Supporting Information

A Mechanochemical Addition/Reduction Cascade Process for the Synthesis of Dual Stereocentered Chiral δ-Hydroxysulfones

Yongjin Zhang, Yanwen Gong, Donghua He, Tianqi Xu, Binhong Jiang, Kun Zhuang,* and Guohua Liu*

Key Laboratory of Resource Chemistry of Ministry of Education, Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, P. R. China. E-mail: ghliu@shnu.edu.cn, zhangkun@shnu.edu.cn.

CONTENTS

Experimental

1. General: Mechanochemical reactions under the ball-mill conditions were conducted using a *Planetary Mill* Focucy (F-P400). The milling instrument consists of a main disk that can rotate at a speed of 200-900 rpm and accommodates four grinding bowls (25 mL). These bowls and balls (5 mm diameter) are made of stainless steel. Chiral ruthenium catalysts, chiral squaramide, α-cyclodextrin, β-cyclodextrin, and γ-cyclodextrin were purchased from Sigma−Aldrich Company Ltd and used as received. The enones (*Org. Lett.*, **2004**, *6*, 2701; *Angew. Chem. Int. Ed.* **2013**, *52*, 5818.) α-nitrosulfones (*Org. Lett*. **2012**, *14*, 3260), and (*S*)-3-((3,5-bis(trifluoromethyl)phenyl)amino)-4-((3,3-dimethyl-1-(piperidin-1-yl)butan-2-yl)amino)cyclobut-3-ene-1,2-dione ([**SA-1**]) (*Org. Biomol. Chem.*, **2014**, *12*, 6425.) were prepared according to the published procedures. All other reagents were obtained from commercial sources and used without further purification. Deuterated solvents were purchased commercially and were degassed and stored over activated 4 Å molecular sieves. The ^{1}H NMR spectra were performed on a Bruker Avance DPX-400 spectrometer. Chemical shifts are given in parts per million (δ units) downfield from tetramethylsilane using the residual solvent signal (Methanol-d_4, δ 3.31) as an internal standard. ^{1}H NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sept, septet; m, multiplet), coupling constant(s) (*J*) in Hertz (Hz), the number of protons. The prefix app is occasionally applied when the true signal multiplicity is unresolved and br indicates the signal in question broadened. ^{13}C{^{1}H} NMR spectra are reported in ppm (δ) relative to residual methanol-d_4 (δ 49.01) unless otherwise noted. The enantiomeric excesses (*ee*) and/or diastereomeric ratios (*dr*) were determined using a Daicel Chiralcel column with the above HPLC setup.

2. General procedures.

2.1. General procedure for the single-step Michael addition under the batch conditions.

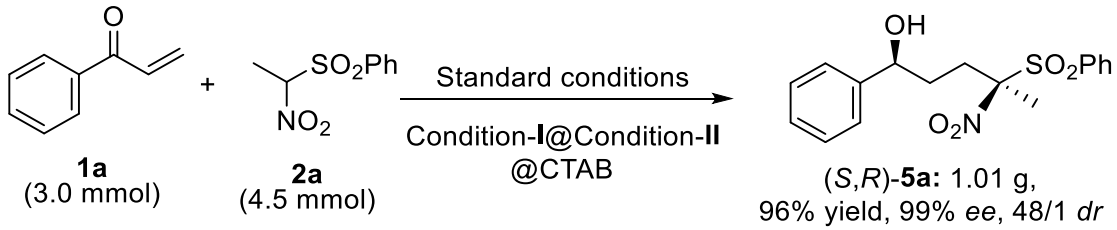
In a typical procedure, 5.0 mol% of [**SA-1**], **1a** (0.20 mmol), **2a** (0.24 mmol), 0.30 equivalent of β-cyclodextrin and 1.0 mL of mesitylene were added sequentially to a 10.0 mL round−bottom flask. The resulting mixture was then stirred at 25 °C for 1 h. During this period, the reaction was monitored by TLC. After completion of the reaction, the water was added, and the aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with aqueous

Na_2CO_3 and then dehydrated with Na_2SO_4. After the evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford (*R*)-**3a**. The *ee* values were determined using HPLC analysis using a UV–Vis detector and Daicel chiral-cel column (Φ 0.46 × 25 cm).

2.2. General procedure for the single-step ATH transformation under the batch conditions.

In a typical reaction, 1.0 mol% of [**Ru-1**], (*R*)-**3a** (95%*ee*, 0.20 mmol), HCO_2Na (2.0 mmol), 0.30 equivalent of *β*-cyclodextrin, 1.0 equivalent of CTAB and 2.0 mL of DMSO/H_2O (v/v = 1:1) were added sequentially to a 10.0 mL round−bottom flask. The resulting mixture was then stirred at 25 °C for 20 h. During this period, the reaction was monitored by TLC. After completion of the reaction, the aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with aqueous Na_2CO_3 and then dehydrated with Na_2SO_4. After the evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford (*S,R*)-**5a**. The *ee* and *dr* values were determined using HPLC analysis using a UV–Vis detector and Daicel chiral-cel column (Φ 0.46 × 25 cm).

2.3. General procedure for the gram-scale preparation of (*S,R*)-**5a** in the addition/reduction cascade process under the ball-milling conditions.



A typical procedure was as follows. In a 100 mL stainless-steel jar, 0.5 mol% of [**SA-1**], **1a** (3.0 mmol), **2a** (4.5 mmol) in 1.0 mL of mesitylene were introduced with 0.30 equivalent of *β*-cyclodextrin on one side, while 1.0 mol% of [**Ru-1**] in 1.0 mL of DMSO/H_2O (v/v = 1/1) were introduced with 0.30 equivalent of *β*-cyclodextrin and 10.0 equivalent of HCO_2Na on the other side, then 1.0 equivalent of CTAB were added into this jar. After this, 9 stainless steel balls (Ø = 5 mm) were added to the system. The sealed jars were placed in a mixing mill and agitated at 550 rpm at 25 °C for 2 h. After completion of the reaction, the products were dissolved in 10.0 mL of ethyl ether,

the jars and balls were washed twice with ethyl ether (2 × 1.0 mL), and the resulting mixture was filtrated. The combined ethyl ether extracts were washed with aqueous Na_2CO_3 and then dehydrated with Na_2SO_4. After evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford (*S,R*)-**5**. The enantiomeric excess (*ee*) and diastereomeric ratio (*dr*) values were determined using HPLC analysis employing a UV–Vis detector and a Daicel chiralcel column (Φ 0.46 × 25 cm).

2.4. Deuterium experiment for the single-step Michael addition under the ball-milling conditions.

The mechanochemical reactions were conducted in a 25 mL stainless-steel ball mill operating at 450 rpm, containing 5 stainless steel balls (Ø = 5 mm). In a typical procedure, 0.5 mol% of [**SA-1**], **1a** (0.20 mmol), and **2a** (0.24 mmol) in 100 μL of C_6D_6 were introduced into 0.30 equivalent of *β*-cyclodextrin in the jar, then 5 stainless steel balls were added to the system. The closed jars were placed into a mixing mill and agitated at 450 rpm at 25 °C for 0.5 h. After completion of the reaction, the products were dissolved in 2.0 mL of ethyl ether, the jars and balls were washed twice with ethyl ether (2 × 1.0 mL), and the resulting mixture was filtrated. The combined ethyl ether extracts were washed with aqueous Na_2CO_3 and then dehydrated with Na_2SO_4. After evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford the desired products (**3a**). The *ee* values were determined using HPLC analysis using a UV–Vis detector and Daicel chiral-cel column (Φ 0.46 × 25 cm).

2.5. Deuterium experiment for the single-step Michael addition under the batch conditions.

In a typical procedure, 5.0 mol% of [**SA-1**], **1a** (0.20 mmol), **2a** (0.24 mmol), 0.30 equivalent of *β*-cyclodextrin and 1.0 mL of C_6D_6 were added sequentially to a 10.0 mL round−bottom flask. The resulting mixture was then stirred at 25 °C for 1 h. During this period, the reaction was monitored by TLC. After completion of the reaction, the water was added, and the aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with aqueous Na_2CO_3 and then dehydrated with Na_2SO_4. After the evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford (*R*)-**3a**.

2.6. Deuterium experiment for the addition/reduction cascade process under the ball-milling conditions.

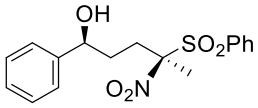
A typical procedure was as follows. In a 25 mL stainless-steel jar, 0.5 mol% of [**SA-1**], **1a** (0.20 mmol), **2a** (0.24 mmol) in 100 μL of C_6D_6 were introduced with 0.30 equivalent of β-cyclodextrin on one side, while 1.0 mol% of [**Ru-1**] in 100 μL of DMSO-d_6/D_2O (v/v = 1/1) were introduced with 0.30 equivalent of β-cyclodextrin and 10.0 equivalent of HCO_2Na on the other side, then 1.0 equivalent of CTAB were added into this jar. After this, 5 stainless steel balls ($\varnothing$ = 5 mm) were added to the system. The sealed jars were placed in a mixing mill and agitated at 450 rpm at 25 °C for 2-3 h. After completion of the reaction, the products were dissolved in 2.0 mL of ethyl ether, the jars and balls were washed twice with ethyl ether (2 × 1.0 mL), and the resulting mixture was filtrated. The combined ethyl ether extracts were washed with aqueous Na_2CO_3 and then dehydrated with Na_2SO_4. After evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford (*S*,*R*)-**5a.**

2.7. Deuterium experiment for the single-step ATH transformation under the batch condition.

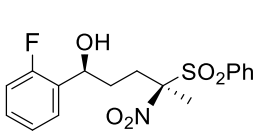
In a typical reaction, 1.0 mol% of [**Ru-1**], (*R*)-**3a** (95%*ee*, 0.20 mmol), HCO_2Na (2.0 mmol), 0.30 equivalent of β-cyclodextrin, 1.0 equivalent of CTAB and 2.0 mL of DMSO-d_6/D_2O (v/v = 1:1) were added sequentially to a 10.0 mL round−bottom flask. The resulting mixture was then stirred at 25 °C for 20 h. During this period, the reaction was monitored by TLC. After completion of the reaction, the aqueous solution was extracted with ethyl ether (3 × 3.0 mL). The combined ethyl ether extracts were washed with aqueous Na_2CO_3 and then dehydrated with Na_2SO_4. After the evaporation of the solvent, the resulting residue was purified by silica gel flash column chromatography to afford (*S*,*R*)-**5a**.

3. Data of chiral products.

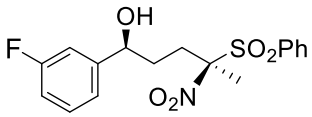
(*S,R*)-**5a**: (*1S,4R*)-4-nitro-1-phenyl-4-(phenylsulfonyl)pentan-1-ol. White solid, 97%, 99% *ee*, 48/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.86 – 7.76 (m, 3H), 7.64 (m, *J* = 9.1, 5.6, 2.1 Hz, 2H), 7.37 – 7.20 (m, 5H), 4.63 (dd, *J* = 7.1, 5.2 Hz, 1H), 2.50 (m, *J* = 14.3, 12.1, 4.2 Hz, 1H), 2.11 (m, 1H), 1.89 (d, *J* = 3.3 Hz, 4H), 1.58 – 1.44 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 143.87, 135.12, 132.91, 130.75, 128.96, 128.04, 127.14, 125.49, 106.91, 72.49, 32.36, 30.09, 15.82. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{19}NO_5SNa]^+$ 372.0876; found: 372.0876.



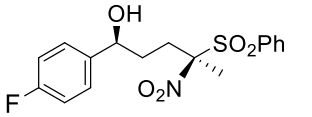
(*S,R*)-**5b:** (*1S,4R*)-1-(2-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 91%, 99% *ee*, 23/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.87 – 6.89 (m, 9H), 4.97 – 4.88 (m, 1H), 2.56 – 2.06 (m, 2H), 2.00 – 1.68 (m, 4H), 1.55 – 1.36 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 164.16, 161.73, 147.06, 135.13, 132.90, 130.75, 128.94, 121.19, 113.69, 112.00, 106.87, 71.57, 32.26, 29.87, 15.79. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{18}FNO_5SNa]^+$ 390.0782; found: 390.0782.



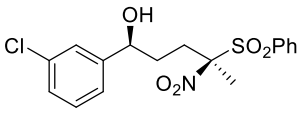
(*S,R*)-**5c:** (*1S,4R*)-1-(3-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 93%, 99% *ee*, 36/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.94 – 7.75 (m, 3H), 7.71 – 7.58 (m, 2H), 7.31 (td, *J* = 7.9, 5.9 Hz, 1H), 7.11 – 6.87 (m, 3H), 4.67 (dd, *J* = 7.1, 4.9 Hz, 1H), 2.46 (m, *J* = 13.7, 12.0, 4.2 Hz, 1H), 2.19 – 2.04 (m, 1H), 2.00 – 1.73 (m, 4H), 1.56 – 1.38 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 130.75, 129.78, 128.95, 121.20, 112.00, 106.99, 71.76, 32.44, 30.23, 15.84. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{18}FNO_5SNa]^+$ 390.0782; found: 390.0782.



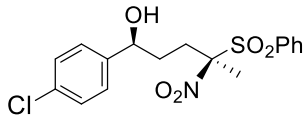
(*S,R*)-**5d:** (*1S,4R*)-1-(4-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 97%, 99% *ee*, 30/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.96 – 7.76 (m, 3H), 7.73 – 7.60 (m, 2H), 7.32 (m, *J* = 10.3, 5.5, 2.7 Hz, 2H), 7.16 – 6.98 (m, 2H), 4.78 – 4.57 (m, 1H), 2.50 (m, *J* = 14.1, 12.1, 4.2 Hz, 1H), 2.21 – 2.03 (m, 1H), 1.98 – 1.80 (m, 4H), 1.50 (m, *J* = 13.1, 11.7, 7.2, 4.3 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 163.33, 135.14, 132.89, 130.76, 128.97, 127.35, 127.28, 114.71, 114.50, 106.89, 71.87, 71.70, 32.37, 29.96, 15.85. HRMS(ESI) calcd for [M-OH$^+$]: [$C_{17}H_{17}FNO_4S]^+$ 350.08568 Found 350.08539.



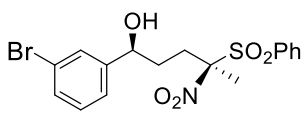
(*S,R*)-**5e:** (*1S,4R*)-1-(3-chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 93%, 99% *ee*, 29/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.22 – 7.02 (m, 9H), 4.65 (dd, *J* = 7.1, 4.8 Hz, 1H), 2.46 (m, *J* = 14.1, 11.9, 4.2 Hz, 1H), 2.19 – 2.11 (m, 1H), 1.87 (d, *J* = 28.2 Hz, 4H), 1.46 (m, *J* = 13.0, 11.6, 7.2, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 146.52, 135.18, 133.91, 132.85, 130.75, 129.57, 128.97, 127.05, 125.51, 123.84, 106.88, 71.55, 32.26, 29.87, 15.81. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{27}H_{25}NO_5SNa]^+$ 498.1346; found: 498.1346.



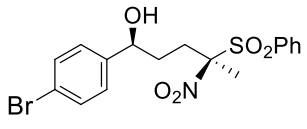
(*S,R*)-**5f:** (*1S,4R*)1-(4-chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 97 %, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.98 – 7.76 (m, 3H), 7.73 – 7.57 (m, 2H), 7.28 (m, *J* = 8.6, 1.8 Hz, 4H), 2.46 (m, *J* = 13.9, 12.1, 4.4, 1.6 Hz, 1H), 2.12 (m, *J* = 13.9, 11.5, 4.4, 1.7 Hz, 1H), 1.99 – 1.76 (m, 4H), 1.56 – 1.37 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 142.82, 135.16, 132.83, 132.65, 130.76, 128.99, 128.08, 127.11, 106.88, 71.59, 32.27, 29.90, 15.87. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{18}ClNO_5SNa]^+$ 406.0486; found: 406.0486.



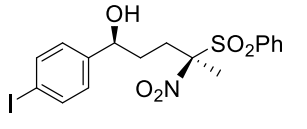
(*S,R*)-**5g:** (*1S,4R*)-1-(3-bromophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 95%, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.86 (dd, *J* = 40.2, 7.9 Hz, 3H), 7.74 – 7.58 (m, 2H), 7.52 – 7.35 (m, 2H), 7.32 – 7.17 (m, 2H), 4.64 (dd, *J* = 7.3, 4.8 Hz, 1H), 2.51 – 2.28 (m, 1H), 2.20 – 2.05 (m, 1H), 1.99 – 1.72 (m, 4H), 1.45 (dd, *J* = 14.5, 9.8 Hz, 1H). ^{13}C NMR (100MHz, Methanol-d_4) δ 146.78, 135.16, 133.88, 130.74, 130.04, 129.84, 128.97, 128.52, 124.27, 122.01, 106.86, 71.48, 32.28, 29.88, 15.77. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{18}BrNO_5SNa]^+$ 449.9981; found: 449.9981.



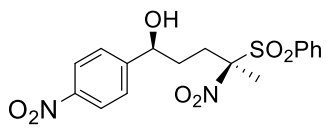
(*S,R*)-**5h:** (*1S,4R*)-1-(4-bromophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 95%, 99% *ee*, 28/1 *dr*.^{1}H NMR (400 MHz, Methanol-d_4) δ 8.04 – 7.76 (m, 4H), 7.76 – 7.59 (m, 3H), 7.49 – 7.43 (m, 1H), 7.24 – 7.19 (m, 1H), 4.73 – 4.48 (m, 1H), 2.45 (m, *J* = 13.9, 12.0, 4.2 Hz, 1H), 2.17 – 2.11 (m, 1H), 1.87 (d, *J* = 25.2 Hz, 4H), 1.47 (dddd, *J* = 17.6, 16.2, 7.9, 3.7 Hz, 1H). ^{13}C NMR (100Hz, Methanol-d_4) δ 143.30, 135.13, 133.89, 131.07, 130.75, 128.97, 127.43, 120.62, 106.86, 71.60, 32.21, 29.88, 15.82. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{18}BrNO_5SNa]^+$ 449.9981; found: 449.9981.



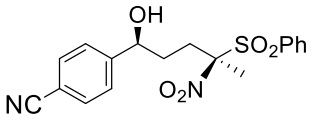
(*S,R*)-**5i:** (*1S,4R*)-1-(4-iodophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 91%, 99% *ee*, 15/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.91 – 7.77 (m, 3H), 7.69 – 7.61 (m, 4H), 7.19 – 6.95 (m, 2H), 4.62 (dd, *J* = 7.1, 4.9 Hz, 1H), 2.27 (m, *J* = 127.7, 14.2, 12.1, 4.3 Hz, 2H), 1.93 – 1.82 (m, 4H), 1.52 – 1.42 (m, 1H).^{13}C NMR (100 MHz, Methanol-d_4) δ 159.87, 145.51, 135.14, 132.88, 130.75, 129.10, 128.97, 117.75, 112.55, 111.00, 106.95, 72.36, 54.28, 32.32, 30.06, 15.84, 15.81. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{18}INO_5SNa]^+$ 497.9843; found: 497.9843.



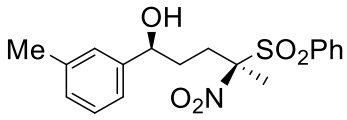
(*S,R*)-**5j:** (*1S,4S*)-4-nitro-1-(4-nitrophenyl)-4-(phenylsulfonyl)pentan-1-ol. White solid, 96%, 99% *ee*, 17/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.23 – 8.11 (m, 2H), 7.80 (td, *J* = 6.8, 1.4 Hz, 3H), 7.69 – 7.59 (m, 2H), 7.57 – 7.47 (m, 2H), 4.83 (dd, *J* = 7.3, 4.4 Hz, 1H), 2.56 – 2.33 (m, 1H), 2.22 (ddd, *J* = 14.2, 12.0, 4.5 Hz, 1H), 2.01 – 1.82 (m, 4H), 1.47 (m, *J* = 13.6, 11.9, 7.2, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 151.83, 147.15, 135.16, 132.80, 130.77, 128.98, 126.52, 126.45, 123.14, 123.09, 106.85, 71.17, 32.15, 29.63, 15.86. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{17}H_{18}N_2O_7SNa]^+$ 417.0727; found: 417.0727.



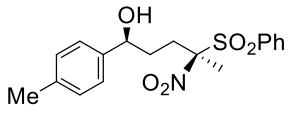
(*S,R*)-**5k:** 4-((*1S,4R*)-1-hydroxy-4-nitro-4-(phenylsulfonyl)pentyl)benzonitrile. White solid, 98%, 99% *ee*, 24/1 *dr*. 1H NMR (400 MHz, Methanol-d_4) δ 7.95 – 7.75 (m, 3H), 7.66 (td, *J* = 8.9, 4.0 Hz, 4H), 7.53 – 7.38 (m, 2H), 4.74 (dd, *J* = 7.3, 4.0 Hz, 1H), 3.03 – 2.11 (m, 2H), 2.00 – 1.68 (m, 4H), 1.51 – 1.38 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 149.98, 135.19, 132.85, 131.93, 130.79, 130.77, 129.00, 126.42, 126.40, 118.39, 110.62, 106.85, 71.37, 32.14, 29.67, 15.87. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{18}H_{18}N_2O_5SNa]^+$ 397.0829; found: 397.0829.



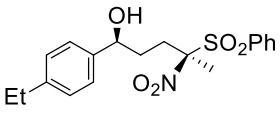
(*S,R*)-**5l:** (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(m-tolyl)pentan-1-ol. White solid, 91%, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.96 – 7.58 (m, 6H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.12 – 7.02 (m, 2H), 4.58 (dd, *J* = 7.2, 5.4 Hz, 1H), 2.55 – 2.01 (m, 5H), 1.86 (d, *J* = 22.2 Hz, 4H), 1.49 (m, *J* = 12.8, 11.4, 7.0, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 143.76, 137.74, 135.14, 135.12, 130.75, 129.01, 128.95, 127.95, 127.81, 126.09, 122.59, 106.94, 72.53, 32.34, 30.11, 20.16, 15.80. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{18}H_{21}NO_5SNa]^+$ 386.1033; found: 386.1033.



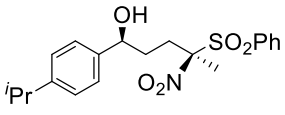
(*S,R*)-**5m:** (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(p-tolyl)pentan-1-ol. White solid, 92%, 99% *ee*, 38/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d4) δ 8.13 – 6.92 (m, 9H), 4.57 (dd, *J* = 7.0, 5.5 Hz, 1H), 2.55 – 1.14 (m, 10H). ^{13}CNMR (100 MHz, Methanol-d_4) δ 140.84, 136.85, 135.07, 132.88, 130.74, 128.93, 128.60, 125.40, 107.05, 72.44, 32.40, 30.39, 19.74, 15.84. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{18}H_{21}NO_5SNa]^+$ 386.1033; found: 386.1033.



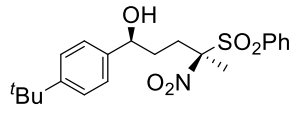
(*S,R*)-**5n:** (*1S,4R*)-1-(3-chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 93%, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d4) δ 7.98 – 7.58 (m, 6H), 7.21 – 7.13 (m, 3H), 4.58 (dd, *J* = 7.0, 5.4 Hz, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.46 (ddd, *J* = 14.3, 12.1, 4.2 Hz, 1H), 2.14 – 1.97 (m, 1H), 1.85 (d, *J* = 20.8 Hz, 4H), 1.57 – 1.41 (m, 1H), 1.21 (d, *J* = 15.2 Hz, 3H).^{13}C NMR (100 MHz, Methanol-d_4) δ 143.42, 141.02, 135.10, 132.92, 130.75, 128.96, 127.49, 125.54, 106.93, 72.42, 32.31, 30.15, 28.13, 14.85. HRMS(ESI) calcd for [M-OH+]: $[C_{18}H_{20}NO_4S]^+$ 346.11076; Found 346.11087.



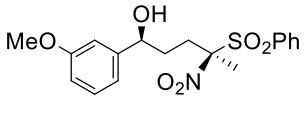
(*S,R*)-**5o:** (*1S,4R)*-1-(4-isopropylphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 91%, 99% *ee*, 16/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.94 – 7.76 (m, 3H), 7.72 – 7.59 (m, 2H), 7.19 (s, 4H), 4.58 (dd, *J* = 7.1, 5.4 Hz, 1H), 2.89 (dq, *J* = 13.8, 6.9 Hz, 1H), 2.47 (m, *J* = 16.0, 12.2, 4.2 Hz, 1H), 2.08 (m, *J* = 14.2, 12.1, 4.4 Hz, 1H), 1.89 (s, 4H), 1.49 (m, *J* = 12.0, 7.0, 4.3 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 148.01, 141.19, 135.09, 132.95, 130.76, 128.94, 126.00, 125.52, 107.42, 72.41, 33.70, 32.30, 30.17, 23.08, 15.78. HRMS(ESI) calcd for [M-OH$^+$]: $[C_{20}H_{24}NO_4S]^+$ 374.14206; Found 374.14227.



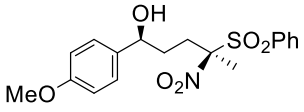
(*S,R*)-**5p:** (*1S,4R*)-1-(4-(tert-butyl)phenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 89%, 99% *ee*, 17/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.96 – 7.89 (m, 2H), 7.87 – 7.78 (m, 2H), 7.76 – 7.60 (m, 3H), 7.42 – 7.13 (m, 2H), 4.60 (t, *J* = 6.3 Hz, 1H), 2.58 – 2.00 (m, 2H), 1.87 (d, *J* = 22.7 Hz, 4H), 1.59 – 0.78 (m, 9H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 135.13, 135.10, 130.76, 129.60, 129.26, 129.00, 128.95, 128.52, 125.23, 124.88, 72.32, 32.27, 30.42, 30.16, 29.38, 15.79, 15.79, 11.86. HRMS(ESI) calcd for [M-OH$^+$]: [$C_{21}H_{26}NO_4S]^+$ 388.15771; Found 388.15778.



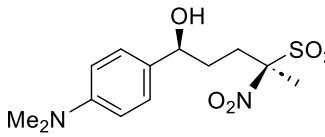
(*S,R*)-**5q:** (*1S,4R*)-1-(3-methoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 96%, 99% *ee*, 40/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.89 – 7.73 (m, 3H), 7.63 (ddq, *J* = 7.9, 6.6, 1.2 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.93 – 6.65 (m, 3H), 4.61 (dd, *J* = 6.9, 5.2 Hz, 1H), 2.47 (m, J = 14.4, 12.2, 4.2 Hz, 1H), 2.18 – 1.99 (m, 1H), 1.99 – 1.78 (m, 4H), 1.49 (m, *J* = 13.1, 12.1, 7.0, 4.2 Hz, 1H).^{13}C NMR (100 MHz, Methanol-d_4) δ 159.87, 145.51, 135.14, 132.88, 130.75, 129.10, 128.97, 117.75, 112.55, 111.00, 106.95, 72.36, 54.28, 32.32, 30.06, 15.84, 15.81. HRMS (ESI): m/z [M+Na]$^+$ calcd for $[C_{18}H_{21}NO_6SNa]^+$ 402.0982; found: 402.0982.



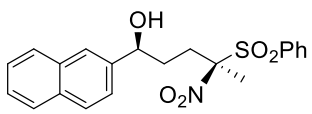
(*S,R*)-**5r:** (*1S,4R*)-1-(4-methoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 98%, 99% *ee*, 24/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.03 – 7.59 (m, 5H), 7.29 – 7.08 (m, 2H), 6.99 – 6.71 (m, 2H), 4.57 (dd, *J* = 6.9, 5.6 Hz, 1H), 3.79 (s, 3H), 2.61 – 1.99 (m, 2H), 2.01 – 1.73 (m, 4H), 1.51 (m, *J* = 13.0, 12.1, 6.9, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 135.77, 135.15, 132.90, 130.75, 128.97, 126.74, 113.41, 106.94, 72.20, 54.33, 32.31, 30.15, 15.86. HRMS (ESI): m/z [M+Na]$^+$ calcd for $[C_{18}H_{21}NO_6SNa]^+$ 402.0982; found: 402.0982.



(*S,R*)-5s: (*1S,4R)*-1-(4-(dimethylamino)phenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 91% yield, 99% *ee*, 10/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d$_4$) δ 7.85 – 7.74 (m, 3H), 7.63 (td, J = 8.0, 7.1, 1.5 Hz, 2H), 7.18 – 7.07 (m, 2H), 6.75 (d, J = 8.4 Hz, 2H), 4.50 (t, J = 6.4 Hz, 1H), 2.92 (d, J = 1.2 Hz, 6H), 2.52 – 2.37 (m, 1H), 2.08 – 1.94 (m, 1H), 1.88 (s, 3H), 1.84 (d, J = 5.4 Hz, 2H), 1.59 – 1.45 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d$_4$) δ 150.48, 135.09, 132.91, 131.73, 130.75, 128.96, 126.43, 112.70, 106.95, 72.55, 39.74, 32.19, 30.29, 15.81. HRMS(ESI) calcd. for [M-OH$^+$]: $C_{19}H_{23}N_2O_4S^+$ 375.13730; Found 375.13726.



(*S,R*)-**5t:** (*1S,4R*)-1-(naphthalen-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 82%, 99% *ee*, 10/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.87 – 7.66 (m, 7H), 7.55 – 7.37 (m, 5H), 4.80 (s, 1H), 2.46 (ddd, *J* = 14.0, 12.2, 4.4 Hz, 1H), 2.19 – 2.07 (m, 1H), 2.04 – 1.80 (m, 4H), 1.69 – 1.53 (m, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 141.19, 135.00, 133.33, 133.06, 132.79, 130.66, 128.81, 127.85, 127.62, 127.29,



125.78, 125.48, 124.22, 123.58, 106.89, 72.47, 32.10, 30.13, 15.73. HRMS (ESI): m/z $[M+Na]^+$ calcd for $[C_{21}H_{21}NO_5SNa]^+$ 422.1033; found: 422.1033.

(*S,R*)-**5u:** (*1S,4R*)-4-((4-fluorophenyl)sulfonyl)-4-nitro-1-phenylpentan-1-ol. White solid, 97%, 99% *ee*, 48/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.95 – 7.66 (m, 4H), 7.50 – 7.30 (m, 5H), 4.83 – 4.67 (m, 1H), 2.60 – 2.36 (m, 1H), 2.23 -2.10(m, *J* = 16.2, 10.7, 4.5, 1.8 Hz, 1H), 2.01 (d, *J* = 1.8 Hz, 4H), 1.62 (dt, *J* = 12.2, 6.8, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 147.75, 145.84, 136.35, 135.46, 133.25, 132.02, 131.10, 129.44, 111.04, 76.29, 36.27, 34.14, 19.66. HRMS (ESI) calcd for [M-OH^+]: [$C_{17}H_{17}FNO_4S]^+$ 350.08568; Found 350.08463.

(*S,R*)-**5v:** (*1S,4R*)-4-((4-chlorophenyl)sulfonyl)-4-nitro-1-phenylpentan-1-ol. White solid, 95%, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.96 – 7.76 (m, 2H), 7.49 – 6.86 (m, 7H), 4.64 (dd, *J* = 7.1, 5.1 Hz, 1H), 2.46 (m, *J* = 14.2, 12.1, 4.2 Hz, 1H), 2.23 – 2.01 (m, 1H), 1.90 (s, 4H), 1.51 (m, *J* = 16.8, 13.1, 7.1, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 168.21, 165.65, 143.85, 134.05, 133.95, 128.94, 128.91, 128.08, 127.17, 125.51, 116.42, 116.18, 107.05, 72.40, 32.36, 30.18, 15.81. HRMS (ESI) calcd for [M-OH^+]: $[C_{17}H_{17}ClNO_4S]^+$ 366.05613; Found 366.05630.

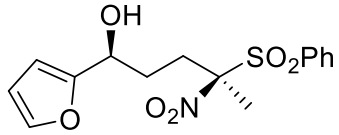
(*S,R*)-**5w:** (*1S,4R*)-4-nitro-1-phenyl-4-tosylpentan-1-ol. White solid, 92% yield, 94%, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.72 – 7.62 (m, 2H), 7.37 – 7.21 (m, 5H), 4.64 (dd, *J* = 7.1, 5.3 Hz, 1H), 2.63 – 2.36 (m, 4H), 2.21 – 1.99 (m, 1H), 1.97 – 1.78 (m, 4H), 1.62 – 1.43 (m, 1H). ^{13}C NMR (400 MHz, Methanol-d_4) δ 146.92, 143.89, 130.75, 129.59, 128.58, 128.07, 127.14, 125.53, 106.88, 72.53, 32.40, 30.10, 20.40, 15.94. HRMS (ESI) calcd for [M-OH^+]: $[C_{18}H_{20}NO_4S]^+$ 346.11076; Found 346.11041.

