Enantioselective 1,2-Difunctionalization of 1,3-Butadiene by Sequential Fluoroalkylation and Carbonyl Allylation

SUPPORTING INFORMATION

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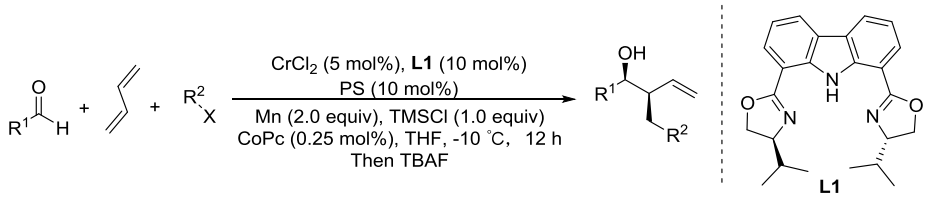
1. General Information

NMR spectra were recorded at room temperature on the following spectrometers: Agilent (400 MHz) and VARIAN (400 MHz). Chemical shifts are given in ppm and coupling constants in Hz. ^{1}H spectra were calibrated in relation to the reference measurement of TMS (0.00 ppm). ^{13}C spectra were calibrated in relation to deuterated solvents, namely $CDCl_3$ (77.16 ppm). The following abbreviations were used for ^{1}H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. When combinations of multiplicities are given the first character noted refers to the largest coupling constant. High performance liquid chromatography (HPLC) was carried out with Agilent 1260 Infinity on a UV spectrophotometric detector (Agilent). For ESI^{+}-spectra an EIˉHR (GC-TOF) spectrometer was applied. Infrared Spectroscopy (IR) was processed on an FT-IR spectrometer named Nicolet 380. The method is denoted in brackets. For the most significant bands the wave number $\tilde{\nu}$ (cm^{-1}) is given.

Chemicals were purchased from commercial suppliers. Unless stated otherwise, all the substrates and solvents were purified and dried according to standard methods prior to use. Reactions requiring inert conditions were carried out in glove box. Buta-1,3-diene is purchased in a THF (1.5 M) solution and the exact concentration was measured by ^{1}H NMR in the presence of diethyl phthalate. CF_3I is purchased in gas tank and bubbled and stored in THF solution, the concentration is measured to be 0.4 M by ^{19}F NMR in the presence of (trifluoromethyl)-benzene.

2. Experimental details

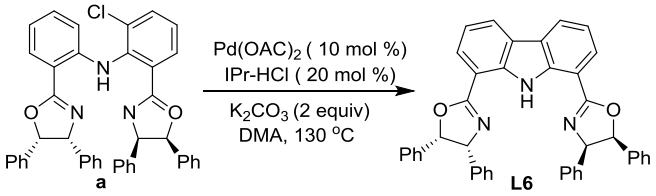
(1). General Procedure



To a mixture of anhydrous chromium(II) chloride (1.2 mg, 0.01 mmol, 5 mol %), 1,8-bis((*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl)-9H-carbazole[1] (**L1**, 7.8 mg, 0.02 mmol, 10 mol %) and Proton sponge (4.3 mg, 0.02 mmol, 10 mol %) was added THF (0.5 mL) under an nitrogen atmosphere. The mixture was stirred vigorously at room temperature for 2 hours. Then phthalocyaninecobalt (II) (0.3 mg, 0.0005 mmol, 0.25 mol %) and manganese powder (22.0 mg, 0.4 mmol, 2.0 equiv.). Then TMSCl (21.7 mg, 0.2 mmol, 1.0 equiv.), aldehyde (0.2 mmol, 1.0 equiv.), 1,3-diene (0.6 mmol, 3.0 equiv.) and alkyl iodides (0.6 mmol, 3.0 equiv.) were added in succession. The resulting suspension was stirred at -10 ^{o}C for 12 h. After the full consumption of aldehyde, the mixture was diluted with undried ethyl acetate, then aqueous *n*-Bu_4NF (1 M) was added, stirred at room temperature and the resulting suspension was filtered over a pad of silica gel using ethyl acetate (EtOAc) as eluent. Volatiles were evaporated in vacuo. The residue was purified by chromatography (Petroleum ether / ethyl acetate = 15/1 to 10/1) afforded the product.

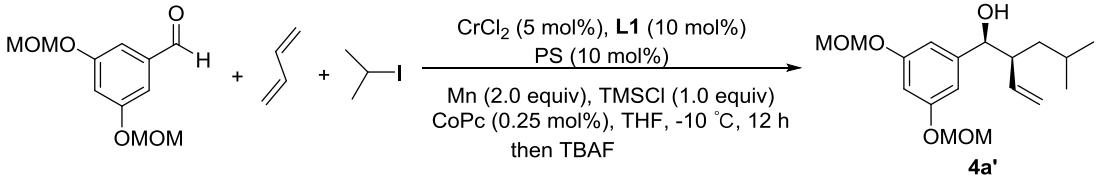
(2). Synthesis and Characterization of Ligand and Products

Synthesis of 1,8-bis((4R,5S)-4,5-diphenyl-4,5-dihydrooxazol-2-yl)-9H-carbazole (L6)

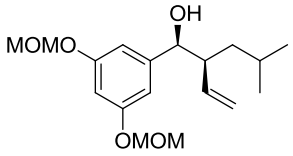


Complex **a** (prepared by the reference, (*Eur. J. Org. Chem.* **2010**, 2121), report methods), (353.1 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.05 mmol), *i*Pr-HCl (38.3 mg, 0.1 mmol) and K_2CO_3 (138.2 mg, 1.0 mmol) were placed in a screw-cap tube equipped with a magnetic stir. Then 5 mL of *N*,*N*-dimethylacetamide (DMA) was added. The reaction was heated under 140 ^{o}C for 12 h. After the reaction was judged by TLC, the heat source was removed and the reaction mixture was allowed to be quenched by water. The resulting suspension was extracted with EtOAc. The combined extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by silica gel chromatography (hexanes/EtOAc = 10/1) to afford 1,8-bis((4R,5S)-4,5- diph-enyl-4,5-dihydro oxazol-2-yl)-9H-carbazole (**L6**) (76.2 mg, 0.125 mmol), as bright yellow powder in 25% yield[1]. Recrystallization with a mixture of Toluene and Hexane afforded pale yellow needles as the ideal product. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.33 (s, 1H), 8.28 (d, *J4* = 7.7 Hz, 2H), 8.07 (d, *J* = 7.4 Hz, 2H), 7.44 – 7.32 (m, 12H), 7.29 – 7.16 (m, 10H), 5.43 (d, *J* = 8.2 Hz, 2H), 5.25 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 141.9, 140.4, 139.4, 129.0, 128.6, 128.6, 127.5, 126.7, 126.3, 126.2, 124.1, 123. 7, 119.1, 110.2, 88.2, 78.5. IR (neat) cm^{-1} ṽ: 3344, 3061, 2088, 1643, 1495, 1132 753, 696. HRMS ($ESI^{(+)}$) : $C_{42}H_{32}N_3O_2$ $[M+H]^+$: calcd. 610.2489, found: 610.2479. $[\alpha]_D^{31}$ = -61.3, (c = 0.81, CH_2Cl_2).

Synthesis of (1S,2S)-1-(3,5-bis(methoxymethoxy)phenyl)-4-methyl-2-vinylpentan-1-ol (4a')



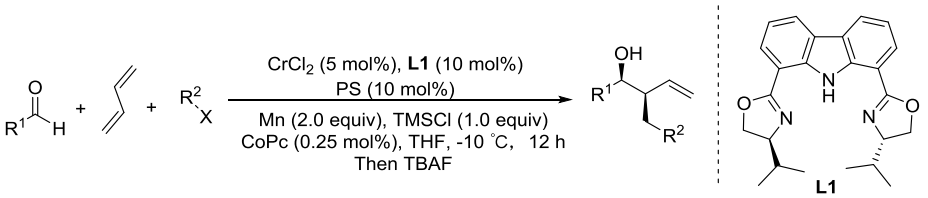
(1S,2S)-1-(3,5-bis(methoxymethoxy)phenyl)-4-methyl-2-vinylpentan-1-ol (4a')



According to the general procedure, **4a'** (51.8 mg, 0.16 mmol) was prepared from 3,5-bis(methoxymethoxy)benzaldehyde (45.3 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 ul, 0.6 mmol, 3.0 equiv.) and 2-iodopropane (102.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 73% yield with spectral properties identical to that reported in the literature, which is confirmed by single crystal X-Ray analysis.[2] The absolute configuration of the product was assigned to be (1*S*, 2*S*). Synthesized **4a'** $[\alpha]_D^{30}$ = -10.66 (c = 0.48, $CHCl_3$), ee = 76%; Reported: $[\alpha]_D^{20}$ = -16.28 (c = 0.86, $CHCl_3$), ee = 94%.

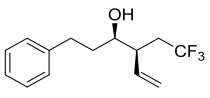
The *anti*-diastereoselectivity of this reaction is in agreement with the well-known behavior of allylic chromium reagents as Type III species (i.e. *anti*-diastereoconvergent agents). The stereochemistry outcome is also in agreement with the results reported in our previous studies.[1]

4a', ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 – 6.65 (m, 3H), 5.77 – 5.56 (m, 1H), 5.29 – 5.20 (m, 1H), 5.18 – 5.14 (m, 4H), 4.28 (d, *J* = 7.7 Hz, 1H), 3.47 (s, 6H), 2.38 (td, *J* = 11.2, 3.7 Hz, 1H), 2.21 (s, 1H), 1.58 – 1.40 (m, 1H), 1.26 – 1.12 (m, 1H), 0.97 – 0.85 (m, 1H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.5 Hz, 3H). HPLC (Chiralcel AD-H column, hexanes:*i*-PrOH = 97:3, 1.0 mL/min, 210 nm), t_{minor} = 23.0 min, t_{major} = 20.2 min, ee = 76%.



The stereochemistry of the series of products was assigned by analogy. The ee was determined by HPLC analysis with Chiralcel OD-H and IE-H *et al*. columns.

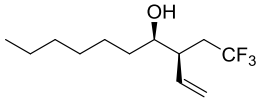
(3R,4S)-1-phenyl-4-(2,2,2-trifluoroethyl)hex-5-en-3-ol (4a)



According to the general procedure **4a** (41.3 mg, 0.16 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and trifluoroiodomethane (117.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 3H), 5.91 – 5.64 (m, 1H), 5.33 – 5.14 (m, 2H), 3.63 (dd, *J* = 8.2, 4.0 Hz, 1H), 2.95 – 2.73 (m, 1H), 2.73 – 2.62 (m, 1H), 2.48 (ddd, *J* = 13.0, 8.7, 4.3 Hz, 1H),

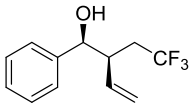
2.43 – 2.16 (m, 2H), 1.85 – 1.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 135.5, 128.7, 128.5, 127.1 (d, *J* = 276.6 Hz), 126.2, 119.0, 72.7, 44.0, 36.7, 35.6 (q, *J* = 27.5 Hz), 32.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.35 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3389, 2926, 1377, 1271, 1249, 1131, 924. HRMS ($EI^{(+)}$, 70 eV): $C_{14}H_{17}OF_3$ $[M]^+$: calcd: 258.1232, found: 258.1230. $[\alpha]_D^{22}$ = 19.2, (c = 0.45, CH_2Cl_2). HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 0.80 mL/min, 214 nm), t_{minor} = 9.6 min, t_{major} = 14.1 min, ee = 94%, dr = 15:1.

(3S,4R)-3-(2,2,2-trifluoroethyl)dec-1-en-4-ol (4b)



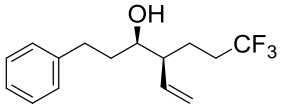
According to the general procedure **4b** (41.8 mg, 0.16 mmol) was prepared from heptanal (22.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and trifluoroiodomethane (117.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.64 (m, 1H), 5.22 (dd, *J* = 10.2, 1H), 5.16 (d, *J* = 17.2 Hz, 1H), 3.59 (d, *J* = 4.0 Hz, 1H), 2.56 – 2.41 (m, 2H), 2.32 – 2.20 (m, 1H), 1.46 – 1.39 (m, 2H), 1.37 – 1.21 (m, 8H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 127.13 (d, *J* = 279.3 Hz), 118.8, 73.3, 43.7, 35.7 (d, *J* = 27.3 Hz), 34.9, 31.9, 29.4, 25.9, 22.7, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.35 (t, *J* = 11.0 Hz, 3F). IR (neat) cm^{-1} ṽ: 2963, 1260, 1191, 1019, 798. HRMS ($EI^{(+)}$, 70 eV): $C_{12}H_{19}F_3$ $[M\text{-}H_2O]^+$: calcd: 220.1439, found: 220.1432. $[\alpha]_D^{22}$ = 14.7, (c = 2.20, CH_2Cl_2). After converting into the corresponding 3,5-dinitro-benzoyl ester[3], enantiomeric ratio was determined by HPLC (Chiralcel OD-H column, CO_2:*i*-PrOH = 90:10, 1.3 mL/min, 214 nm), t_{minor} = 6.9 min, t_{major} = 7.8 min, ee = 90%, dr = 15:1.

(1S,2S)-1-phenyl-2-(2,2,2-trifluoroethyl)but-3-en-1-ol (4c)



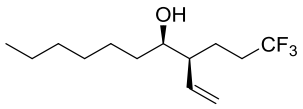
According to the general procedure **4c** (28.1 mg, 0.12 mmol) was prepared from benzaldehyde (21.2 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and trifluoroiodomethane (117.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 61% yield. Major isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.31 (dd, *J* = 6.4, 3.7 Hz, 3H), 5.76 – 5.61 (m, 1H), 5.23 (dd, *J* = 27.1, 13.8 Hz, 2H), 4.59 (d, *J* = 5.5 Hz, 1H), 2.74 (ddd, *J* = 12.8, 9.6, 4.7 Hz, 1H), 2.17 – 1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 136.1, 128.5, 127.7 (dd, *J* = 109.3, 91.4 Hz), 126.6, 119.5, 118.2, 75.5, 46.1, 35.0 (q, *J* = 27.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.05 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3413, 2926, 1376, 1252, 1133, 1051, 922, 702. HRMS ($EI^{(+)}$, 70 eV): $C_{12}H_{11}F_3$ $[M\text{-}H_2O]^+$: calcd: 212.0813, found: 212.0819. $[\alpha]_D^{22}$ = -21.7, (c = 1.04, CH_2Cl_2). HPLC (Chiralcel OD-H column, CO_2:*i*-PrOH = 98:2, 1.3 mL/min, 214 nm), t_{minor} = 21.8 min, t_{major} = 16.0 min, ee = 83%, dr = 4:1.

(3R,4S)-7,7,7-trifluoro-1-phenyl-4-vinylheptan-3-ol (4d)



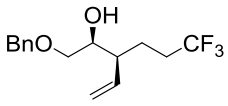
According to the general procedure **4d** (92.6 mg, 0.34 mmol) was prepared from 3-phenylpropanal (53.7 mg, 0.4 mmol, 1.0 equiv.), 1,3-diene (800 uL, 1.2 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (251.9 mg, 1.2 mmol, 3.0 equiv.) as colorless oil in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 5.86 – 5.57 (m, 1H), 5.27 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.20 – 5.10 (m, 1H), 3.63 – 3.46 (m, 1H), 2.93 – 2.75 (m, 1H), 2.68 (ddd, *J* = 13.7, 9.4, 6.8 Hz, 1H), 2.23 – 2.03 (m, 2H), 2.00 (d, *J* = 5.6 Hz, 1H), 1.87 – 1.70 (m, 3H), 1.68 – 1.58 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 136.9, 128.6, 128.5, 127.4 (d, *J* = 276.1 Hz), 126.0, 119.5, 73.1, 49.7, 36.7, 32.2, 31.96 (q, *J* = 28.5 Hz), 23.24 (dd, *J* = 5.4, 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ - 66.32 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3399, 3066, 2928, 1603, 1495, 1252, 1130, 803, 699. HRMS (EI$^{(+)}$, 70 eV): $C_{15}H_{19}F_3O$ $[M]^+$: calcd: 254.1282, found: 254.1283. $[\alpha]_D^{22}$ = 25.2, (c = 0.96, CH_2Cl_2). HPLC (Chiralcel IC-H column, CO_2:*i*-PrOH = 98:2, 1.3 mL/min, 230 nm), t_{minor} = 10.8 min, t_{major} = 13.9 min, ee = 92.5%, dr = 10:1.

(4S,5R)-1,1,1-trifluoro-4-vinylundecan-5-ol (4e)



According to the general procedure **4e** (42.9 mg, 0.17 mmol) was prepared from heptanal (22.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodo- ethane (126.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (dt, *J* = 17.3, 9.8 Hz, 1H), 5.25 (d, *J* = 10.3 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 3.50 (d, *J* = 4.2 Hz, 1H), 2.22 – 1.93 (m, 3H), 1.84 – 1.71 (m, 1H), 1.71 – 1.58 (m, 1H), 1.48 – 1.20 (m, 10H), 0.88 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 127.4 (d, *J* = 276.3 Hz), 119.3, 73.9, 49.4, 35.0, 32.2, 31.9, 29.4, 25.8, 23.4, 22.8, 14.2.^{19}F NMR (376 MHz, $CDCl_3$) δ - 66.35 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3365, 2929, 2858, 1495, 1386, 1252, 1143, 919. HRMS (EI$^{(+)}$, 70 eV): $C_{13}H_{21}F_3$ $[M\text{-}H_2O]^+$: calcd: 234.1595, found: 234.1602. $[\alpha]_D^{22}$ = 26.2, (c = 0.91, CH_2Cl_2). After converting into the corresponding 3,5-dinitro-benzoyl ester[3], enantiomeric ratio was determined by HPLC (LUX 5u(Amylose-2, 0.46*25 cm, 5 um) column, CH_3CN:H_2O = 80:20, 0.7 mL/min, 214 nm), t_{minor} = 8.2 min, t_{major} = 20.6 min, ee = 92%, dr = 10:1.

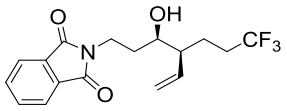
(2S,3S)-1-(benzyloxy)-3-(2,2,2-trifluoroethyl)pent-4-en-2-ol (4f)



According to the general procedure **4f** (43.2 mg, 0.15 mmol) was prepared from 2-(benzyloxy)acetaldehyde (30.0 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (126.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 5H), 5.72 – 5.63 (m, 1H), 5.19 (dd, *J* = 10.3, 1.6 Hz, 1H), 5.07 (dd, *J* = 17.2, 1.7 Hz, 1H), 4.54 (s, 2H), 3.78 (td, *J* = 7.6, 3.9 Hz, 1H), 3.52 – 3.41 (m, 2H), 2.18 – 2.07 (m, 2H), 2.04 – 1.95 (m, 1H), 1.82 – 1.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 136.8, 128.6, 128.0, 127.9, 127.4 (d, *J* = 275.9 Hz), 118.8, 73.6, 72.8, 72.4, 46.2, 31.9 (d, *J* = 28.5 Hz), 23.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.27 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3457, 2926, 1259, 1097, 1021, 799. HRMS (EI$^{(+)}$, 70 eV): $C_{15}H_{19}O_2F_3$ $[M]^+$: calcd: 288.1337, found: 288.1338. $[\alpha]_D^{20}$ = 15.3, (c = 2.07, CH_2Cl_2). HPLC (Chiralcel AD-H column,

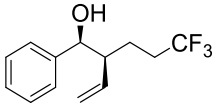
CO_2:*i*-PrOH = 99:1, 1.5 mL/min, 214 nm), t_{minor} = 33.9 min, t_{major} = 29.0 min, ee = 89%, dr = 8:1.

2-((3R,4R)-7,7,7-trifluoro-3-hydroxy-4-vinylheptyl)isoindoline-1,3-dione (4g)



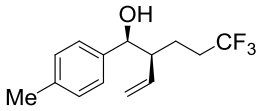
According to the general procedure **4g** (51.2 mg, 0.15 mmol) was prepared from 3-(1,3-dioxoisoindolin-2-yl)propanal (40.6 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (126.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2H), 5.73 – 5.61 (m, 1H), 5.22 (dd, *J* = 10.3, 1.6 Hz, 1H), 5.09 (dd, *J* = 17.2, 1.2 Hz, 1H), 3.94 – 3.79 (m, 2H), 3.50 (dd, *J* = 4.2, 2.7 Hz, 1H), 2.87 (s, 1H), 2.18 – 1.90 (m, 3H), 1.80 – 1.66 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 136.6, 134.3, 132.1, 127.4 (d, *J* = 276.3 Hz), 123.5, 119.3, 70.6, 49.3, 34.8, 34.1, 32.0 (q, *J* = 28.5 Hz), 23.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.33 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3519, 2962, 1709, 1398, 1260, 1019, 798. HRMS (EI$^{(+)}$, 70 eV): $C_{17}H_{18}NO_3F_3$ $[M+1]^+$: calcd: 341.1239, found: 341.1244. $[\alpha]_D^{22}$ = 12.9, (c = 0.75, CH_2Cl_2). HPLC (Chiralcel IE-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 210 nm), t_{minor} = 22.7 min, t_{major} = 19.2 min, ee = 94% dr = 10:1.

(1S,2S)-5,5,5-trifluoro-1-phenyl-2-vinylpentan-1-ol (4h)



According to the general procedure **4h** (39.1 mg, 0.16 mmol) was prepared from benzaldehyde (21.2 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (126.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 5.77 – 5.54 (m, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 4.48 (d, *J* = 7.5 Hz, 1H), 2.41 – 2.28 (m, 1H), 2.09 – 2.03 (m, 1H), 1.97 – 1.82 (m, 1H), 1.54 – 1.34 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 137.6, 128.4, 128.0, 127.1 (d, *J* = 276.4 Hz), 126.7, 120.0, 76.7, 51.5, 31.74 (dd, *J* = 57.2, 28.6 Hz), 22.76 (q, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ - 66.34 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3413, 2948, 2876, 1454, 1254, 1133, 1038, 921,700. HRMS (EI$^{(+)}$, 70 eV): $C_{13}H_{13}F_3$ $[M-H_2O]^+$: calcd: 226.0969, found: 229.0971. $[\alpha]_D^{22}$ = -19.8, (c = 0.42, CH_2Cl_2). HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 210 nm), t_{minor} = 17.1 min, t_{major} = 13.3 min, ee = 89%, dr = 6:1.

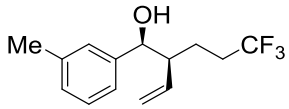
(1S,2S)-5,5,5-trifluoro-1-(p-tolyl)-2-vinylpentan-1-ol (4i)



According to the general procedure **4i** (85.3 mg, 0.33 mmol) was prepared from 4-methylbenzaldehyde (48.1 mg, 0.4 mmol, 1 equiv.), 1,3-diene (800 uL, 1.2 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (251.9 mg, 1.2 mmol, 3.0 equiv.) as colorless oil in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.09 (m, 4H), 5.65 – 5.57 (m, 1H), 5.27 (dd, *J* = 9.6, 2.0 Hz, 1H),

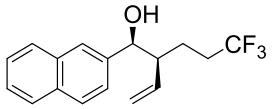
5.17 (dd, *J* = 17.2, 0.8 Hz, 1H), 4.40 (d, *J* = 7.3 Hz, 1H), 2.34 (s, 3H), 2.28 (dd, *J* = 13.7, 6.7 Hz, 1H), 2.16 – 1.99 (m, 1H), 1.98 – 1.80 (m, 1H), 1.58 – 1.47 (m, 1H), 1.45 – 1.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 137.9, 137.7, 129.2, 127.5 (dd, *J* = 258.1, 57.8 Hz), 126.8, 119.8, 76.60, 51.58, 31.84 (q, *J* = 28.5 Hz), 22.84 (d, *J* = 2.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ - 66.32 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3415, 2978, 1387, 1254, 1134, 1041, 791, 649. HRMS (EI$^{(+)}$, 70 eV): $C_{14}H_{15}F_3$ [M-H_2O]$^+$: calcd: 240.1126, found: 240.1128. $[\alpha]_D^{20}$ = -21.9, (c = 0.38, CH_2Cl_2). HPLC (Chiralcel IE-H column, hexanes:*i*-PrOH = 98:2, 0.6 mL/min, 210 nm), t_{minor} = 10.3 min, t_{major} = 11.3 min, ee = 88%, dr = 5:1.

(1S,2S)-5,5,5-trifluoro-1-(m-tolyl)-2-vinylpentan-1-ol (4j)



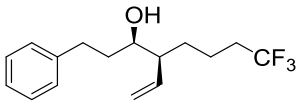
According to the general procedure **4j** (85.2 mg, 0.33 mmol) was prepared from 3-methylbenzaldehyde (48.1 mg, 0.4 mmol, 1 equiv.), 1,3-diene (800 uL, 1.2 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (251.9 mg, 1.2 mmol, 3.0 equiv.) as colorless oil in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 6.0 Hz, 1H), 7.13 – 7.07 (m, 3H), 5.66 – 5.57 (m, 1H), 5.29 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.18 (dd, *J* = 17.2, 1.1 Hz, 1H), 4.40 (dd, *J* = 7.3, 1.6 Hz, 1H), 2.35 (s, 3H), 2.30 (dd, *J* = 13.9, 6.9 Hz, 1H), 2.16 – 2.02 (m, 1H), 1.95 – 1.82 (m, 1H), 1.56 – 1.48 (m, 1H), 1.45 – 1.38 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 138.23, 137.8, 128.9, 128.4, 127.3 (d, *J* = 271.4 Hz), 124.0, 120.0, 76.8, 51.6, 31.9 (q, *J* = 28.5 Hz), 22.9 (d, *J* = 2.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ - 66.32 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3424, 2874, 1387, 1254, 1134, 1039, 921, 817. HRMS (EI$^{(+)}$, 70 eV): $C_{14}H_{17}OF_3$ [M]$^+$: calcd: 258.1232, found: 258.1236. $[\alpha]_D^{20}$ = -20.3, (c = 0.40, CH_2Cl_2). HPLC (Chiralcel AD-H column, CO_2:*i*-PrOH = 98:2, 1.3 mL/min, 220 nm), t_{minor} = 12.0 min, t_{major} = 12.5 min, ee = 85%, dr = 5:1.

(1S,2S)-5,5,5-trifluoro-1-(naphthalen-2-yl)-2-vinylpentan-1-ol (4k)



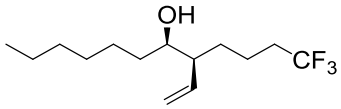
According to the general procedure **4k** (1.50 g, 5.11 mmol) was prepared from 2-naphthaldehyde (1.00 g, 6.40 mmol, 1.0 equiv.), 1,3-diene (12.8 mL, 19.20 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iod-oethane (4.03 g, 19.20 mmol, 3.0 equiv.) at r.t. for 24 h, as yellow oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 3H), 7.75 (s, 1H), 7.56 – 7.48 (m, 2H), 7.45 (dd, *J* = 8.5, 1.3 Hz, 1H), 5.71 – 5.62 (m, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 5.20 (d, *J* = 17.1 Hz, 1H), 4.62 (d, *J* = 7.2 Hz, 1H), 2.54 – 2.36 (m, 2H), 2.16 – 2.05 (m, 1H), 2.00 – 1.85 (m, 1H), 1.65 – 1.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 137.5, 133.3, 133.2, 128.4, 128.1, 127.8, 127.2 (d, *J* = 276.2 Hz), 126.3, 126.1, 126.0, 124.5, 120.1, 76.8, 51.5, 31.8 (q, *J* = 28.5 Hz), 23.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ - 66.23 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3427, 2958, 2899, 1256, 1135, 1043,820. HRMS (EI$^{(+)}$, 70 eV): $C_{17}H_{17}OF_3$ [M]$^+$: calcd: 294.1232, found: 294.1229. $[\alpha]_D^{20}$ = -19.3, (c = 1.24, CH_2Cl_2). HPLC (Chiralcel IE-H column, hexanes:*i*-PrOH = 99:1, 0.4 mL/min, 210 nm), t_{minor} = 31.4 min, t_{major} = 33.8 min, ee = 86%, dr = 7:1.

(3R,4S)-8,8,8-trifluoro-1-phenyl-4-vinyloctan-3-ol (4l)



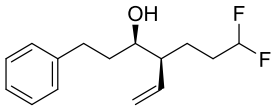
According to the general procedure **4l** (45.8 mg, 0.16 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (134.4 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 5.70 – 5.57 (m, 1H), 5.23 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.13 (dd, *J* = 17.2, 1.8 Hz, 1H), 3.56 – 3.44 (m, 1H), 3.00 – 2.73 (m, 1H), 2.72 – 2.62 (m, 1H), 2.10 – 1.97 (m, 3H), 1.84 – 1.57 (m, 4H), 1.51 – 1.38 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 137.8, 128.7, 128.6, 127.3 (d, *J* = 229.0 Hz), 126.0, 119.0, 73.1, 50.4, 36.7, 33.8 (d, *J* = 28.3 Hz), 32.3, 29.9, 20.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ - 66.29 (t, *J* = 11.0 Hz, 3F). IR (neat) cm^{-1} ṽ: 3395, 2935, 1252, 1135, 920, 699. HRMS ($EI^{(+)}$, 70 eV): $C_{16}H_{19}F_3$ $[M\text{-}H_2O]^+$: calcd: 268.1439, found: 268.1432. $[\alpha]_D^{20}$ = 20.2, (c = 0.50, CH_2Cl_2). HPLC (Chiralcel AD-H column, hexanes :*i*-PrOH = 99:1, 0.6 mL/min, 214 nm), t_{minor} = 21.7 min, t_{major} = 23.0 min, ee = 89%, dr = 10:1.

(5S,6R)-1,1,1-trifluoro-5-vinyldodecan-6-ol (4m)



According to the general procedure **4m** (38.9 mg, 0.15 mmol) was prepared from heptanal (22.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1-trifluoro-2-iodoethane (134.4 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63 (dt, *J* = 17.2, 9.8 Hz, 1H), 5.22 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.11 (dd, *J* = 17.2, 1.8 Hz, 1H), 3.47 (dd, *J* = 7.0, 3.6 Hz, 1H), 2.06 (ddd, *J* = 17.4, 11.7, 6.7 Hz, 3H), 1.70 – 1.59 (m, 2H), 1.55 – 1.40(m, 5H) 1.37 – 1.16 (m, 7H), 0.88 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 127.3 (d, *J* = 276.3 Hz), 118.6, 73.8, 50.1, 35.0, 33.8 (d, *J* = 28.4 Hz), 32.0, 30.0, 29.5, 25.8, 22.8, 20.1, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.41 (t, *J* = 10.9 Hz, 3F). IR (neat) cm^{-1} ṽ: 3388, 2929, 2857, 1388, 1254, 1141, 998. HRMS ($EI^{(+)}$, 70 eV): $C_{14}H_{23}F_3$ $[M\text{-}H_2O]^+$: calcd: 248.1752, found: 248.1745. $[\alpha]_D^{20}$ = 18.3, (c = 0.27, CH_2Cl_2). After converting into the corresponding 3,5-dinitro-benzoyl ester[3], enantiomeric ratio was determined by HPLC (Chiralcel IE-H column, hexanes:*i*-PrOH = 99.6:0.4, 0.36 mL/min, 210 nm), t_{minor} = 19.7 min, t_{major} = 20.6 min, ee = 94%, dr = 10:1.

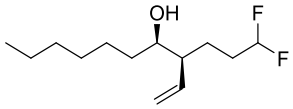
(3R,4S)-7,7-difluoro-1-phenyl-4-vinylheptan-3-ol (4n)



According to the general procedure **4n** (35.6 mg, 0.14 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1-difluoro-2-iodoethane (115.2 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.13 (m, 3H), 5.85 (dt, *J* = 56.9, 4.3 Hz, 1H), 5.72 – 5.55 (m, 1H), 5.24 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.13 (dd, *J* = 17.2, 0.9 Hz, 1H), 3.51 (dd, *J* = 8.4, 4.1 Hz, 1H), 2.92 – 2.75 (m, 1H), 2.75 – 2.57 (m, 1H), 2.05 (ddd, *J* = 14.3, 9.4, 4.5 Hz, 1H),

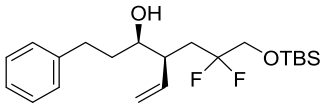
1.96 – 1.63 (m, 5H), 1.56 – 1.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 137.3, 128.4, 125.9, 119.1, 117.4 (t, *J* = 238.9 Hz), 73.0, 49.9, 36.6, 32.2 (t, *J* = 20.9 Hz), 31.9, 23.11. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.00 (dtd, *J* = 56.8, 17.6, 5.0 Hz, 2F). IR (neat) cm^{-1} ṽ: 3466, 3027, 2931, 1453, 1402, 1112, 918. HRMS ($EI^{(+)}$, 70 eV): $C_{15}H_{18}F_2$ $[M\text{-}H_2O]^+$: calcd: 236.1377, found: 236.1383. $[\alpha]_D^{20}$ = 26.0, (c = 0.89, CH_2Cl_2). HPLC (Chiralcel IC-H column, CO_2:*i*-PrOH = 95:5, 1.3 mL/min, 214 nm), t_{minor} = 8.2 min, t_{major} = 10.7 min, ee = 92%, dr = 15:1.

(4S,5R)-1,1-difluoro-4-vinylundecan-5-ol (4o)



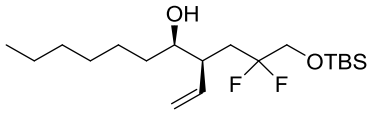
According to the general procedure **4o** (33.2 mg, 0.14 mmol) was prepared from heptanal (22.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1-difluoro-2-iodoethane (115.2 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dt, *J* = 56.8, 4.2 Hz, 1H), 5.70 – 5.57 (m, 1H), 5.23 (dd, *J* = 10.3, 1.9 Hz, 1H), 5.12 (dd, *J* = 17.2, 1.9 Hz, 1H), 3.50 (d, *J* = 3.7 Hz, 1H), 2.11 – 1.98 (m, 1H), 1.95 – 1.75(m, 2H), 1.72 – 1.64 (m, 2H), 1.57 – 1.39 (m, 4H), 1.29 (dd, *J* = 19.4, 10.1 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 118.8, 117.2, 73.7, 49.7, 34.8, 32.1, 31.8, 29.3, 25.7, 23.2, 22.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.95 (dtd, *J* = 56.9, 17.5, 2.9 Hz, 2F). IR (neat) cm^{-1} ṽ: 3389, 2956, 2857, 1458, 1402, 1252, 1120, 916. HRMS ($EI^{(+)}$, 70 eV): $C_{13}H_{22}F_2$ $[M\text{-}H_2O]^+$: calcd: 216.1690, found: 216.1692. $[\alpha]_D^{20}$ = 20.2, (c = 1.76, CH_2Cl_2). After converting into the corresponding 3,5-dinitro-benzoyl ester[3], enantiomeric ratio was determined by HPLC (Chiralcel AD-H column, CO_2:*i*-PrOH = 99:1, 1.3 mL/min, 214 nm), t_{minor} = 20.8 min, t_{major} = 23.4 min, ee = 95%, dr > 15:1.

(3R,4S)-7-((tert-butyldimethylsilyl)oxy)-6,6-difluoro-1-phenyl-4-vinylheptan-3-ol (4p)



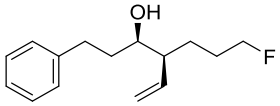
According to the general procedure, **4p** (66.1 mg, 0.17 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and (2-bromo-2,2-difluoroetho-xy)(tert-butyl)dimethylsilane (165.1 mg, 0.6 mmol, 3.0 equiv.); $ZrCp_2Cl_2$ (60.0 mg, 0.2 mmol, 1.0 equiv.) instead of TMSCl (21.7 mg, 0.2 mmol, 1.0 equiv.), as colorless oil in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.4 Hz, 3H), 5.93 – 5.66 (m, 1H), 5.18 (dd, *J* = 17.0, 14.1 Hz, 2H), 3.73 (t, *J* = 12.5 Hz, 2H), 3.62 (dd, *J* = 8.4, 4.2 Hz, 1H), 2.95 – 2.76 (m, 1H), 2.76 – 2.59 (m, 1H), 2.60 – 2.41 (m, 1H), 2.25 – 2.06 (m, 2H), 1.82 – 1.69 (m, 2H), 0.92 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 137.7, 128.5, 126.0, 123.6, 118.0, 73.0, 64.77 (t, *J* = 34.3 Hz), 44.1, 36.6, 34.6 (t, *J* = 23.1 Hz), 32.4, 25.9, 18.3, -5.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.52 – -103.88 (m, 1F), -103.96 – -104.95 (m, 1F). IR (neat) cm^{-1} ṽ: 2963, 1409, 1261, 1090, 1020, 799. HRMS ($EI^{(+)}$, 70 eV): $C_{21}H_{34}O_2F_2Si$ $[M]^+$: calcd: 384.2296, found: 384.2302. $[\alpha]_D^{22}$ = 13.9, (c = 2.27, CH_2Cl_2). HPLC (Chiralcel AD-H column, CO_2:*i*-PrOH = 98:2, 1.3 mL/min, 214 nm), t_{minor} = 12.1 min, t_{major} = 17.2 min, ee = 89%, dr > 15:1.

(4S,5R)-1-((tert-butyldimethylsilyl)oxy)-2,2-difluoro-4-vinylundecan-5-ol (4q)



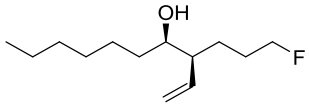
According to the general procedure, **4q** (58.3 mg, 0.16 mmol) was prepared from heptanal (22.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and (2-bromo-2,2-difluoroethoxy)-(tert-butyl)dimethylsilane (165.1 mg, 0.6 mmol, 3.0 equiv.); $ZrCp_2Cl_2$ (60.0 mg, 0.2 mmol, 1.0 equiv.) instead of TMSCl (21.7 mg, 0.2 mmol, 1.0 equiv.), as colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 – 5.66 (m, 1H), 5.25 – 5.05 (m, 2H), 3.72 (t, *J* = 12.5 Hz, 2H), 3.56 (dd, *J* = 7.0, 3.4 Hz, 1H), 2.43 (td, *J* = 8.8, 4.5 Hz, 1H), 2.26 – 1.96 (m, 3H), 1.55 – 1.19 (m, 12H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 123.6, 117.4 (t, *J* = 238.9 Hz), 73.7, 64.8 (t, *J* = 34.3 Hz), 43.9, 34.8, 34.6, 31.9, 29.5, 25.92, 25.86, 22.8, 18.4, 14.2, -5.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.82 – -103.82 (m, 1F), -103.84 – -104.86 (m, 1F). IR (neat) cm^{-1} ν̃: 2963, 1261, 1092, 1020, 799. HRMS (EI$^{(+)}$, 70 eV): $C_{19}H_{38}O_2F_2Si$ $[M]^+$: calcd: 364.2609, found: 364.2603. $[\alpha]_D^{20}$ = 17.1, (c = 1.84, CH_2Cl_2). After converting into the corresponding 3,5-dinitro-benzoyl ester[3], enantiomeric ratio was determined by HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 90:10, 0.70 mL/min, 214 nm), t_{major} = 7.6 min, t_{minor} = 8.6 min, ee = 92%, dr = 10:1.

(3R,4S)-7-fluoro-1-phenyl-4-vinylheptan-3-ol (4r)



According to the general procedure **4r** (25.5 mg, 0.11 mmol) was prepared 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1-fluoro-3-iodopropane (104.4 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.15 (m, 3H), 5.64 (dt, *J* = 17.2, 9.8 Hz, 1H), 5.22 (dd, *J* = 10.3, 1.7 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 4.43 (dt, *J* = 47.2, 5.9 Hz, 2H), 3.55 – 3.47 (m, 1H), 2.89 – 2.78 (m, 1H), 2.74 – 2.59 (m, 1H), 2.11 – 2.00 (m, 1H), 1.87 – 1.63 (m, 5H), 1.51 – 1.37 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 138.0, 128.42, 128.38, 125.8, 118.7, 84.0 (d, *J* = 164.4 Hz), 73.0, 50.2, 36.6, 32.1, 28.4, 28.2, 26.3, 26.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.23 – -218.91 (m, 1F). IR (neat) cm^{-1} ν̃: 2963, 1407, 1260, 1088, 1019, 798. HRMS (EI$^{(+)}$, 70 eV): $C_{15}H_{19}F$ $[M\text{-}H_2O]^+$: calcd: 218.1471, found: 218.1463. $[\alpha]_D^{22}$ = 26.3, (c = 0.40, CH_2Cl_2). HPLC (Chiralcel IE-H column, hexanes:*i*-PrOH = 99:1, 0.5 mL/min, 210 nm), t_{minor} = 26.9 min, t_{major} = 27.5 min, ee = 92%, dr = 15:1.

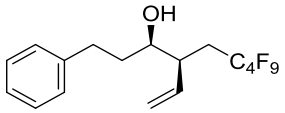
(4S,5R)-1-fluoro-4-vinylundecan-5-ol (4s)



According to the general procedure **4s** (26.4 mg, 0.12 mmol) was prepared from heptanal (22.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.), and 1-fluoro-3-iodopropane (104.4 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (dt, *J* = 17.5, 9.7 Hz, 1H), 5.21 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.11 (dd, *J* = 17.3, 1.2 Hz, 1H), 4.44 (dt, *J* = 47.2,

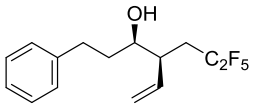
5.7 Hz, 2H), 3.48 (dd, *J* = 10.1, 5.9 Hz, 1H), 2.07 – 2.01 (m, 1H), 1.84 – 1.58 (m, 3H), 1.56 – 1.22 (m, 11H), 0.88 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 118.3, 84.1 (d, *J* = 164.4 Hz), 73.7, 49.9, 34.8, 31.8, 29.4, 28.3, 26.3, 25.7, 22.6, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -218.22 – -218.78 (m, 1F). IR (neat) cm^{-1} ṽ: 3394, 3074, 2956, 2856, 1460, 1000, 913. HRMS ($EI^{(+)}$, 70 eV): $C_{13}H_{23}F$ $[M-H_2O]^+$: calcd: 198.1784, found: 198.1780. $[\alpha]_D^{22}$ = 22.5, (c = 1.58, CH_2Cl_2). After converting into the corresponding 3,5-dinitro-benzoyl ester[3], enantiomeric ratio was determined by HPLC (Chiralcel ID-H column, hexanes:*i*-PrOH = 99:1, 0.7 mL/min, 214 nm), t_{minor} = 9.2 min, t_{major} = 10.2 min, ee = 93%, dr = 15:1.

(3R,4S)-6,6,7,7,8,8,9,9,9-nonafluoro-1-phenyl-4-vinylnonan-3-ol (4t)



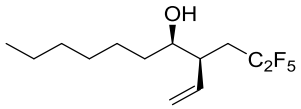
According to the general procedure **4t** (65.3 mg, 0.16 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1,2,2,3,3,4,4-nonafluor-o-4-iodobutane (207.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 6.9 Hz, 3H), 5.86 – 5.69 (m, 1H), 5.20 (dd, *J* = 21.9, 13.7 Hz, 2H), 3.66 (dd, *J* = 8.4, 4.1 Hz, 1H), 2.90 – 2.75 (m, 1H), 2.73 – 2.55 (m, 2H), 2.34 – 2.13 (m, 2H), 1.81 – 1.70 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.5, 135.7, 128.5, 128.4, 126.1, 118.6, 118.0, 73.1, 42.4, 36.5, 36.0, 32.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.08 (m, 3F), -110.93 – -112.44 (m, 1F), -113.04 – -114.52 (m, 1F), -123.07 – -124.99 (m, 2F), -125.71 – -126.17 (m, 2F). IR (neat) cm^{-1} ṽ: 3438, 2944, 1354, 1218, 1130, 1048, 698. HRMS ($EI^{(+)}$, 70 eV): $C_{17}H_{17}OF_9$ $[M]^+$: calcd: 408.1136, found: 408.1132. $[\alpha]_D^{22}$ = 14.3, (c = 0.10, CH_2Cl_2). HPLC (LUX 5u (cellulose-1, 0.46*25 cm, 5 um) column, CH_3CN:H_2O = 90:10, 0.7 mL/min, 254 nm), t_{minor} = 5.2 min, t_{major} = 6.0 min, ee = 86%, dr = 15:1.

(3R,4S)-6,6,7,7,7-pentafluoro-1-phenyl-4-vinylheptan-3-ol (4u)



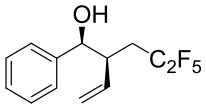
According to the general procedure **4u** (48.1 mg, 0.16 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1,2,2-pentafluoro-2-iodo-ethane(147.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.21 (t, *J* = 7.1 Hz, 3H), 5.83 – 5.69 (m, 1H), 5.21 (dd, *J* = 23.1, 13.8 Hz, 2H), 3.73 – 3.57 (m, 1H), 2.92 – 2.75 (m, 1H), 2.74 – 2.56 (m, 2H), 2.45 – 2.06 (m, 2H), 1.97 – 1.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 137.5, 135.8, 128.6, 128.5, 126.2, 118.8, 118.1, 73.1, 42.6, 36.6, 32.4, 32.0 (t, *J* = 21.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.86 (s, 3F), -116.59 (m, 2F). IR (neat) cm^{-1} ṽ: 3456, 2943, 1453, 1190, 1049, 924,698. HRMS ($EI^{(+)}$, 70 eV): $C_{15}H_{17}OF_5$ $[M]^+$: calcd: 308.1200, found: 308.1202. $[\alpha]_D^{23}$ = 29.1, (c = 0.66, CH_2Cl_2). HPLC (Chiralcel AD-H column, CO_2:*i*-PrOH = 95:5, 1.3 mL/min, 214 nm), t_{minor} = 5.9 min, t_{major} = 7.1 min, ee = 95%, dr = 15:1.

(4S,5R)-1,1,1,2,2-pentafluoro-4-vinylundecan-5-ol (4v)



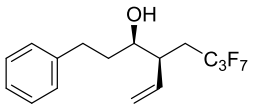
According to the general procedure **4v** (44.3 mg, 0.16 mmol) was prepared from heptanal (22.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1,2,2-pentafluoro-2-io-do-ethane(147.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.59 (m, 1H), 5.20 (dd, *J* = 23.8, 13.8 Hz, 2H), 3.73 – 3.47 (m, 1H), 2.59 (m, 1H), 2.45 – 2.09 (m, 2H), 1.54 – 1.21 (m, 10H), 0.89 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.7, 135.8, 118.4, 117.6, 73.6, 42.2, 34.7, 31.9 (t, *J* = 20.6 Hz), 31.7, 29.2, 25.8, 22.6, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.98 (s, 3F), -116.69 (m, 2F). IR (neat) cm^{-1} ṽ: 3387, 2930, 1464, 1193, 1056, 922, 700. HRMS ($EI^{(+)}$, 70 eV): $C_{13}H_{19}F_5$ $[M\text{-}H_2O]^+$: calcd: 270.1407, found: 270.1406. $[\alpha]_D^{23}$ = 21.4, (c = 0.86, CH_2Cl_2). After converting into the corresponding 3,5-dinitro-benzoyl ester[3], enantiomeric ratio was determined by HPLC (Chiralcel OJ-H column, CO_2:*i*-PrOH = 98:2, 1.3 mL/min, 254 nm), t_{minor} = 6.2 min, t_{major} = 6.6 min, ee = 95.5%, dr > 15:1.

(1S,2S)-4,4,5,5,5-pentafluoro-1-phenyl-2-vinylpentan-1-ol (4w)



According to the general procedure **4w** (39.2 mg, 0.14 mmol) was prepared from benzaldehyde (21.2 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1,2,2-pentafluoro-2-iodo-ethane (147.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.32 – 7.25 (m, 3H), 5.84 – 5.53 (m, 1H), 5.16 (dd, *J* = 32.9, 13.7 Hz, 2H), 4.61 (d, *J* = 3.8 Hz, 1H), 2.84 (dt, *J* = 8.7, 4.2 Hz, 1H), 2.32 – 1.91 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.2, 136.2, 128.2 (t, *J* = 21.6 Hz), 128.0, 126.5, 119.2, 118.0, 75.8, 44.6, 31.4 (t, *J* = 20.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.0 (s, 3F), -115.0 – -1183. (m, 2F). IR (neat) cm^{-1} ṽ: 2962, 1452, 1392, 1197, 1043, 925, 702. HRMS ($EI^{(+)}$, 70 eV): $C_{13}H_{11}F_5$ $[M\text{-}H_2O]^+$: calcd: 262.0781, found: 262.0791. $[\alpha]_D^{22}$ = -17.9, (c = 1.36, CH_2Cl_2). HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 95:5, 1.0 mL/min, 214 nm), t_{minor} = 6.5 min, t_{major} = 8.9 min, ee = 86%, dr = 15:1.

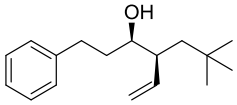
(3R,4S)-6,6,7,7,8,8,8-heptafluoro-1-phenyl-4-vinyloctan-3-ol (4x)



According to the general procedure **4x** (57.3 mg, 0.16 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 1,1,1,2,2,3,3-heptafluoro-3-iodopropane (177.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 6.8 Hz, 3H), 5.81 – 5.69 (m, 1H), 5.20 (dd, *J* = 21.9, 13.8 Hz, 2H), 3.65 (dd, *J* = 8.6, 4.2 Hz, 1H), 2.85 – 2.74 (m, 1H), 2.73 – 2.56 (m, 2H), 2.44 – 2.07 (m, 2H), 1.84 – 1.67 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.5, 135.7, 128.5, 128.4, 126.1, 118.7, 73.1, 42.4, 36.5, 36.1, 31.87 (dd, *J* = 35.1, 13.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.42 (t, *J* = 9.8 Hz, 3F), -109.73 – -117.08 (m, 2F), -127.84 (s, 2F). IR

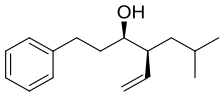
(neat) cm^{-1} ṽ: 3418, 2945, 1496, 1222, 1172, 923, 700. HRMS ($EI^{(+)}$, 70 eV): $C_{16}H_{17}OF_5$ $[M]^+$: calcd: 358.1168, found: 358.1181. $[\alpha]_D^{23}$ = 16.9, (c = 1.06, CH_2Cl_2). HPLC (Chiralcel OD-H column, CO_2:*i*-PrOH = 90:10, 1.3 mL/min, 214 nm), t_{minor} = 4.8 min, t_{major} = 6.6 min, ee = 96%, dr = 15:1.

(3R,4S)-6,6-dimethyl-1-phenyl-4-vinylheptan-3-ol (4y)



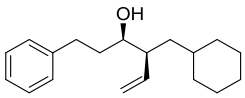
According to the general procedure **4y** (43.4 mg, 0.18 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 2-iodo-2-methylpropane (110.4 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.24 – 7.14 (m, 3H), 5.68 (dt, *J* = 17.4, 9.8 Hz, 1H), 5.12 (dd, *J* = 20.2, 13.8 Hz, 2H), 3.45 – 3.30 (m, 1H), 2.91 – 2.75 (m, 1H), 2.66 (ddd, *J* = 13.7, 10.1, 6.5 Hz, 1H), 2.23 – 2.11 (m, 1H), 1.89 – 1.78 (m, 1H), 1.73 – 1.60 (m, 1H), 1.35 (dd, *J* = 11.9, 4.1 Hz, 2H), 0.89 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 141.4, 128.6, 128.5, 125.9, 117.6, 74.2, 47.2, 44.8, 36.4, 32.5, 31.3, 30.3. IR (neat) cm^{-1} ṽ: 3384, 3066, 1495, 1222, 910,698. HRMS ($EI^{(+)}$, 70 eV): $C_{17}H_{26}O$ $[M]^+$: calcd: 246.1984, found: 246.1992. $[\alpha]_D^{31}$ = 43.4, (c = 0.90, CH_2Cl_2). HPLC (Chiralcel AD-H column, hexanes:*i*-PrOH = 99.5:0.5, 0.6 mL/min, 210 nm), t_{minor} = 16.3 min, t_{major} = 18.7 min, ee = 91%, dr > 15:1.

(3R,4S)-6-methyl-1-phenyl-4-vinylheptan-3-ol (4z)



According to the general procedure **4z** (39.9 mg, 0.17 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and 2-iodopropane (102.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.14 (m, 3H), 5.60 (dt, *J* = 17.3, 9.9 Hz, 1H), 5.14 (ddd, *J* = 18.5, 13.7, 1.4 Hz, 2H), 3.46 – 3.37 (m, 1H), 2.87 – 2.76 (m, 1H), 2.66 (ddd, *J* = 13.7, 10.0, 6.5 Hz, 1H), 2.19 – 2.03 (m, 1H), 1.89 – 1.77 (m, 1H), 1.76 – 1.65 (m, 1H), 1.55 (ddd, *J* = 17.2, 11.8, 6.6 Hz, 1H), 1.36 – 1.10 (m, 2H), 0.86 (dd, *J* = 21.4, 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 139.0, 128.6, 128.5, 125.9, 118.1, 73.3, 48.6, 40.0, 36.7, 32.3, 25.4, 24.0, 21.4. IR (neat) cm^{-1} ṽ: 3408, 3067, 1454, 914, 699. HRMS ($EI^{(+)}$, 70 eV): $C_{16}H_{22}$ $[M\text{-}H_2O]^+$: calcd: 214.1722, found: 214.1729. $[\alpha]_D^{31}$ = 21.9, (c = 1.60, CH_2Cl_2). HPLC (Chiralcel AD-H column, hexanes:*i*-PrOH = 99.6:0.4, 0.6 mL/min, 210 nm), t_{minor} = 19.7 min, t_{major} = 22.2 min, ee = 93%, dr = 15:1.

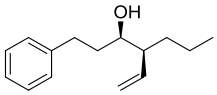
(3R,4S)-4-(cyclohexylmethyl)-1-phenylhex-5-en-3-ol (4aa)



According to the general procedure **4aa** (39.0 mg, 0.14 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and iodocyclohexane (126.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29

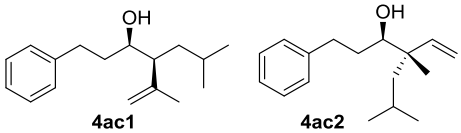
(t, *J* = 7.4 Hz, 2H), 7.19 (dd, *J* = 14.0, 7.3 Hz, 3H), 5.60 (ddd, *J* = 18.3, 17.2, 9.8 Hz, 1H), 5.15 (dd, *J* = 33.8, 13.8 Hz, 2H), 3.42 (dd, *J* = 8.6, 5.2 Hz, 1H), 2.88 – 2.76 (m, 1H), 2.72 – 2.61 (m, 1H), 2.24 – 2.10 (m, 1H), 1.89 – 1.78 (m, 1H), 1.78 – 1.55 (m, 7H), 1.33 – 1.06 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 139.1, 128.6, 128.5, 125.9, 118.1, 73.3, 47.7, 38.6, 36.7, 34.9, 34.7, 32.4, 32.3, 26.8, 26.5, 26.3. IR (neat) cm^{-1} ṽ: 3459, 3065, 1261, 1172, 913, 699. HRMS (EI$^{(+)}$, 70 eV): $C_{19}H_{28}O$ $[M]^+$: calcd: 272.2140, found: 272.2145. $[\alpha]_D^{31}$ = 35.1, (c = 0.99, CH_2Cl_2). HPLC (Chiralcel OJ-H column, CO_2:*i*-PrOH = 95:5, 1.3 mL/min, 214 nm), t_{major} =10.8 min, t_{minor} = 11.5 min, ee = 90%, dr = 15:1.

(3R,4S)-1-phenyl-4-vinylheptan-3-ol (4ab)



According to the general procedure **4ab** (14.0 mg, 0.064 mmol) was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), 1,3-diene (400 uL, 0.6 mmol, 3.0 equiv.) and iodoethane (93.6 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 32% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (dd, *J* = 14.1, 7.1 Hz, 3H), 5.70 – 5.54 (m, 1H), 5.15 (dd, *J* = 32.2, 14.4 Hz, 2H), 3.47 (dd, *J* = 7.5, 4.8 Hz, 1H), 2.92 – 2.77 (m, 1H), 2.75 – 2.61 (m, 1H), 2.15 – 1.94 (m, 1H), 1.77 (ddd, *J* = 14.1, 9.5, 5.8 Hz, 2H), 1.43 – 1.21 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 138.9, 128.6, 128.5, 125.9, 118.2, 73.1, 50.5, 36.7, 33.0, 32.3, 20.6, 14.2. IR (neat) cm^{-1} ṽ: 3438, 3067, 1495, 913 699. HRMS (EI$^{(+)}$, 70 eV): $C_{15}H_{20}$ $[M\text{-}H_2O]^+$: calcd: 200.1565, found: 200.1563. $[\alpha]_D^{31}$ = 26.8, (c = 1.30, CH_2Cl_2). HPLC (Chiralcel AD-H column, hexanes:*i*-PrOH = 99.5:0.5, 0.6 mL/min, 210 nm), t_{minor} = 20.95 min, t_{major} = 23.98 min, ee = 85%, dr = 15:1.

