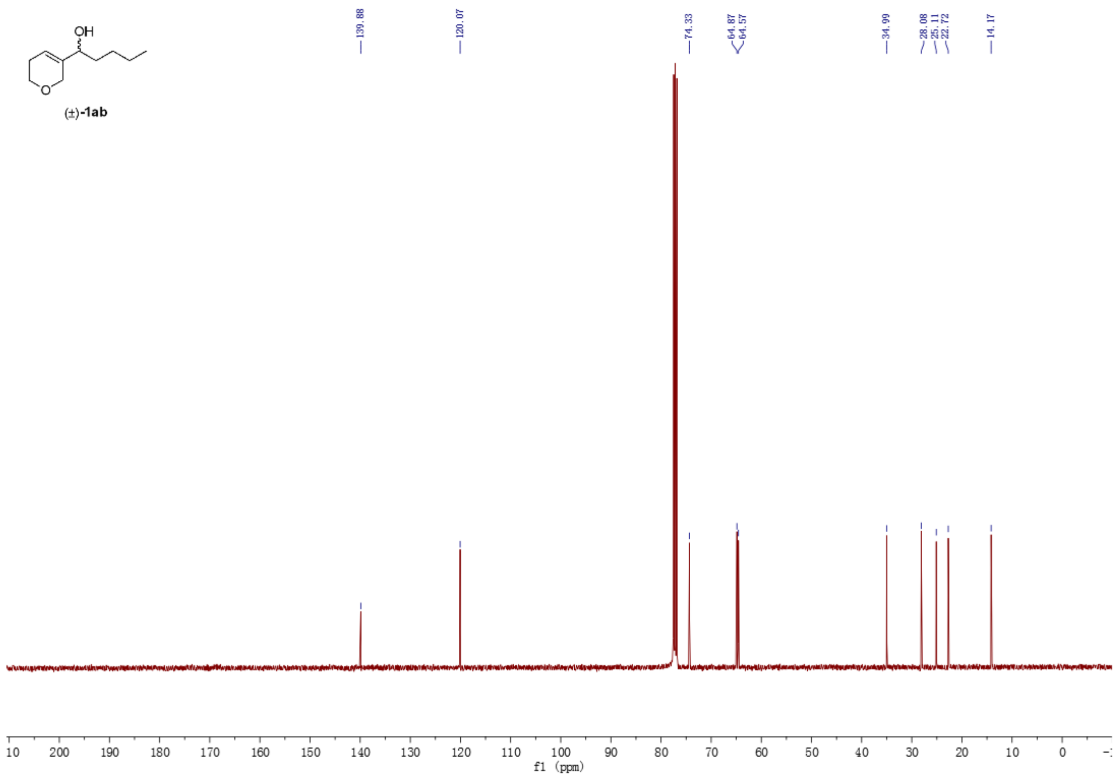




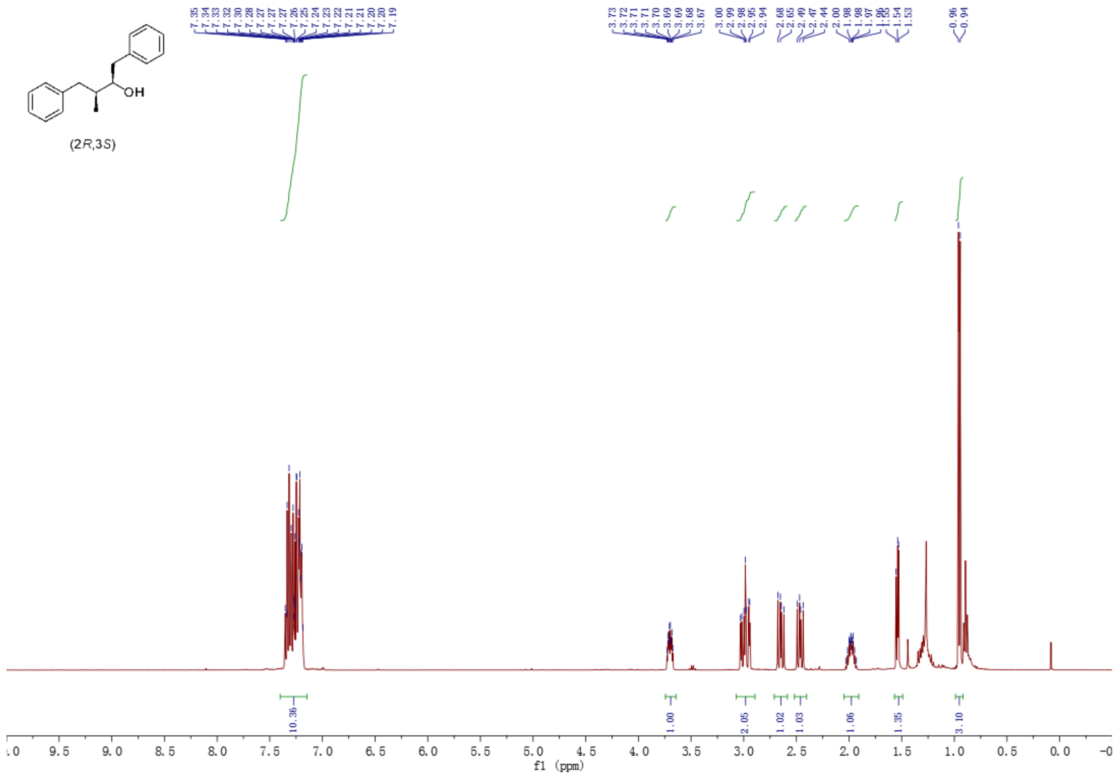


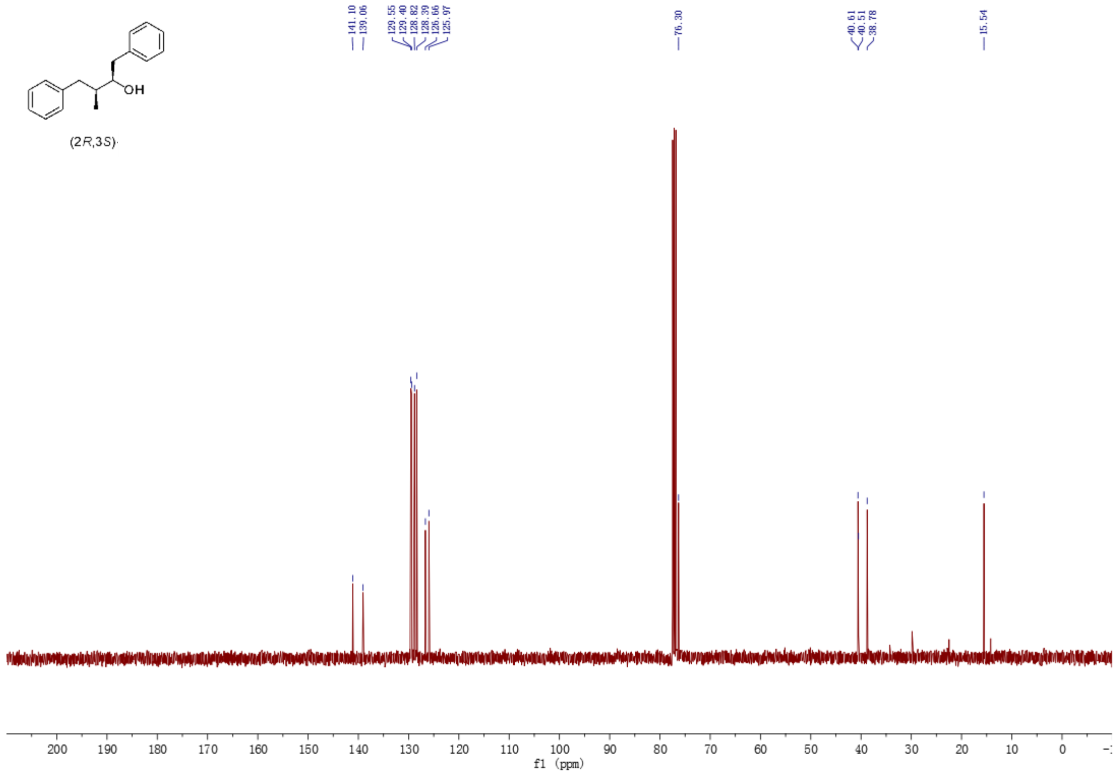


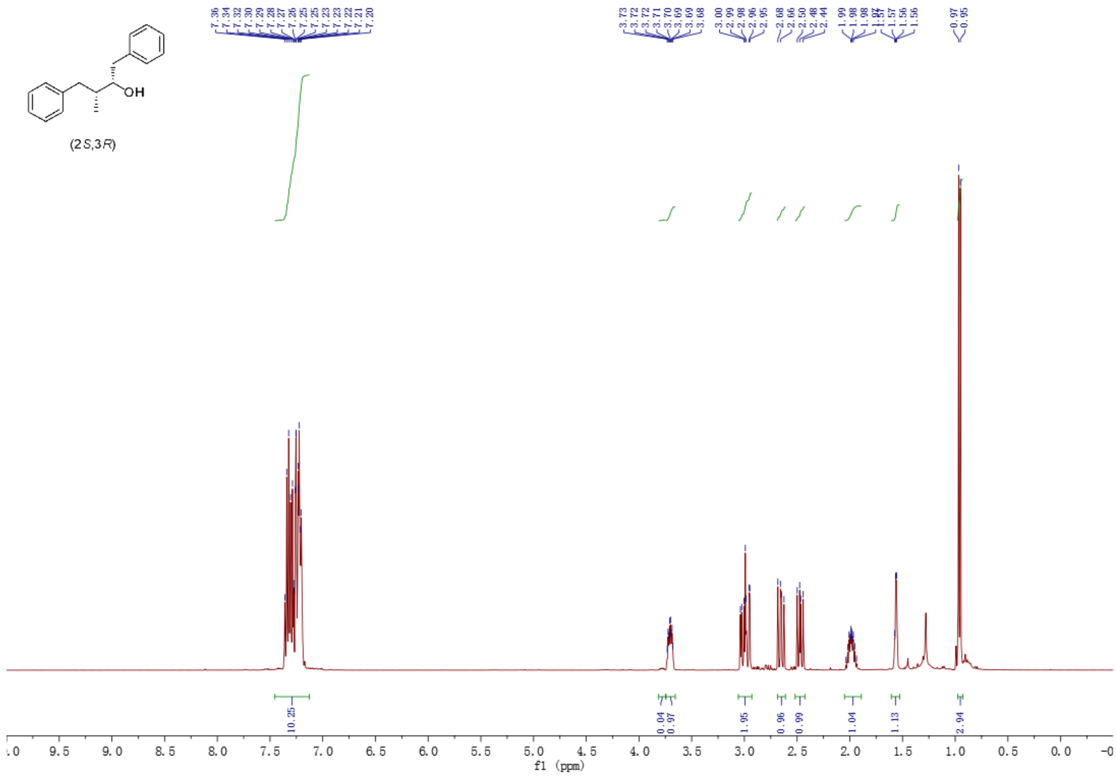
(±)-**1ab**

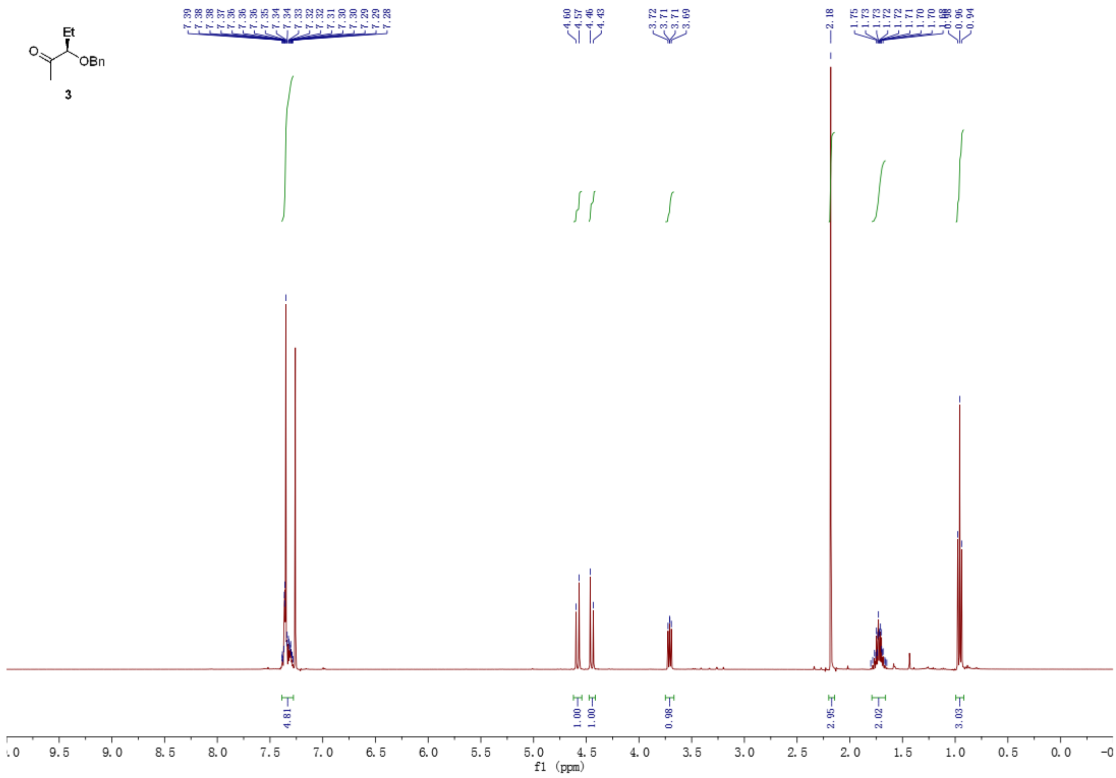


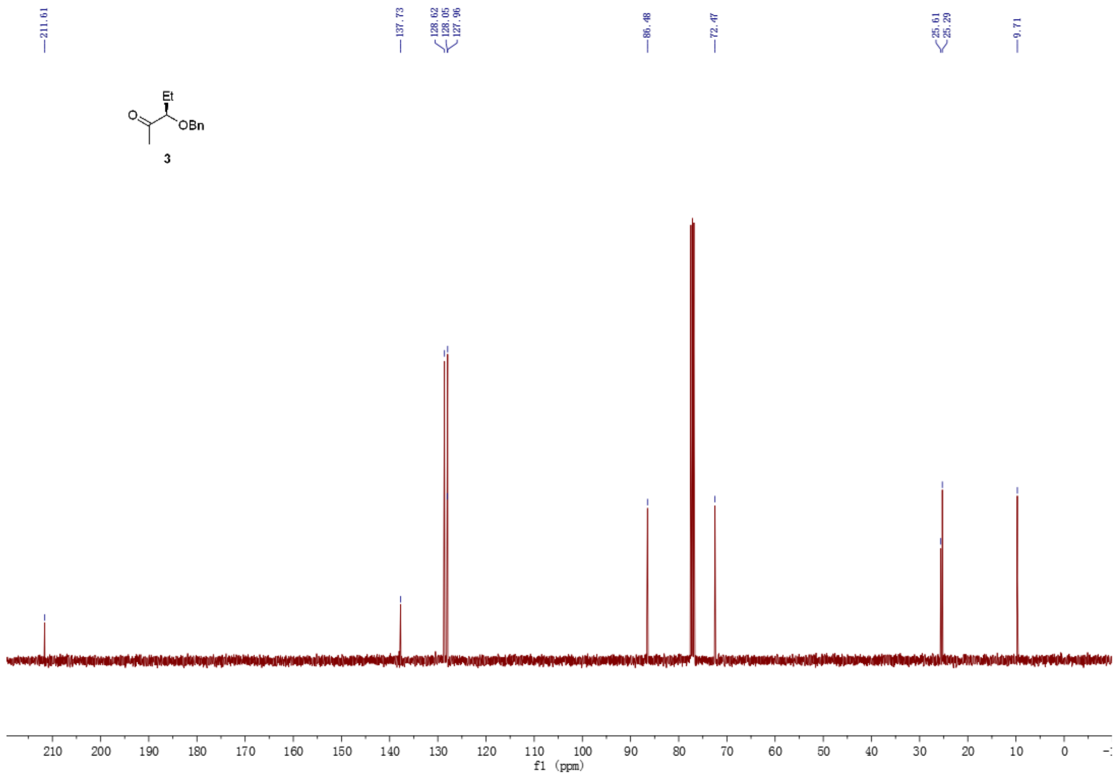
(±)-**1ab**


OH
(2R,3S)
7.35 7.34 7.33 7.32 7.30 7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19
3.73 3.72 3.71 3.70 3.69 3.69 3.68 3.67 3.00 2.99 2.98 2.95 2.94 2.68 2.65 2.49 2.47 2.44 2.00 1.98 1.98 1.97 1.54 1.53
0.96 0.94
10.36 1.00 2.05 1.02 1.03 1.06 1.35 3.10
f1 (ppm)