(*S,R*)-**5x:** (*1S,4R*)-4-nitro-1-phenyl-4-(phenylsulfonyl)hexan-1-ol. White solid, 93%, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.84 – 7.73 (m, 3H), 7.67 – 7.57 (m, 2H), 7.37 (d, *J* = 4.3 Hz, 4H), 7.34 – 7.25 (m, 1H), 4.67 (dd, *J* = 7.0, 5.6 Hz, 1H), 2.51 – 2.24 (m, 4H), 2.18 – 2.00 (m, 1H), 1.77 (m, *J* = 13.2, 11.9, 6.9, 5.2 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 144.03, 135.03, 133.40, 130.51, 128.92, 128.08, 127.19, 125.65, 110.25, 72.99, 32.84, 26.68, 23.81, 7.00. HRMS (ESI) calcd for [M-OH^+]: [$C_{18}H_{20}NO_4S]^+$ 346.11076; Found 346.11087.

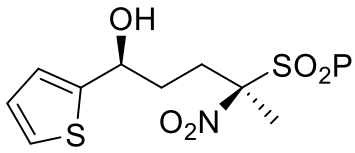
(*S,R*)-**5y**: (*1S,4S*)-4-nitro-1,5-diphenyl-4-(phenylsulfonyl)pentan-1-ol. White solid, 98%, 99% *ee*, >50/1 *dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.92 (d, *J* = 7.8 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.20 (m, 8H), 7.12 – 7.00 (m, 2H), 4.52 (t, *J* = 6.3 Hz, 1H), 3.73 – 3.46 (m, 2H), 2.52 – 1.89 (m, 4H). ^{13}C NMR (100MHz, Methanol-d_4) δ 144.00, 135.14, 134.13, 131.97, 130.99, 129.90, 128.96, 128.51,

127.97, 127.81, 127.07, 125.63, 109.93, 73.52, 38.89, 32.87, 27.82. HRMS (ESI) calcd for [M-OH$^+$]: [$C_{23}H_{22}NO_4S$]$^+$ 408.12969; Found 408.12973.

(*S,R*)-5z: (*1S,4R*)-1-(furan-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 94% yield, 99% *ee*, 49/1*dr*. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.94 – 7.80 (m, 3H), 7.68 (t, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 1.8 Hz, 1H), 6.36 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.27 (d, *J* = 3.3 Hz, 1H), 4.64 (dd, *J* = 7.3, 5.5 Hz, 1H), 2.18 (m, *J* = 14.2, 12.0, 4.5 Hz, 1H), 2.03 (m,, 1H), 1.94 (s, 3H), 1.60 (m, 1H).^{13}C NMR (100 MHz, Methanol-d_4) δ 155.96, 141.84, 135.20, 135.16, 132.88, 130.78, 129.02, 109.77, 105.82, 66.05, 29.79, 29.23, 15.96. HRMS (ESI) m/z [M+Na]$^+$ calcd for [$C_{15}H_{17}NO_6SNa$]$^+$ 362.0669; found: 362.0669.



(*S,R*)-5z': (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(thiophen-2-yl)pentan-1-ol. White solid, 94% yield, 99% ee, 32/1dr. ^{1}H NMR (400 MHz, Methanol-d$_4$) δ 7.95 – 7.78 (m, 3H), 7.72 – 7.57 (m, 2H), 7.32 (dd, J = 4.8, 1.5 Hz, 1H), 7.01 – 6.91 (m, 2H), 2.58 (m, 1H), 2.17 (m,, 1H), 2.05 – 1.88 (m, 4H), 1.68 – 1.54 (m, 1H).^{13}C NMR (100 MHz, Methanol-d_4) δ 147.90, 135.22, 132.83, 130.78, 129.05, 126.30, 124.10, 123.41, 106.90, 68.52, 32.78, 29.98, 16.04. HRMS (ESI) m/z [M+Na]$^+$ calcd for $C_{15}H_{17}NO_5S_2Na$]$^+$ 378.0440; found: 378.0440. .



(*S,R*)-5 z'': (*1S,4R*)-1-(benzo[d][1,3]dioxol-5-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol. White solid, 92% yield, 99% ee, 32/1dr. ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.90 – 7.78 (m, 3H), 7.71 – 7.59 (m, 2H), 6.85 – 6.64 (m, 3H), 5.94 (s, 2H), 4.56 (dd, J = 6.9, 5.5 Hz, 1H), 2.47 (m, 1H), 2.17 – 2.01 (m, 1H), 1.96 – 1.78 (m, 4H), 1.49 (m, , 1H). ^{13}C NMR (100 MHz, Methanol-d_4) δ 147.81, 146.95, 137.89, 135.16, 132.87, 130.77, 128.98, 118.94, 107.54, 106.94, 105.81, 100.93, 72.34, 32.36, 30.44, 30.10, 15.85. HRMS(ESI) calcd. for [M-OH$^+$]: C18H18NO6S$^+$ 376.08493; Found 376.08494.

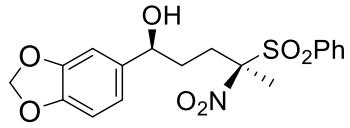
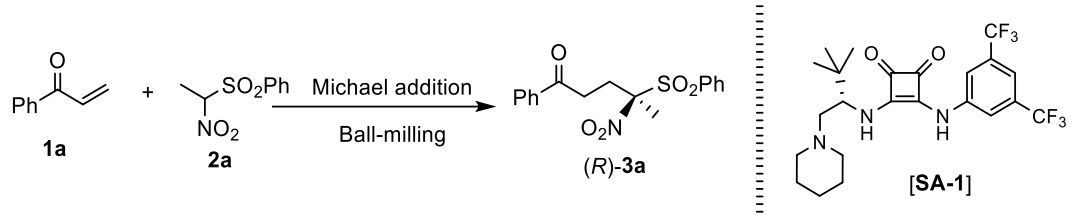


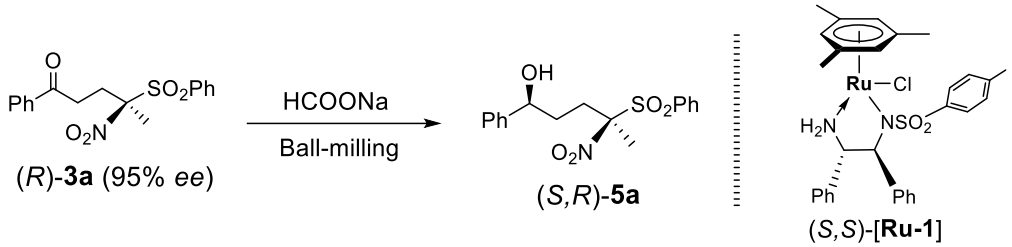
Table S1. Optimizing the single-step Michael addition reaction under the ball-milling conditions.[a]



Entry	Loading of [**SA-1**] (mol%) /Mesitylene (μL)/Additive/Milling speed (rpm)	Time (minute)	Yield (%)	*ee* (%)
1	10.0 mol%/--/--/450	30	99	72
2	1.0 mol%/--/--/450	30	99	86
3	1.0 mol%/100μL/--/450	30	99	89
4	0.5 mol%/100μL/--/450	30	99	91
5	0.5 mol%/100μL/--/350	30	93	91
6	0.5 mol%/100μL/--/550	30	99	90
7	0.5 mol%/75μL/--/450	30	89	88
8	0.5 mol%/125μL/--/450	30	99	90
9	0.4 mol%/100μL/--/450	30	83	91
10	0.5 mol%/100μL/CTAB(1 equivalents)/450	30	99	91
11	0.5 mol%/100μL/β-CD (0.3 equivalents)/450	30	98	95
12	0.5 mol%/100μL/β-CD (0.25 equivalents)/450	30	91	95
13	0.5 mol%/100μL/β-CD (0.35 equivalents)/450	30	99	94
14	0.5 mol%/100μL/β-CD(0.3 equivalents)/450	20	93	95
15	0.5 mol%/100μL/β-CD(0.3 equivalents)/450	40	99	92

[a] Reaction conditions: [**SA-1**] (0.40-10.0 mol%), **1a** (0.20 mmol), **2a** (0.24 mmol), and/or additive, air atmosphere. [b] All yields were determined using ^{1}H NMR spectroscopy, and the *ee* values were determined by a chiral HPLC analysis.

Table S2. Optimizing the single-step ATH transformation under the ball-milling conditions.[a]

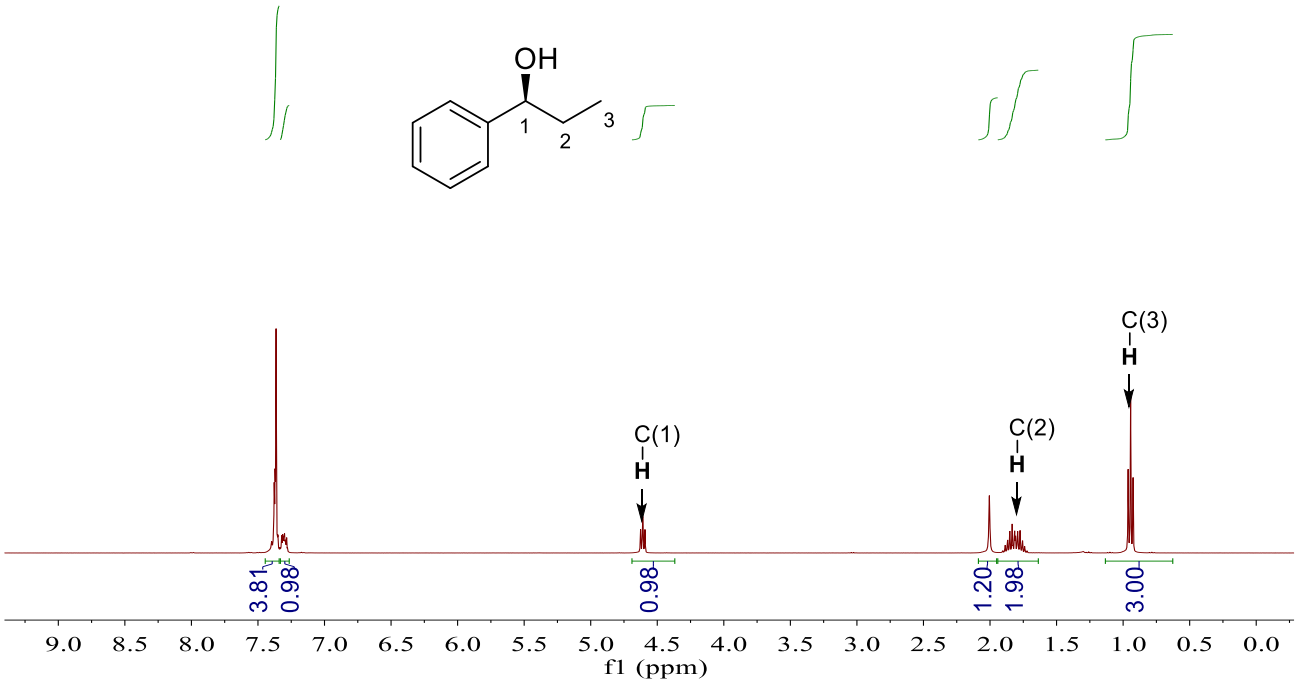


Entry	Loading of [**Ru-1**](mol%)/ DMSO-H_2O (μL)/Additive/Milling speed (rpm)	Time (h)	Yield (%)	*ee/dr* (%)
1	1.2 mol%/100 μL/--/450	2.5	72	97/32:1
2	1.0 mol%/100 μL/--/450	2.5	57	99(48:1)
3	0.8 mol%/100 μL/--/450	2.5	38	99(48:1)
4	1.0 mol%/100 μL/--/350	2.5	44	99(48:1)
5	1.0 mol%/100 μL/--/550	2.5	66	99(40:1)
6	1.0 mol%/80 μL/--/450	2.5	51	99(48:1)
7	1.0 mol%/120 μL/--/450	2.5	62	99(42:1)
8	1.0 mol%/100μL/*β*-CD(0.25 equivalents)/450	2.5	69	99(48:1)
9	1.0 mol%/100μL/*β*-CD(0.25 equivalents) + CTAB/450	2.5	91	99(48:1)
10	1.0 mol%/100μL/*β*-CD(0.30 equivalents) + CTAB/450	2.5	98	99(48:1)
11	1.0 mol%/100μL/*β*-CD(0.35 equivalents) + CTAB/450	2.5	98	99(48:1)
12	1.0 mol%/100μL/*β*-CD(0.3 equivalents) + CTAB/450	2.0	93	99(48:1)
13	1.0 mol%/100μL/*β*-CD(0.3 equivalents) + CTAB/450	3.0	98	99(48:1)

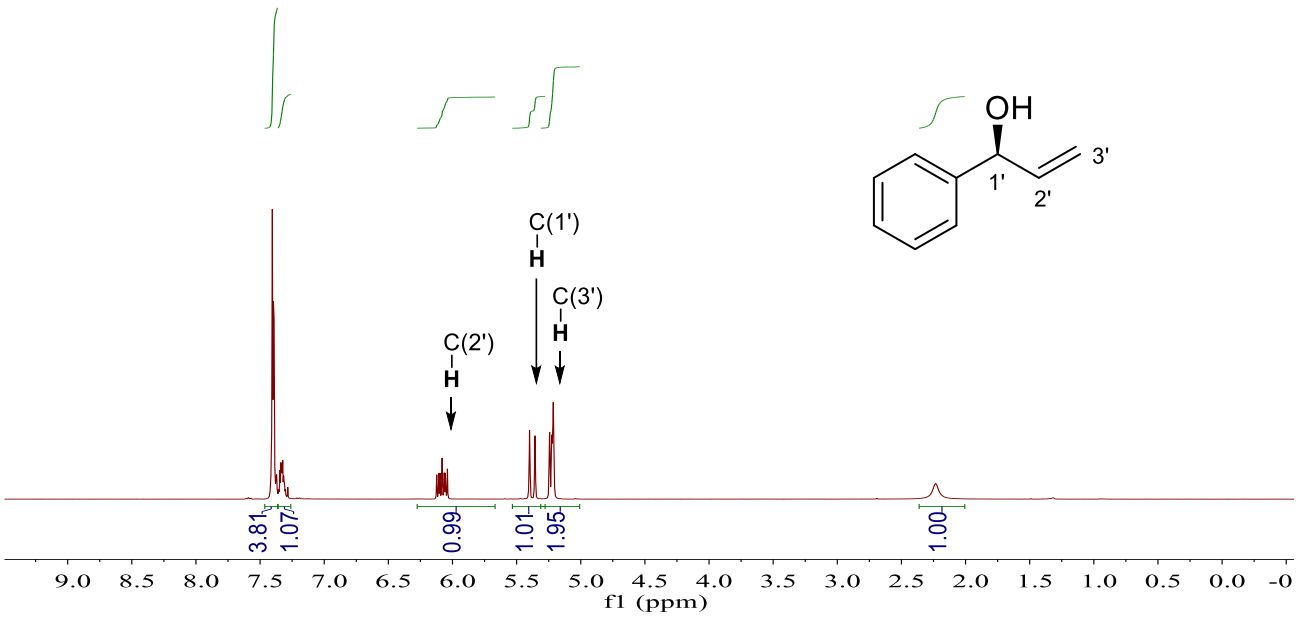
[a] Reaction conditions: MesRuTsDPEN (0.8-1.2 mol%), (*R*)-**3a** (95%*ee*, 0.20 mmol), 5.0 equivalent of HCOONa, 80-120μL of DMSO/H_2O (v/v = 1/1), 0.25-0.35 equivalent of *β*-cyclodextrin, and/or 1.0 equivalent of CTAB, air atmosphere, 400-800 rpm at 25 °C for 2 h. [b] All yields were determined using ^{1}H NMR spectroscopy, and the *ee* and *dr* values were determined by a chiral HPLC analysis.

Figure S1. The contrastive ^{1}H–NMR spectra in the reactions of **1a** in Equation 3 of Scheme 1.

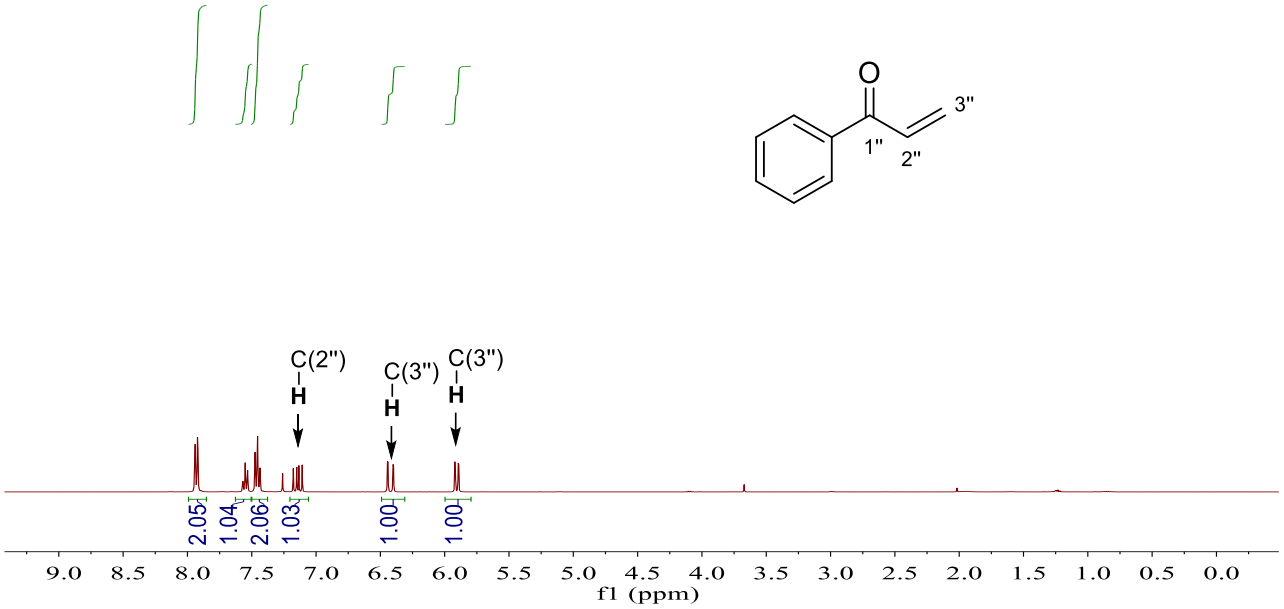
(a) The standard ^{1}H-NMR spectrum of by-products of (*S*)-1-phenylpropan-1-ol ((*R*)-**4a**).



(b) The standard ^{1}H-NMR spectrum of by-products of (*S*)-1-phenylpropan-1-ol.



(c) The standard ^{1}H-NMR spectrum of **1a.**



(d) The obtained ^{1}H-NMR spectrum of the mixed products in the reaction of **1a** under the ball-milling conditions.

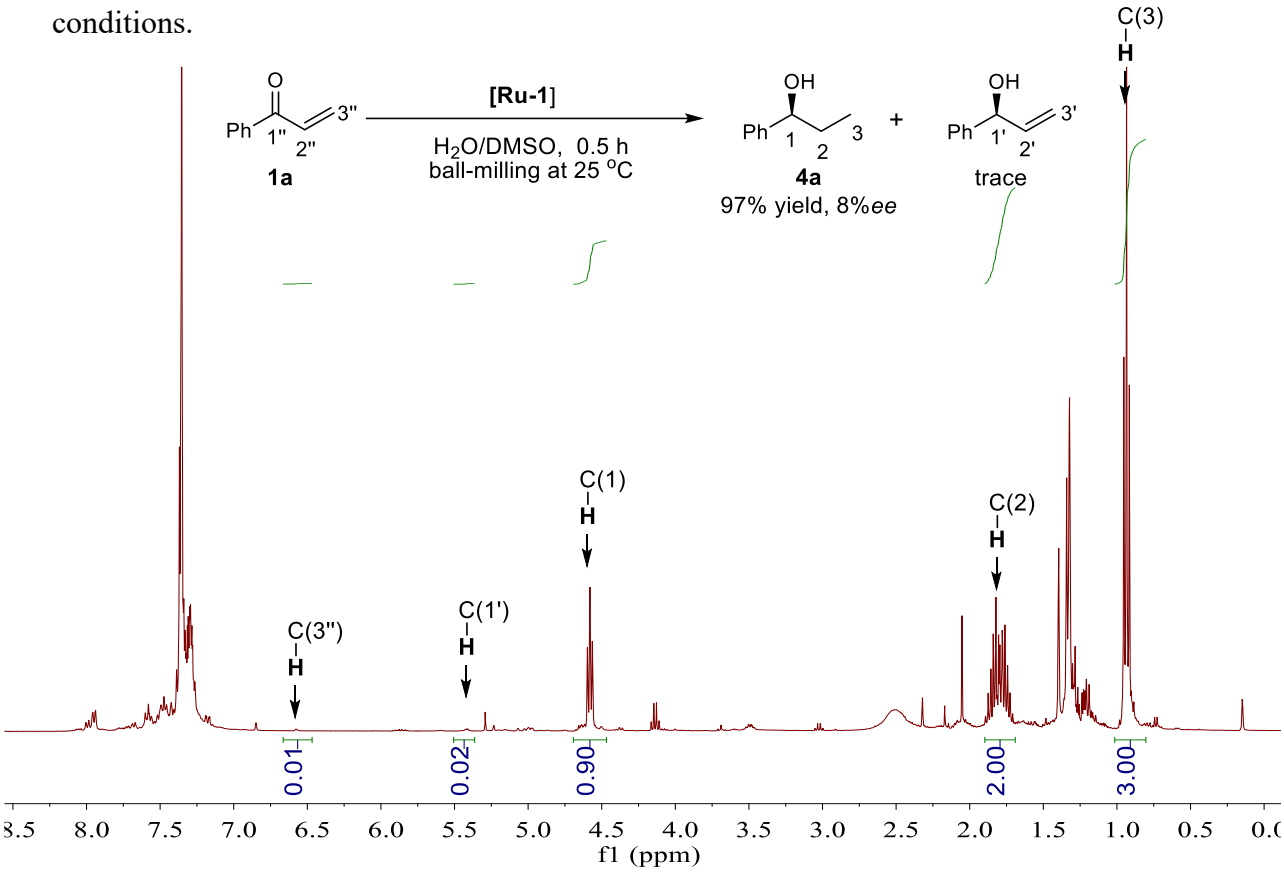
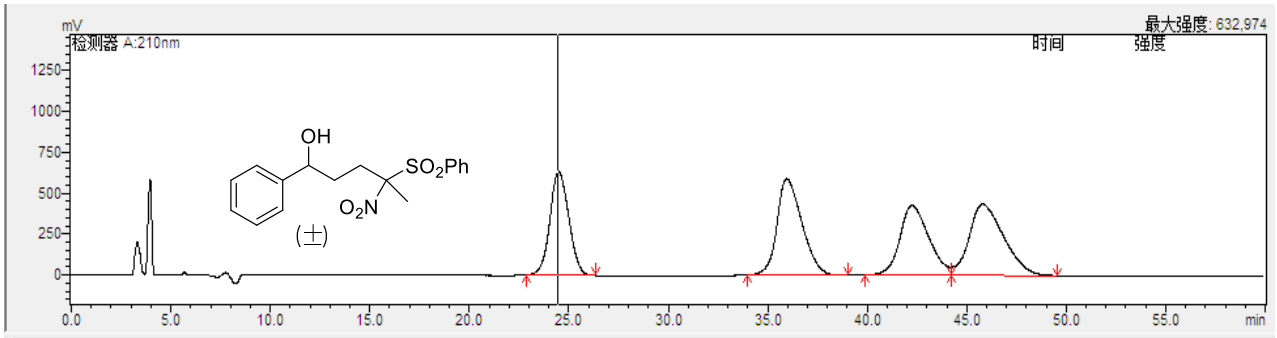


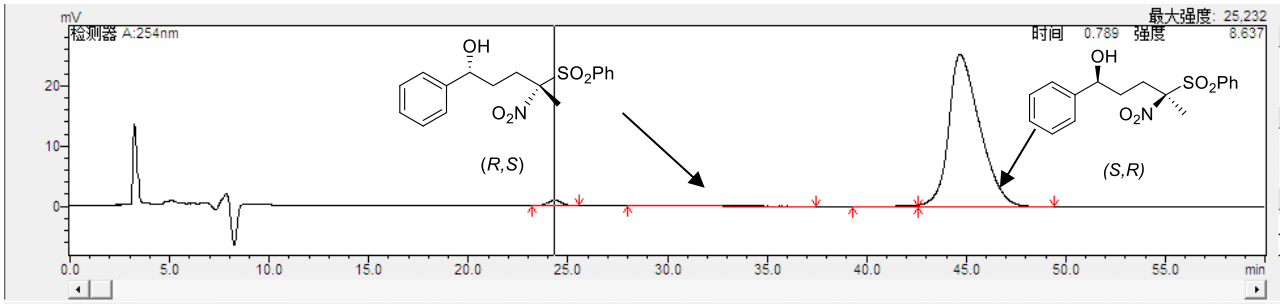
Figure S2. HPLC analyses of chiral products

(*S,R*)-**5a:** (*1S,4R*)-4-nitro-1-phenyl-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel OZ-H, detected at 210 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

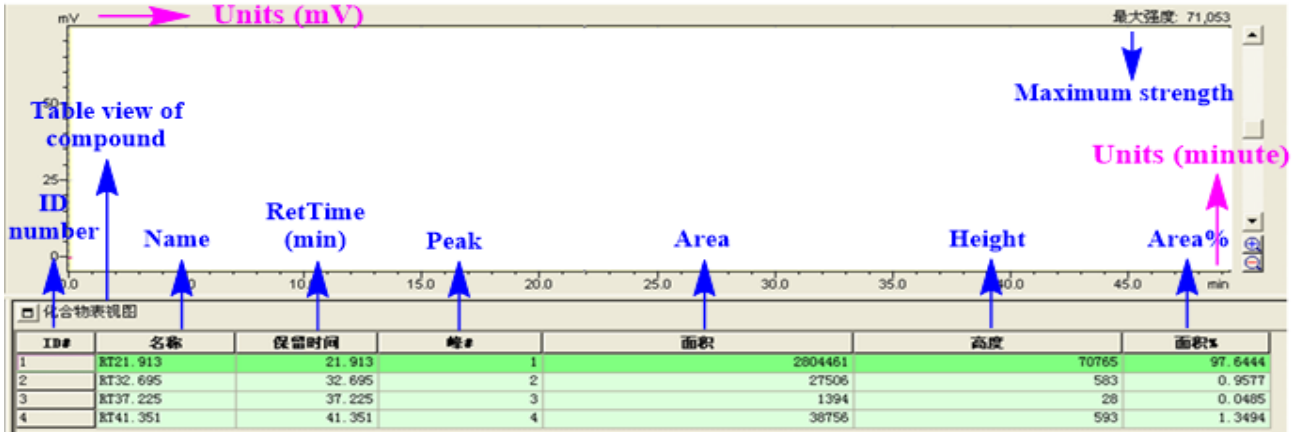
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT24.479	24.479	1	41830690	634196	22.0681
2	RT35.956	35.956	2	51571862	590095	27.2071
3	RT42.247	42.247	3	43465077	428502	22.9303
4	RT45.796	45.796	4	52685358	435373	27.7945



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT24.312	24.312	1	47295	913	1.6797
2	RT30.496	30.496	2	20383	88	0.7239
3	RT42.554	42.554	3	10315	243	0.3663
4	RT44.681	44.681	4	2737689	25247	97.2301

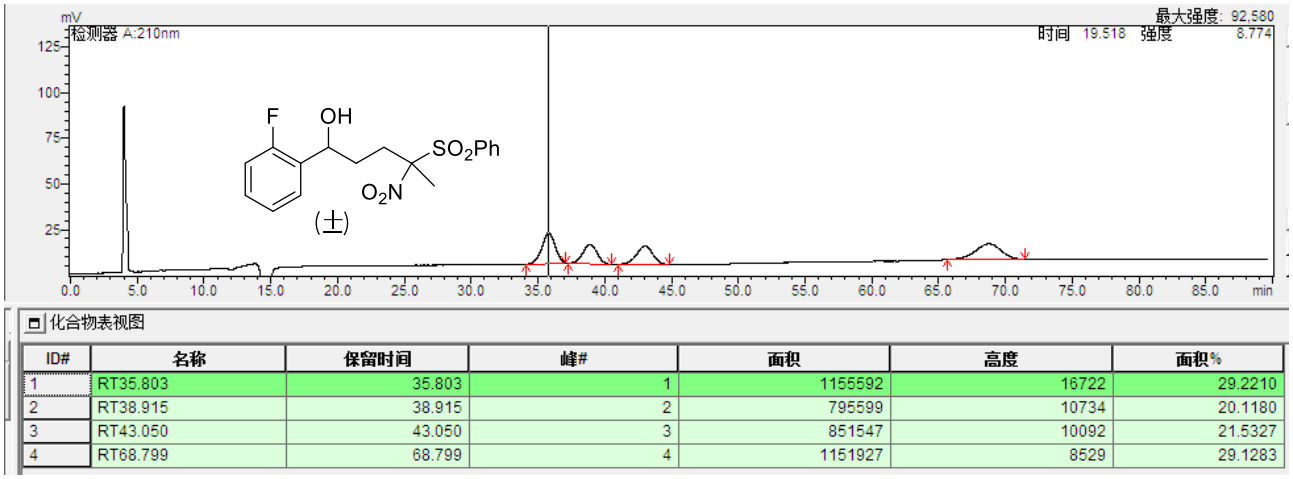
<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



化合物表视图

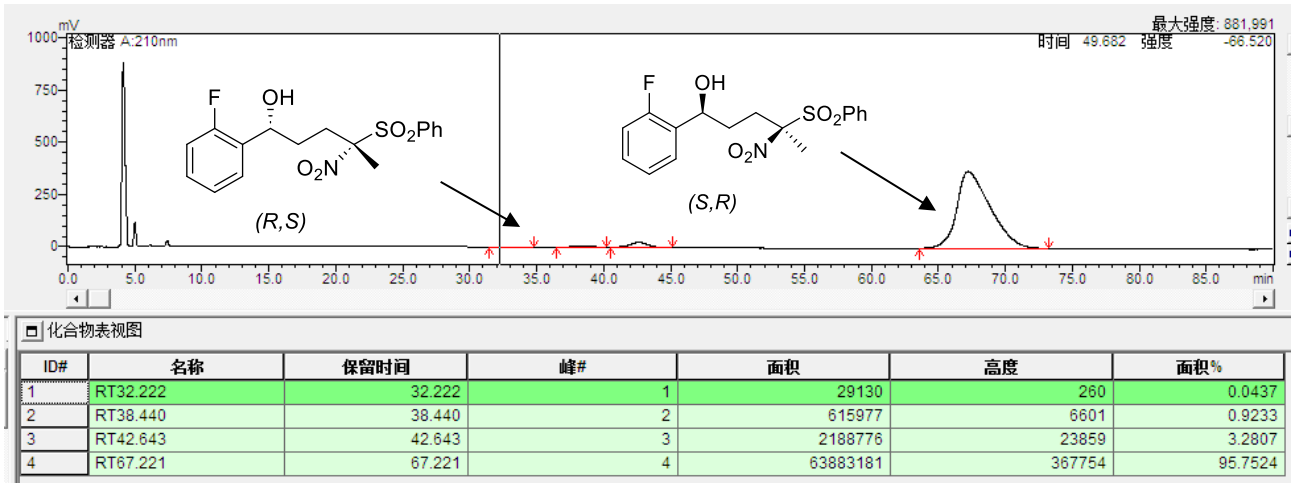
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5b: (*1S,4S*)-1-(2-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol** (HPLC: Chiracel OZ-H, detected at 210 nm, eluent: n-hexane/2-propanol = 93/7, flow rate = 0.8mL/min, 25°C).