(3R,4S)-6-methyl-1-phenyl-4-(prop-1-en-2-yl)heptan-3-ol (4ac1) and **(3R,4S)-4,6-dimethyl-1-phenyl-4-vinylheptan-3-ol (4ac2)**



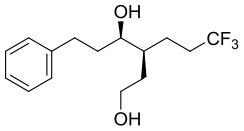
According to the general procedure **4ac1** and **4ac2**, (**4ac1**/**4ac2** = 3.3/1), (30.1 mg, 0.12 mmol) , was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol, 1.0 equiv.), isoprene (40.9 mg, 0.6 mmol, 3.0 equiv.) 2-iodopropane (102.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 61% yield.

4ac1: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.15 (m, 3H), 4.99 (s, 1H), 4.87 (s, 1H), 3.45 (t, *J* = 8.6 Hz, 1H), 2.95 – 2.83 (m, 1H), 2.68 (ddd, *J* = 13.6, 10.6, 6.1 Hz, 1H), 2.19 (ddd, *J* = 11.8, 8.3, 3.7 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.68 (s, 3H), 1.66 – 1.60 (m, 1H), 1.45 (ddd, *J* = 13.5, 6.6, 3.4 Hz, 1H), 1.39 – 1.29 (m, 1H), 1.15 – 1.04 (m, 1H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.7, 128.6, 128.5, 125.9, 115.7, 71.4, 52.2, 38.1, 36.8, 32.2, 25.6, 24.3, 21.3, 18.7. HRMS (EI$^{(+)}$, 70 eV): $C_{17}H_{24}$ $[M\text{-}H_2O]^+$: calcd: 228.1878, found: 288.1876. HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 210 nm), t_{minor} = 5.4 min, t_{major} = 8.4 min, ee = 98%, dr > 15:1.

According to the general procedure without chair ligand **L1** and Proton sponge**, 4ac1** and **4ac2**, (**4ac1**/**4ac2** = 1/2), (32.0 mg, 0.13 mmol), was prepared from 3-phenylpropanal (26.8 mg, 0.2 mmol,

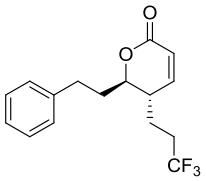
1.0 equiv.), isoprene (40.9 mg, 0.6 mmol, 3.0 equiv.) 2-iodopropane (102.0 mg, 0.6 mmol, 3.0 equiv.) as colorless oil in 65% yield. **4ac2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.20 (dd, *J* = 16.6, 7.5 Hz, 3H), 5.76 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 5.06 (d, *J* = 17.6 Hz, 1H), 3.22 (d, *J* = 10.4 Hz, 1H), 3.02 – 2.86 (m, 1H), 2.66 – 2.50 (m, 1H), 1.87 – 1.74 (m, 1H), 1.63 – 1.52 (m, 2H), 1.32 – 1.17 (m, 2H), 0.98 (s, 3H), 0.86 (dd, *J* = 12.8, 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 142.7, 128.6, 128.5, 125.9, 115.3, 77.0, 46.3, 45.8, 33.6, 32.9, 25.4, 25.1, 24.6, 16.7. HRMS ($EI^{(+)}$, 70 eV): $C_{17}H_{24}$ $[M\text{-}H_2O]^+$: calcd: 228.7878, found: 288.1881. HPLC (Chiralcel OD-H column, hexanes:*i*-PrOH = 98:2, 1.0 mL/min, 210 nm), t_{minor} = 5.8 min, t_{major} = 10.5 min, ee = 18%, dr > 15:1.

(3S,4R)-6-phenyl-3-(3,3,3-trifluoropropyl)hexane-1,4-diol (5)



A screw-cap tube equipped with a magnetic stir, solution of **4d** (54.4 mg, 0.2 mmol, 1.0 equiv.) in 5 mL of THF, was added a solution of 9-BBN in THF solution (1.2 mL, 0.5 M, 0.6 mmol, 3.0 equiv.). The solution was then heated to reflux for 3 h. The reaction mixture was cooled at 0 °C and H_2O (0.7 mL), sodium perborate (277.7 mg, 1.8 mmol, 9.0 equiv.) and sodium hydroxide (66.7 mg, 1.8 mmol, 9.0 equiv.) were added, after which the mixture was stirred at 50 °C in an oil bath for 4 h. The phases were then separated and the aqueous layer was extracted with ethyl acetate (3*15 mL). The organic extracts were combined, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (silicagel, Petroleum ether / ethyl acetate = 3/1 to 1/1) to **5** (44.1 mg, 0.15 mmol) as a yellow oil in 75% yield[4]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 3.73 – 3.61 (m, 2H), 3.60 – 3.54 (m, 1H), 3.12 (s, 2H), 2.87 – 2.74 (m, 1H), 2.70 – 2.60 (m, 1H), 2.17 – 2.01(m, 3H), 1.84 – 1.70 (m, 4H), 1.67 – 1.52 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 128.6, 18.5, 127.25 (d, *J* = 259.1 Hz), 126.1, 72.5, 59.4, 40.5, 36.7, 32.7, 31.8 (d, *J* = 28.4 Hz), 31.18, 22.75 (d, *J* = 2.8 Hz). IR (neat) cm^{-1} ν̃: 3336, 2944, 1495, 1454, 1257, 1141, 1054, 700, 656. HRMS ($EI^{(+)}$, 70 eV): $C_{15}H_{19}OF_3$ $[M\text{-}H_2O]^+$: calcd: 272.1388, found: 272.1396. $[\alpha]_D^{33}$ = 13.5, (c = 0.91, CH_2Cl_2).

(5S,6R)-6-phenethyl-5-(3,3,3-trifluoropropyl)-5,6-dihydro-2H-pyran-2-one (6)



To a solution of **4d** (108.8 mg, 0.4 mmol, 1 equiv.) in CH_2Cl_2 (5.0 mL) at 0 °C, then was added dropwise DIPEA (0.4 mL, 2.4 mmol, 6 equiv.) followed by acryloyl chloride (0.15 mL, 1.2 mmol, 3 equiv.). The resulting reaction mixture was stirred at room temperature for 2 h and quenched with water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (2*20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure to afford the desired ester. Then, to a solution of the corresponding ester (0.40 mmol, 1.00 equiv.) in anhydrous toluene (0.02 M) was added Hoveyda-Grubb II (3 mol %, 75.2 mg). Resulting mixture

was heated at 80 °C for 6 h. After this time, all volatiles were removed under reduced pressure. Crude was purified by column chromatography by using appropriate eluent to afford the desired *α,β*-unsaturated lactone **6** (95.4 mg, 0.32 mmol) in 80% yield[5]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.22 (dd, *J* = 10.3, 4.5 Hz, 3H), 6.72 (dd, *J* = 9.9, 3.7 Hz, 1H), 6.07 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.28 – 4.15 (m, 1H), 2.91 (ddd, *J* = 14.2, 9.2, 5.2 Hz, 1H), 2.83 – 2.70 (m, 1H), 2.20 – 2.03 (m, 3H), 2.01 – 1.91 (m, 1H), 1.90 – 1.76 (m, 1H), 1.73 – 1.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 147.0, 140.7, 128.7, 128.60, 128.56, 126.6 (d, *J* = 276.4 Hz), 126.4, 121.8, 80.2, 36.8, 35.1, 31.2, 30.5 (d, *J* = 29.3 Hz), 23.80. IR (neat) cm^{-1} $\tilde{\nu}$: 3027, 2960, 1725, 1496, 1257, 1142, 1028, 800, 702, 656. HRMS ($EI^{(+)}$, 70 eV): $C_{16}H_{17}O_2F_3$ $[M]^+$: calcd: 298.1181, found: 298.1184. $[\alpha]_D^{33}$ = 55.4, (c =0.65, CH_2Cl_2).

(3). <u>References</u>

[1] (a) Chen, W.; Yang, Q.; Zhou, T.; Tian, Q.; Zhang, G. *Org. Lett.* **2015**, *17*, 5236. (b) Tian, Q.; Bai, J.; Chen, B.; Zhang, G. *Org. Lett.* **2016**, *18*, 1828. (c) Guo, R.; Yang, Q.; Tian, Q.; Zhang, G. *Sci. Rep.* **2017**, *7*, 4873. (d) Liu, H.; Du, D. *Eur. J. Org. Chem.* **2010**, 2121.

[2] Wu, J.-J.; Lorenzo, P.; Zhong, S.; Ali, M.; Butts, C. P.; Myers, E. L.; Aggarwal, V. K. *Nature*, **2017**, *547*, 436.

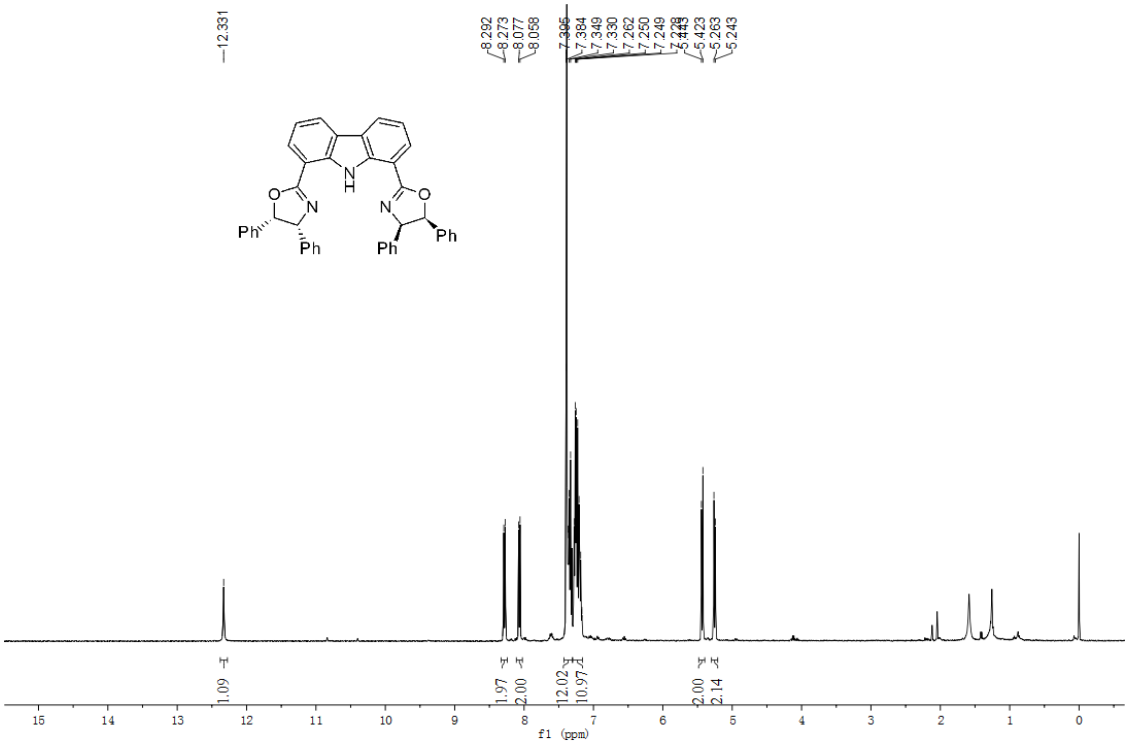
[3] Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140.

[4] (a) Denmark, S. E.; Fu, J. *Org. Lett.* **2002**, *4*, 1951. (b) Denmark, S. R.; Fu, J.; Lawler, M. J. *J. Org. Chem.* **2006**, *71*, 1523.

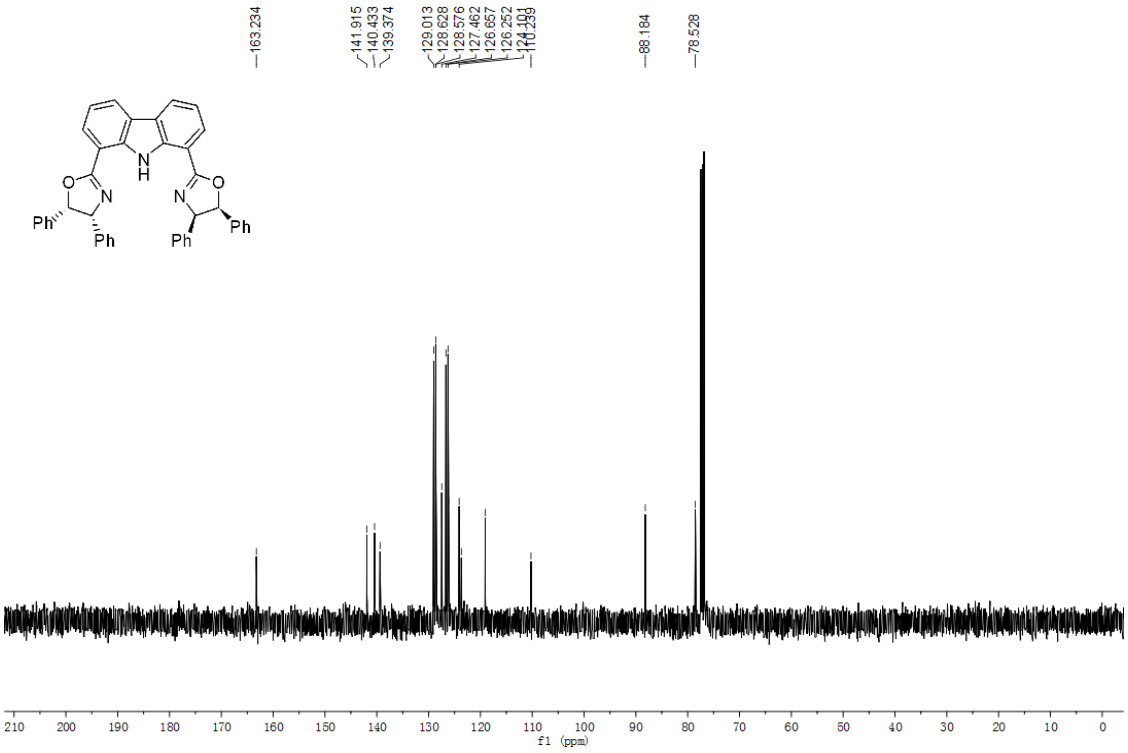
[5] Hemelaere, R.; Carreaux, F.; Carboni, B. *Chem. Eur. J.* **2014**, *20*, 14518.

3. Copies of NMR specta and HPLC chromatographs

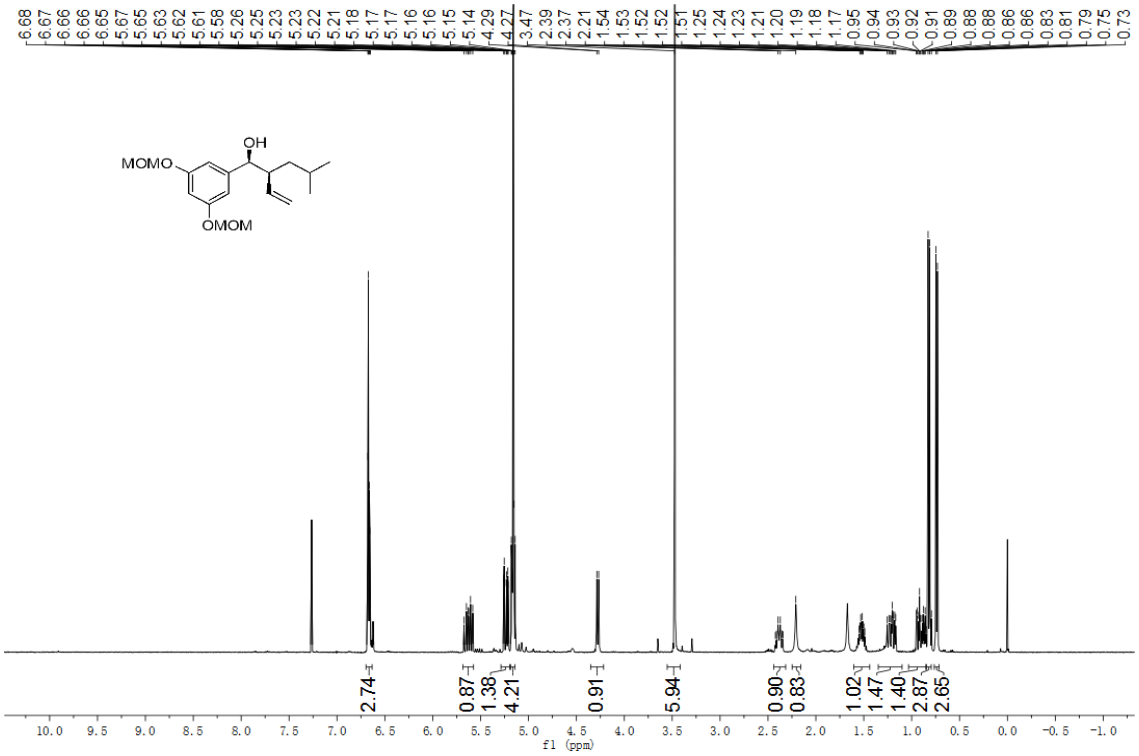
1,8-bis((4R,5S)-4,5-diphenyl-4,5-dihydrooxazol-2-yl)-9H-carbazole (L6)-^{1}H NMR



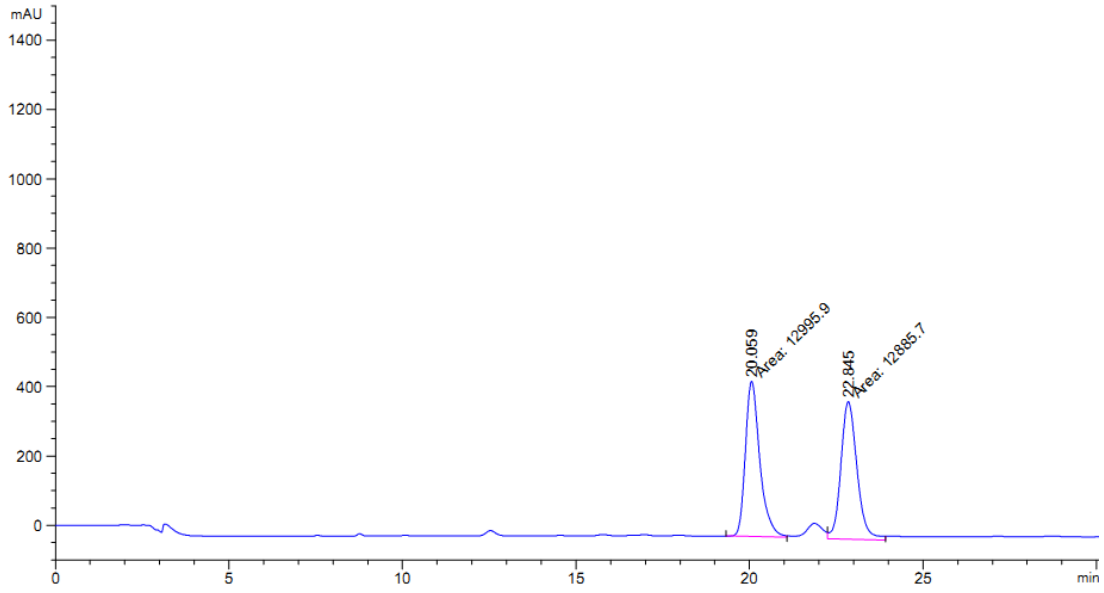
1,8-bis((4R,5S)-4,5-diphenyl-4,5-dihydrooxazol-2-yl)-9H-carbazole (L6)-^{13}C NMR



4a' -^{1}H NMR

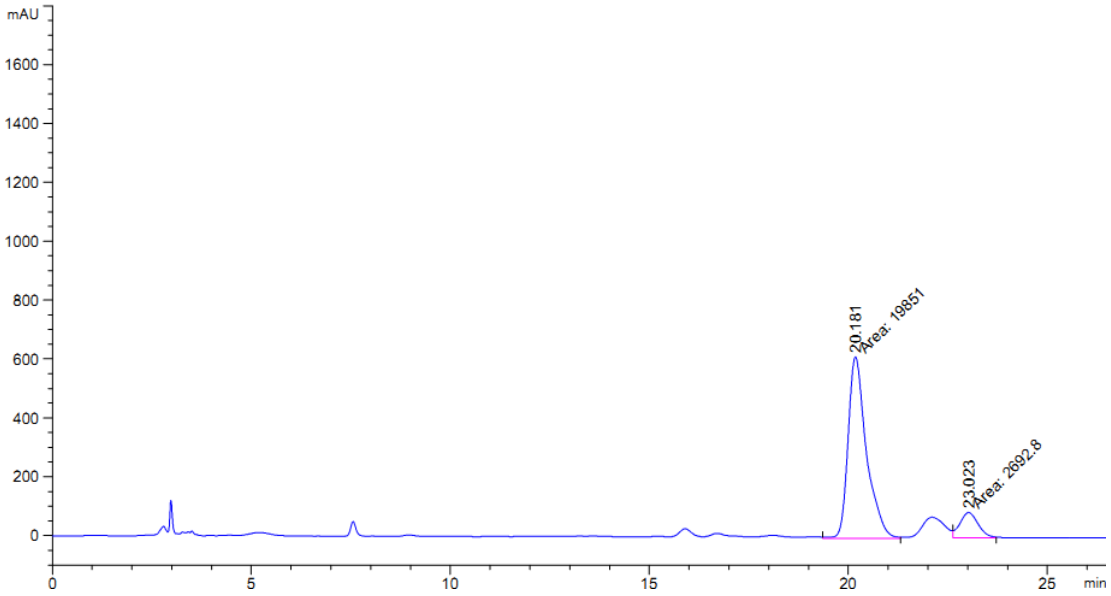


4a' - HPLC (racemic)



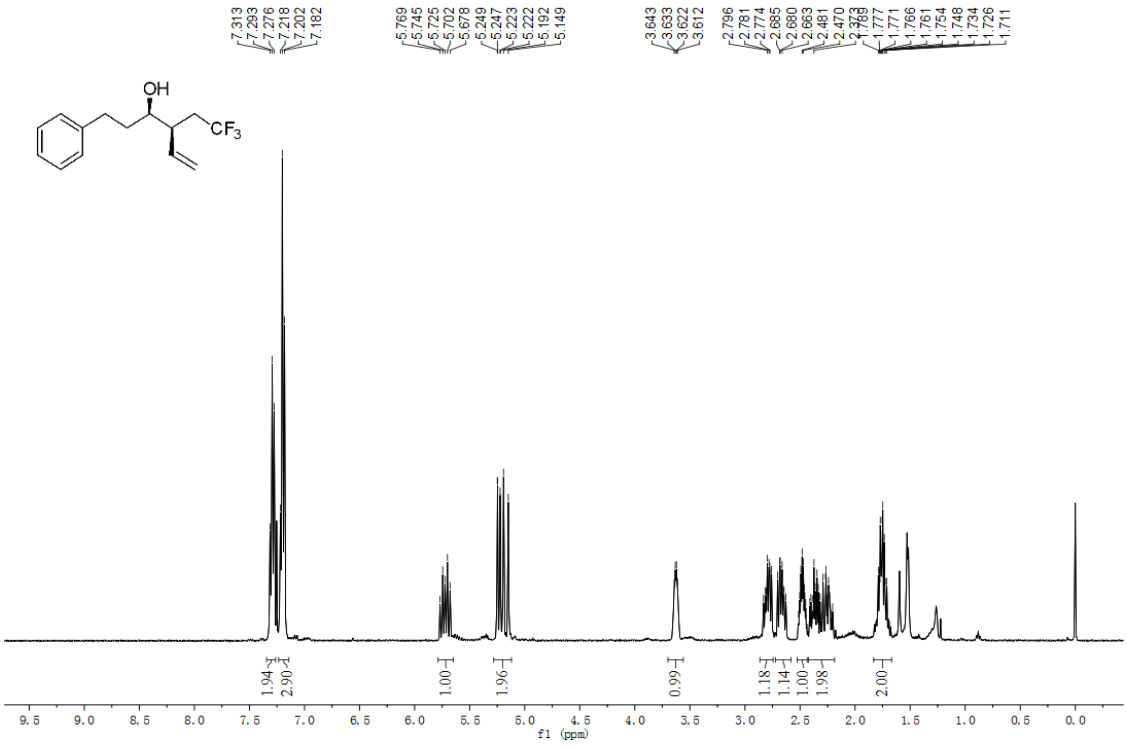
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.059	MM	0.4836	1.29959e4	447.91943	50.2130
2	22.845	MM	0.5414	1.28857e4	396.67532	49.7870

4a' -HPLC (76% ee)

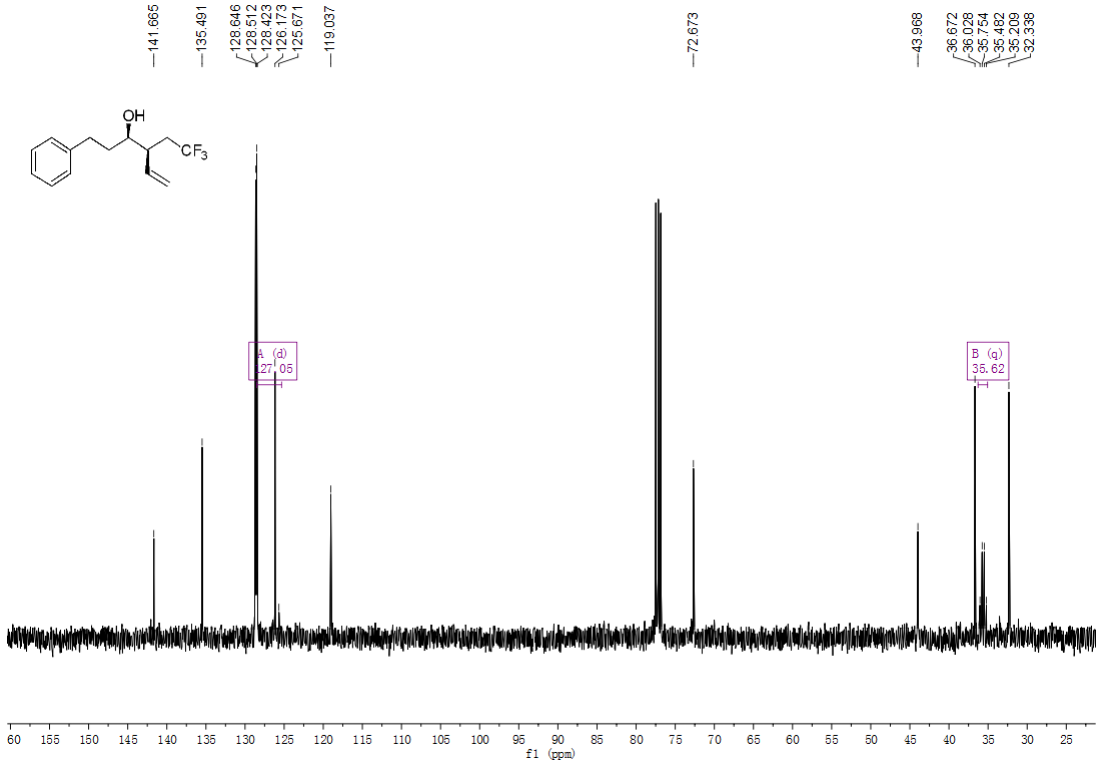


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.181	MM	0.5363	1.98510e4	616.87842	88.0553
2	23.023	MM	0.5269	2692.79810	85.17909	11.9447

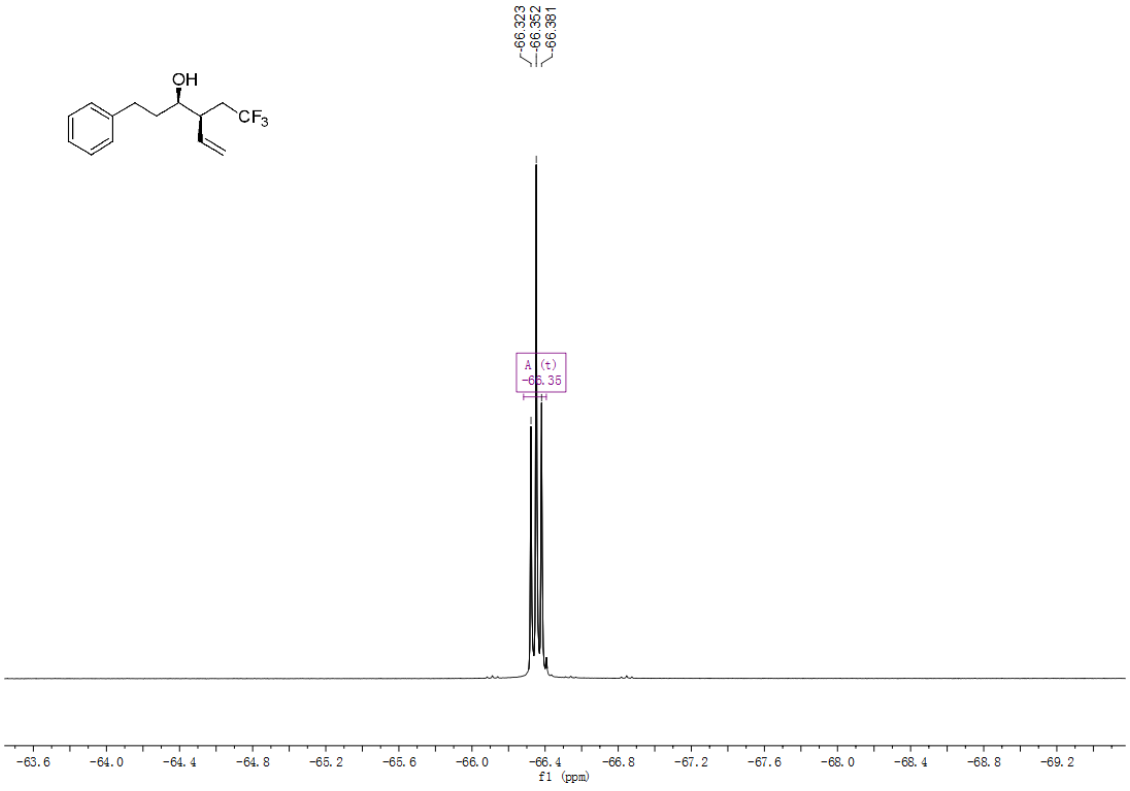
4a-^{1}H NMR



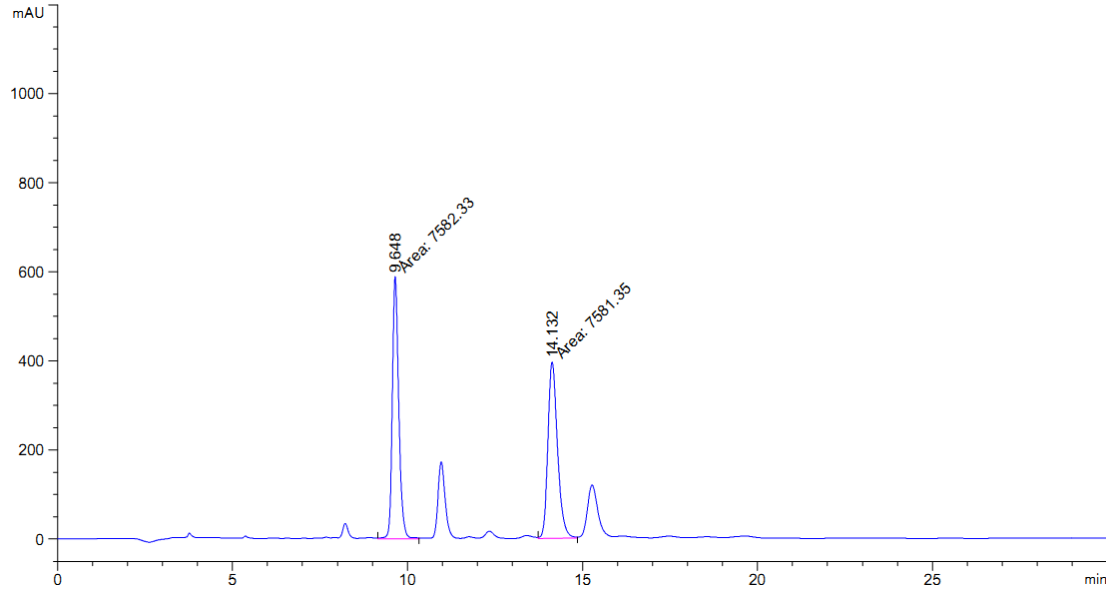
4a-^{13}C NMR



4a-^{19}F NMR

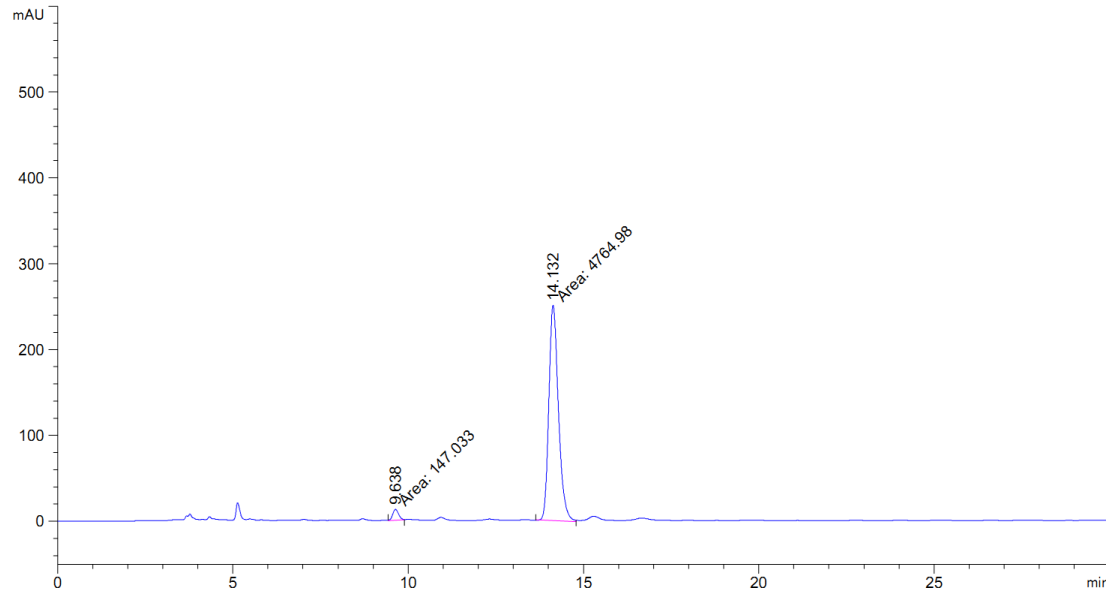


4a-HPLC (racemic)



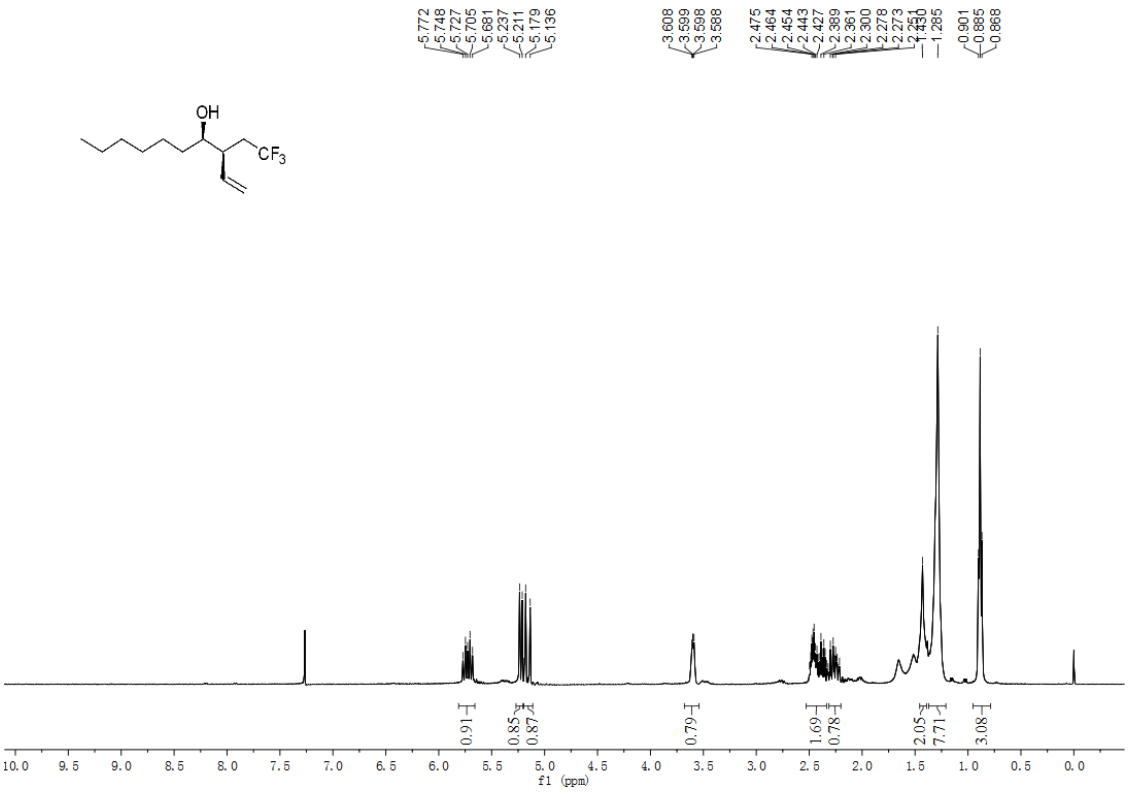
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.648	MM	0.2144	7582.33008	589.55975	50.0032
2	14.132	FM	0.3193	7581.34521	395.67136	49.9968

4a-HPLC (94% ee)

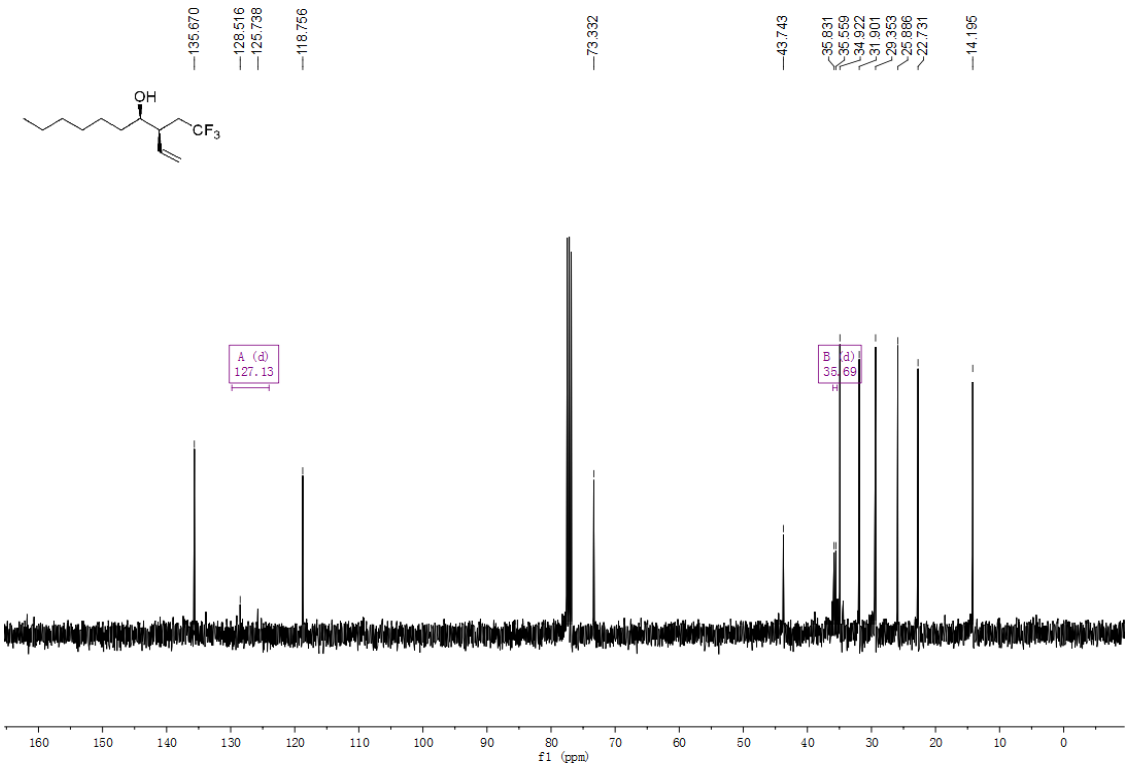


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.638	MM	0.1925	147.03337	12.72716	2.9933
2	14.132	MM	0.3168	4764.98145	250.69984	97.0067

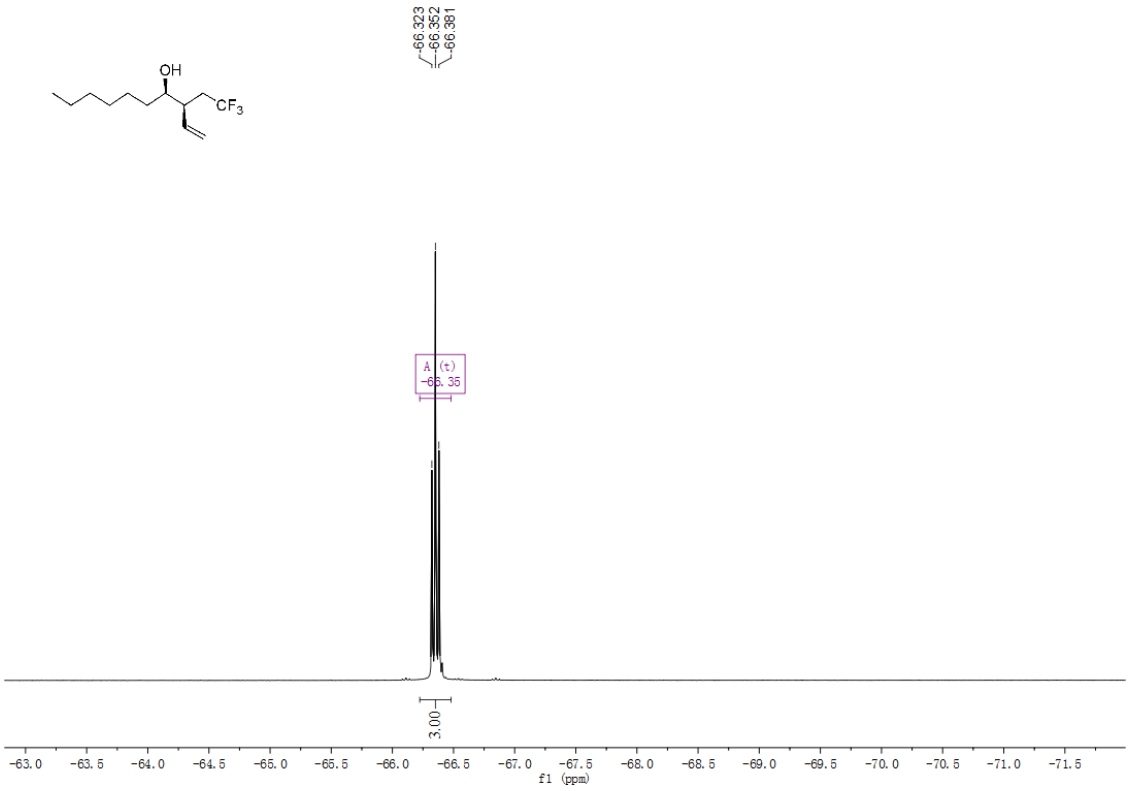
4b-^{1}H NMR



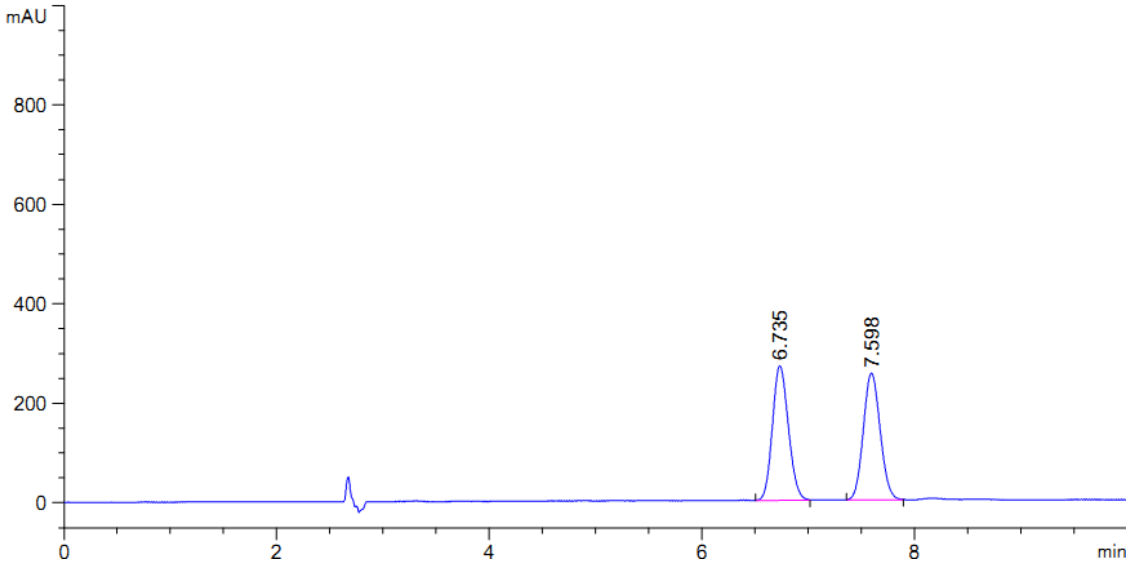
4b-^{13}C NMR



4b-^{19}F NMR

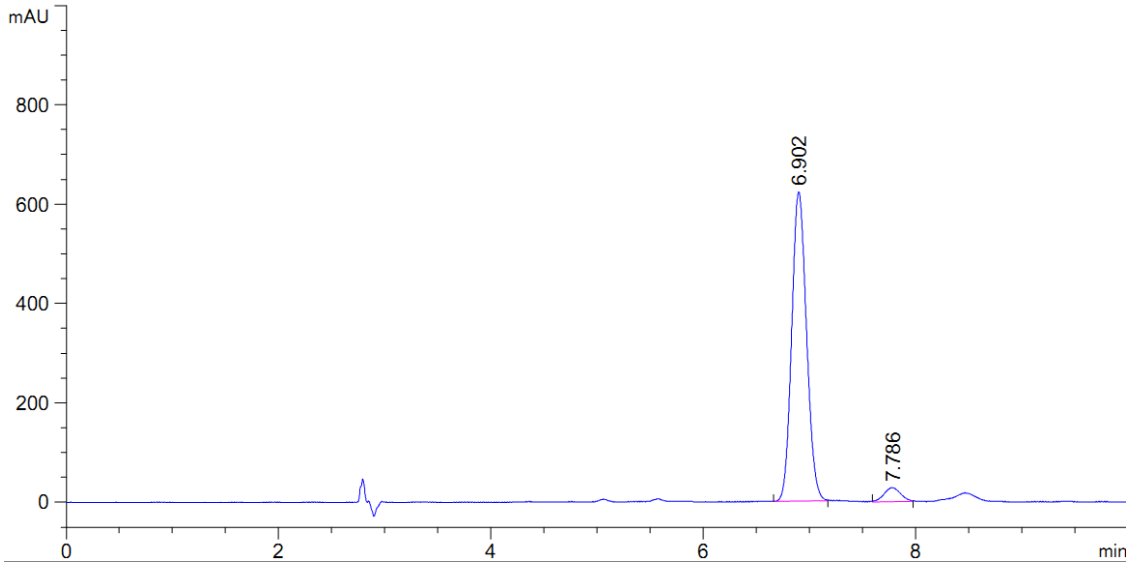


4b-HPLC (racemic)



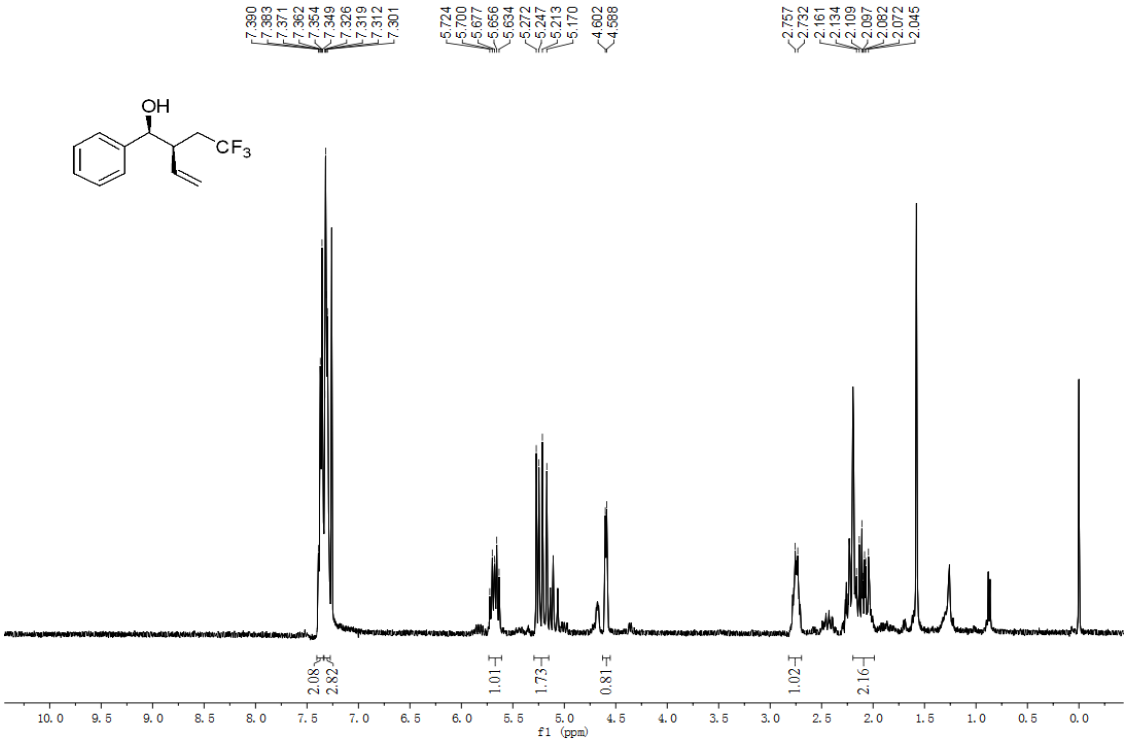
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.735	VV	0.1642	2831.62158	270.43591	50.1186
2	7.598	VV	0.1704	2818.22339	255.11540	49.8814

4b-HPLC (90% ee)

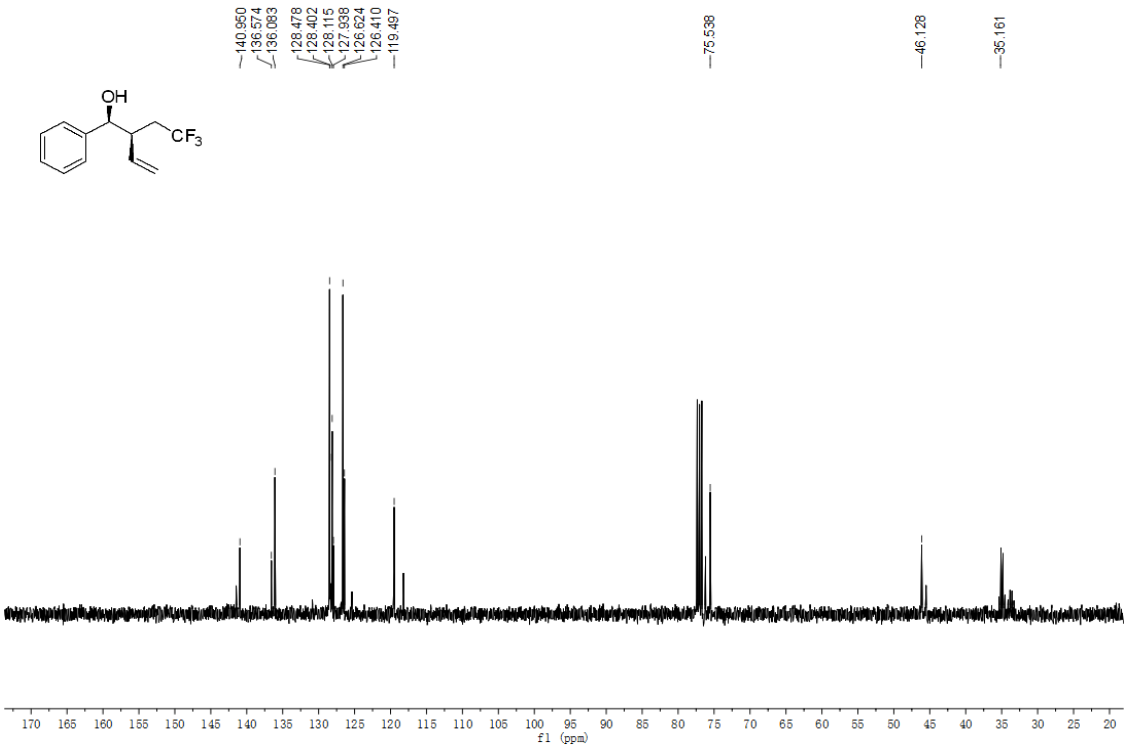


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.902	BV	0.1481	6039.08057	622.97534	95.1963
2	7.786	VV	0.1308	304.73859	28.14204	4.8037