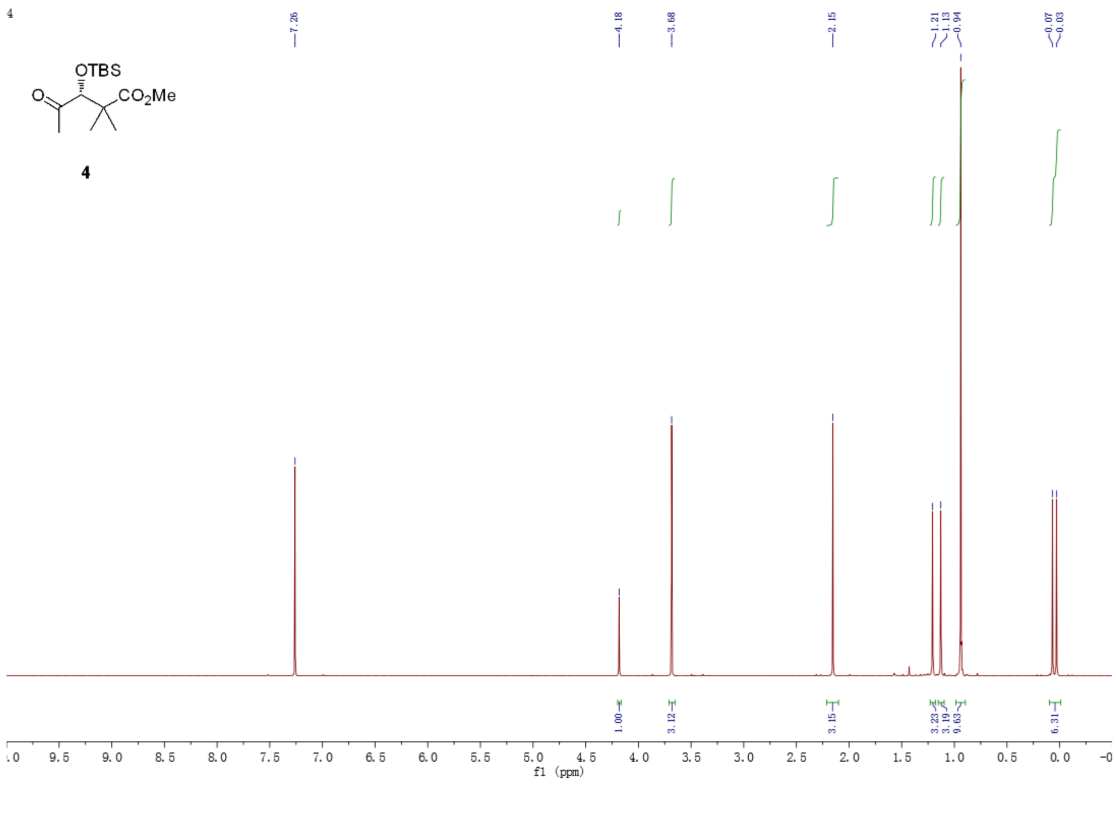

OH
(2R,3S)
141.10 139.06 129.55 129.40 128.82 128.39 126.66 125.97
76.30
40.61 40.51 38.78
15.54
f1 (ppm)


OH
(2S,3R)
f1 (ppm)


Et
O
OBn
3
f1 (ppm)