化合物表视图

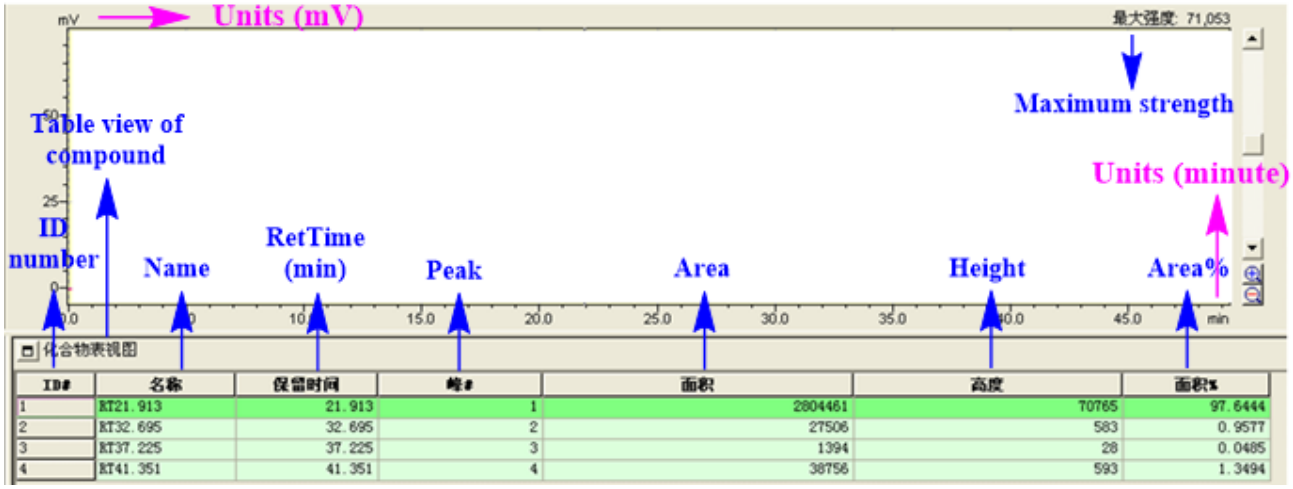
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT35.803	35.803	1	1155592	16722	29.2210
2	RT38.915	38.915	2	795599	10734	20.1180
3	RT43.050	43.050	3	851547	10092	21.5327
4	RT68.799	68.799	4	1151927	8529	29.1283



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.222	32.222	1	29130	260	0.0437
2	RT38.440	38.440	2	615977	6601	0.9233
3	RT42.643	42.643	3	2188776	23859	3.2807
4	RT67.221	67.221	4	63883181	367754	95.7524

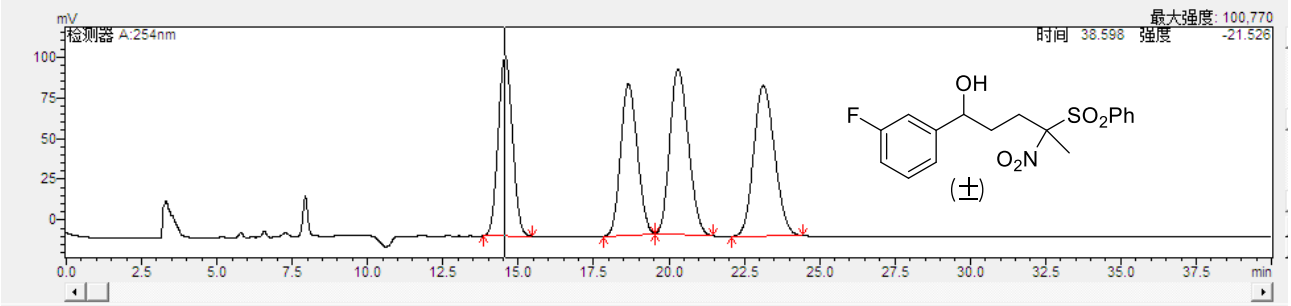
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

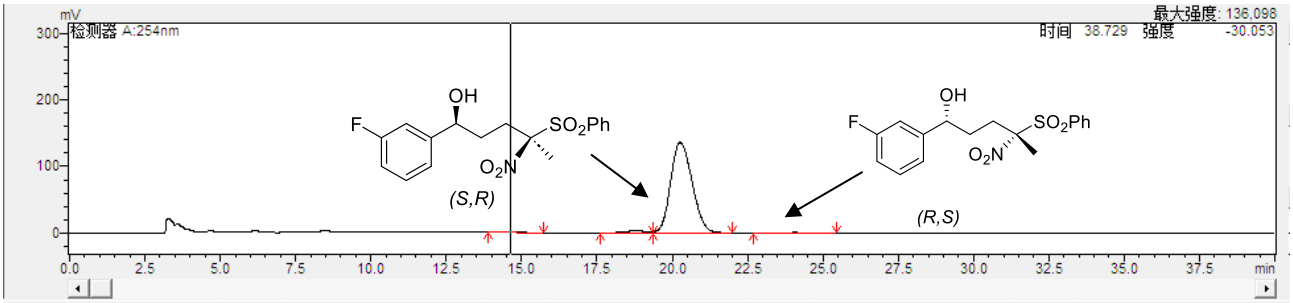
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5c: (*1S,4R*)-1-(3-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC:** Chiracel IC, detected at 254 nm, eluent: n-hexane/2-propanol = 85/15, flow rate = 1.0mL/min, 25°C).



化合物表视图

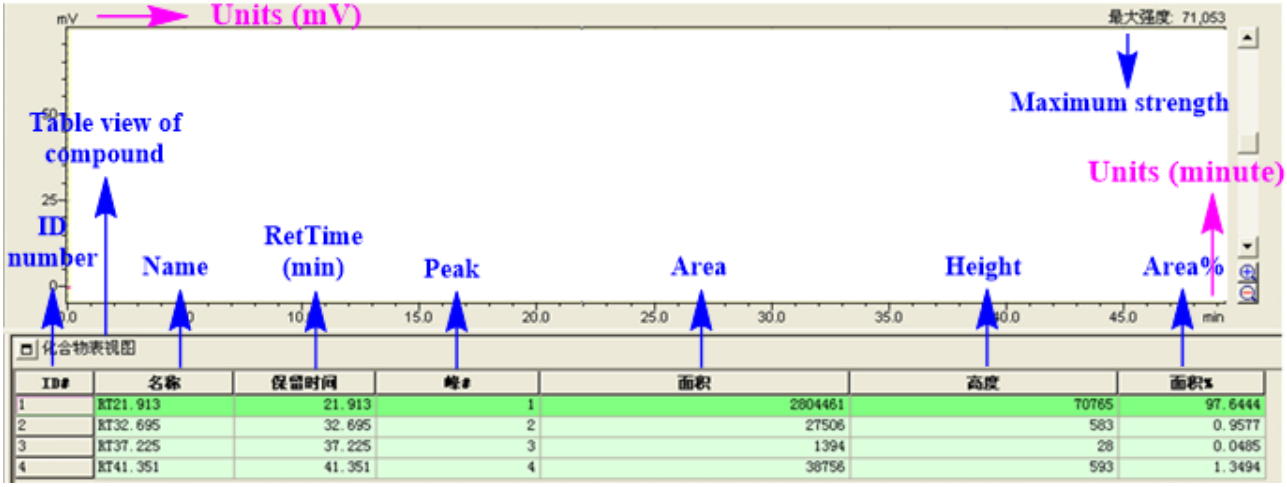
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT14.559	14.559	1	3648915	110506	22.7361
2	RT18.653	18.653	2	3583499	92491	22.3285
3	RT20.303	20.303	3	4350229	101442	27.1060
4	RT23.132	23.132	4	4466329	92279	27.8294



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT14.633	14.633	1	55347	1556	0.7983
2	RT18.788	18.788	2	131077	2912	1.8907
3	RT20.262	20.262	3	6725363	135615	97.0093
4	RT24.026	24.026	4	20911	348	0.3016

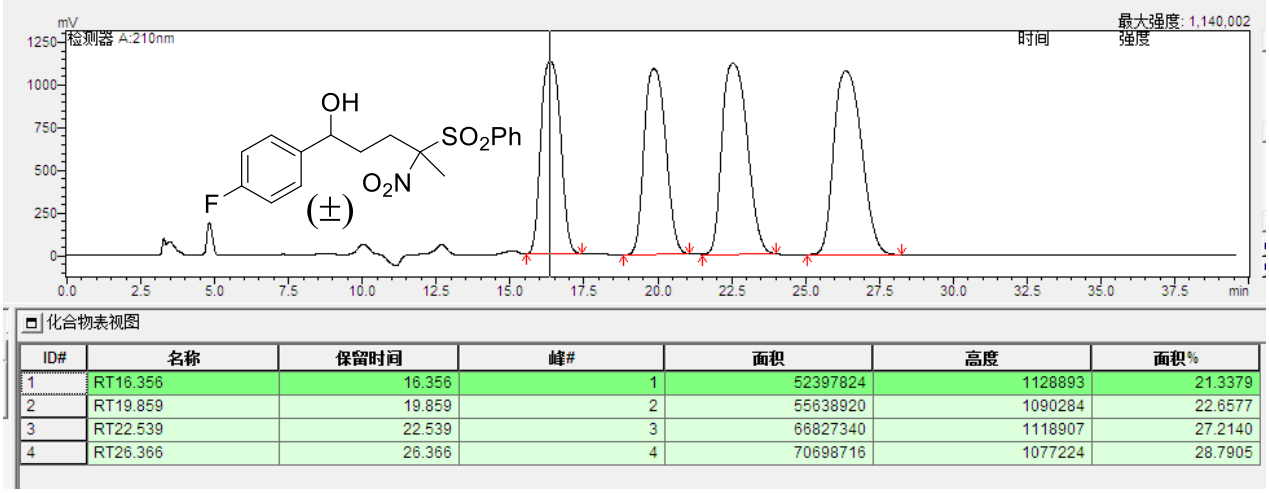
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

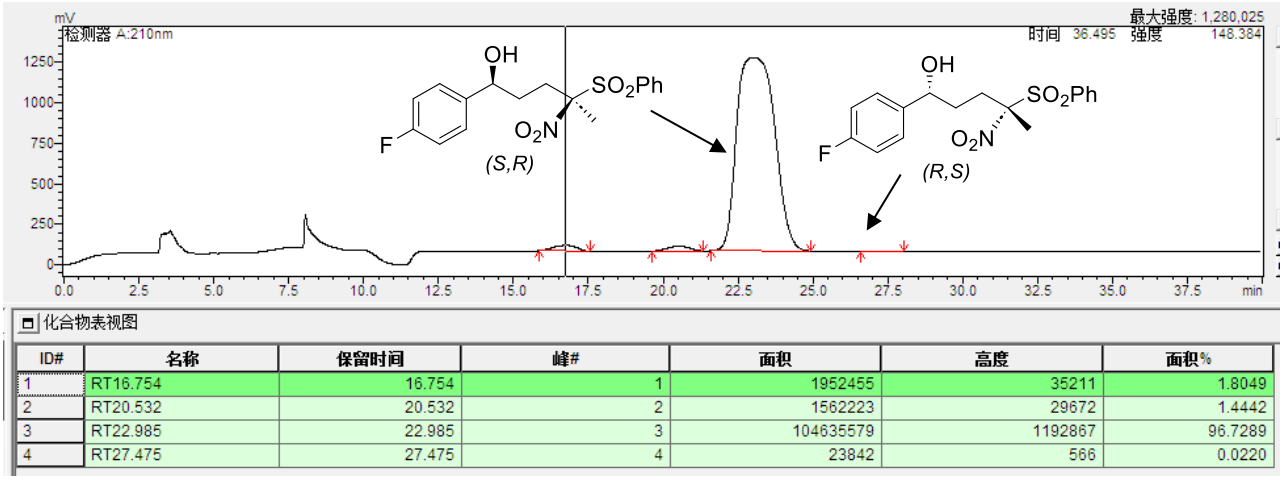
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*R*)-**5d:** (*1S*,*4R*)-1-(4-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 210 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT16.356	16.356	1	52397824	1128893	21.3379
2	RT19.859	19.859	2	55638920	1090284	22.6577
3	RT22.539	22.539	3	66827340	1118907	27.2140
4	RT26.366	26.366	4	70698716	1077224	28.7905



化合物表视图

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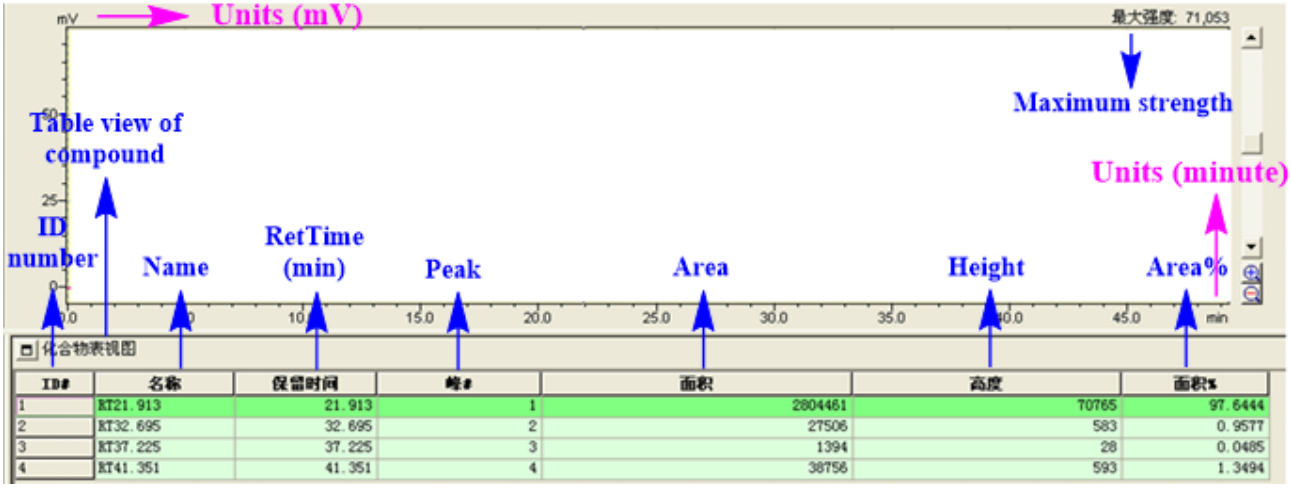
1	RT16.754	16.754	1	1952455	35211	1.8049
2	RT20.532	20.532	2	1562223	29672	1.4442
3	RT22.985	22.985	3	104635579	1192867	96.7289
4	RT27.475	27.475	4	23842	566	0.0220

Translation of all characters (Chinese) in the above two frameworks to English is as follows:



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ID#	名称	保留时间	峰#	面积	高度	面积%
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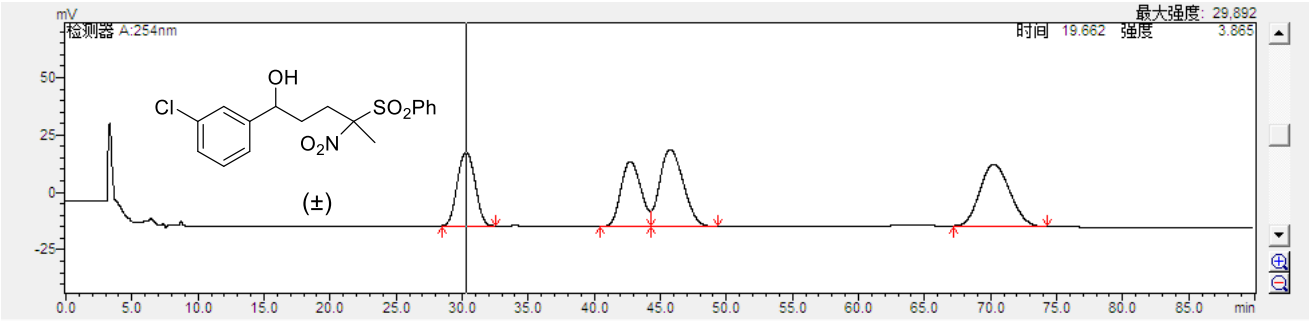
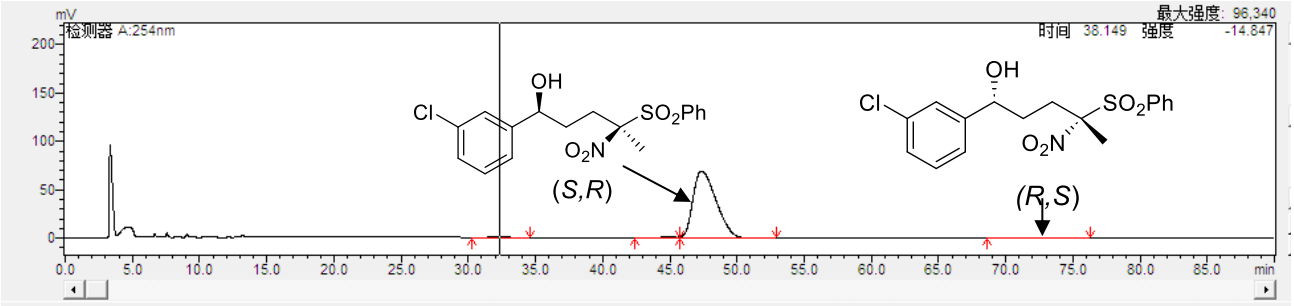
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5e:** (*1S,4R*)-1-(3,9-dihydropyren-4-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 0.7mL/min, 25°C).



化合物表视图

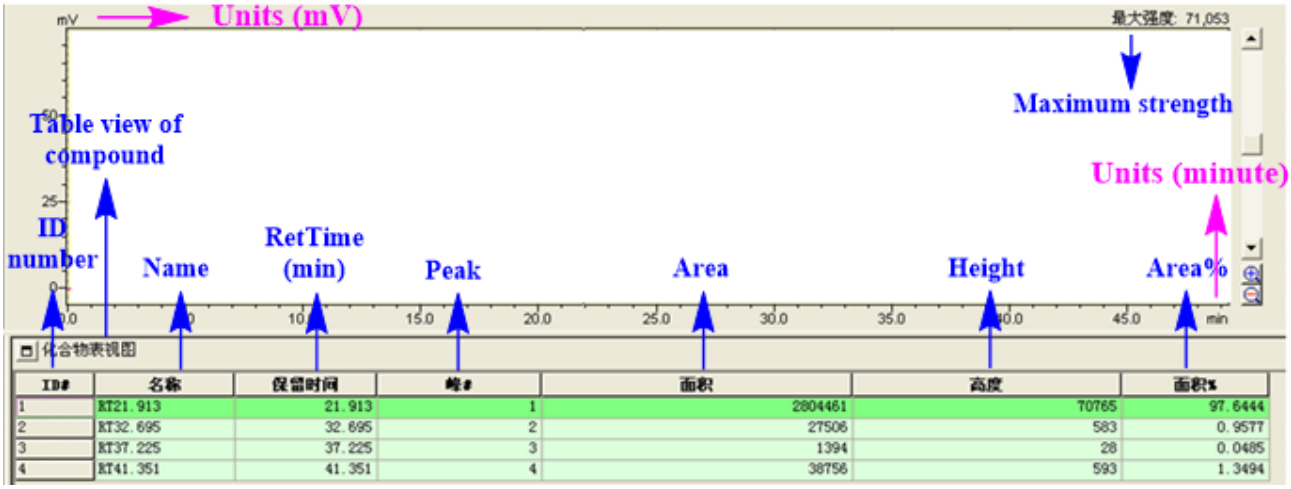
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT30.295	30.295	1	3008082	31866	20.8013
2	RT42.706	42.706	2	2993623	28233	20.7013
3	RT45.731	45.731	3	4187877	33505	28.9597
4	RT70.232	70.232	4	4271458	26955	29.5377



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.329	32.329	1	163859	1787	1.8931
2	RT44.860	44.860	2	122568	1306	1.4161
3	RT47.365	47.365	3	8309778	69342	96.0063
4	RT72.195	72.195	4	59245	364	0.6845

Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
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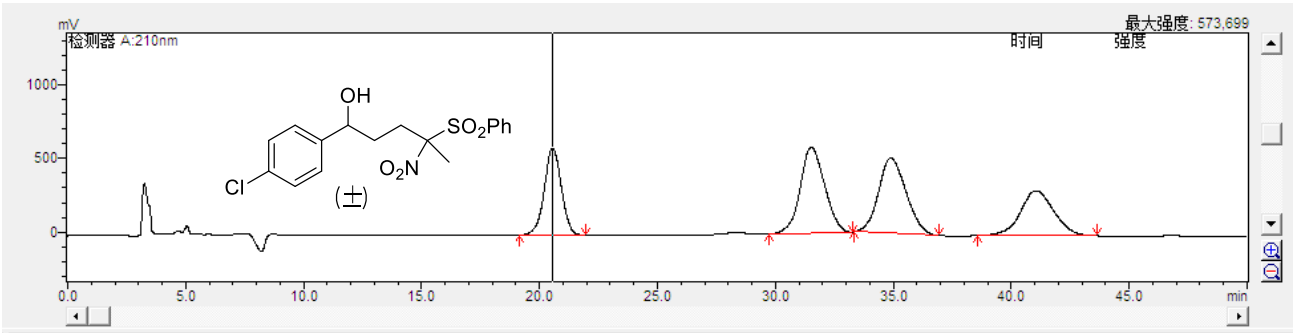
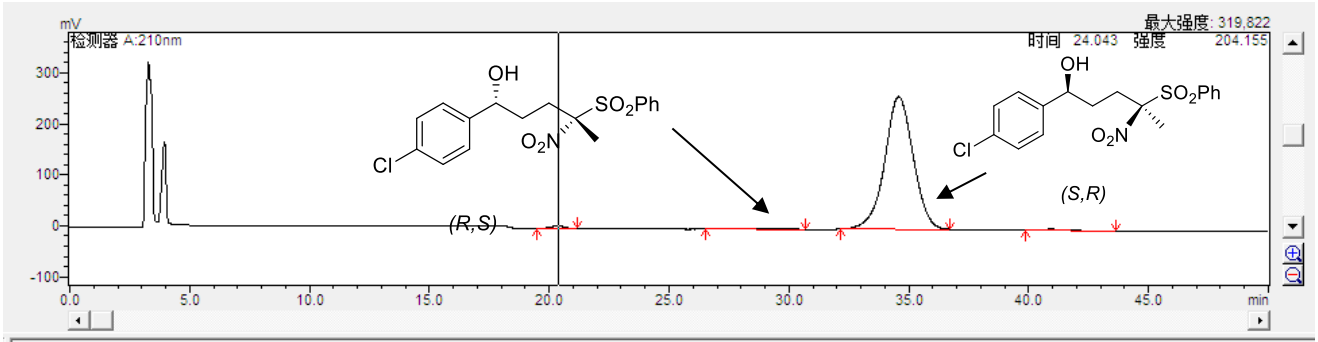
(*S,R*)-**5f: (*1S,4R*-1-(4-chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC:** Chiracel OZ-H, detected at 210, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.547	20.547	1	29781562	592168	20.7569
2	RT31.507	31.507	2	41911147	580709	29.2109
3	RT34.887	34.887	3	41670021	509897	29.0429
4	RT41.036	41.036	4	30114985	304413	20.9893



化合物表视图

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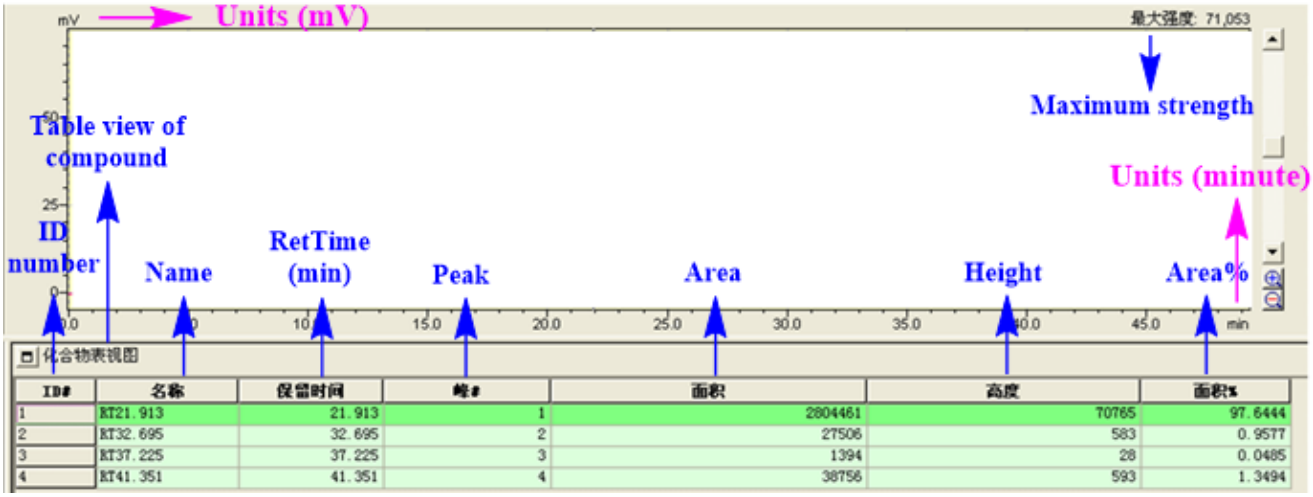
1	RT20.367	20.367	1	217121	5012	0.9805
2	RT28.156	28.156	2	210018	2277	0.9484
3	RT34.569	34.569	3	21547949	260286	97.3108
4	RT40.951	40.951	4	168352	2166	0.7603

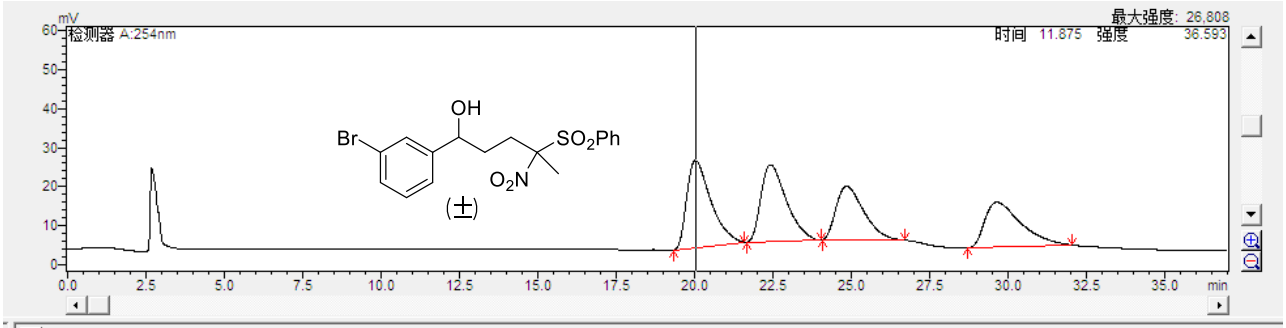
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5f: (*1S,4S*)-1-(3-bromophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC:** Chiracel OD-3, detected at 254 nm, eluent: n-hexane/2-propanol = 85/15, flow rate = 1.0mL/min, 25°C).



化合物表视图

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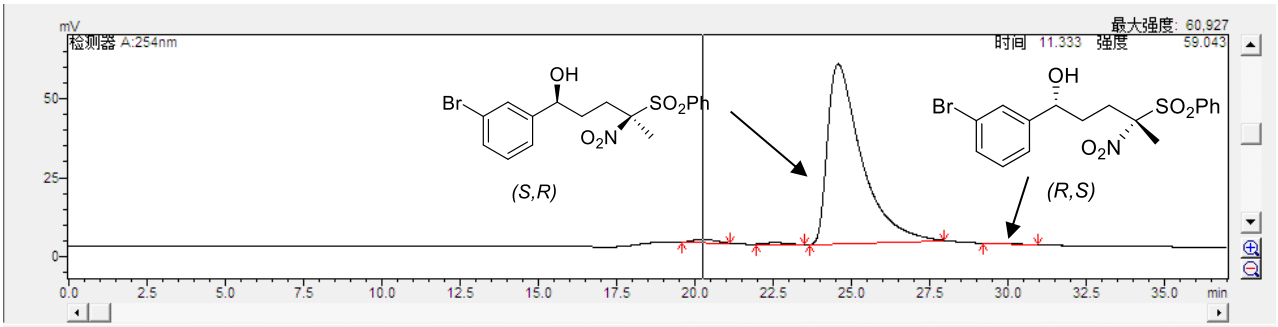
1	RT20.023	20.023	1	1201402	22487	29.2681
2	RT22.418	22.418	2	1119598	19766	27.2753
3	RT24.842	24.842	3	848259	13770	20.6650
4	RT29.644	29.644	4	935553	11570	22.7916



化合物表视图

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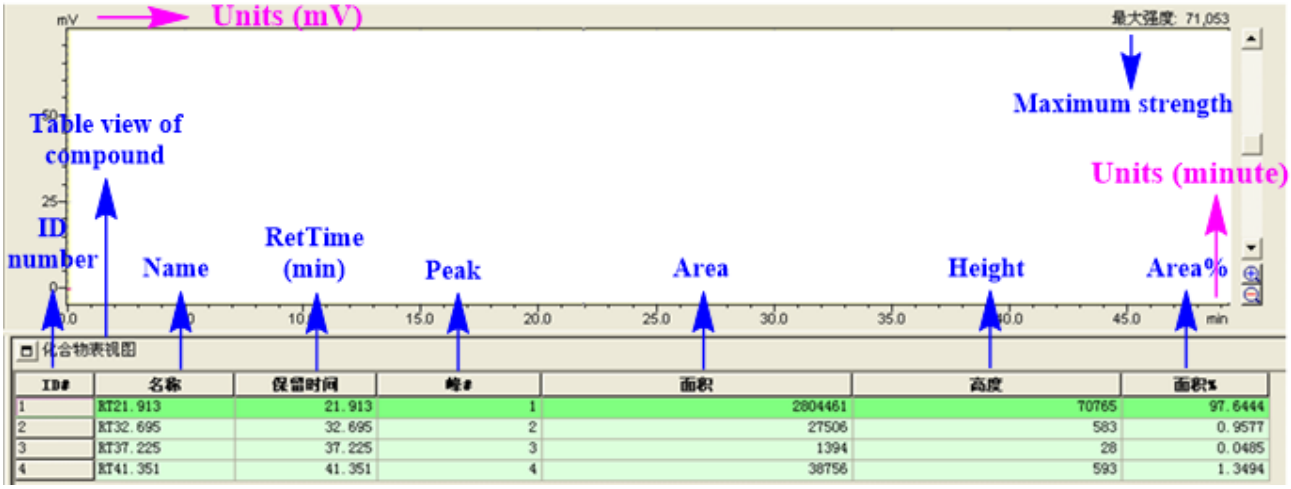
1	RT20.260	20.260	1	48219	1056	1.1051
2	RT22.566	22.566	2	26199	561	0.6005
3	RT24.570	24.570	3	4280230	56768	98.0998
4	RT29.235	29.235	4	8490	4	0.1946

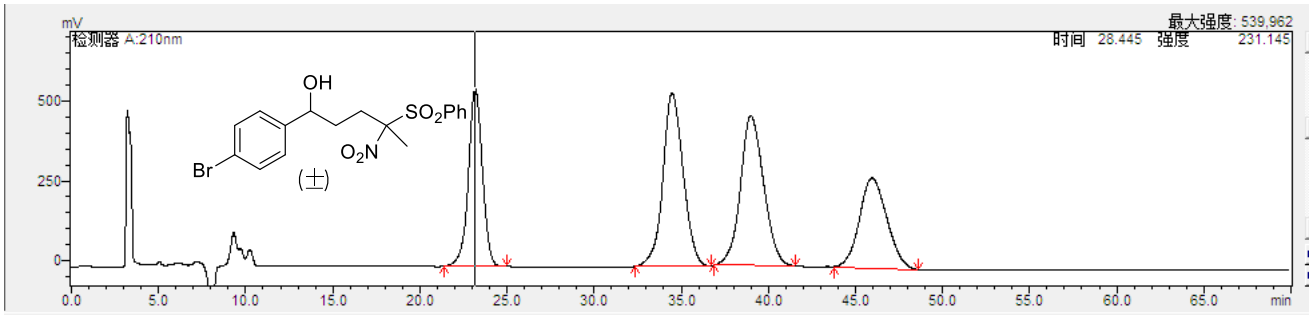
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

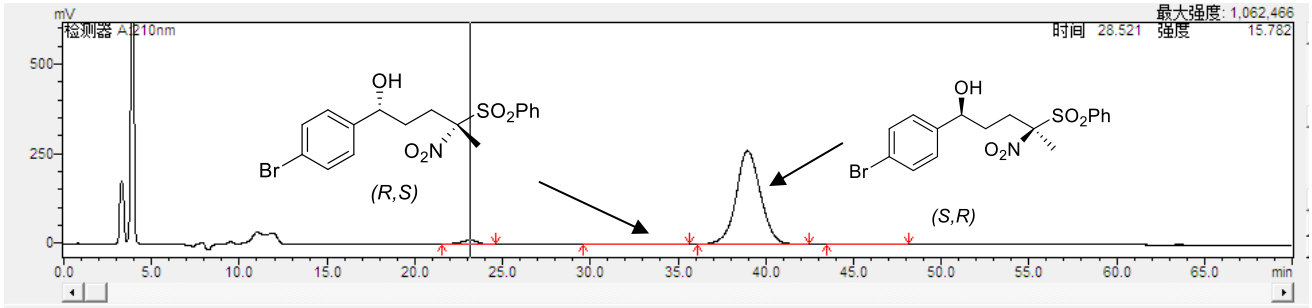
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*R*)-**5h: (*1S*,*4R*)-1-(4-bromophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC:** Chiracel OZ-H, detected at 210 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