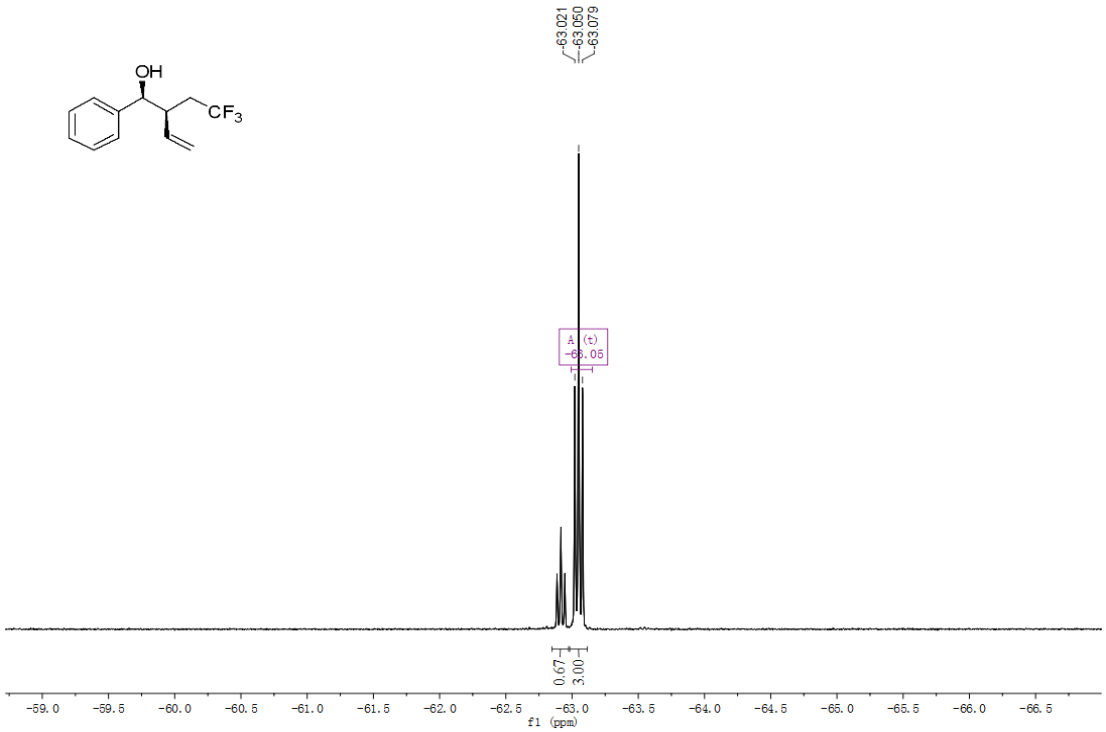
4c-^{1}H NMR



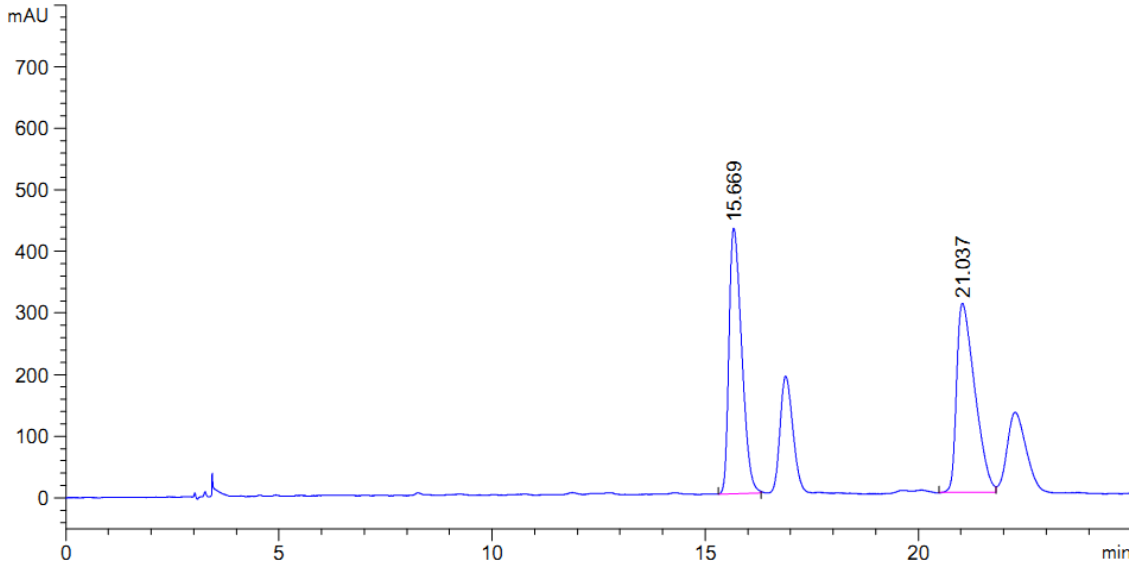
4c-^{13}C NMR



4c-^{19}F NMR

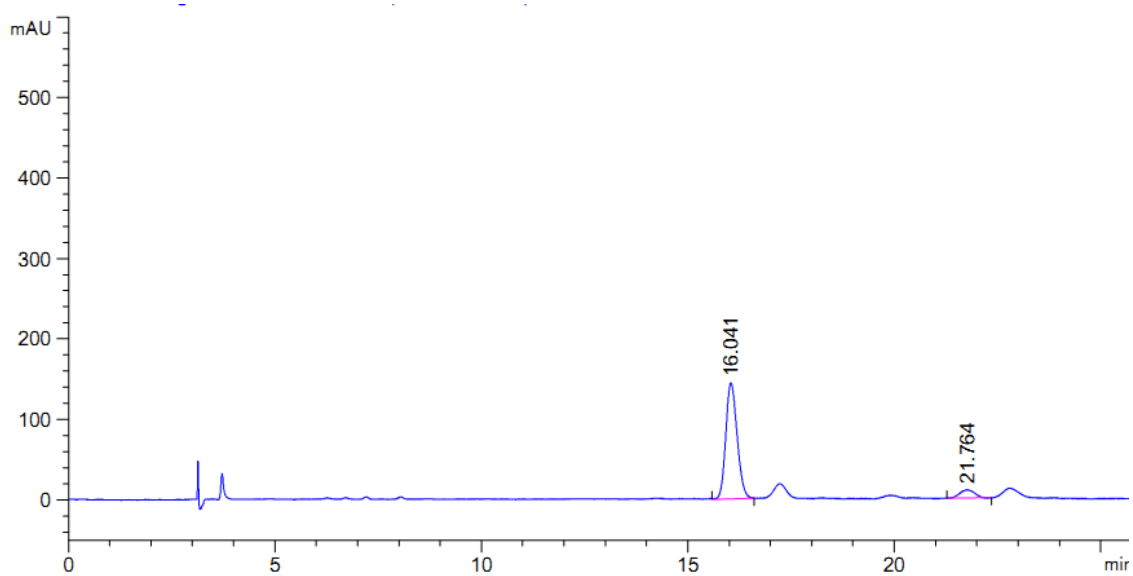


4c-HPLC (racemic)



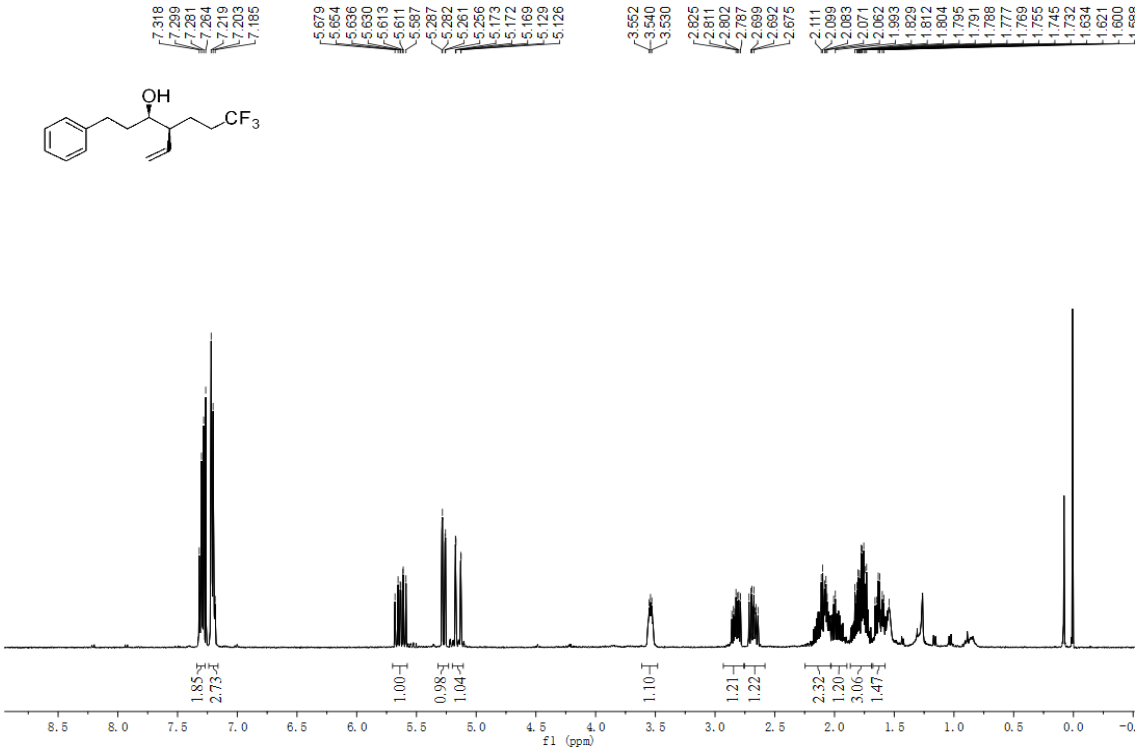
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.669	VV	0.2988	8922.70215	431.35559	49.4423
2	21.037	MF R	0.4718	9123.98633	306.96979	50.5577

4c-HPLC (83% ee)

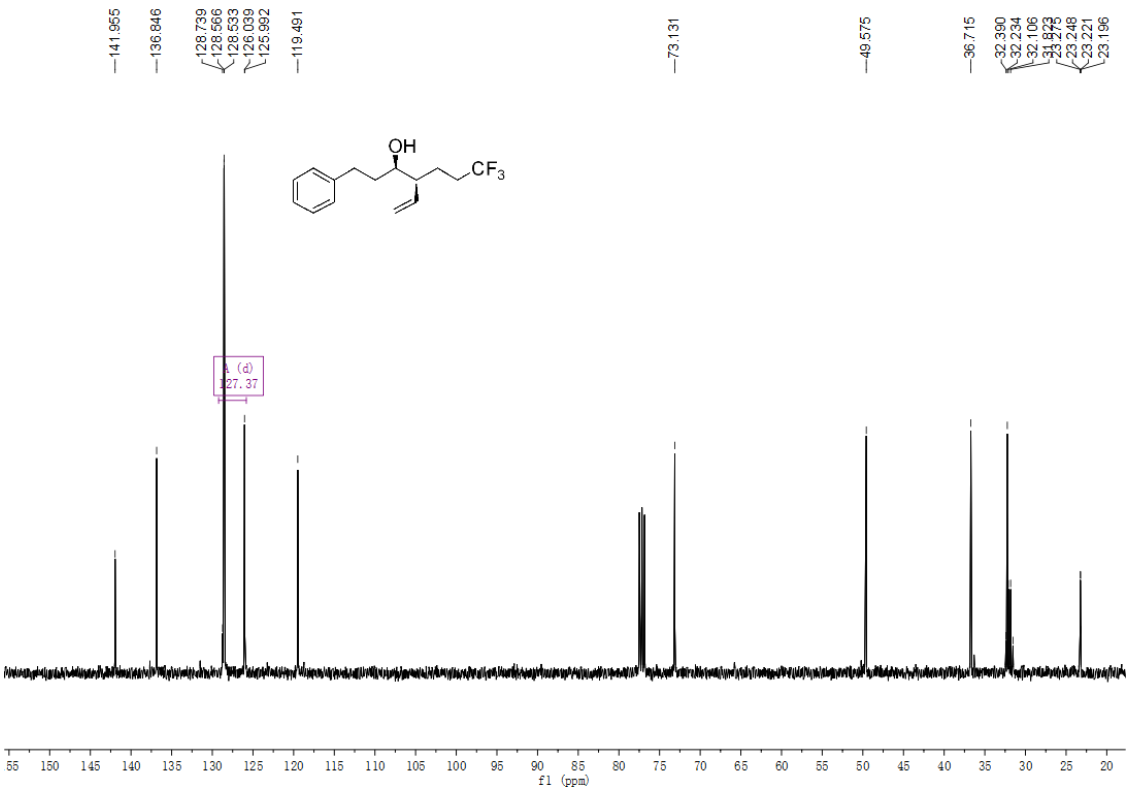


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.041	MM R	0.3097	2745.57202	144.23727	91.5923
2	21.764	MF R	0.3833	252.02942	10.17521	8.4077

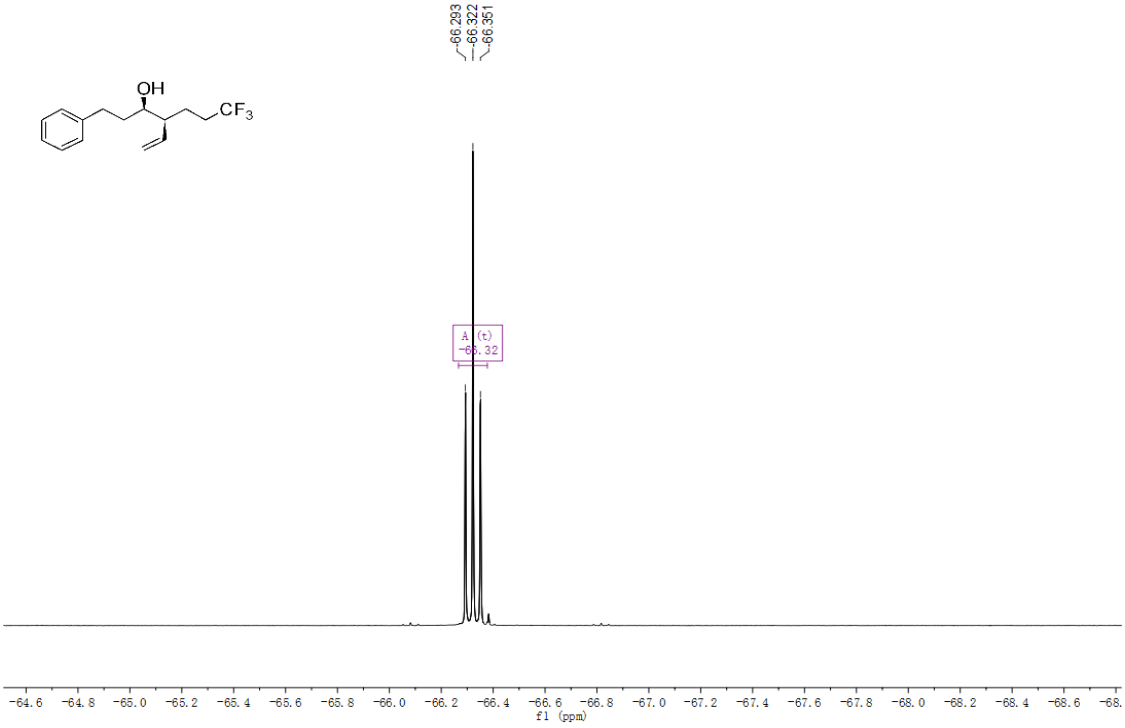
4d-^{1}H NMR



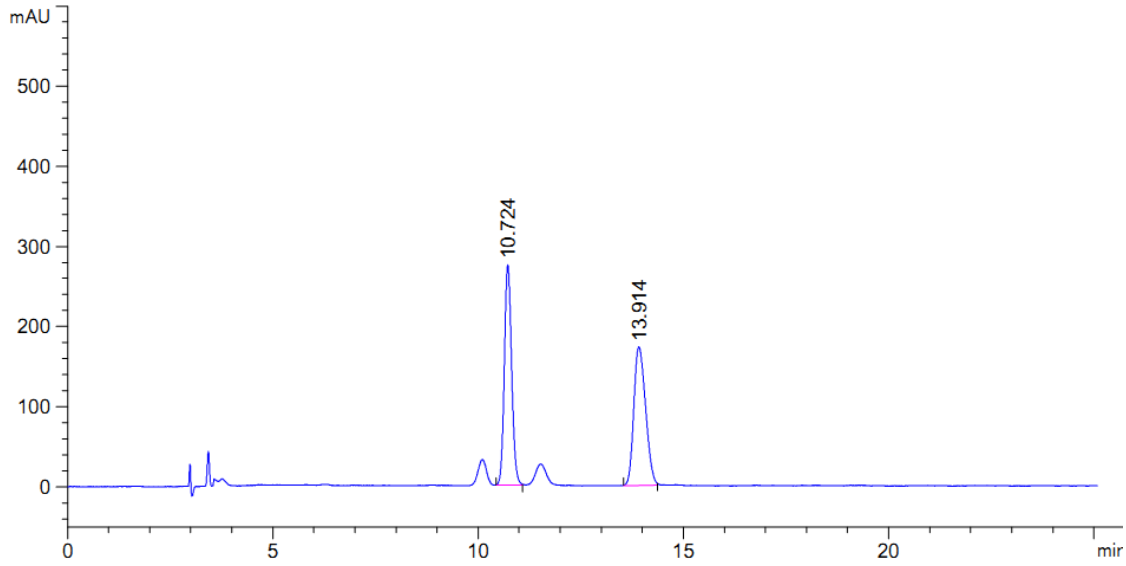
4d-^{13}C NMR



4d-^{19}F NMR

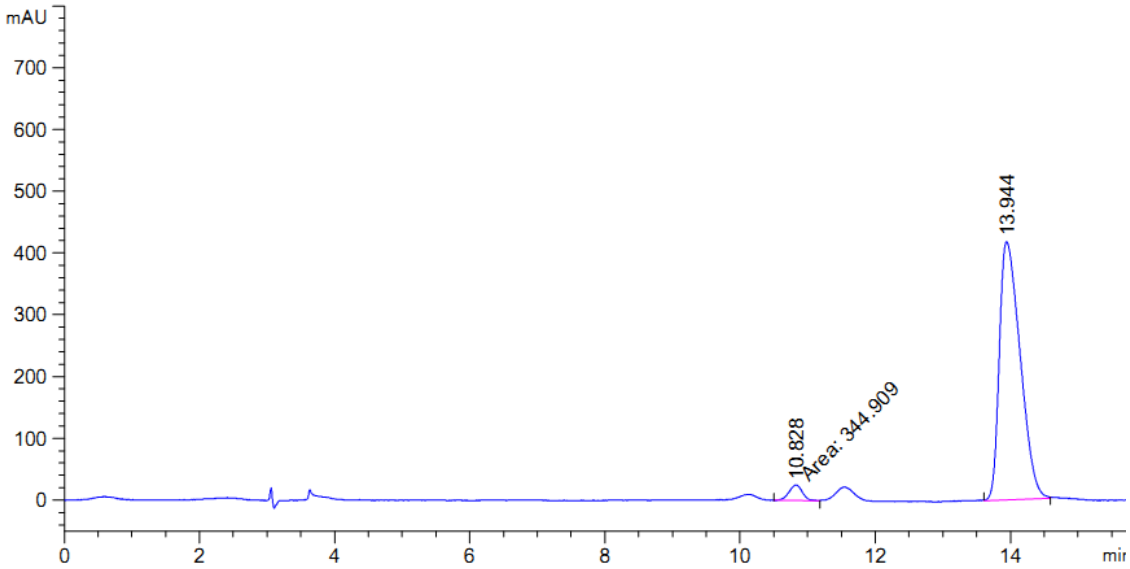


4d-HPLC (racemic)



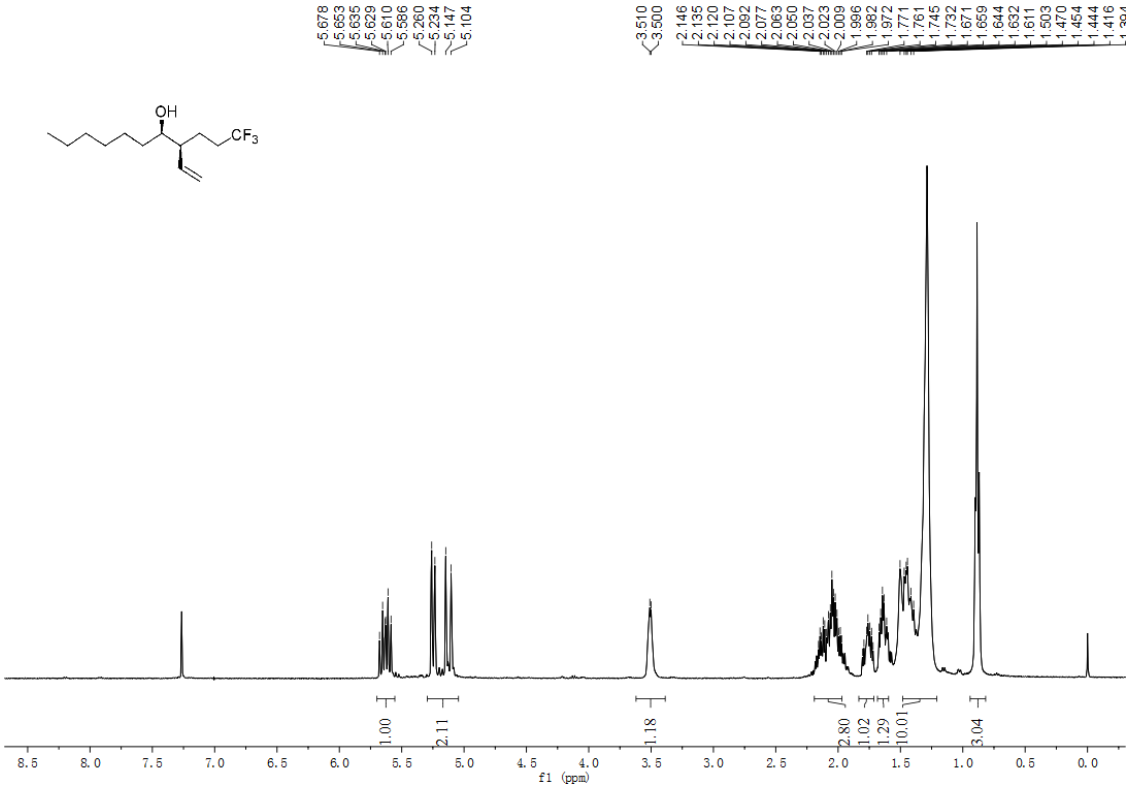
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.724	VV	0.1798	3378.43799	275.04321	49.5591
2	13.914	VV	0.2459	3438.55078	173.01938	50.4409

4d-HPLC (92.5% ee)

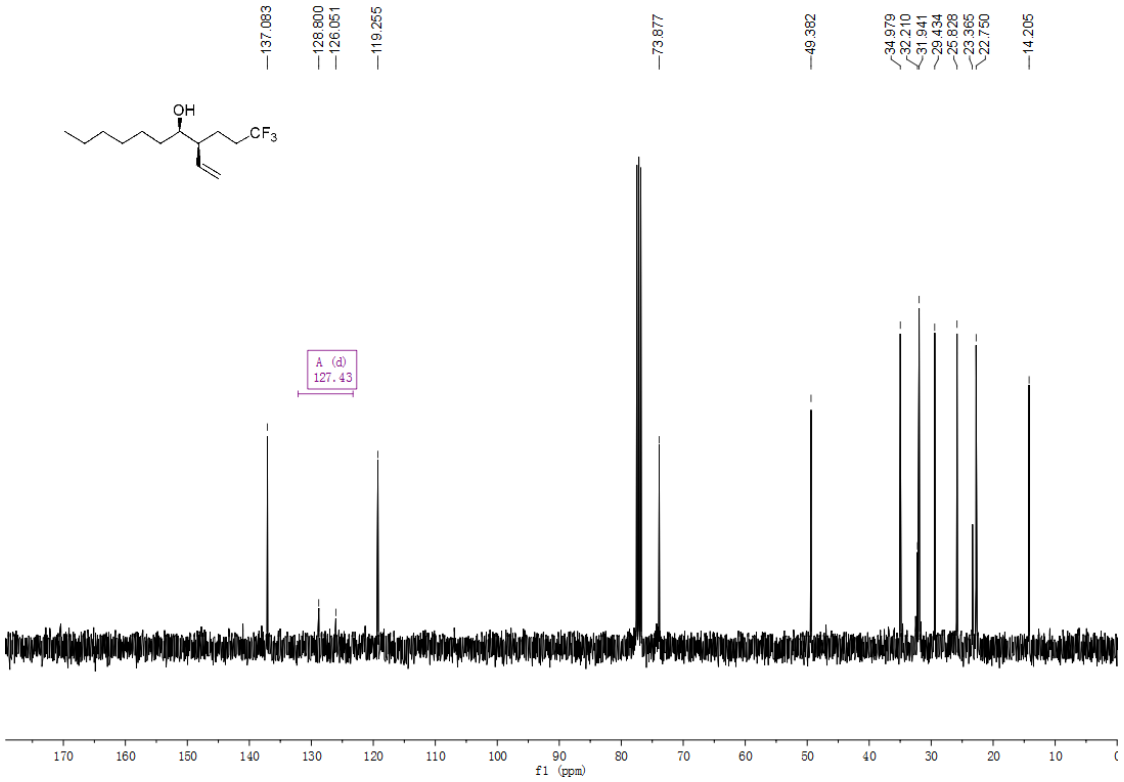


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.828	MM	0.2290	344.90863	25.10596	3.7180
2	13.944	VV	0.3044	8931.80566	417.82788	96.2820

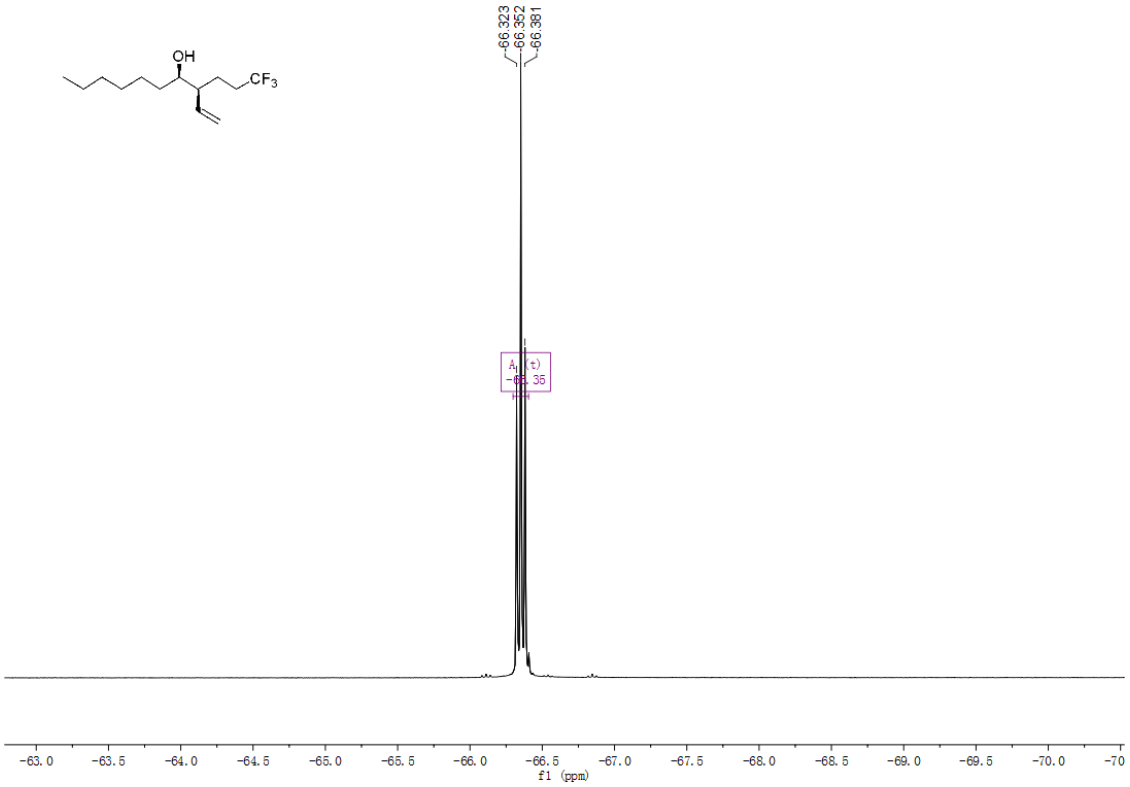
4e-^{1}H NMR



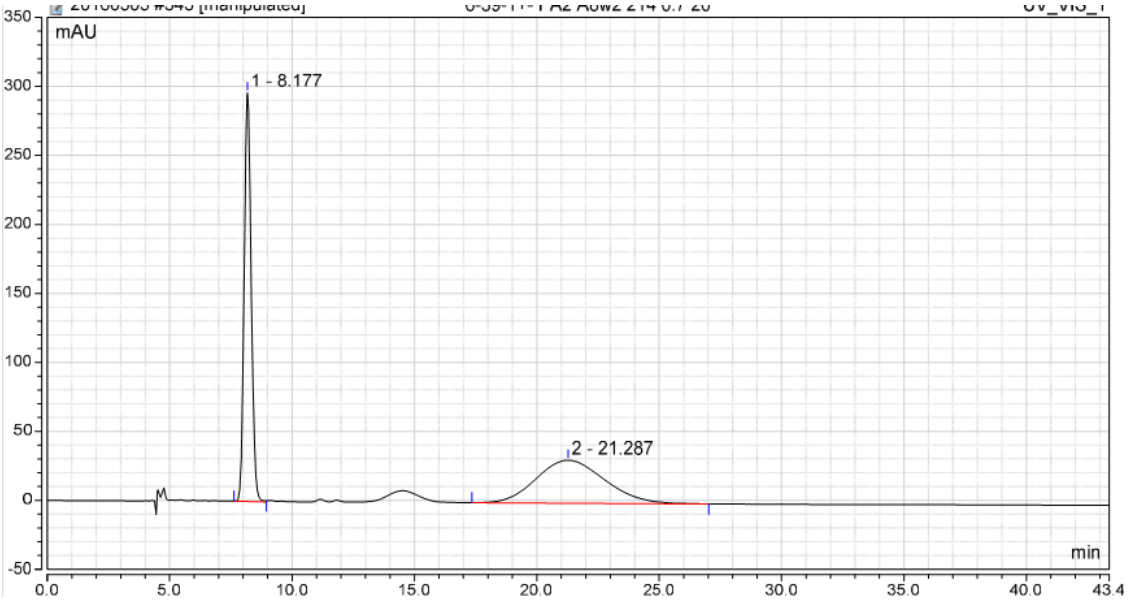
4e-^{13}C NMR



4e-^{19}F NMR

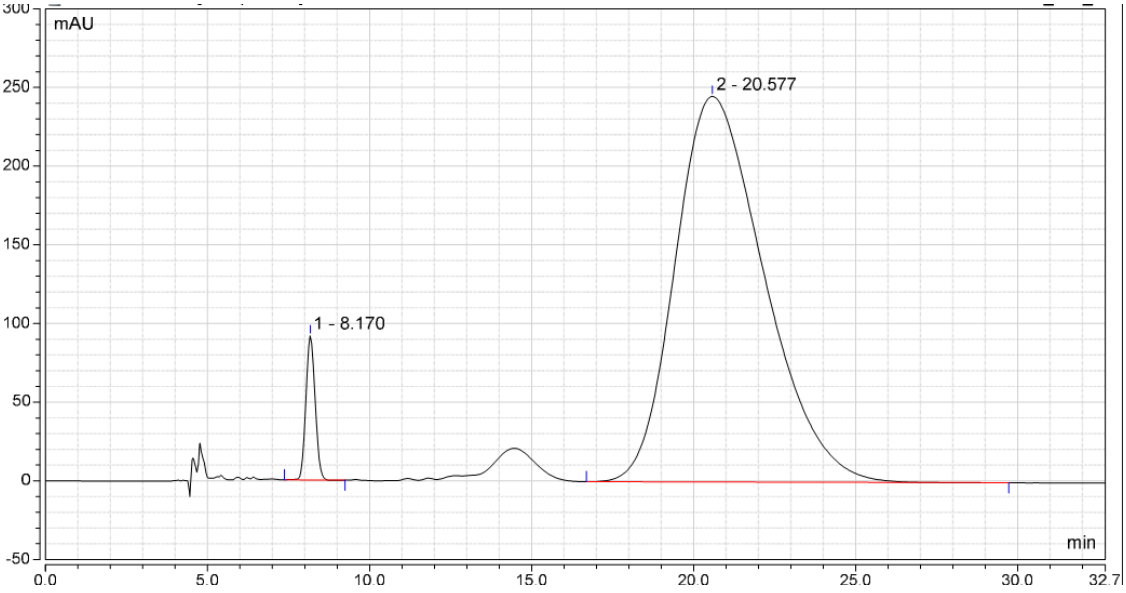


4e-HPLC (racemic)



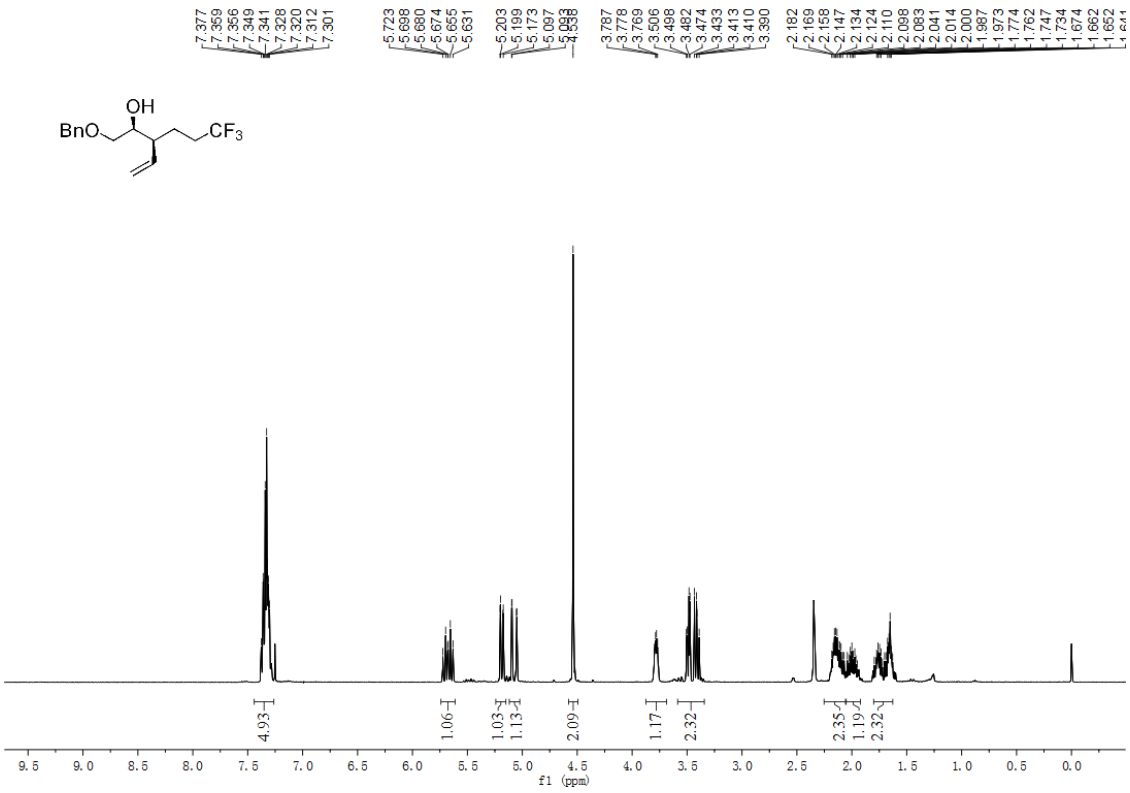
Integration Results				
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.177	98.558	296.367	49.34
2	21.287	101.180	31.139	50.66
Total:		**199.738**	**327.507**	**100.00**

4e-HPLC (92.5% ee)

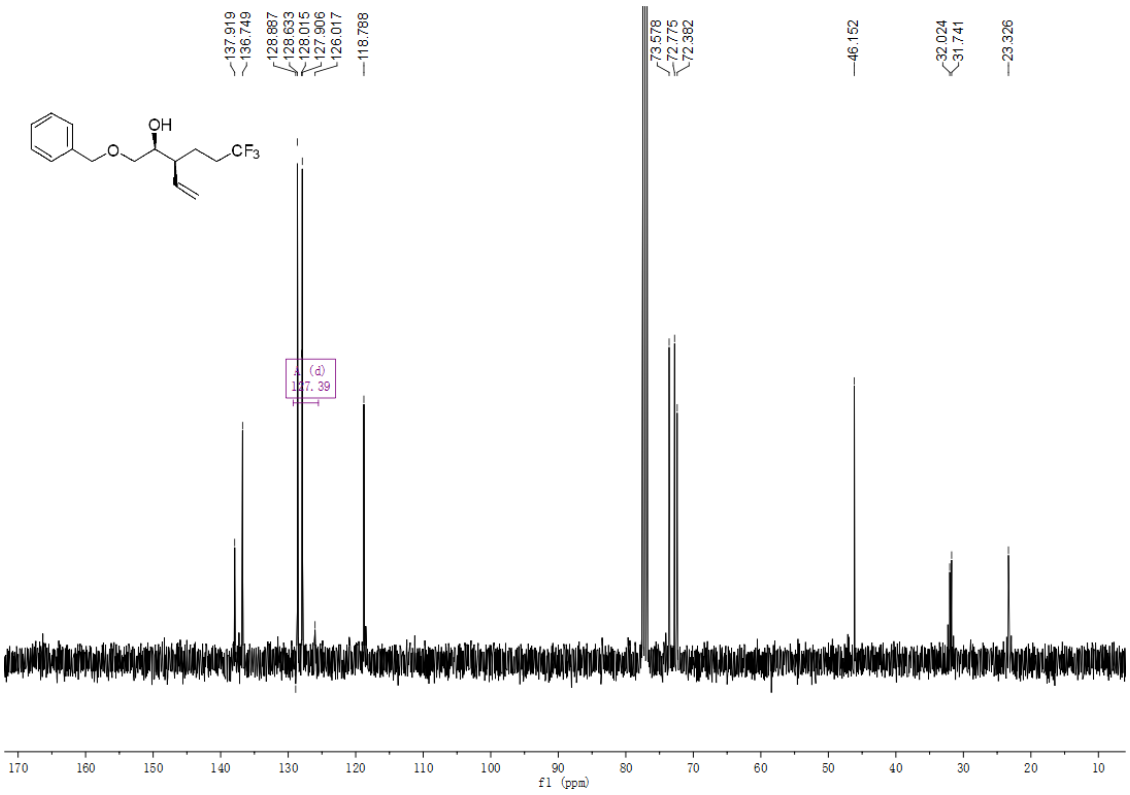


Integration Results				
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	8.170	30.163	91.717	3.72
2	20.577	780.103	245.104	96.28
Total:		**810.266**	**336.821**	**100.00**

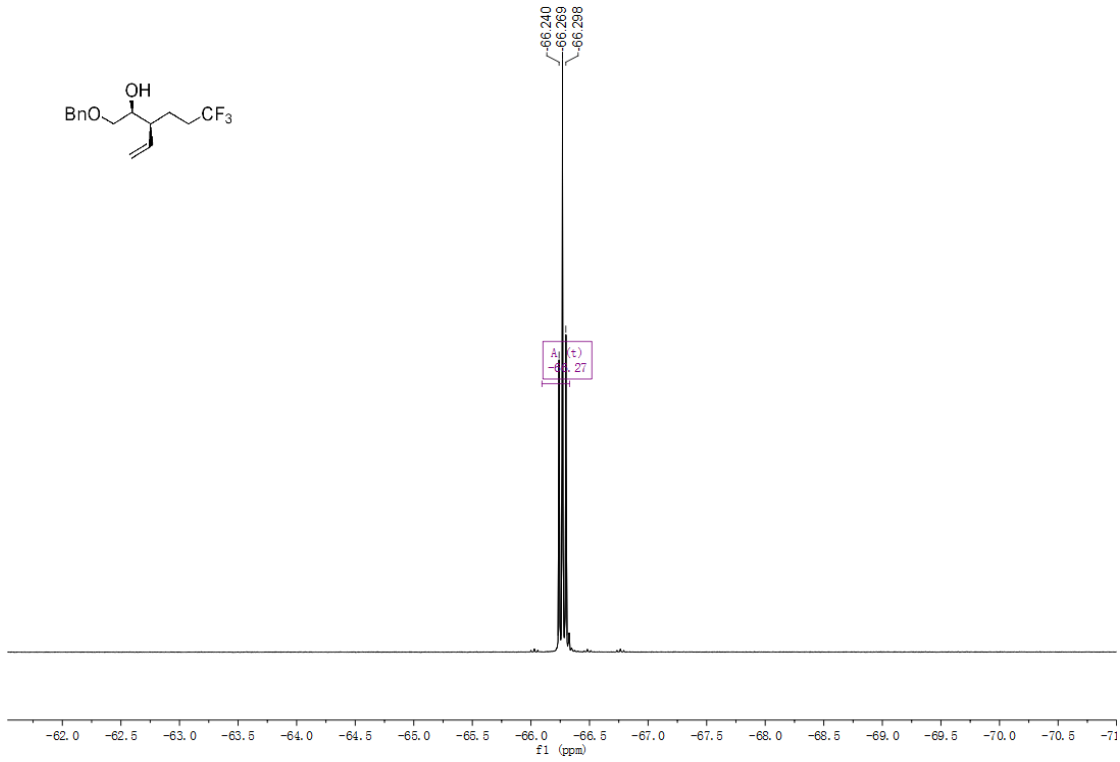
4f-^{1}H NMR



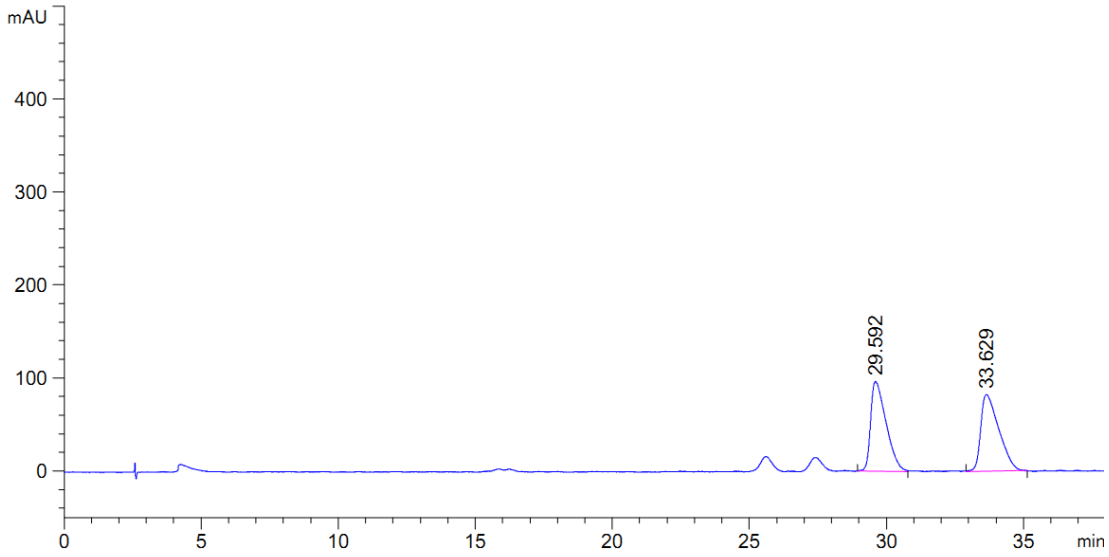
4f-^{13}C NMR



4f-^{19}F NMR

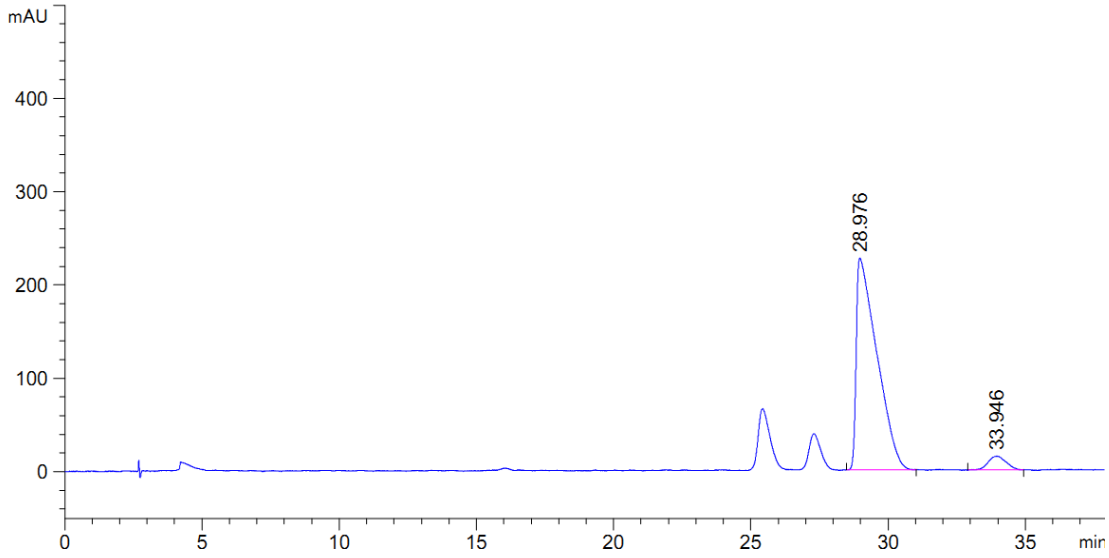


4f-HPLC (racemic)



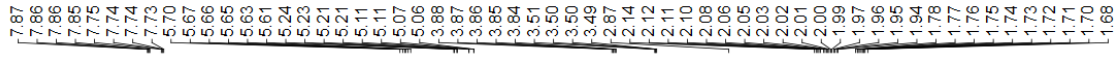
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.592	MM R	0.5729	3770.39795	96.51539	50.0871
2	33.629	MM R	0.6907	3757.28857	82.42394	49.9129

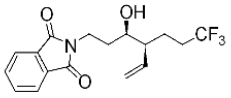
4f-HPLC (89% ee)

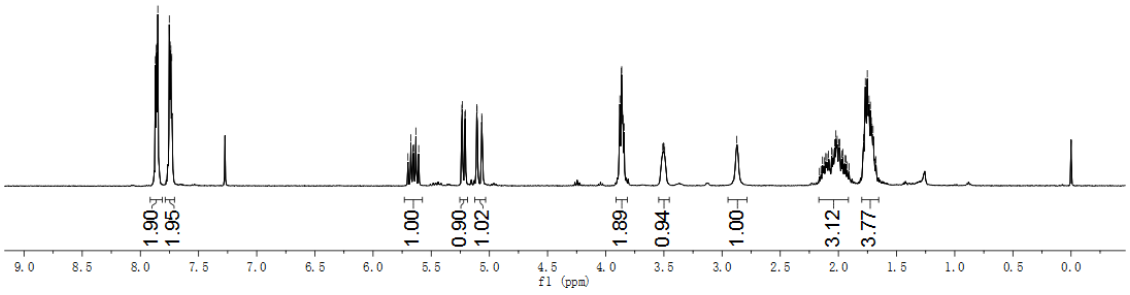


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.976	MM R	0.8466	1.18589e4	226.97078	94.5506
2	33.946	MM R	0.7204	683.48401	15.13064	5.4494

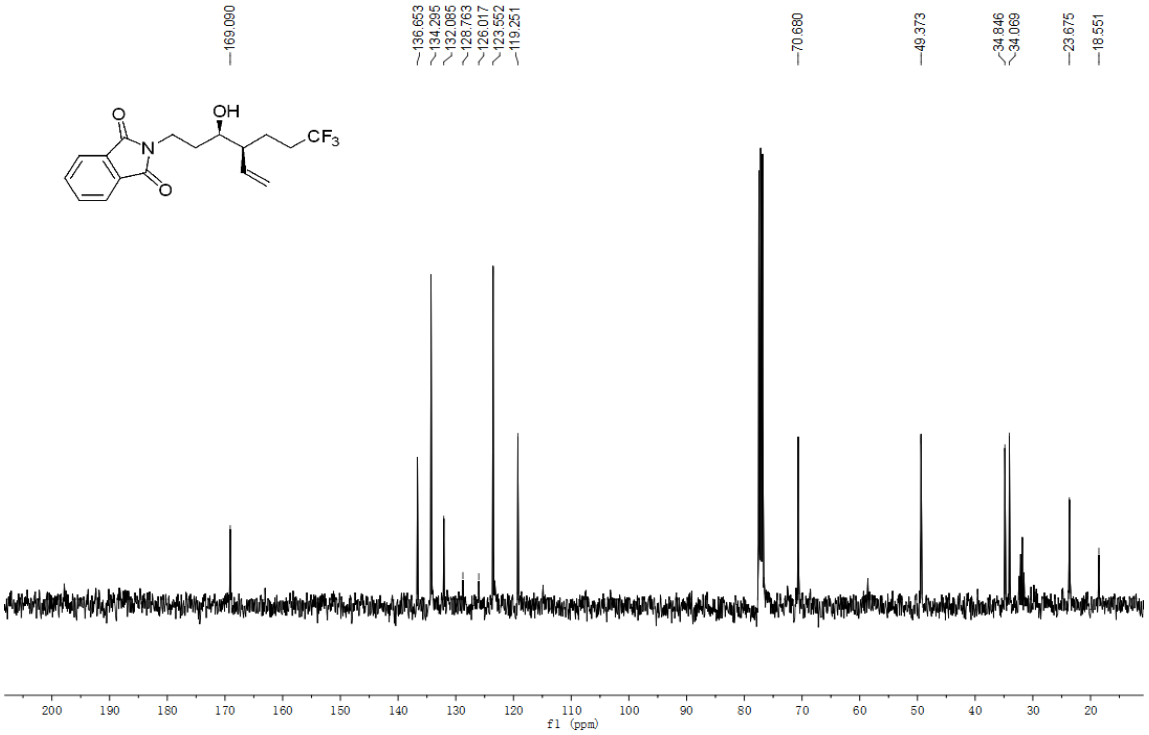
4g-^{1}H NMR



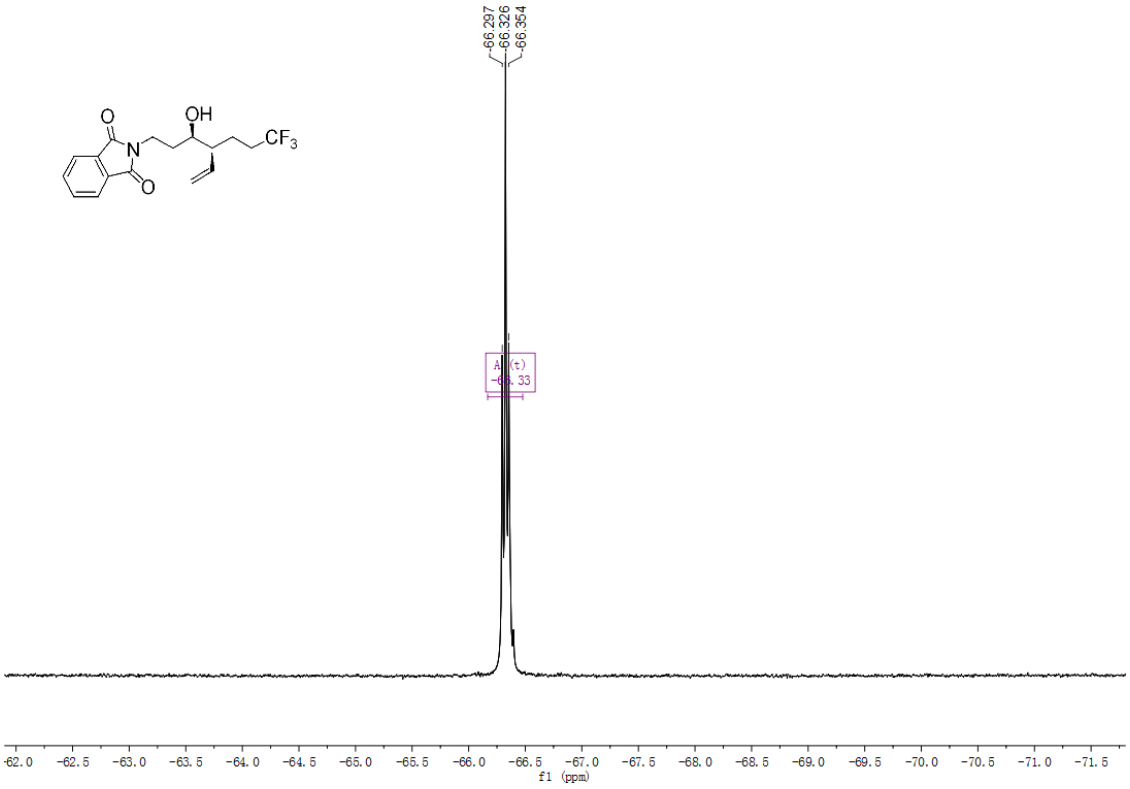




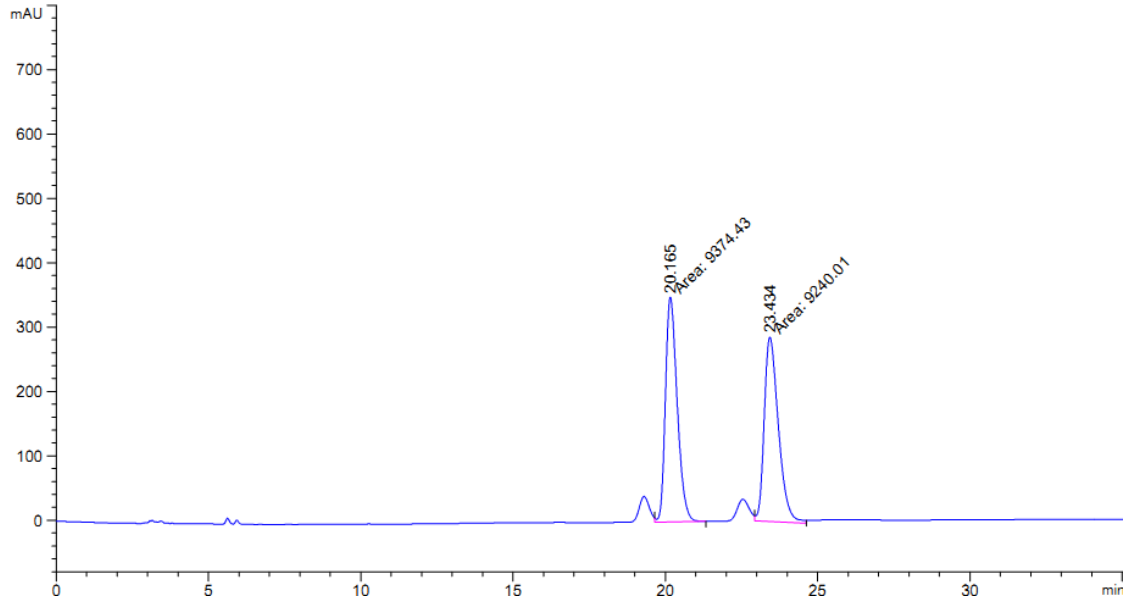
4g-^{13}C NMR



4g-^{19}F NMR

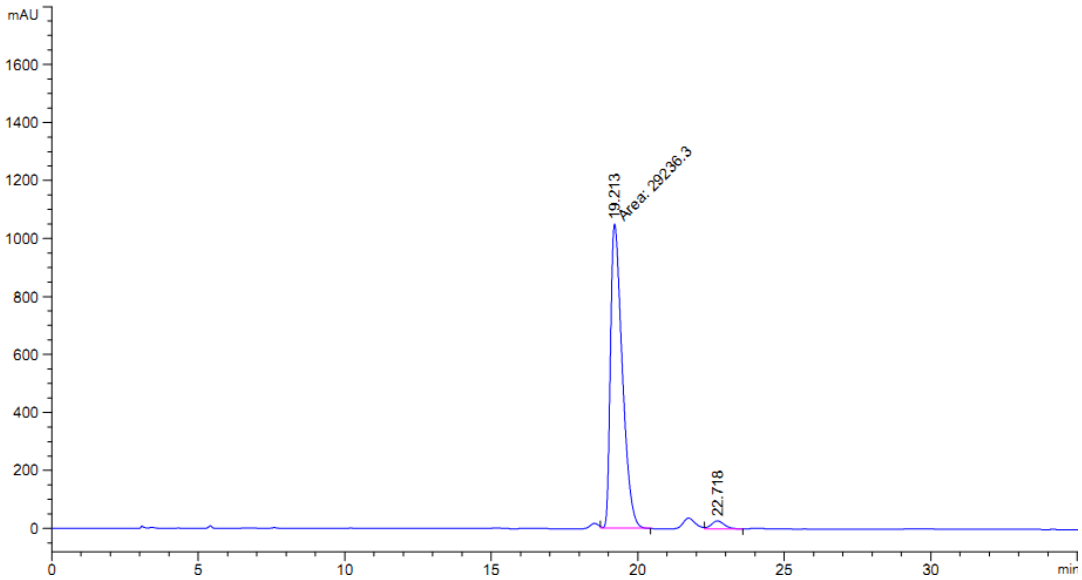


4g-HPLC (racemic)



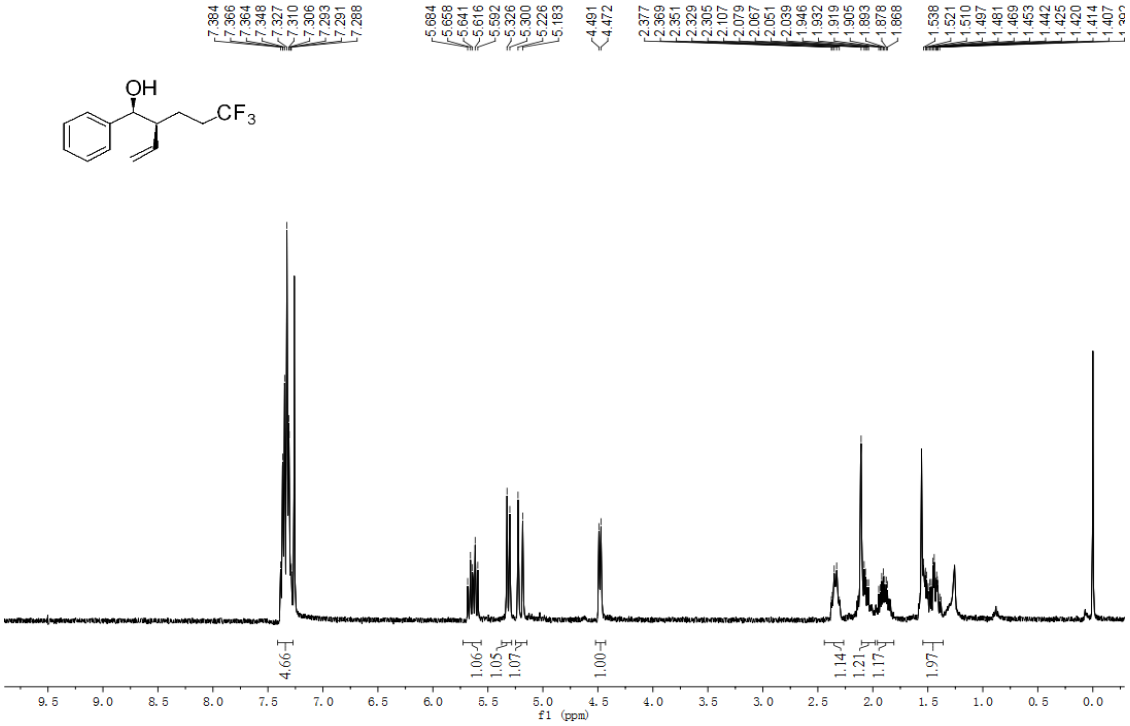
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.165	FM	0.4481	9374.42773	348.69205	50.3611
2	23.434	MM	0.5381	9240.00879	286.20432	49.6389