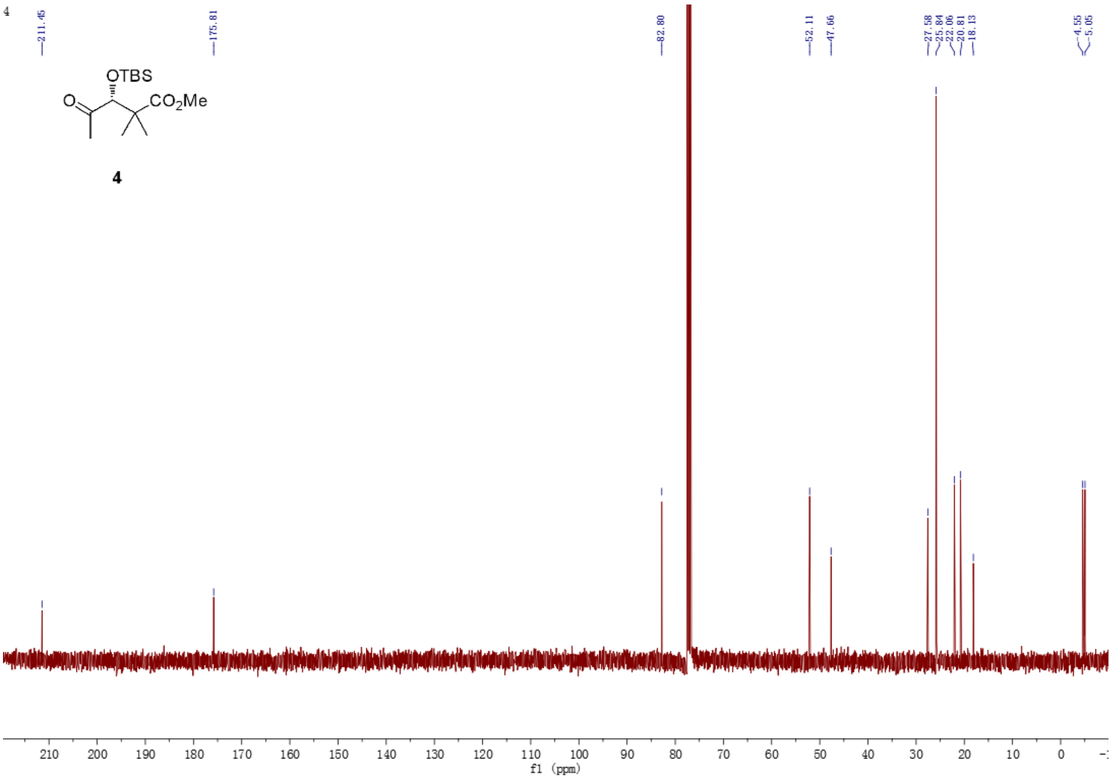


3



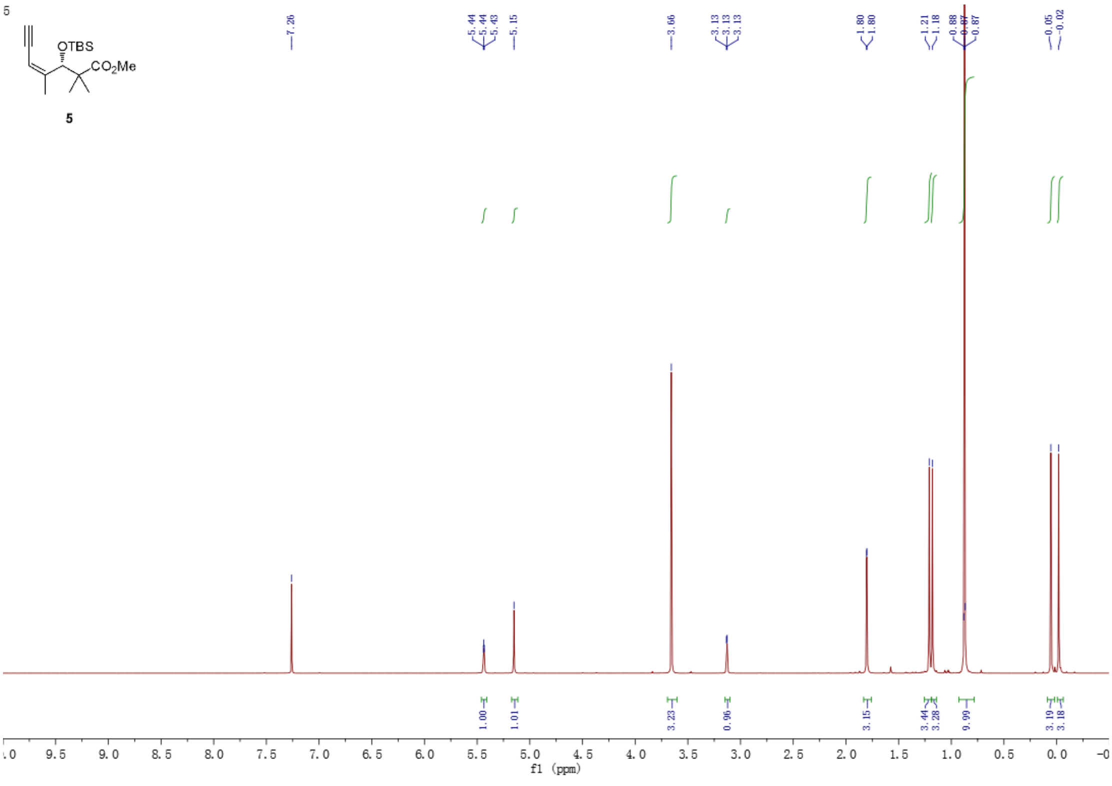
4

4

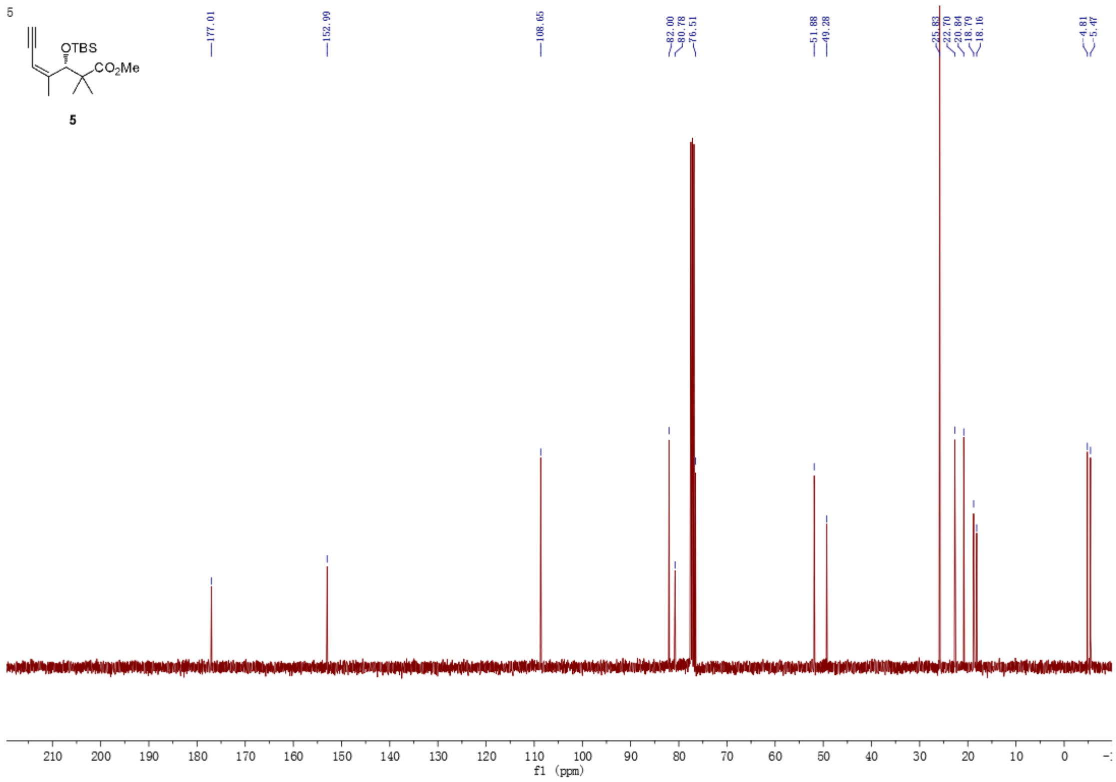


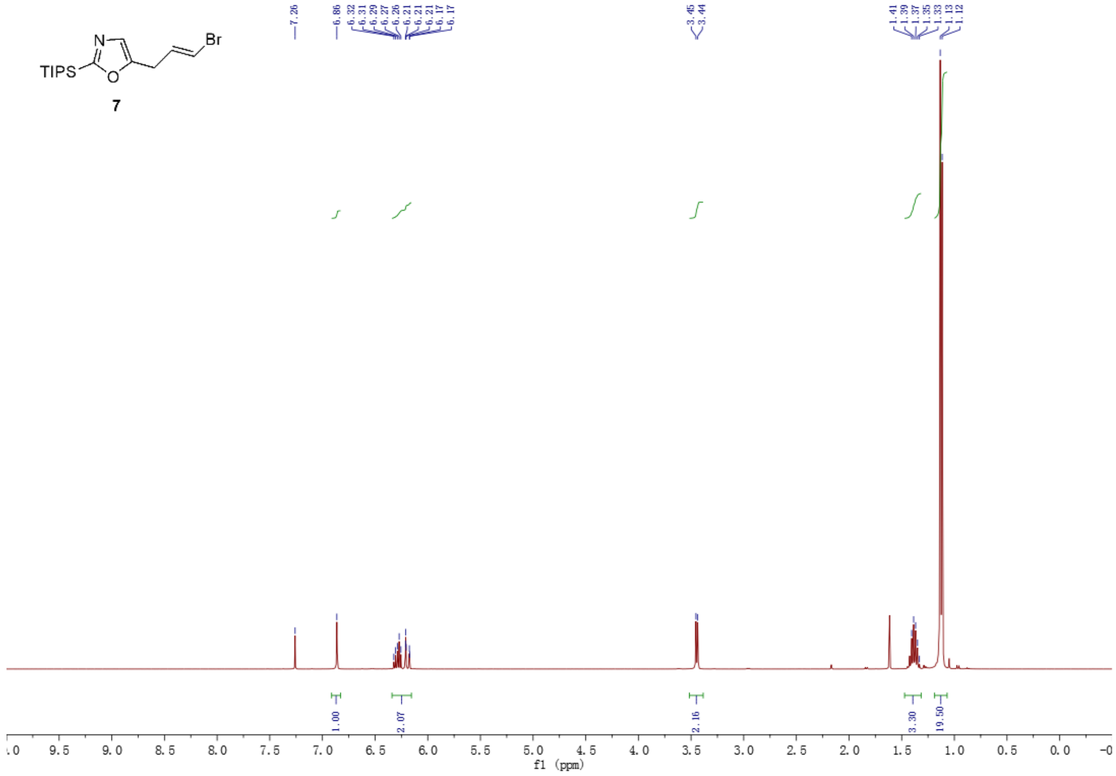
4

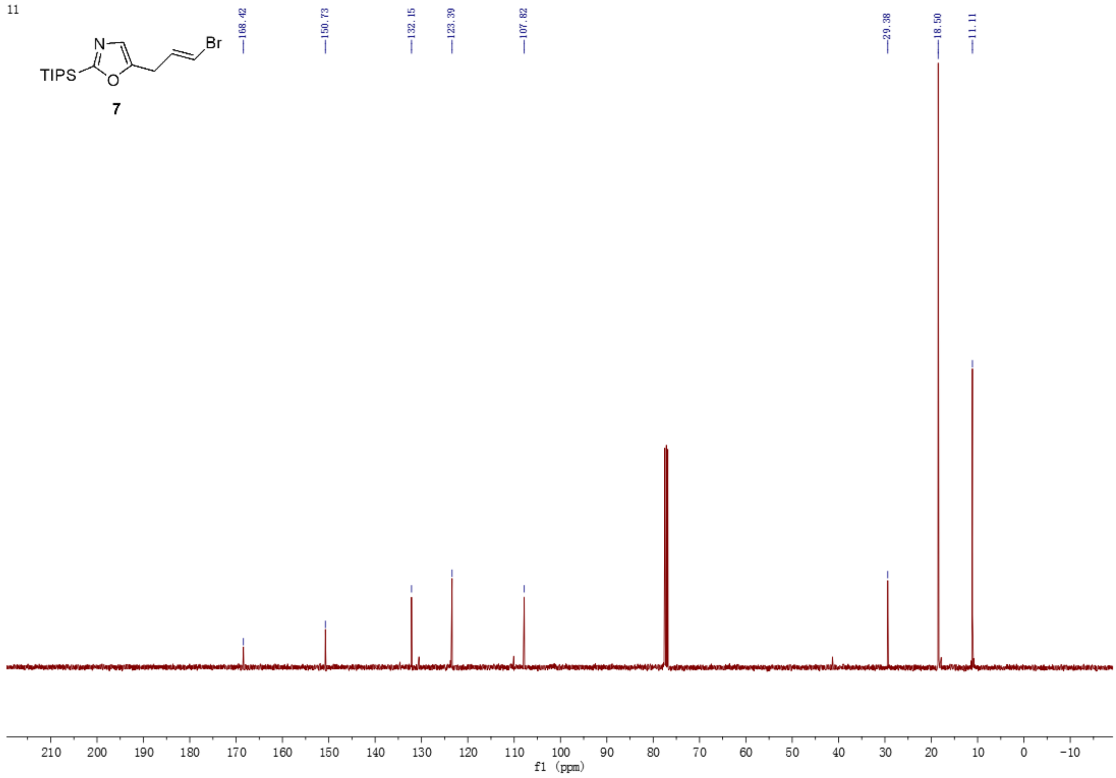
5

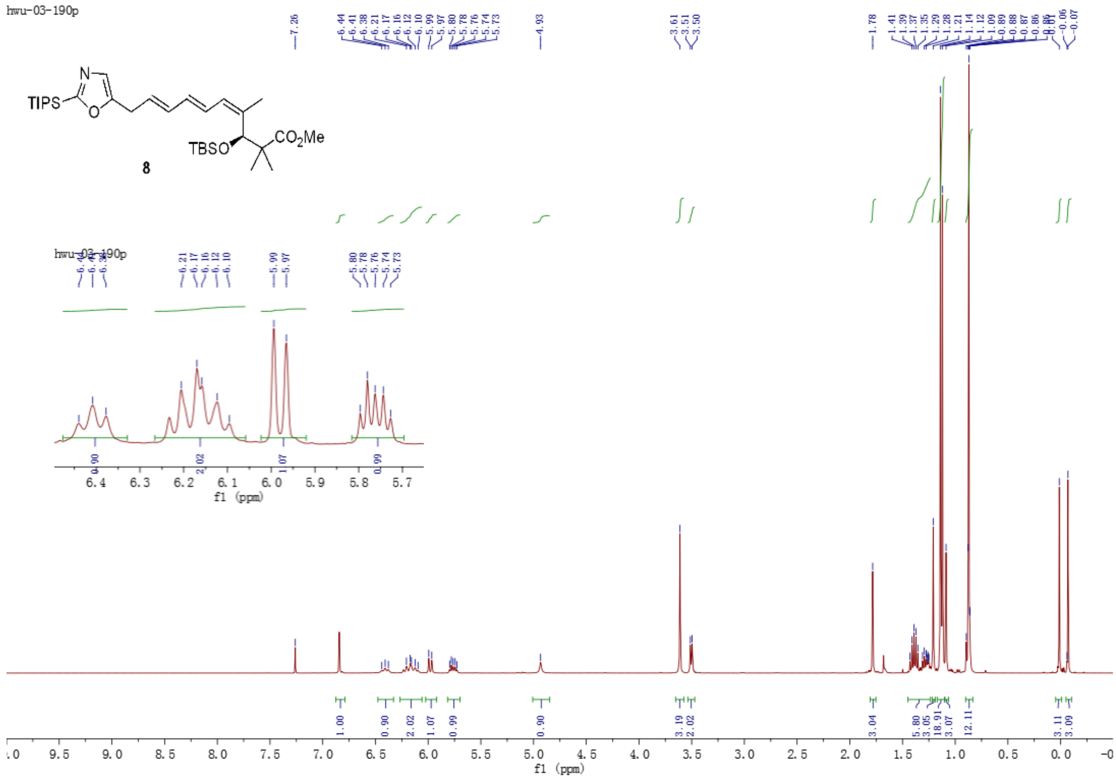


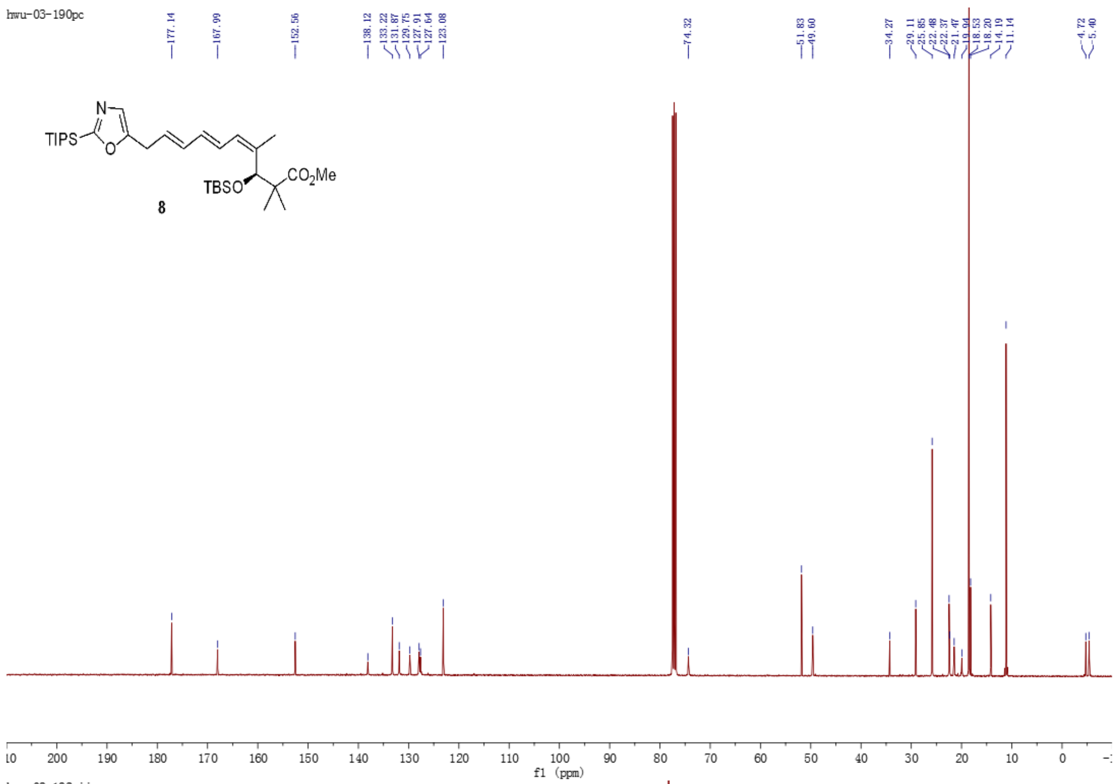
5

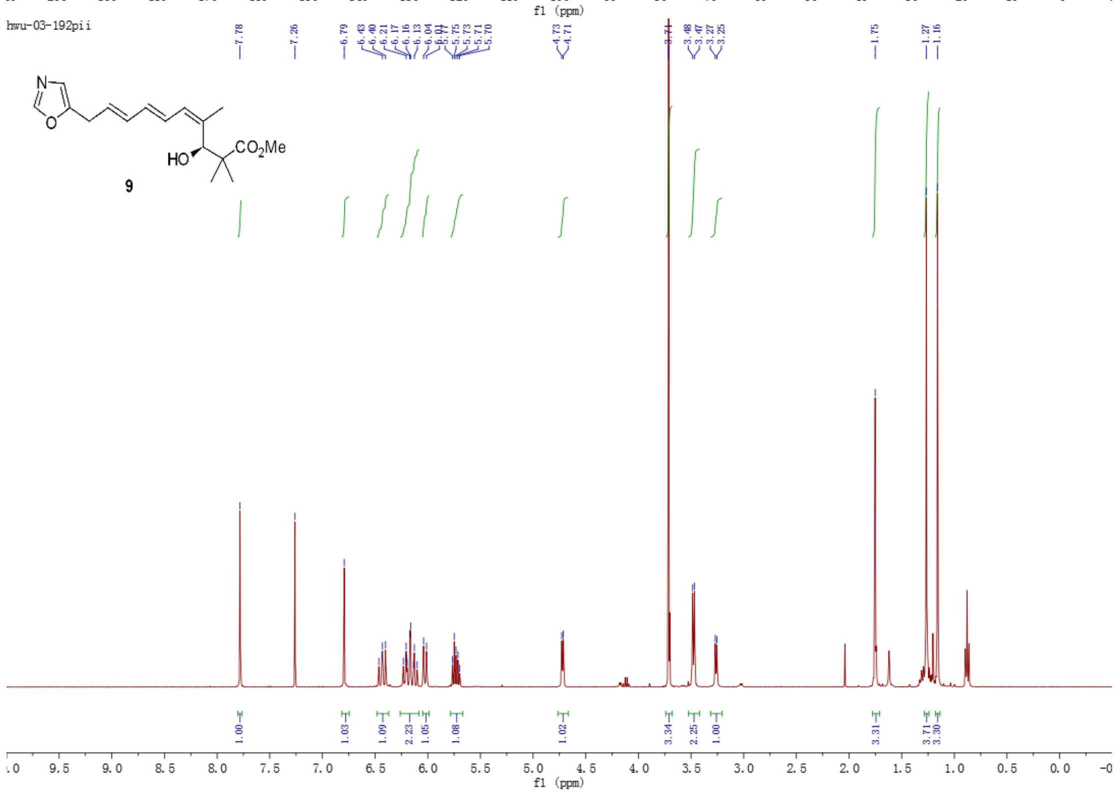




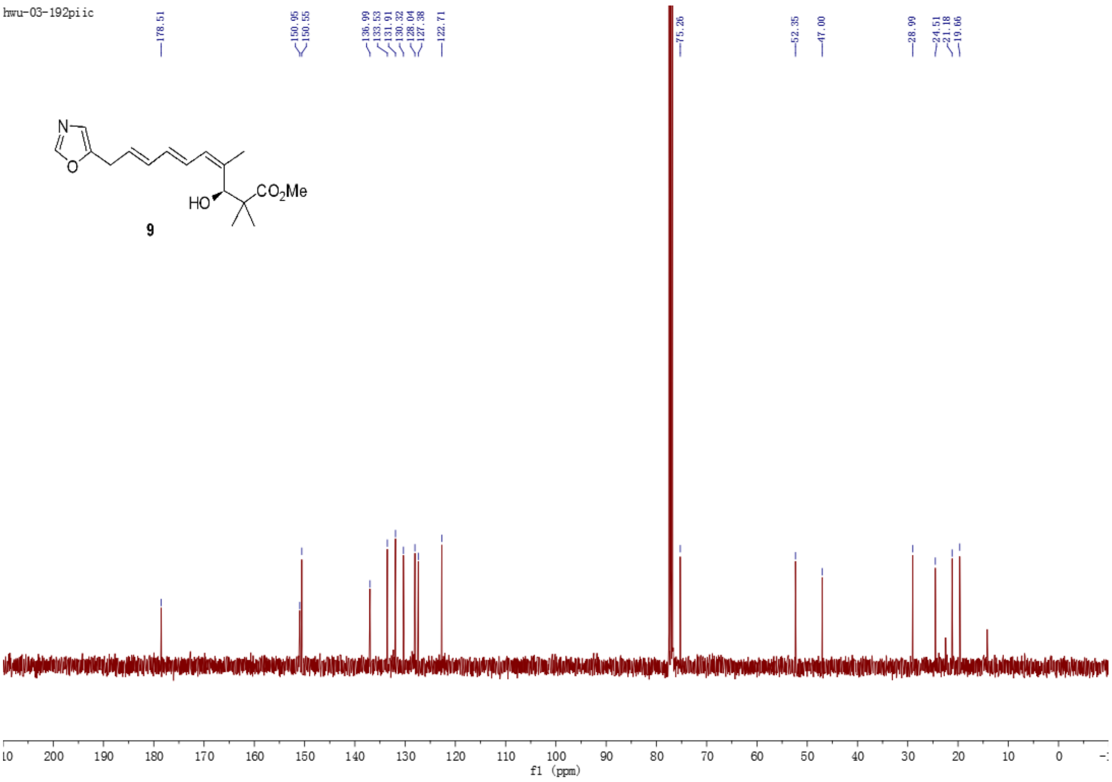




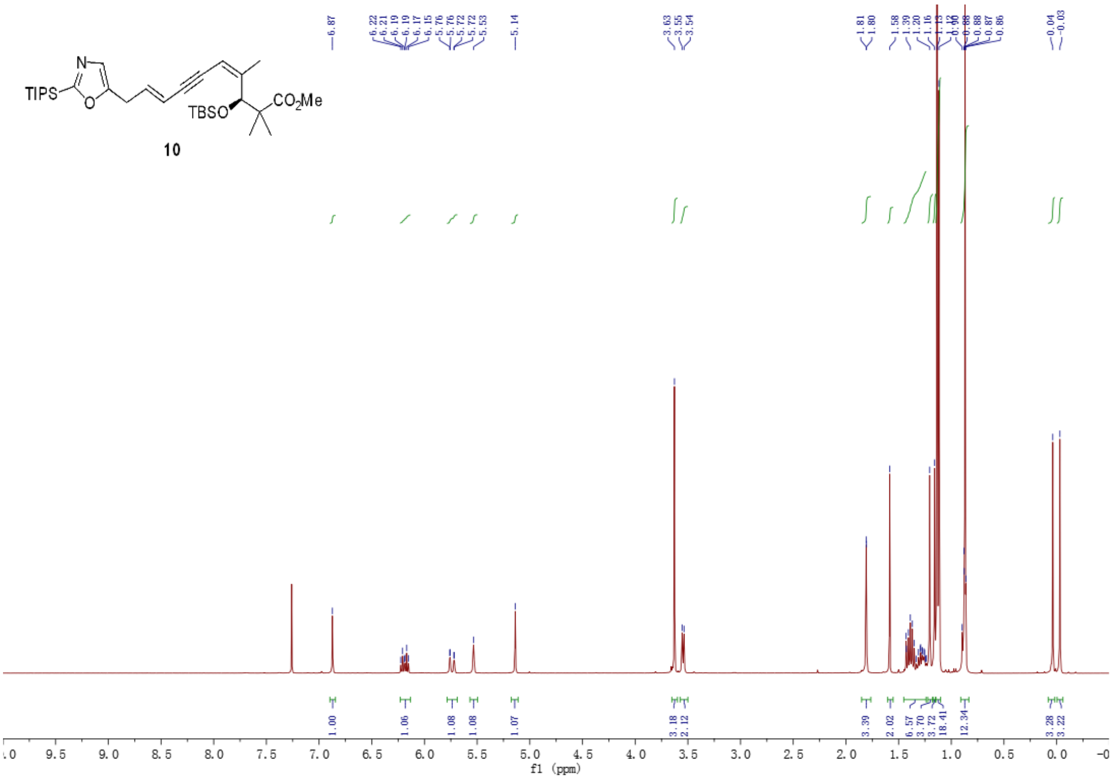




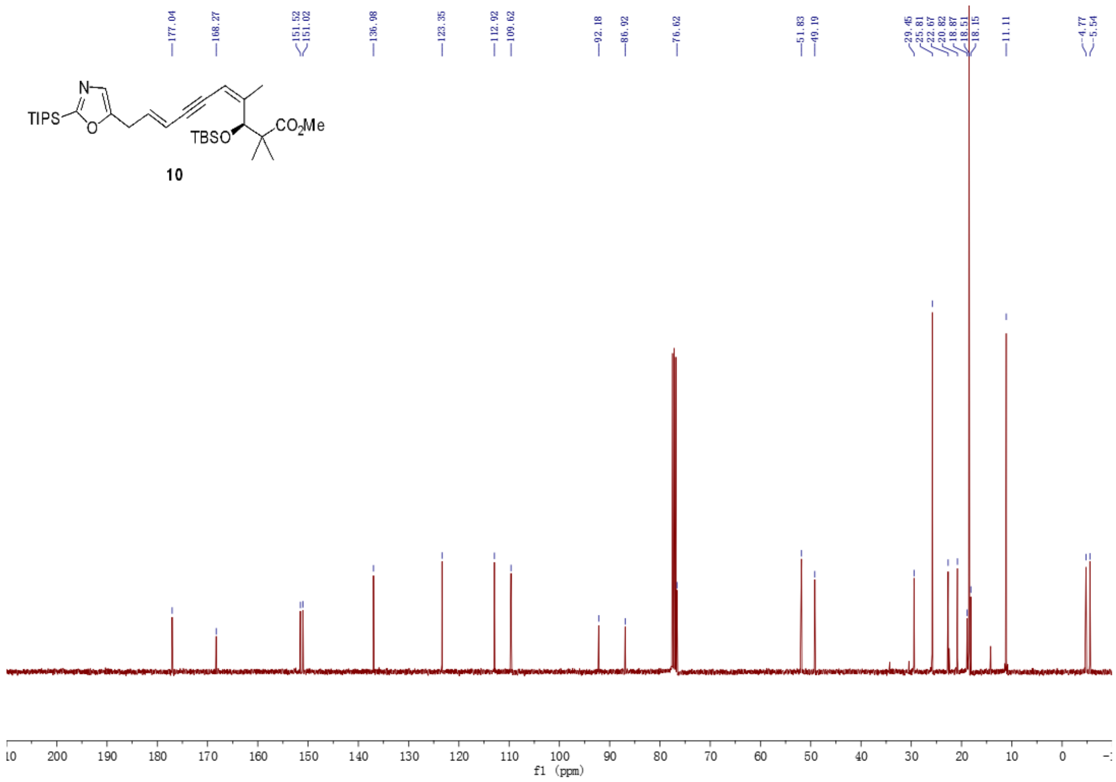
hwu-03-192piic



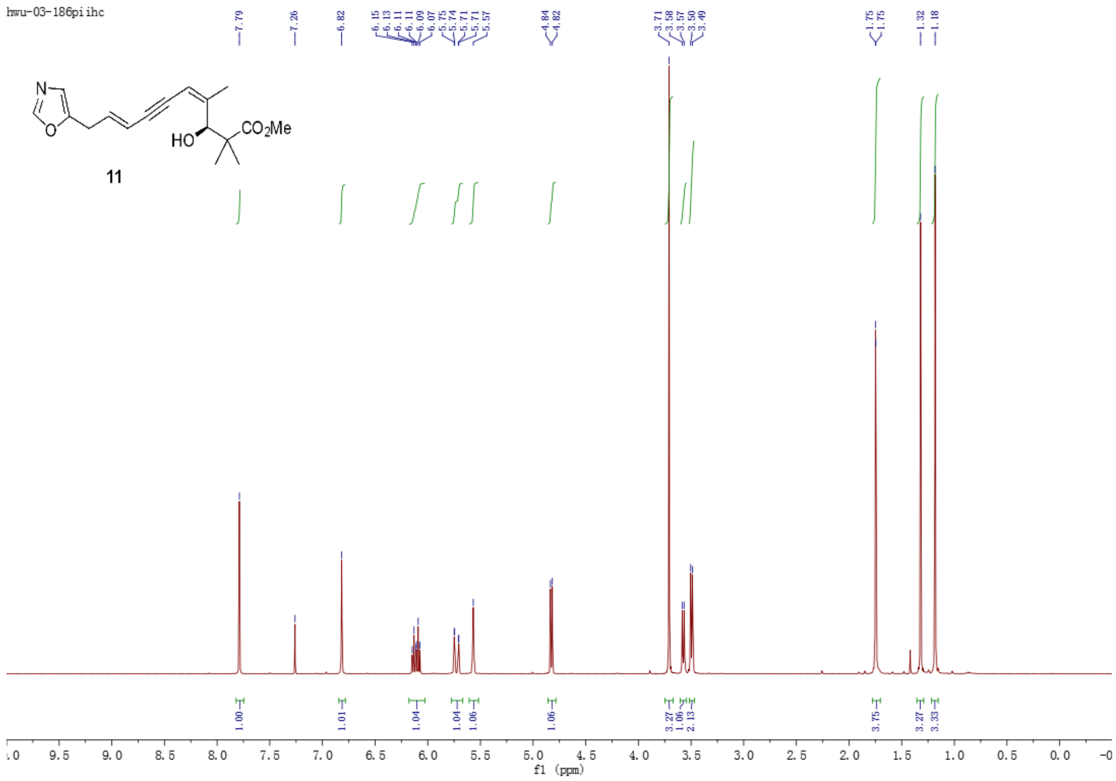
9



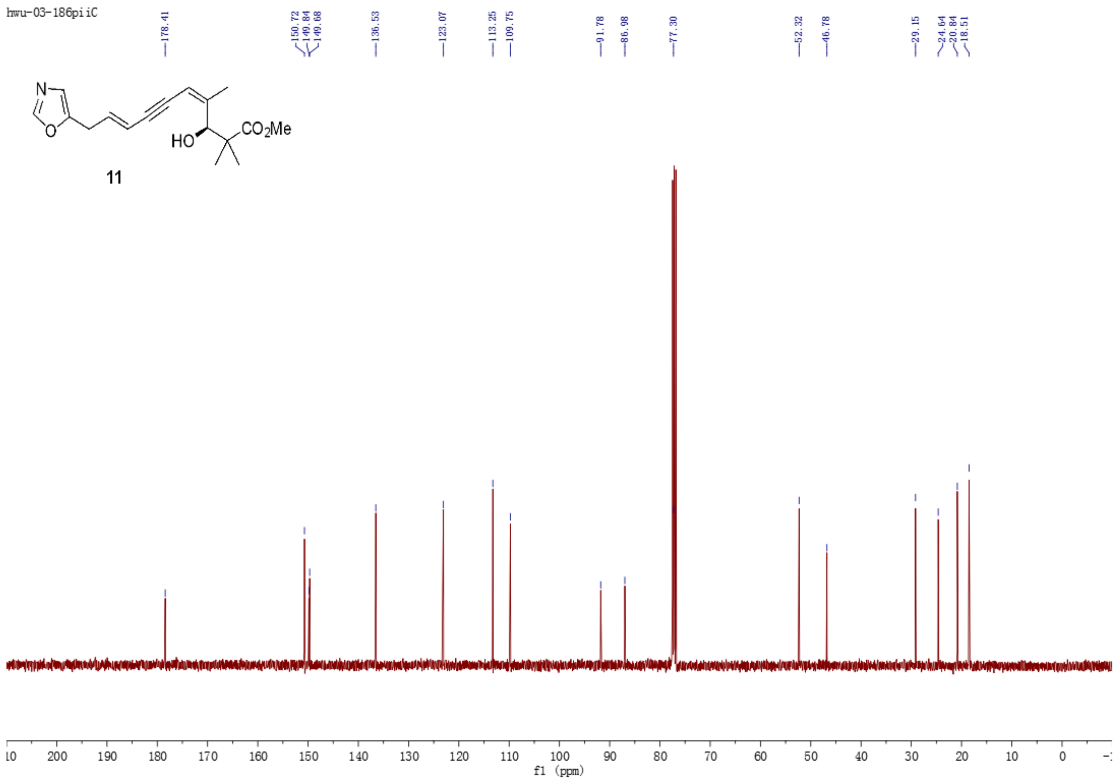
10



TIPS
N
O
TBSO
CO2Me