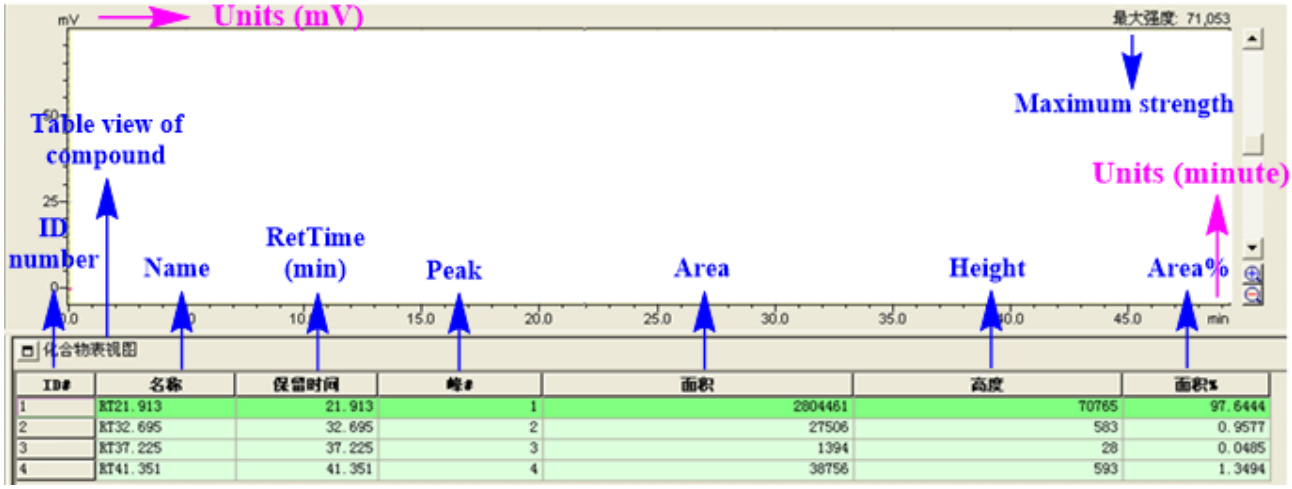
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT23.171	23.171	1	31169259	557536	20.8689
2	RT34.469	34.469	2	43665388	540527	29.2355
3	RT39.000	39.000	3	43601590	468341	29.1928
4	RT45.939	45.939	4	30921079	281576	20.7028



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT23.180	23.180	1	725485	11600	2.7590
2	RT34.001	34.001	2	27550	250	0.1048
3	RT38.955	38.955	3	25348893	261877	96.4005
4	RT44.798	44.798	4	193460	1853	0.7357

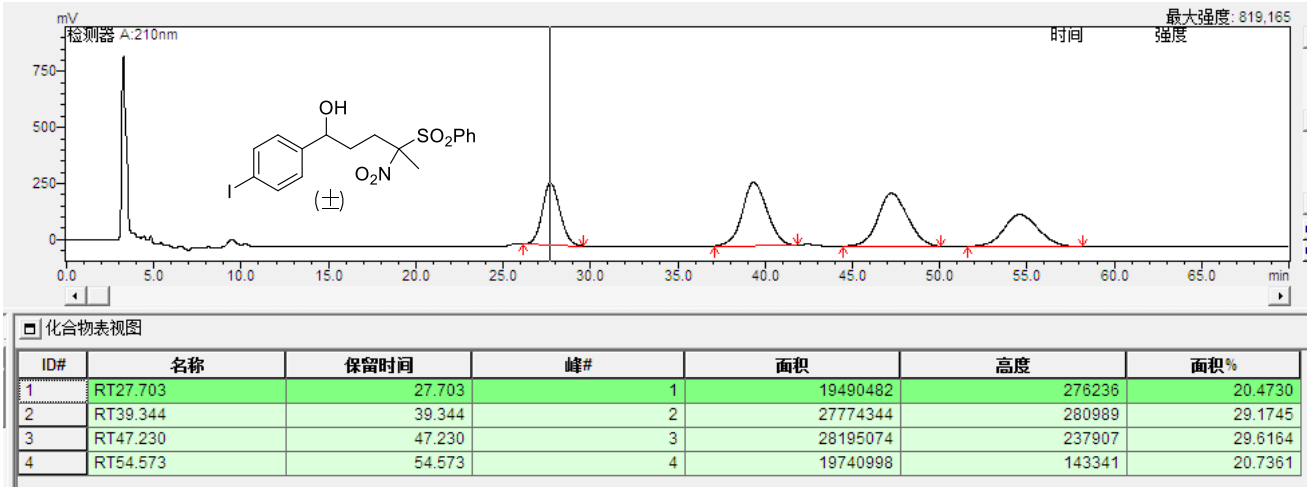
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

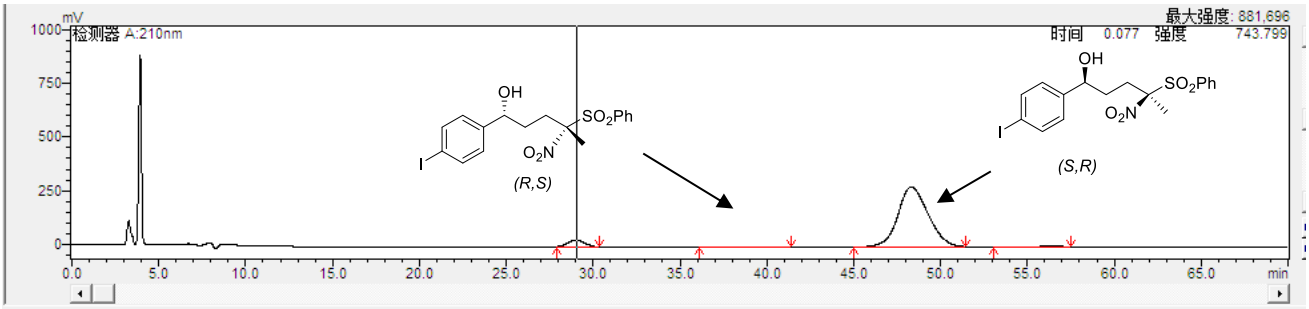
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5i: (*1S,4R*)-1-(4-iodophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC:** Chiracel OZ-H, detected at 210 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

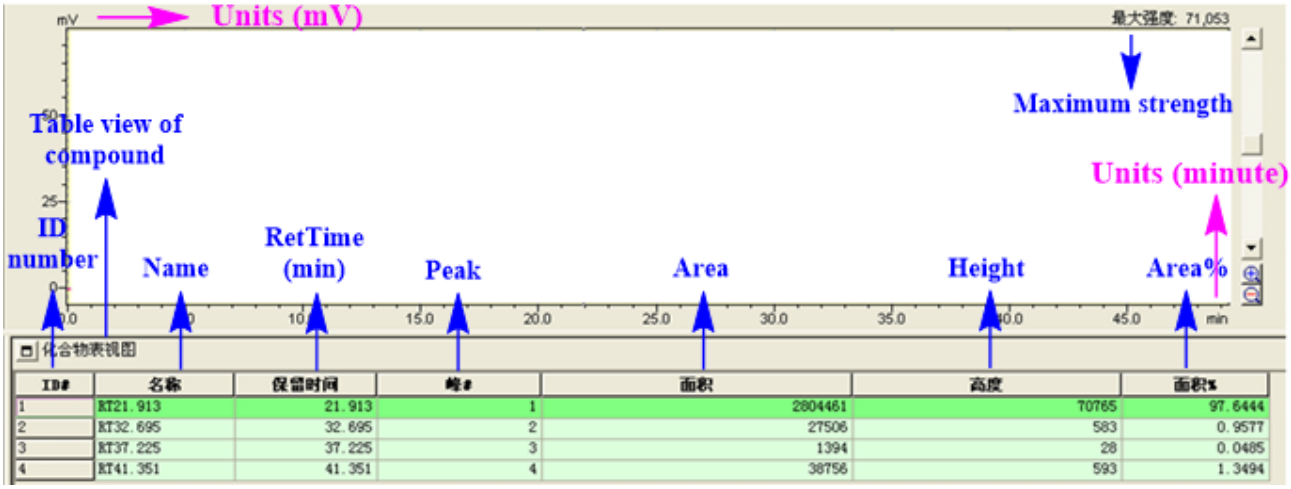
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.703	27.703	1	19490482	276236	20.4730
2	RT39.344	39.344	2	27774344	280989	29.1745
3	RT47.230	47.230	3	28195074	237907	29.6164
4	RT54.573	54.573	4	19740998	143341	20.7361



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT29.021	29.021	1	2132491	32281	5.9106
2	RT38.053	38.053	2	87658	1436	0.2430
3	RT48.317	48.317	3	33707023	278195	93.4260
4	RT56.358	56.358	4	151666	1767	0.4204

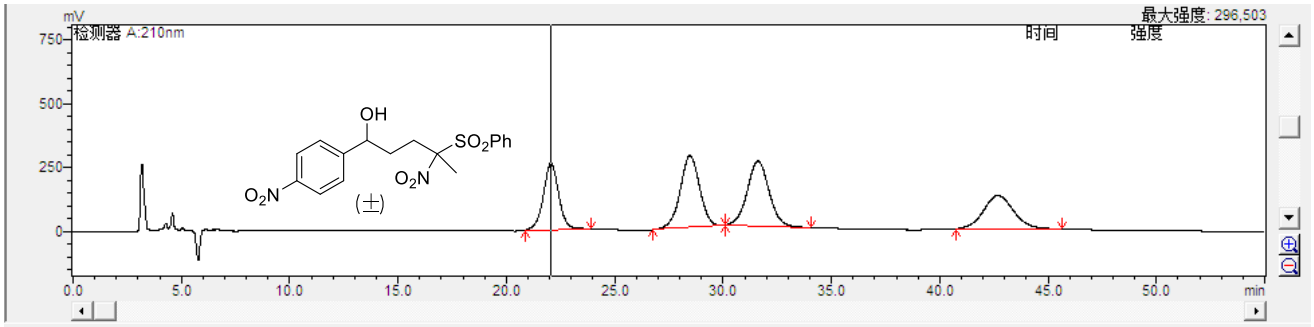
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

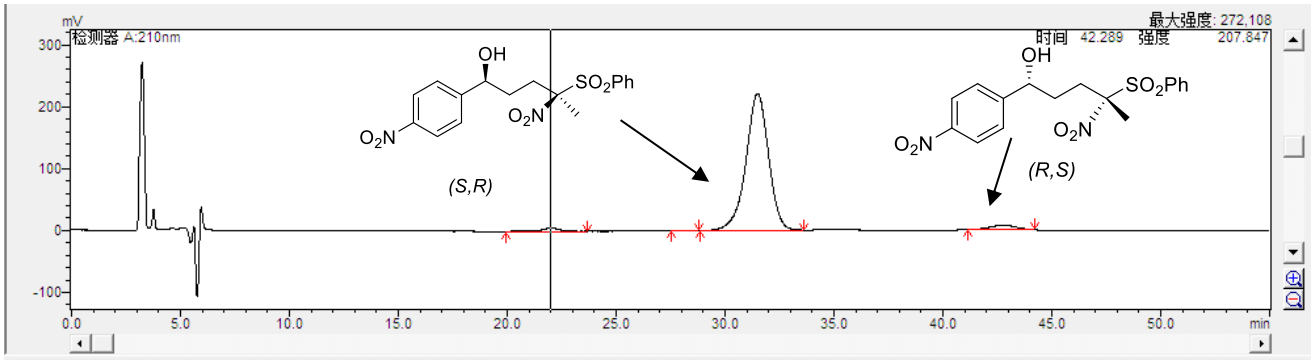
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5j: (*1S,4R*)-4-nitro-1-(4-nitrophenyl)-4-(phenylsulfonyl)pentan-1-ol (HPLC:** Chiracel OZ-H, detected at 210 nm, eluent: n-hexane/2-propanol = 85/15, flow rate = 1.0mL/min, 25°C).



化合物表视图

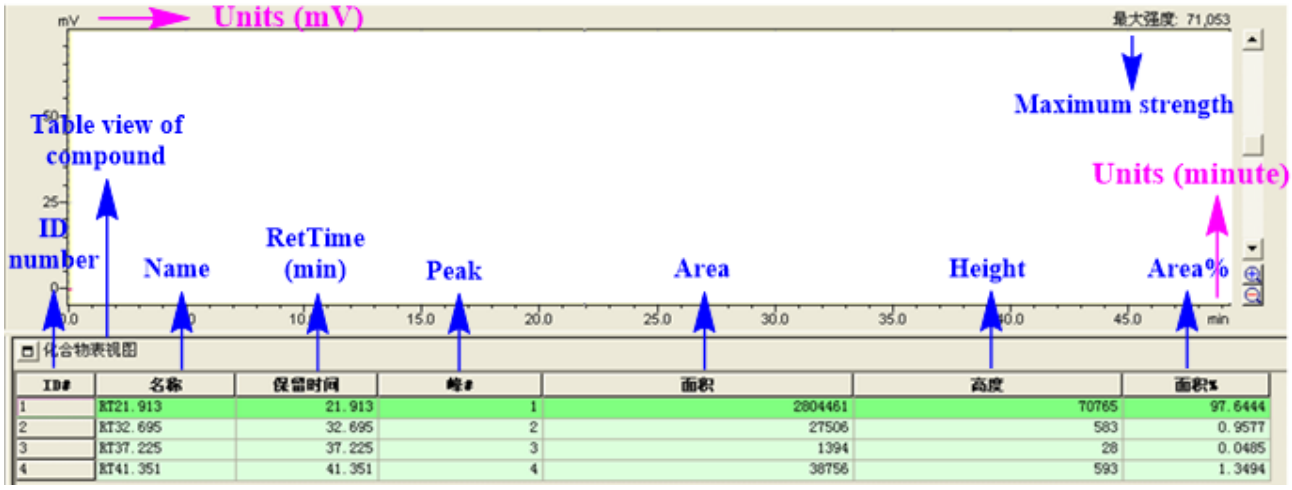
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.053	22.053	1	12877688	260158	21.1271
2	RT28.469	28.469	2	17516260	281109	28.7372
3	RT31.605	31.605	3	17859488	254769	29.3003
4	RT42.684	42.684	4	12699917	130910	20.8355



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.011	22.011	1	300337	5589	1.7814
2	RT28.689	28.689	2	2417	64	0.0143
3	RT31.490	31.490	3	15926786	220956	94.4666
4	RT42.758	42.758	4	630166	7324	3.7377

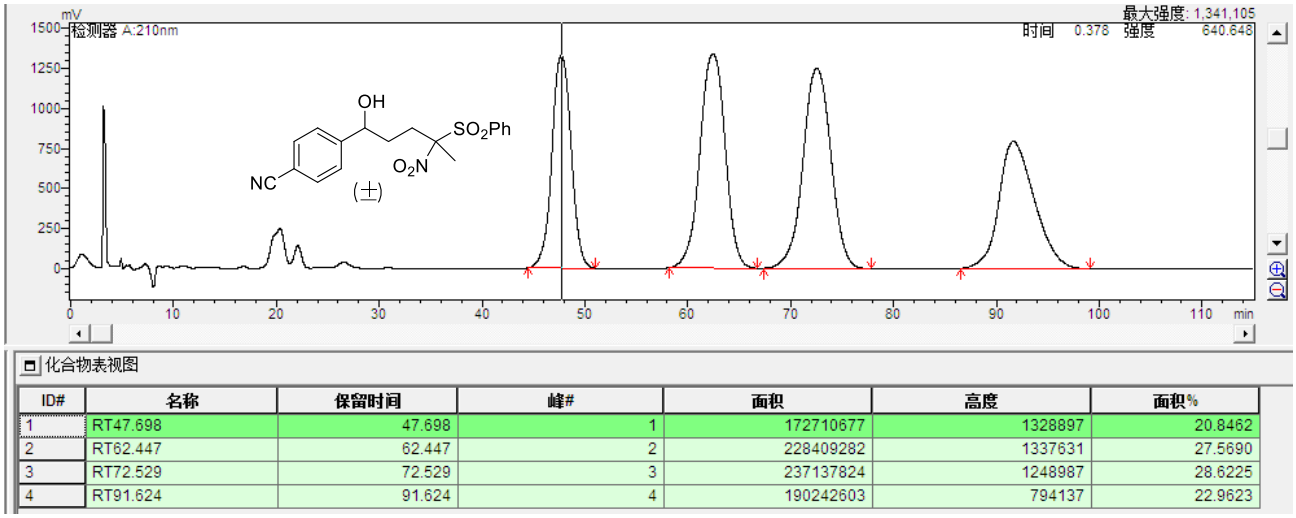
<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



化合物表视图

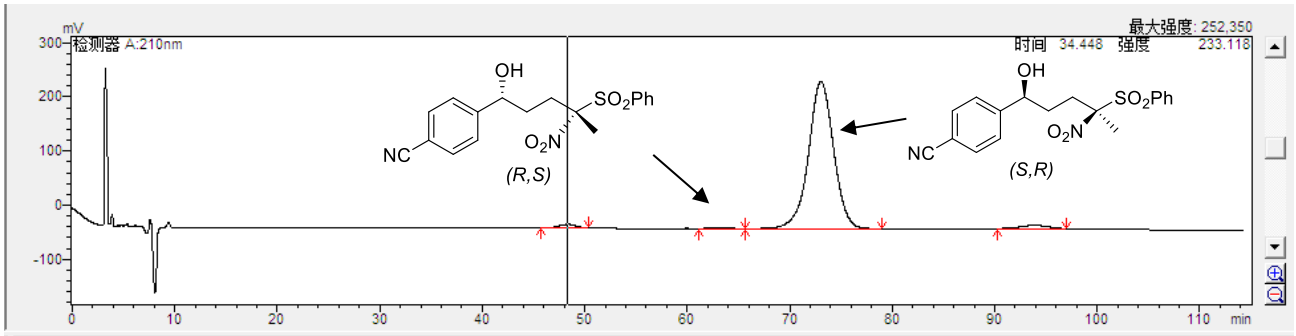
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5k: 4-((*1S,4S*)-1-hydroxy-4-nitro-4-(phenylsulfonyl)pentyl)benzonitrile:** (HPLC: Chiracel OZ-H, detected at 210nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

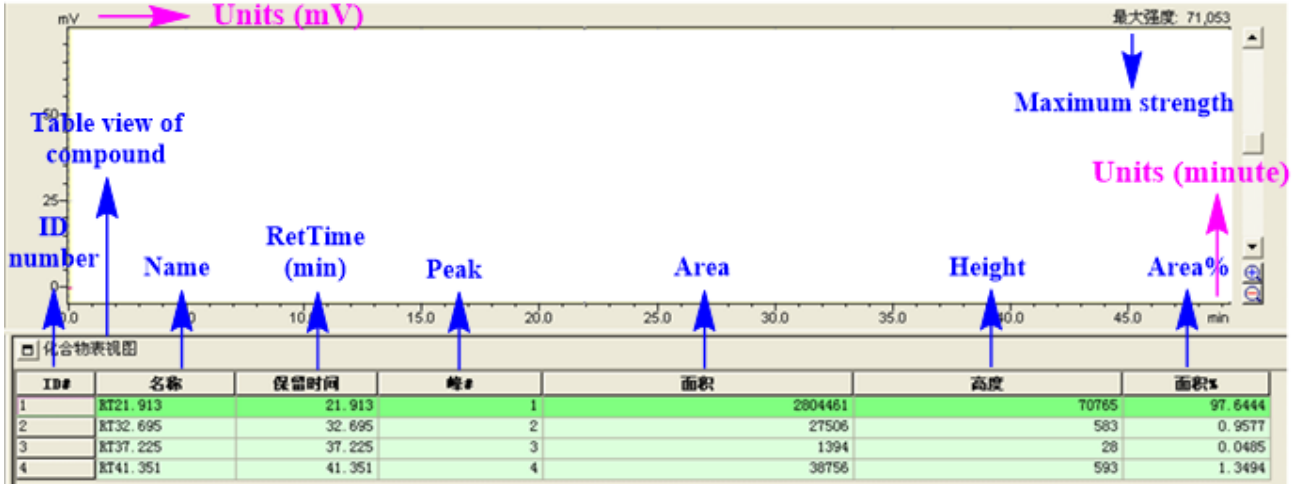
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT47.698	47.698	1	172710677	1328897	20.8462
2	RT62.447	62.447	2	228409282	1337631	27.5690
3	RT72.529	72.529	3	237137824	1248987	28.6225
4	RT91.624	91.624	4	190242603	794137	22.9623



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT48.353	48.353	1	734642	6692	1.5191
2	RT62.851	62.851	2	76105	519	0.1574
3	RT73.046	73.046	3	46393108	272475	95.9296
4	RT93.815	93.815	4	1157784	6329	2.3940

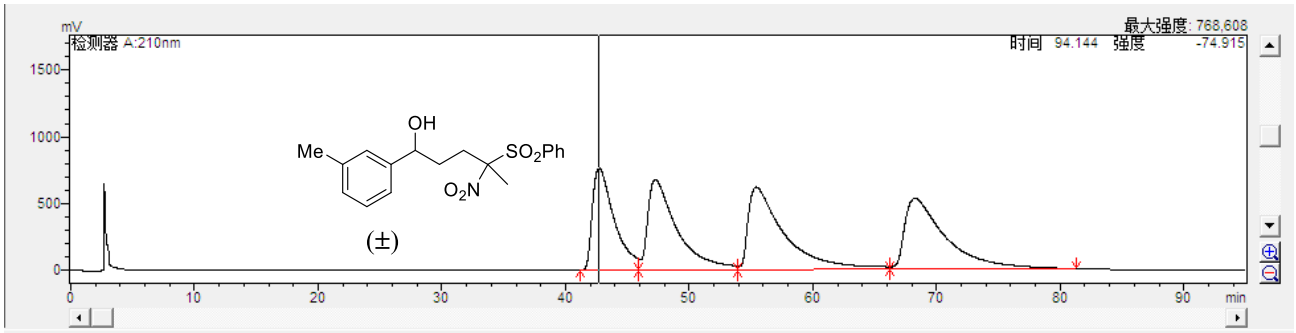
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

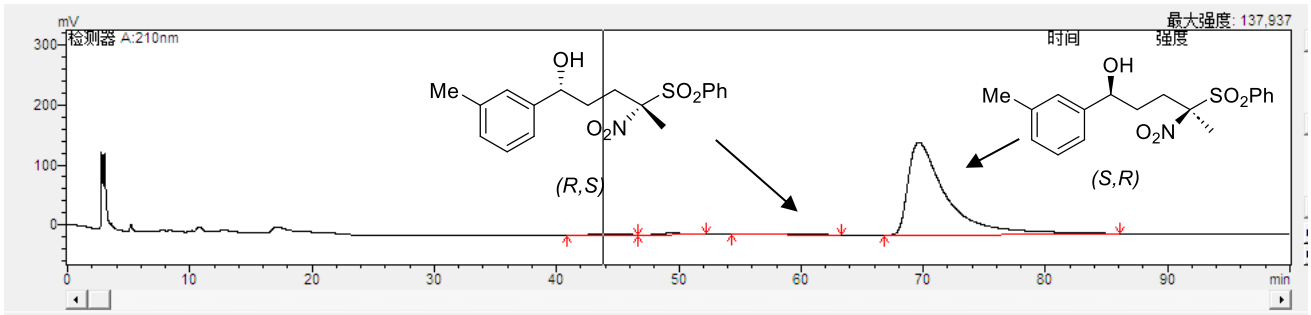
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5l: (*1S,4S*)-4-nitro-4-(phenylsulfonyl)-1-(m-tolyl)pentan-1-ol (HPLC:** Chiracel OD3, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25°C).



化合物表视图

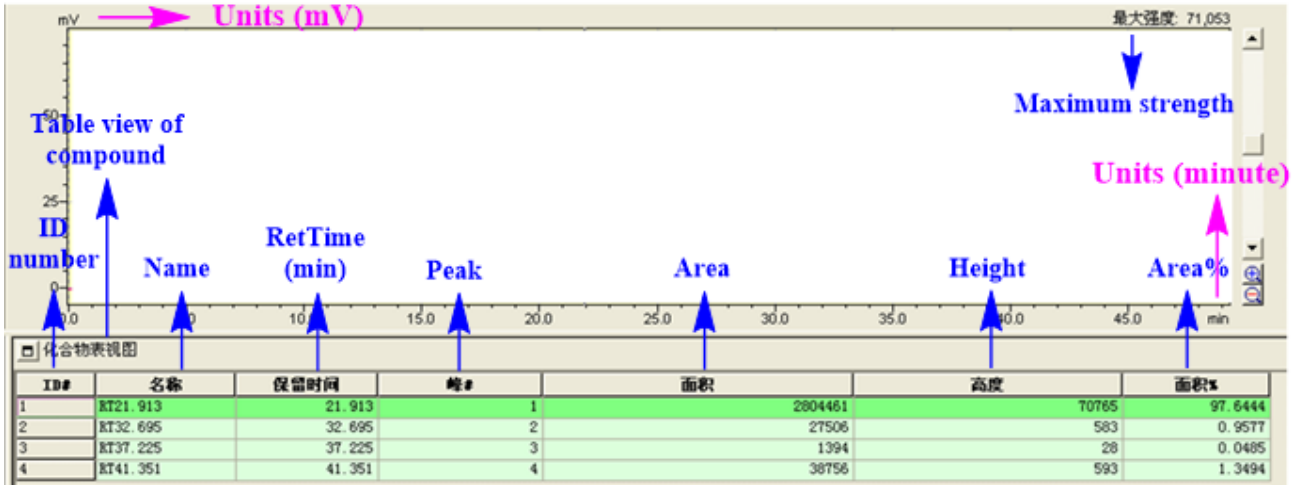
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT42.708	42.708	1	93919484	766368	20.6057
2	RT47.258	47.258	2	112321604	678279	24.6431
3	RT55.414	55.414	3	126639940	618703	27.7845
4	RT68.257	68.257	4	122912956	529535	26.9668



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT43.803	43.803	1	198838	1802	0.5839
2	RT49.540	49.540	2	279184	2495	0.8199
3	RT56.235	56.235	3	84877	236	0.2493
4	RT69.635	69.635	4	33488301	154263	98.3469

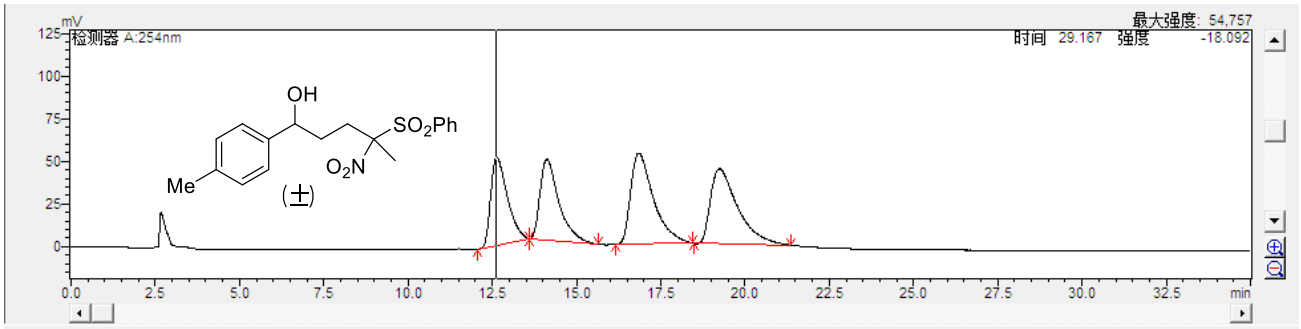
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

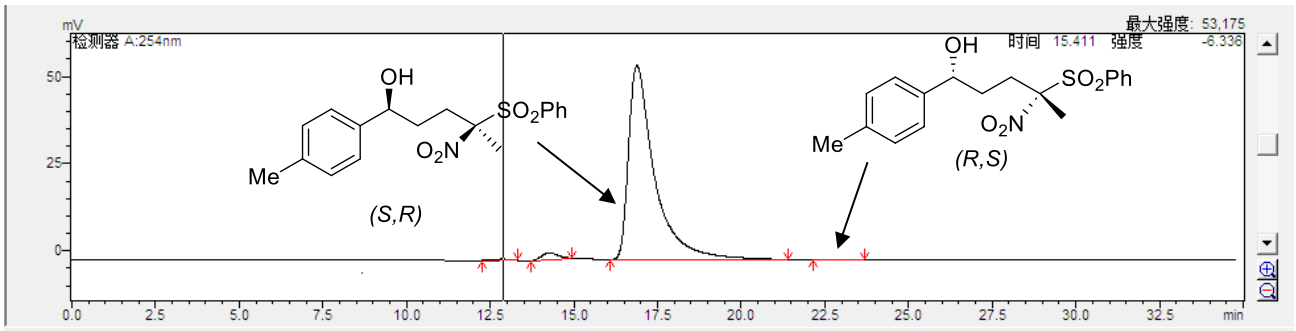
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5m: (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(p-tolyl)pentan-1-ol (HPLC:** Chiracel OD-3, detected at 254 nm, eluent: n-hexane/2-propanol = 85/15, flow rate = 1.0mL/min, 25°C).



化合物表视图

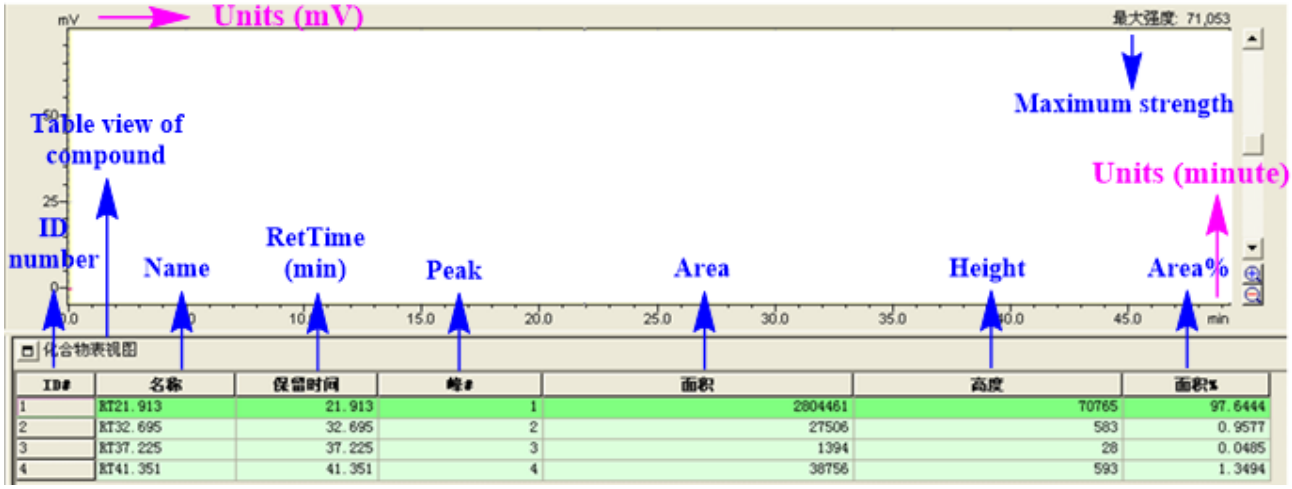
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.632	12.632	1	1765330	51677	20.4824
2	RT14.119	14.119	2	1855279	47599	21.5260
3	RT16.845	16.845	3	2520710	53340	29.2467
4	RT19.237	19.237	4	2477465	44046	28.7449



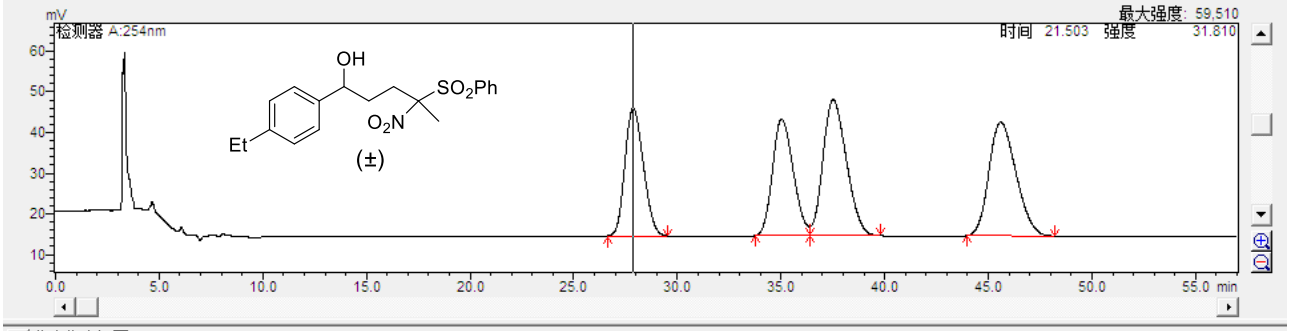
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.886	12.886	1	12327	401	0.3976
2	RT14.252	14.252	2	66140	1993	2.1334
3	RT16.881	16.881	3	3018131	55634	97.3505
4	RT22.518	22.518	4	3674	53	0.1185

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

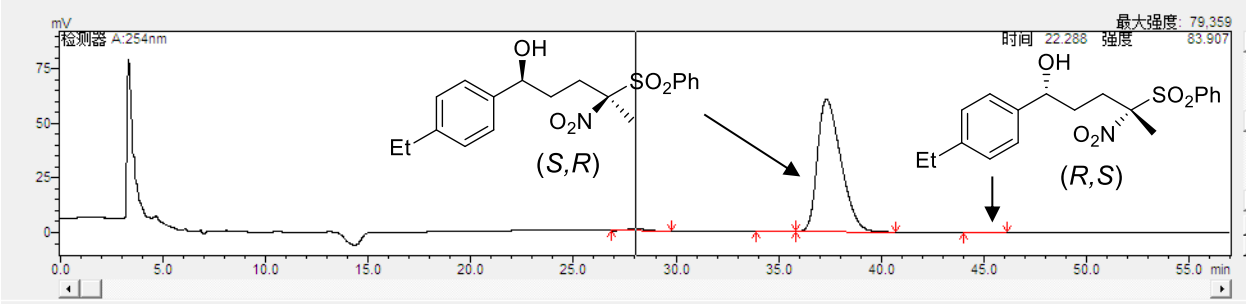


(*S,R*)-**5n: (*1S,4R*)-1-(4-ethylphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC:** Chiracel IC, detected at 254 nm, eluent: n-hexane/2-propanol = 93/7, flow rate = 1.0 mL/min, 25°C).