4g-HPLC (94% ee)

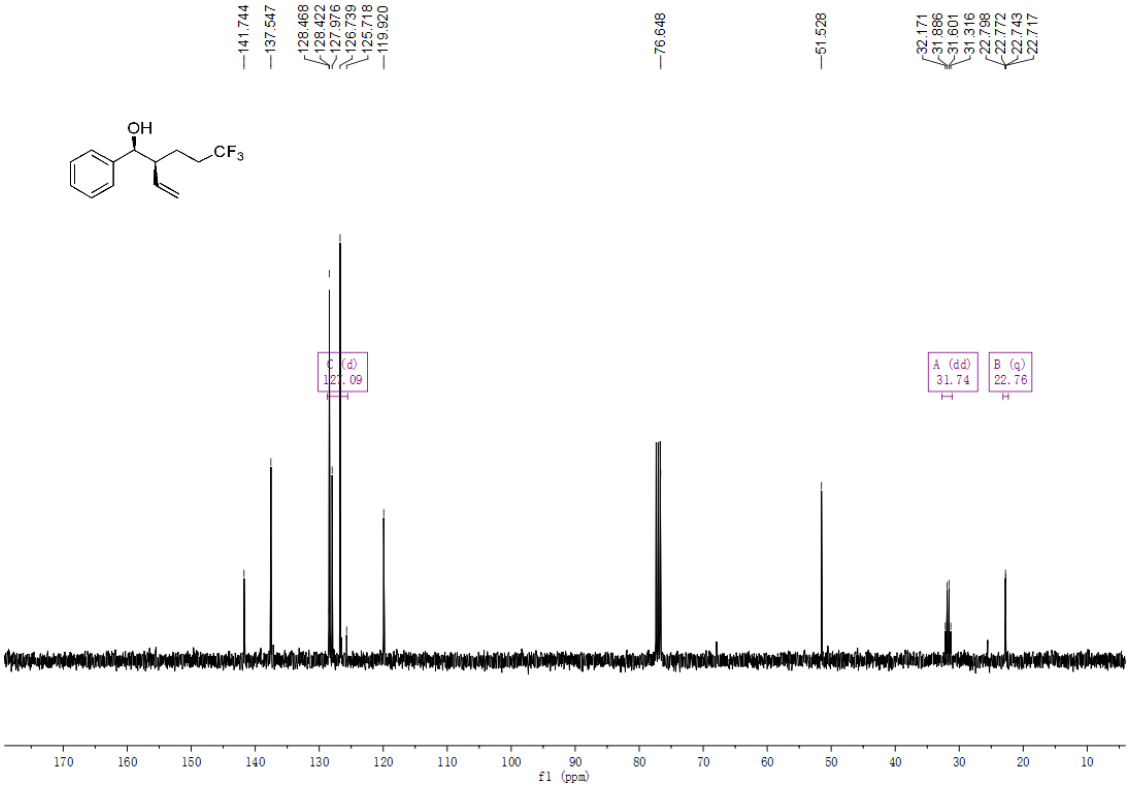


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.213	MM	0.4653	2.92363e4	1047.29602	97.1756
2	22.718	VB	0.4695	849.76550	27.65277	2.8244

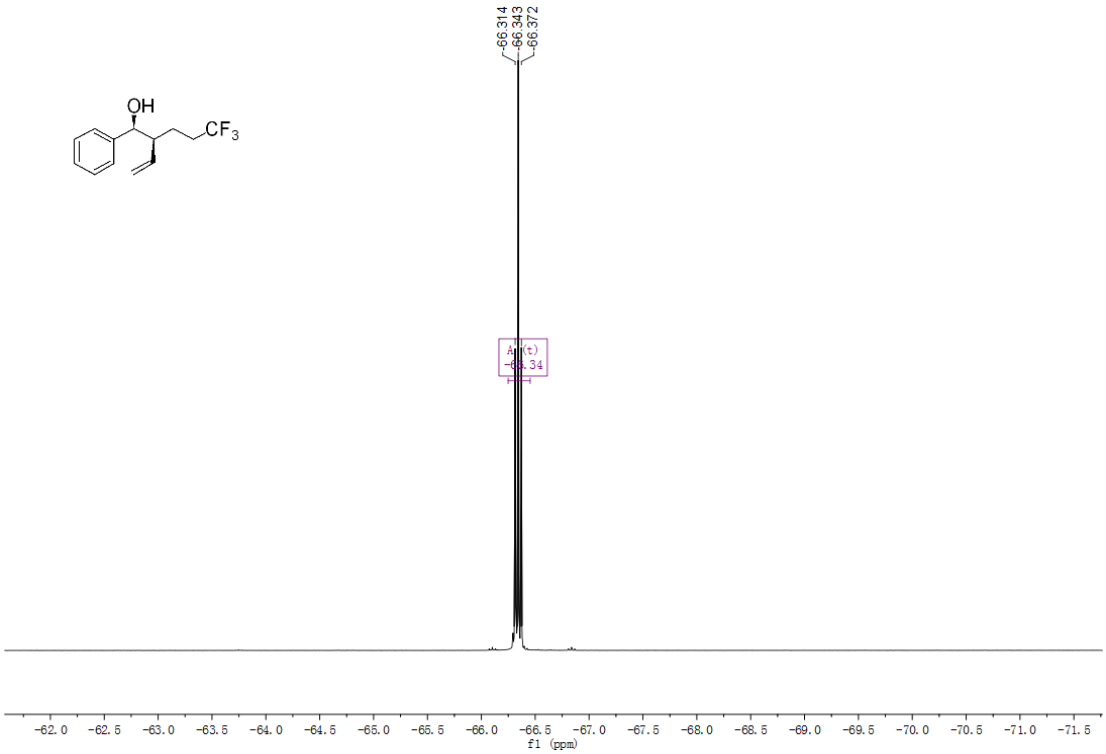
4h-^{1}H NMR



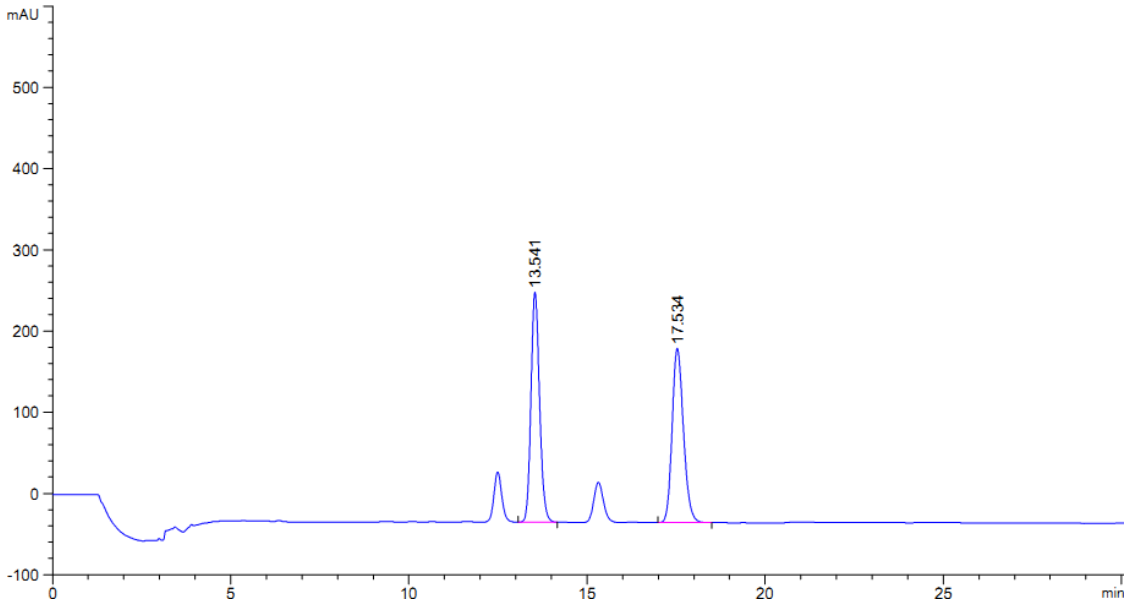
4h-^{13}C NMR



4h-^{19}F NMR

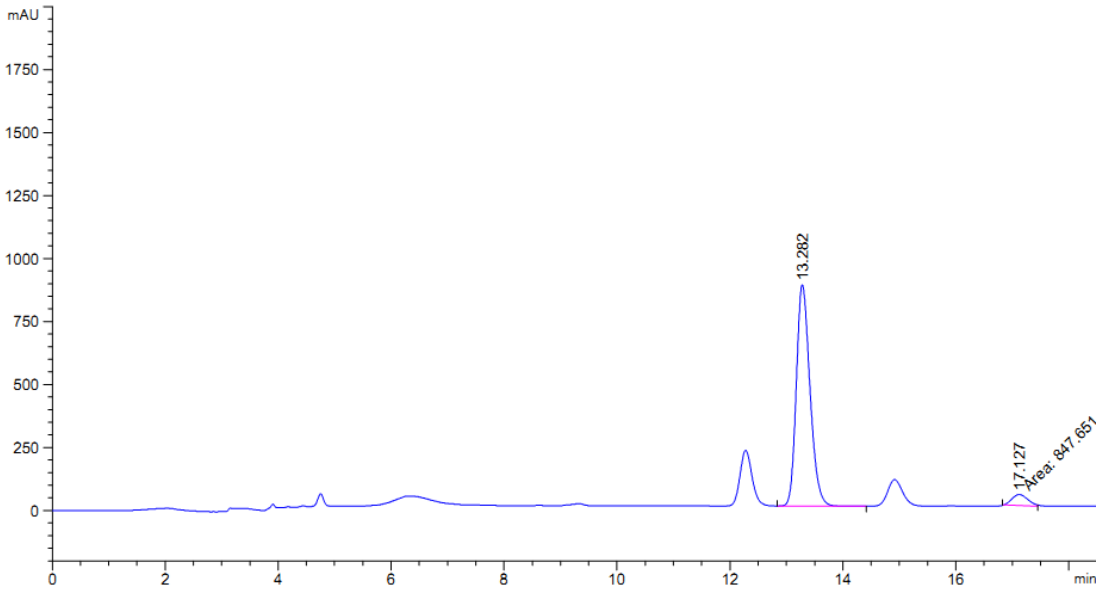


4h-HPLC (racemic)



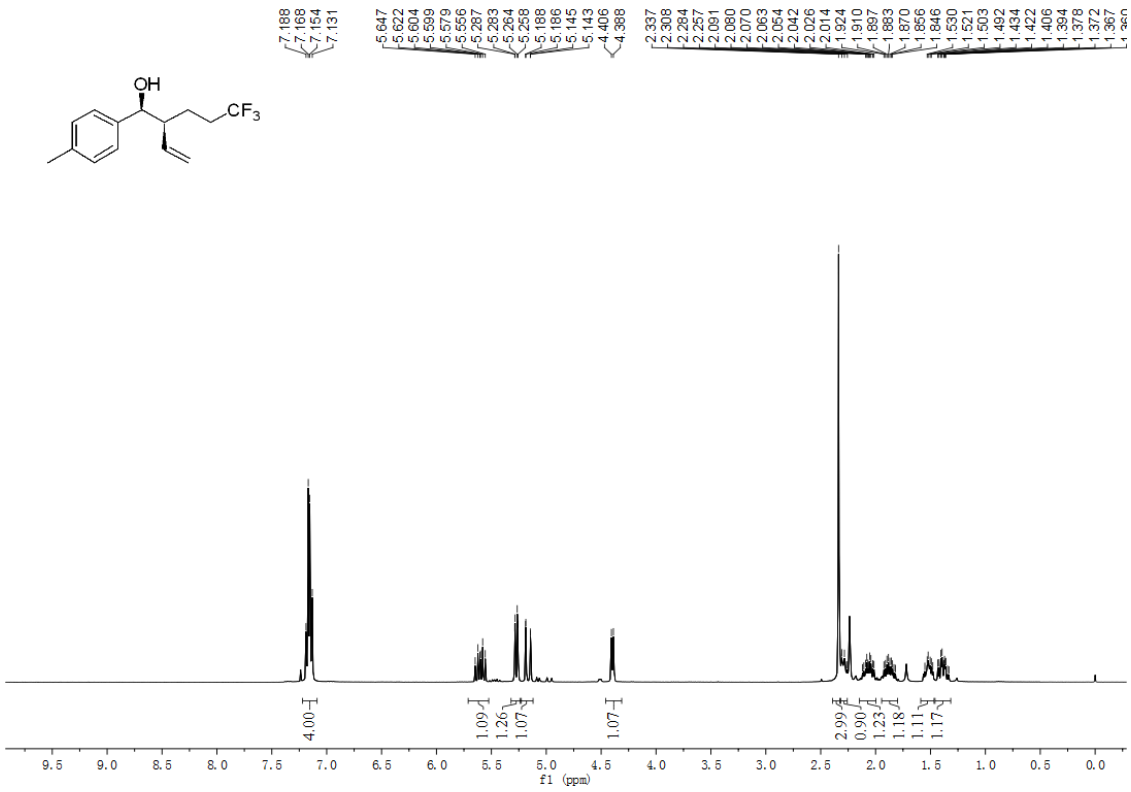
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.541	BB	0.2578	4726.03027	283.00250	49.9603
2	17.534	BB	0.3395	4733.53760	214.49738	50.0397

4h-HPLC (89% ee)

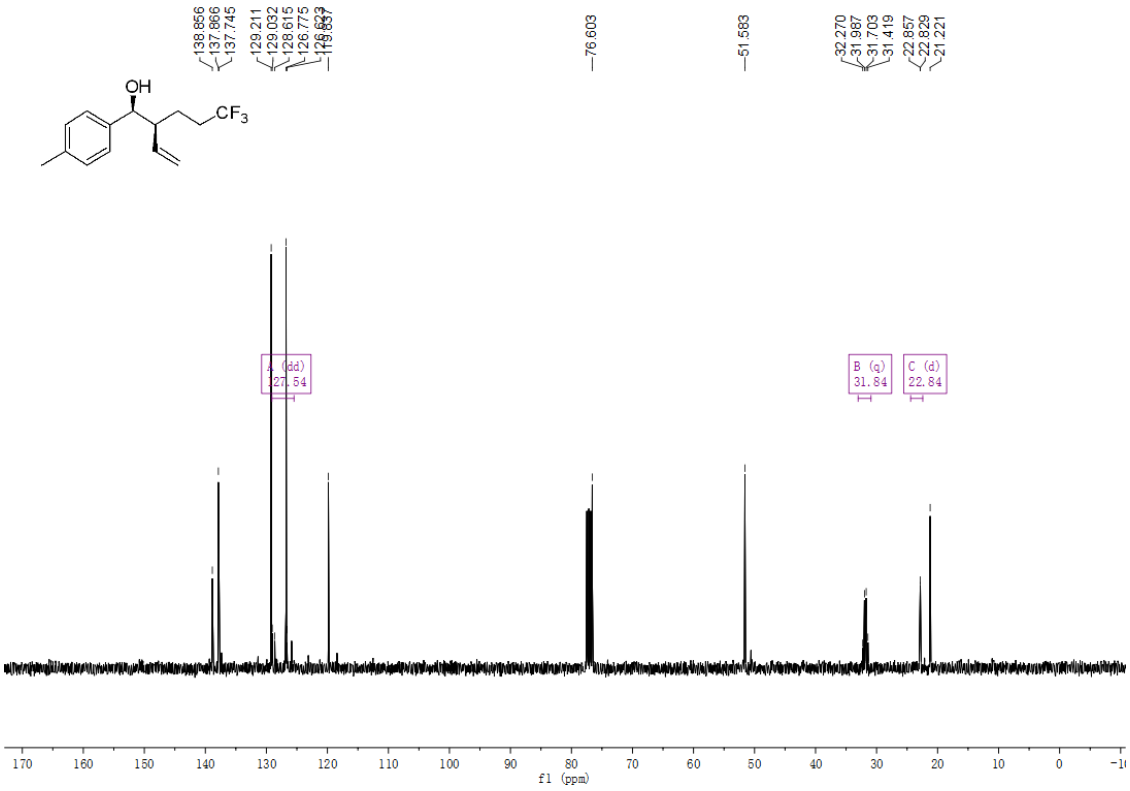


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.282	VB	0.2597	1.48208e4	878.85553	94.5901
2	17.127	MM	0.3242	847.65070	43.57822	5.4099

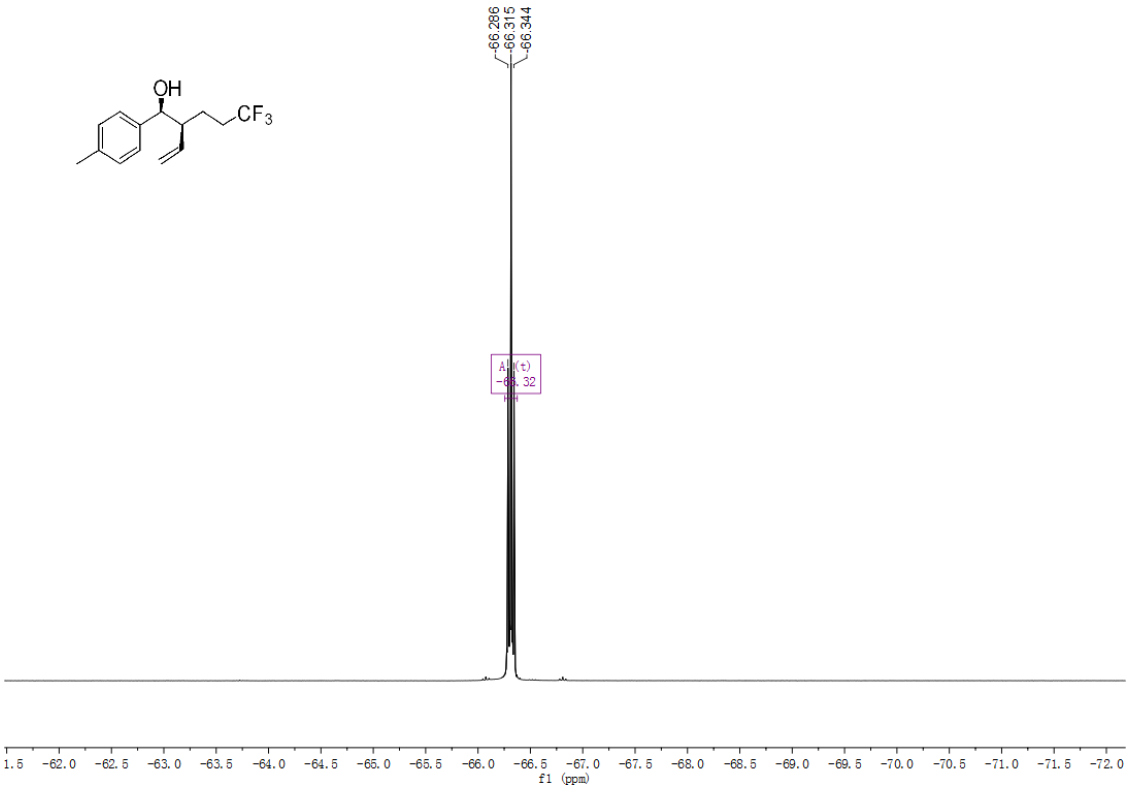
4i-^{1}H NMR



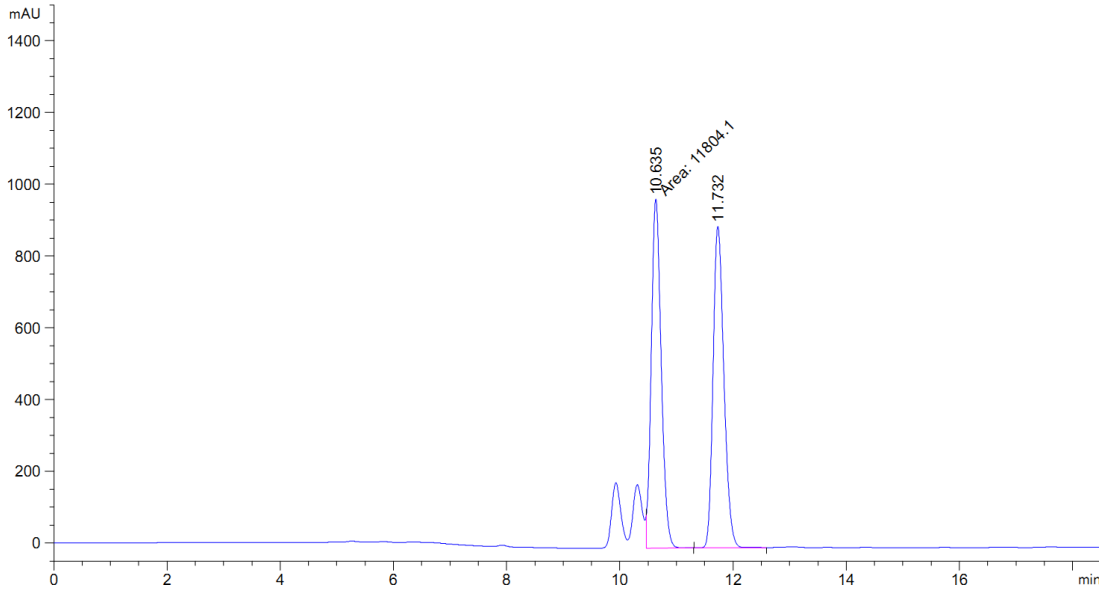
4i-^{13}C NMR



4i-^{19}F NMR

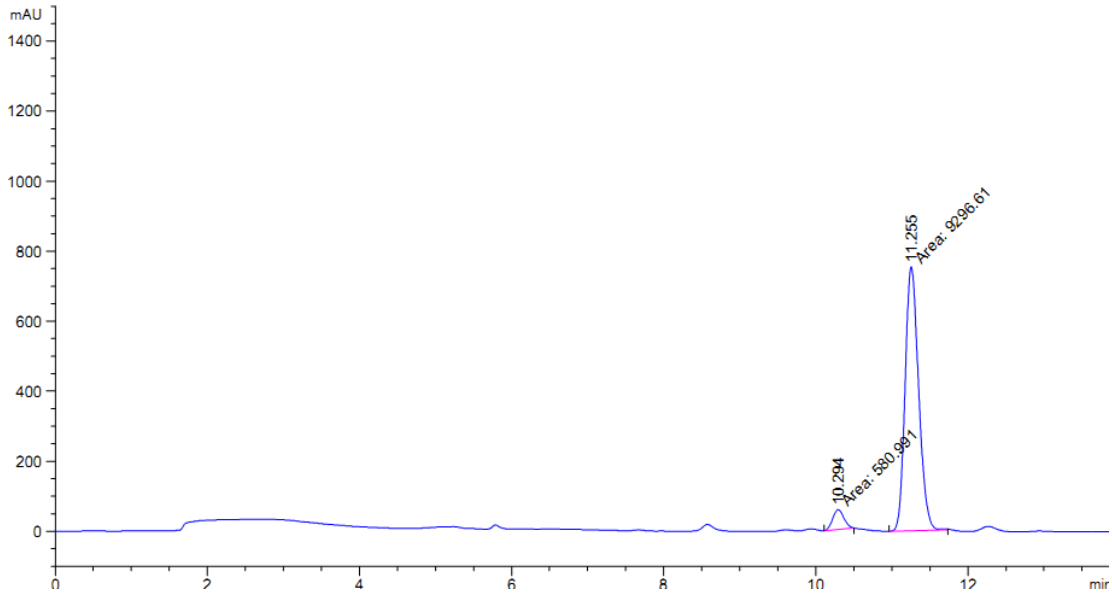


4i-HPLC (racemic)



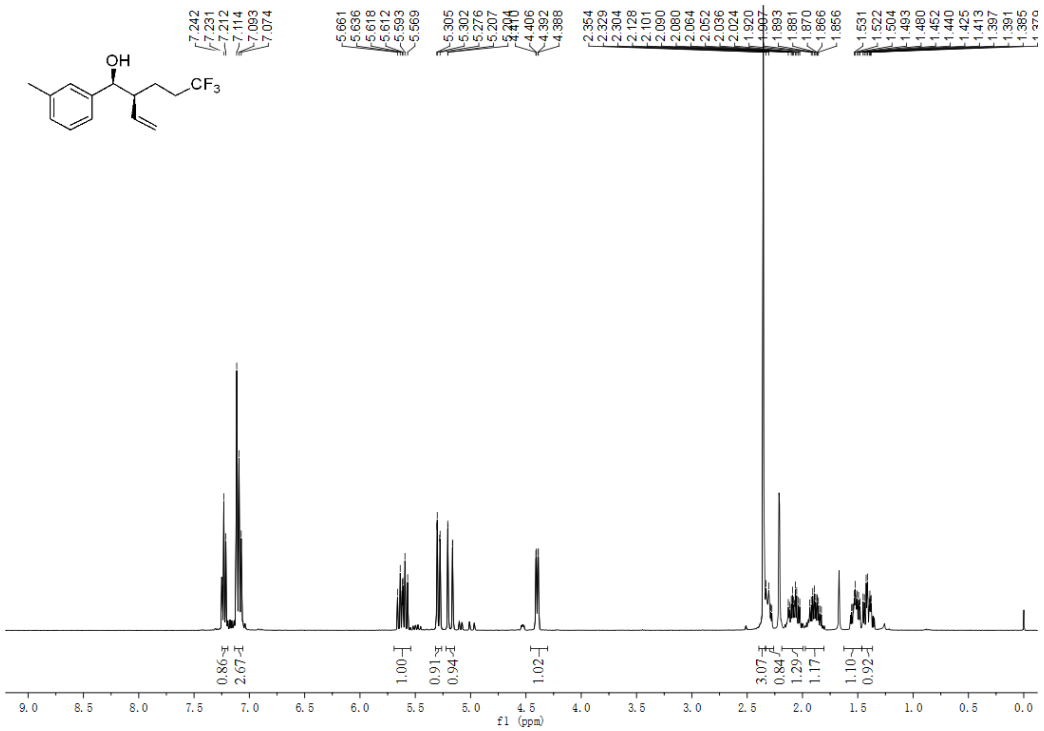
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.635	FM	0.2022	1.18041e4	973.00195	49.6980
2	11.732	BV R	0.2062	1.19475e4	896.30811	50.3020

4i-HPLC (88% ee)

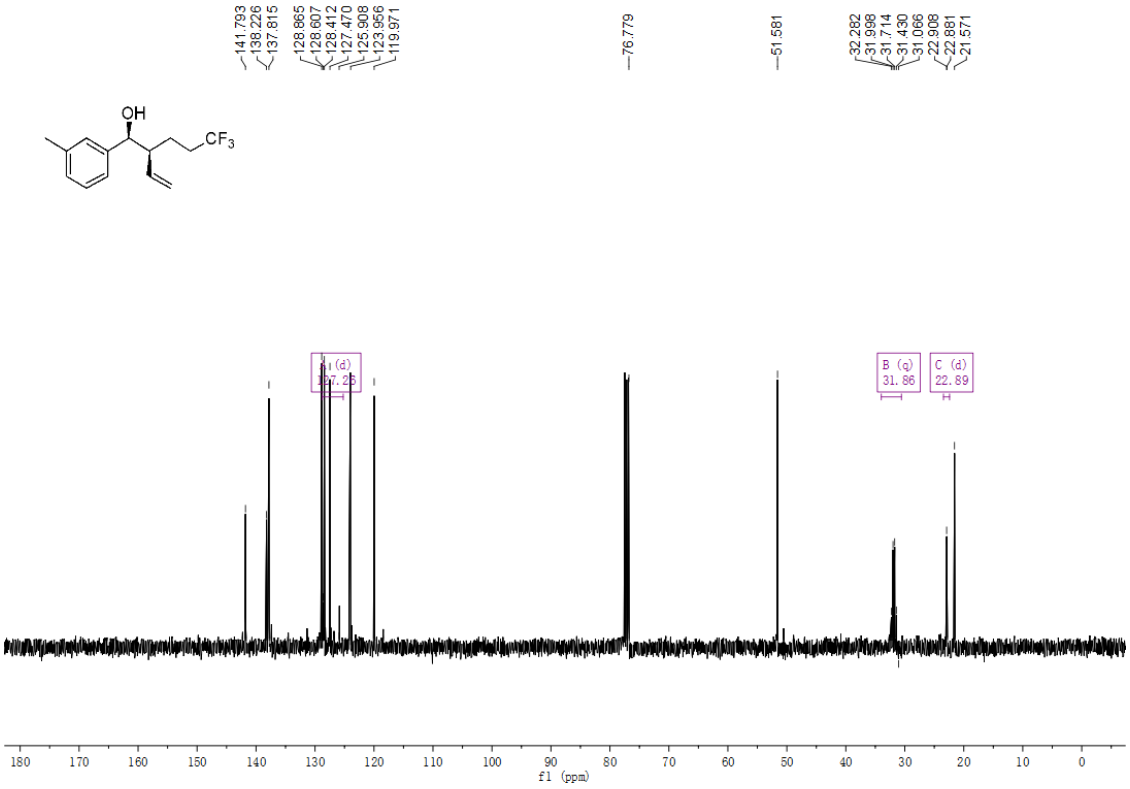


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.294	MM	0.1713	580.99146	56.52156	5.8819
2	11.255	MM	0.2054	9296.61035	754.24615	94.1181

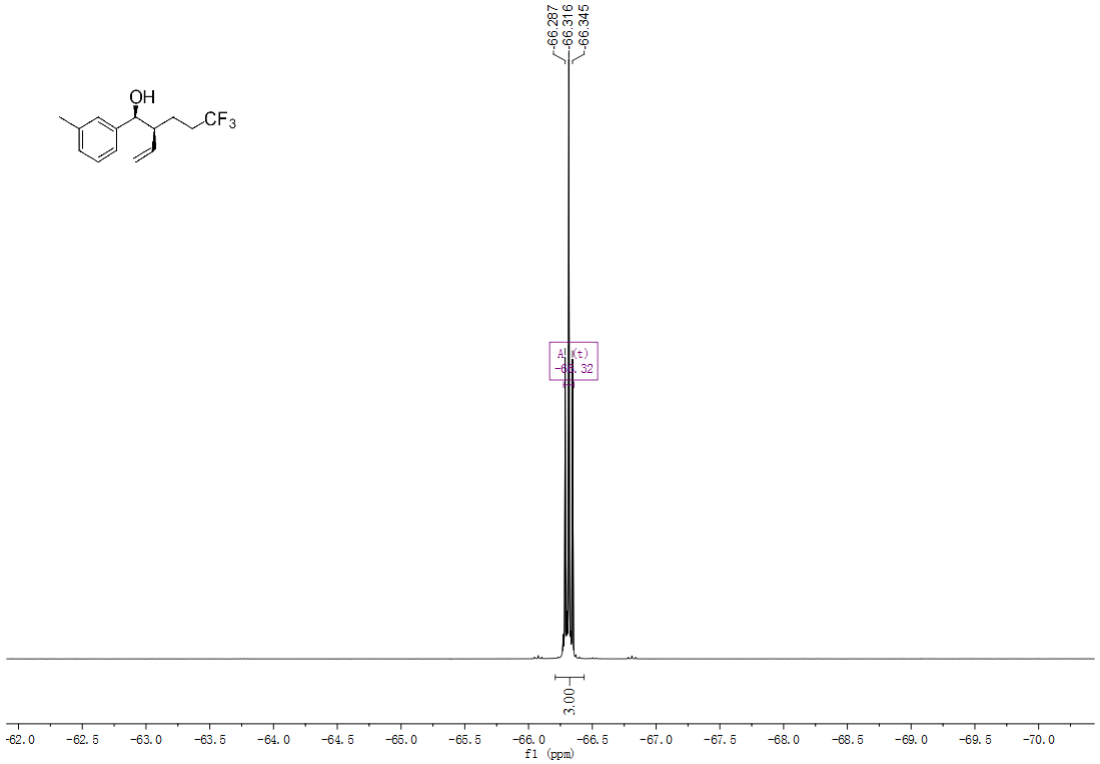
4j-^{1}H NMR



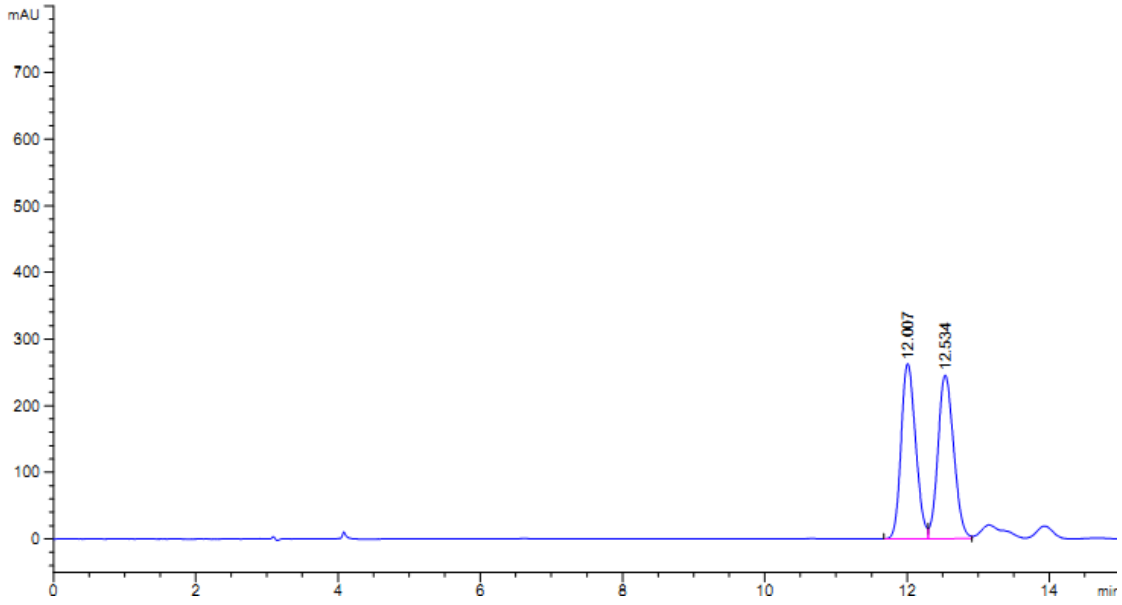
4j-^{13}C NMR



4j-^{19}F NMR

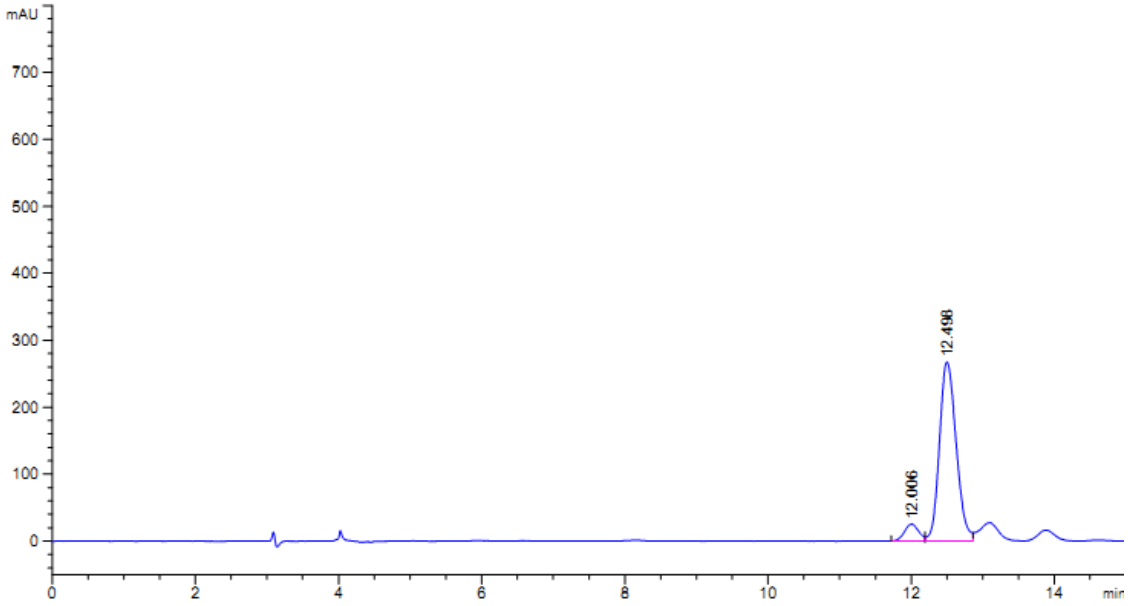


4j-HPLC (racemic)



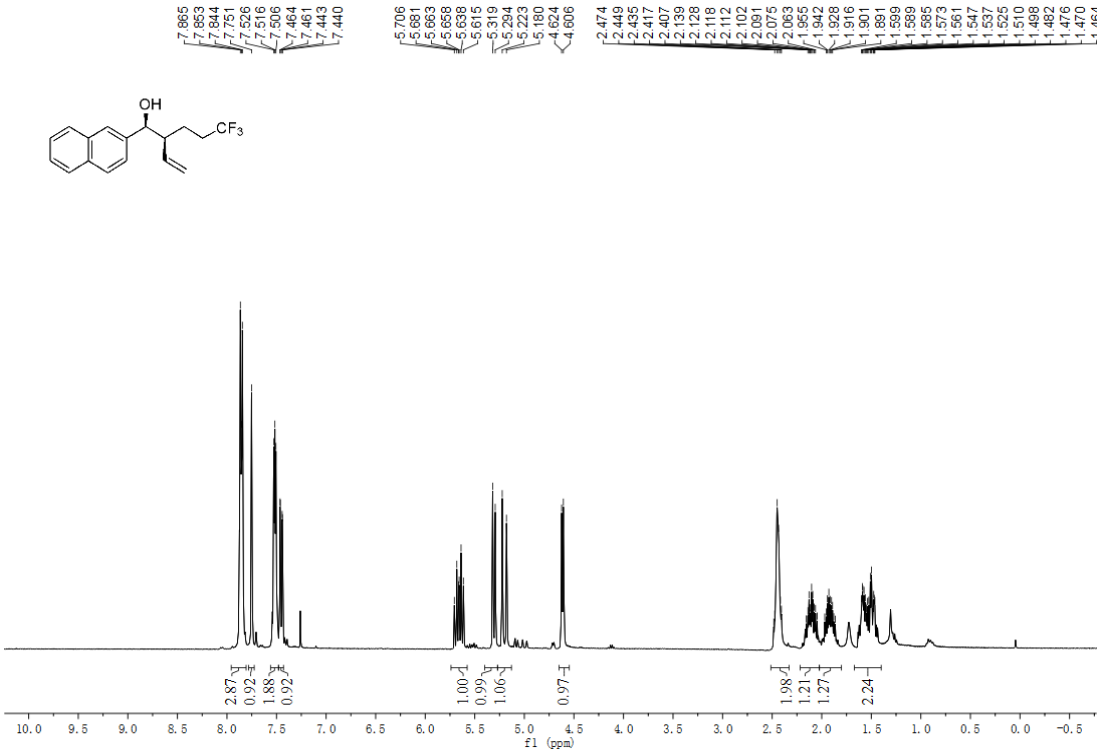
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.007	BV	0.2145	3729.14038	262.80182	49.6949
2	12.534	VV	0.2367	3774.92603	245.03404	50.3051

4j-HPLC (85% ee)

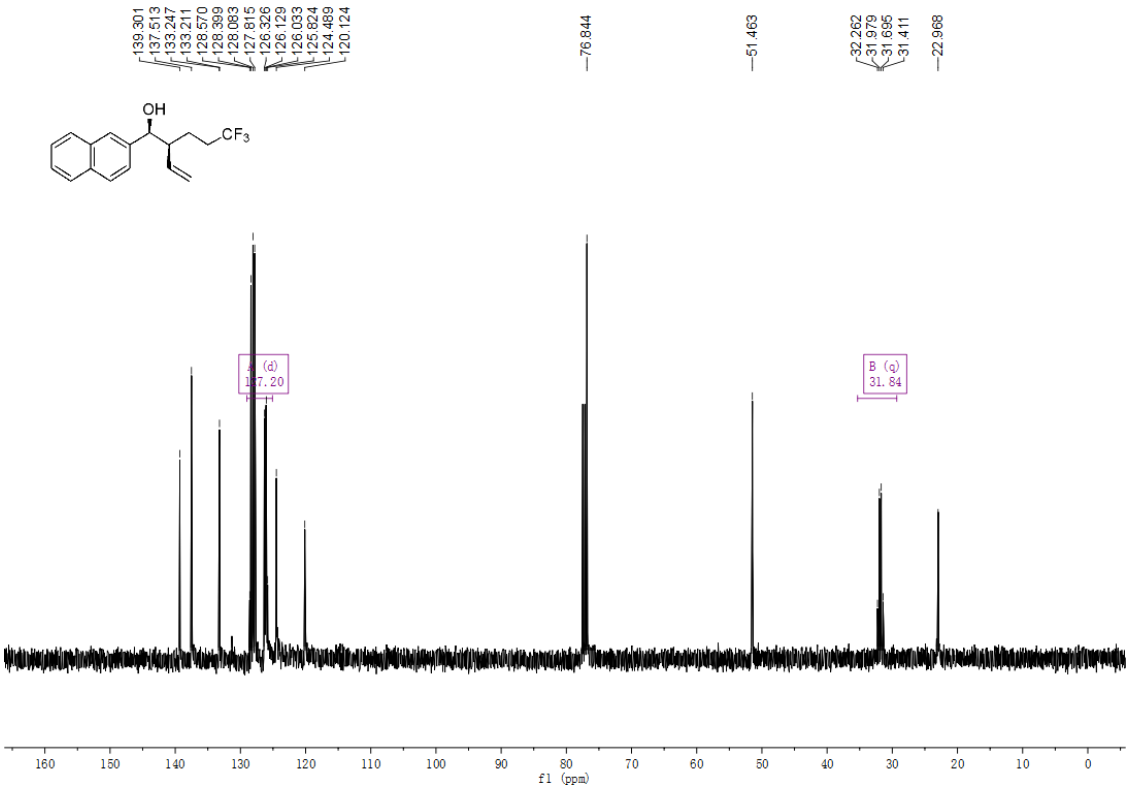


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.006	BV	0.1672	348.62225	25.23074	7.4541
2	12.498	VV	0.2539	4328.31396	267.26263	92.5459

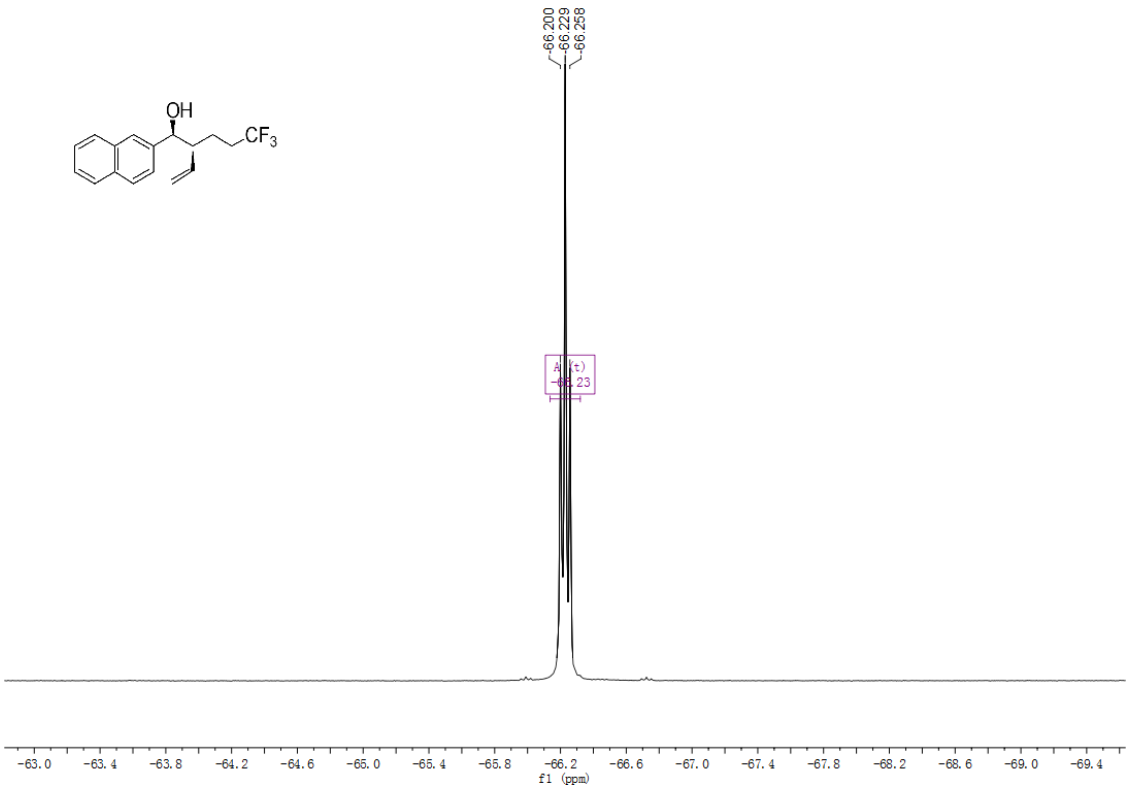
4k-^{1}H NMR



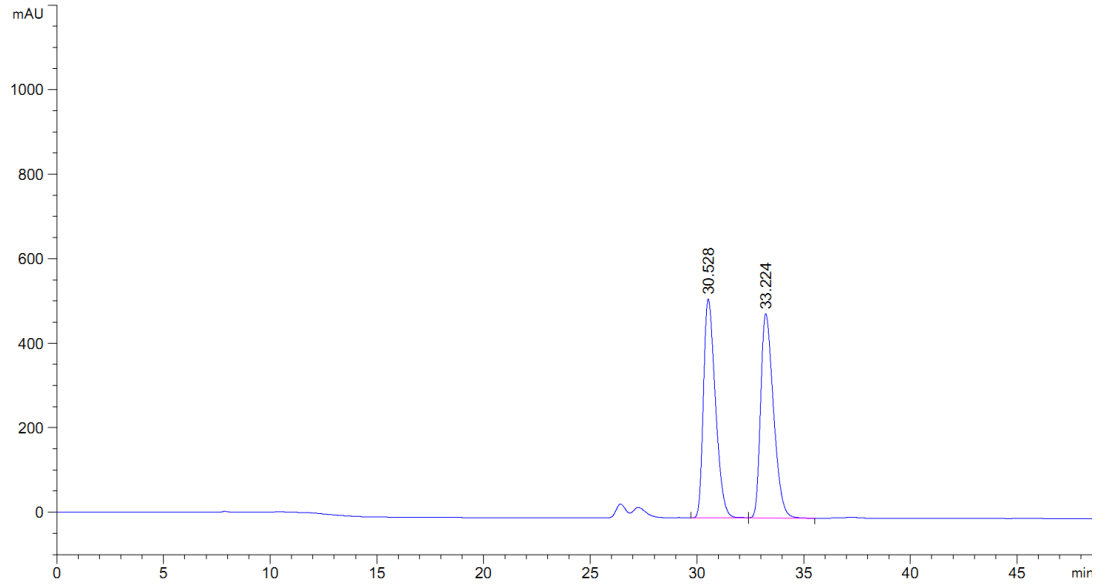
4k-^{13}C NMR



4k-^{19}F NMR

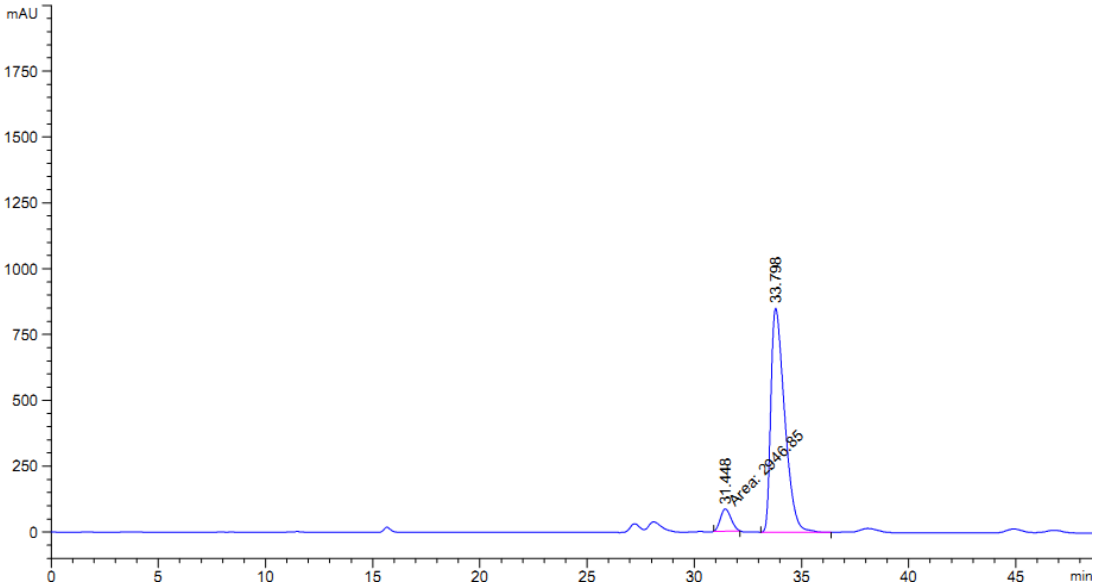


4k-HPLC (racemic)



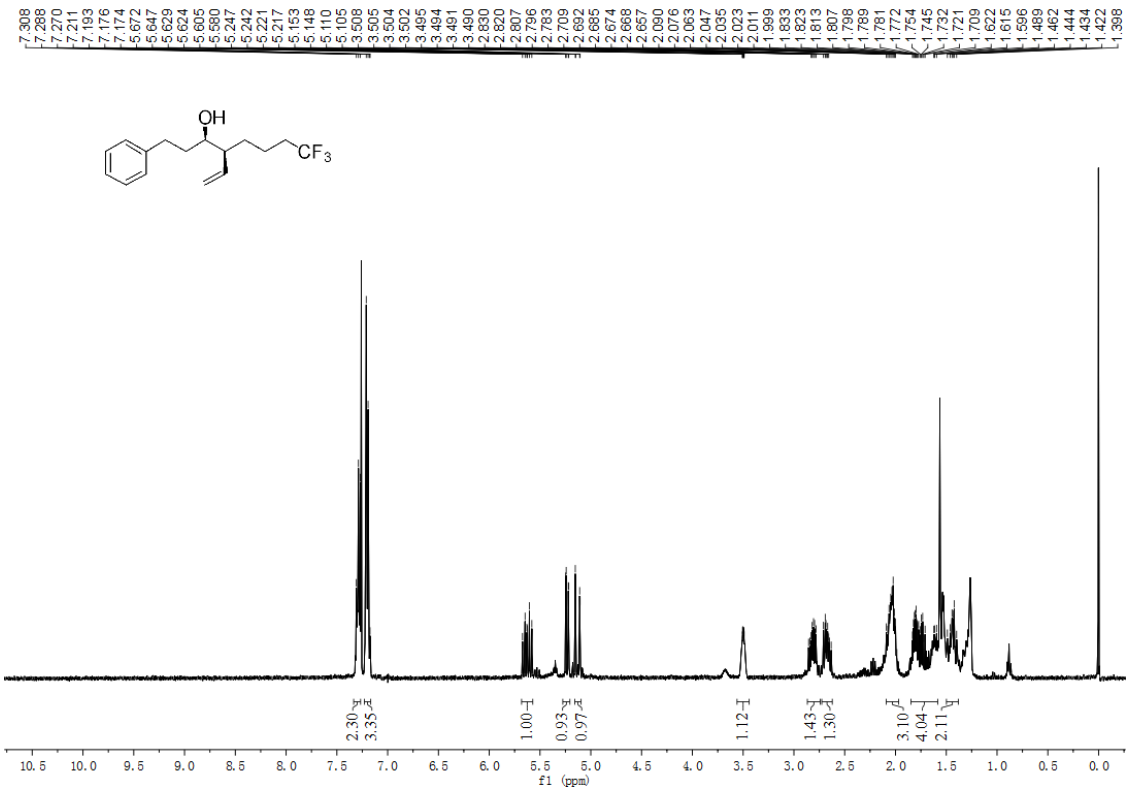
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.528	BB	0.6024	2.01300e4	517.94702	49.8485
2	33.224	BB	0.6498	2.02523e4	483.39133	50.1515

4k-HPLC (85% ee)

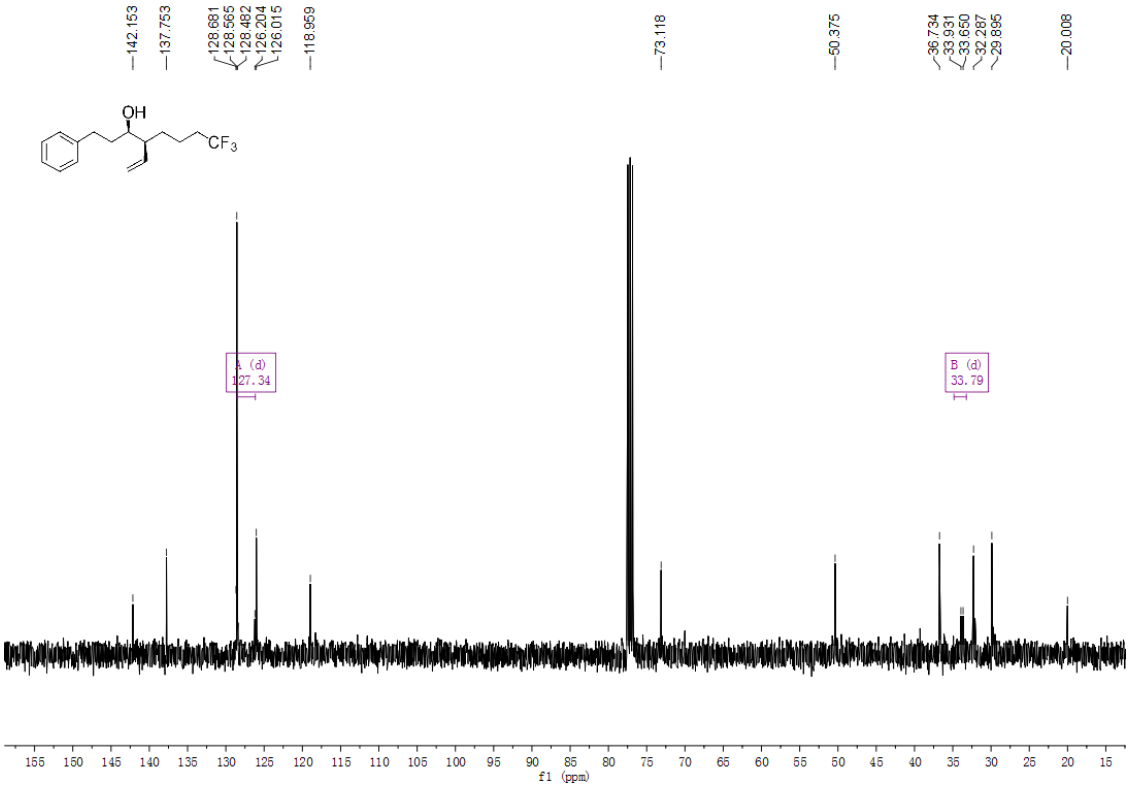


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.448	MM	0.5775	2946.84741	85.04205	7.1604
2	33.798	VB	0.6828	3.82081e4	851.04938	92.8396