10
177.04
168.27
151.52
151.02
136.98
123.35
112.92
109.62
92.18
86.92
76.62
51.83
49.19
29.45
25.81
22.67
20.82
18.87
18.51
18.15
11.11
-4.77
-5.54
f1 (ppm)

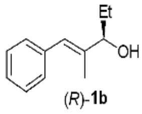


hwu-03-186pi ihc
N
O
HO
CO2Me
11
7.79
7.26
6.82
6.15
6.13
6.11
6.11
6.09
6.07
5.75
5.74
5.71
5.71
5.57
4.84
4.82
3.71
3.58
3.57
3.50
3.49
1.75
1.75
1.32
1.18
1.00
1.01
1.04
1.04
1.06
1.06
3.27
1.06
2.13
3.75
3.27
3.33
f1 (ppm)

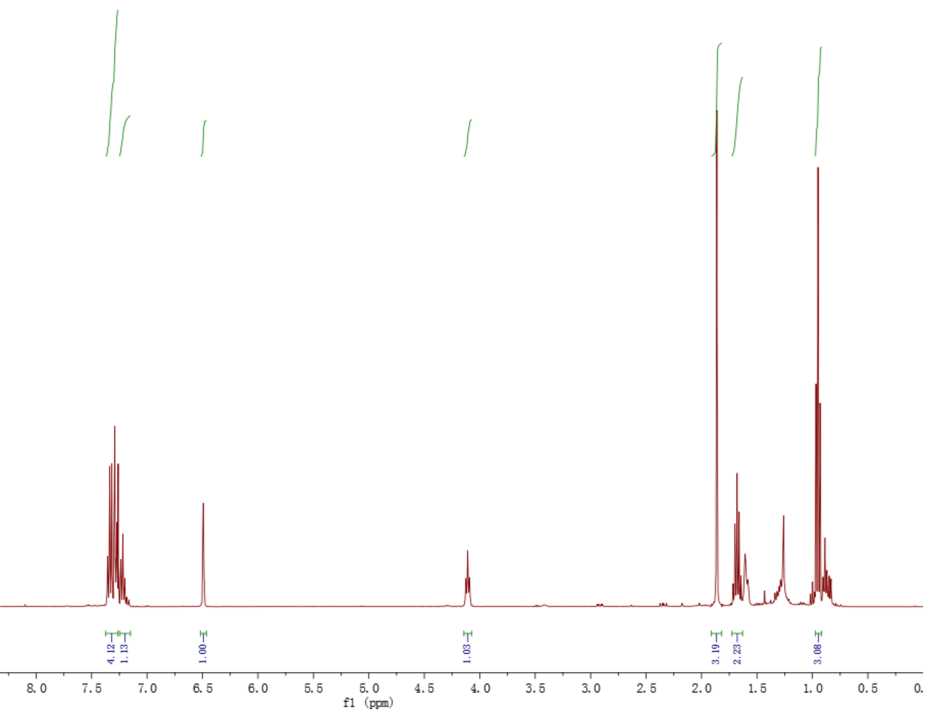

hwu-03-186piiC
178.41
150.72
149.84
149.68
136.53
123.07
113.25
109.75
91.78
86.98
77.30
52.32
46.78
29.15
24.64
20.84
18.51
HO
CO2Me
N
O
11
f1 (ppm)