化合物表视图

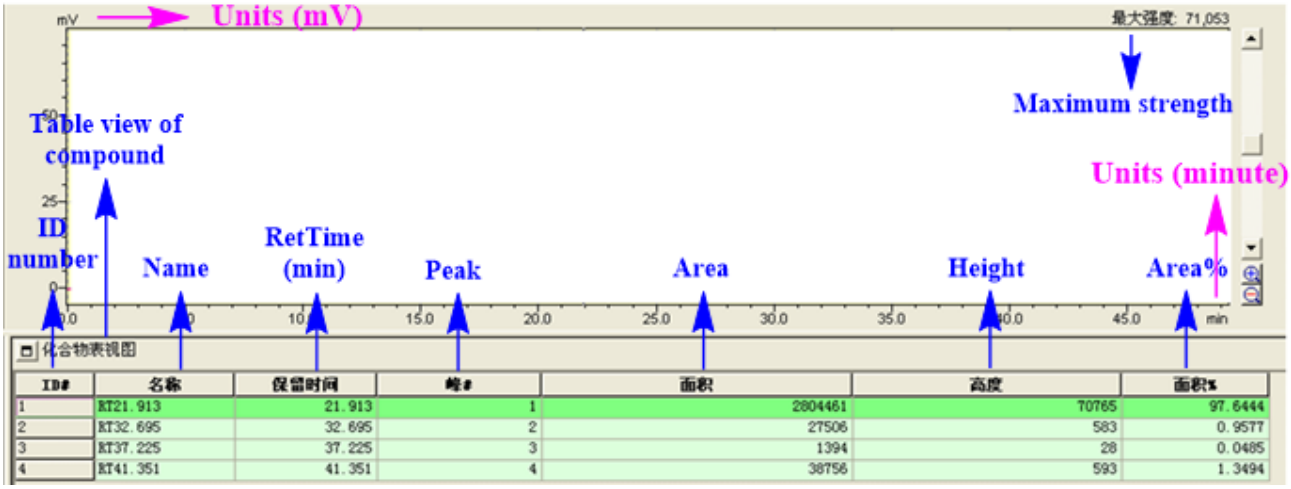
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.865	27.865	1	1947921	31436	21.3301
2	RT35.022	35.022	2	1995818	28591	21.8546
3	RT37.511	37.511	3	2635326	33458	28.8573
4	RT45.596	45.596	4	2553193	27966	27.9580



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT28.029	28.029	1	66374	1039	1.3390
2	RT35.404	35.404	2	31355	475	0.6325
3	RT37.333	37.333	3	4855807	60849	97.9596
4	RT45.747	45.747	4	3414	74	0.0689

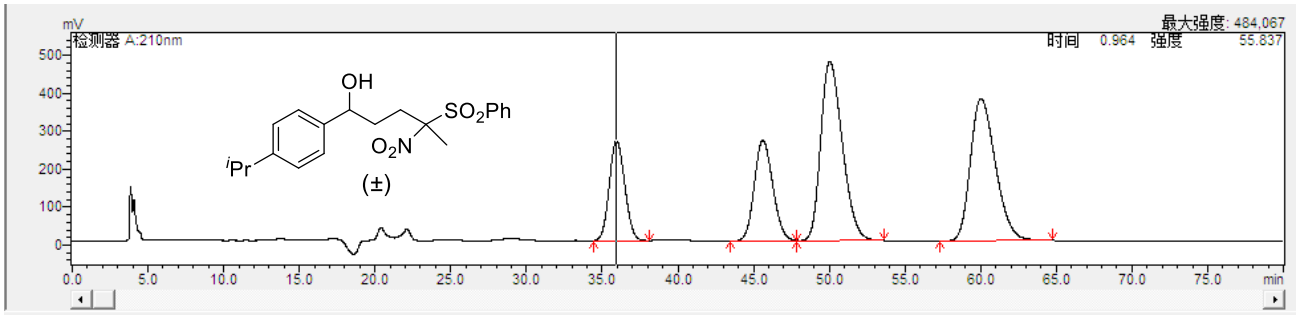
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

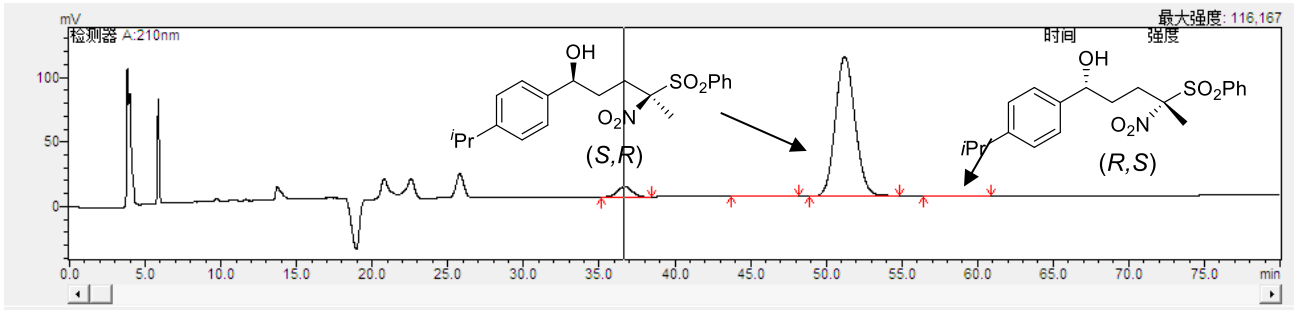
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5o:** (*1S,4R*)-1-(4-isopropylphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 210 nm, eluent: n-hexane/2-propanol = 93/7, flow rate = 0.9 mL/min, 25°C).



化合物表视图

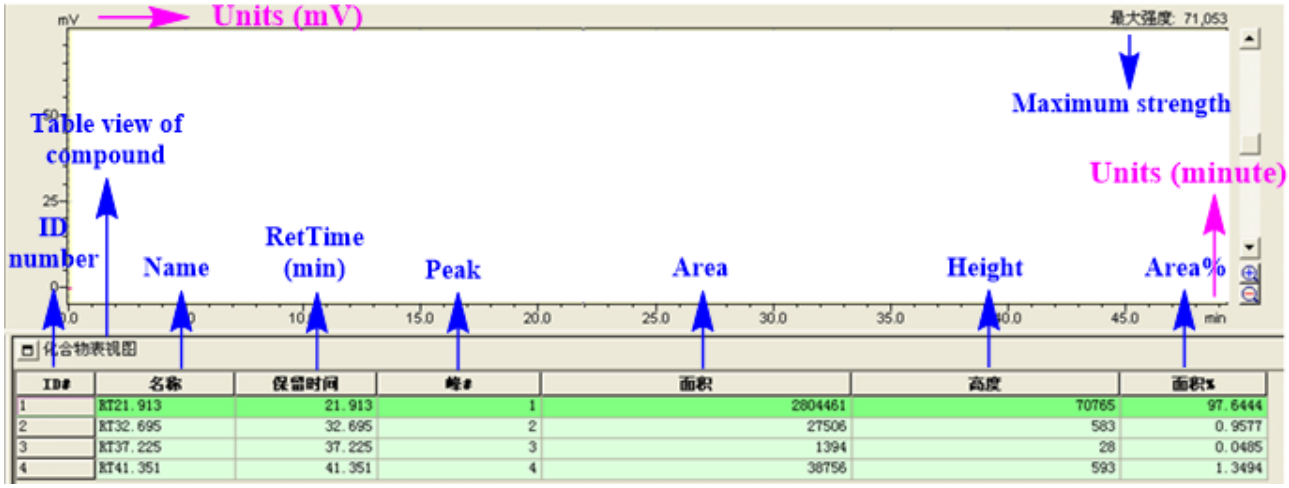
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT35.952	35.952	1	18728561	263163	14.2580
2	RT45.607	45.607	2	22467721	264959	17.1046
3	RT50.035	50.035	3	46907898	472175	35.7108
4	RT60.022	60.022	4	43250711	375195	32.9266



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT36.668	36.668	1	534338	8067	5.1520
2	RT45.319	45.319	2	73736	532	0.7110
3	RT51.207	51.207	3	9739223	107888	93.9043
4	RT57.907	57.907	4	24138	289	0.2327

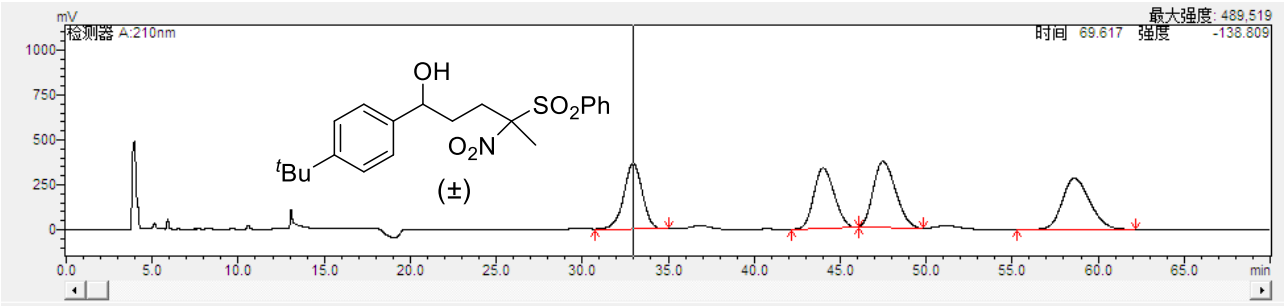
<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



化合物表视图

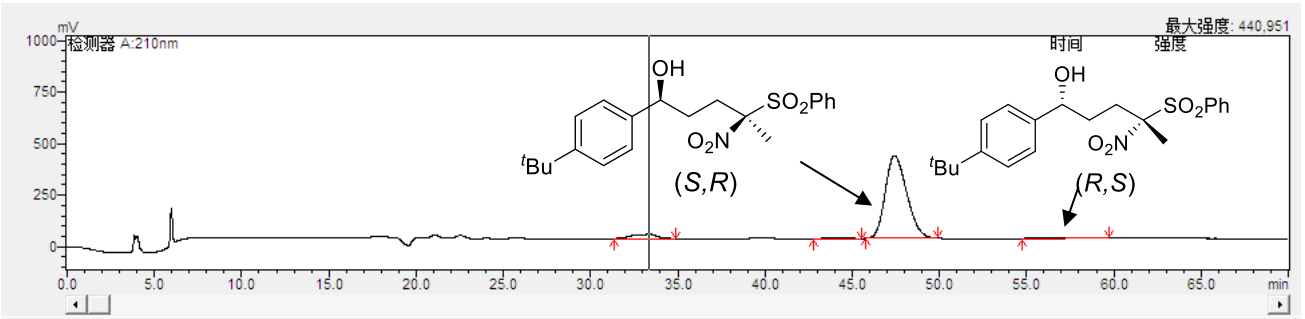
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5p:** (*1S,4R*)-1-(4-(tert-butyl)phenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 210 nm, eluent: n-hexane/2-propanol = 93/7, flow rate = 0.9 mL/min, 25°C).



化合物表视图

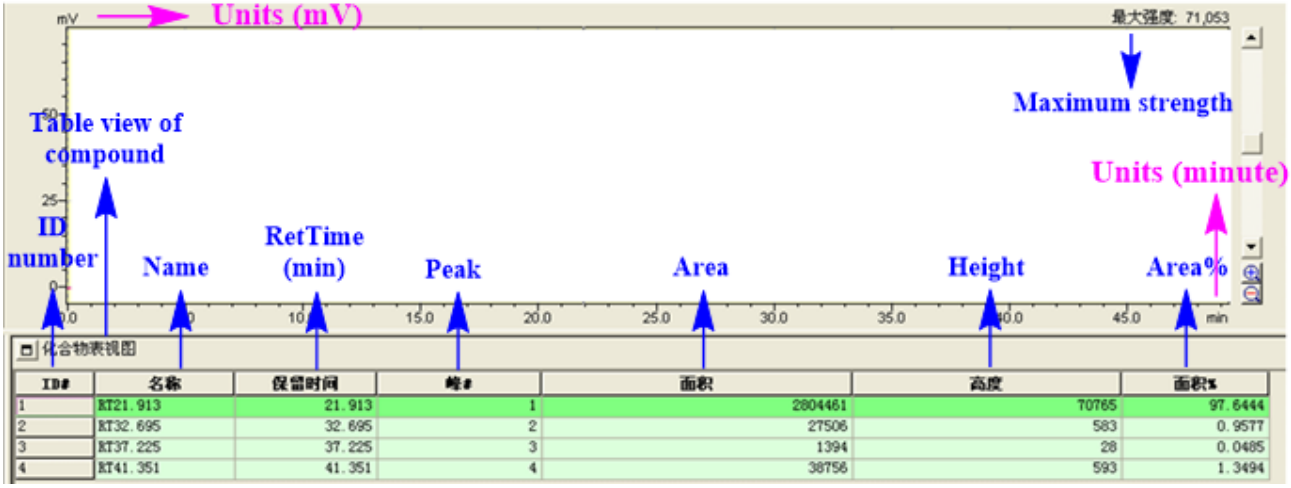
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.951	32.951	1	27206116	363516	22.8017
2	RT44.005	44.005	2	27442638	333833	23.0000
3	RT47.489	47.489	3	33372437	368621	27.9698
4	RT58.625	58.625	4	31294770	283736	26.2285



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT33.346	33.346	1	1930080	20826	5.2880
2	RT44.277	44.277	2	107082	1389	0.2934
3	RT47.425	47.425	3	34354355	400578	94.1232
4	RT56.220	56.220	4	107848	747	0.2955

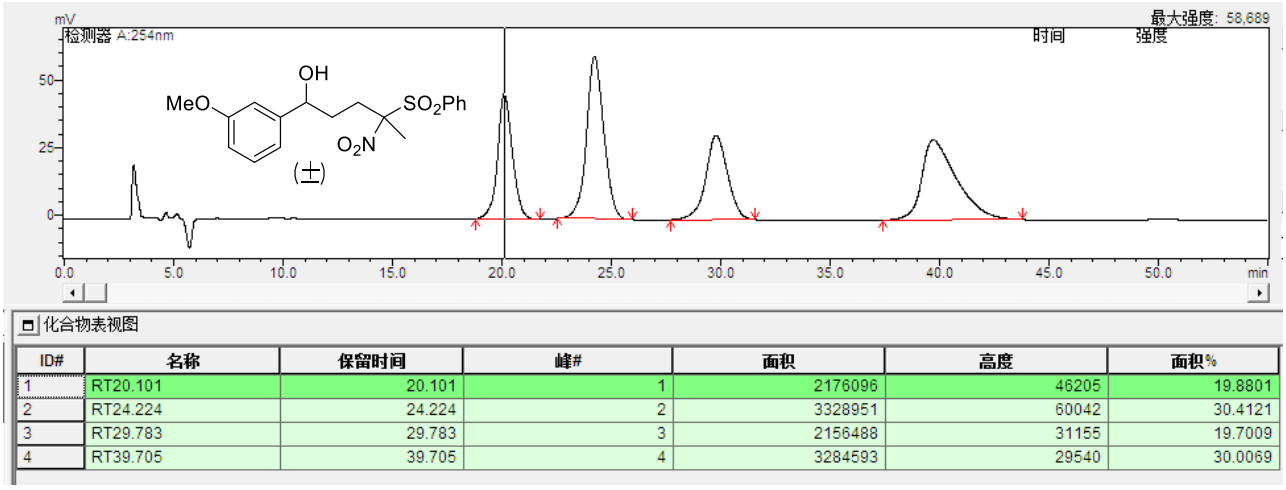
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

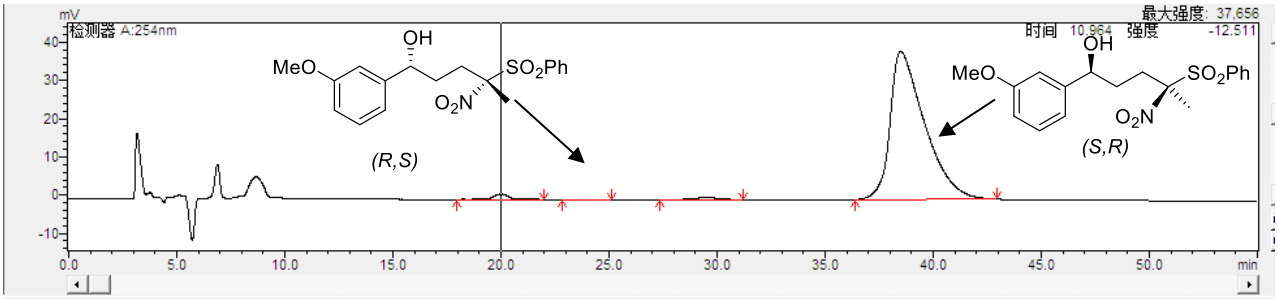
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5q:** (*1S,4R*)-1-(3-methoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel OZ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 85/15, flow rate = 1.0mL/min, 25°C).



化合物表视图

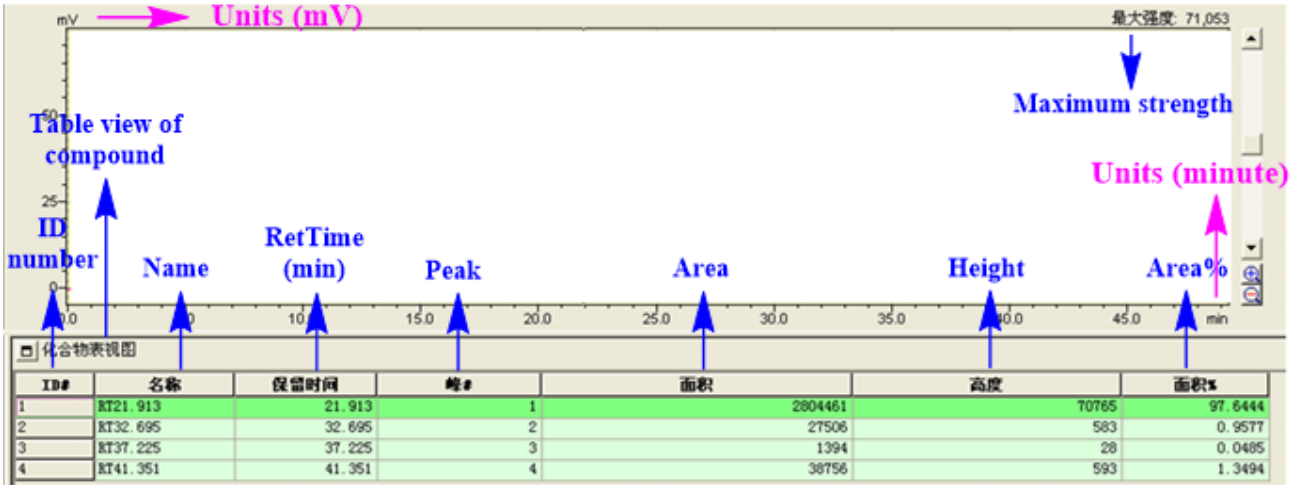
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.101	20.101	1	2176096	46205	19.8801
2	RT24.224	24.224	2	3328951	60042	30.4121
3	RT29.783	29.783	3	2156488	31155	19.7009
4	RT39.705	39.705	4	3284593	29540	30.0069



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.005	20.005	1	73701	1431	1.6647
2	RT24.245	24.245	2	1084	25	0.0245
3	RT29.514	29.514	3	38557	531	0.8709
4	RT38.497	38.497	4	4314016	38804	97.4400

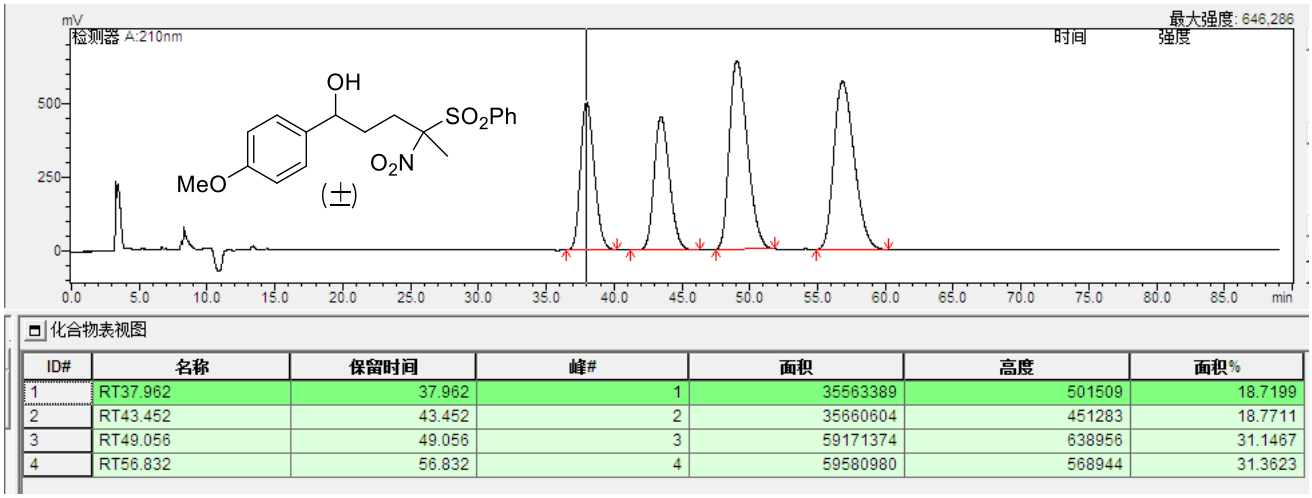
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

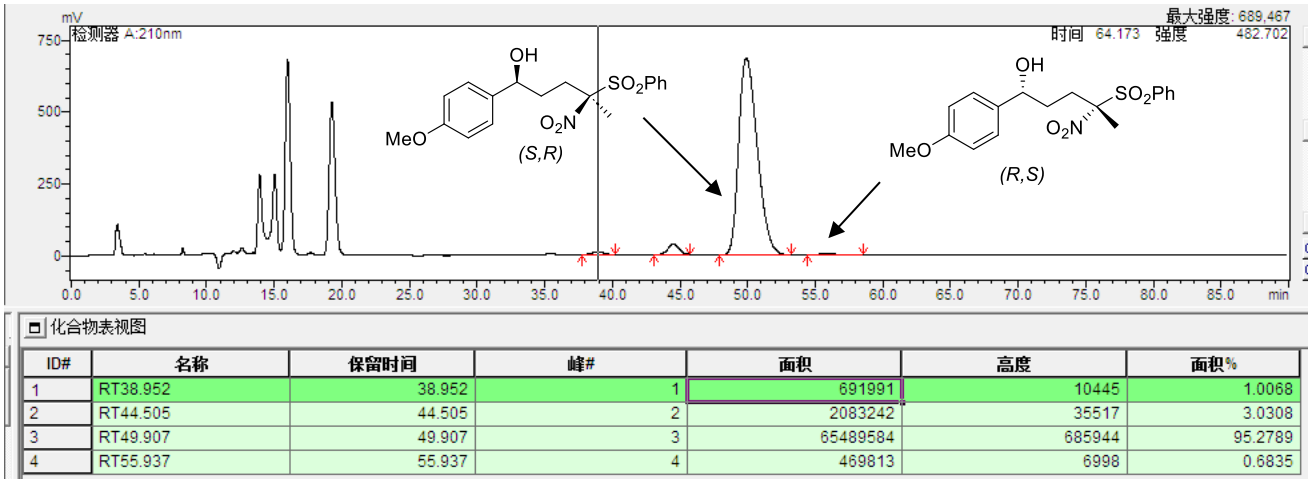
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5r:** (*1S,4R*)-1-(4-methoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 210 nm, eluent: n-hexane/2-propanol = 85/15, flow rate = 1.0mL/min, 25°C).



化合物表视图

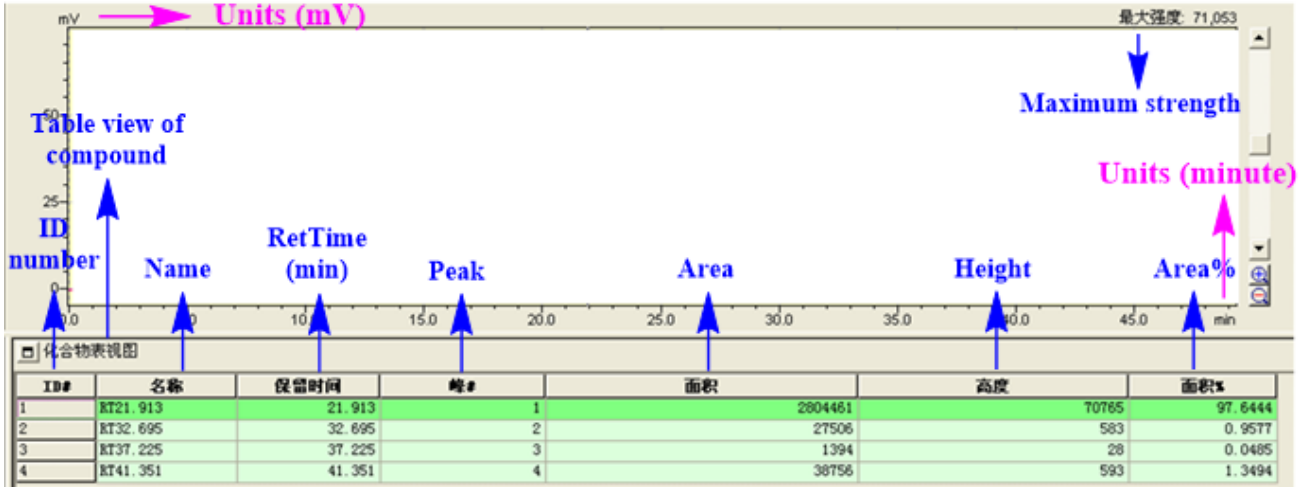
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT37.962	37.962	1	35563389	501509	18.7199
2	RT43.452	43.452	2	35660604	451283	18.7711
3	RT49.056	49.056	3	59171374	638956	31.1467
4	RT56.832	56.832	4	59580980	568944	31.3623



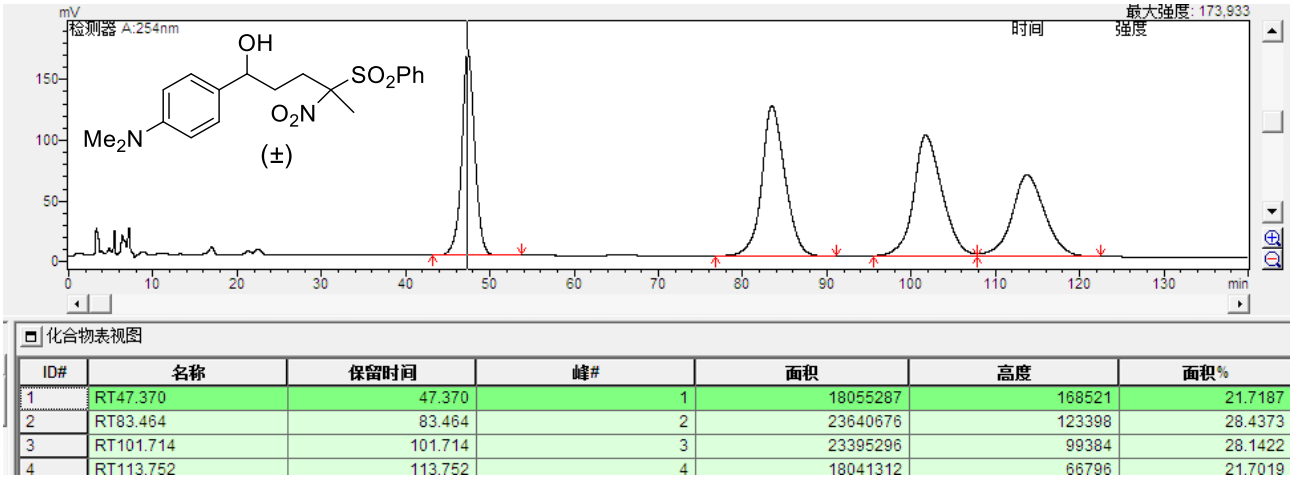
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT38.952	38.952	1	691991	10445	1.0068
2	RT44.505	44.505	2	2083242	35517	3.0308
3	RT49.907	49.907	3	65489584	685944	95.2789
4	RT55.937	55.937	4	469813	6998	0.6835

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

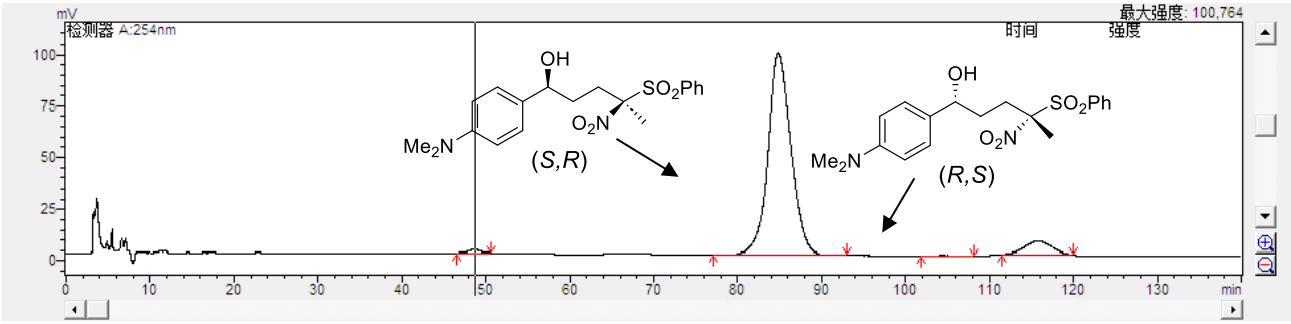


(*S*,*R*)-**5s:** (*1S*,*4R*)-1-(4-(dimethylamino)phenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel OZ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25°C).