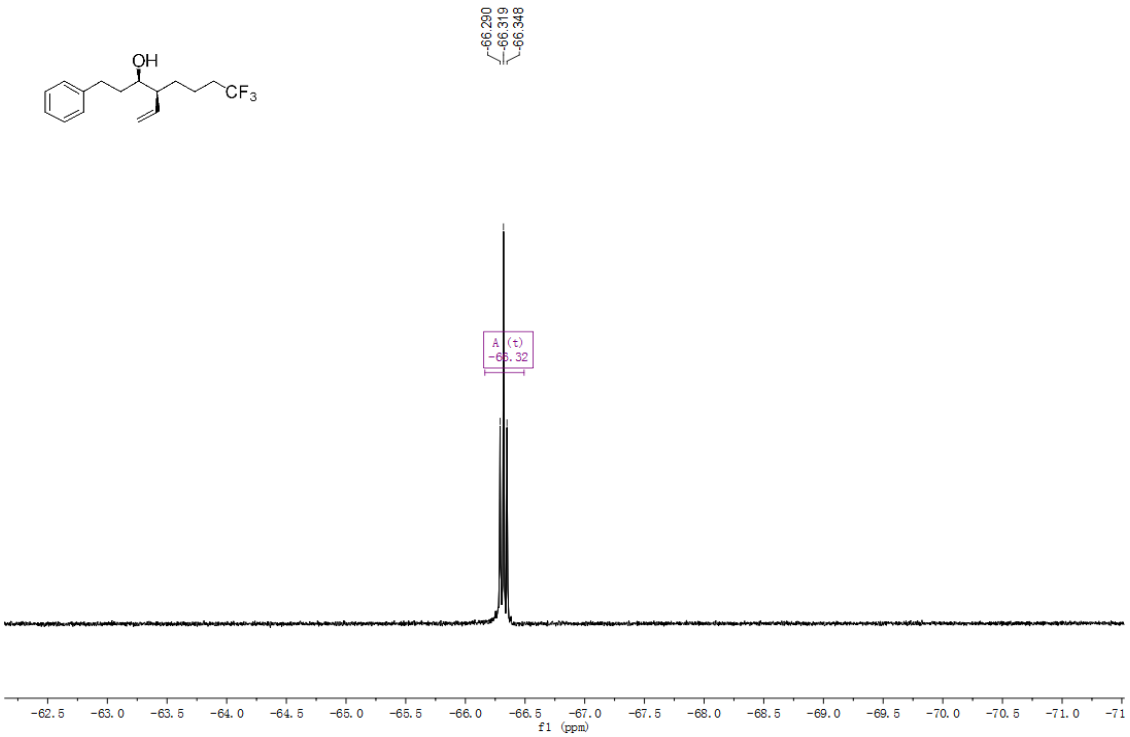
4l-^{1}H NMR



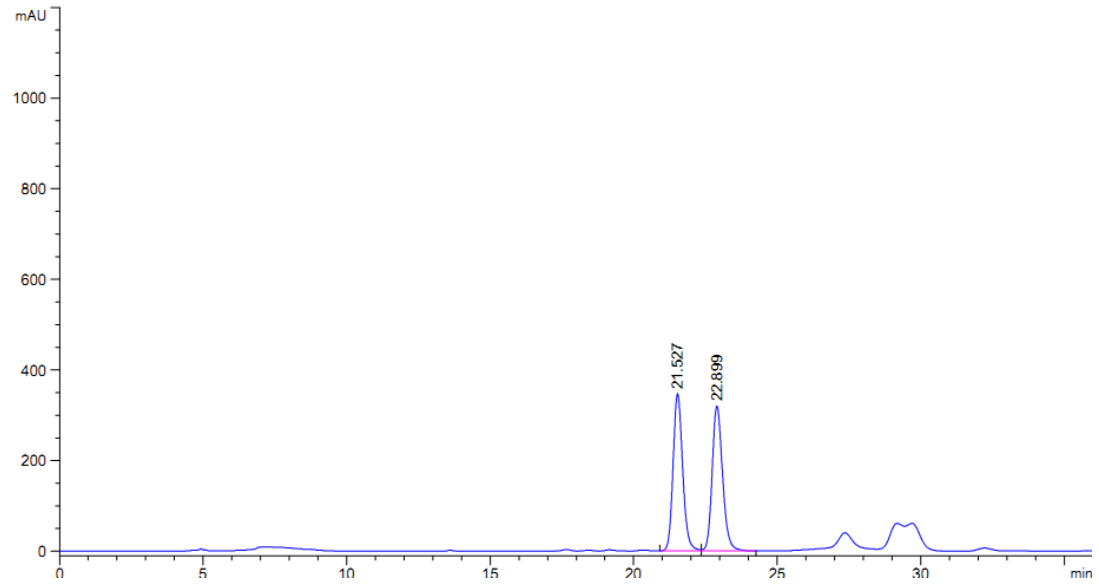
4l-^{13}C NMR



4l-^{19}F NMR

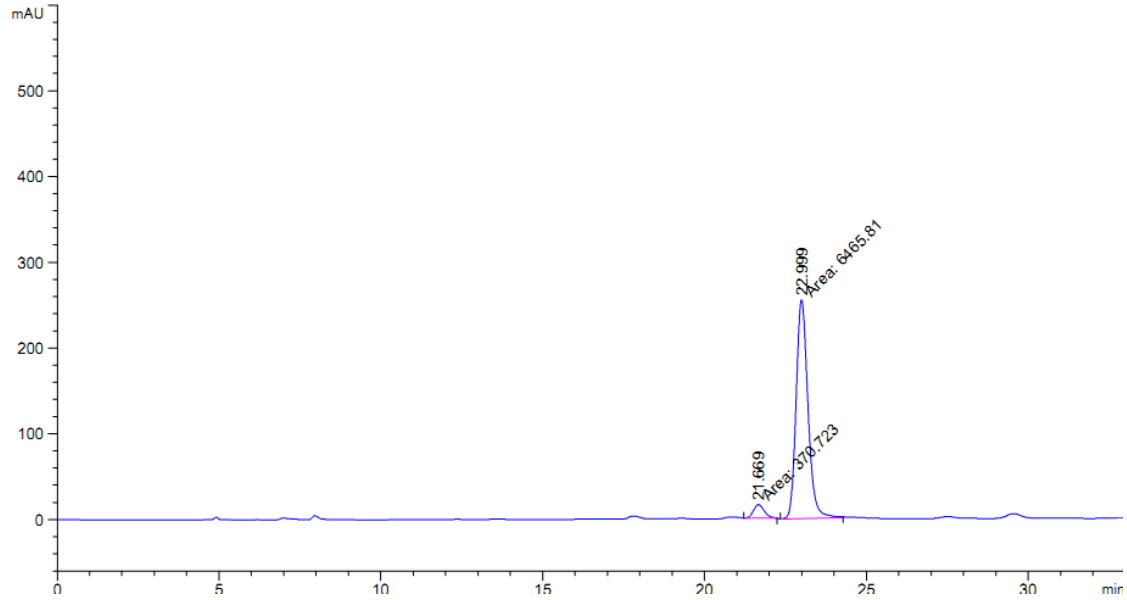


4l-HPLC (racemic)



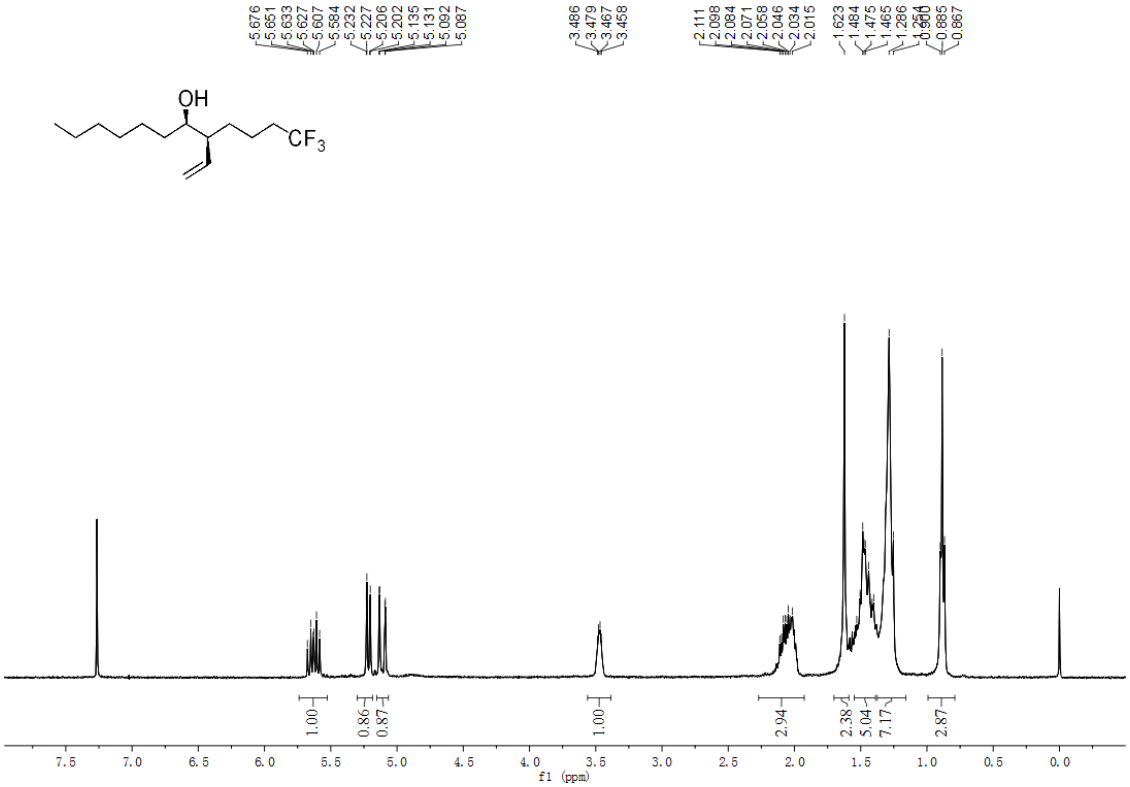
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.527	BV	0.3573	8055.09424	346.33676	49.9620
2	22.899	VB	0.3877	8067.34375	319.41202	50.0380

4l-HPLC (89% ee)

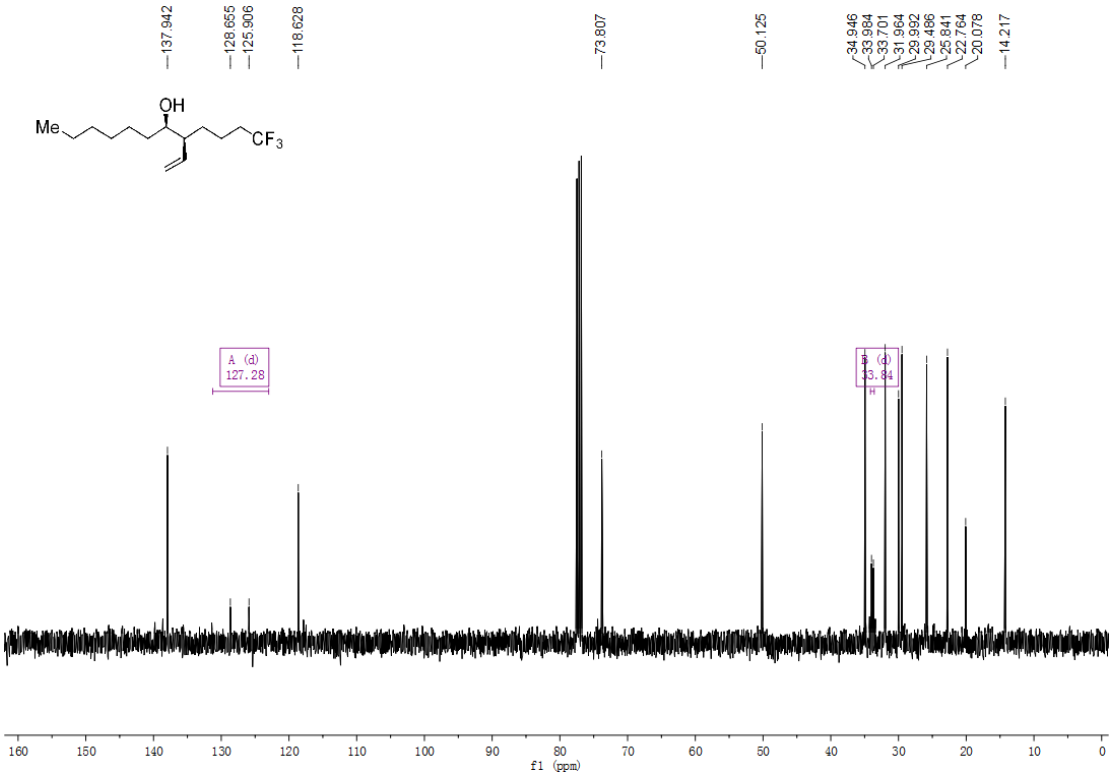


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.669	MM	0.3887	370.72278	15.89609	5.4227
2	22.999	MM	0.4227	6465.81299	254.95238	94.5773

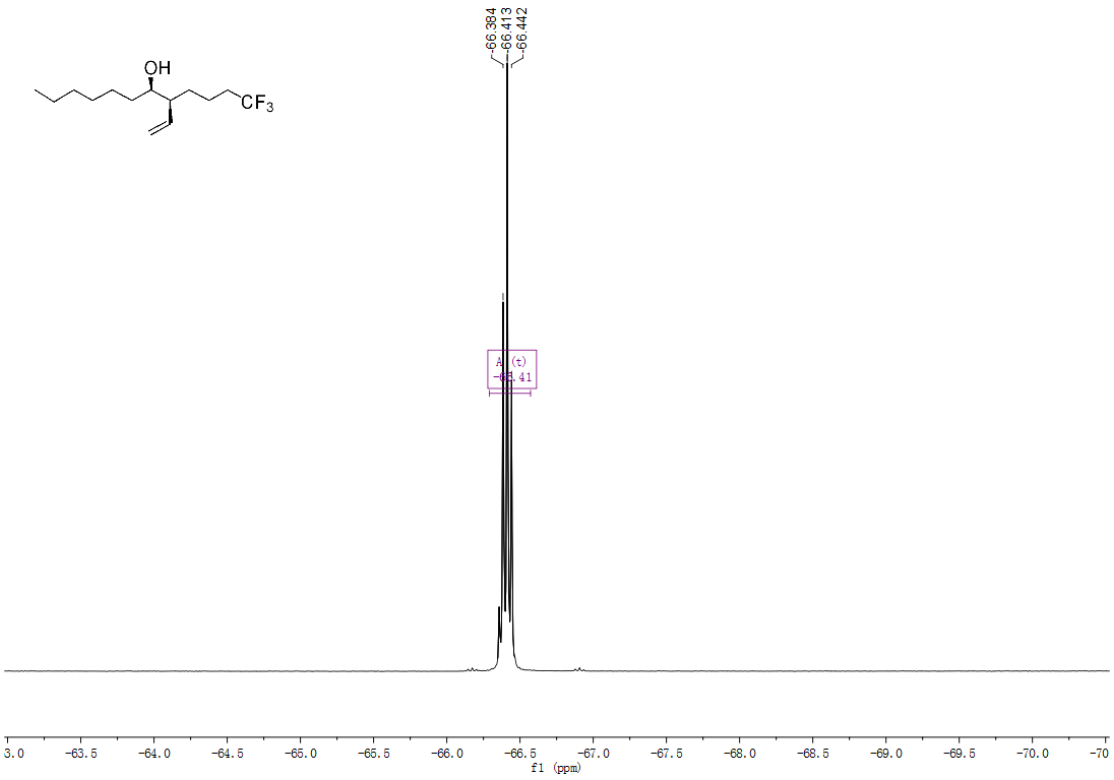
4m-^{1}H NMR



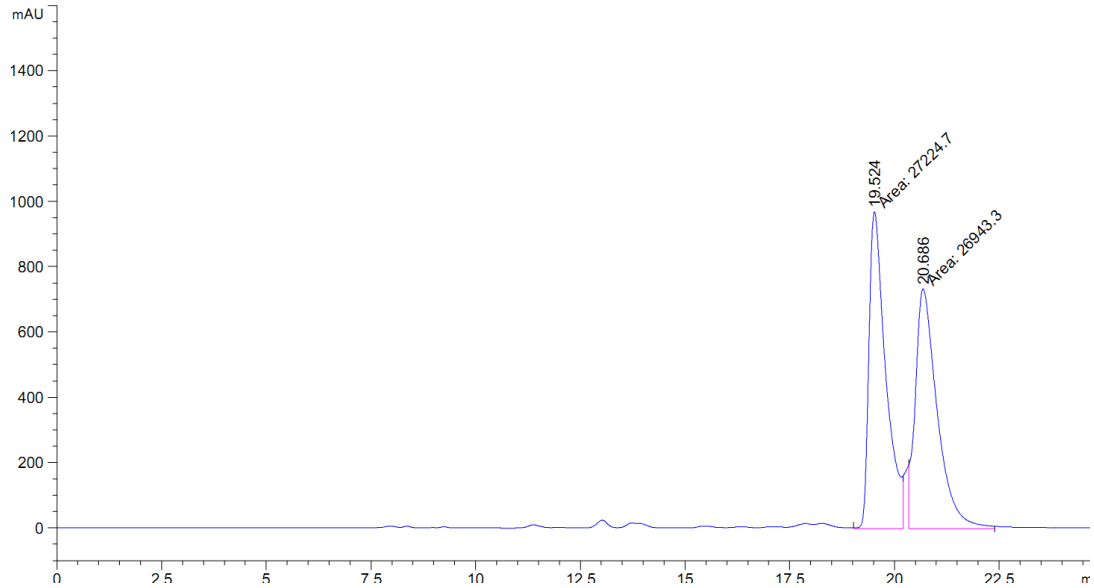
4m-^{13}C NMR



4m-^{19}F NMR

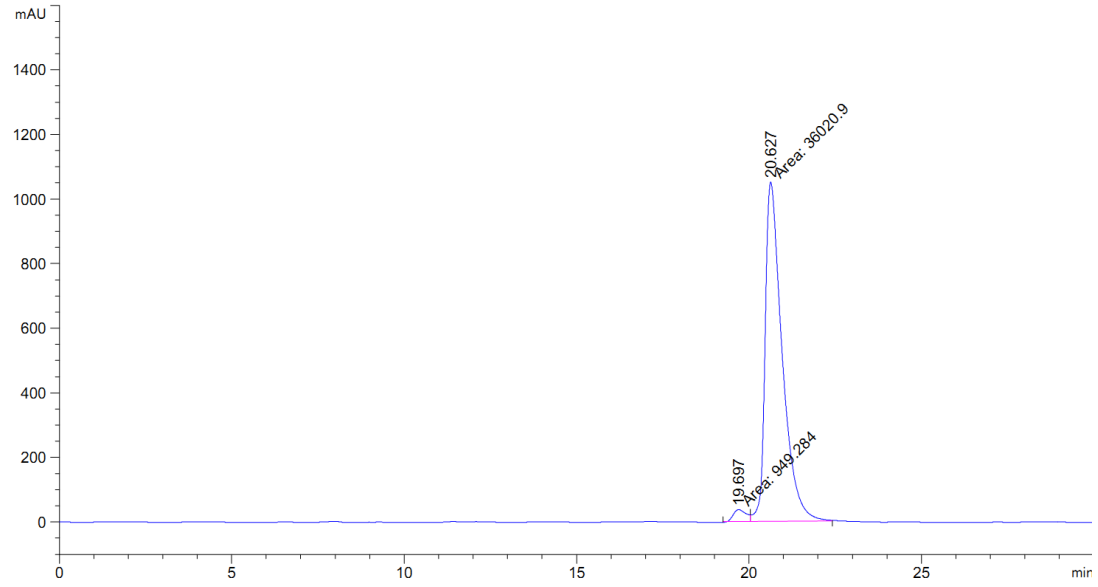


4m-HPLC (racemic)



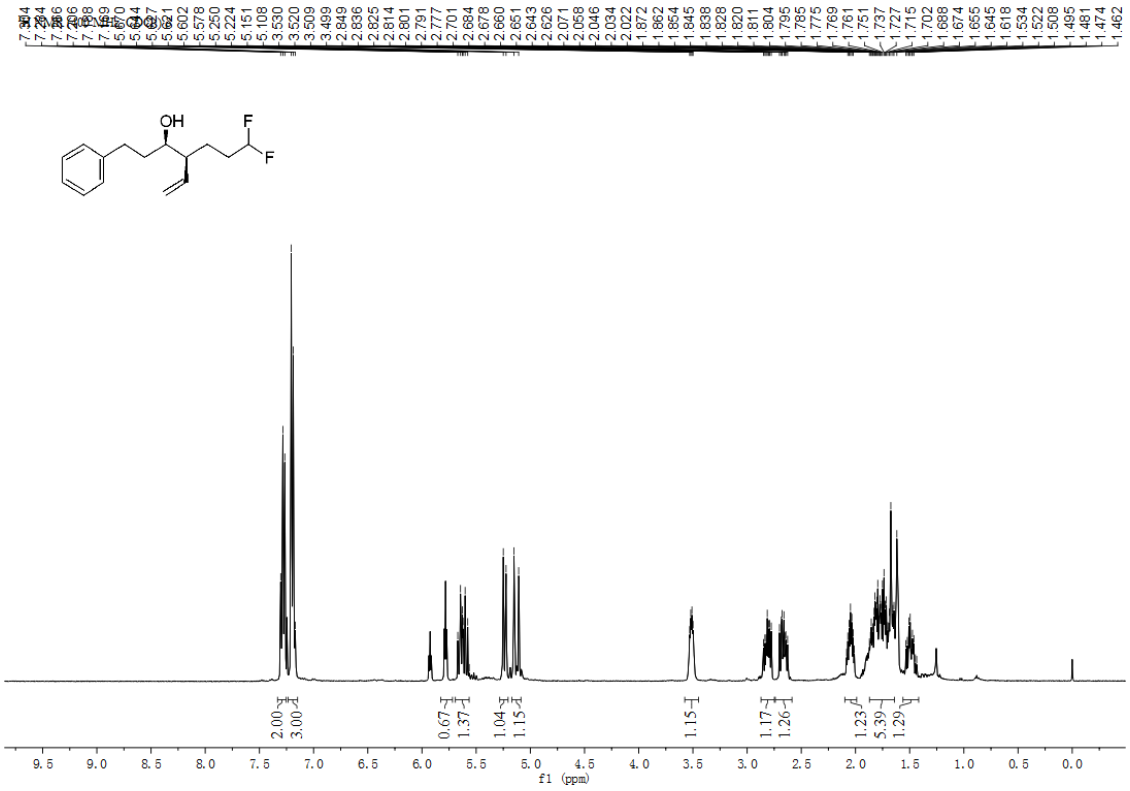
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.524	MM	0.4671	2.72247e4	971.48285	50.2598
2	20.686	MM	0.6109	2.69433e4	735.12720	49.7402

4m-HPLC (94% ee)

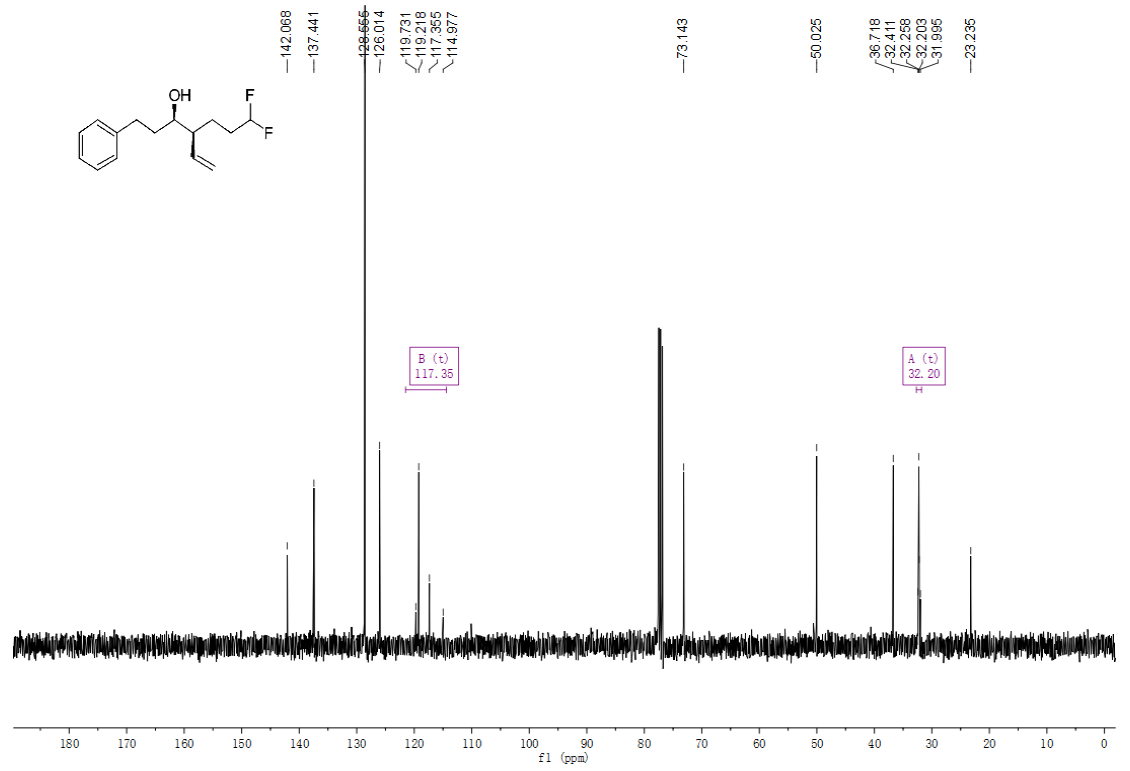


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.697	MF	0.4314	949.28375	36.67225	2.5677
2	20.627	FM	0.5712	3.60209e4	1050.94446	97.4323

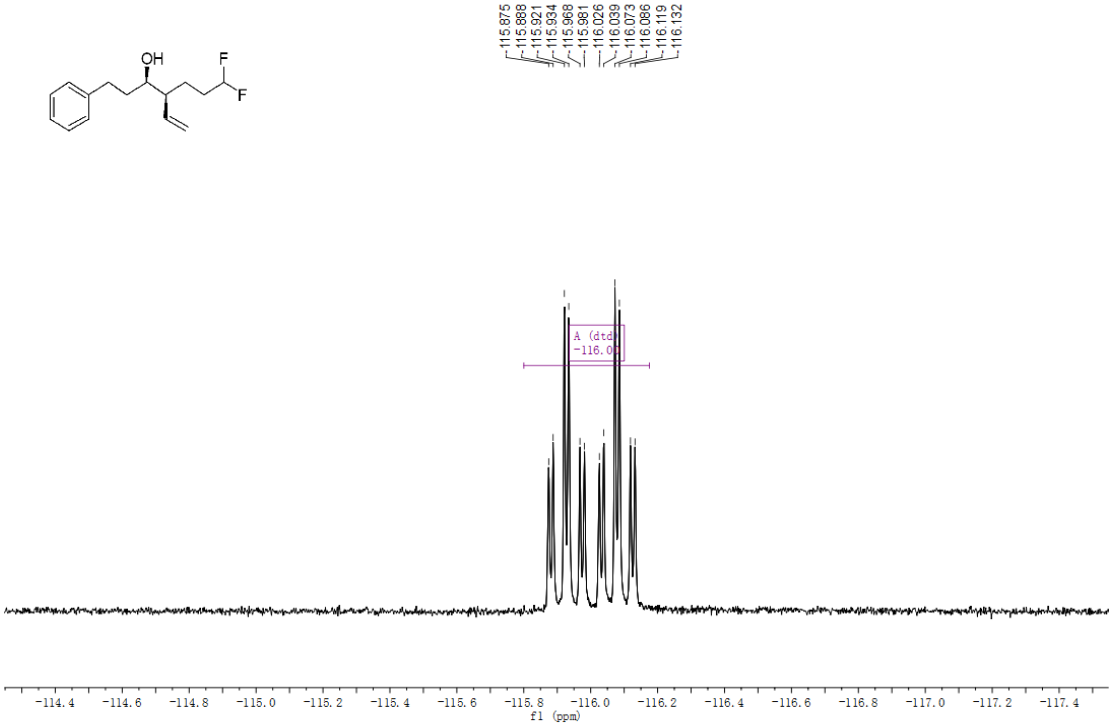
4n-^{1}H NMR



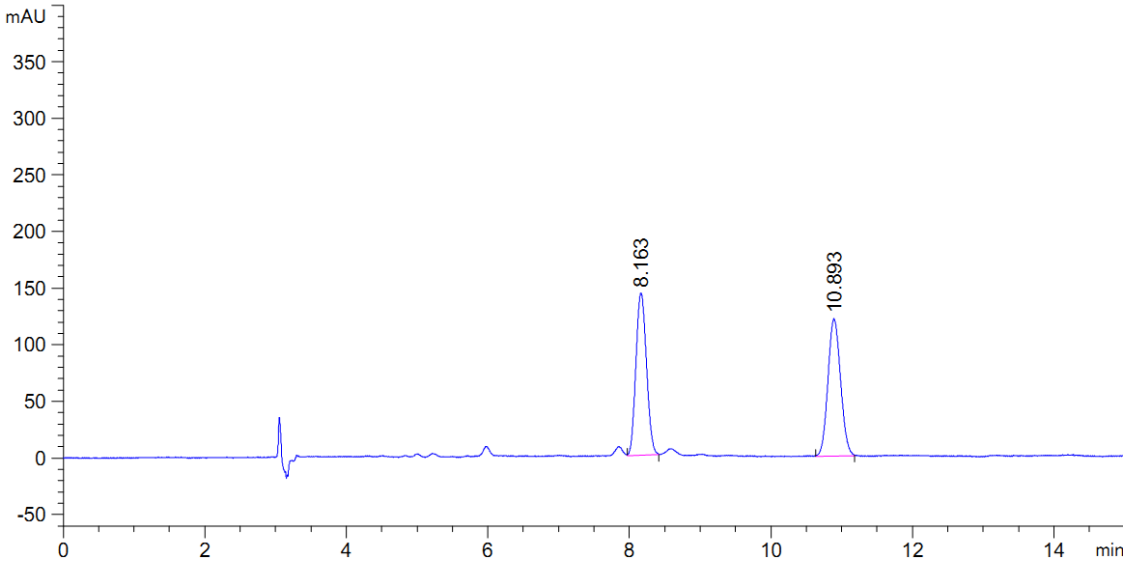
4n-^{13}C NMR



4n-^{19}F NMR

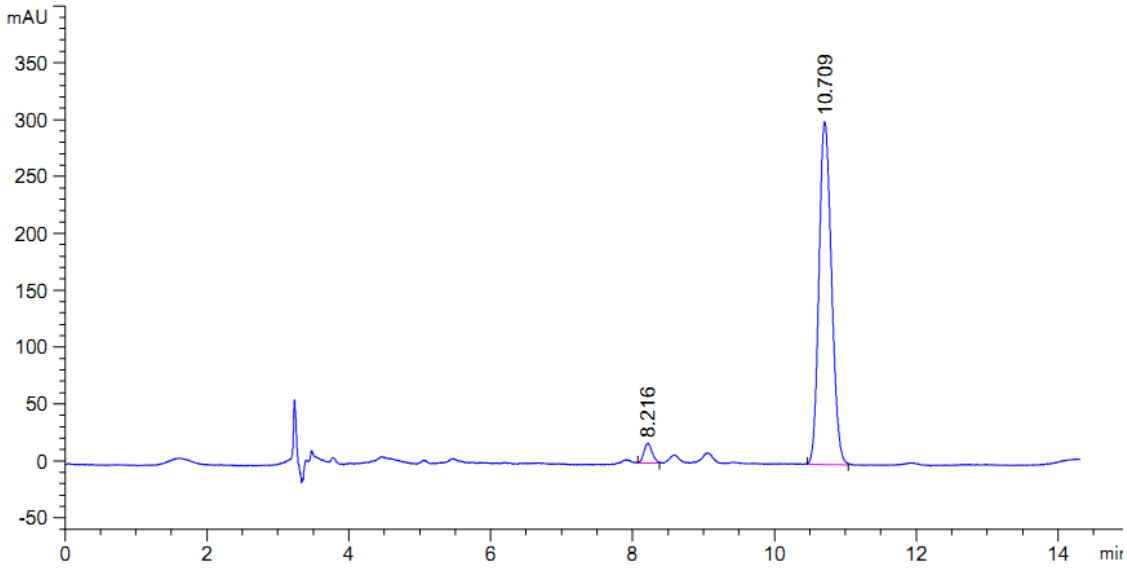


4n-HPLC (racemic)



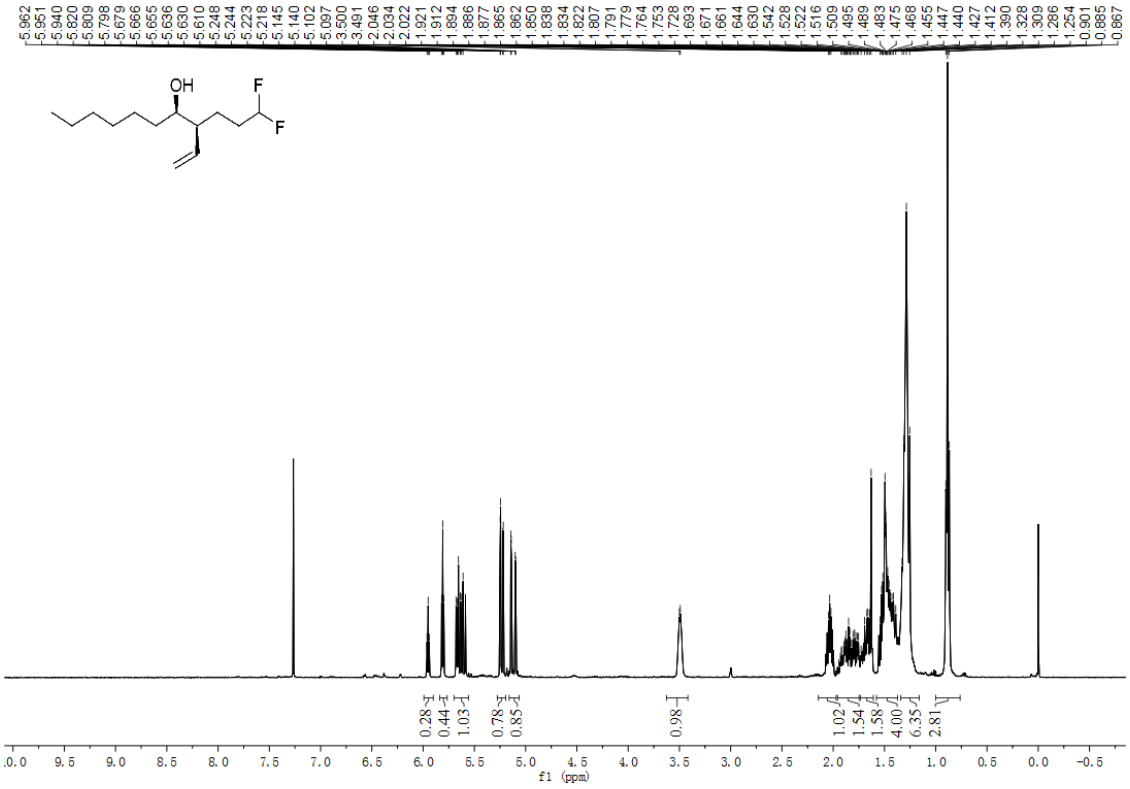
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.163	VV	0.1564	1489.46436	143.16858	49.6878
2	10.893	VV	0.1648	1508.18311	121.48673	50.3122

4n-HPLC (92% ee)

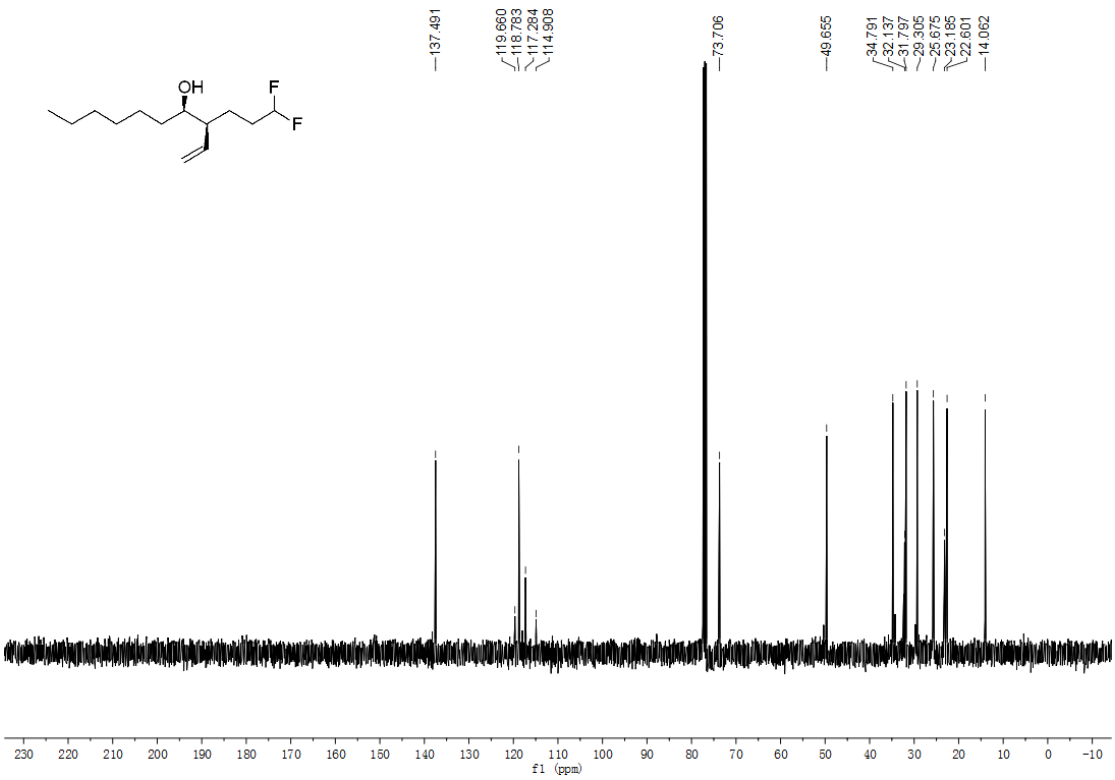


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.216	VV	0.0991	139.14682	17.42791	3.6299
2	10.709	VV	0.1854	3694.16382	301.54813	96.3701

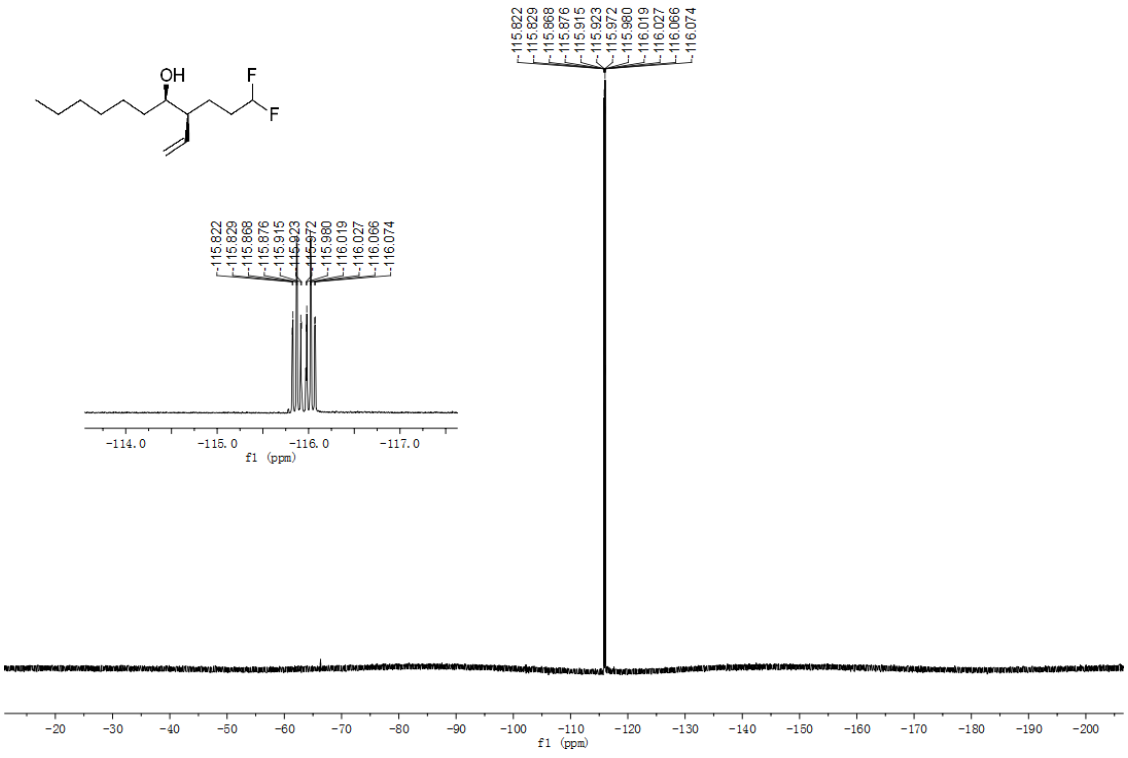
4o-^{1}H NMR



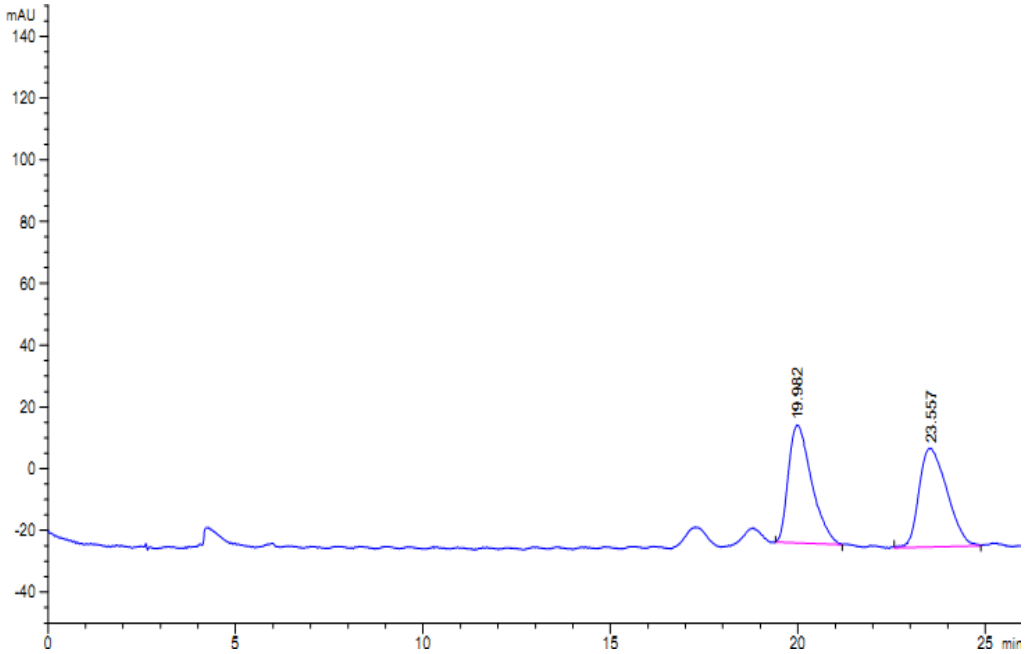
4o-^{13}C NMR



4o-^{19}F NMR

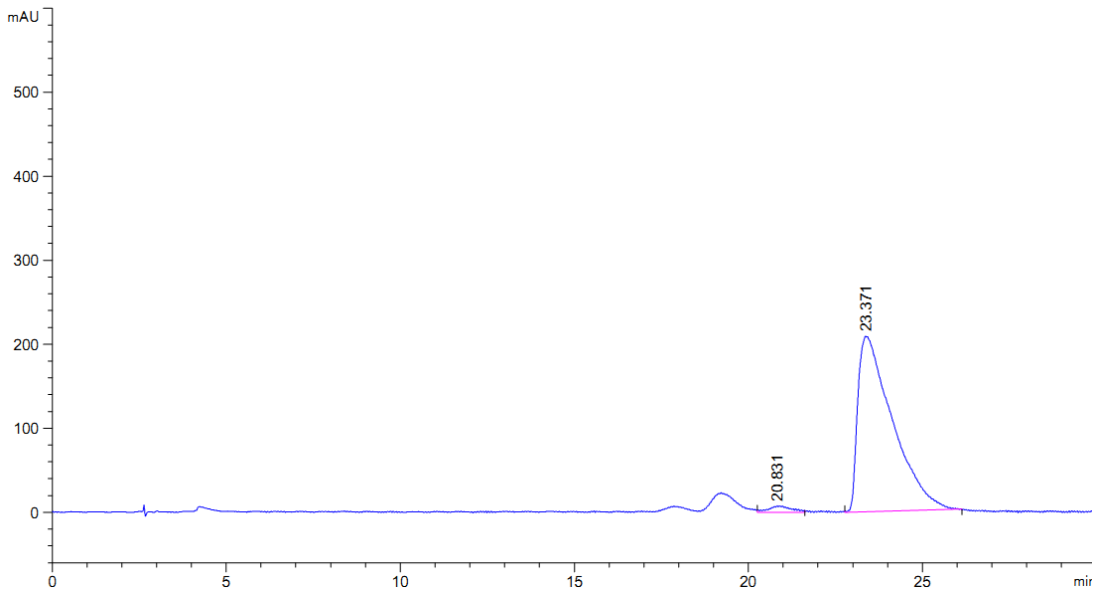


4o-HPLC (racemic)



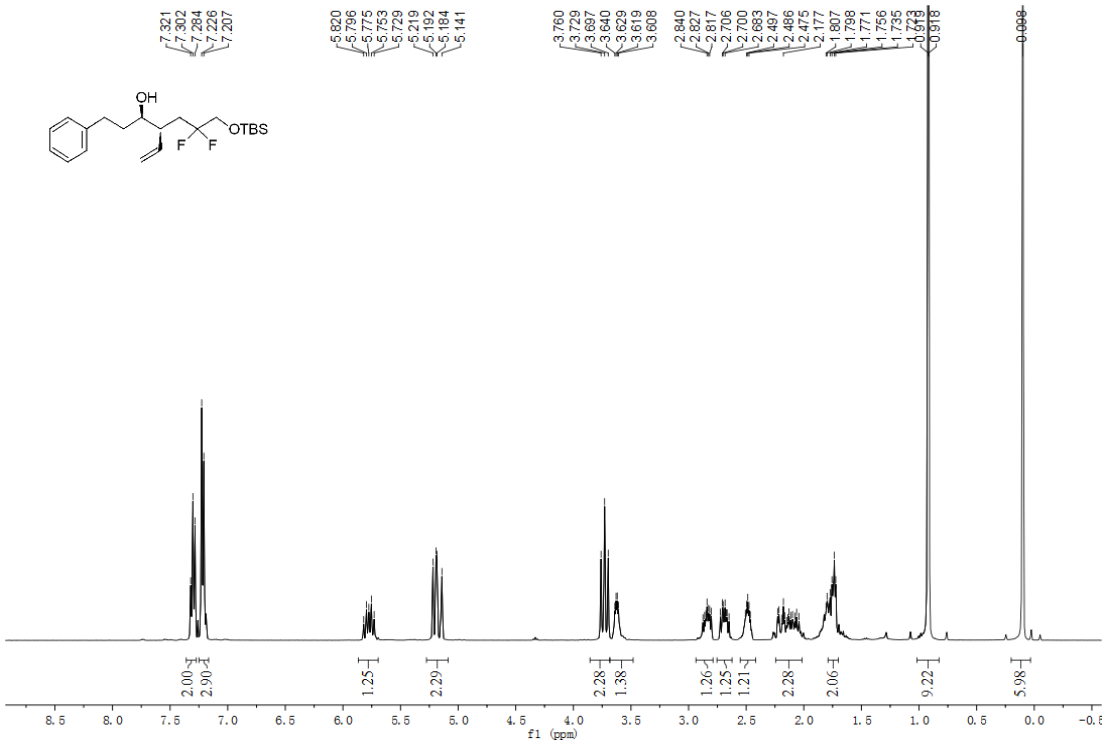
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.982	BB	0.5212	1648.10669	38.13494	49.8883
2	23.557	MM R	0.7992	1655.48779	31.95133	50.1117

4o-HPLC (95% ee)

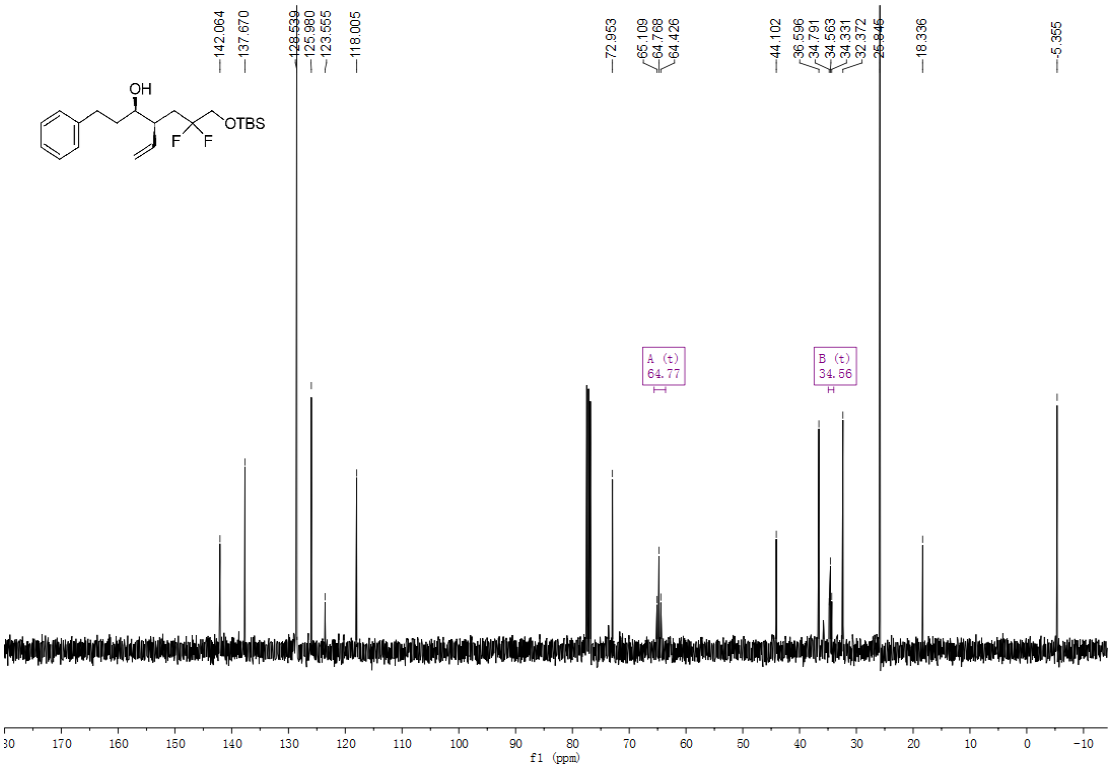


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.831	MM R	0.6904	358.35342	7.77520	2.4218
2	23.371	MM R	1.0884	1.44386e4	208.78365	97.5782

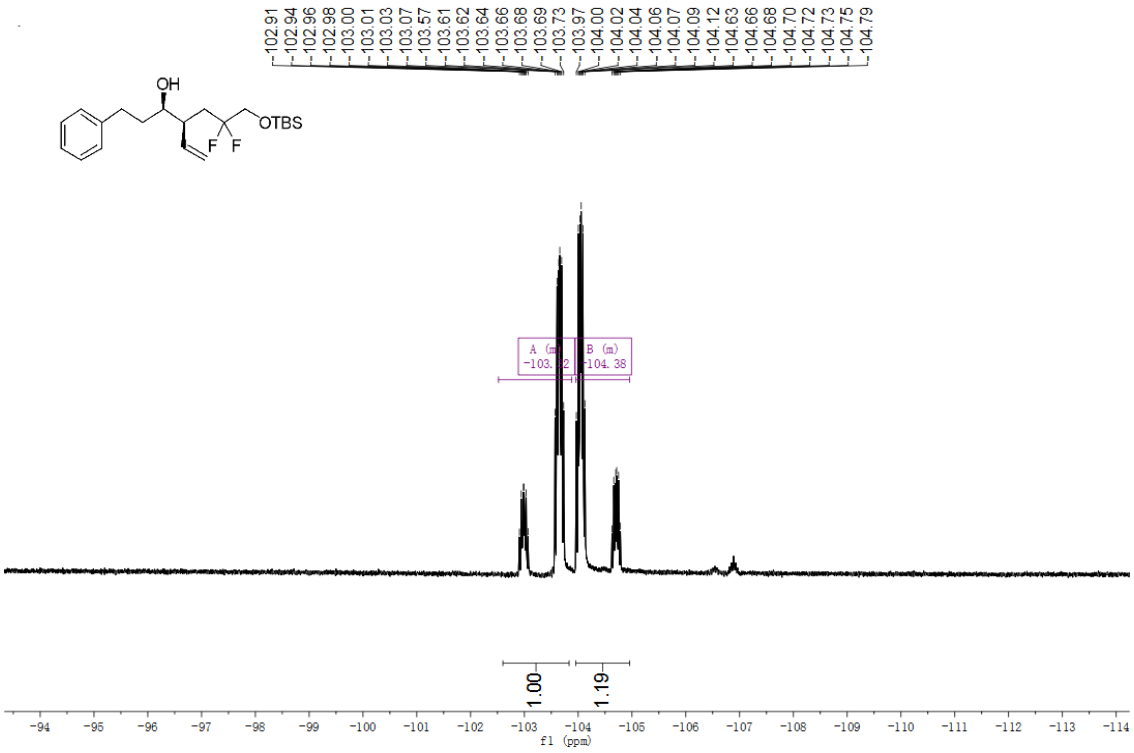
4p-^{1}H NMR



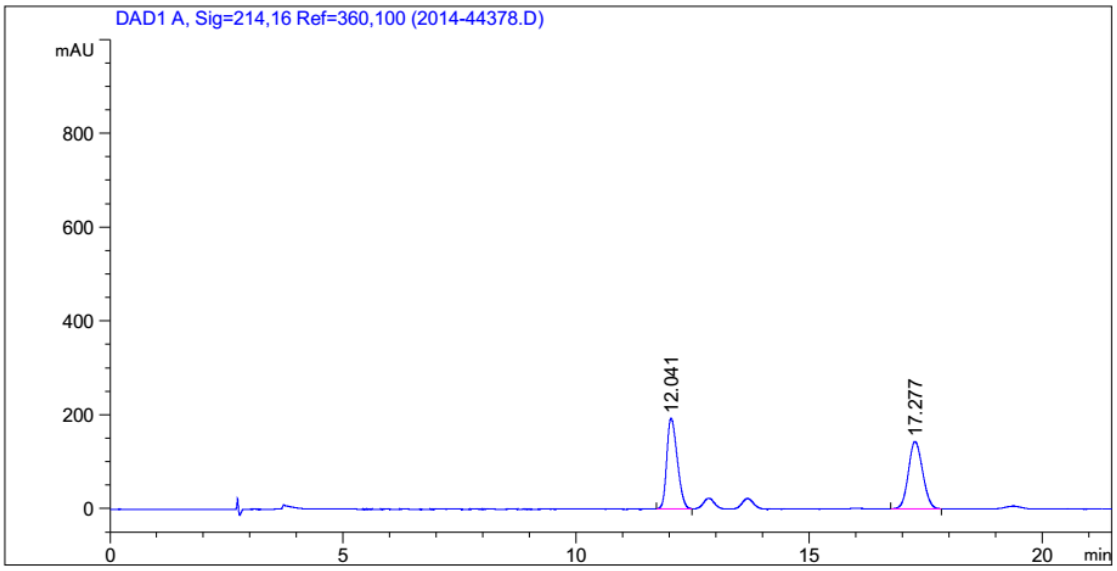
4p-^{13}C NMR



4p-^{19}F NMR

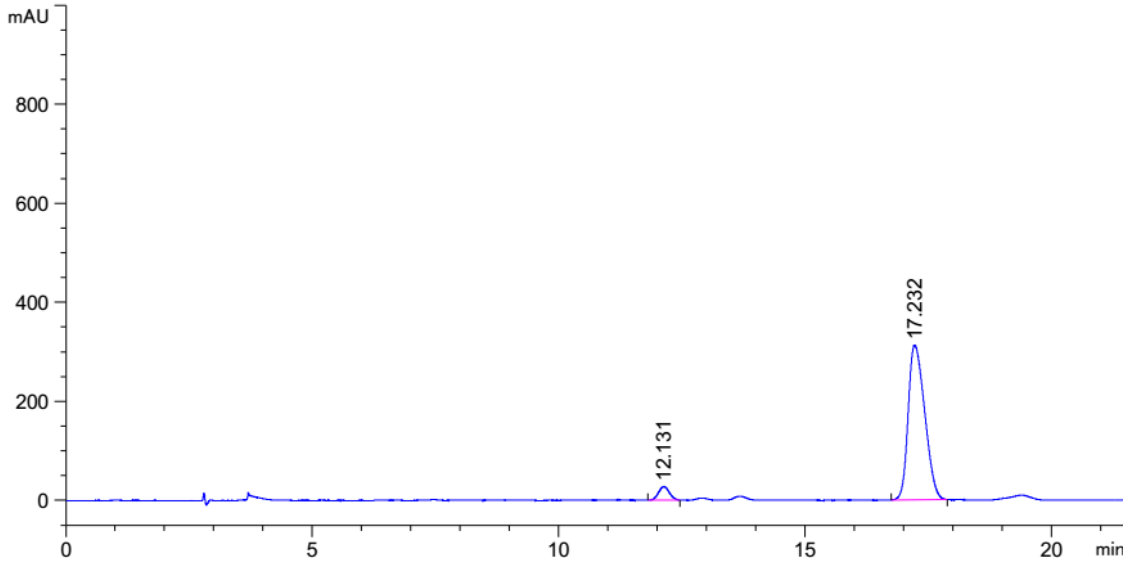


4p-HPLC (racemic)