^{1}H and ^{19}F NMR of resolved allylic alcohols

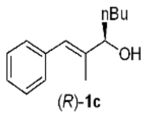
hwu-190211-203-56asmr.10.fid



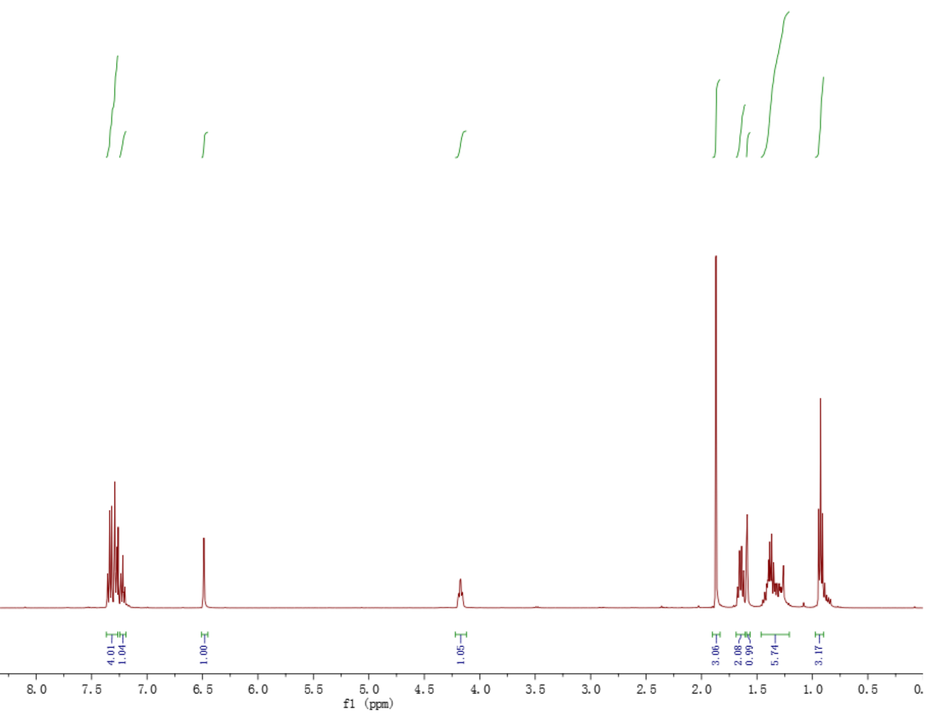
(*R*)-**1b**



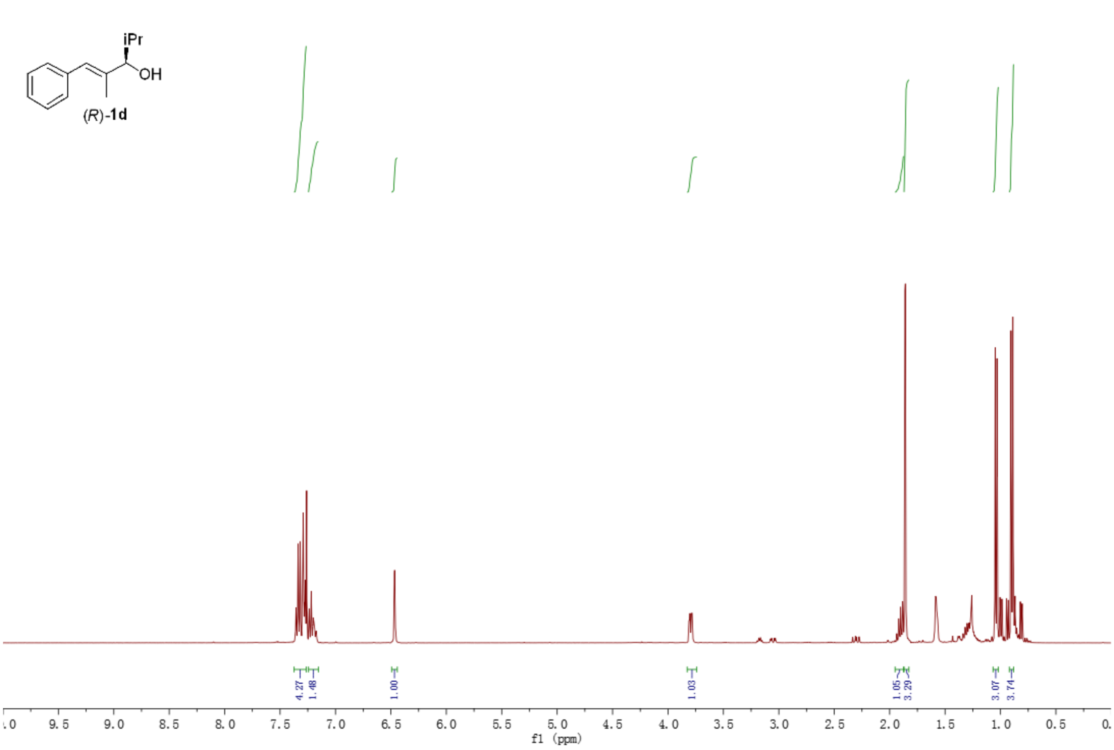
hwu-190214-203-62a3smr.10.fid



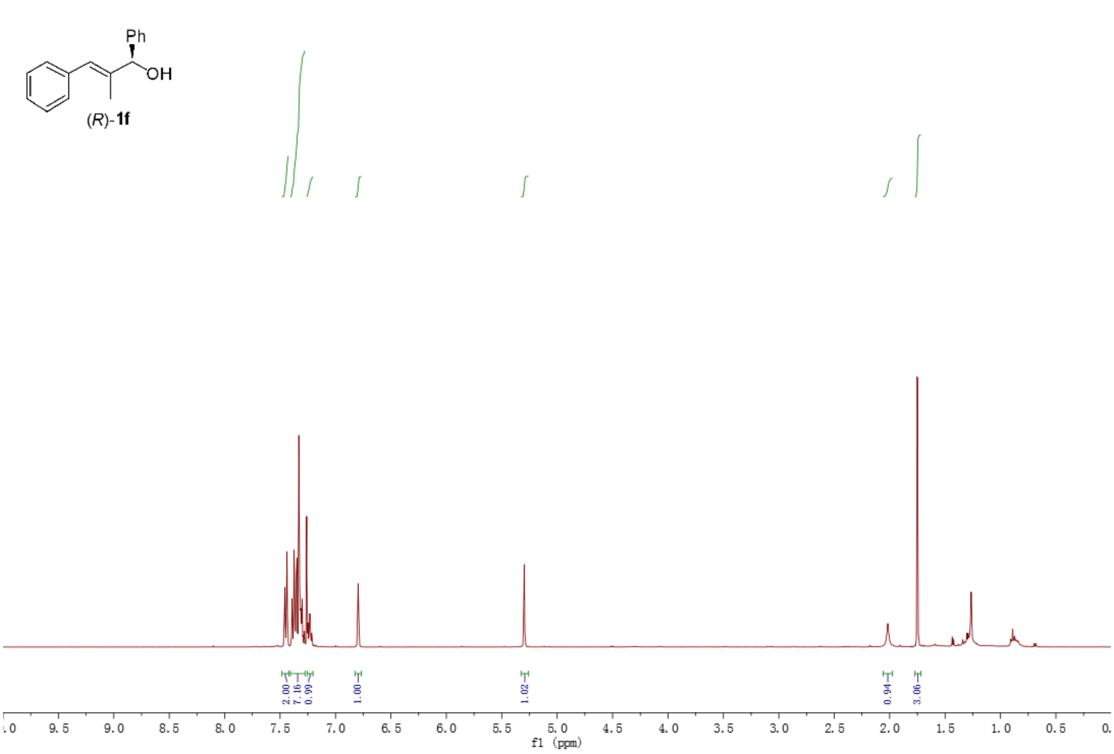
(*R*)-**1c**

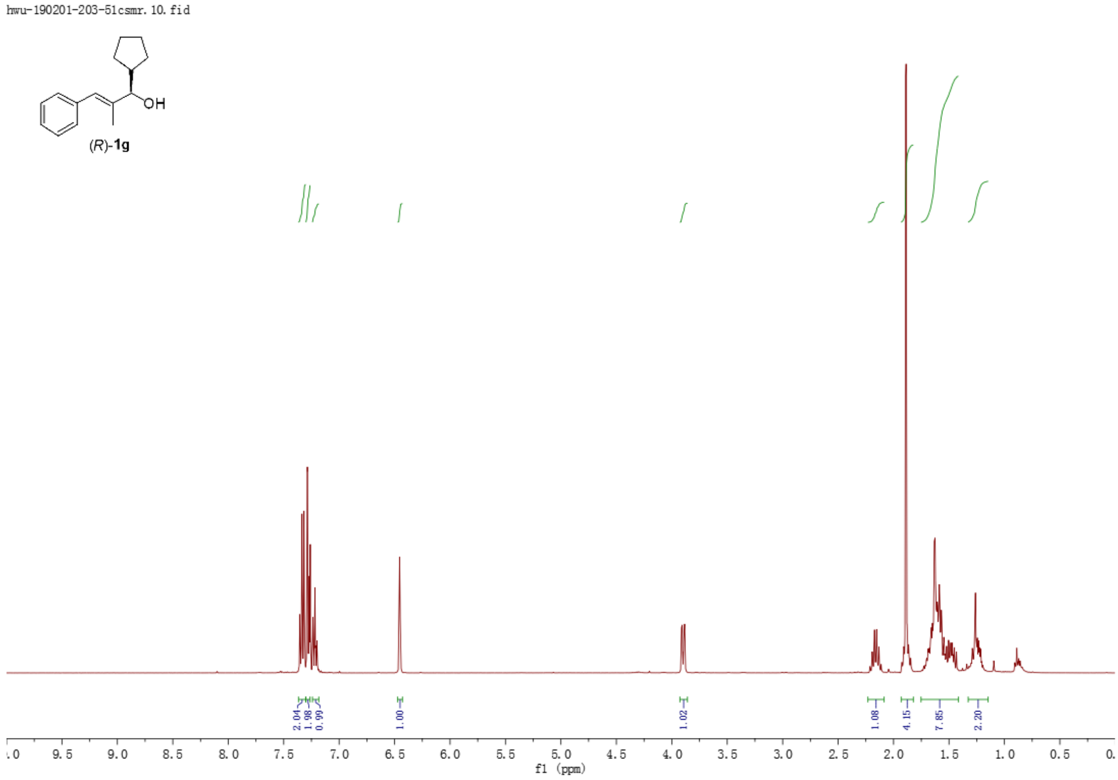


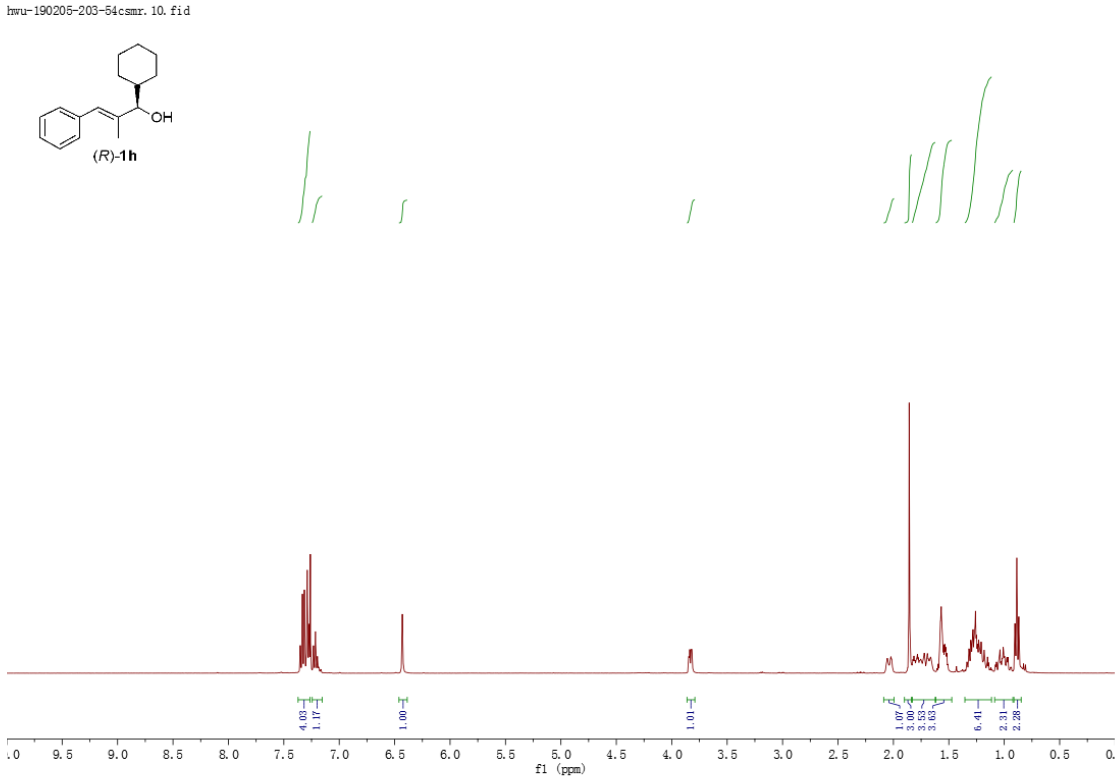
hwu-190219-203-64asmr.10.fid



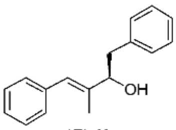
hwu-190221-203-64c4smr.10.fid



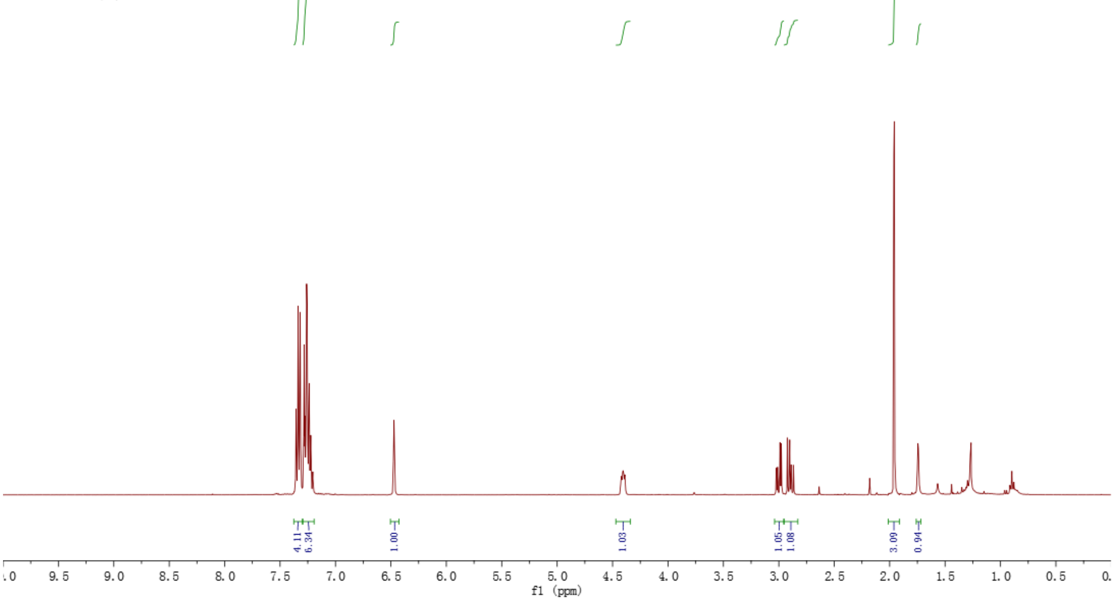

hwu-190201-203-51csmr.10.fid
OH
(R)-1g
2.04
1.98
0.99
1.00
1.02
1.08
4.15
7.85
2.20
f1 (ppm)


hwu-190205-203-54csmr.10.fid
OH
(R)-1h
4.03
1.17
1.00
1.01
1.07
3.00
3.53
3.63
6.41
2.31
2.28
f1 (ppm)