化合物表视图

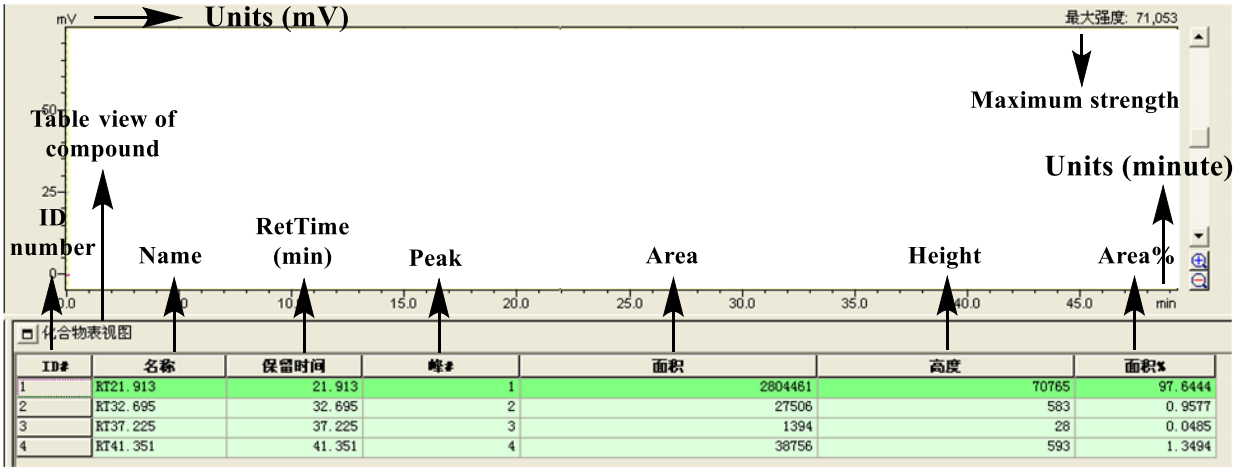
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT47.370	47.370	1	18055287	168521	21.7187
2	RT83.464	83.464	2	23640676	123398	28.4373
3	RT101.714	101.714	3	23395296	99384	28.1422
4	RT113.752	113.752	4	18041312	66796	21.7019



化合物表视图

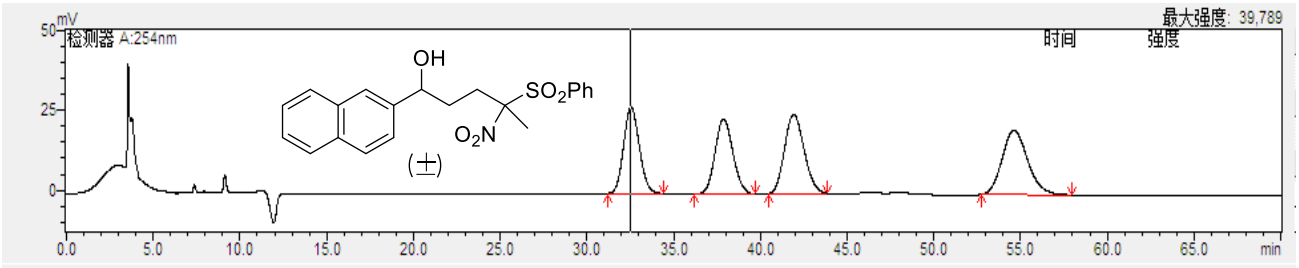
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT48.638	48.638	1	167897	1615	0.8207
2	RT84.829	84.829	2	18708890	98050	91.4536
3	RT104.540	104.540	3	19455	117	0.0951
4	RT115.789	115.789	4	1561015	6676	7.6306

Translation of all characters (Chinese) in the above two frameworks to English is as follows:



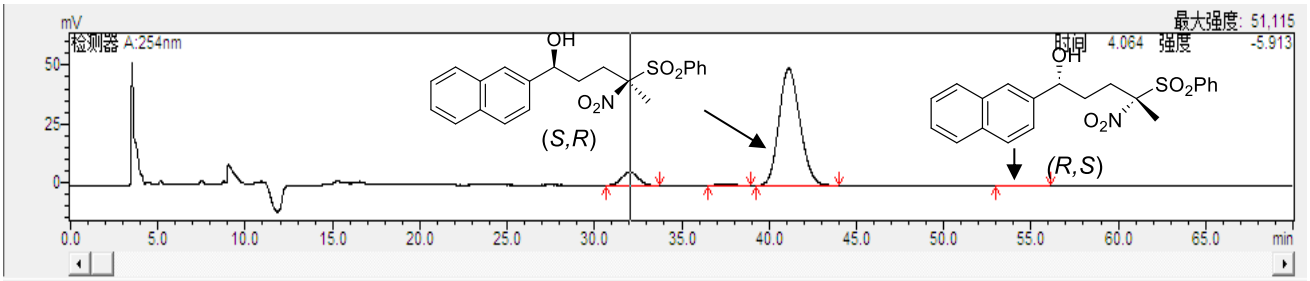
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5t:** (*1S,4R*)-1-(naphthalen-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

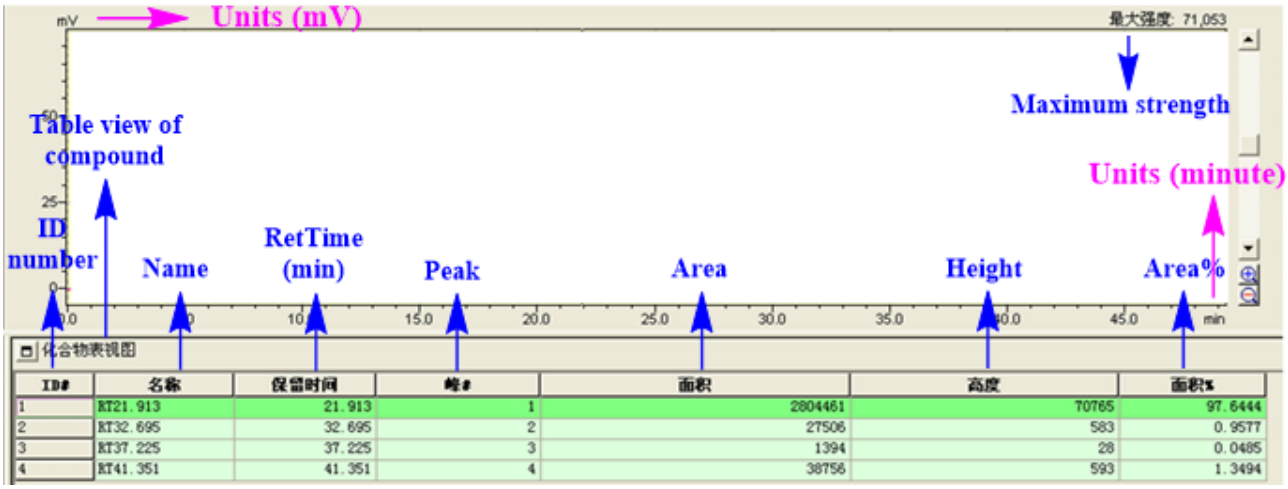
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.540	32.540	1	1721054	27208	23.0221
2	RT37.877	37.877	2	1704211	23671	22.7968
3	RT41.923	41.923	3	1967070	24973	26.3130
4	RT54.624	54.624	4	2083330	20226	27.8681



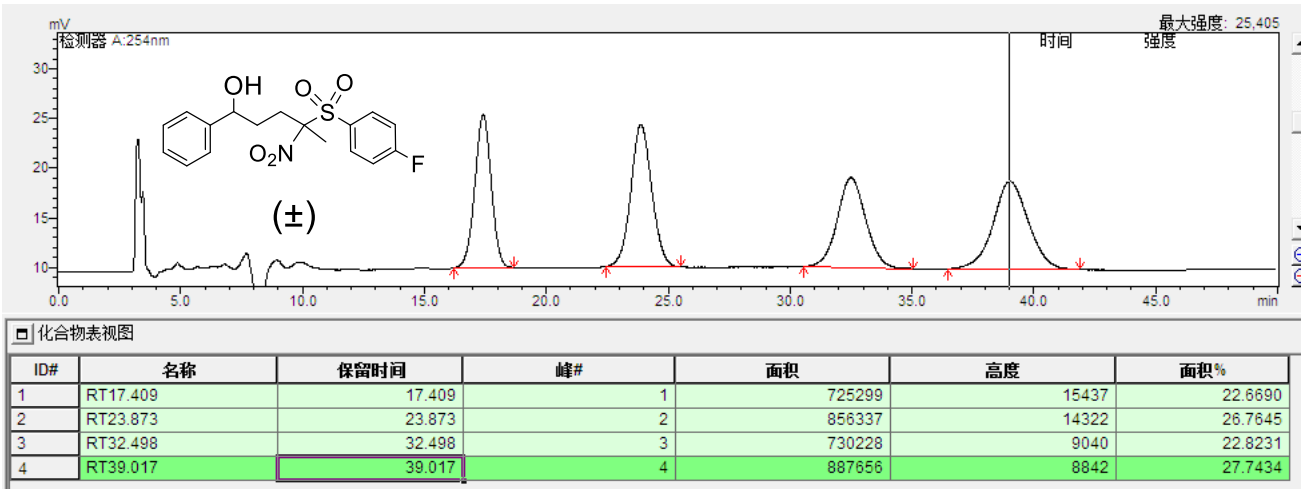
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.028	32.028	1	382296	5790	8.3076
2	RT37.494	37.494	2	28299	372	0.6150
3	RT41.120	41.120	3	4184560	50088	90.9340
4	RT54.044	54.044	4	6602	66	0.1435

<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>

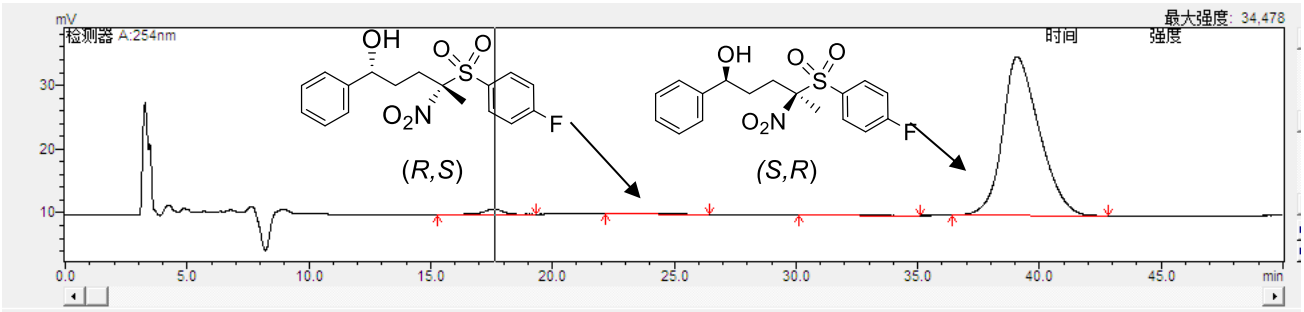


(*S,R*)-**5u:** (*1S,4R*)-4-((4-fluorophenyl)sulfonyl)-4-nitro-1-phenylpentan-1-ol (HPLC: Chiracel OZ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25°C).



化合物表视图

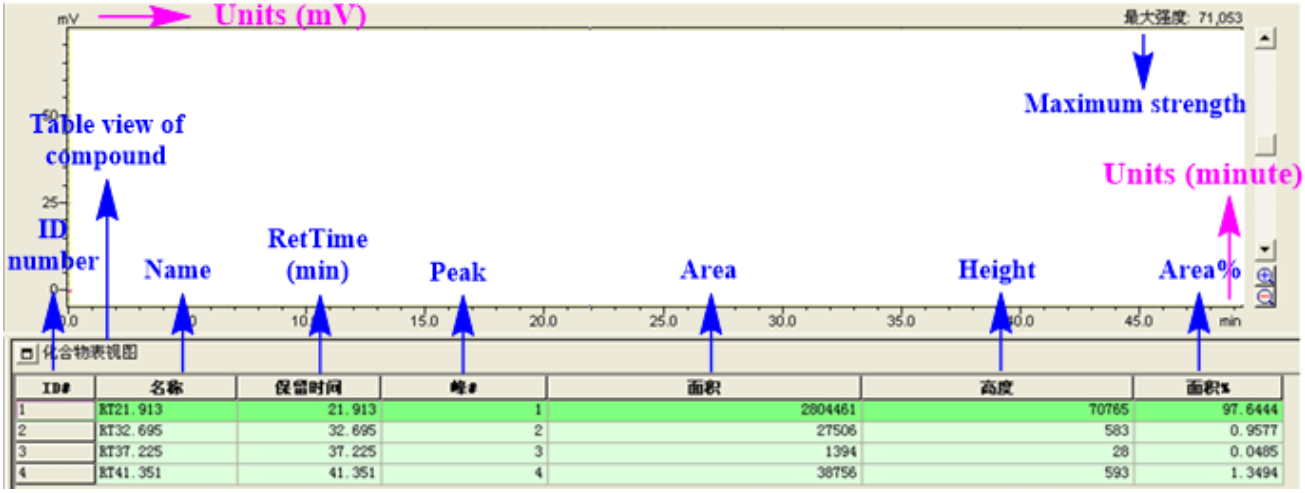
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.409	17.409	1	725299	15437	22.6690
2	RT23.873	23.873	2	856337	14322	26.7645
3	RT32.498	32.498	3	730228	9040	22.8231
4	RT39.017	39.017	4	887656	8842	27.7434



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.608	17.608	1	48013	871	1.7872
2	RT24.147	24.147	2	7356	75	0.2738
3	RT32.903	32.903	3	6459	124	0.2404
4	RT39.083	39.083	4	2624666	24904	97.6986

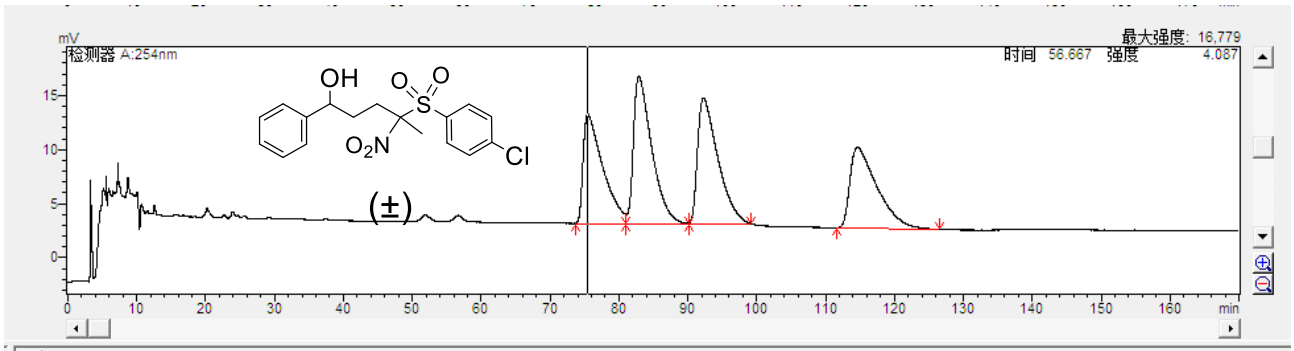
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

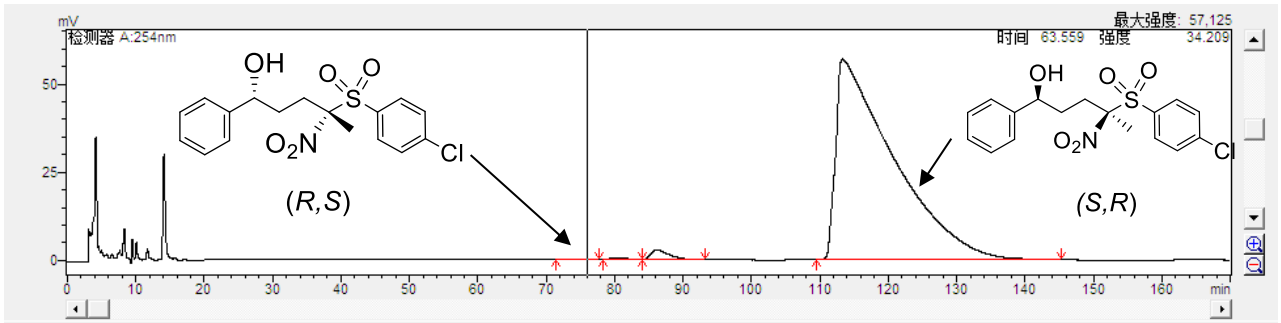
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*R*)-**5v:** (1*S*,4*R*)-4-((4-chlorophenyl)sulfonyl)-4-nitro-1-phenylpentan-1-ol (HPLC: Chiracel OJ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25°C).



化合物表视图

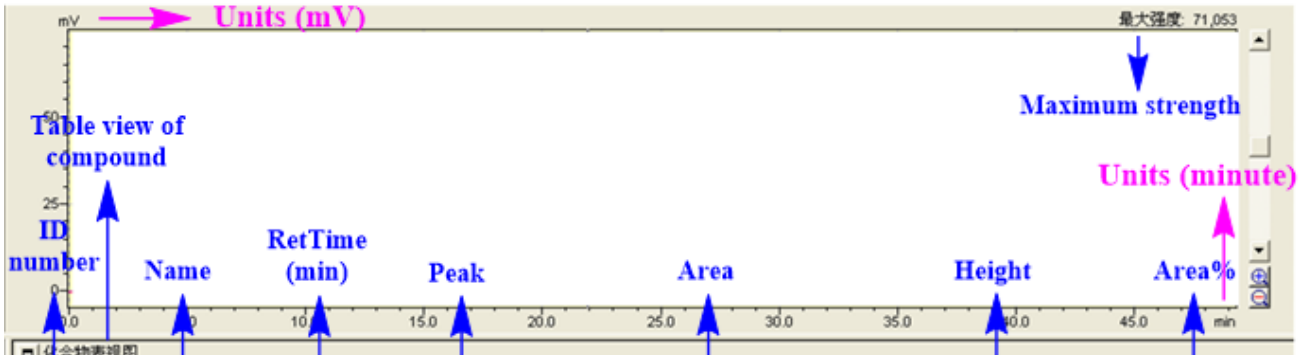
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT75.465	75.465	1	2010611	10107	22.4291
2	RT82.889	82.889	2	2516043	13630	28.0674
3	RT92.325	92.325	3	2392993	11602	26.6947
4	RT114.677	114.677	4	2044641	7461	22.8087



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT76.063	76.063	1	23331	127	0.0687
2	RT80.613	80.613	2	51893	359	0.1527
3	RT86.187	86.187	3	479195	2681	1.4104
4	RT113.286	113.286	4	33421576	56935	98.3682

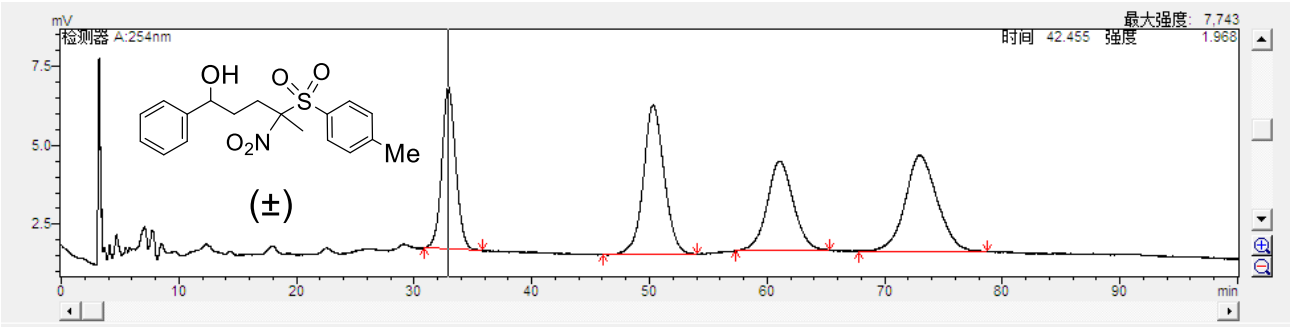
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

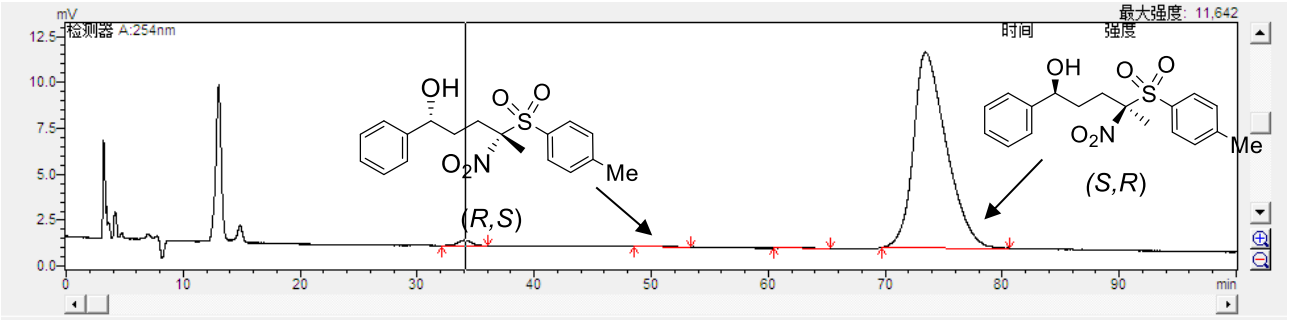
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*R*)-**5w: (1*S*,4*R*)-4-nitro-1-phenyl-4-tosylpentan-1-ol** (HPLC: Chiracel OZ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25°C).



化合物表视图

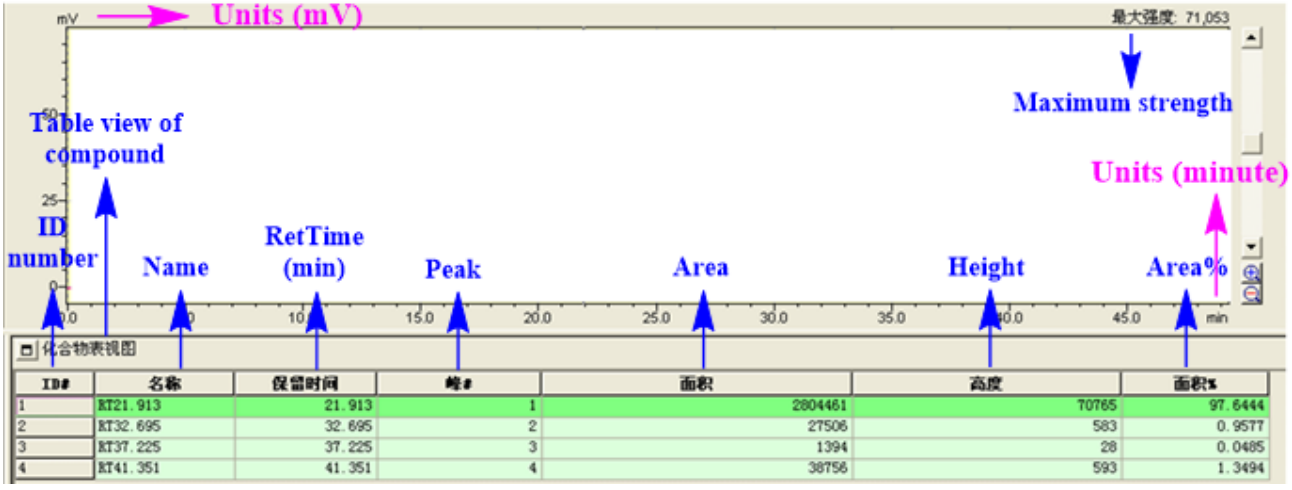
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.911	32.911	1	422903	5130	20.9282
2	RT50.331	50.331	2	577529	4721	28.5802
3	RT61.004	61.004	3	438731	2838	21.7115
4	RT73.011	73.011	4	581571	3055	28.7802



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT34.086	34.086	1	24789	317	1.1726
2	RT48.660	48.660	2	896	7	0.0424
3	RT62.357	62.357	3	7823	69	0.3701
4	RT73.409	73.409	4	2080408	10639	98.4149

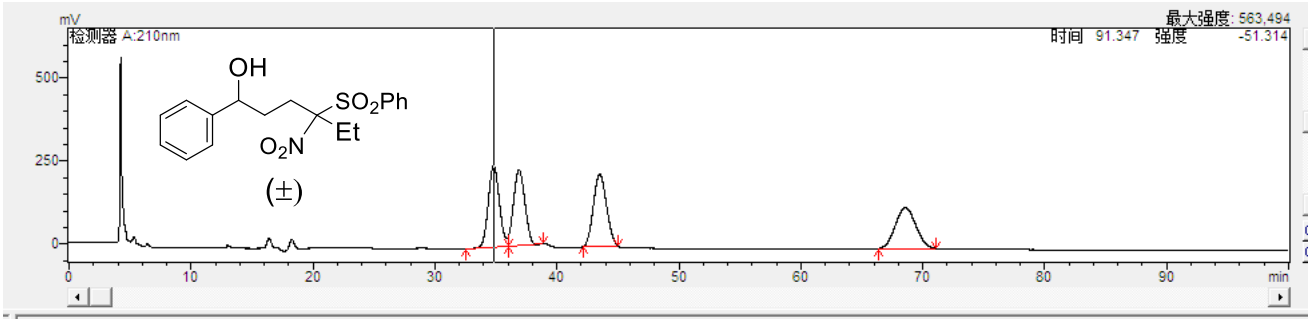
<u>Translation of all characters (Chinese) in the above two frameworks to English is as follows:</u>



化合物表视图

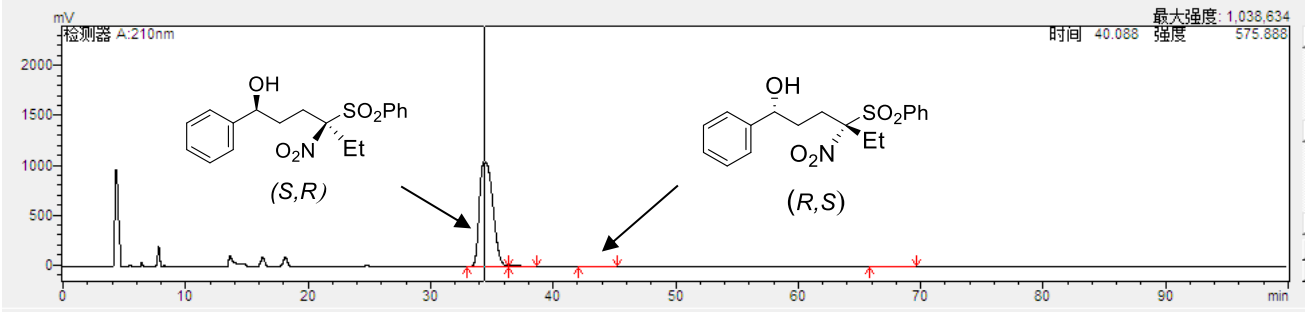
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-**5x:** (1S,4R)-4-nitro-1-phenyl-4-(phenylsulfonyl)hexan-1-ol (HPLC: Chiralpak IC, elute: Hexanes/i-PrOH =90/10, detector: 210 nm, flow rate: 1.0 mL/min, 25 °C).



化合物表视图

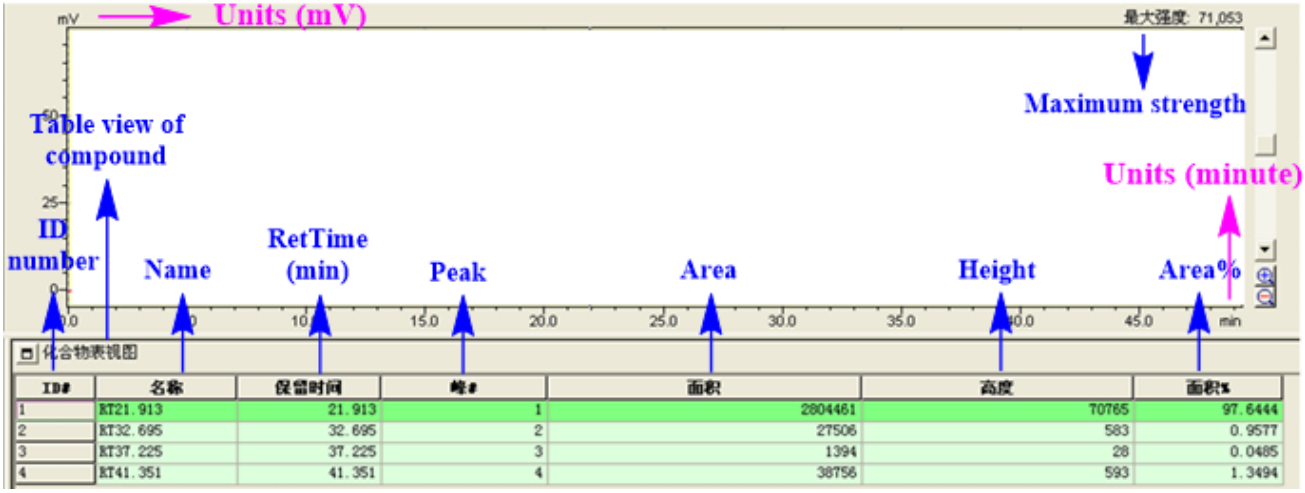
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT34.806	34.806	1	15367559	244757	25.2427
2	RT36.886	36.886	2	14499038	227415	23.8160
3	RT43.495	43.495	3	16410621	217170	26.9560
4	RT68.557	68.557	4	14602119	123964	23.9853



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT34.423	34.423	1	80598257	1057644	98.1747
2	RT36.853	36.853	2	865316	14679	1.0540
3	RT43.553	43.553	3	629059	8486	0.7662
4	RT69.628	69.628	4	4103	70	0.0050

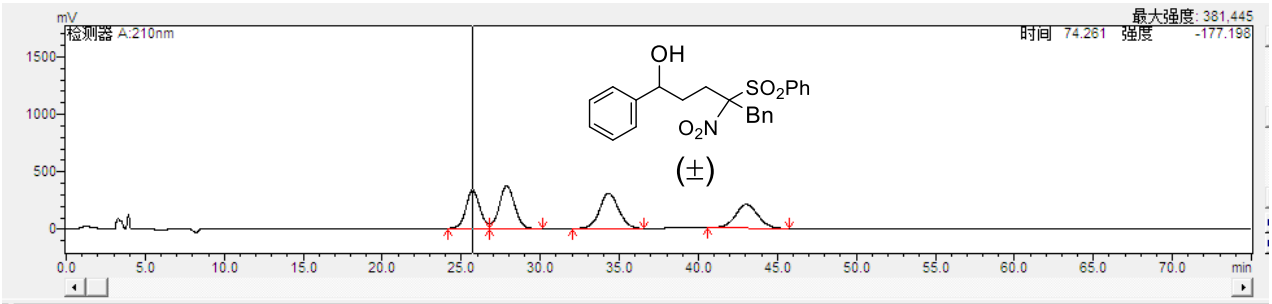
Translation of all characters (Chinese) in the above two frameworks to English is as follows:



化合物表视图

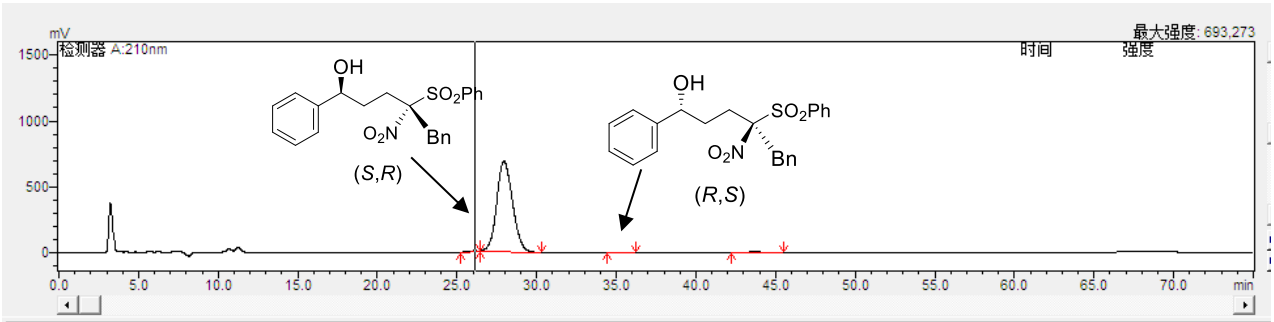
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S,R*)-5y: (*1S,4S*)-4-nitro-1,5-diphenyl-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 210 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0mL/min, 25°C).



化合物表视图

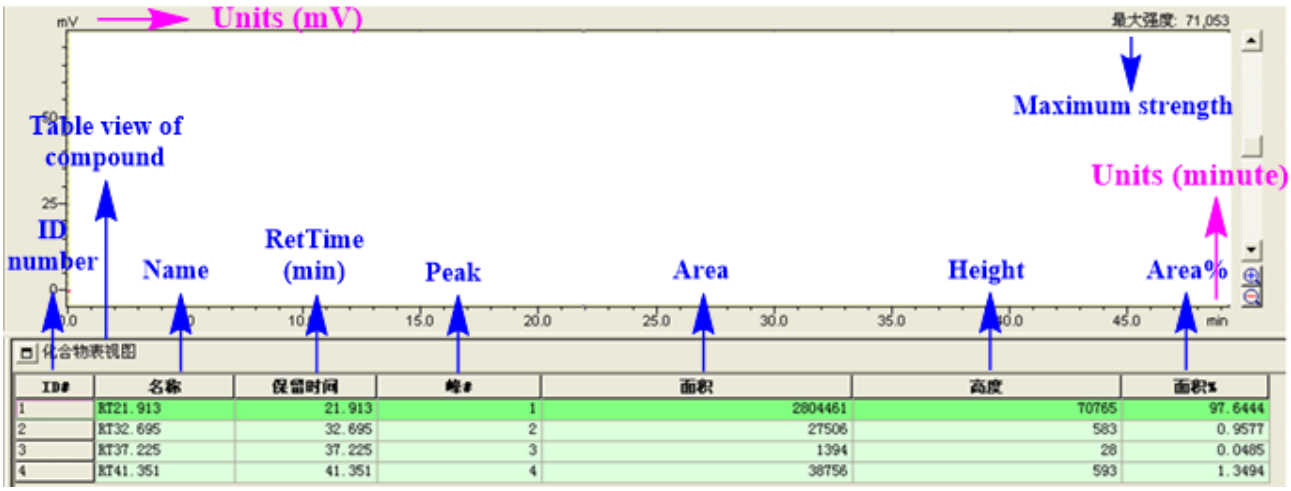
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT25.707	25.707	1	20612354	334492	22.3498
2	RT27.862	27.862	2	25101891	374597	27.2177
3	RT34.309	34.309	3	25949297	307978	28.1365
4	RT43.032	43.032	4	20562780	207341	22.2960



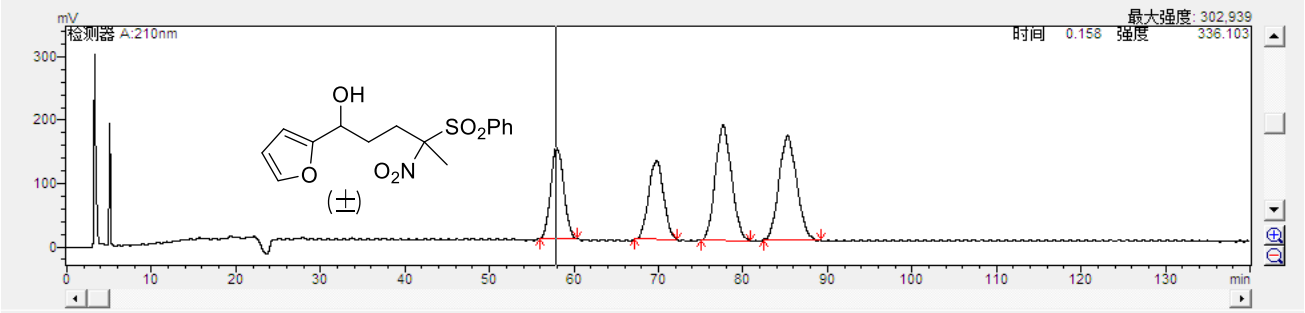
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT26.084	26.084	1	139822	3632	0.2939
2	RT27.935	27.935	2	47086352	685346	98.9633
3	RT35.215	35.215	3	25092	361	0.0527
4	RT43.700	43.700	4	328320	3407	0.6900

Translation of all characters (Chinese) in the above two frameworks to English is as follows:

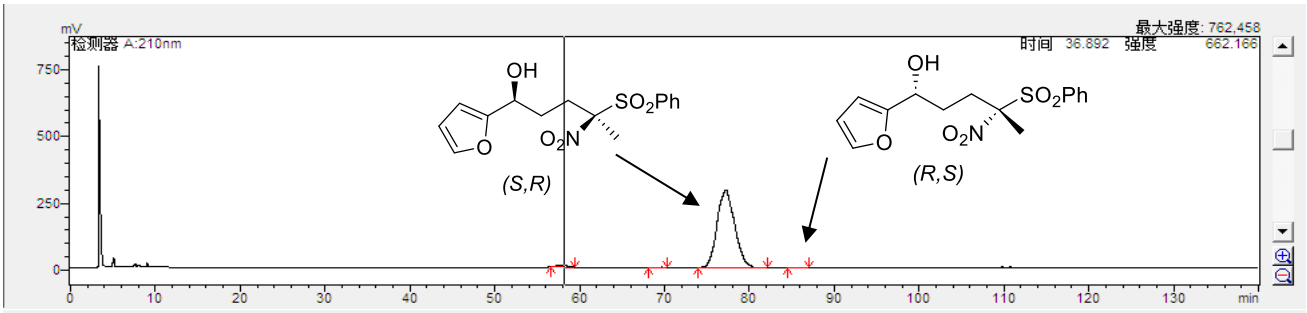


(*S,R*)-**3z:** (*1S,4R*)-1-(furan-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel IC, detected at 210 nm, eluent: n-hexane/2-propanol = 95/5, flow rate = 1.0mL/min, 25°C).