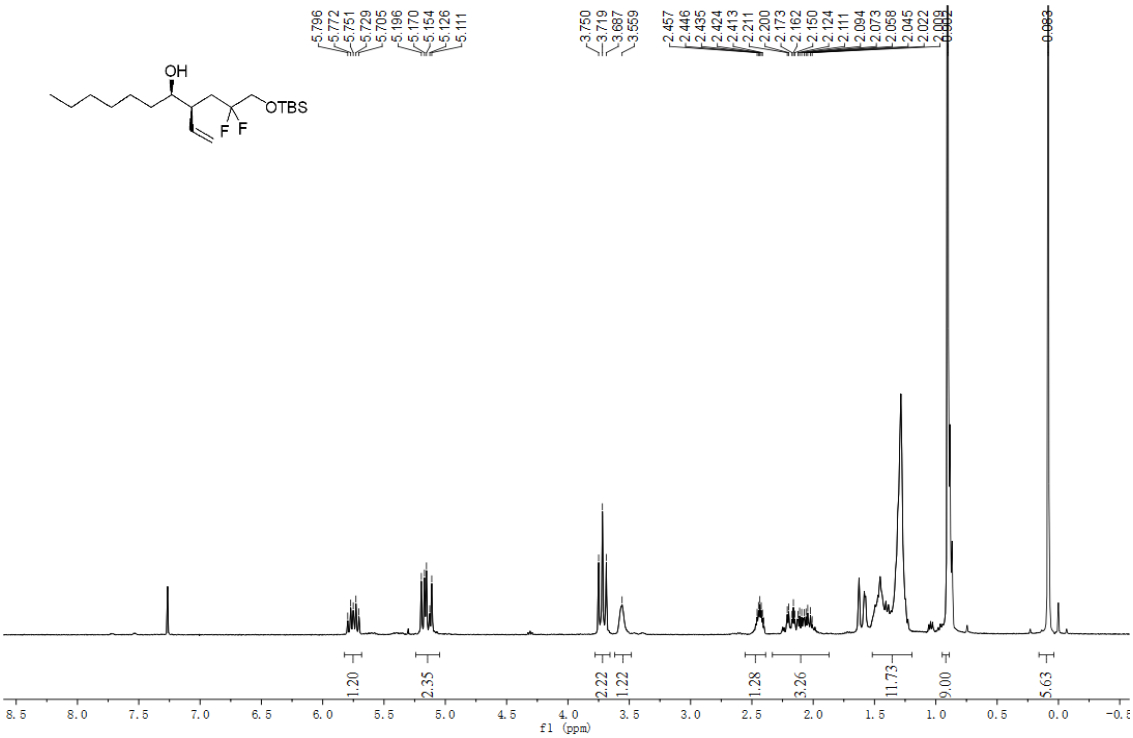
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.041	BV	0.2236	3015.22388	193.68507	49.6523
2	17.277	VV	0.2690	3057.44971	143.80447	50.3477

4p-HPLC (89% ee)

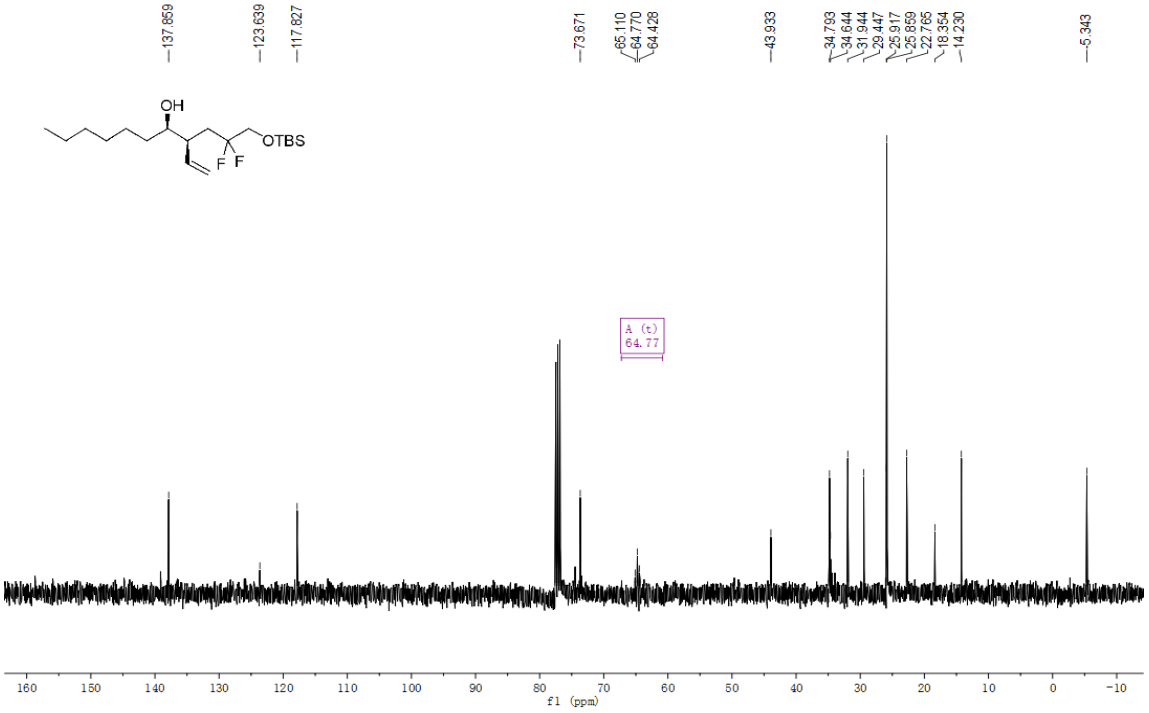


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.131	VV	0.1871	433.39957	27.68544	5.5816
2	17.232	VV	0.3228	7331.38086	312.92477	94.4184

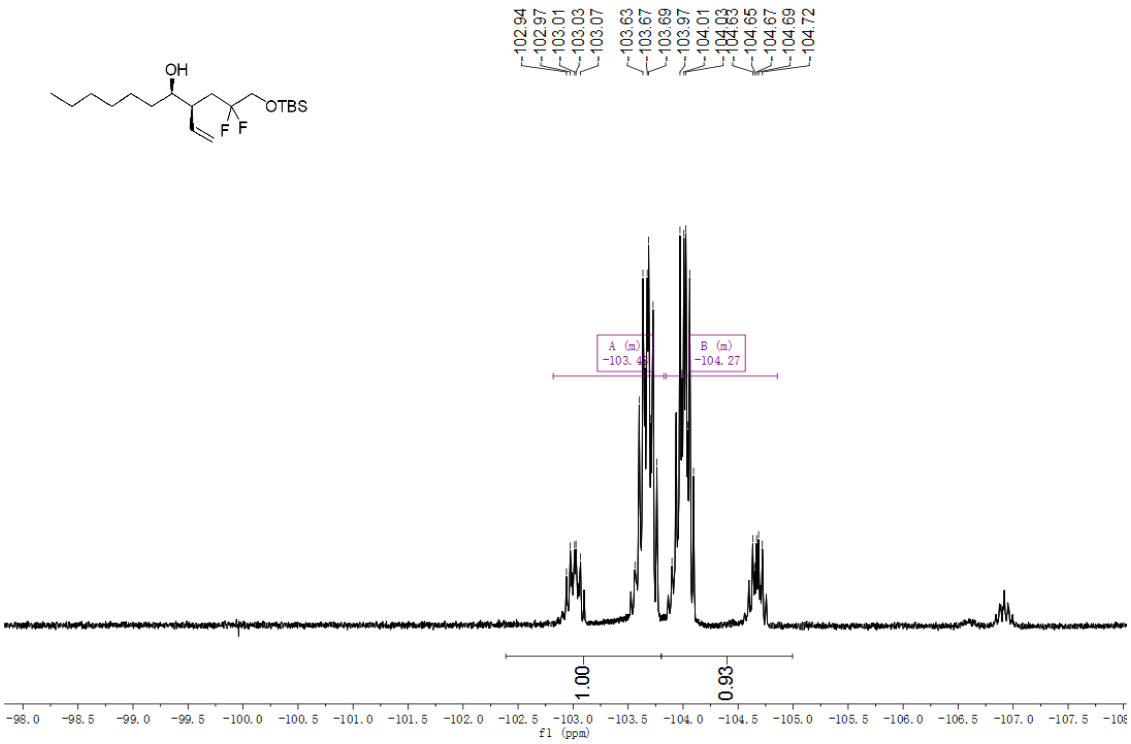
4q-^{1}H NMR



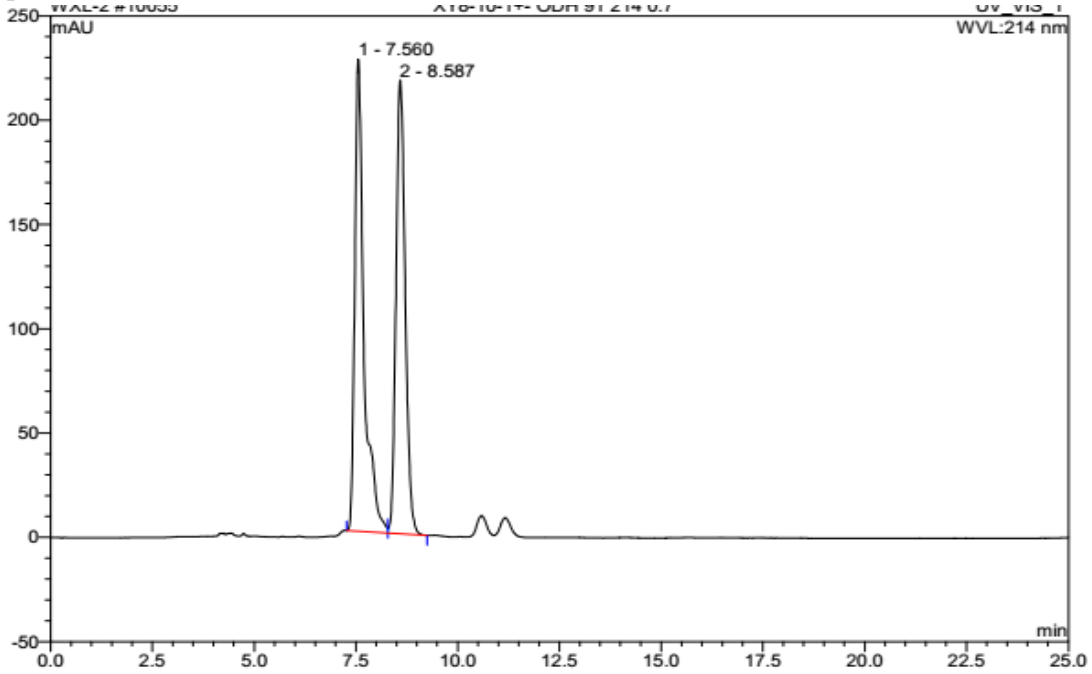
4q-^{13}C NMR



4q-^{19}F NMR

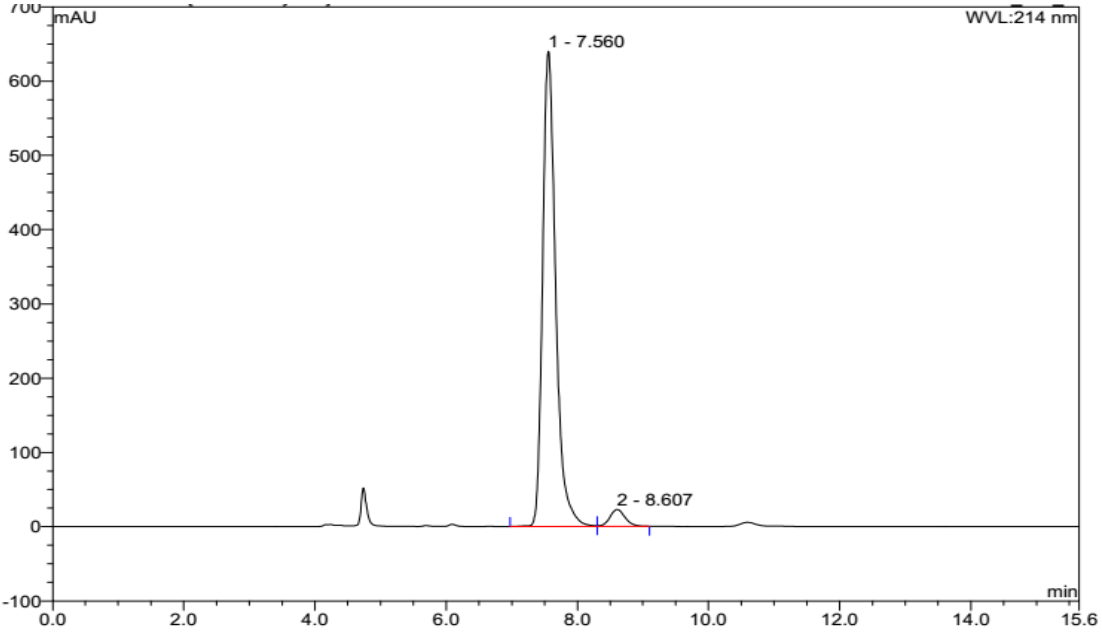


4q- HPLC (racemic)



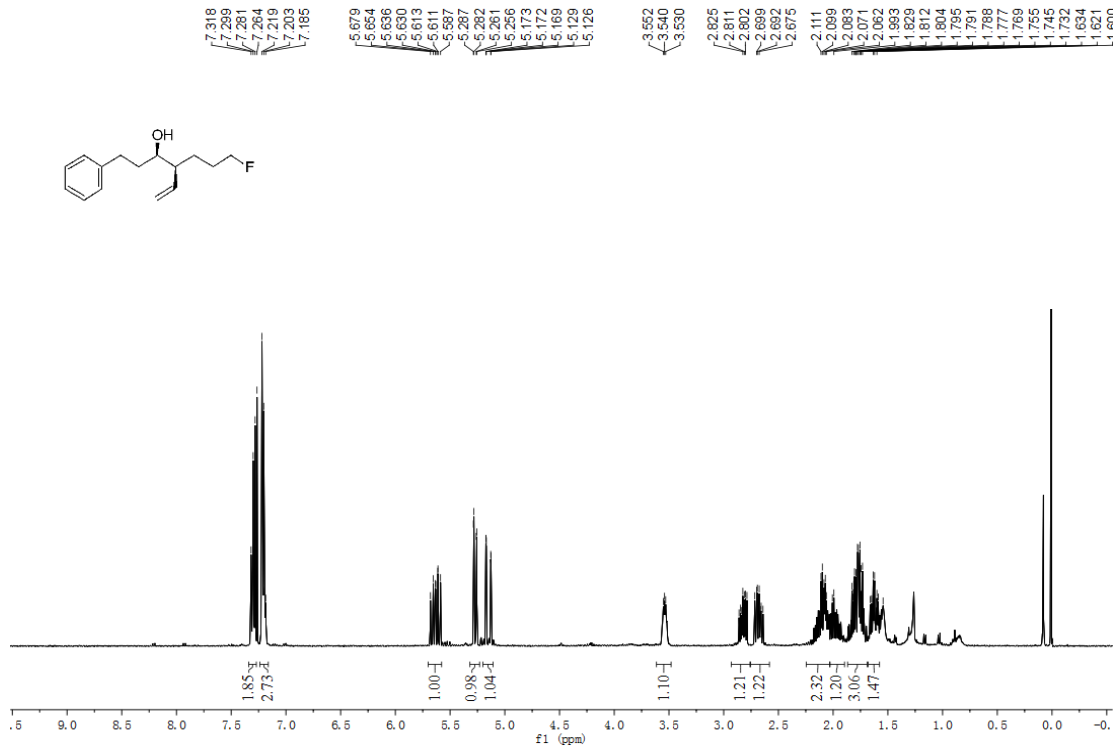
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.56	n.a.	226.291	59.454	50.97	n.a.	BM
2	8.59	n.a.	217.677	57.184	49.03	n.a.	MB
Total:			443.968	116.638	100.00	0.000	

4q- HPLC (92% ee)

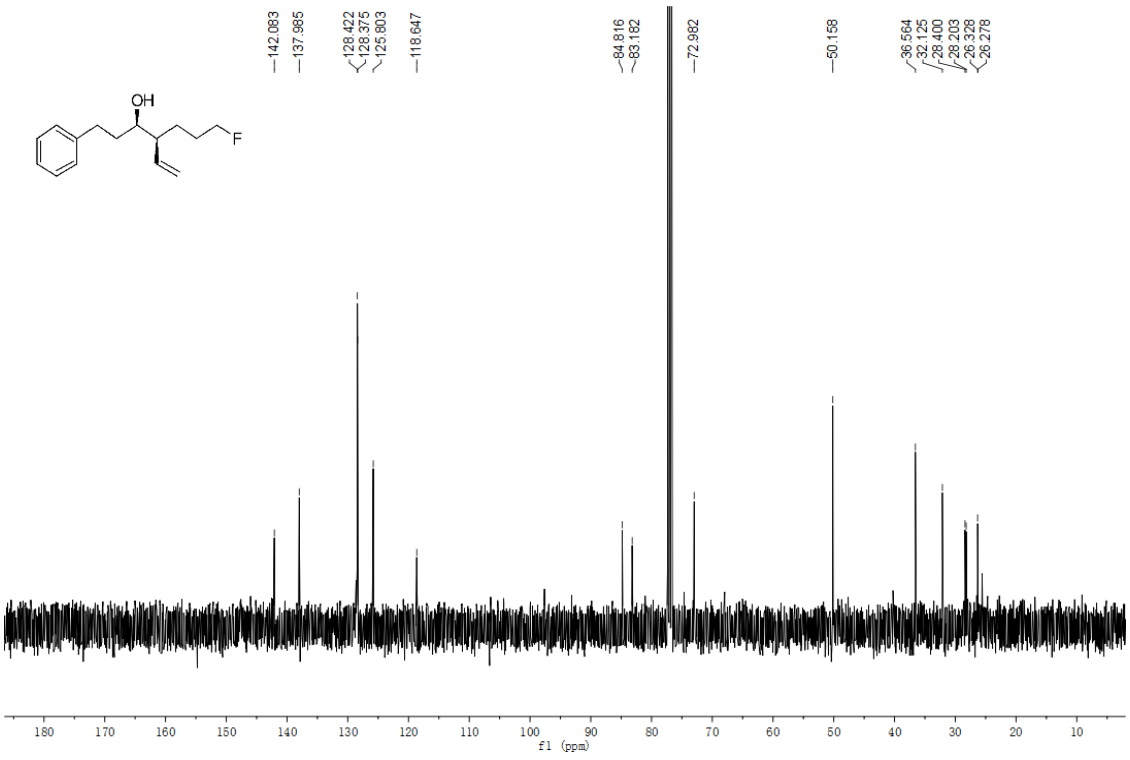


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.56	n.a.	639.970	147.586	96.08	n.a.	BM
2	8.61	n.a.	22.568	6.028	3.92	n.a.	MB
Total:			662.538	153.614	100.00	0.000	

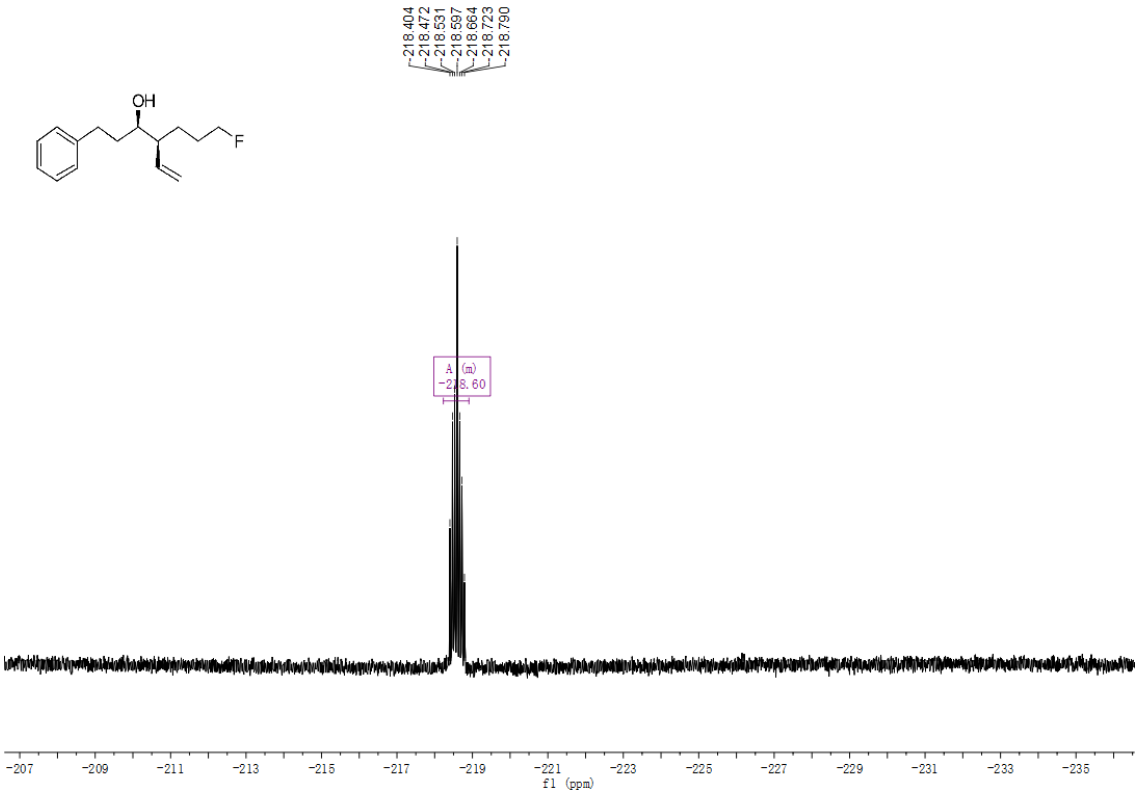
4r-^{1}H NMR



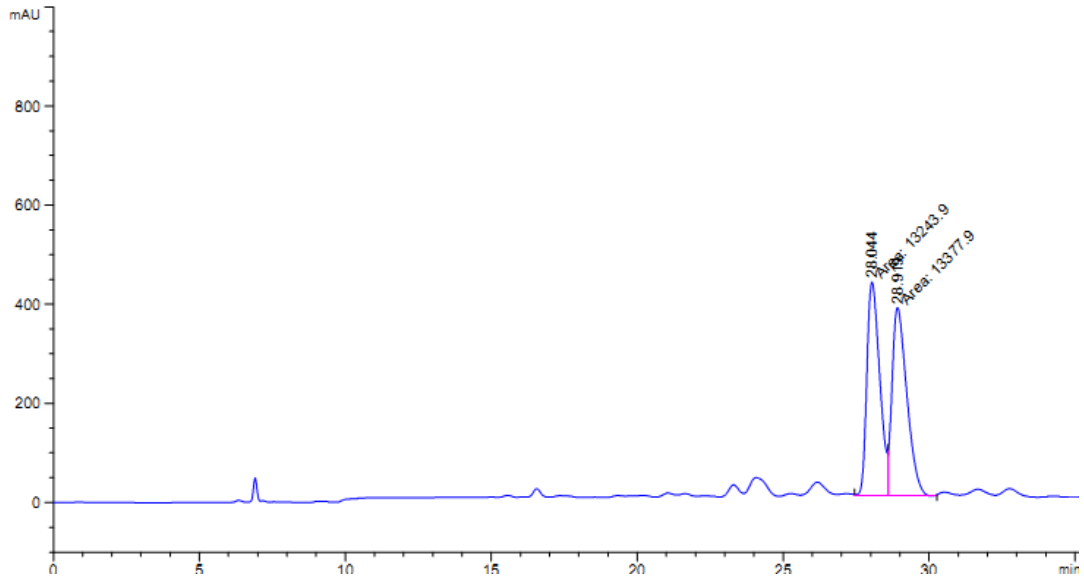
4r-^{13}C NMR



4r-^{19}F NMR

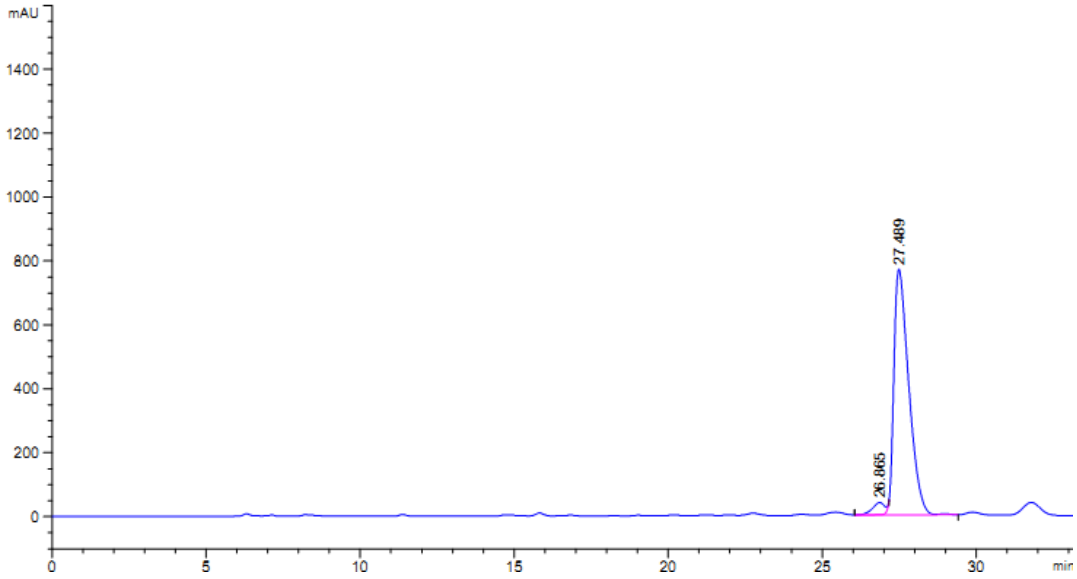


4r-HPLC (racemic)



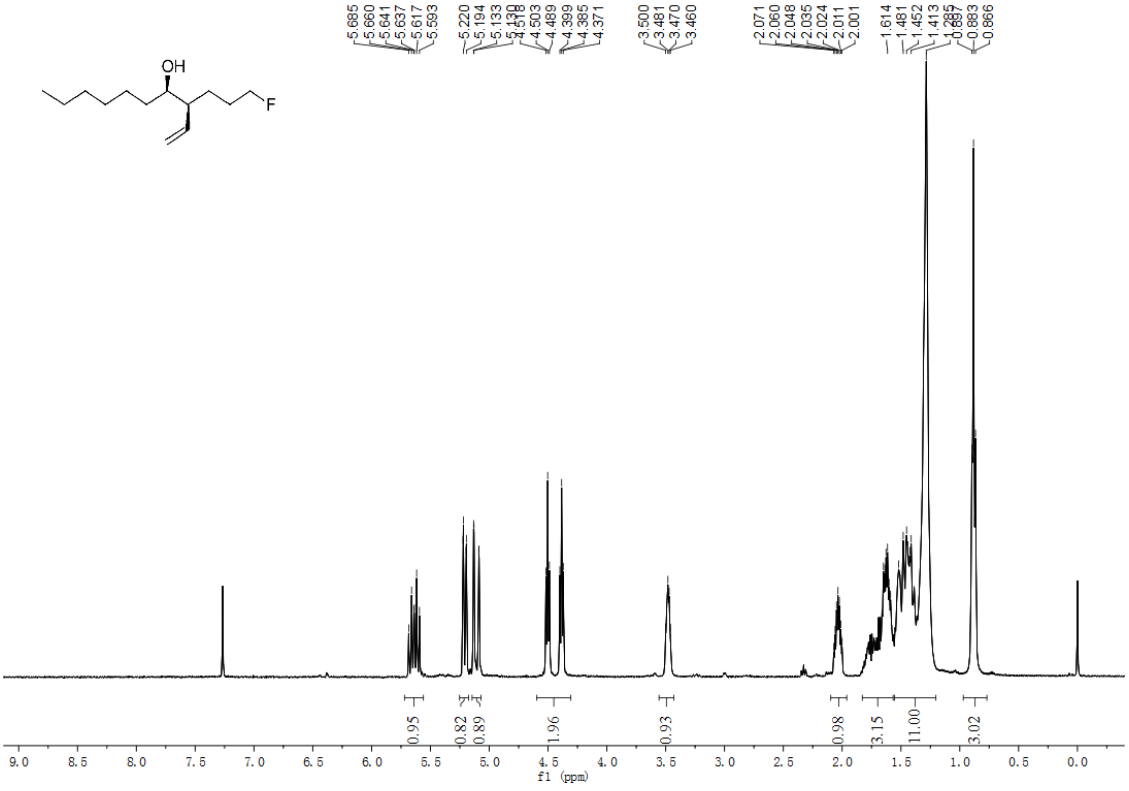
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.044	MF	0.5124	1.32439e4	430.80746	49.7483
2	28.919	FM	0.5877	1.33779e4	379.38007	50.2517

4r-HPLC (92% ee)

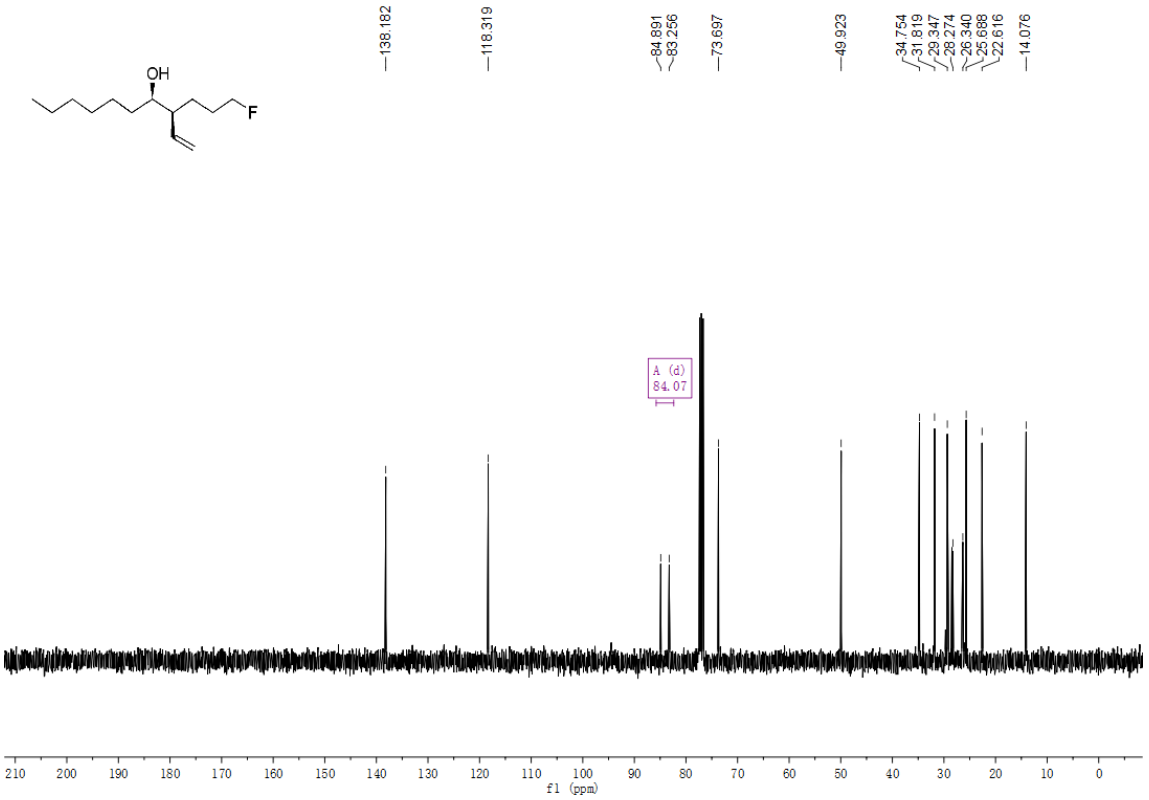


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.865	BV E	0.4113	1053.65186	38.62127	3.9114
2	27.489	VV R	0.5111	2.58846e4	769.30652	96.0886

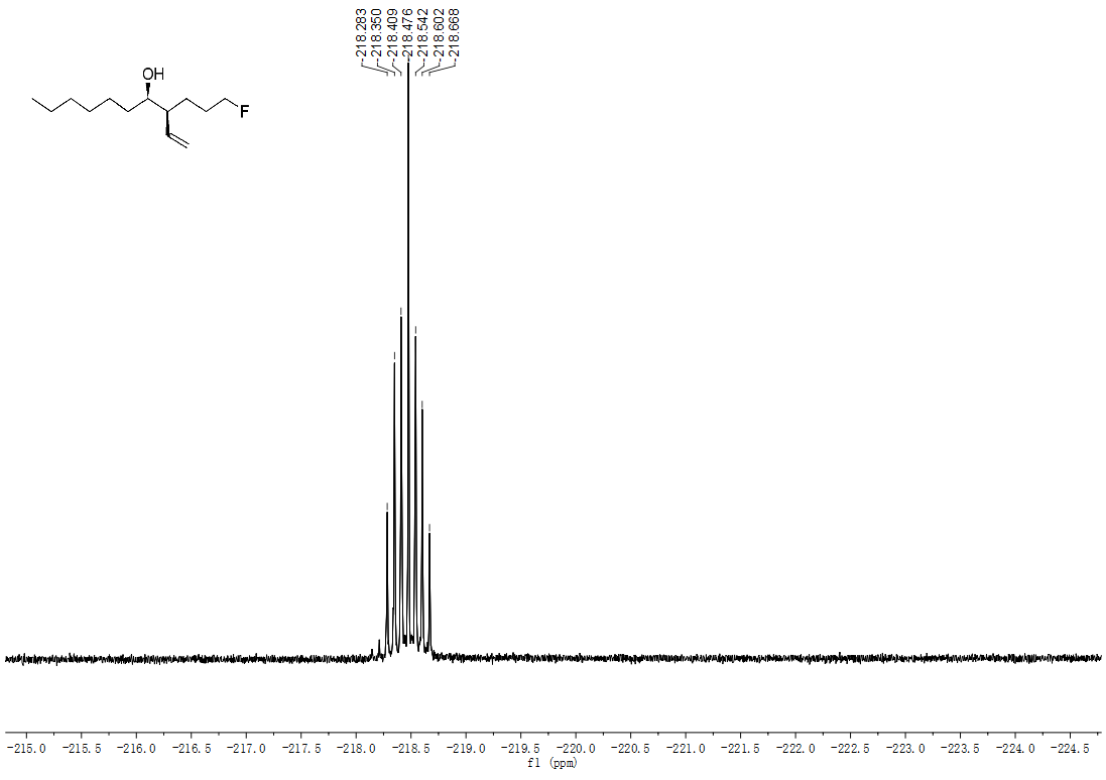
4s-^{1}H NMR



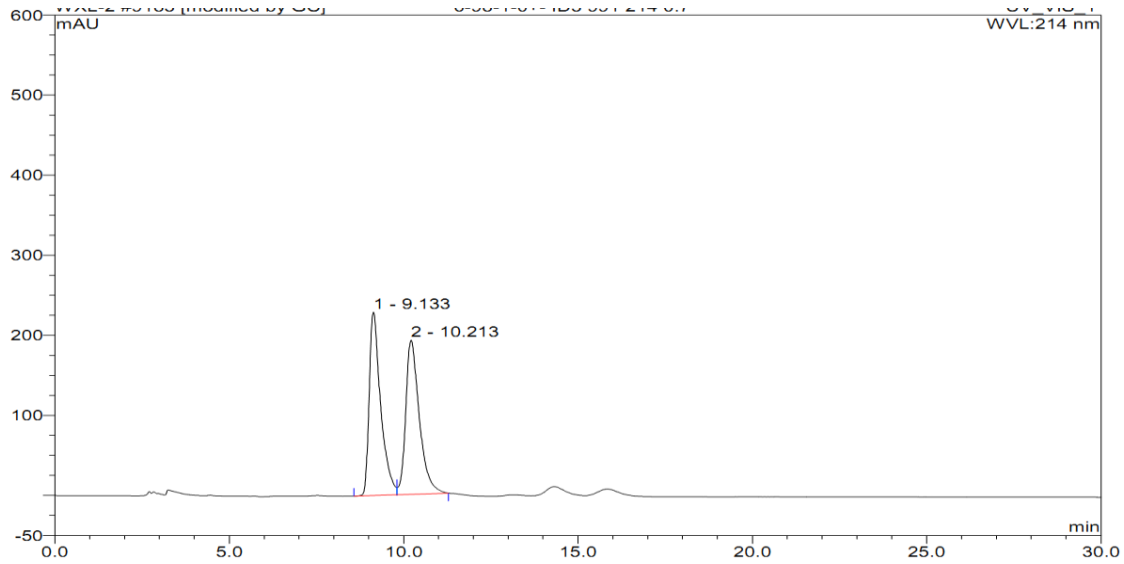
4s-^{13}C NMR



4s-^{19}F NMR

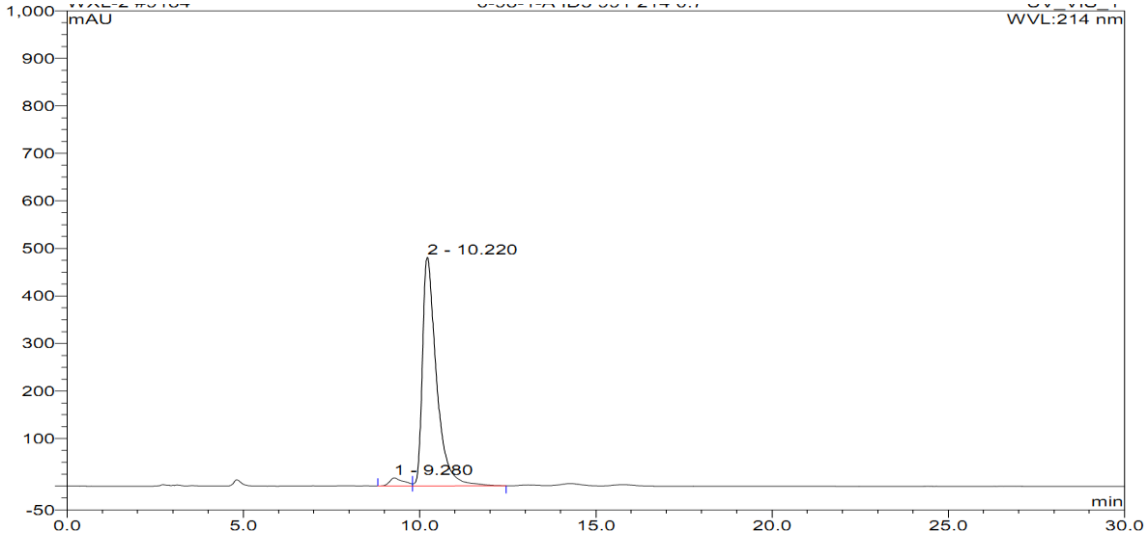


4s-HPLC (racemic)



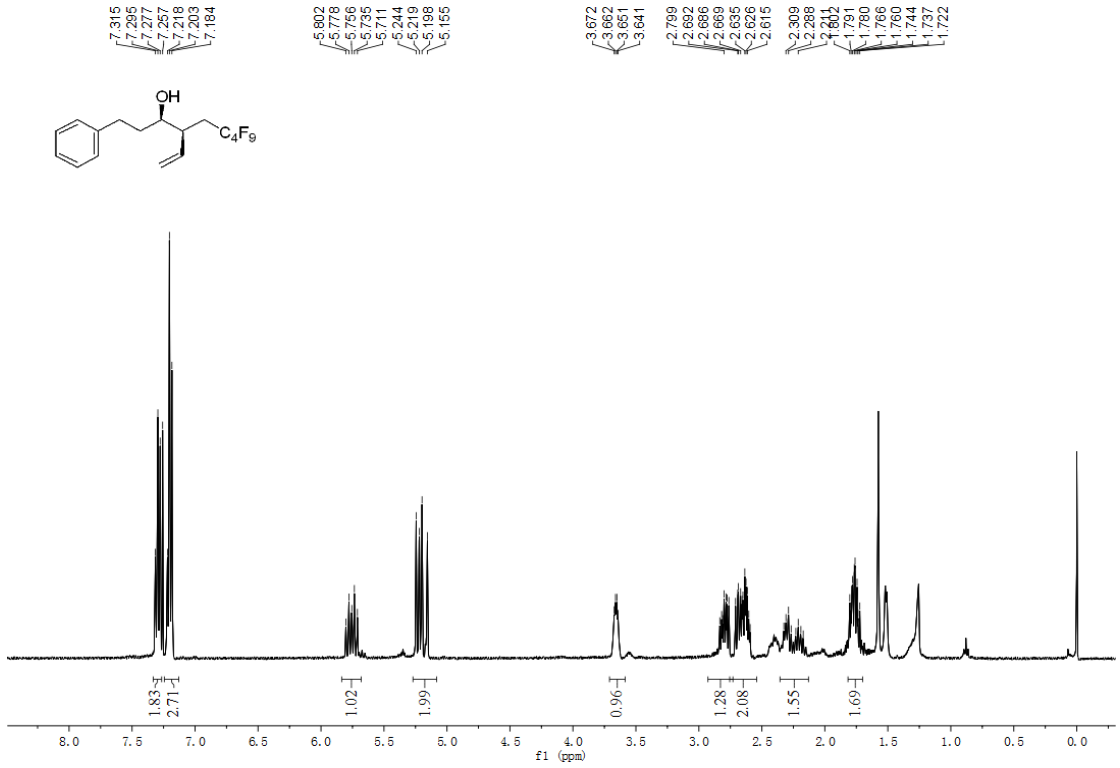
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %
1	9.13	n.a.	229.123	87.604	50.09
2	10.21	n.a.	192.779	87.306	49.91
Total:			421.903	174.910	100.00

4s-HPLC (93% ee)

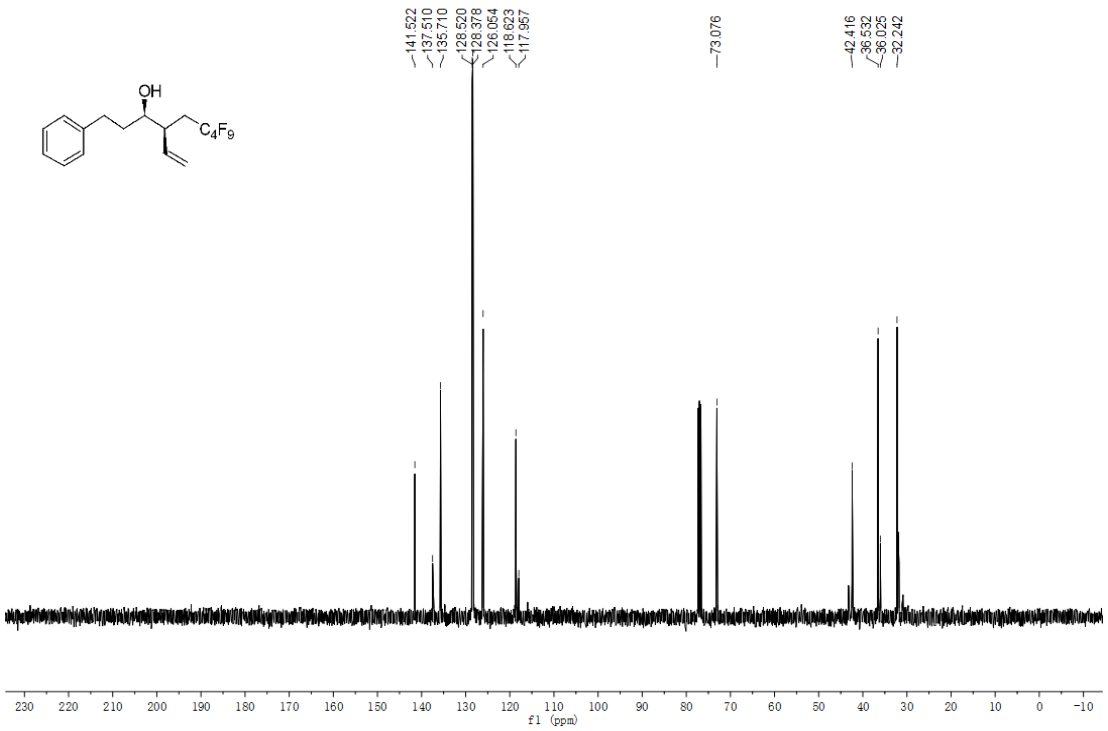


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %
1	9.28	n.a.	16.650	7.752	3.37
2	10.22	n.a.	481.163	222.099	96.63
Total:			497.814	229.851	100.00

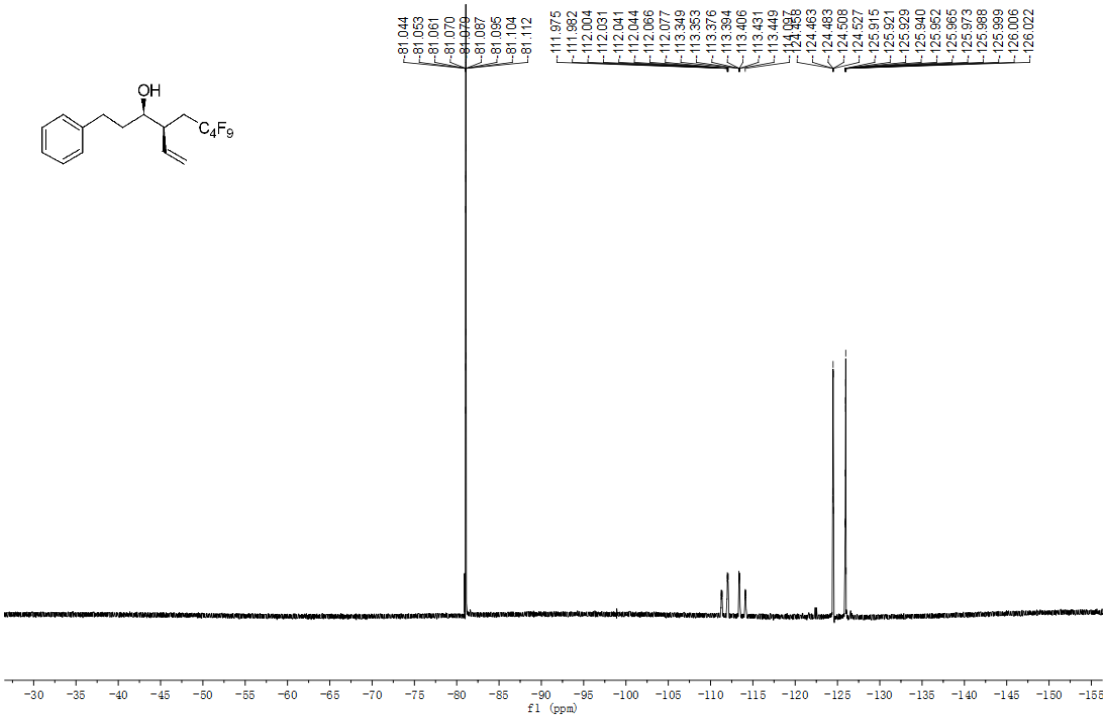
4t-^{1}H NMR



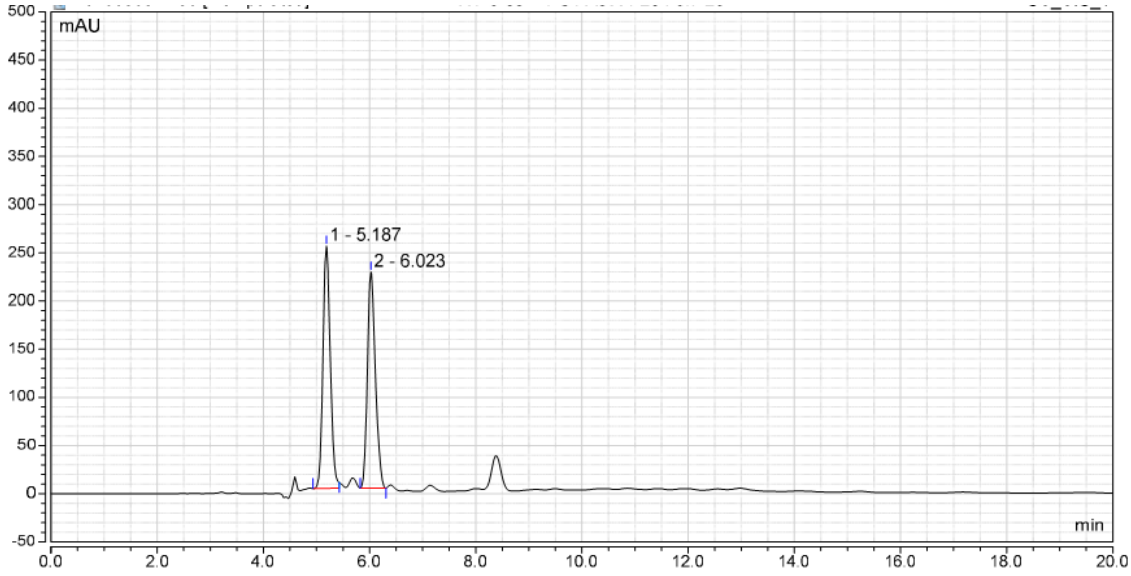
4t-^{13}C NMR



4t-^{19}F NMR

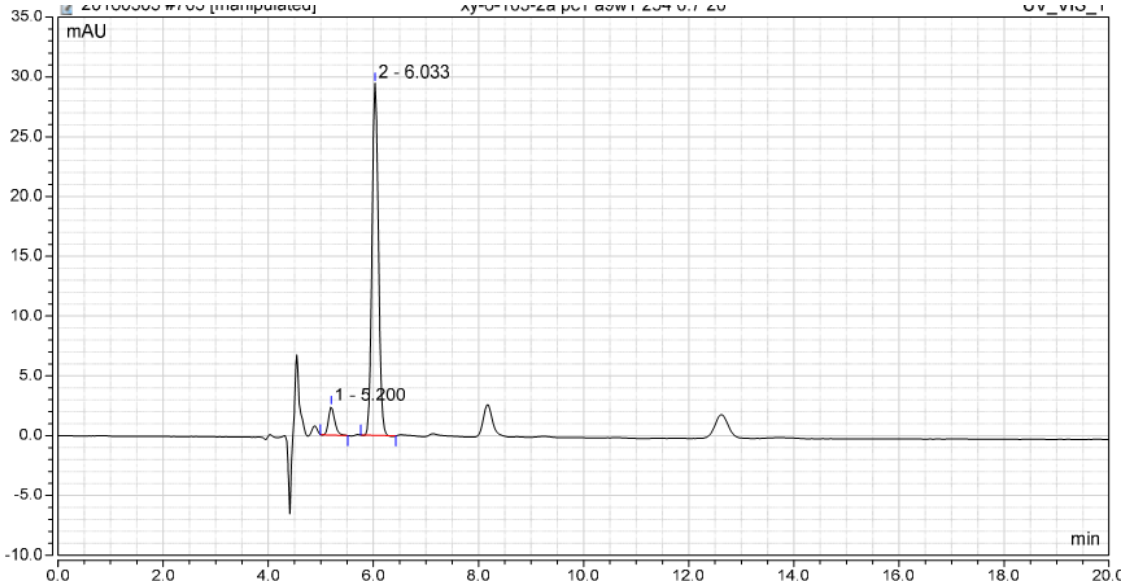


4t-HPLC (racemic)



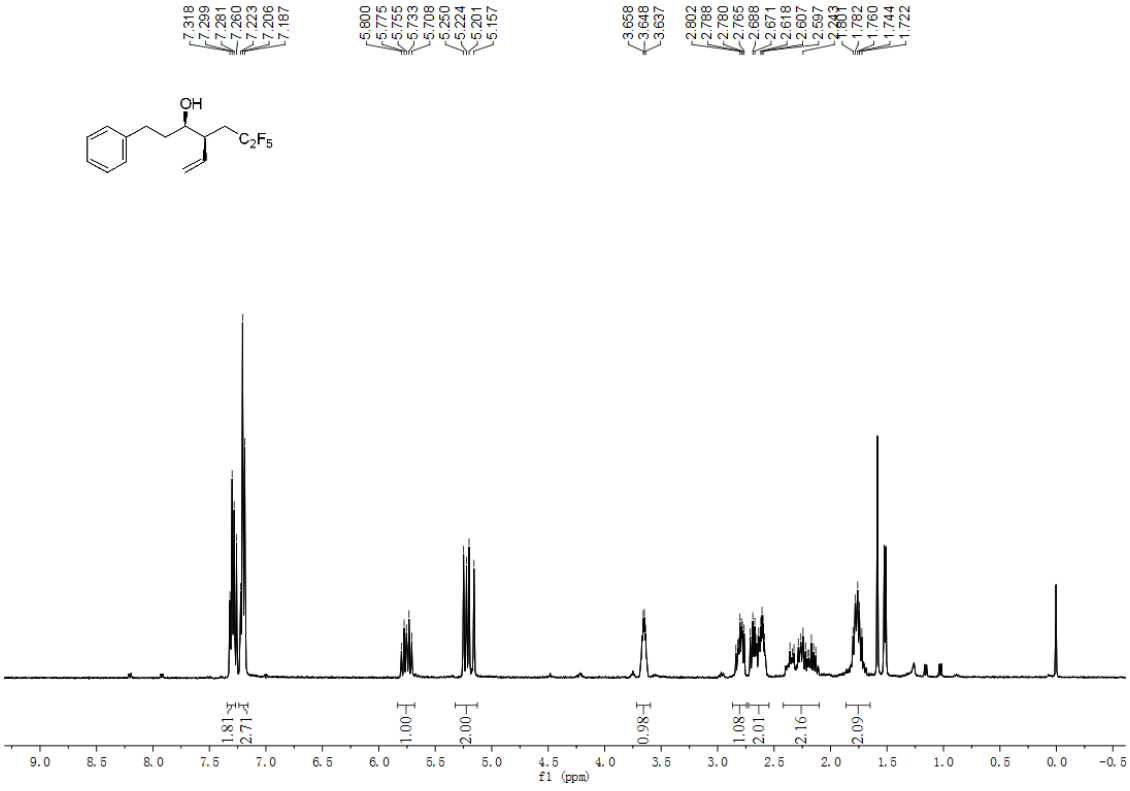
Integration Results				
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	5.187	40.241	251.625	50.71
2	6.023	39.111	224.347	49.29
Total:		**79.352**	**475.972**	**100.00**

4t-HPLC (86% ee)

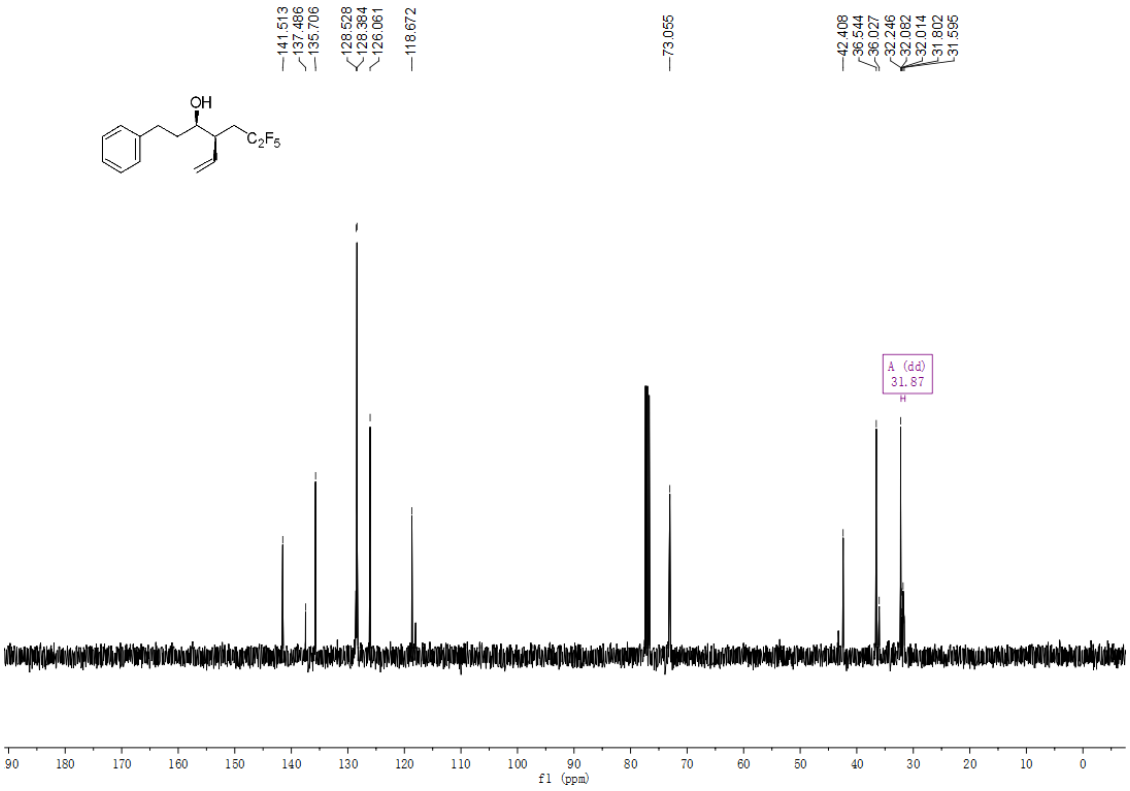


Integration Results				
No.	Retention Time min	Area mAU*min	Height mAU	Relative Area %
1	5.200	0.323	2.395	7.21
2	6.033	4.163	29.451	92.79
Total:		**4.486**	**31.846**	**100.00**