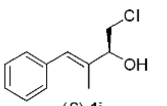
hwu-190201-203-51bsmr.10.fid



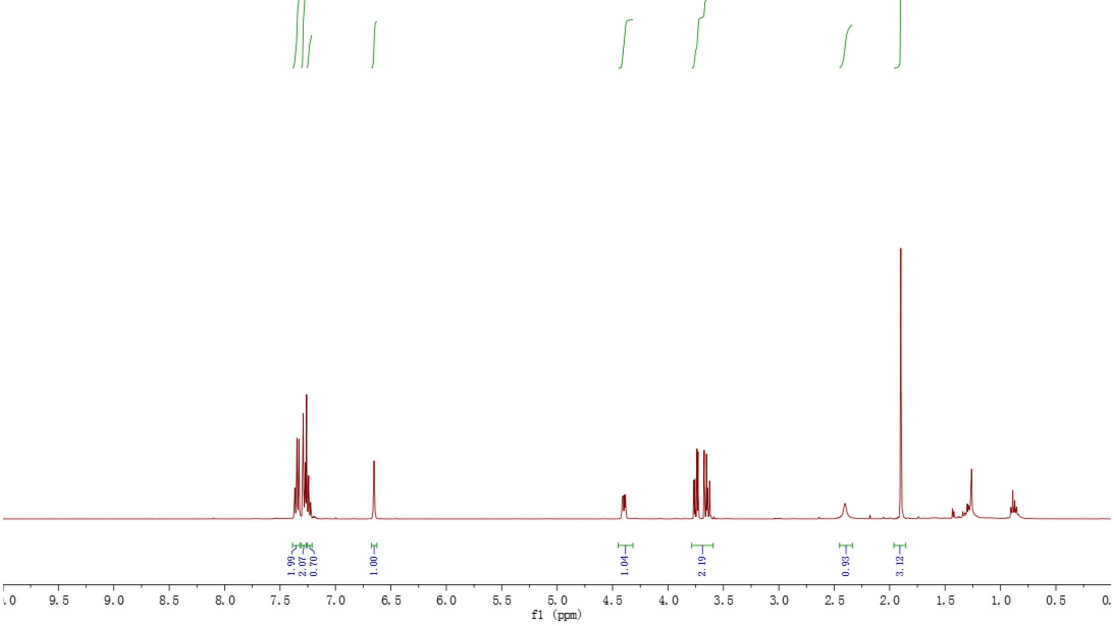
(*R*)-**1i**

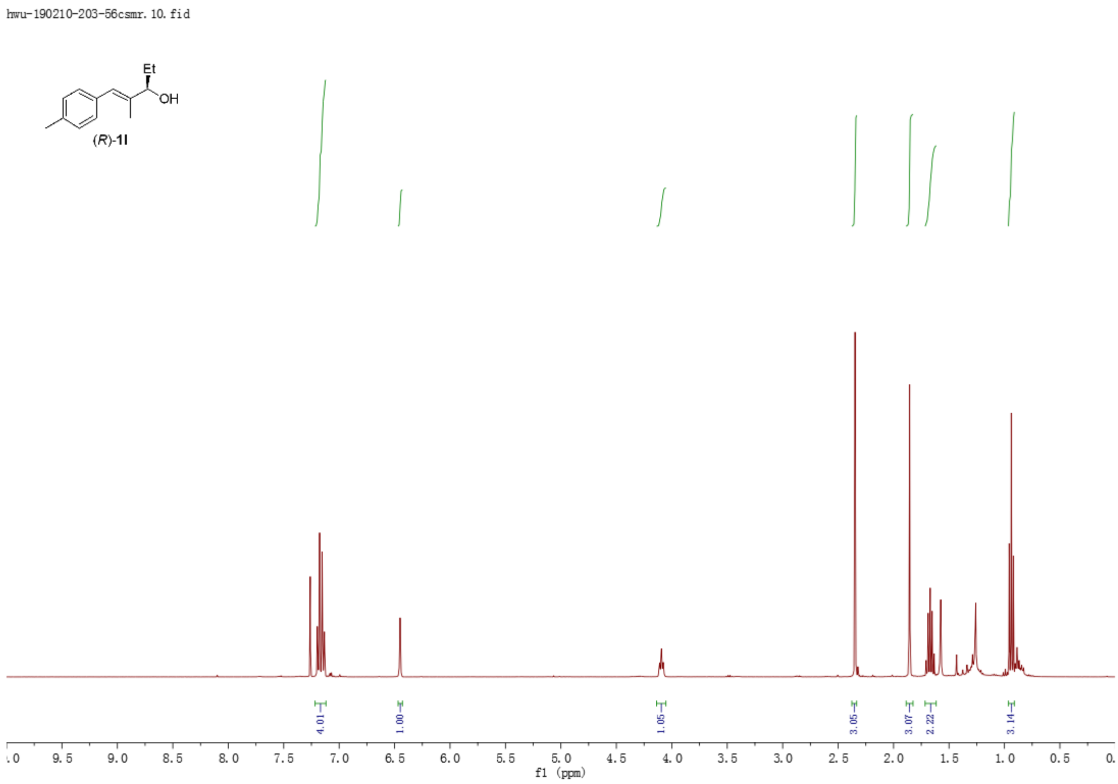


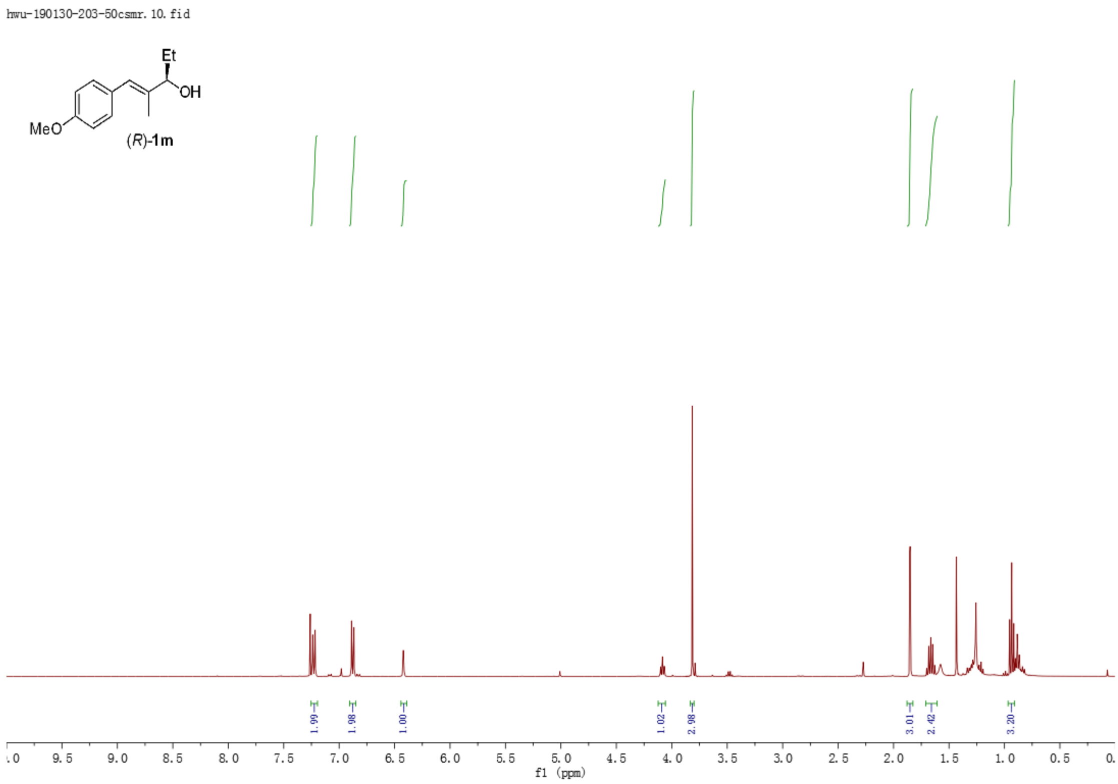
hwu-190221-203-67asmr.10.fid

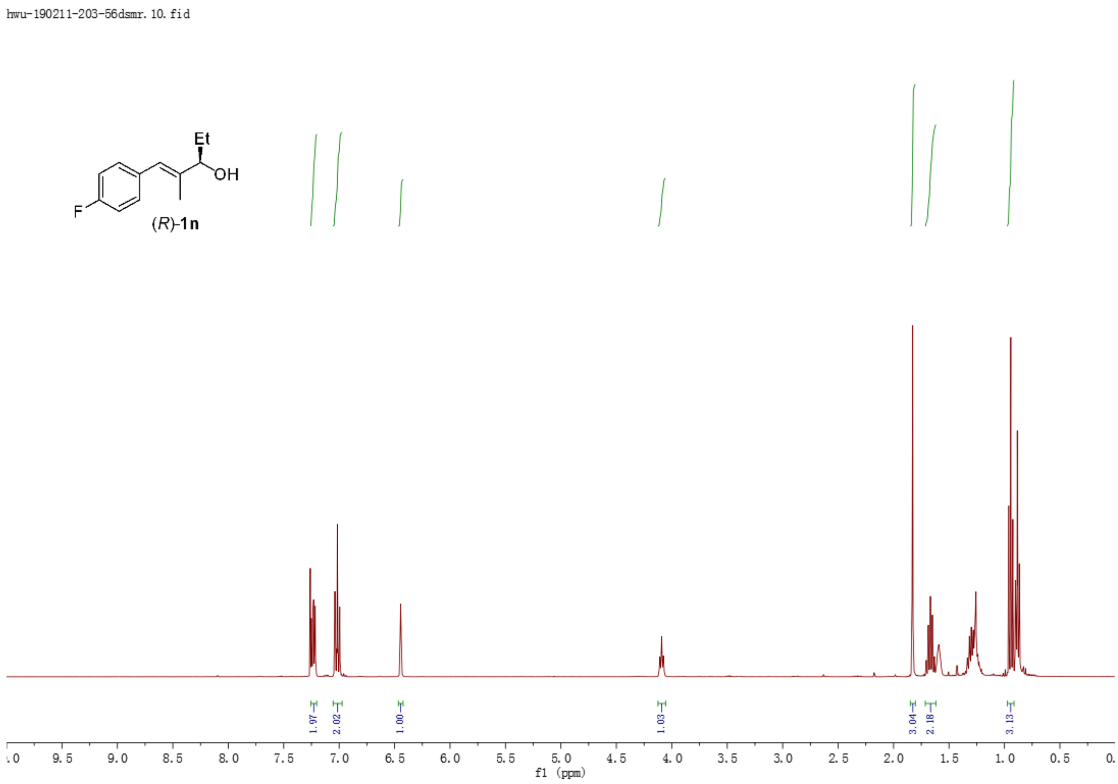


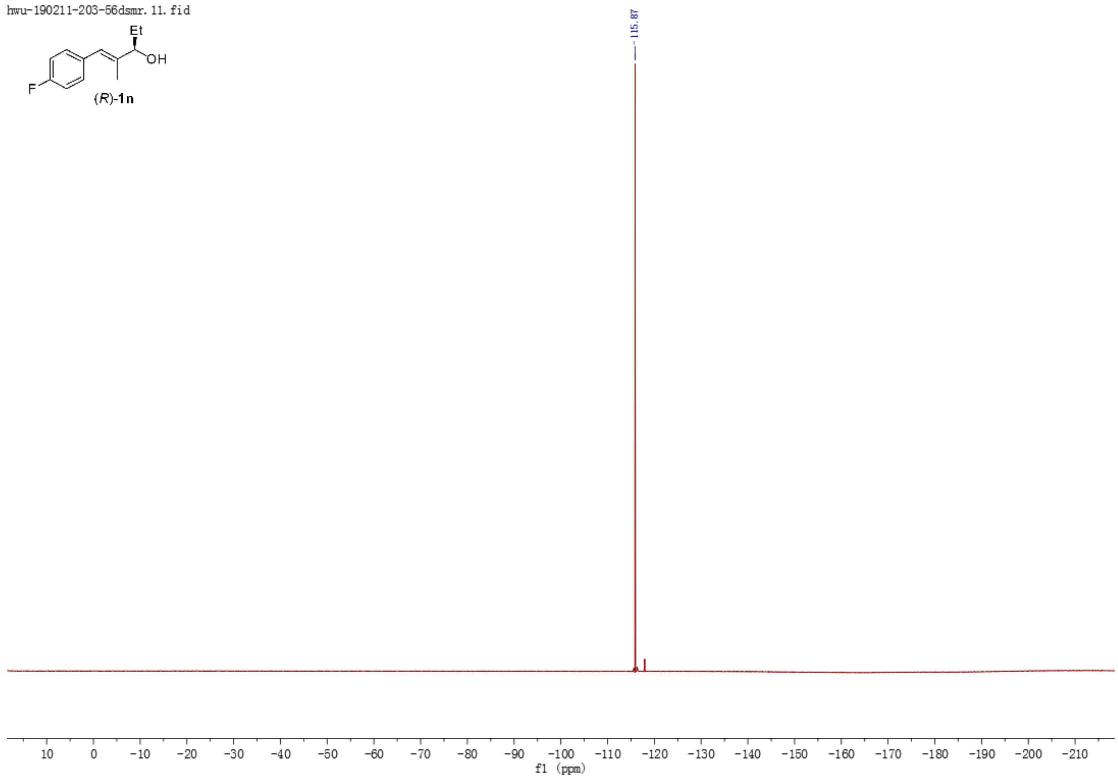
(*S*)-**1j**

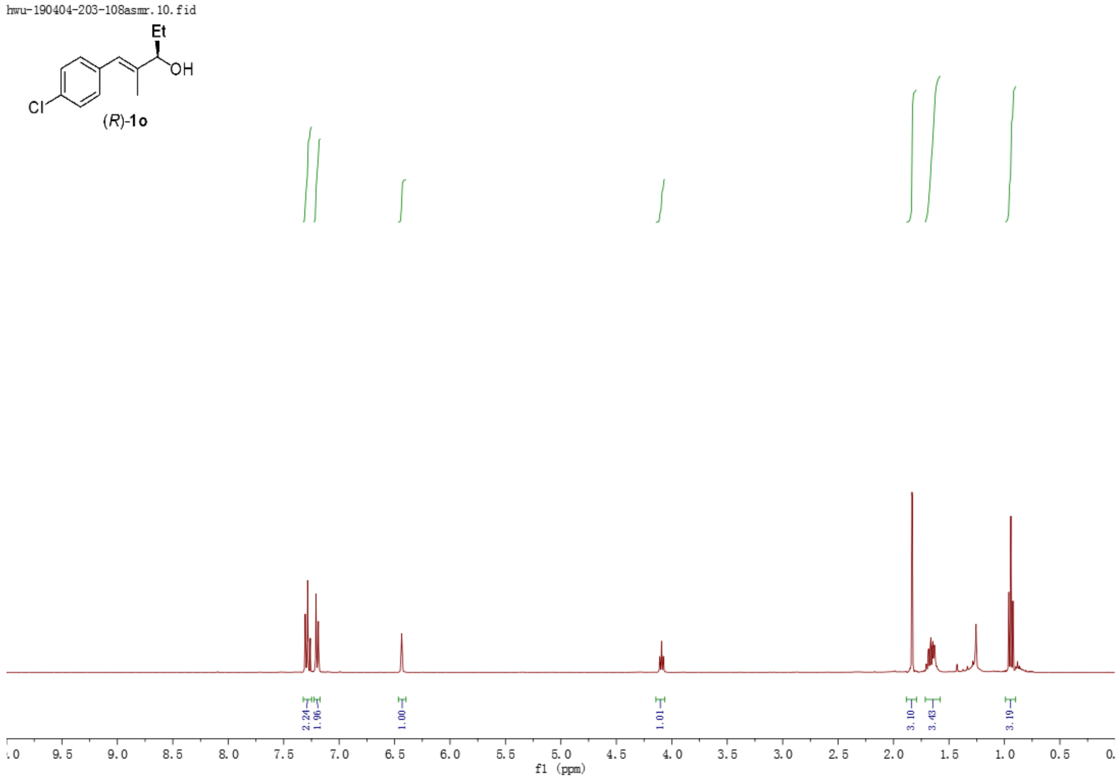


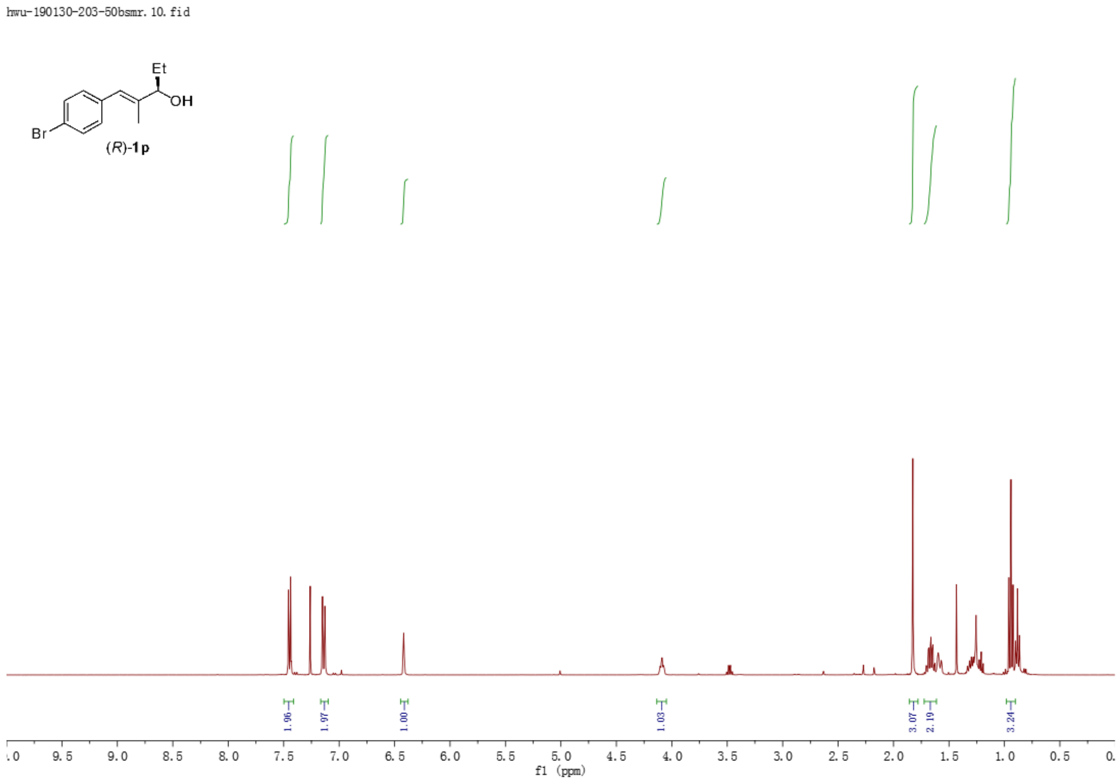

hwu-190210-203-56csmr.10.fid
Et
OH
(R)-1l
4.01
1.00
1.05
3.05
3.07
2.22
3.14
f1 (ppm)

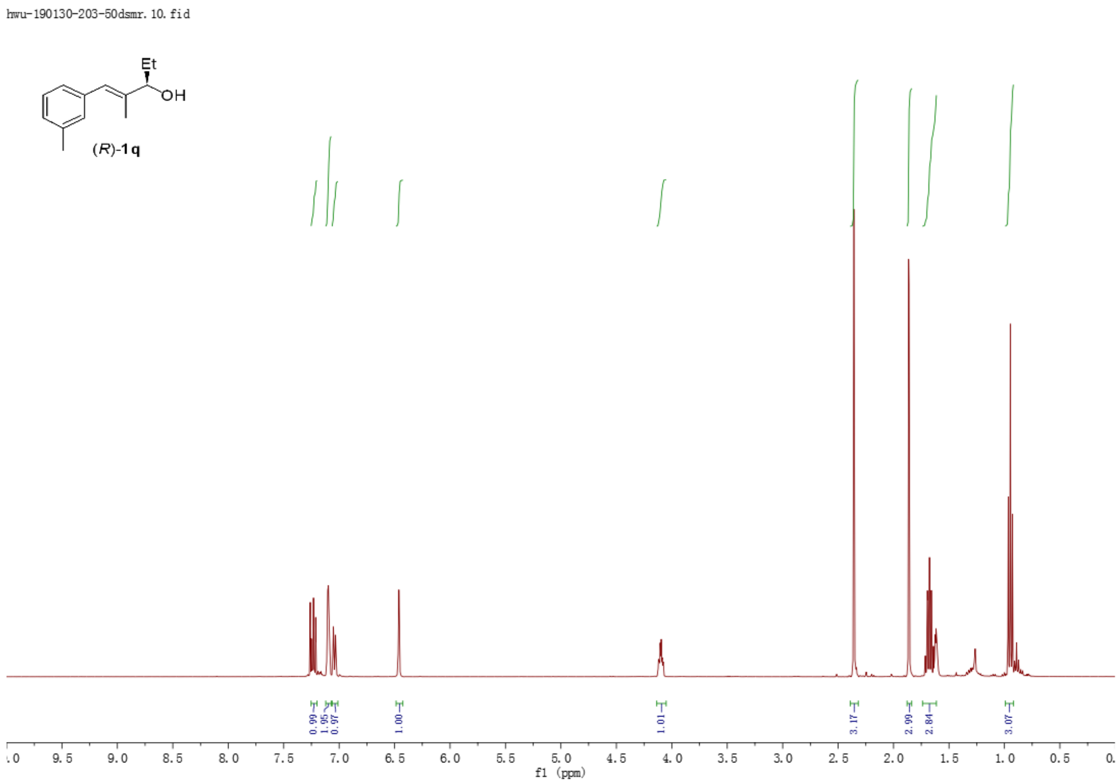

hwu-190130-203-50csmr.10.fid
Et
OH
MeO
(R)-1m
1.99
1.98
1.00
1.02
2.98
3.01
2.42
3.20
f1 (ppm)

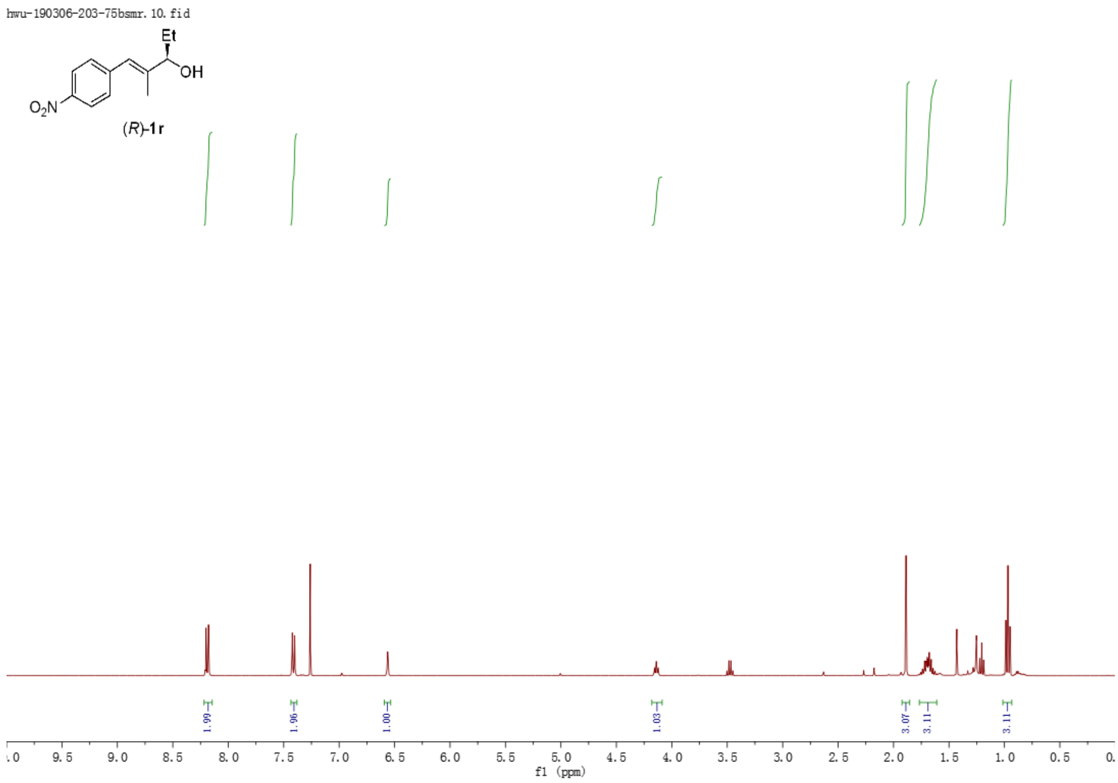

hwu-190211-203-56dsmr.10.fid
Et
OH
F
(R)-1n
1.97
2.02
1.00
1.03
3.04
2.18
3.13
f1 (ppm)


hwu-190211-203-56dsmr.11.fid
Et
OH
F
(R)-1n
-115.87
f1 (ppm)

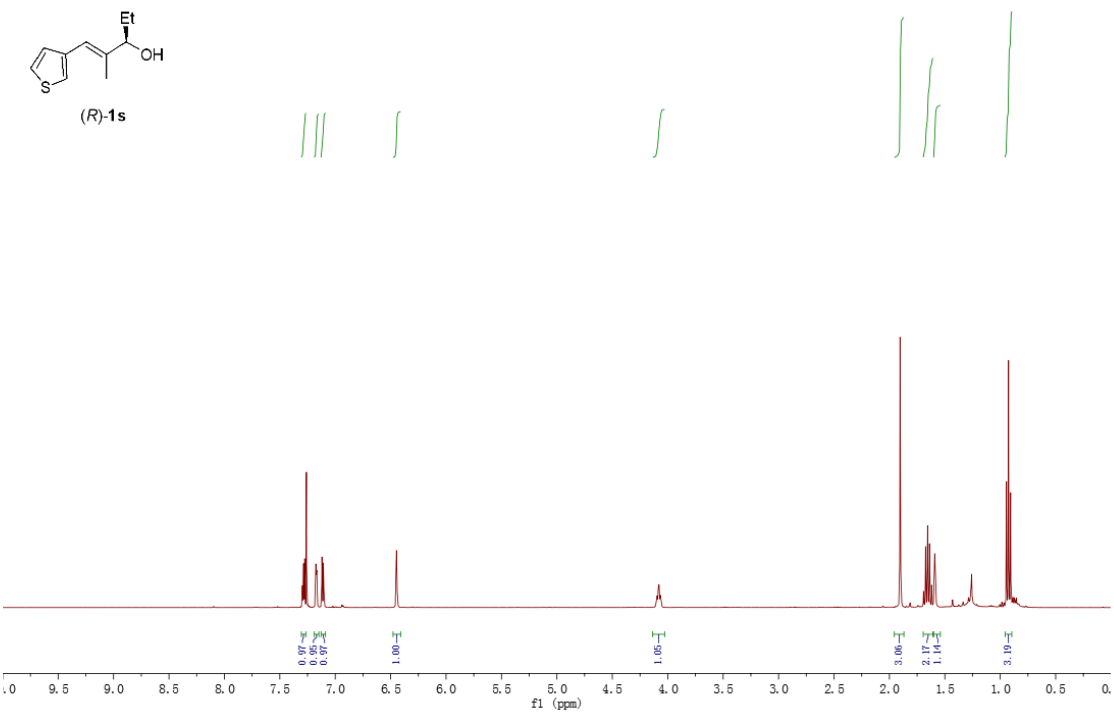

hwu-190404-203-108asmr.10.fid
Et
OH
Cl
(R)-1o
2.24
1.96
1.00
1.01
3.10
3.43
3.19
f1 (ppm)


hwu-190130-203-50bsmr.10.fid
Et
OH
Br
(R)-1p
1.96
1.97
1.00
1.03
3.07
2.19
3.24
f1 (ppm)

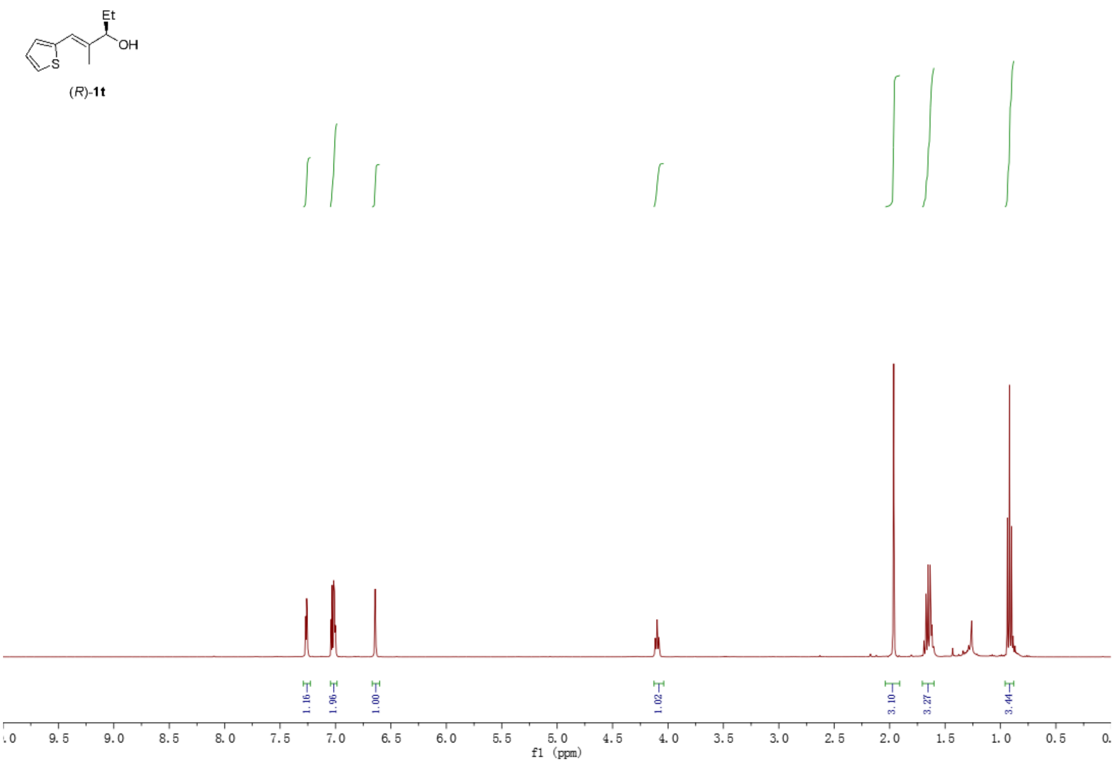

hwu-190130-203-50dsmr.10.fid
Et
OH
(R)-1q
0.99
1.95
0.97
1.00
1.01
3.17
2.99
2.84
3.07
f1 (ppm)


hwu-190306-203-75bsmr.10.fid
Et
OH
O_2N
(R)-1r
1.99
1.96
1.00
1.03
3.07
3.11
3.11
f1 (ppm)