化合物表视图

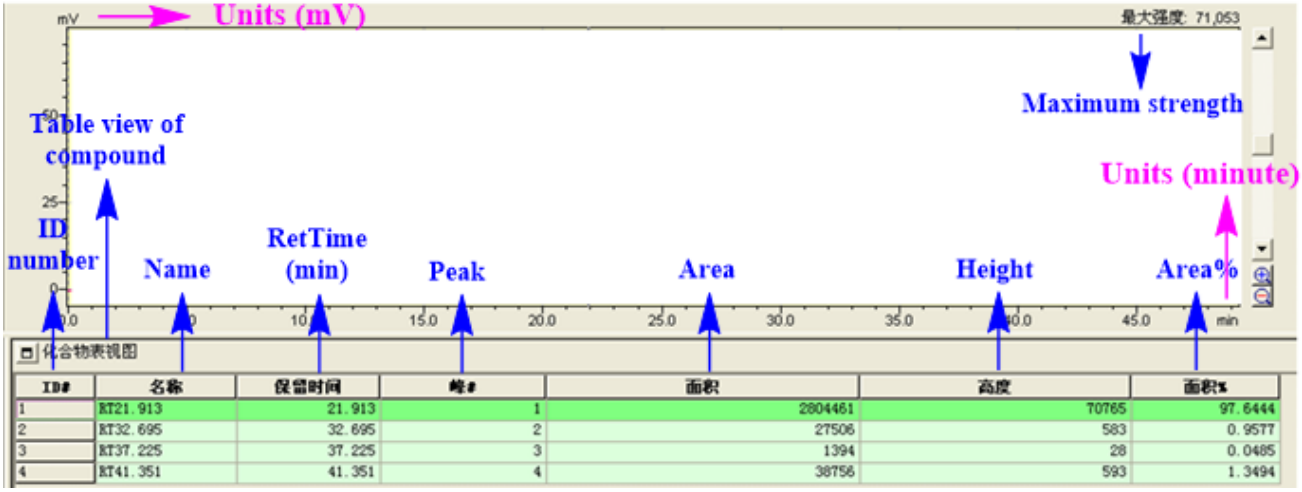
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT57.900	57.900	1	15445020	143581	19.5622
2	RT69.831	69.831	2	15332173	124094	19.4193
3	RT77.648	77.648	3	24321392	182369	30.8047
4	RT85.285	85.285	4	23854824	164800	30.2138



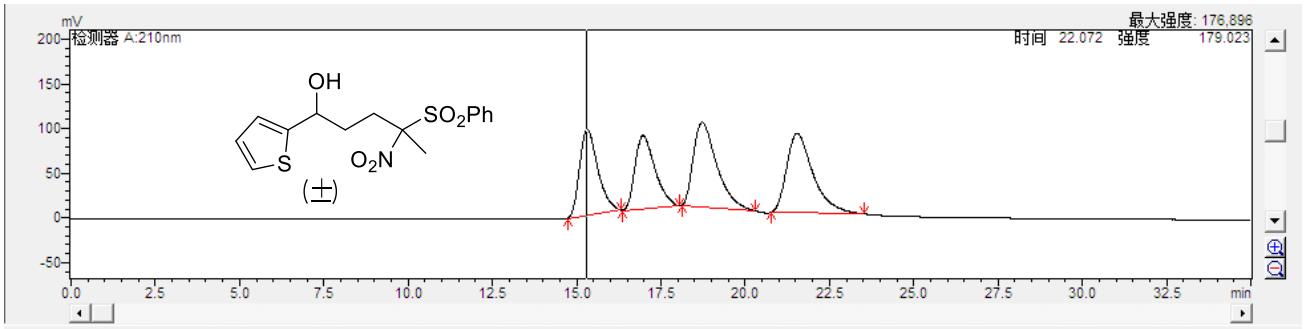
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT58.141	58.141	1	678009	7605	1.5911
2	RT69.660	69.660	2	129027	2277	0.3028
3	RT77.214	77.214	3	41748309	290809	97.9695
4	RT84.929	84.929	4	58230	1784	0.1366

Translation of all characters (Chinese) in above two frameworks to English is as follows:

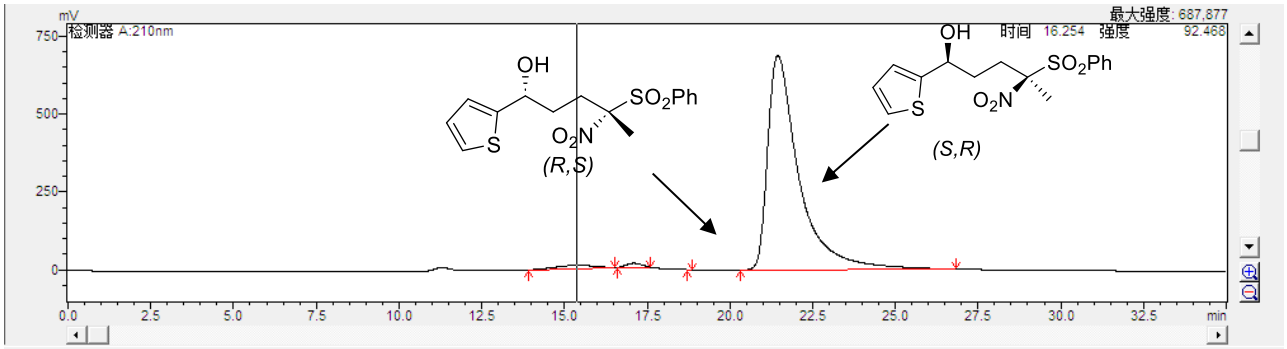


(*S,R*)-**3z'**: (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(thiophen-2-yl)pentan-1-ol (HPLC: Chiracel OD-3, detected at 210 nm, eluent: n-hexane/2-propanol = 85/15, flow rate = 1.0mL/min, 25°C).



化合物表视图

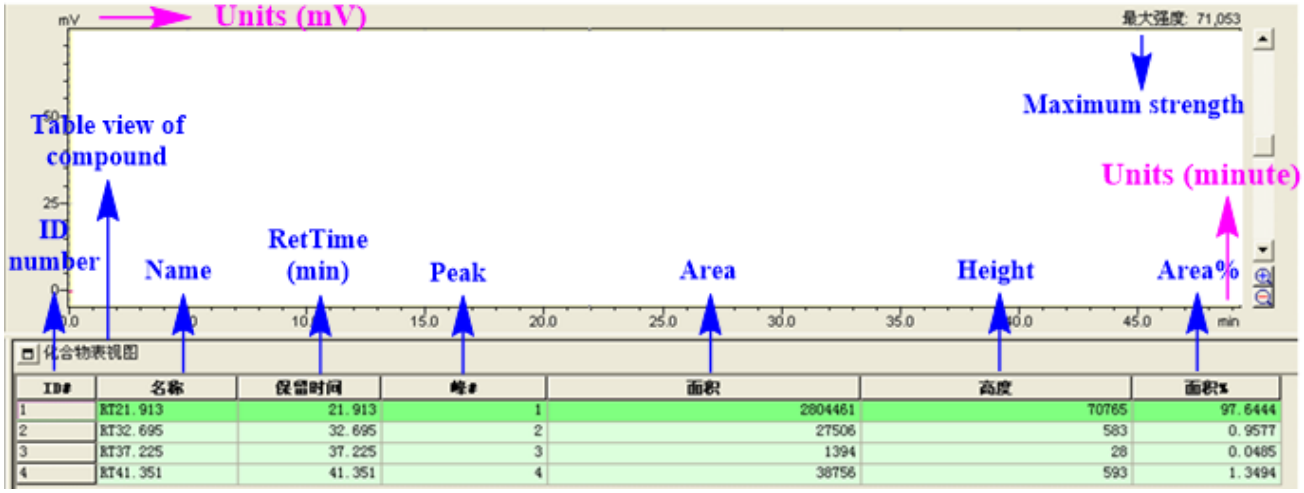
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT15.312	15.312	1	3639061	96298	22.0427
2	RT16.966	16.966	2	3388834	81920	20.5270
3	RT18.719	18.719	3	4609747	94829	27.9224
4	RT21.535	21.535	4	4871491	88867	29.5079



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT15.388	15.388	1	895739	12562	1.9140
2	RT17.088	17.088	2	414877	12859	0.8865
3	RT18.717	18.717	3	190	3	0.0004
4	RT21.450	21.450	4	45488104	688504	97.1991

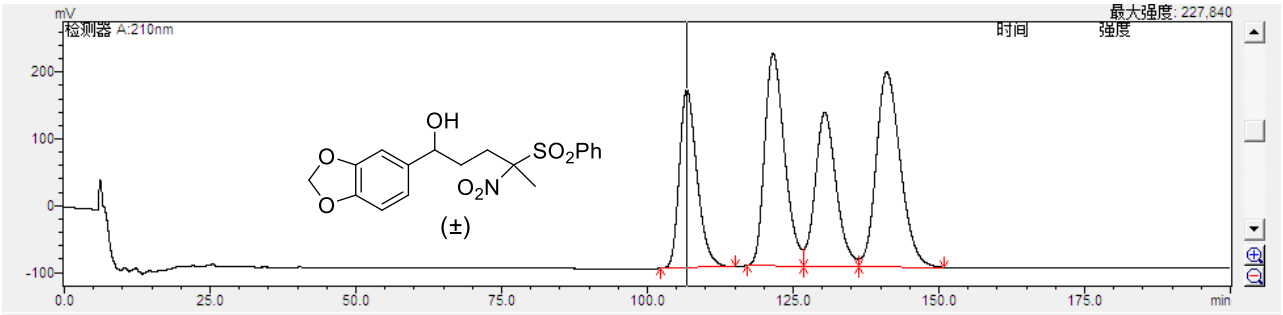
Translation of all characters (Chinese) in above two frameworks to English is as follows:



化合物表视图

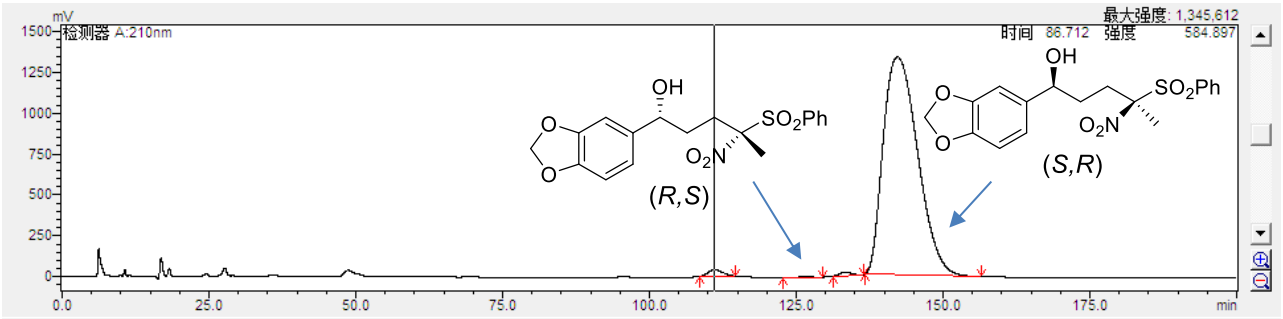
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

(*S*,*R*)-**3z''**: (*1S*,*4R*)-1-(benzo[d][1,3]dioxol-5-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol (HPLC: Chiracel OZ-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, 25°C).



化合物表视图

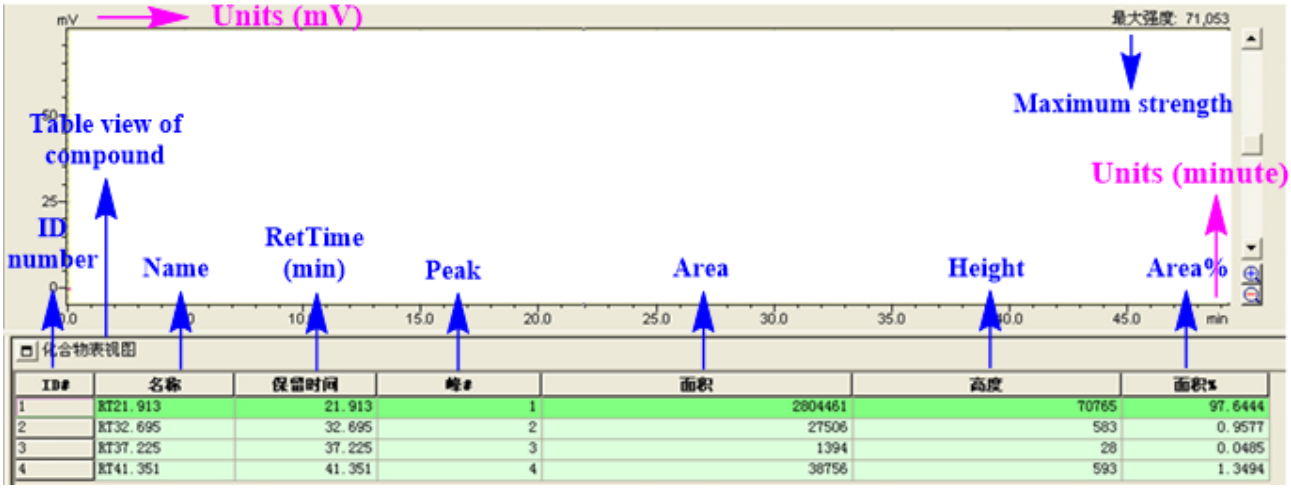
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT106.777	106.777	1	56492390	267174	20.6062
2	RT121.577	121.577	2	75802278	317523	27.6497
3	RT130.430	130.430	3	57602236	229720	21.0110
4	RT141.081	141.081	4	84255398	291490	30.7331



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT111.129	111.129	1	7212167	39833	1.2933
2	RT126.771	126.771	2	102438	652	0.0184
3	RT133.442	133.442	3	3143072	21548	0.5636
4	RT142.225	142.225	4	547186937	1335241	98.1247

Translation of all characters (Chinese) in above two frameworks to English is as follows:

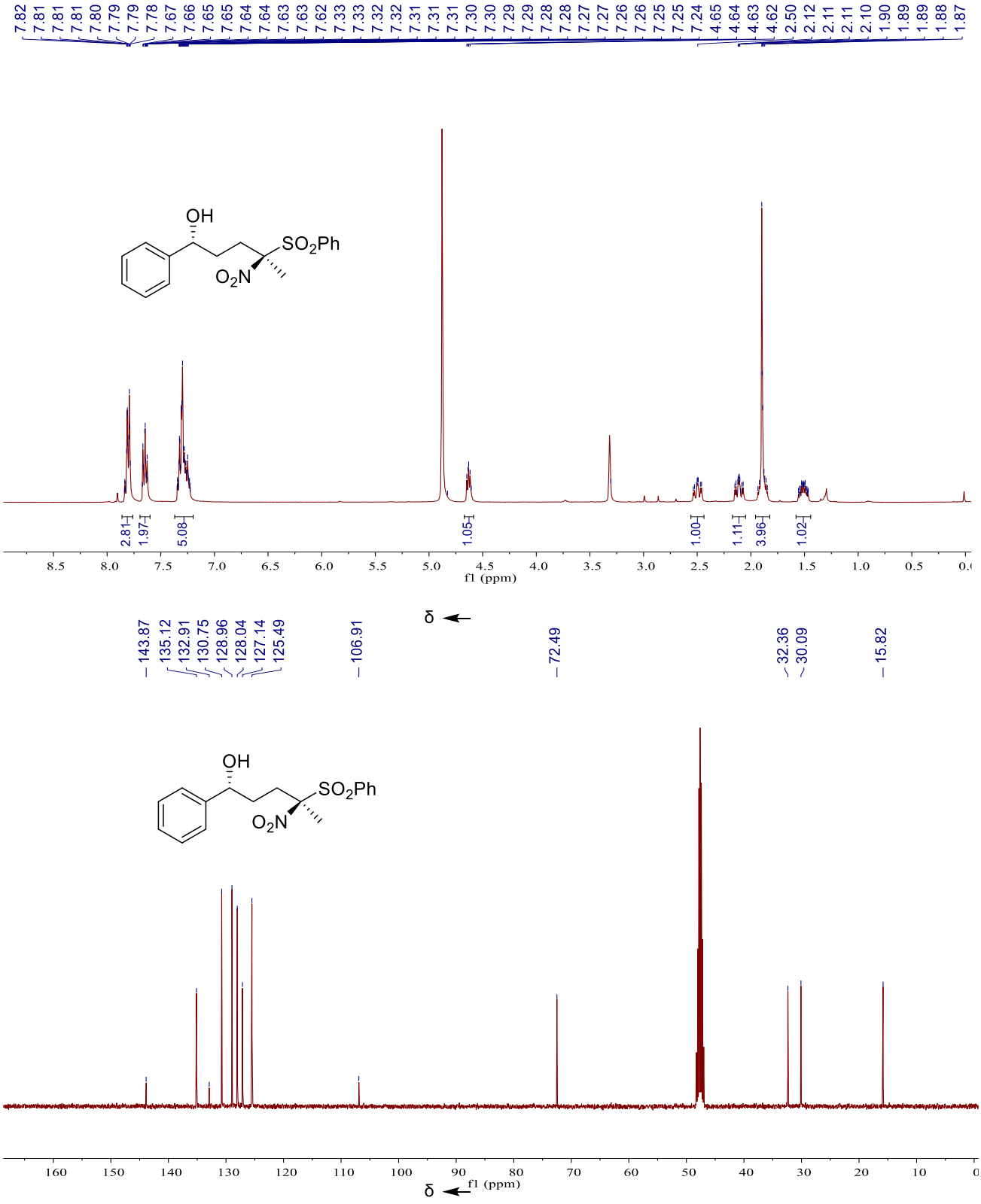


化合物表视图

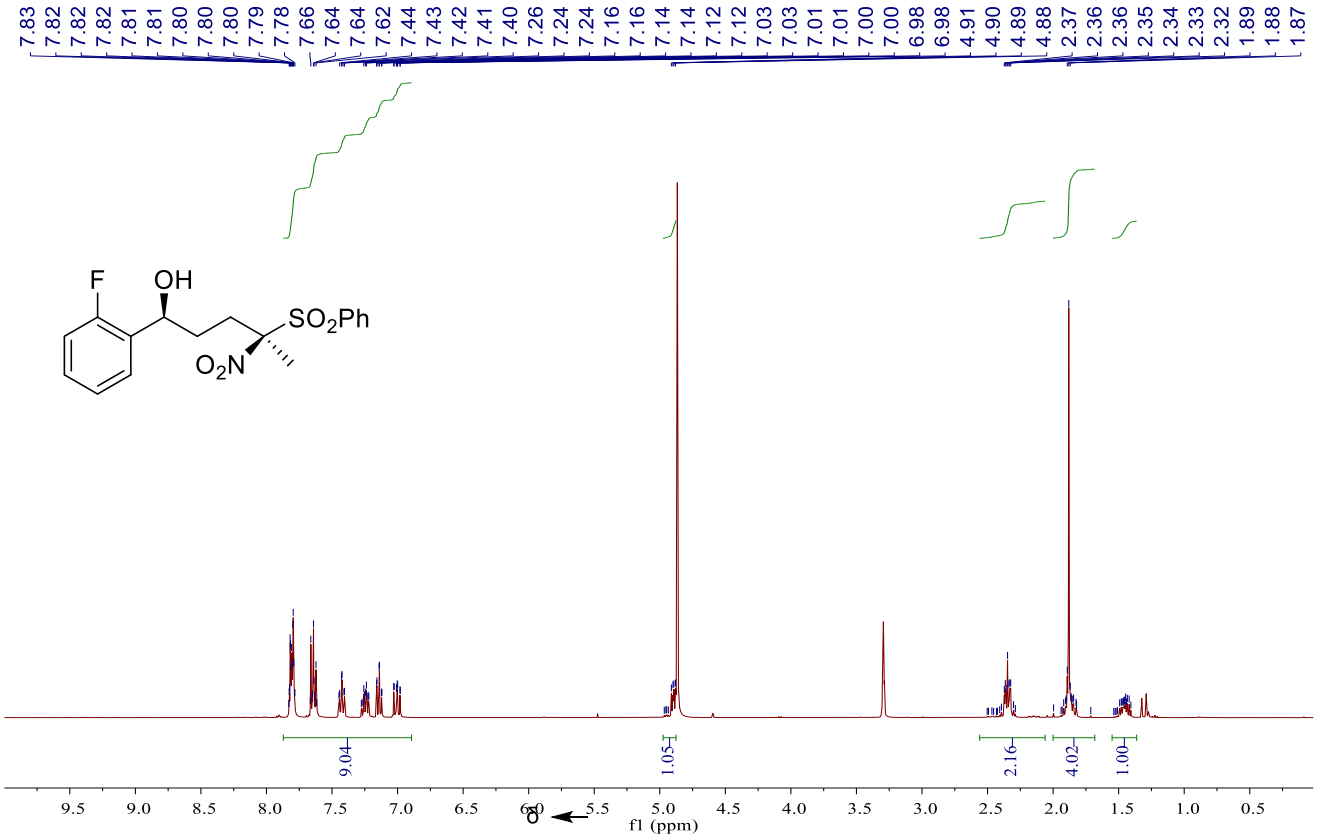
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.913	21.913	1	2804461	70765	97.6444
2	RT32.695	32.695	2	27506	583	0.9577
3	RT37.225	37.225	3	1394	28	0.0485
4	RT41.351	41.351	4	38756	593	1.3494

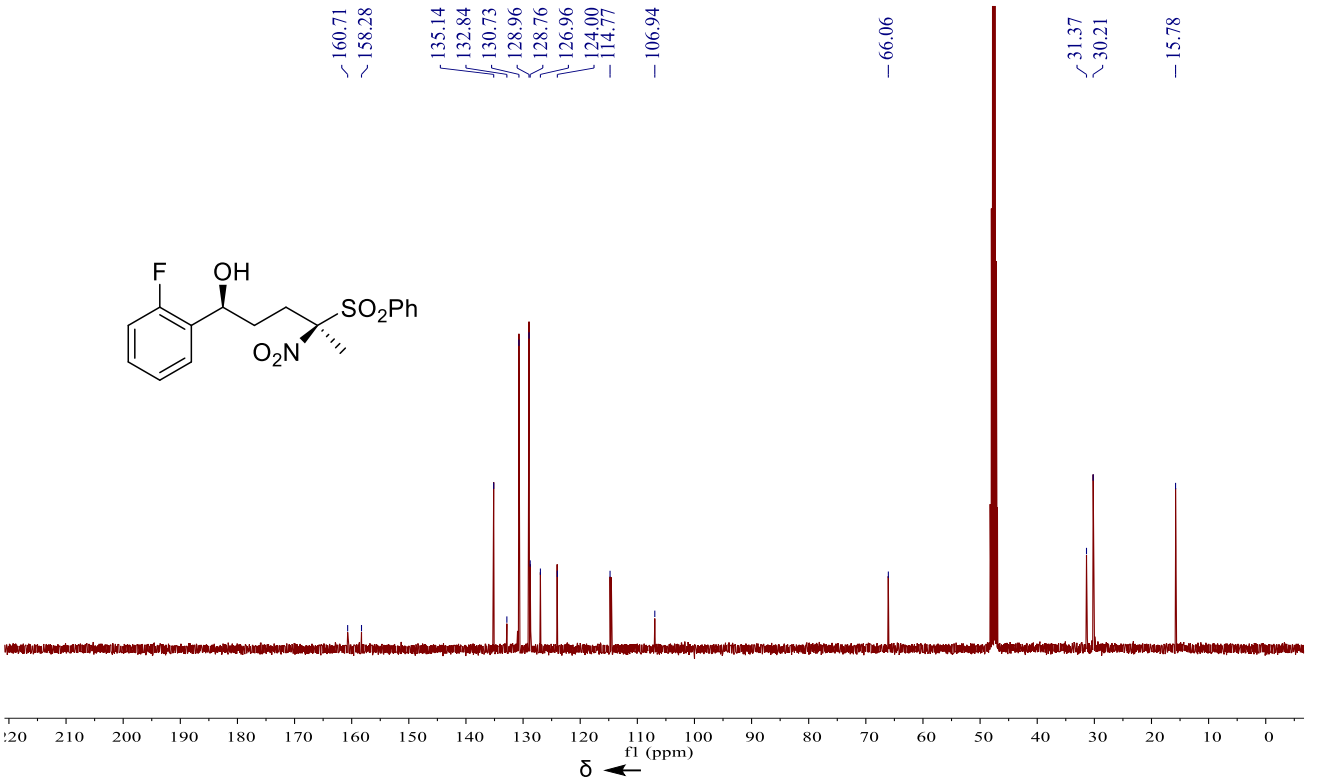
Figure S3. Characterization of chiral products **(**The ^{1}H NMR, ^{13}C NMR, and/or ^{19}F NMR spectra of all chiral products).

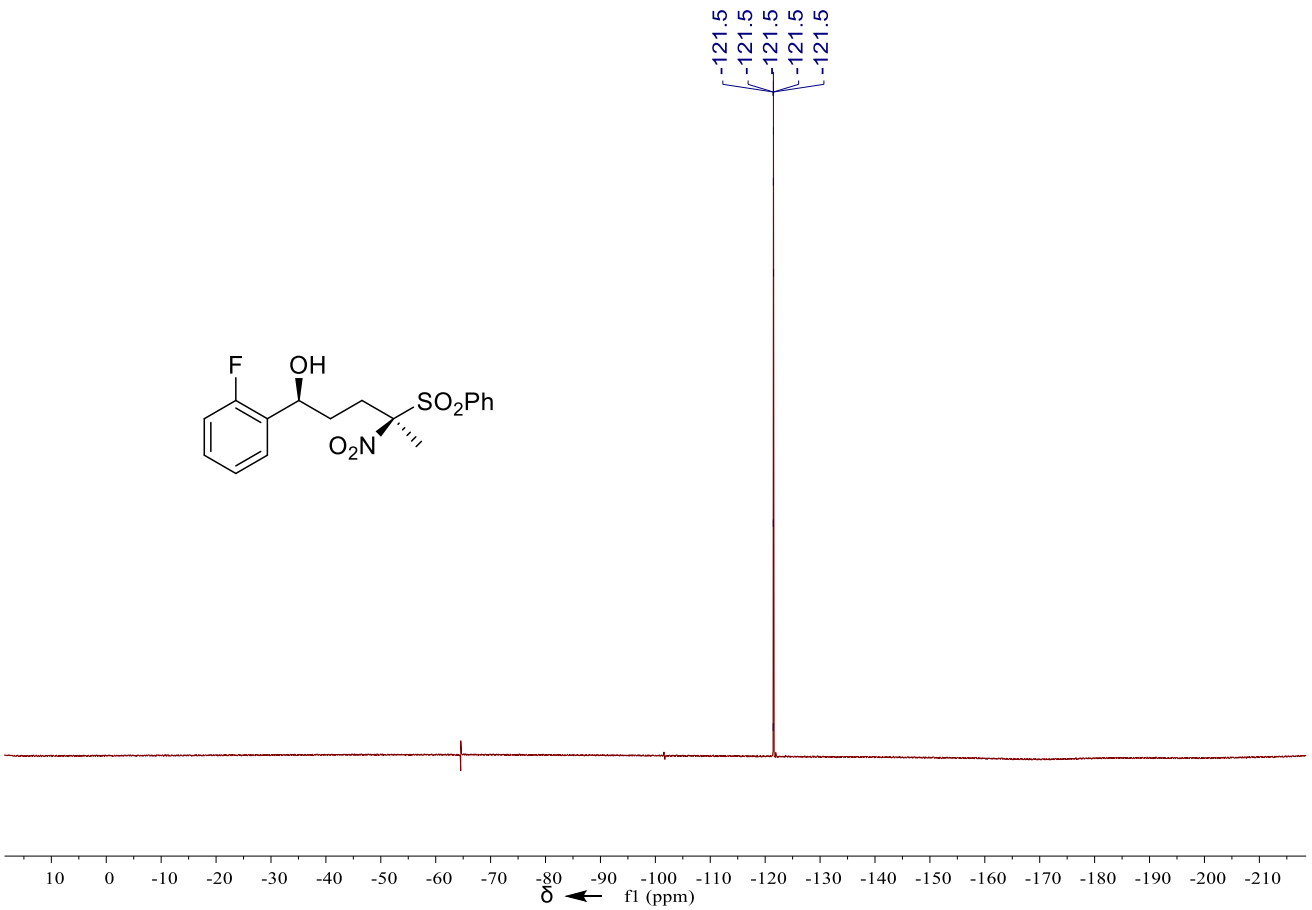
(*S,R*)-5a: (*1S,4R*)-4-nitro-1-phenyl-4-(phenylsulfonyl)pentan-1-ol.



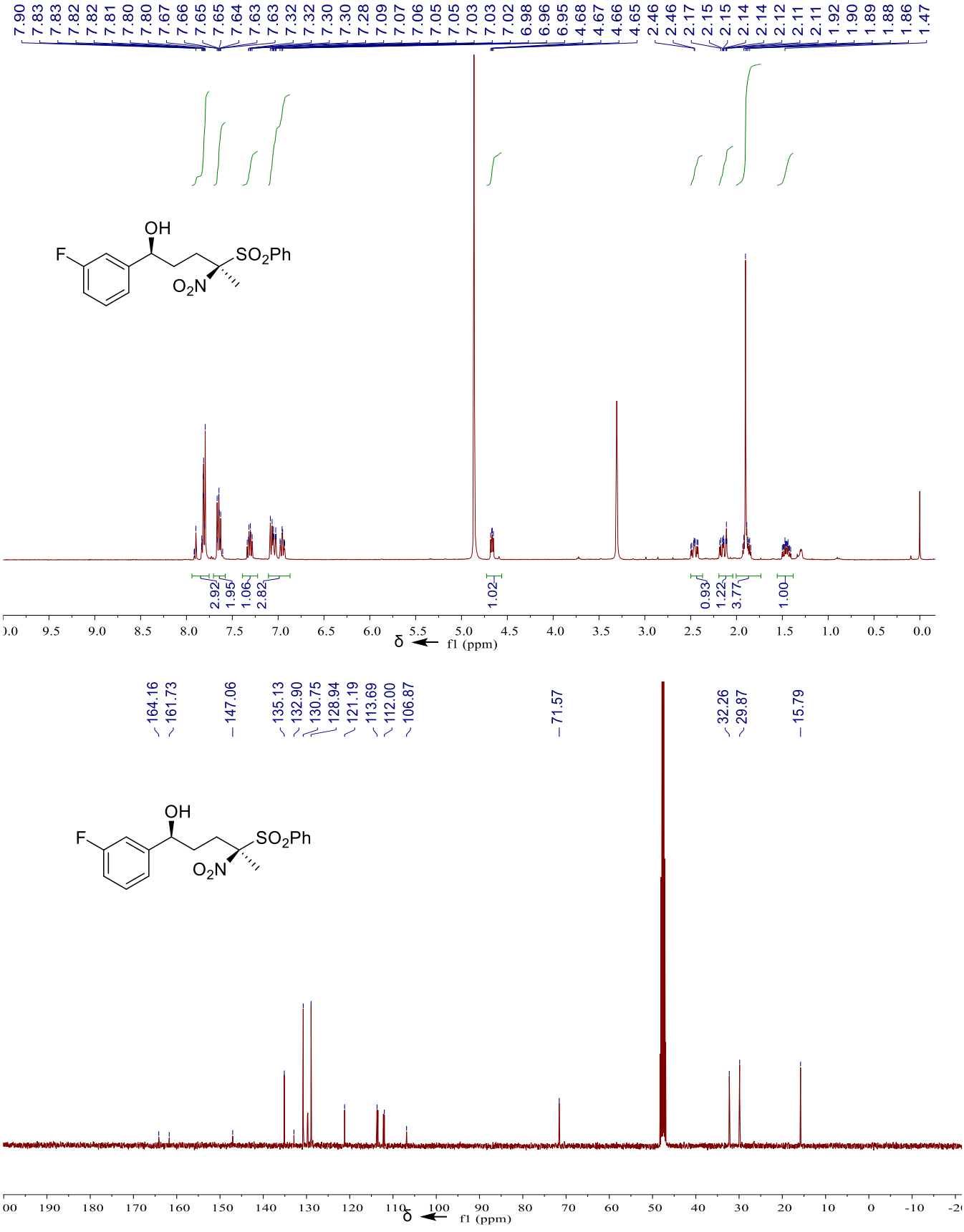
(*S,R*)-5b: (*1S,4R*)-1-(2-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.