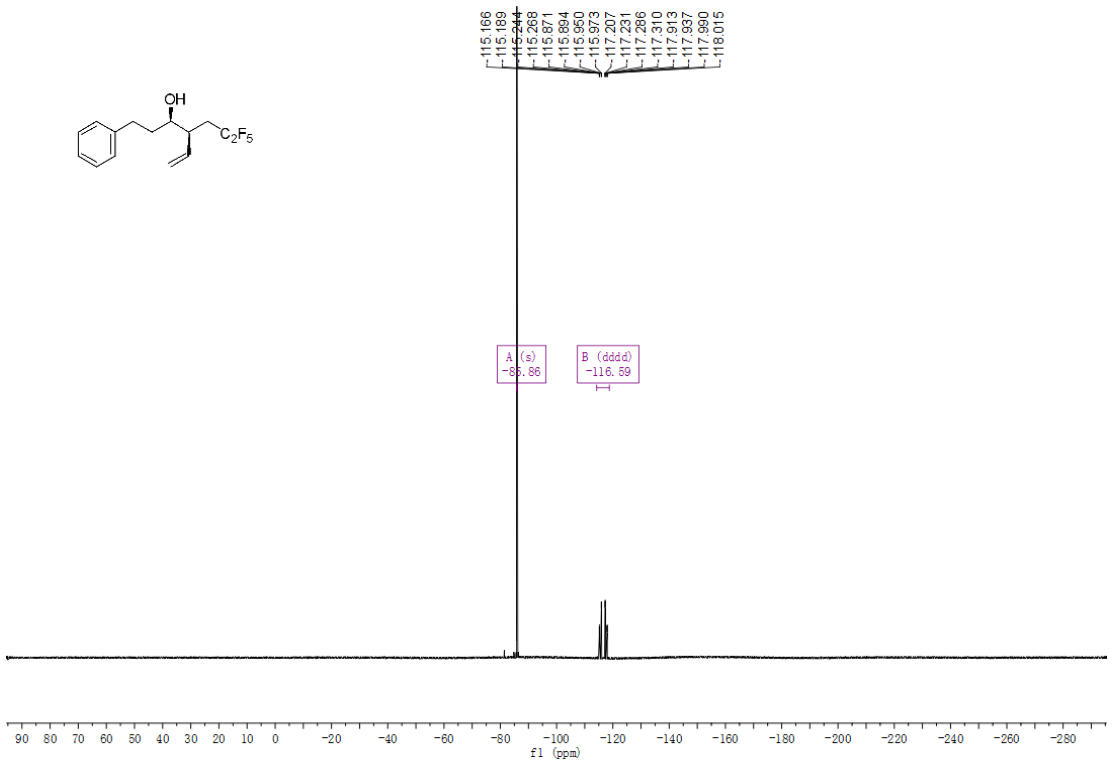
4u-^{1}H NMR



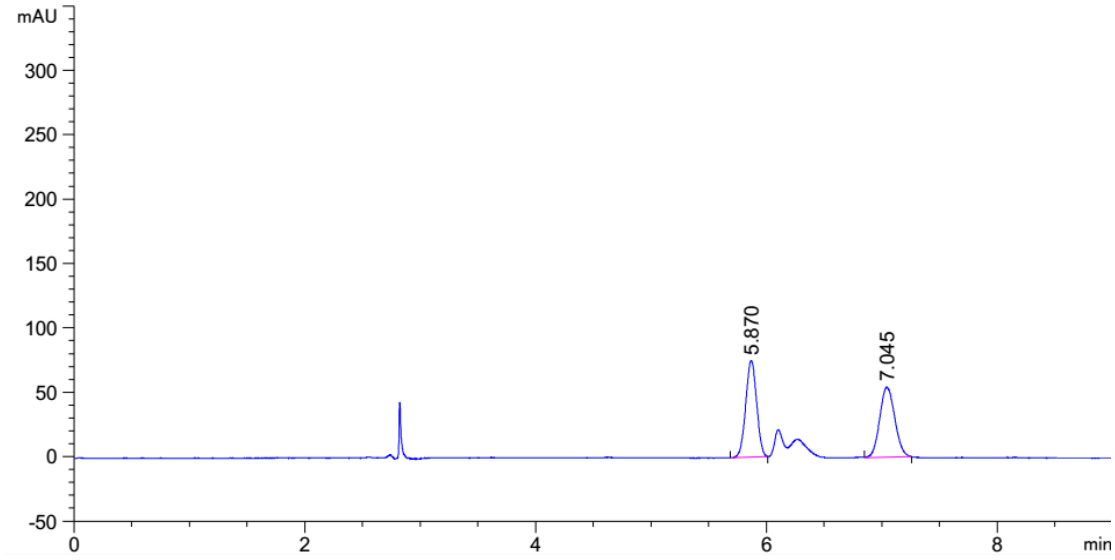
4u-^{13}C NMR



4u-^{19}F NMR

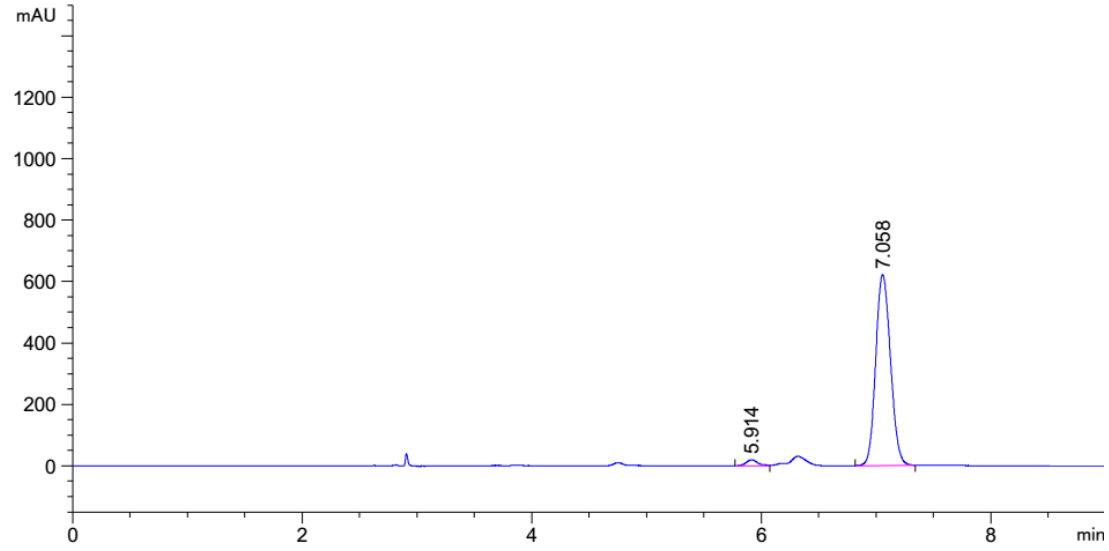


4u-HPLC (racemic)



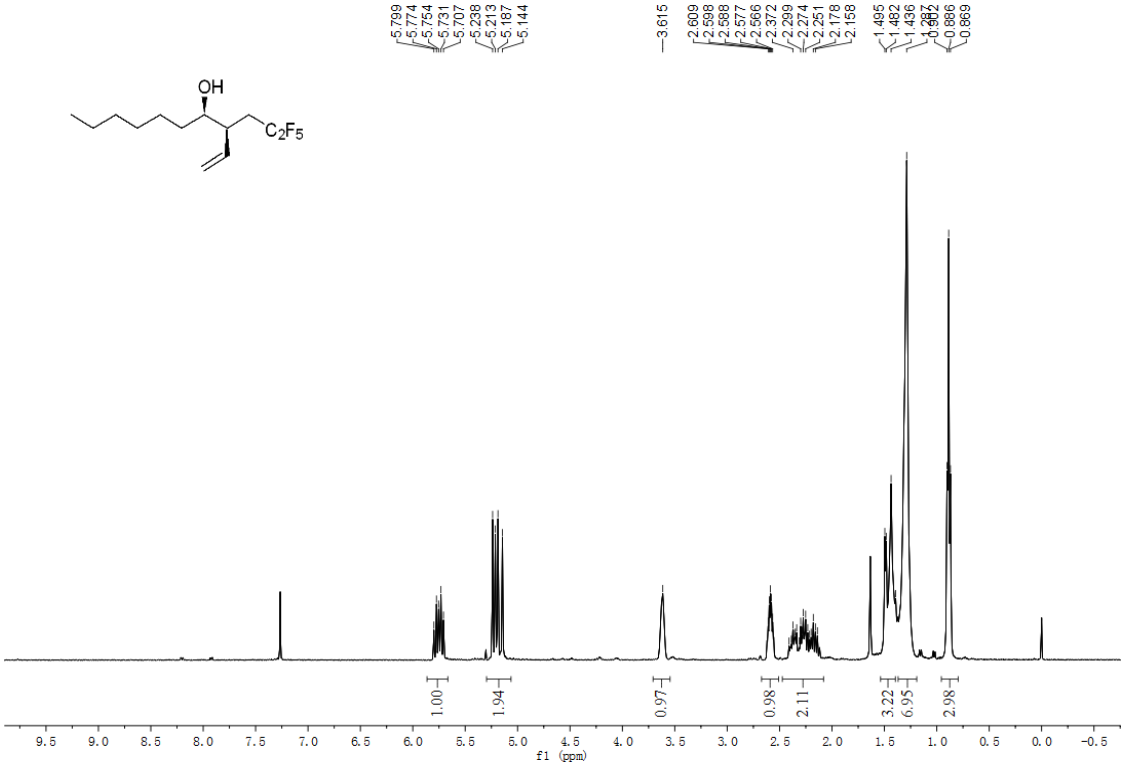
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.870	BB	0.1029	494.88611	75.04329	49.9866
2	7.045	MM R	0.1432	495.15137	54.49219	50.0134

4u-HPLC (95% ee)

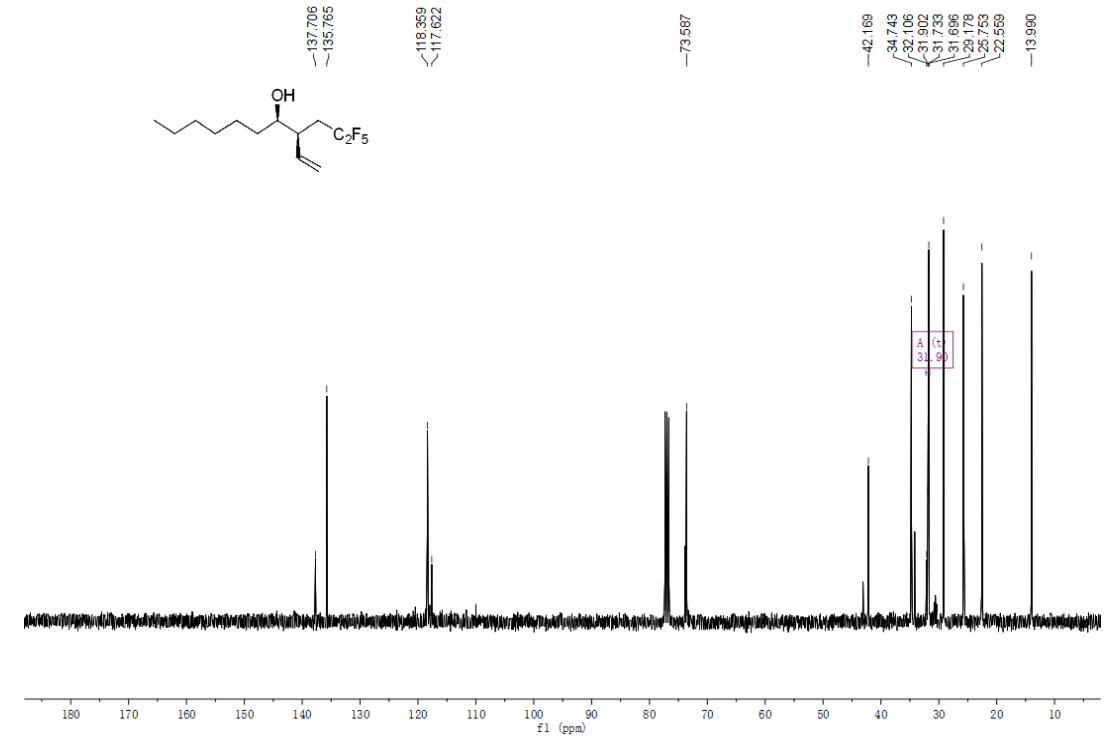


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.914	BV	0.1017	134.87636	19.25086	2.3632
2	7.058	VV	0.1401	5572.44189	621.42535	97.6368

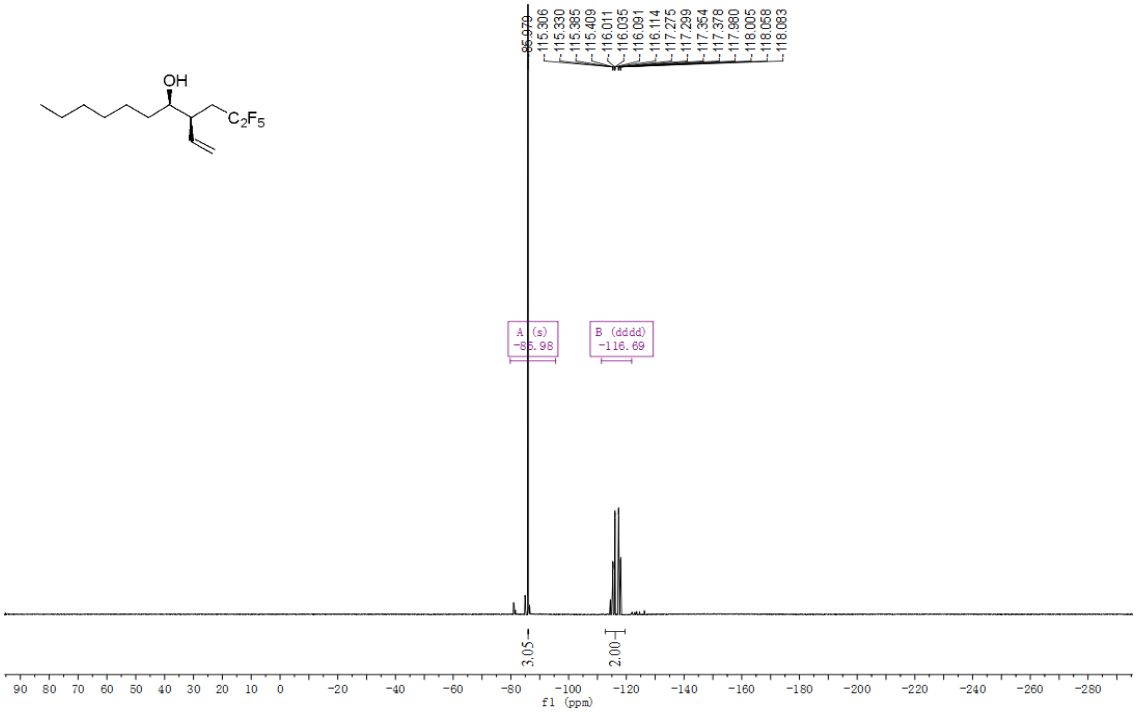
4v-^{1}H NMR



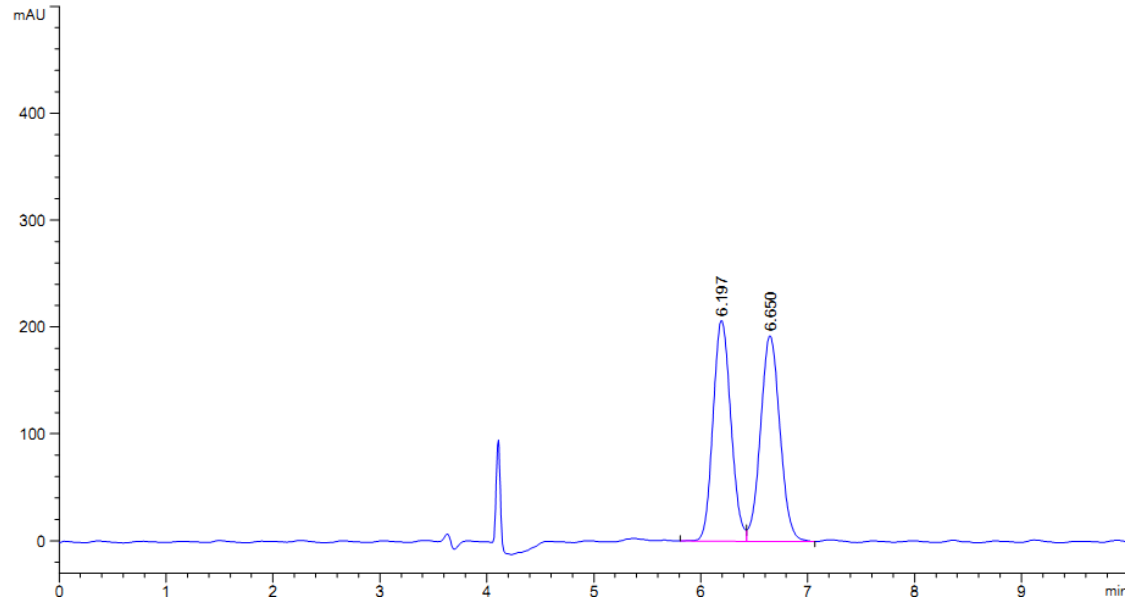
4v-^{13}C NMR



4v-^{19}F NMR

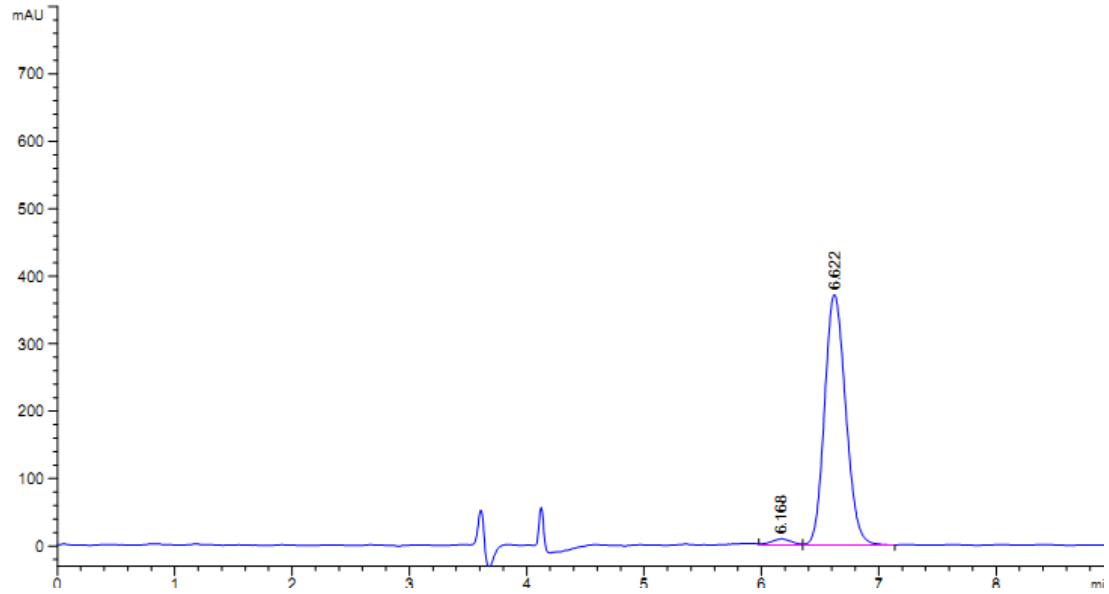


4v-HPLC (racemic)



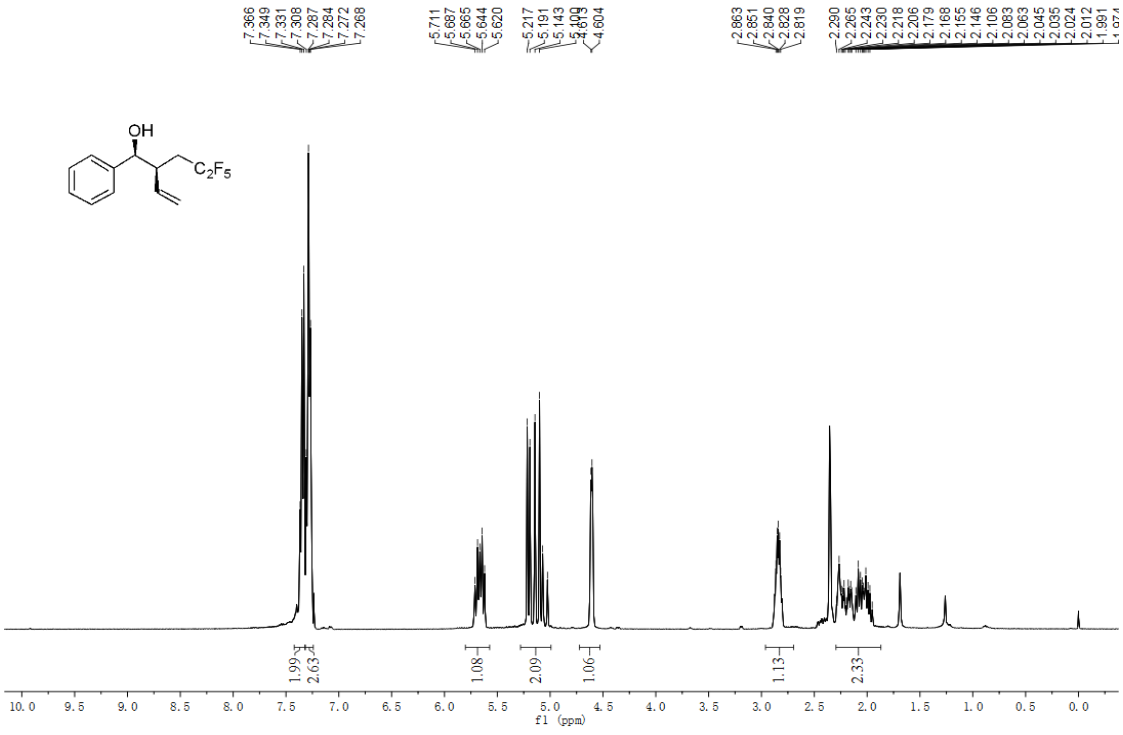
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.197	BV	0.1815	2397.58716	206.44864	49.6347
2	6.650	VB	0.1956	2432.87549	192.28307	50.3653

4v-HPLC (95.5% ee)

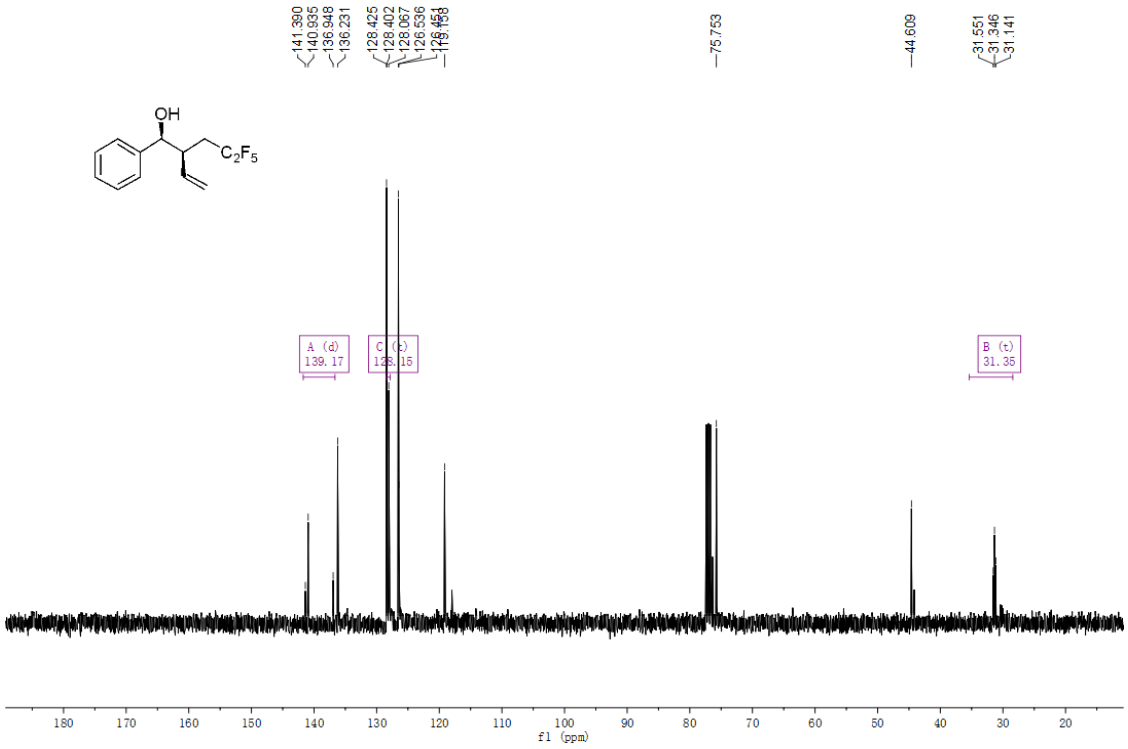


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.168	VV	0.1522	105.74618	8.79742	2.2293
2	6.622	VB	0.1956	4637.73047	371.55017	97.7707

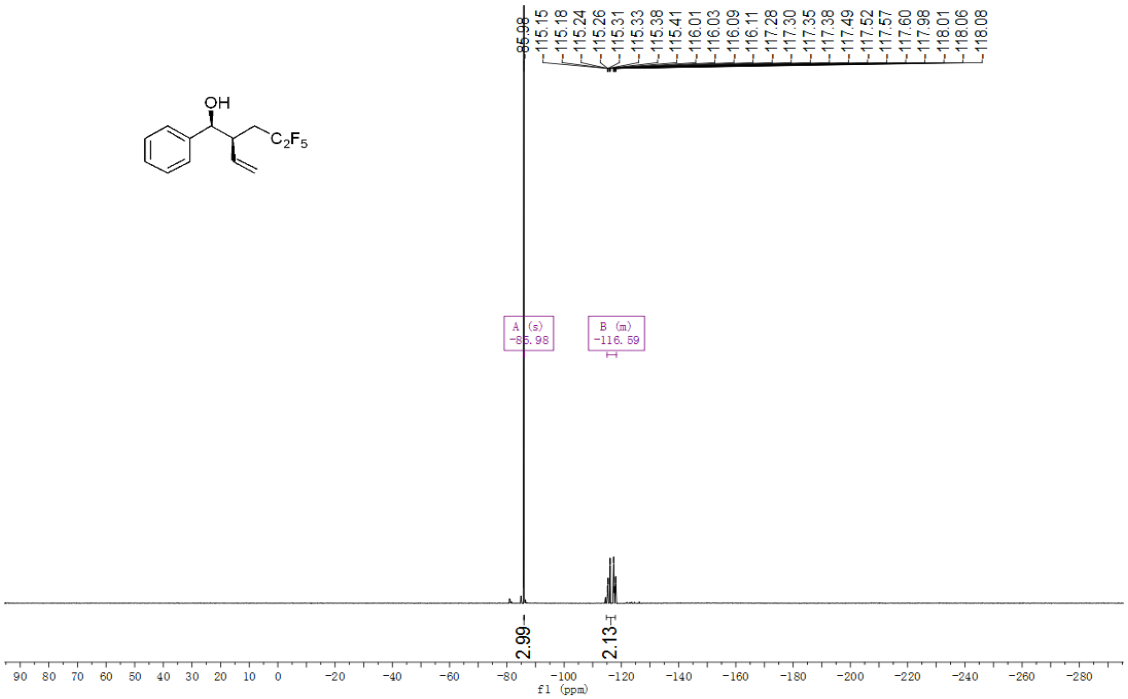
4w-^{1}H NMR



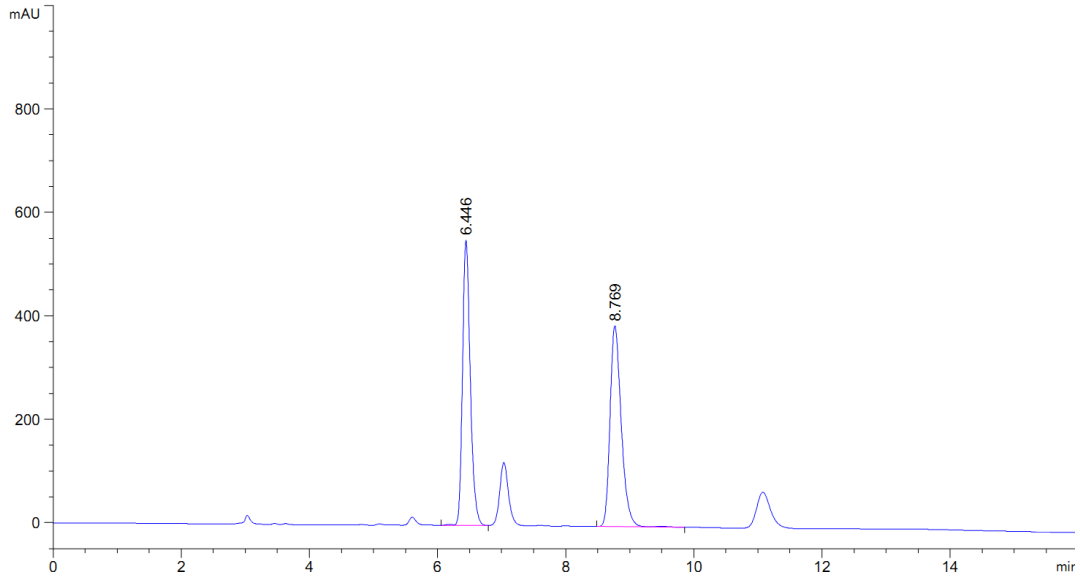
4w-^{13}C NMR



4w-^{19}F NMR

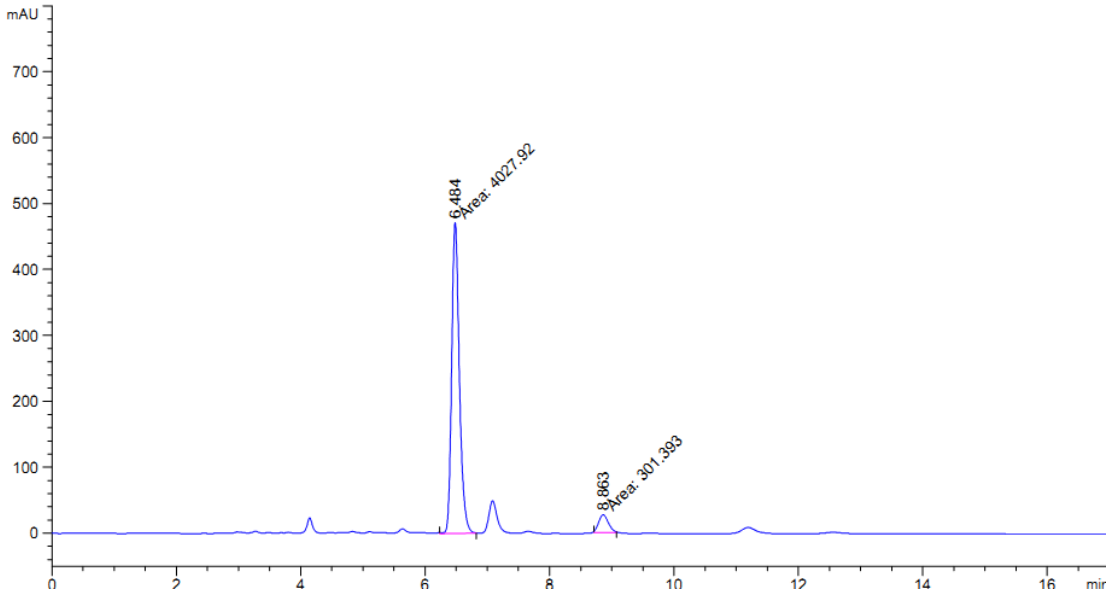


4w-HPLC (racemic)



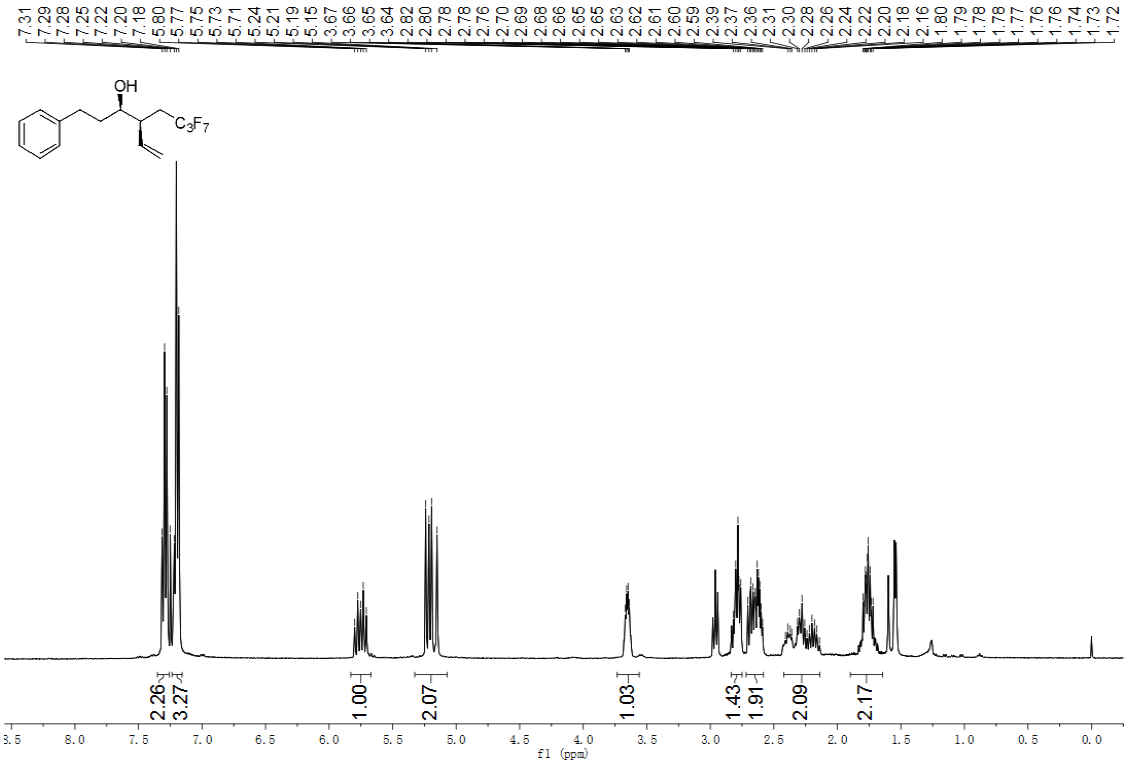
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.446	VB R	0.1290	4651.01025	551.87213	49.6730
2	8.769	BV R	0.1856	4712.25293	388.22336	50.3270

4w-HPLC (86% ee)

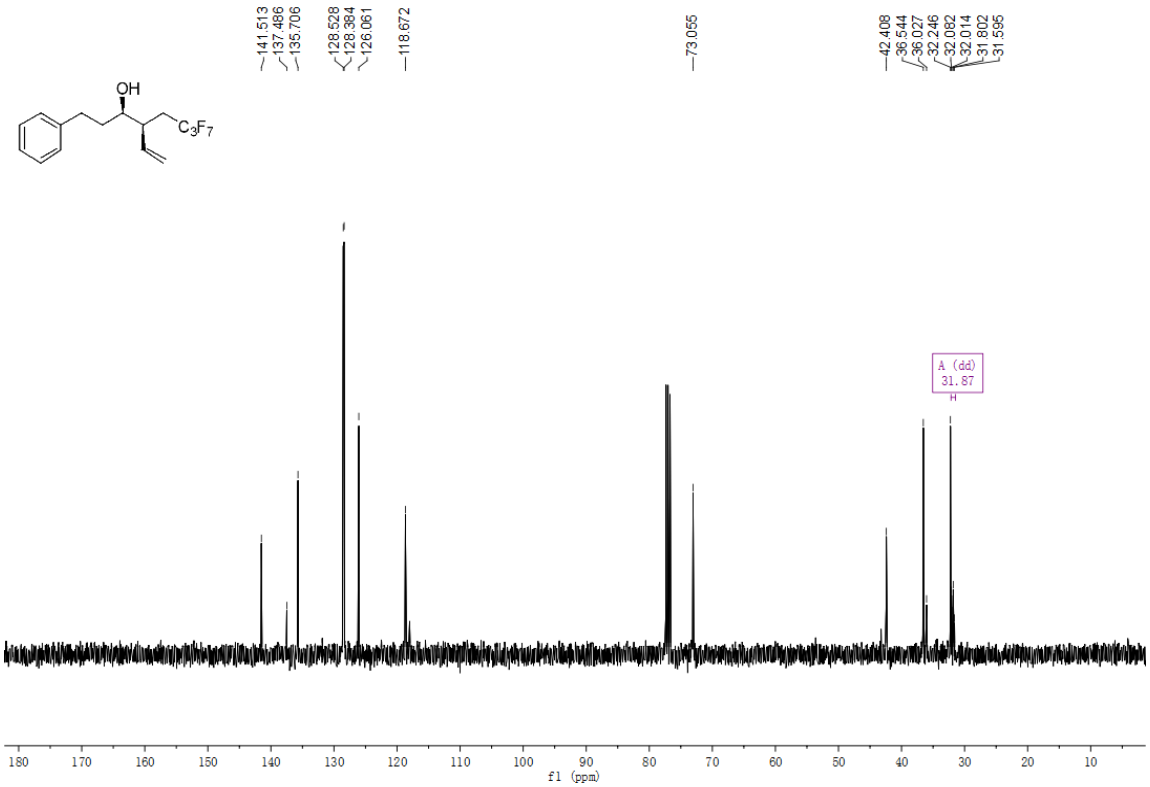


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.484	MM	0.1424	4027.92139	471.37369	93.0383
2	8.863	MM	0.1844	301.39334	27.23466	6.9617

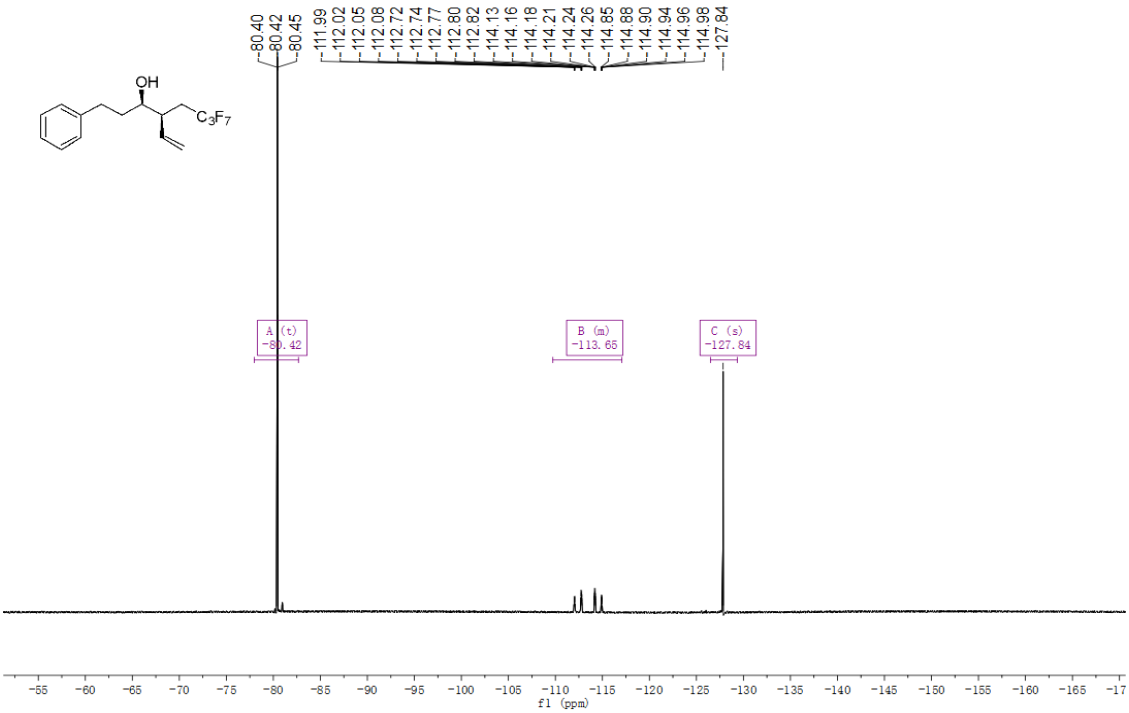
4x-^{1}H NMR



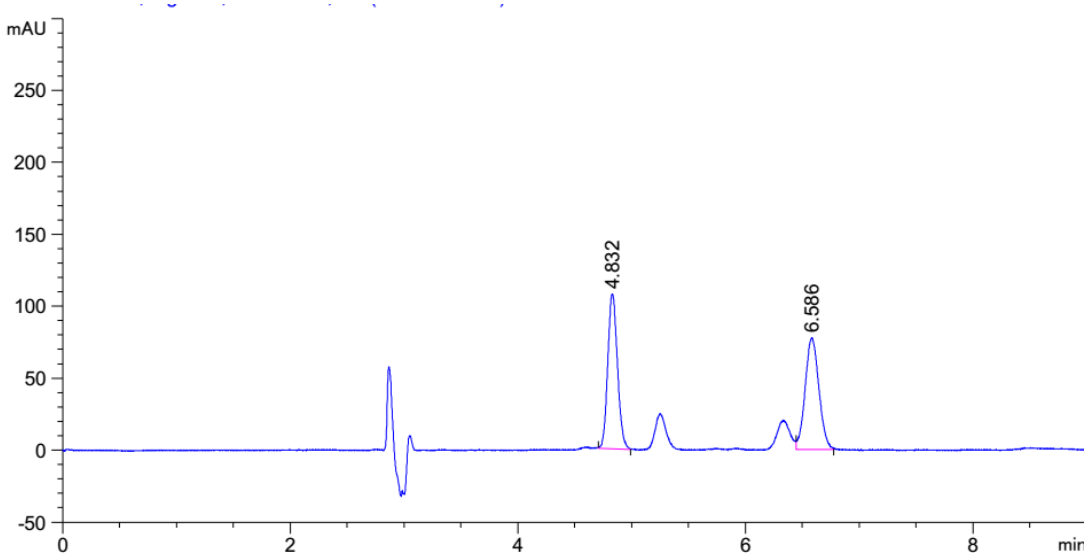
4x-^{13}C NMR



4x-^{19}F NMR

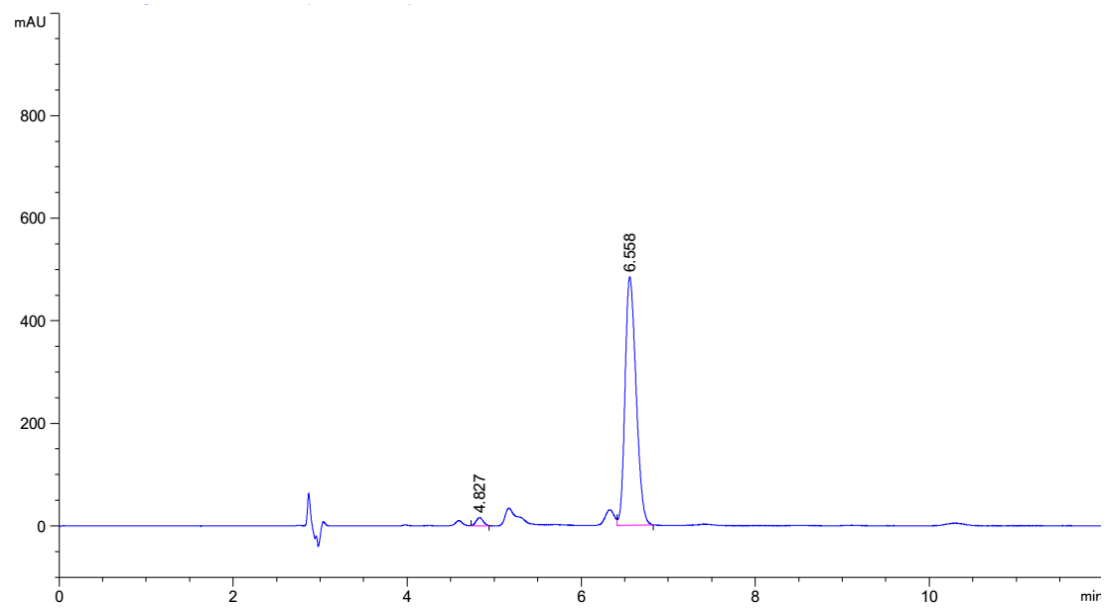


4x-HPLC (racemic)



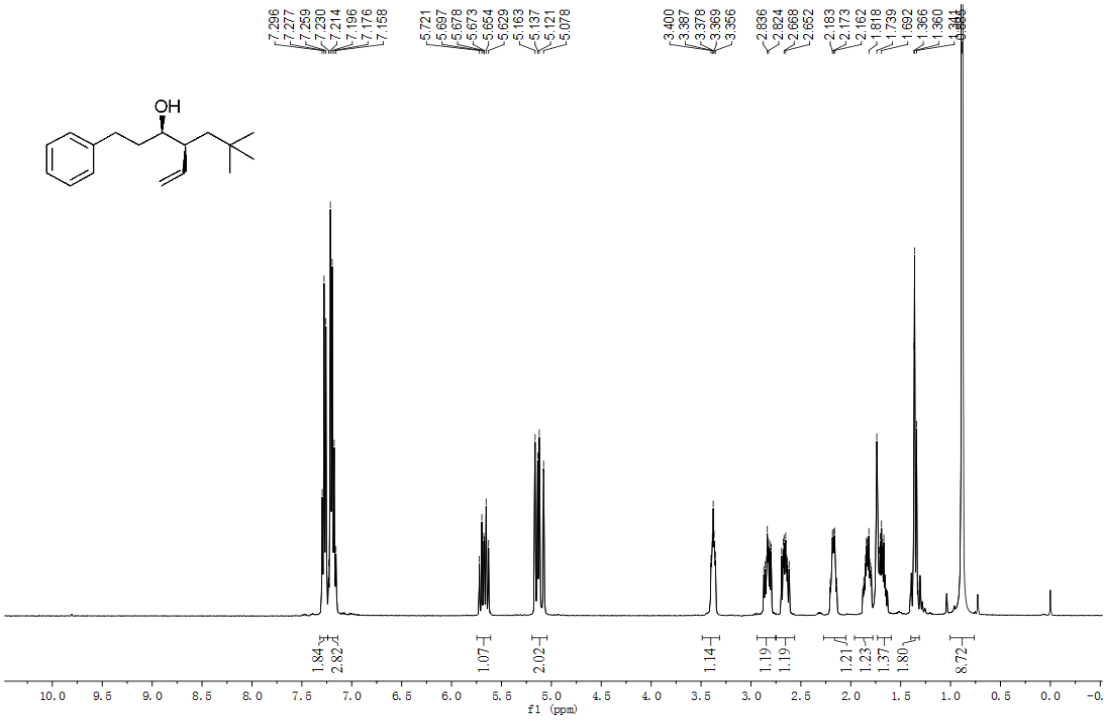
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.832	VV	0.0945	636.62933	107.66635	49.2881
2	6.586	VV	0.1194	655.01886	77.64507	50.7119

4x-HPLC (96% ee)

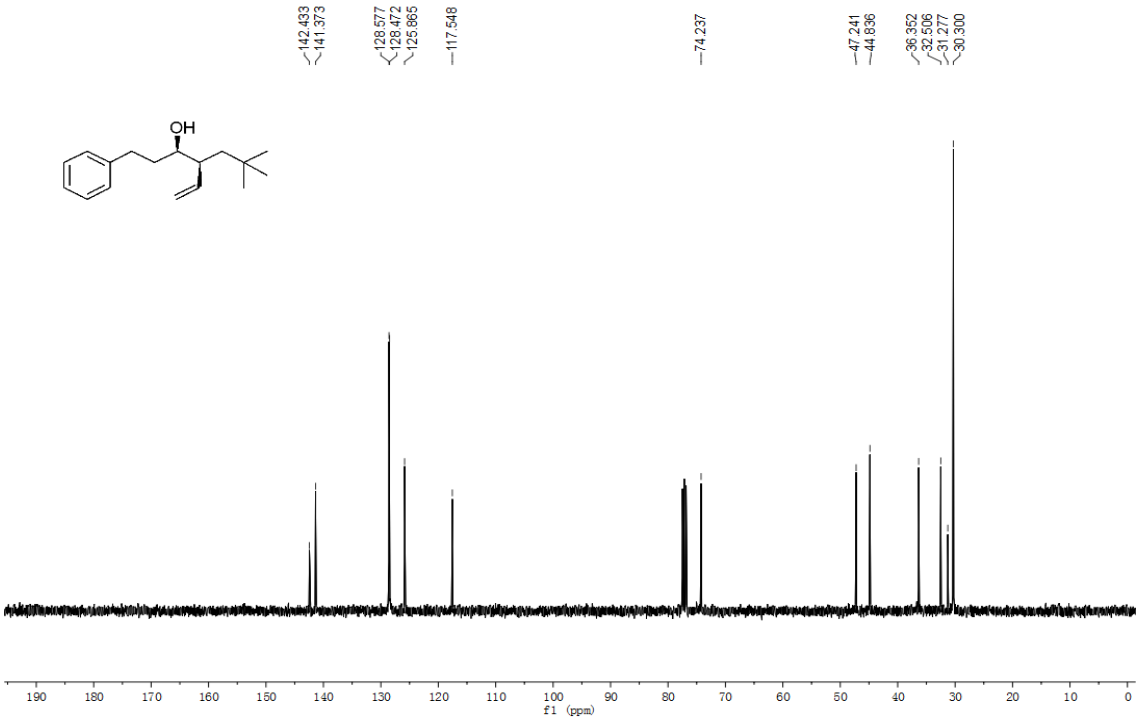


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.827	VV	0.0792	91.71584	16.15630	2.1097
2	6.558	VV	0.1365	4255.60645	484.19662	97.8903

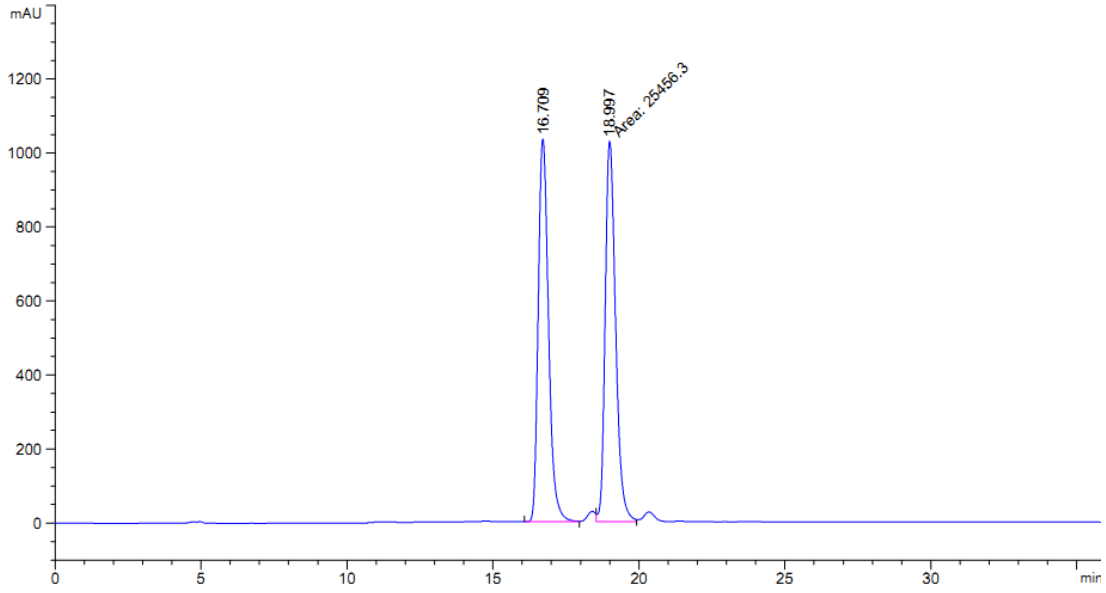
4y-^{1}H NMR



4y-^{13}C NMR

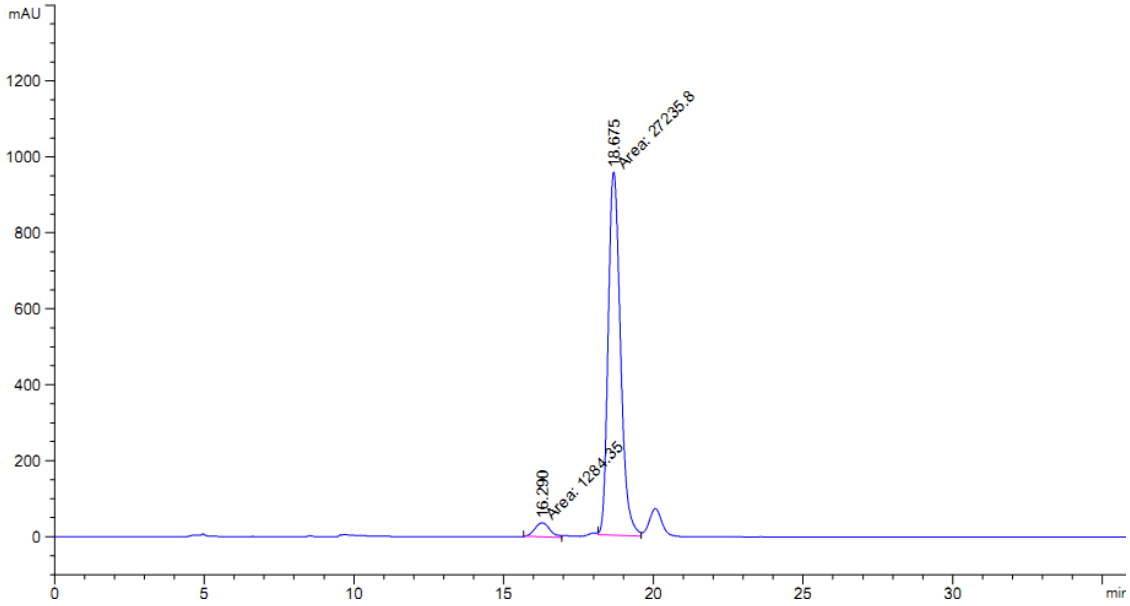


4y-HPLC (racemic)



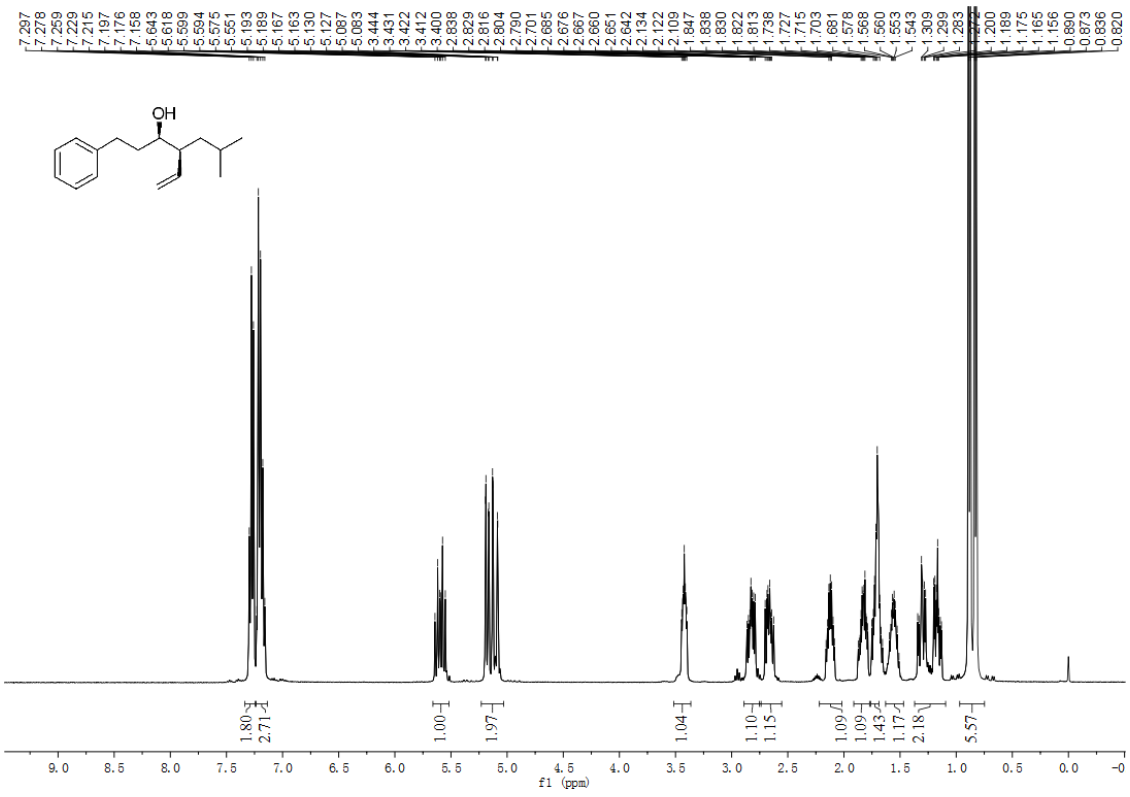
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.709	BB	0.3829	2.53316e4	1033.73682	49.8772
2	18.997	FM	0.4128	2.54563e4	1027.89185	50.1228