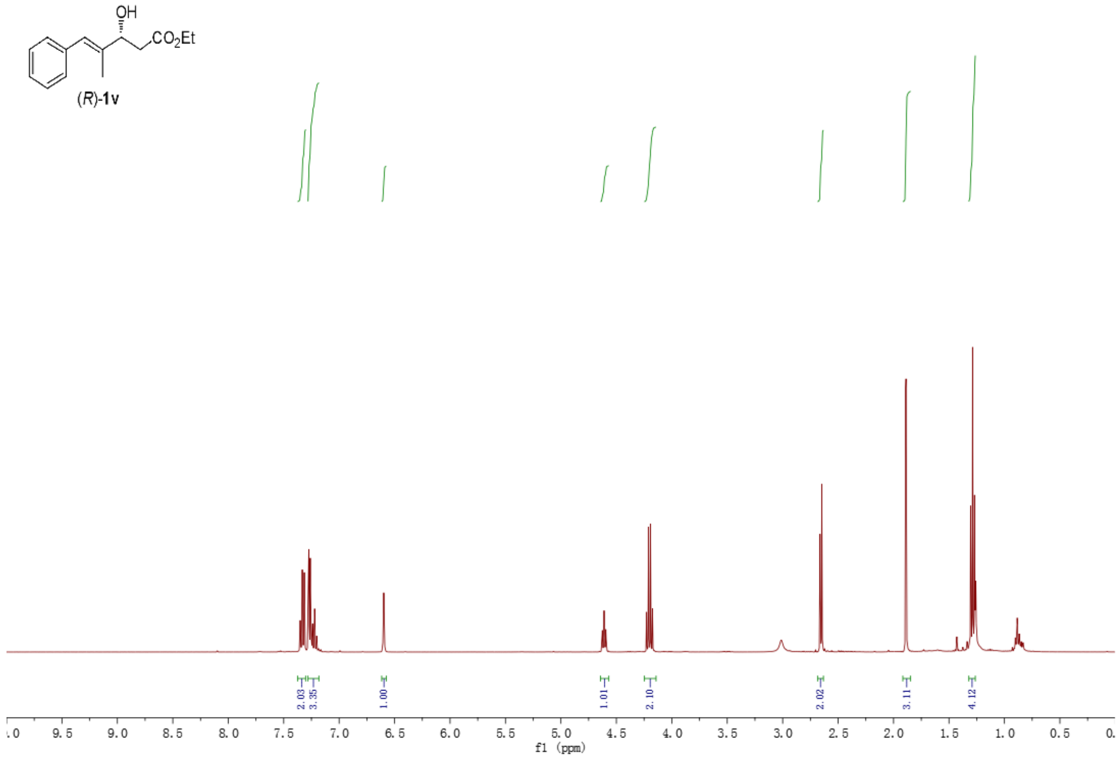
hwu-190224-203-69asmr.10.fid



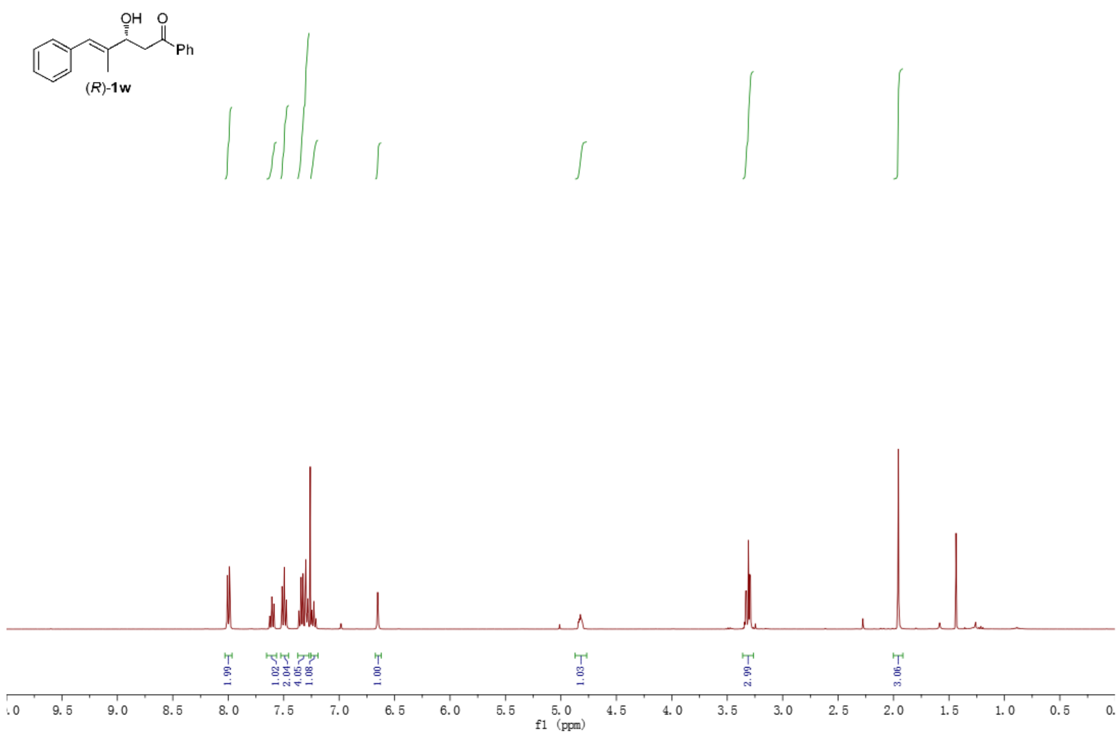
hwu-190214-203-59bsmr.10.fid



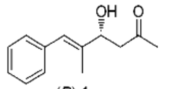
hwu-190219-203-64dsmr.10.fid



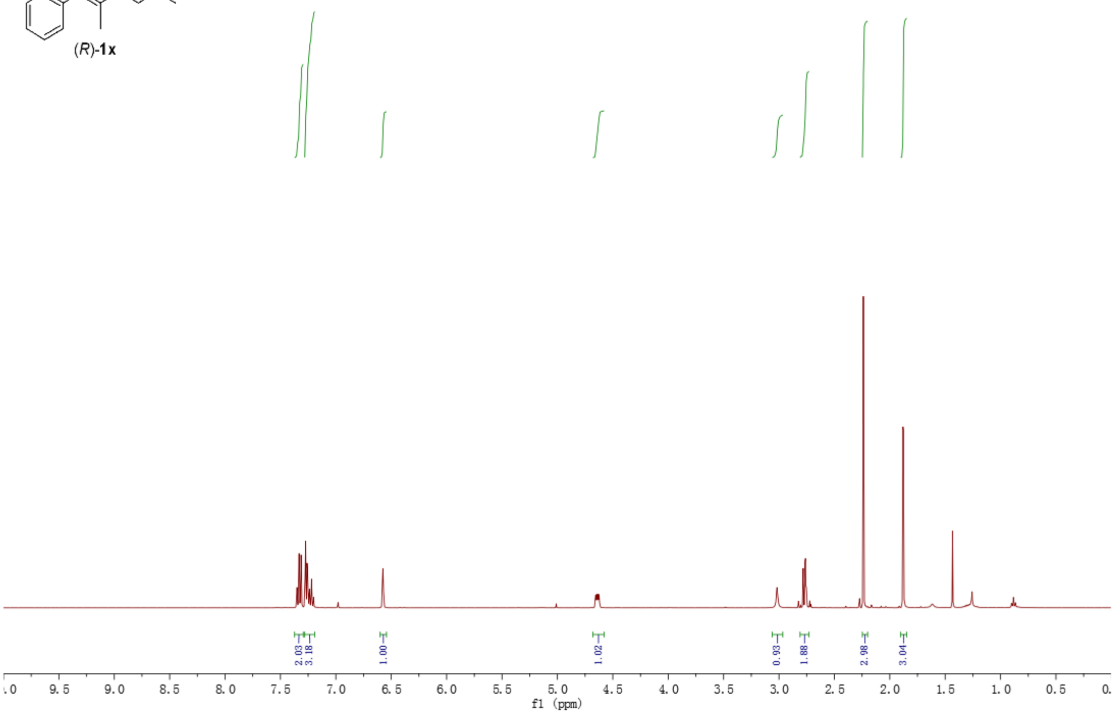
hwu-190306-203-79csmr.10.fid



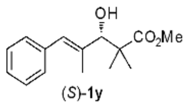
hwu-190405-203-110a2smr.10.fid



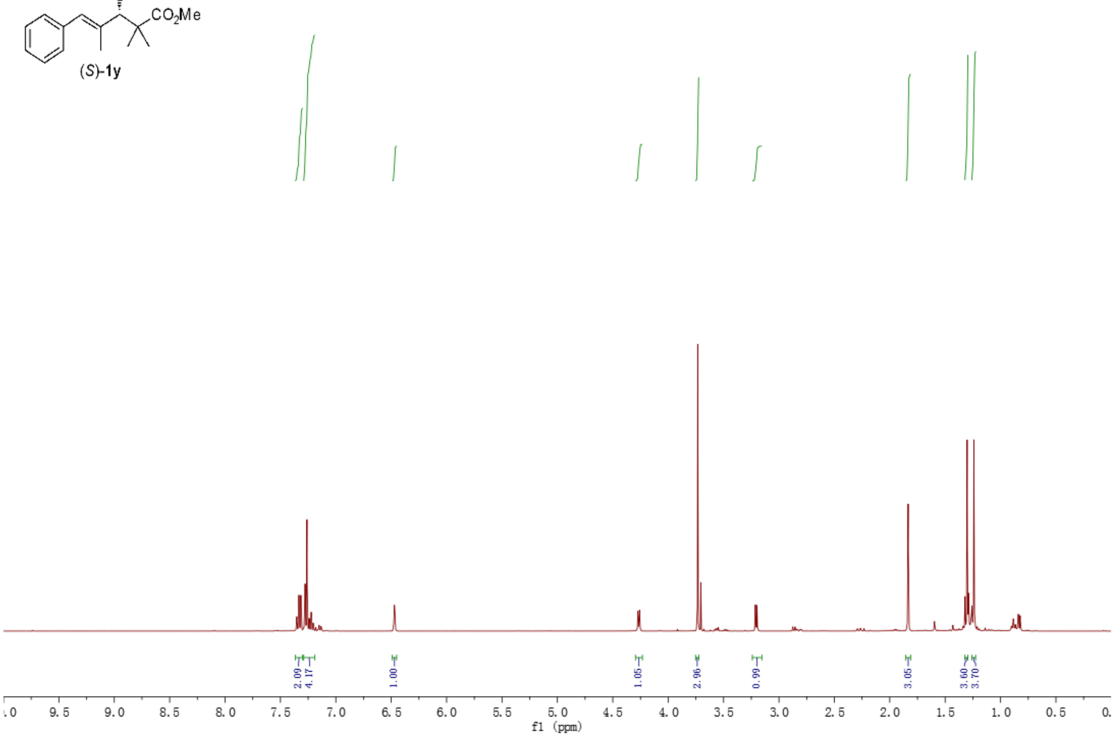
(R)-1x



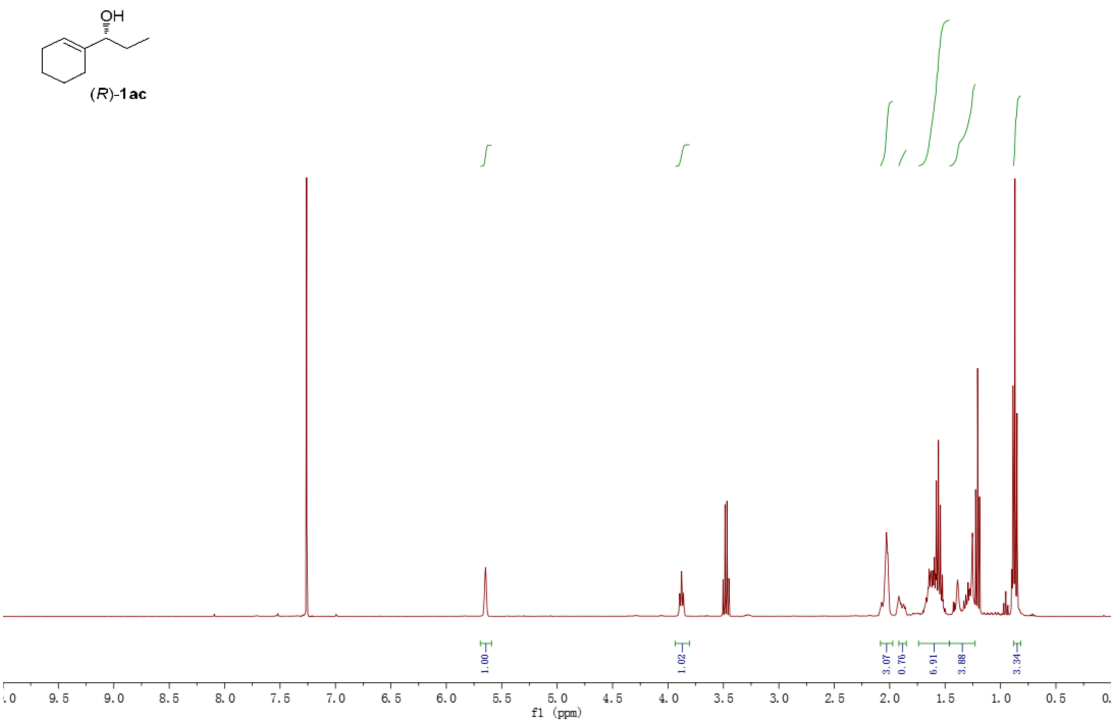
hwu-190224-203-68csmr.10.fid



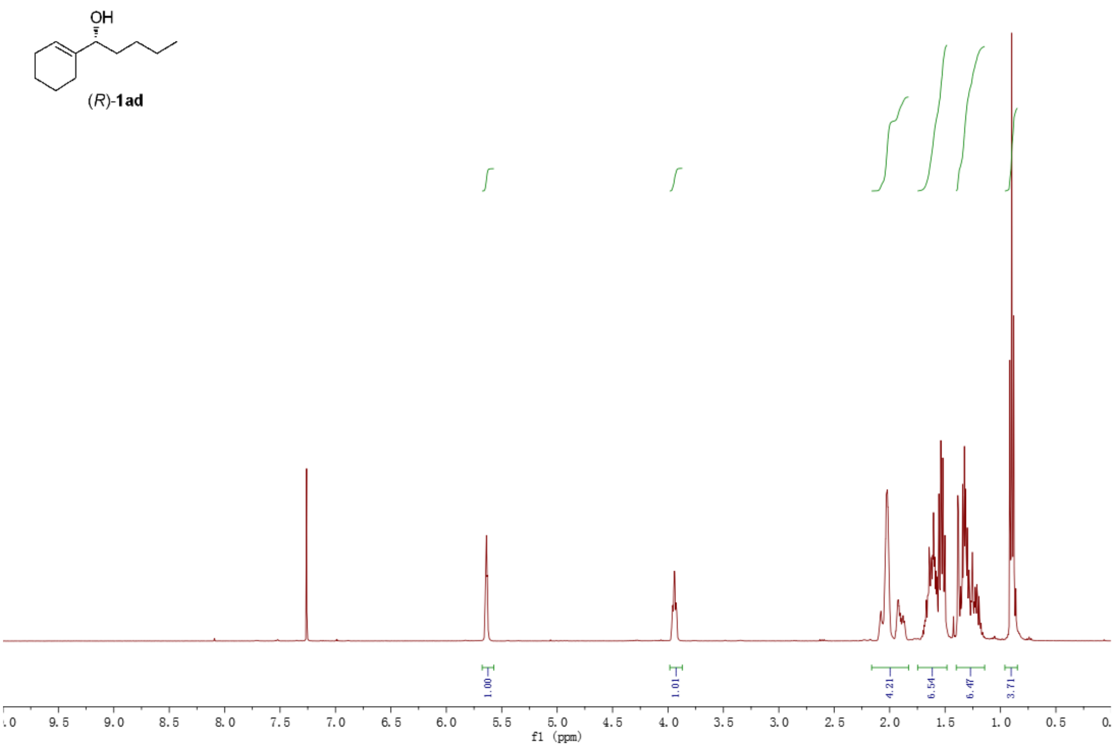
(S)-1y

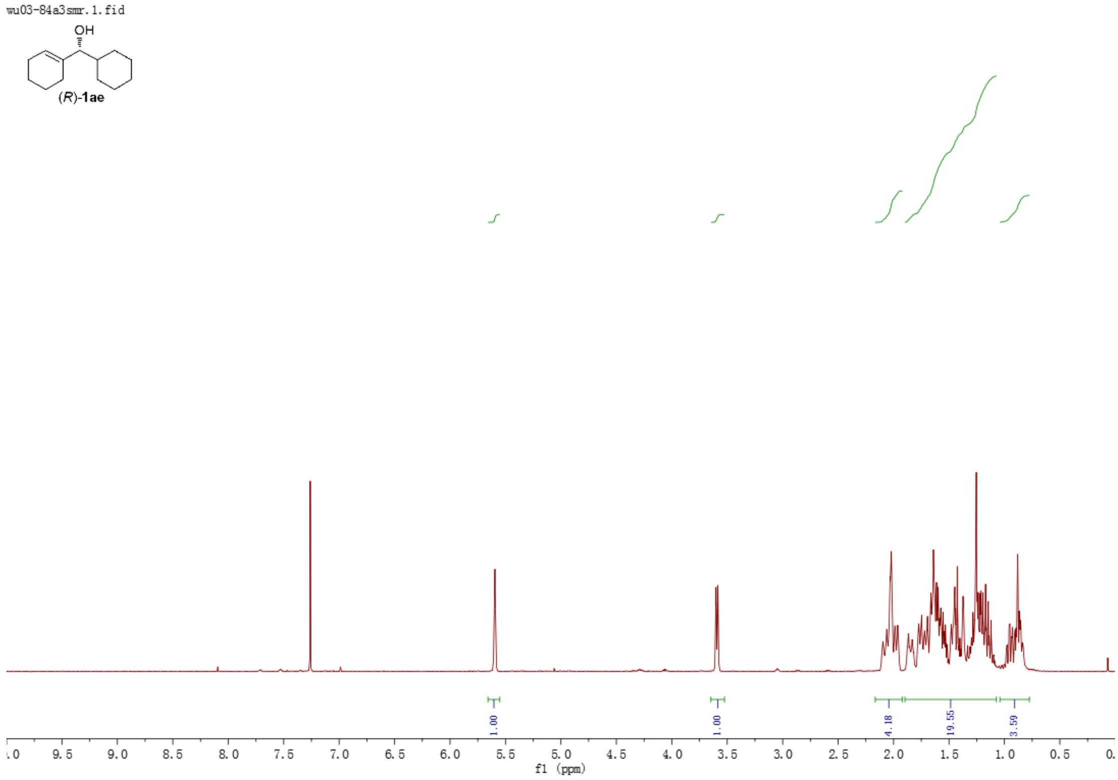


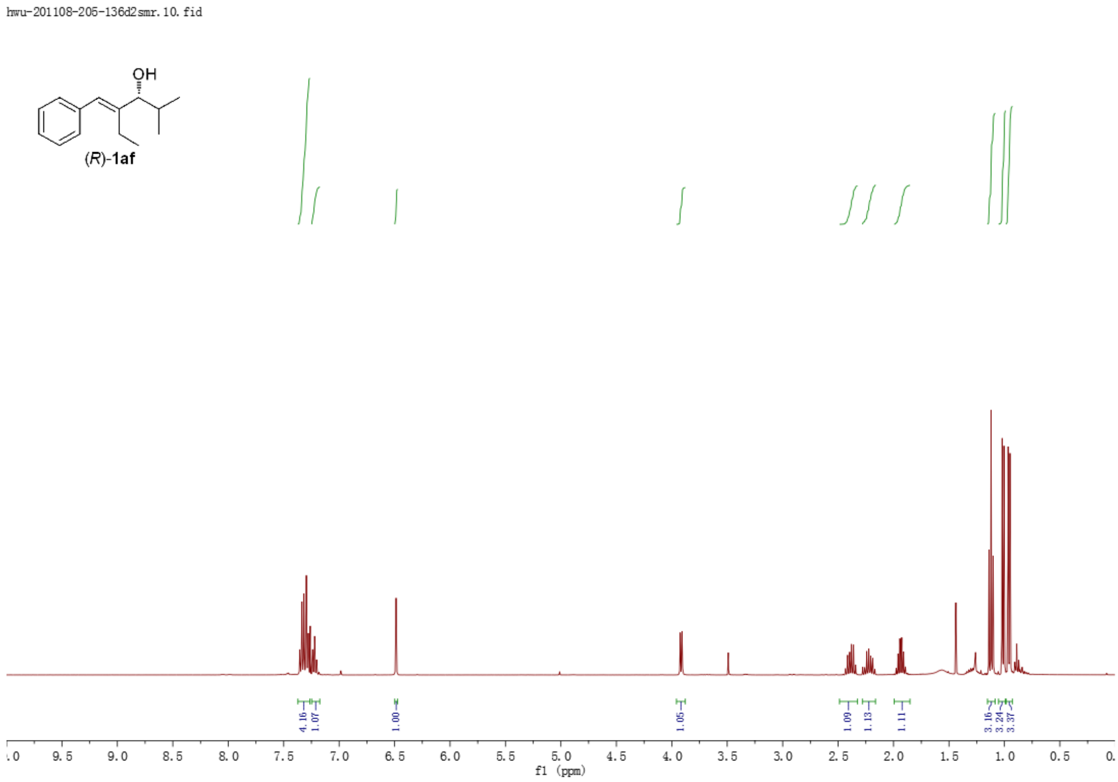
hwu-190305-203-79dsmr.10.fid



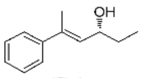
hwu-190324-203-100asmr.10.fid



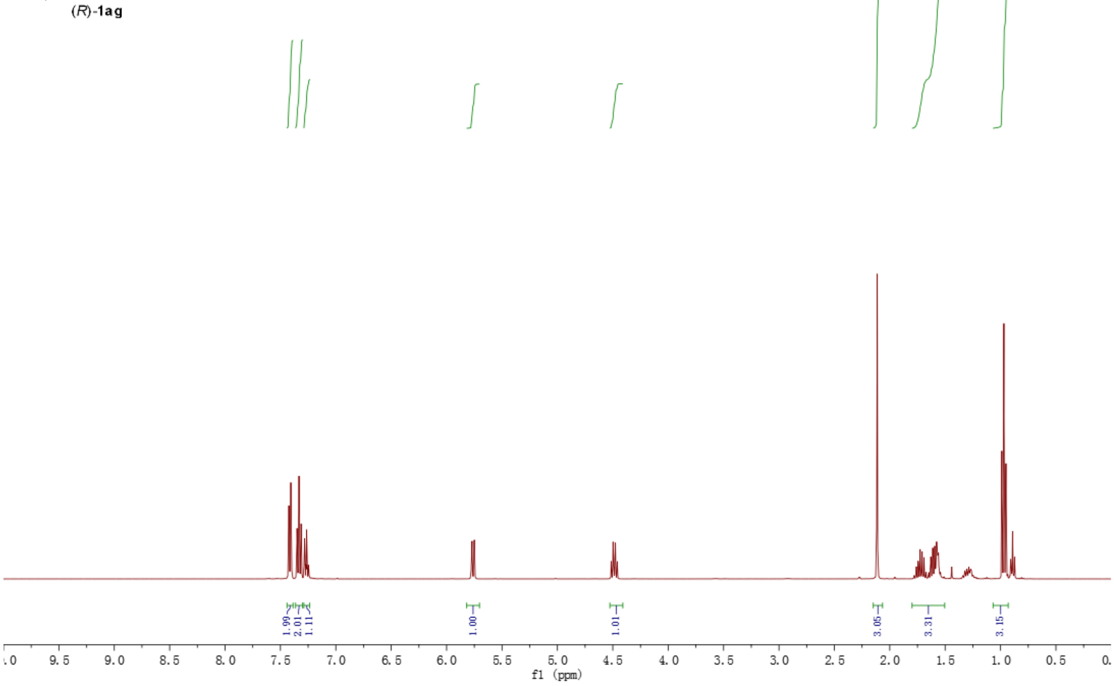

wu03-84a3smr.1.fid
OH
(R)-1ae
f1 (ppm)


hwu-201108-205-136d2smr.10.fid
OH
(R)-1af
f1 (ppm)

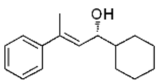
hwu-201108-205-148smr.10.fid



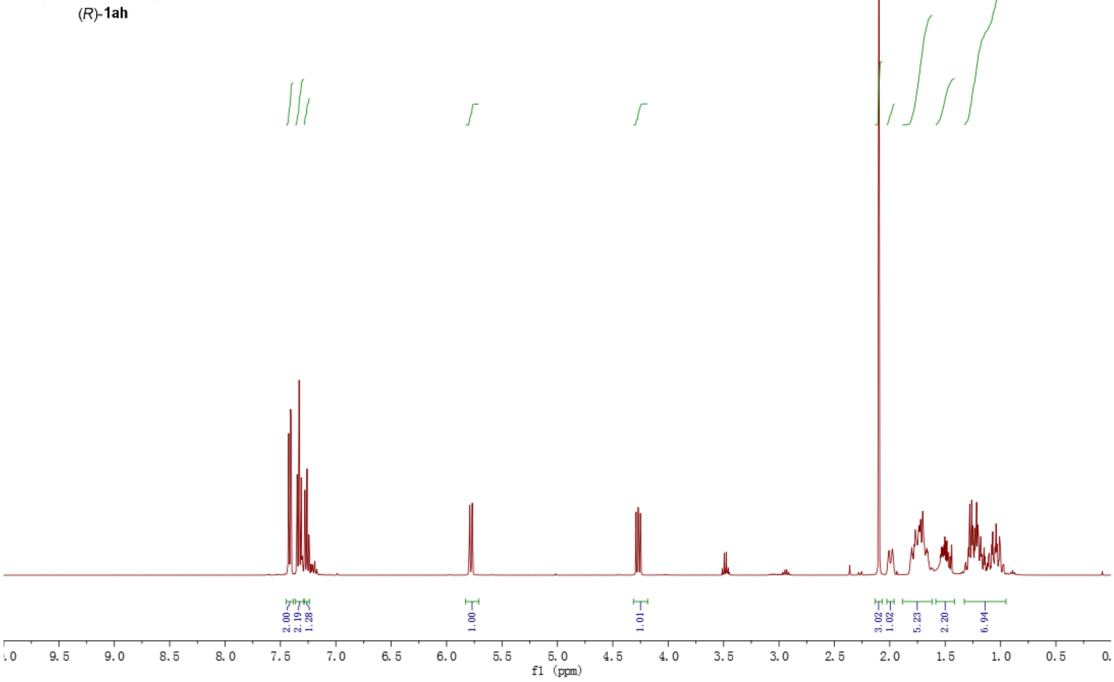
(R)-1ag



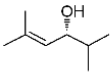
hwu-201108-205-147dsmr.10.fid



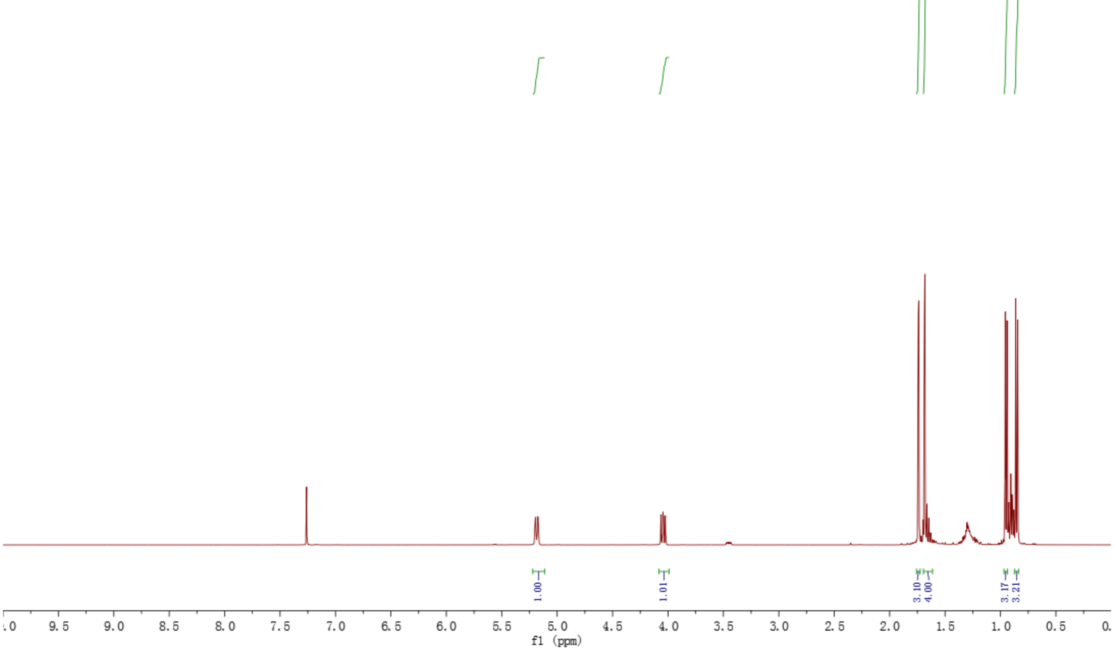
(R)-1ah



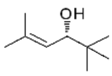
hwu-201108-205-147bsmr.10.fid



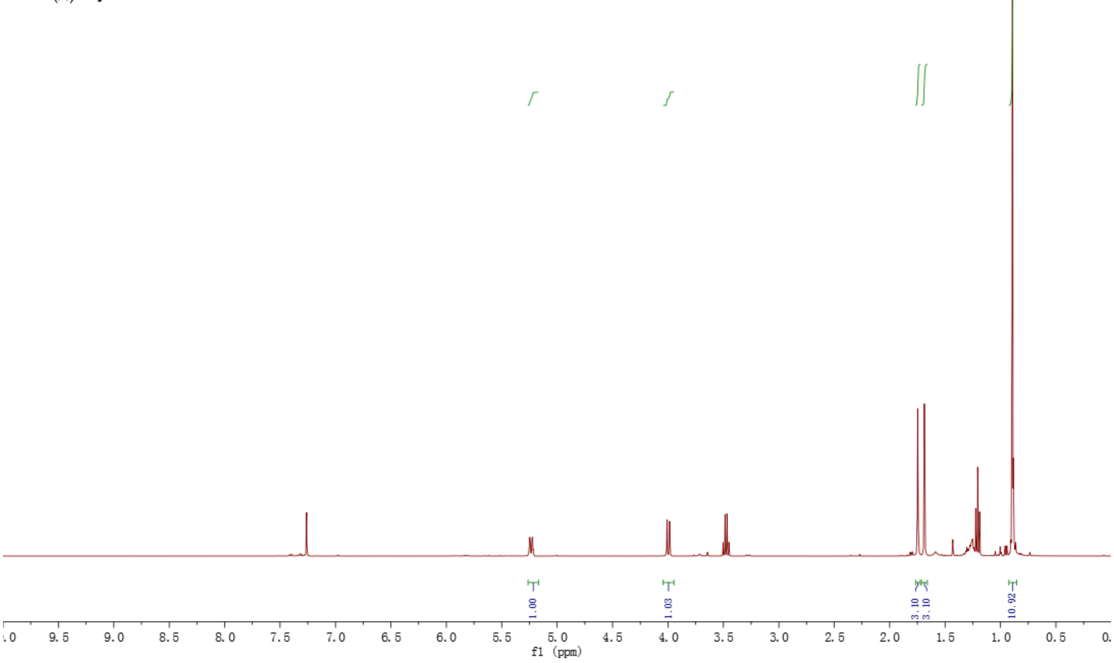
(*R*)-**1ai**

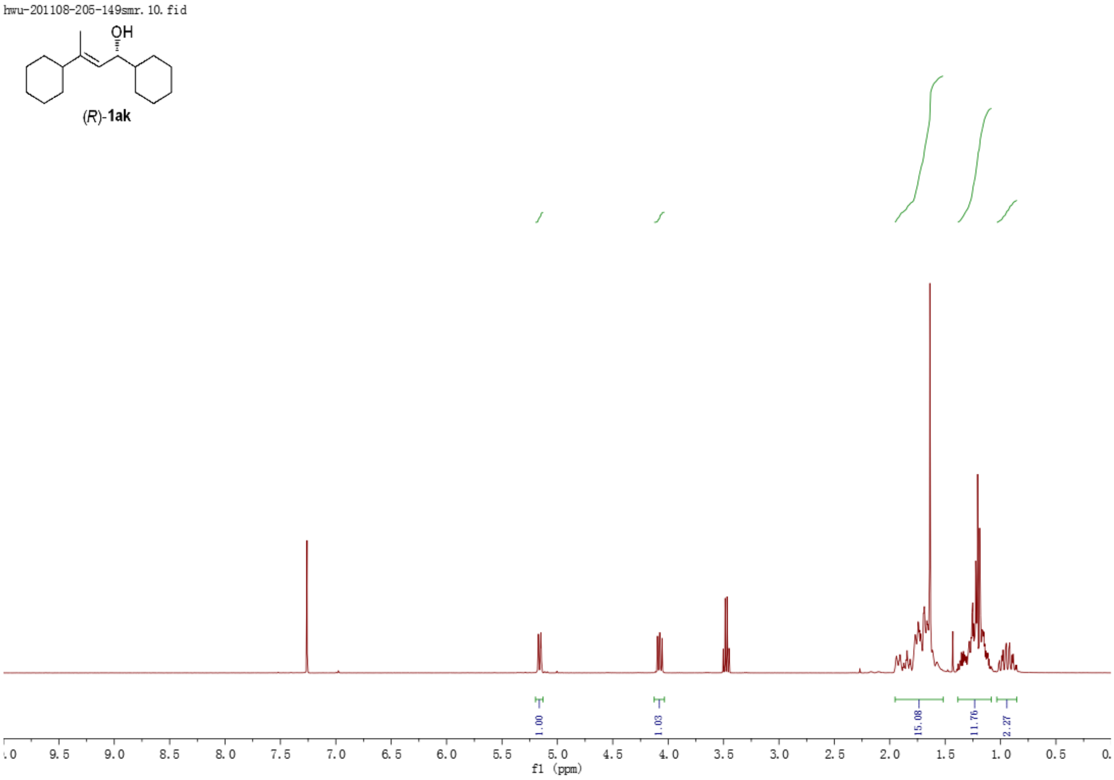


hwu-201108-205-147asmr.10.fid



(*R*)-**1aj**




hwu-201108-205-149smr.10.fid
OH
(R)-1ak
1.00
1.03
15.08
11.76
2.27
f1 (ppm)

9. References

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