4y-HPLC (91% ee)

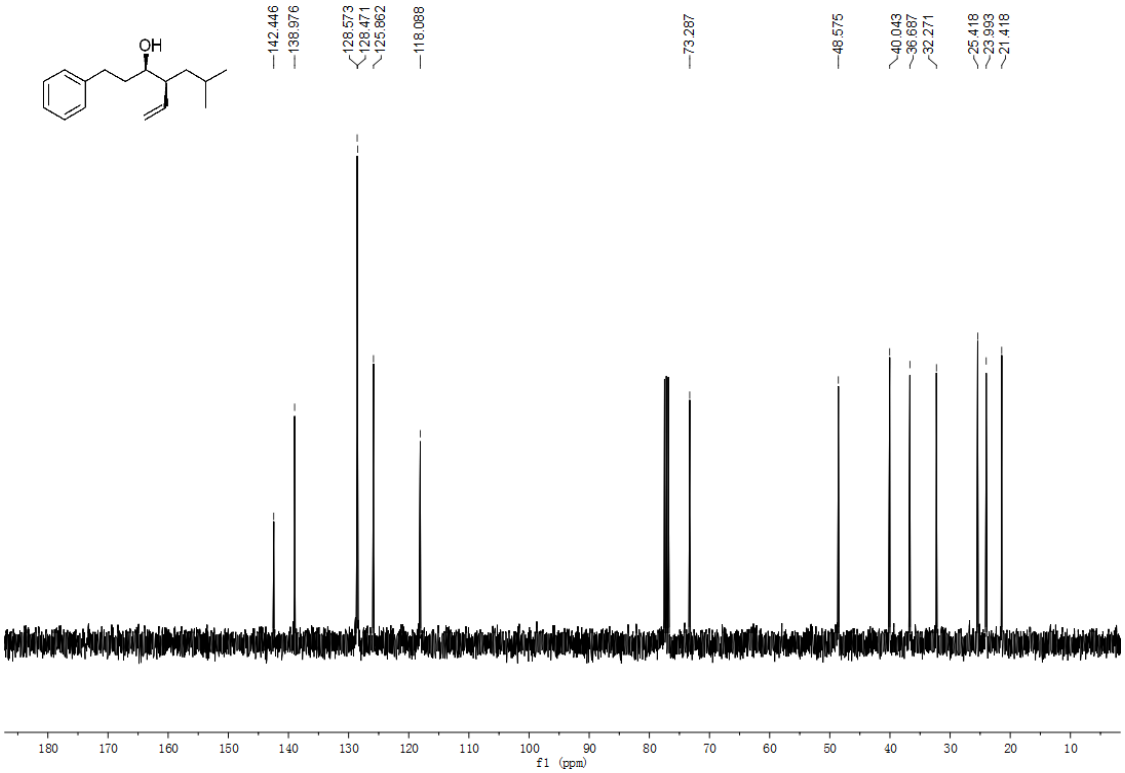


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.290	MM	0.5891	1284.35144	36.33853	4.5033
2	18.675	MM	0.4746	2.72358e4	956.48358	95.4967

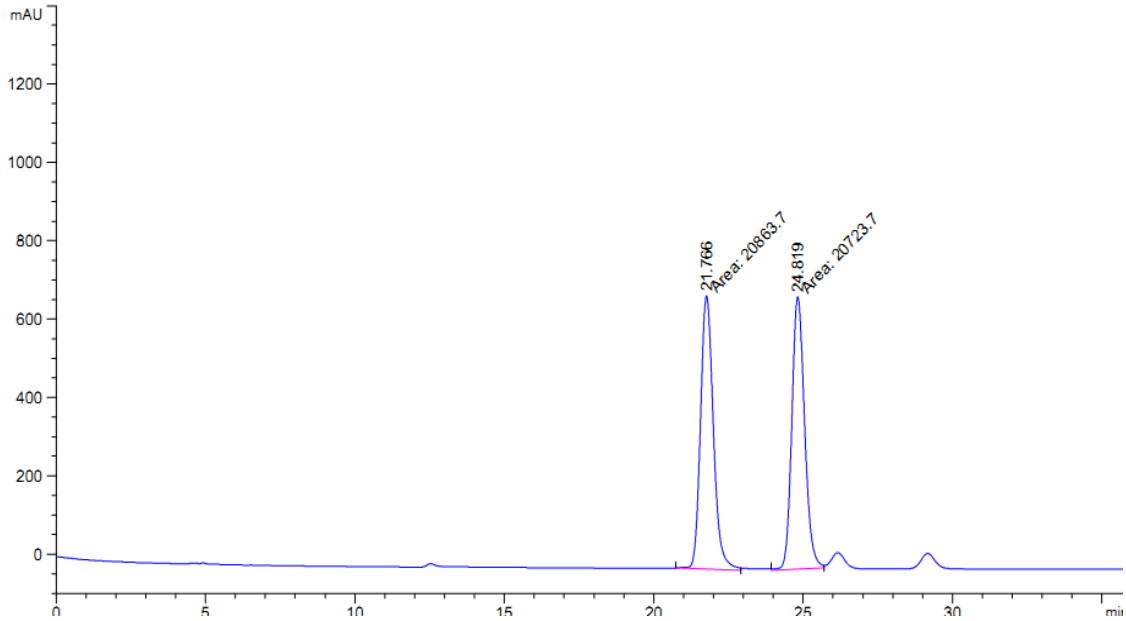
4z-^{1}H NMR



4z-^{13}C NMR

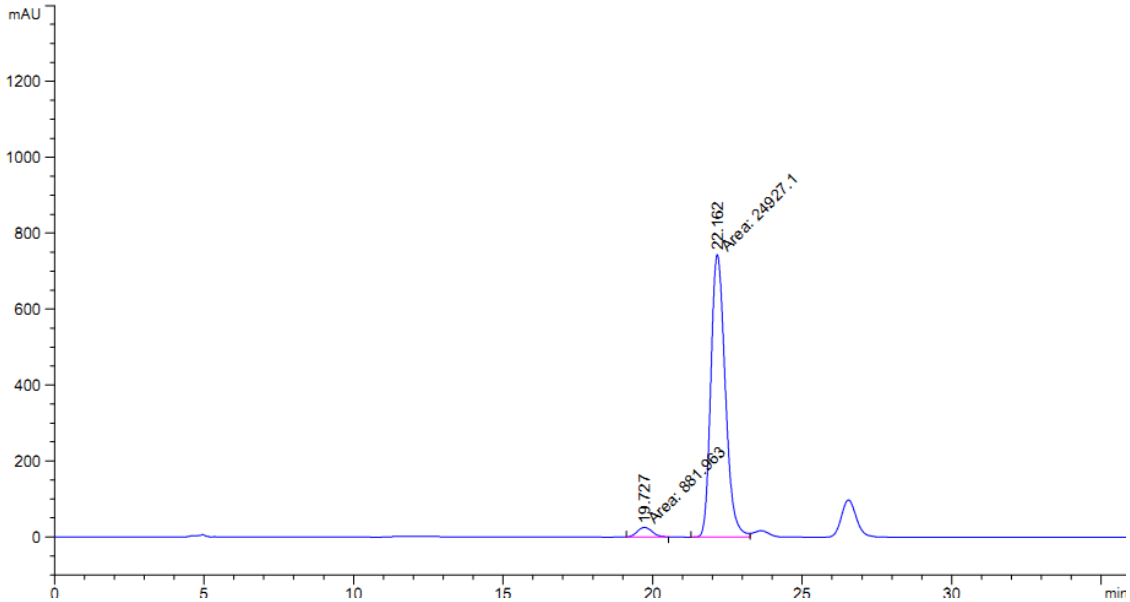


4z-HPLC (racemic)



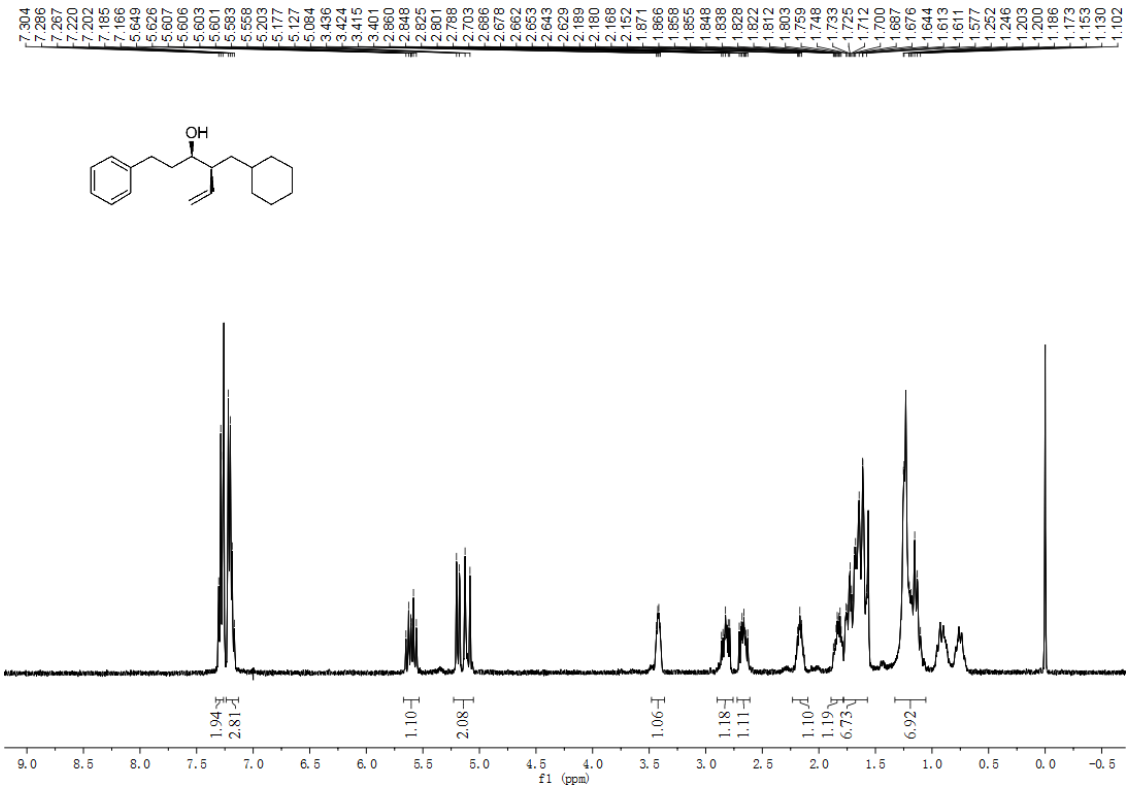
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.766	MM	0.4985	2.08637e4	697.54065	50.1683
2	24.819	MM	0.4964	2.07237e4	695.80939	49.8317

4z-HPLC (93% ee)

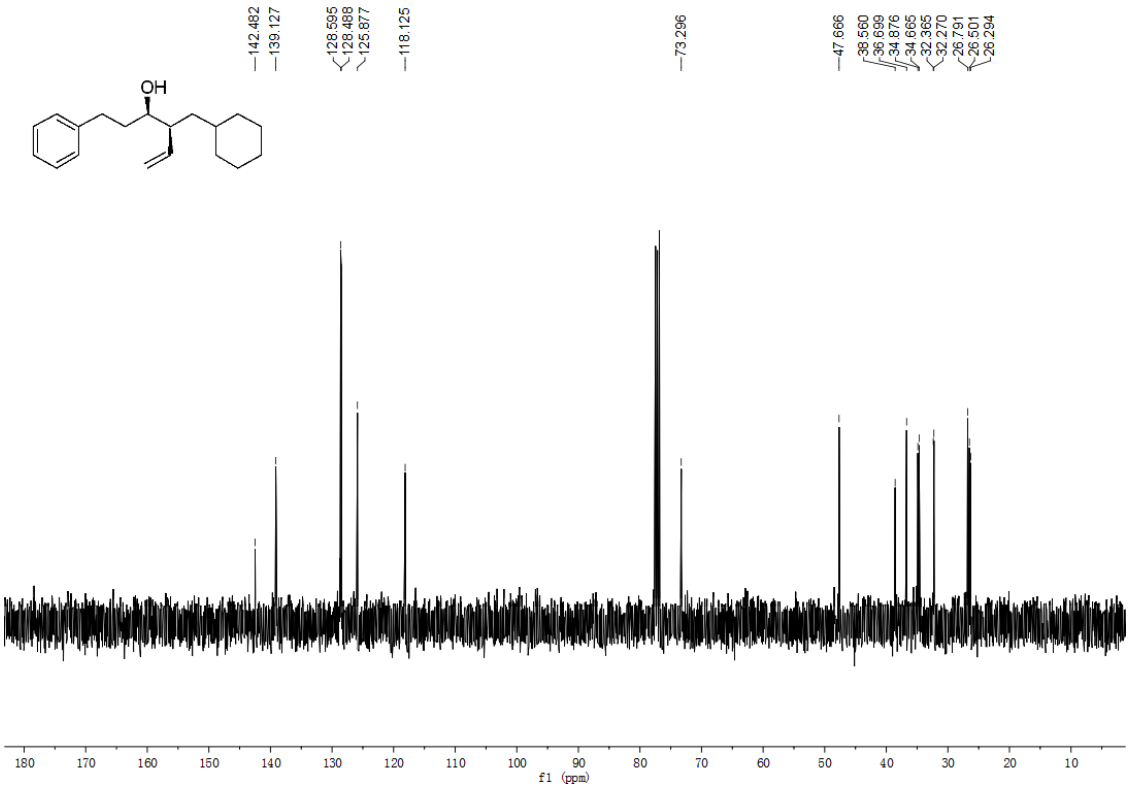


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.727	MM	0.5823	881.96295	25.24392	3.4173
2	22.162	MM	0.5584	2.49271e4	744.02155	96.5827

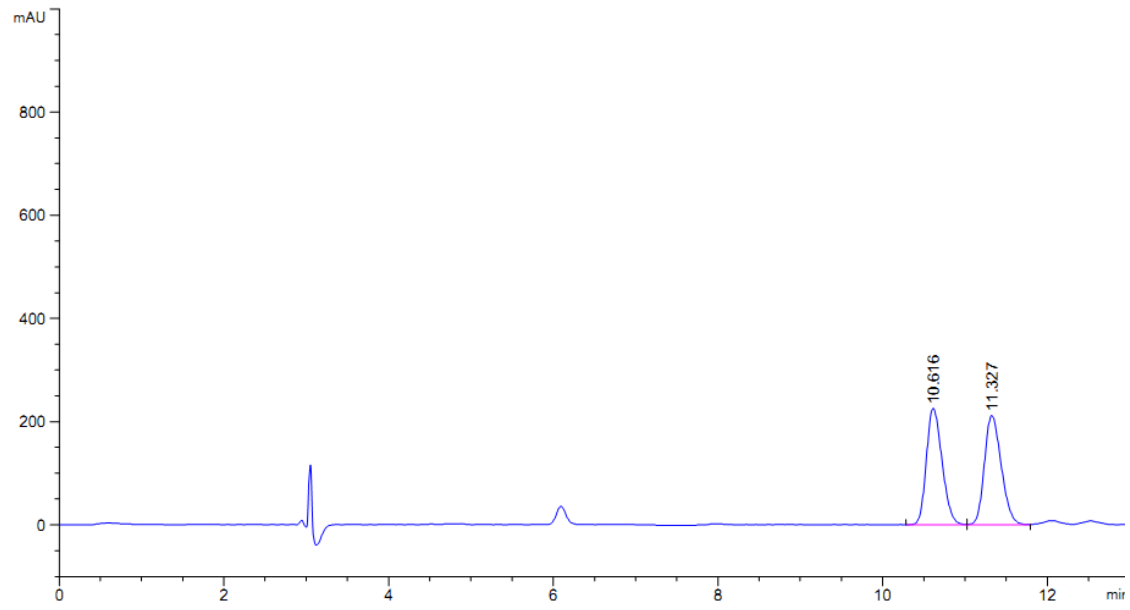
4aa-^{1}H NMR



4aa-^{13}C NMR

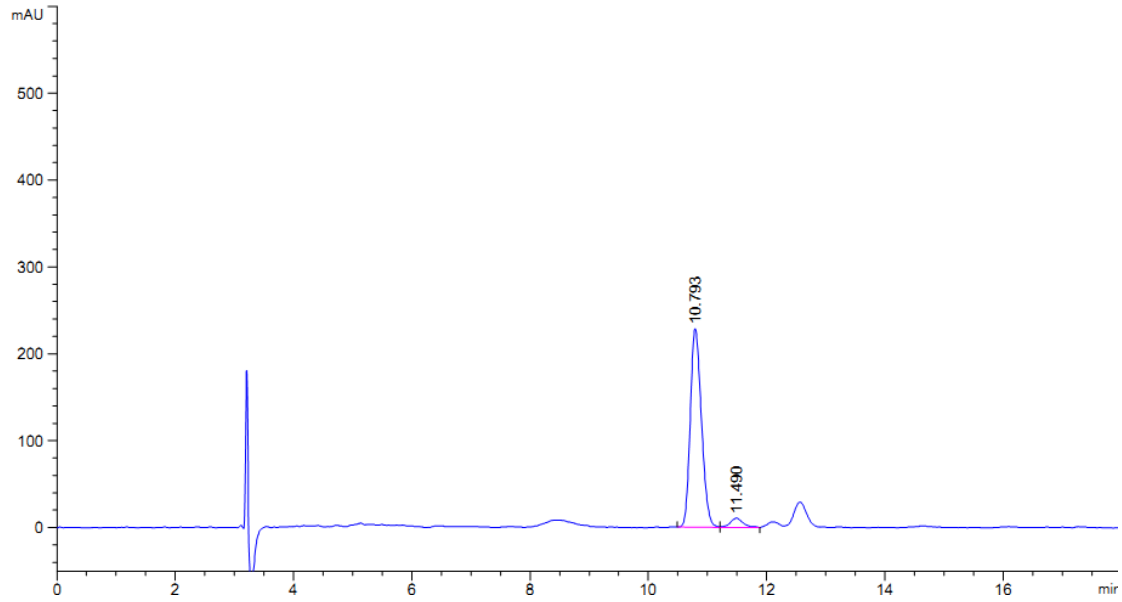


4aa-HPLC (racemic)



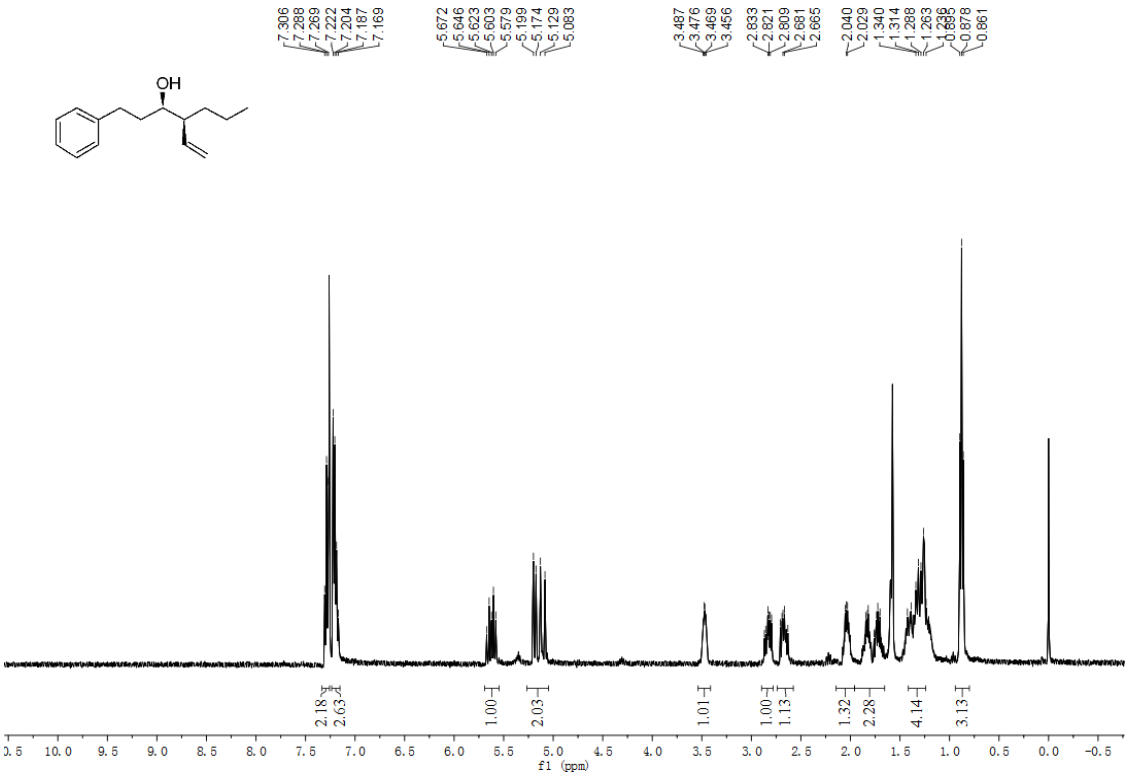
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.616	BV	0.2062	2986.45850	225.92451	49.7665
2	11.327	VV	0.2218	3014.47925	212.16443	50.2335

4aa-HPLC (90% ee)

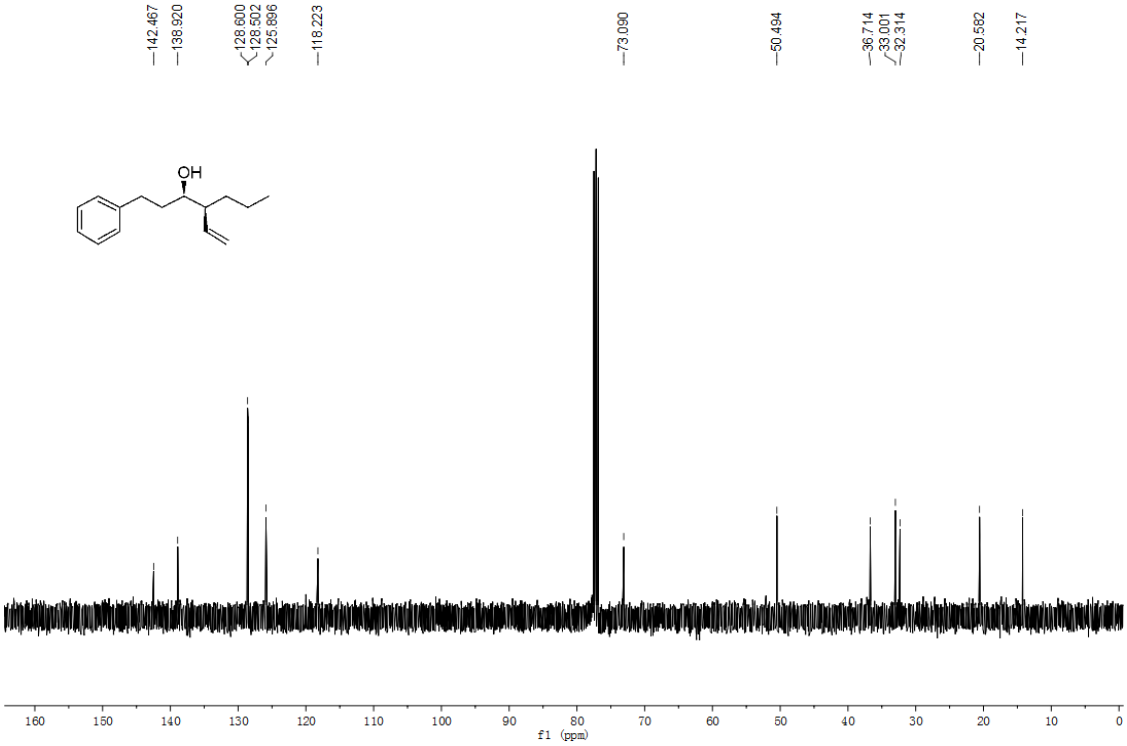


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.793	BV	0.2028	2991.42529	228.37743	94.9856
2	11.490	VB	0.1958	157.92134	10.48013	5.0144

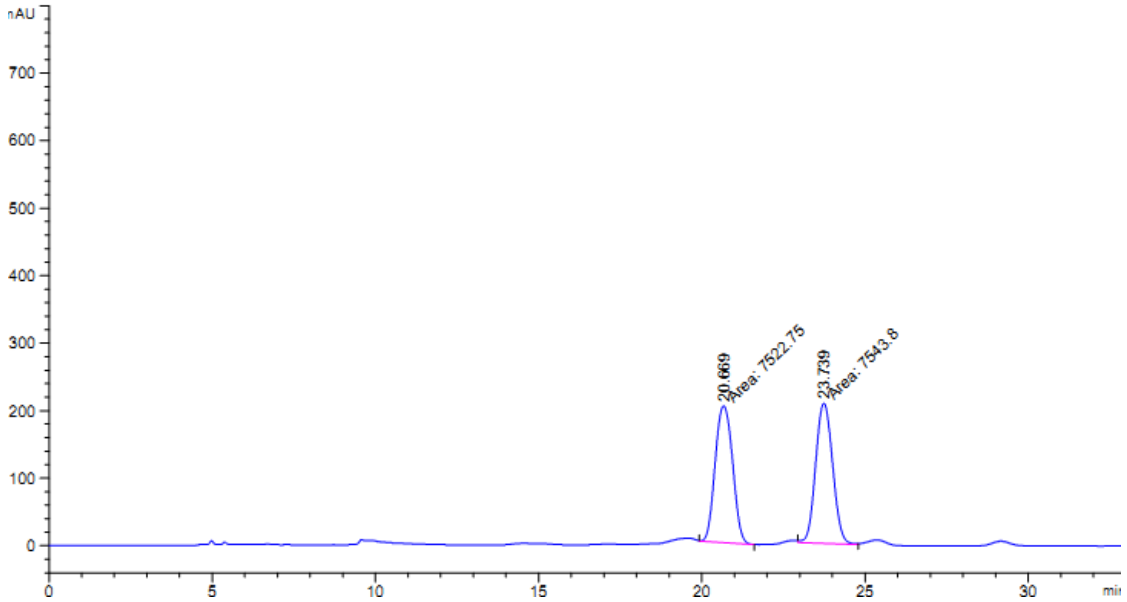
4ab-^{1}H NMR



4ab-^{13}C NMR

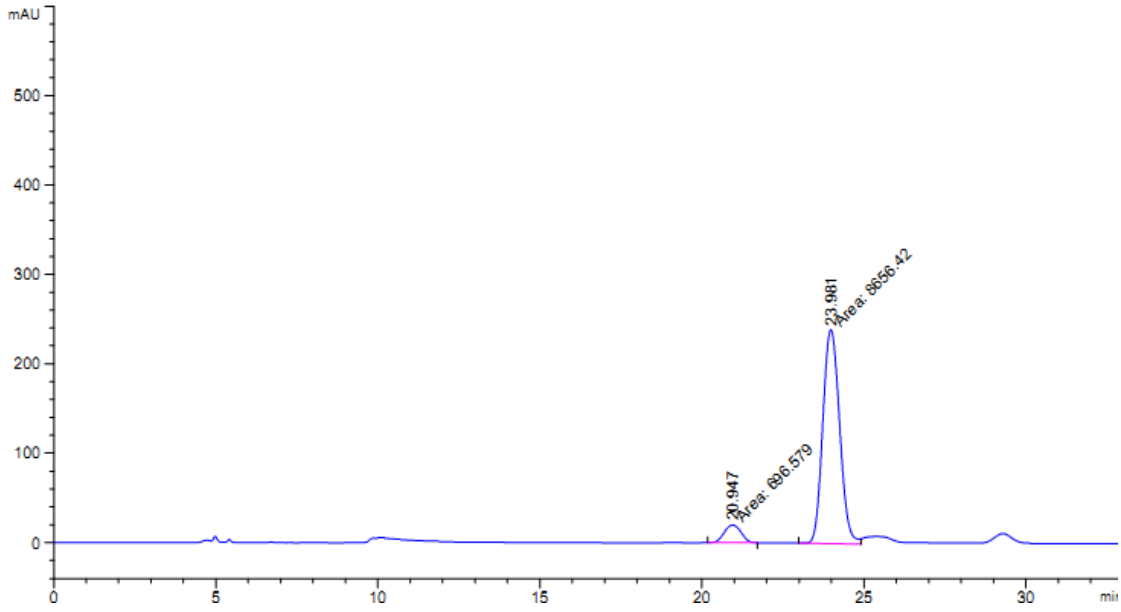


4ab-HPLC (racemic)



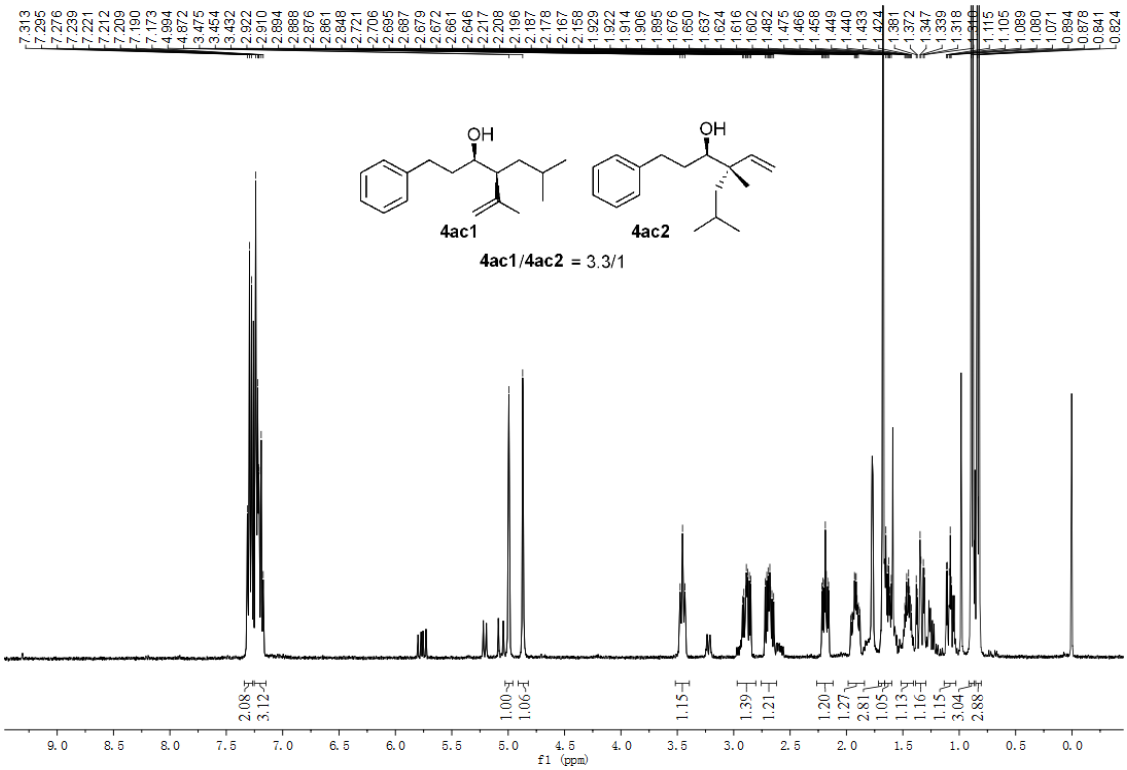
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.669	FM	0.6191	7522.74805	202.50607	49.9301
2	23.739	MM	0.6054	7543.80225	207.67487	50.0699

4ab-HPLC (85% ee)

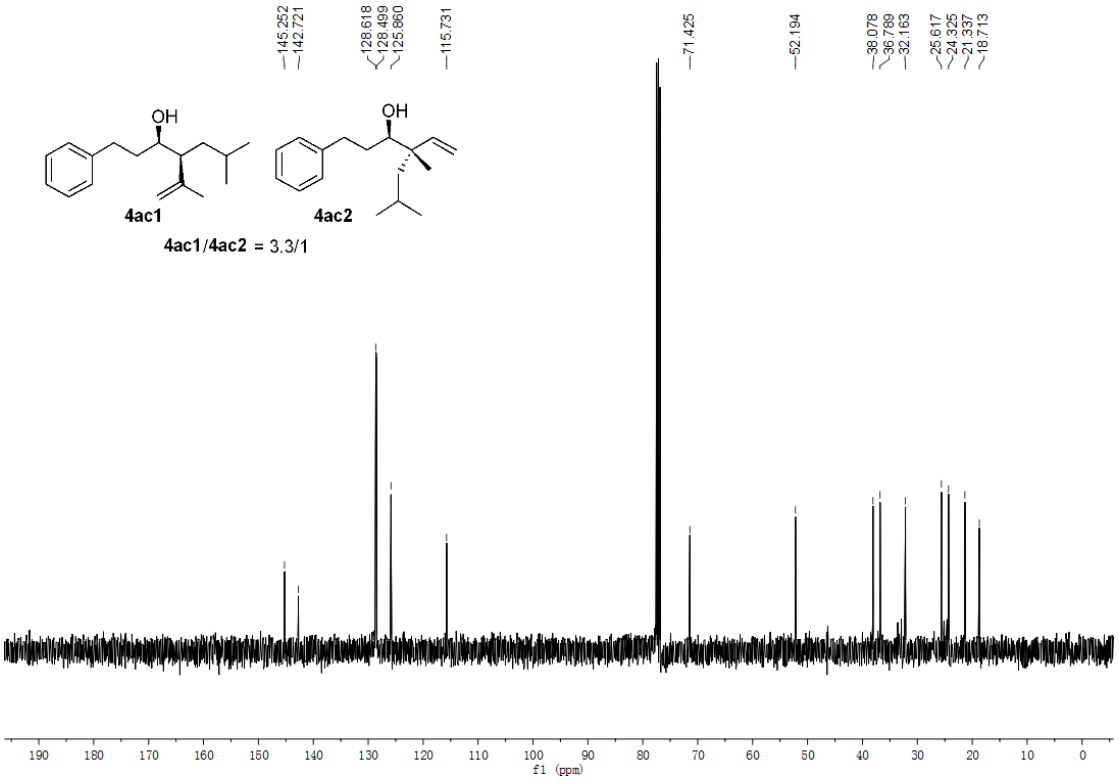


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.947	MM	0.5977	696.57892	19.42451	7.4476
2	23.981	MM	0.6031	8656.42480	239.21062	92.5524

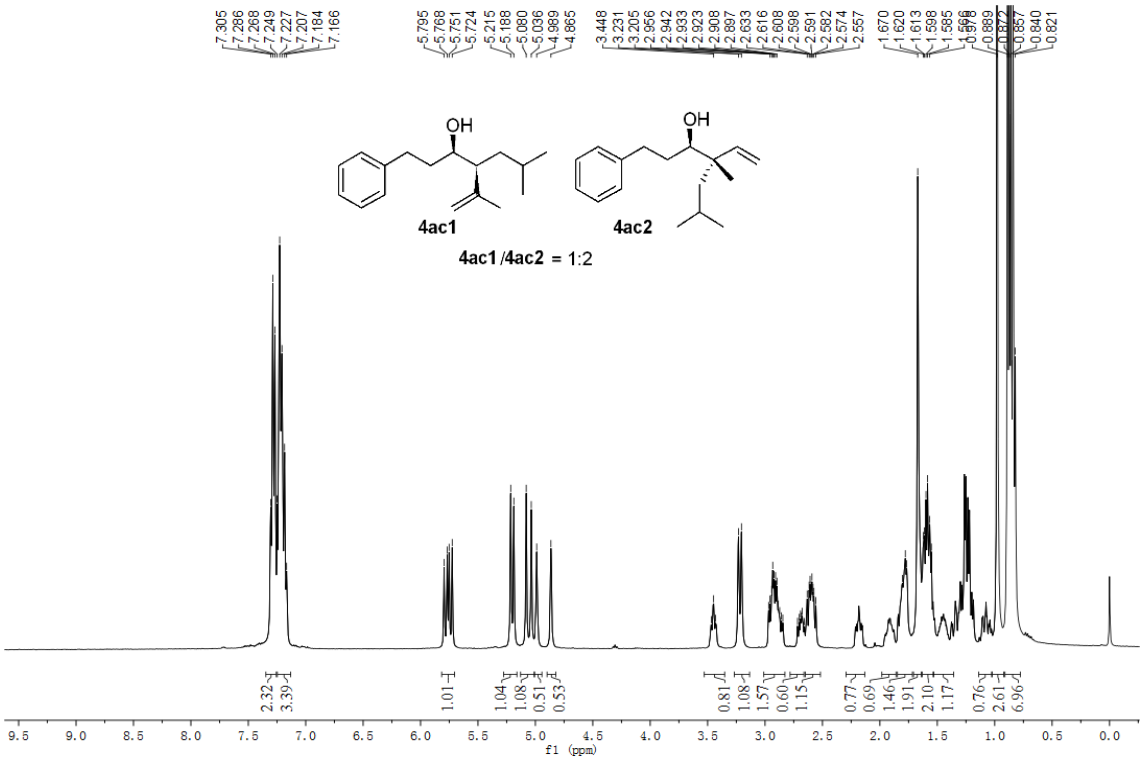
4ac1-^{1}H NMR (98% ee)



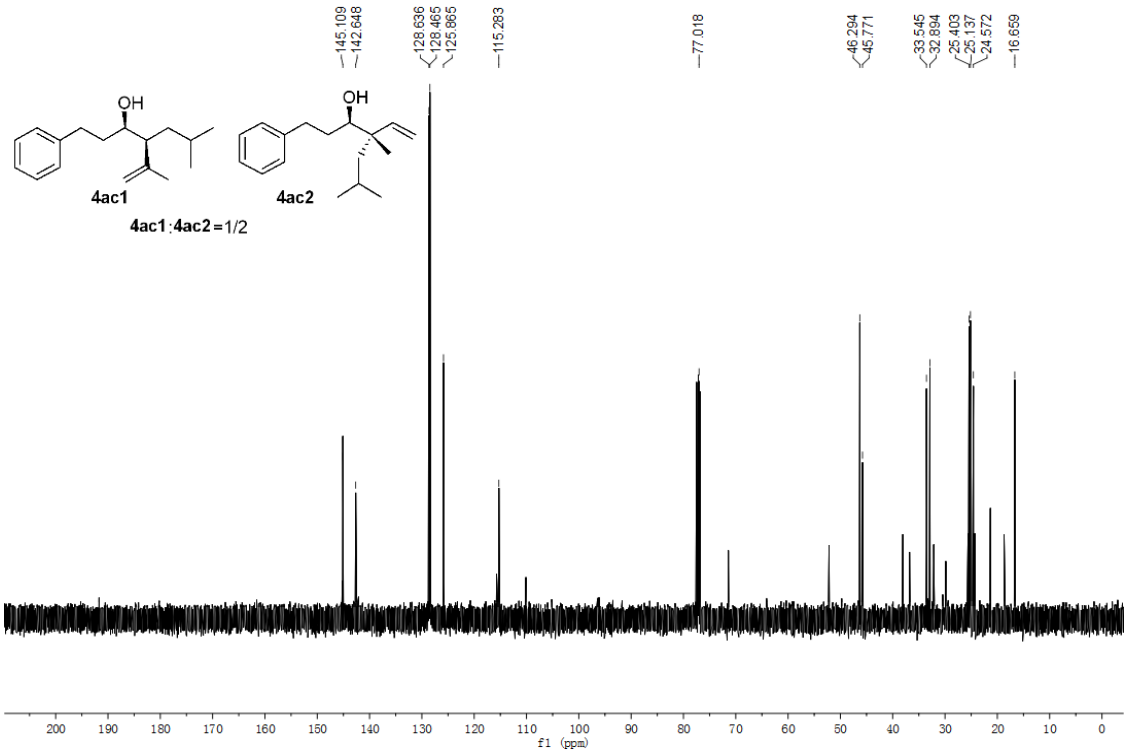
4ac1-^{13}C NMR (98% ee)



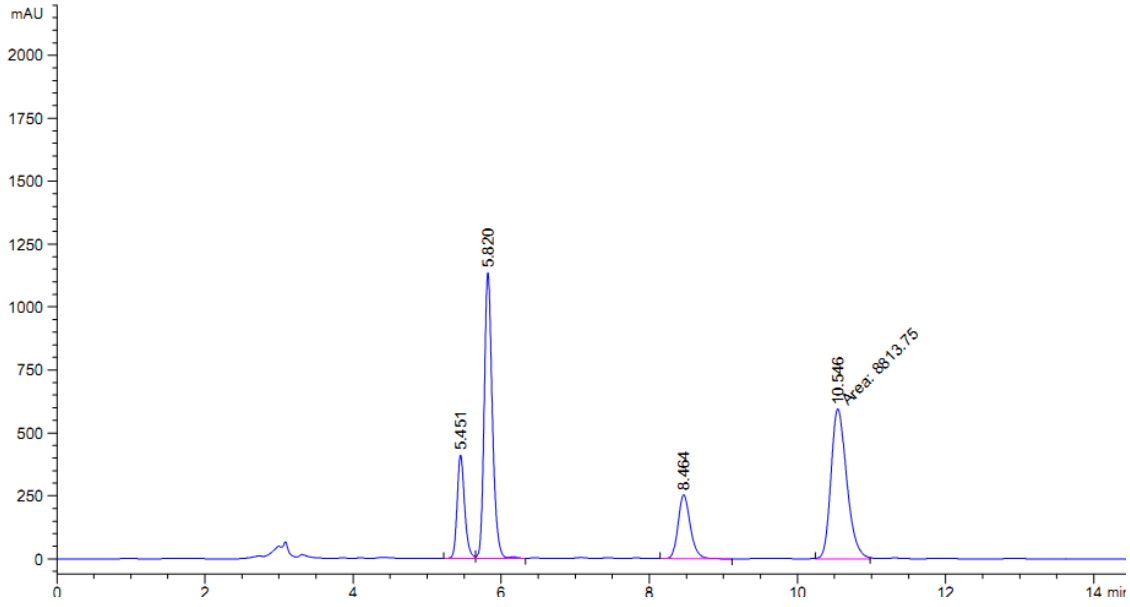
4ac2-^{1}H NMR (racemic)



4ac2-^{13}C NMR (racemic)

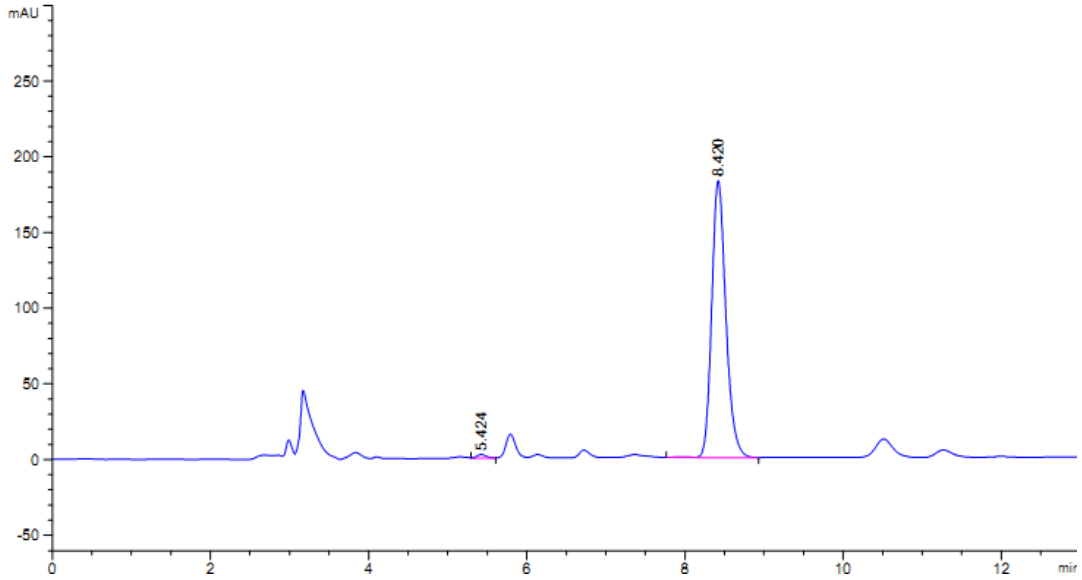


4ac1 and **4ac2**- HPLC (racemic)



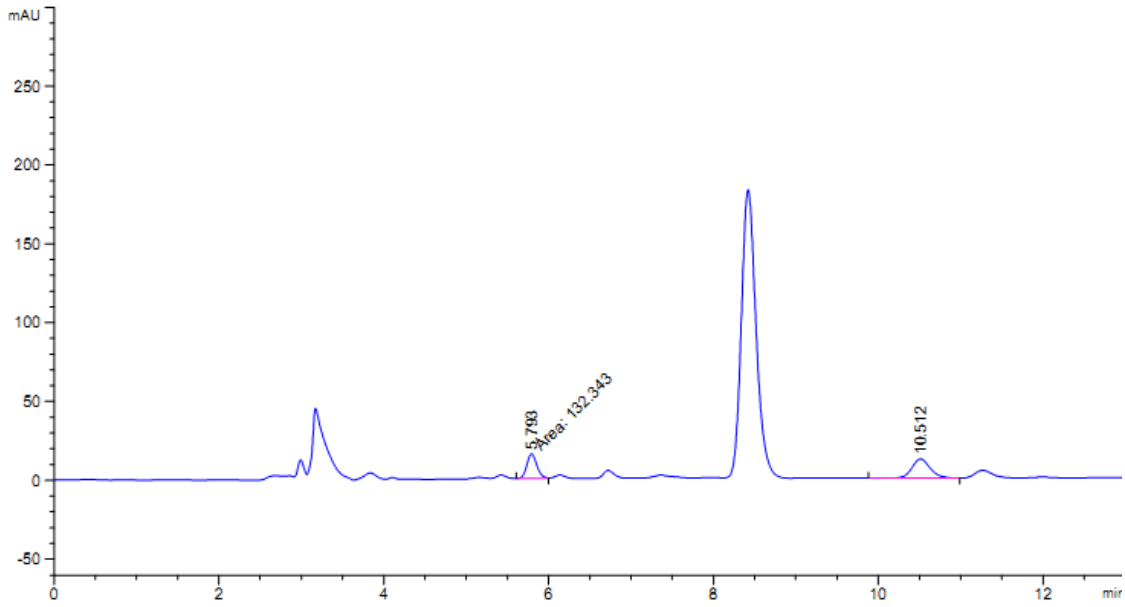
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.451	BV	0.1077	2912.32666	411.09518	12.4568
2	5.820	VV R	0.1173	8732.84375	1135.82727	37.3528
3	8.464	BB	0.1763	2920.40186	253.71291	12.4914
4	10.546	FM	0.2467	8813.75195	595.47772	37.6989

4ac1-HPLC (98% ee)



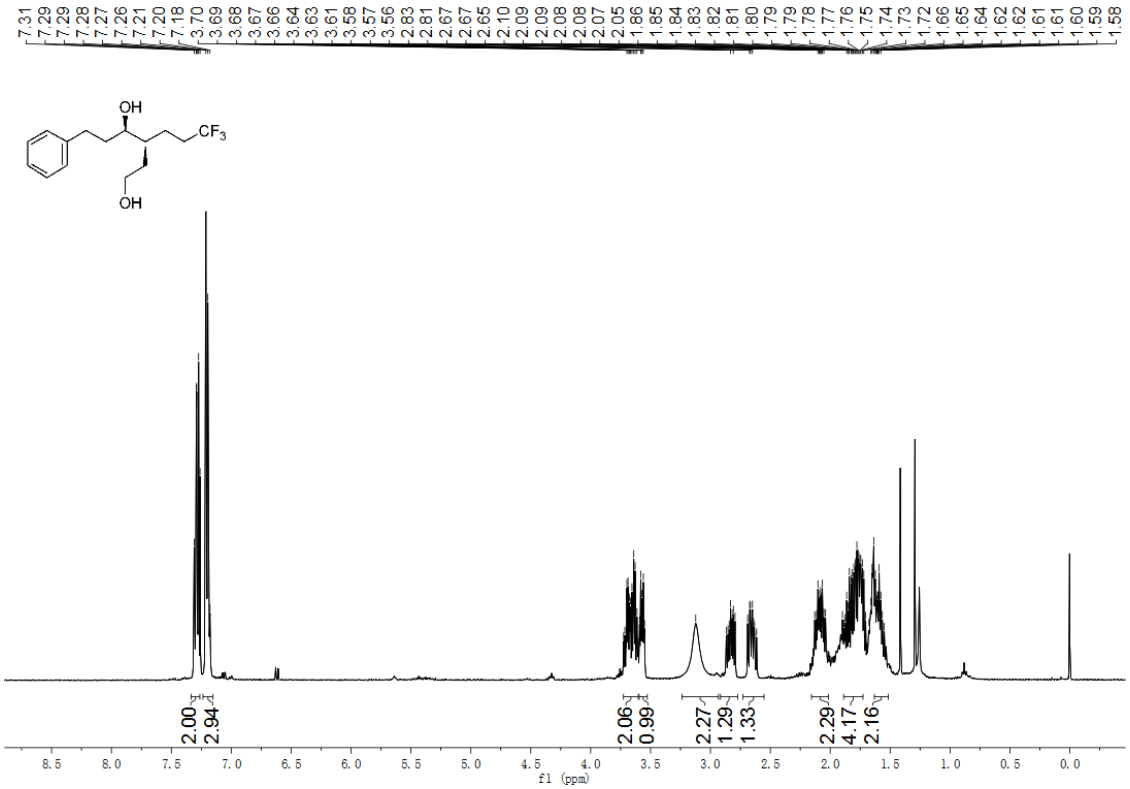
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.424	VB	0.1232	18.40837	2.30433	0.8002
2	8.420	VB R	0.1905	2282.06323	182.97598	99.1998

4ac2-HPLC (18% ee)

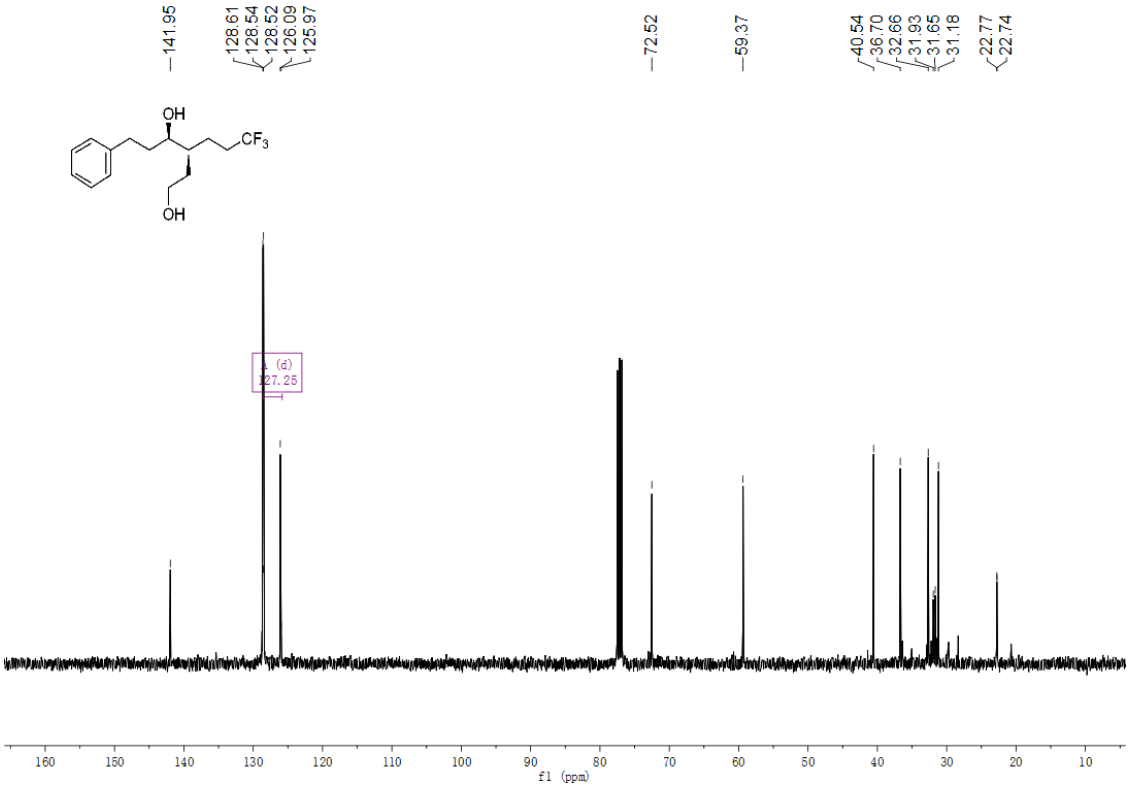


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.793	MF	0.1412	132.34335	15.61635	41.1781
2	10.512	BB	0.2380	189.04900	12.11740	58.8219

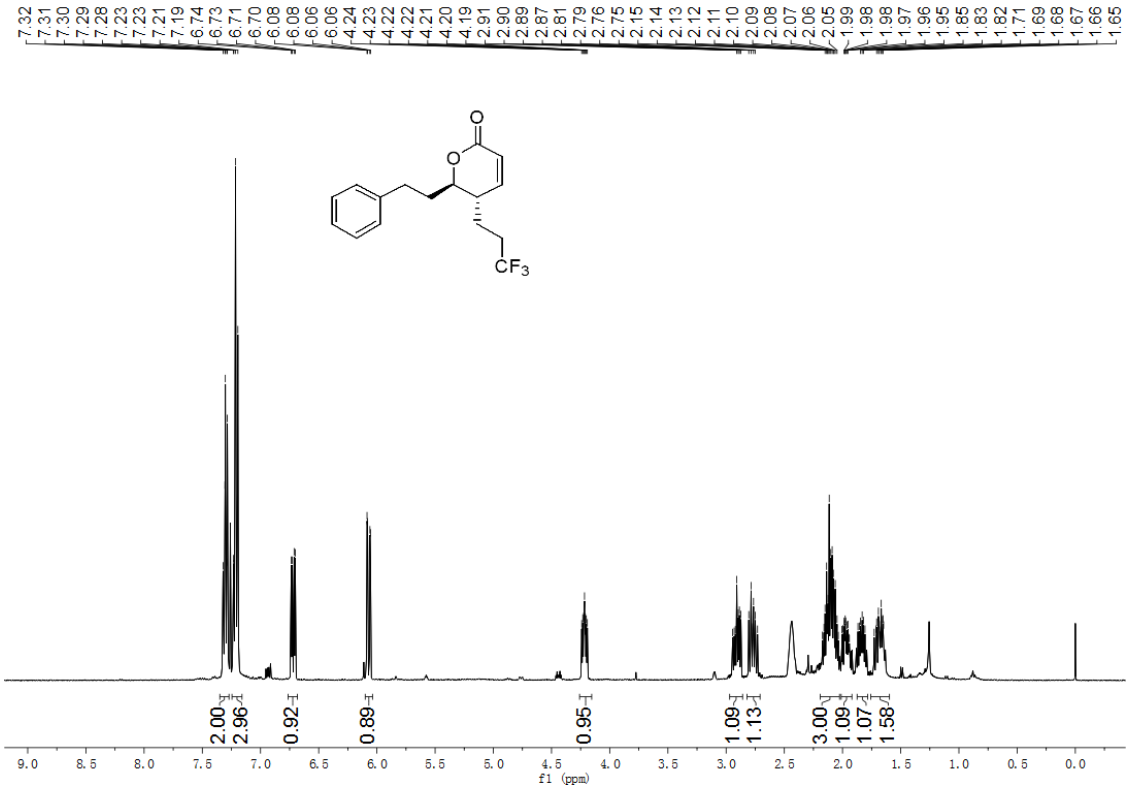
5-^{1}H NMR



5-^{13}C NMR



6-^{1}H NMR



6-^{13}C NMR