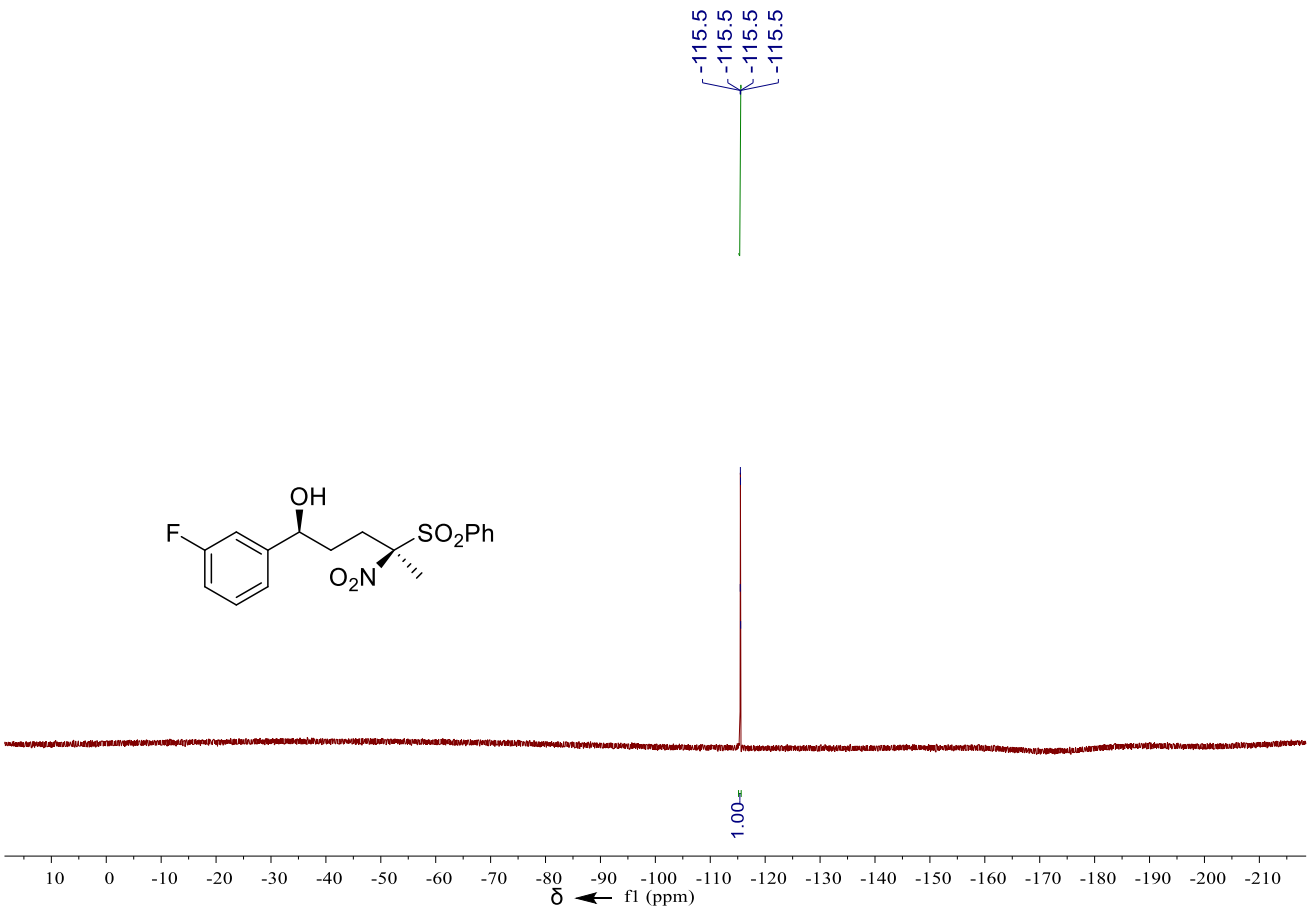




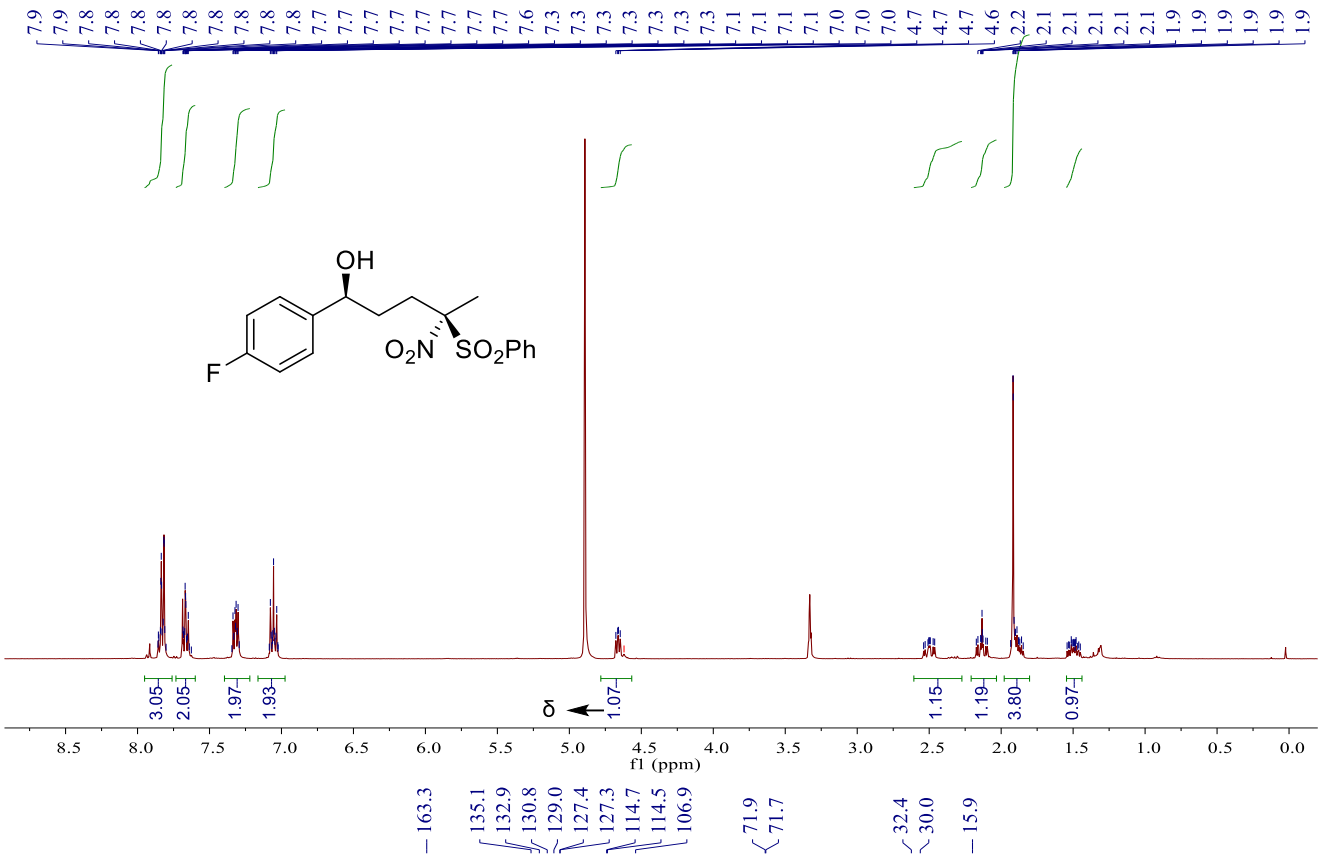

-121.5
-121.5
-121.5
-121.5
-121.5
F
OH
SO2Ph
O2N
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
δ
f1 (ppm)

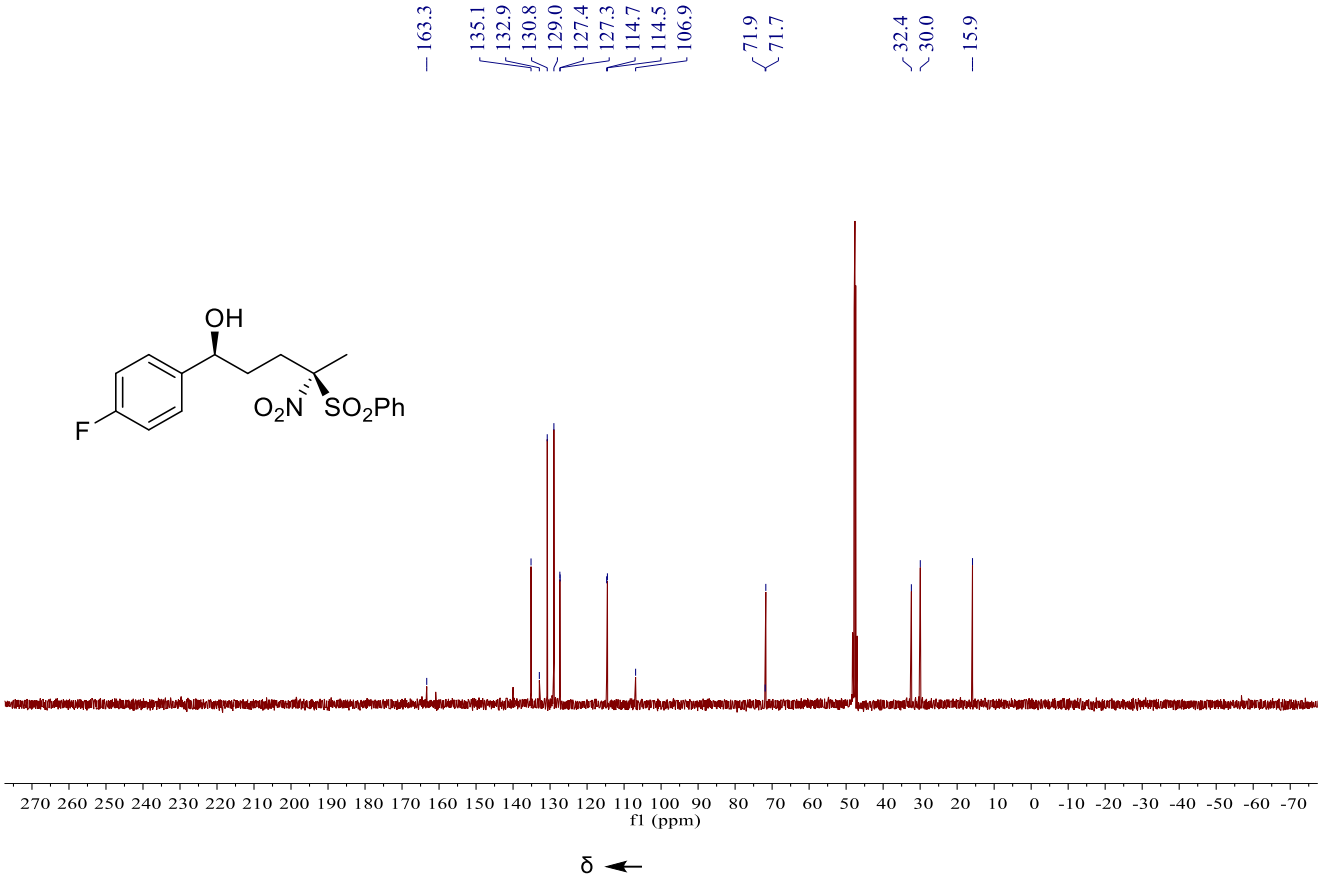
(*S,R*)-5c: (*1S,4S*)-1-(3-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.

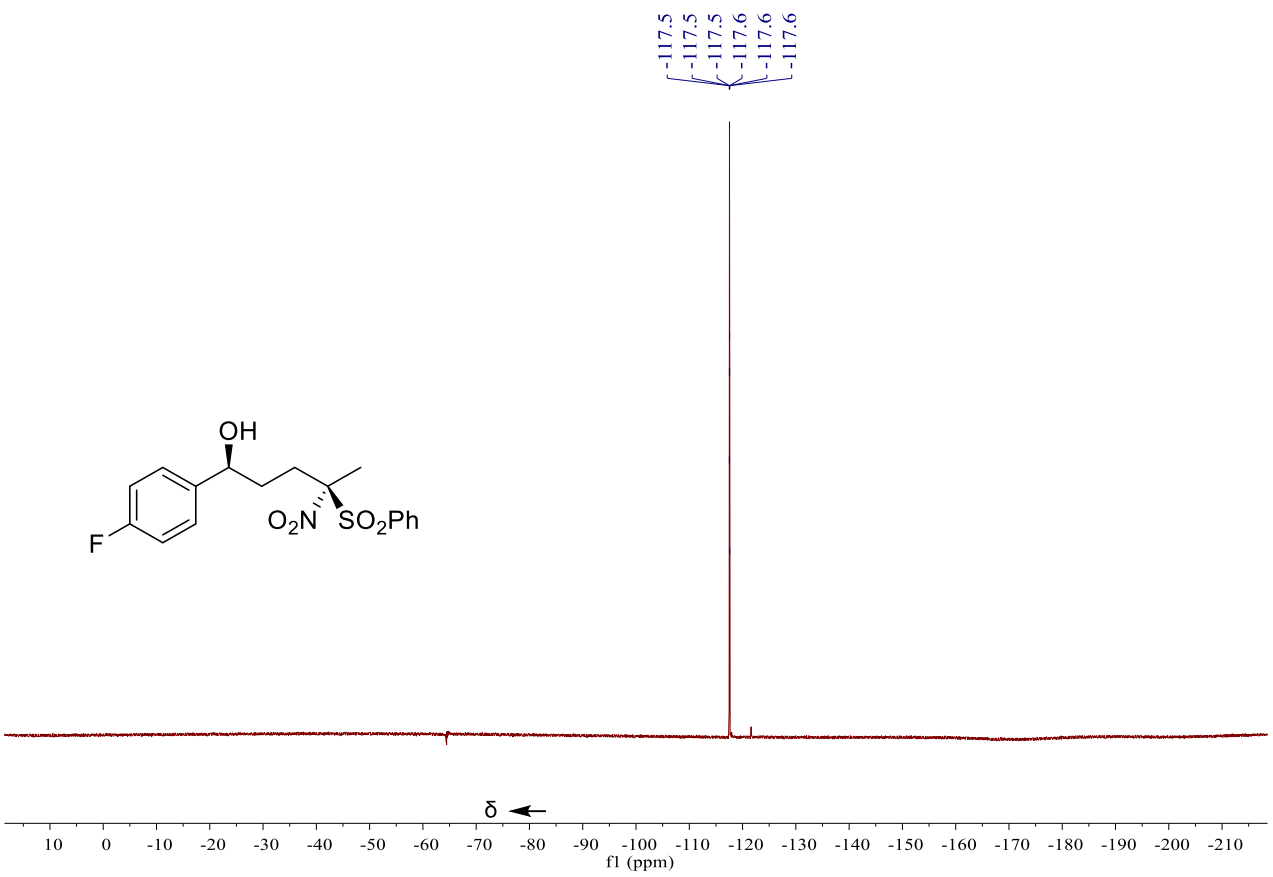



-115.5
-115.5
-115.5
-115.5
OH
F
SO2Ph
O2N
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
δ
f1 (ppm)

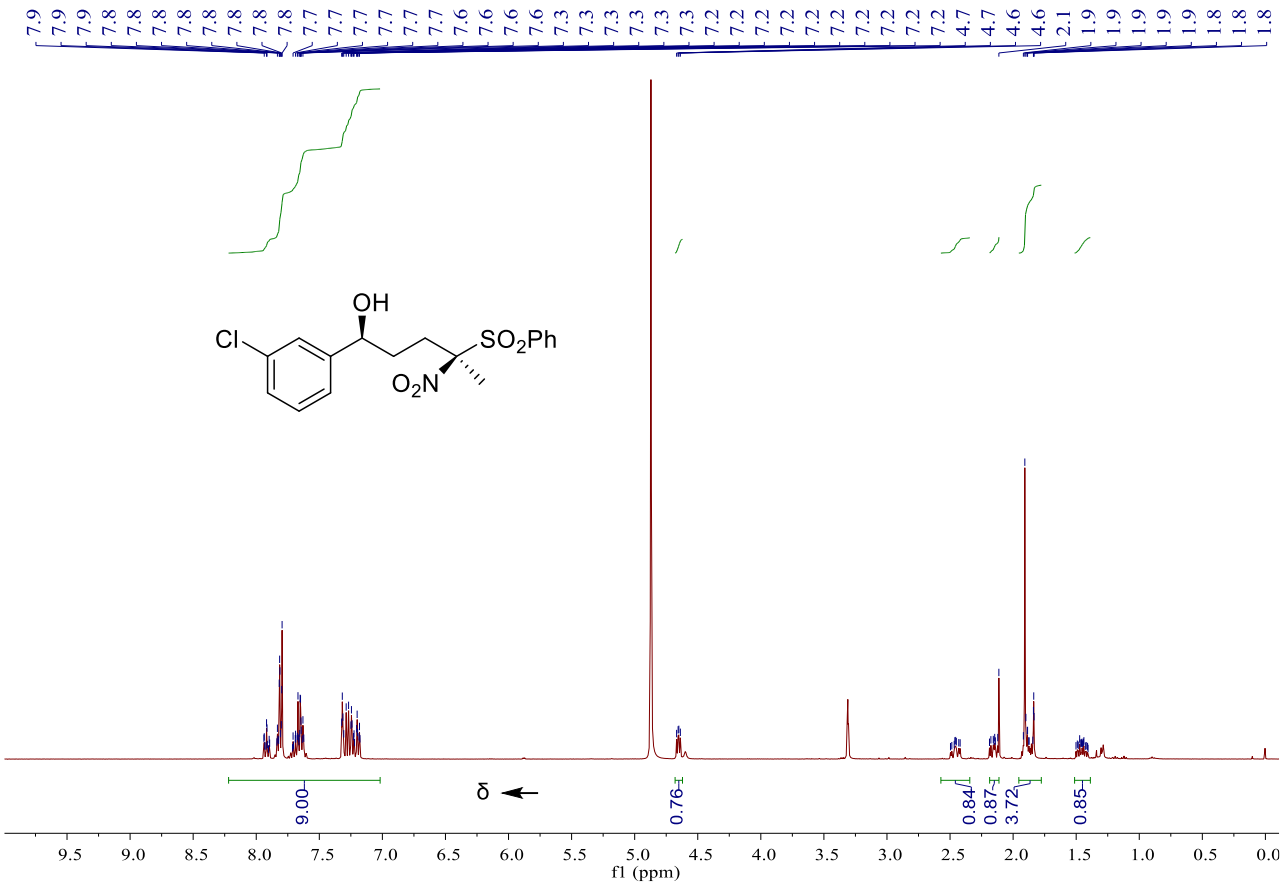
(*S,R*)-**5d**: **(*1S,4R*)-1-(4-fluorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.**

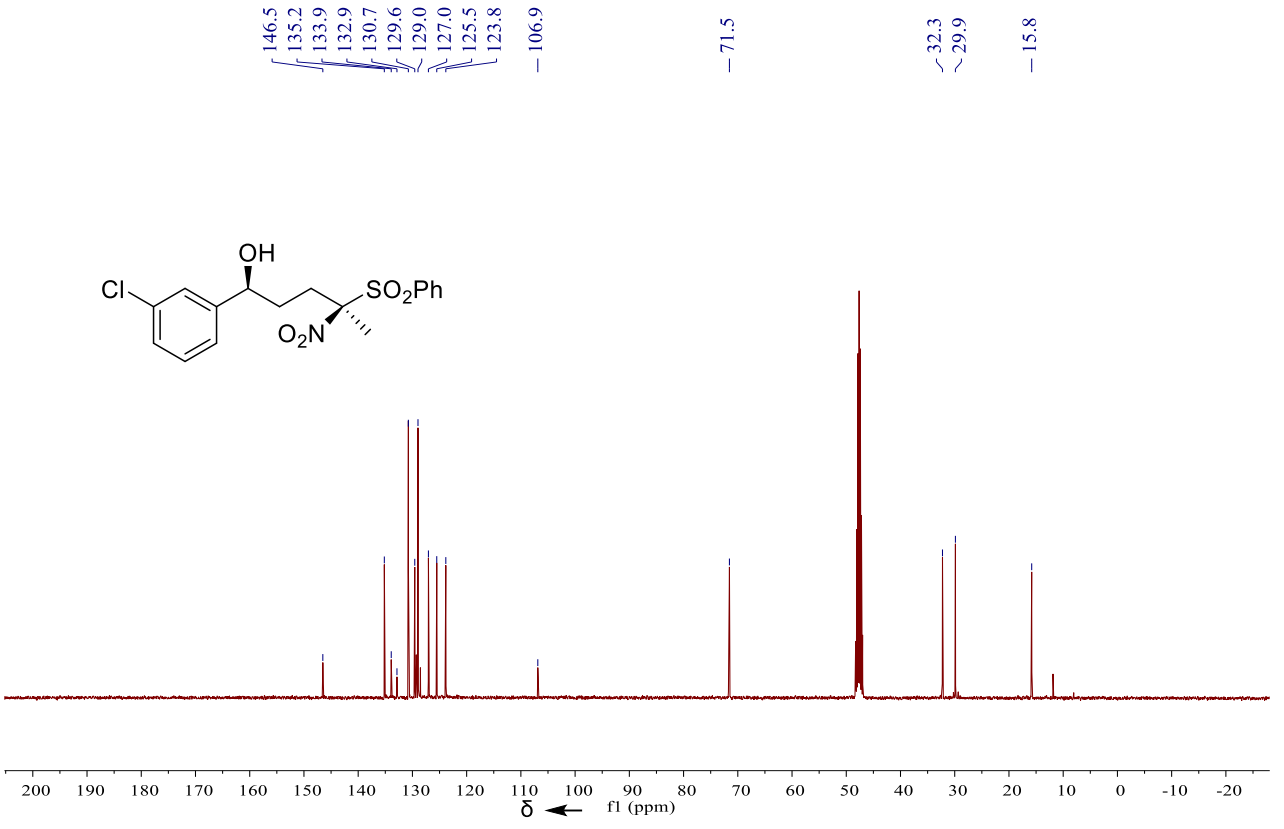




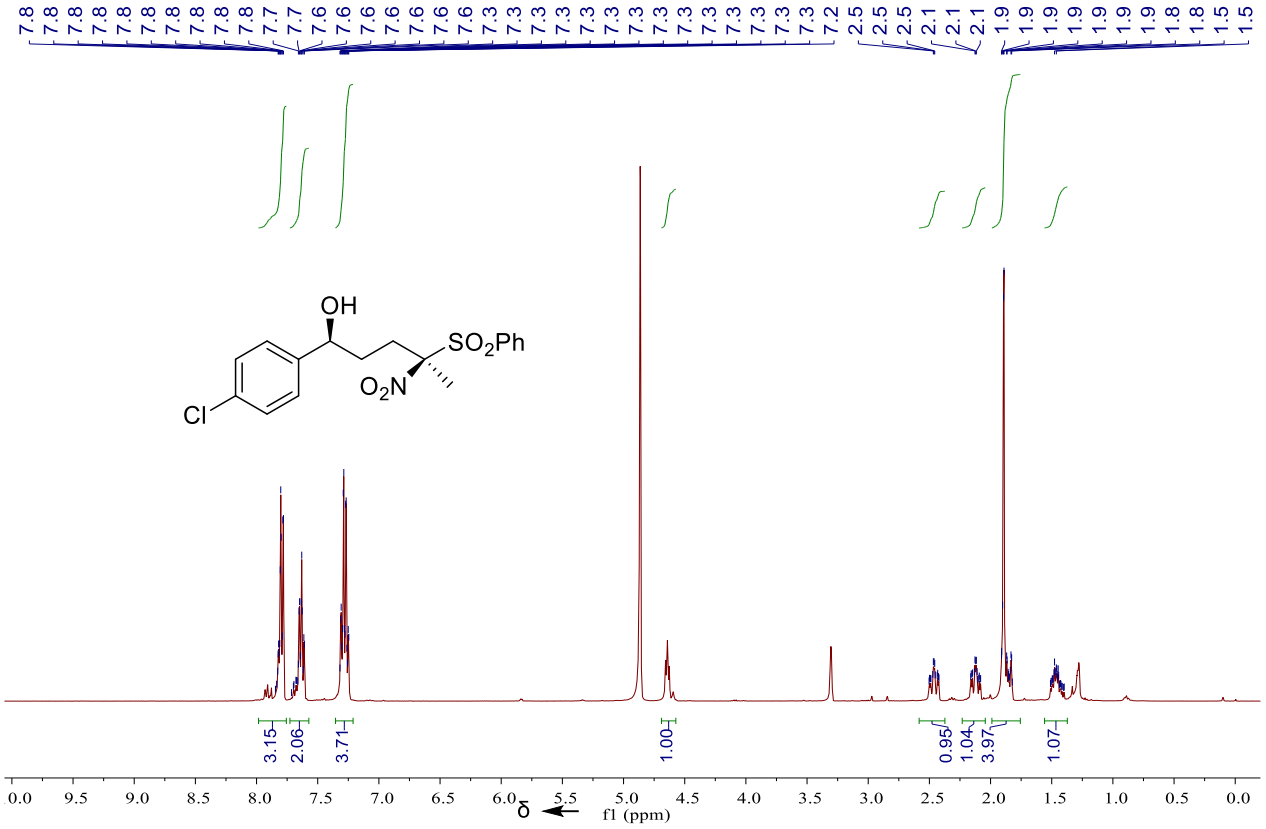

-117.5
-117.5
-117.5
-117.6
-117.6
-117.6
OH
F
O2N
SO2Ph
δ
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

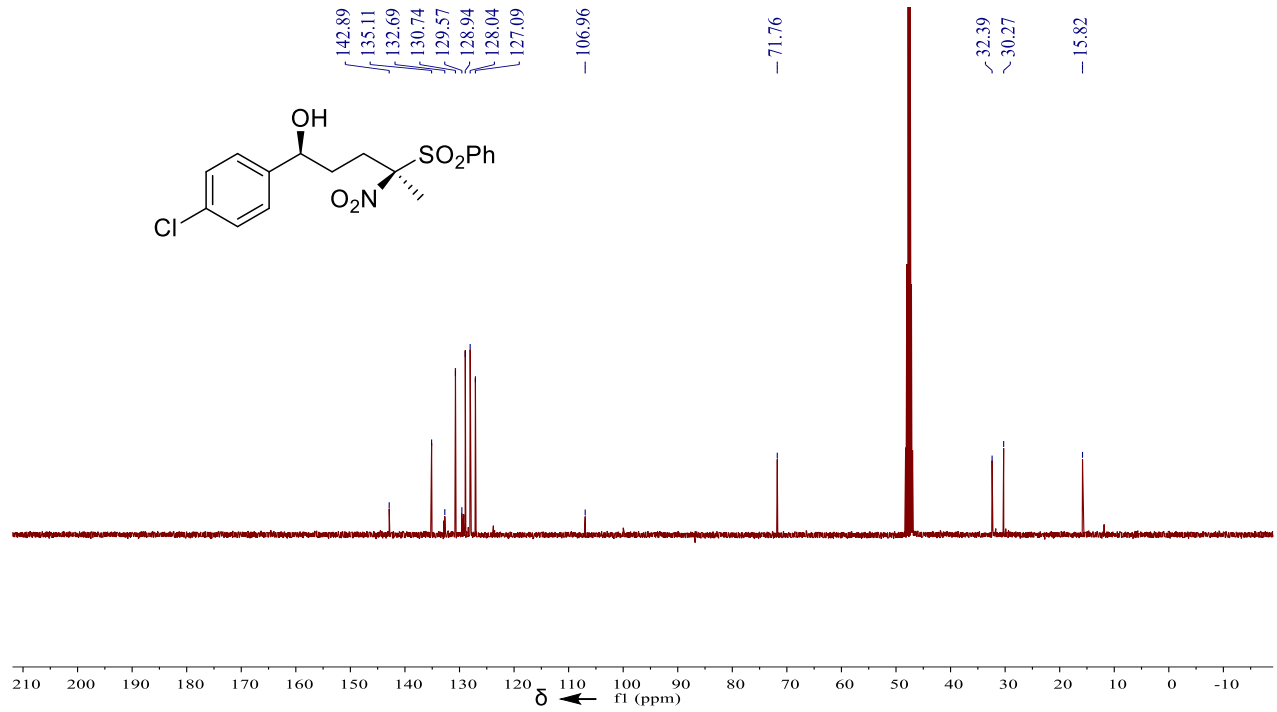
(*S,R*)-**5e:** (*1S,4R)*-1-(3-chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.



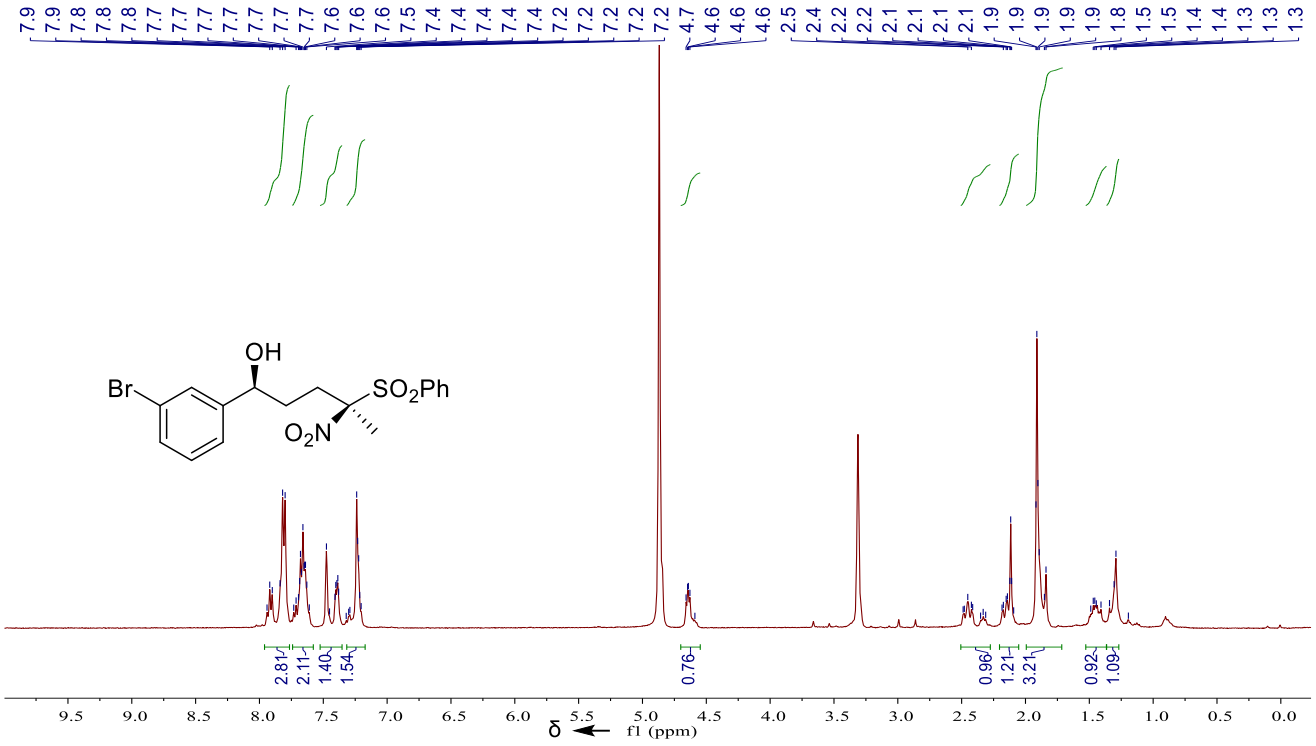


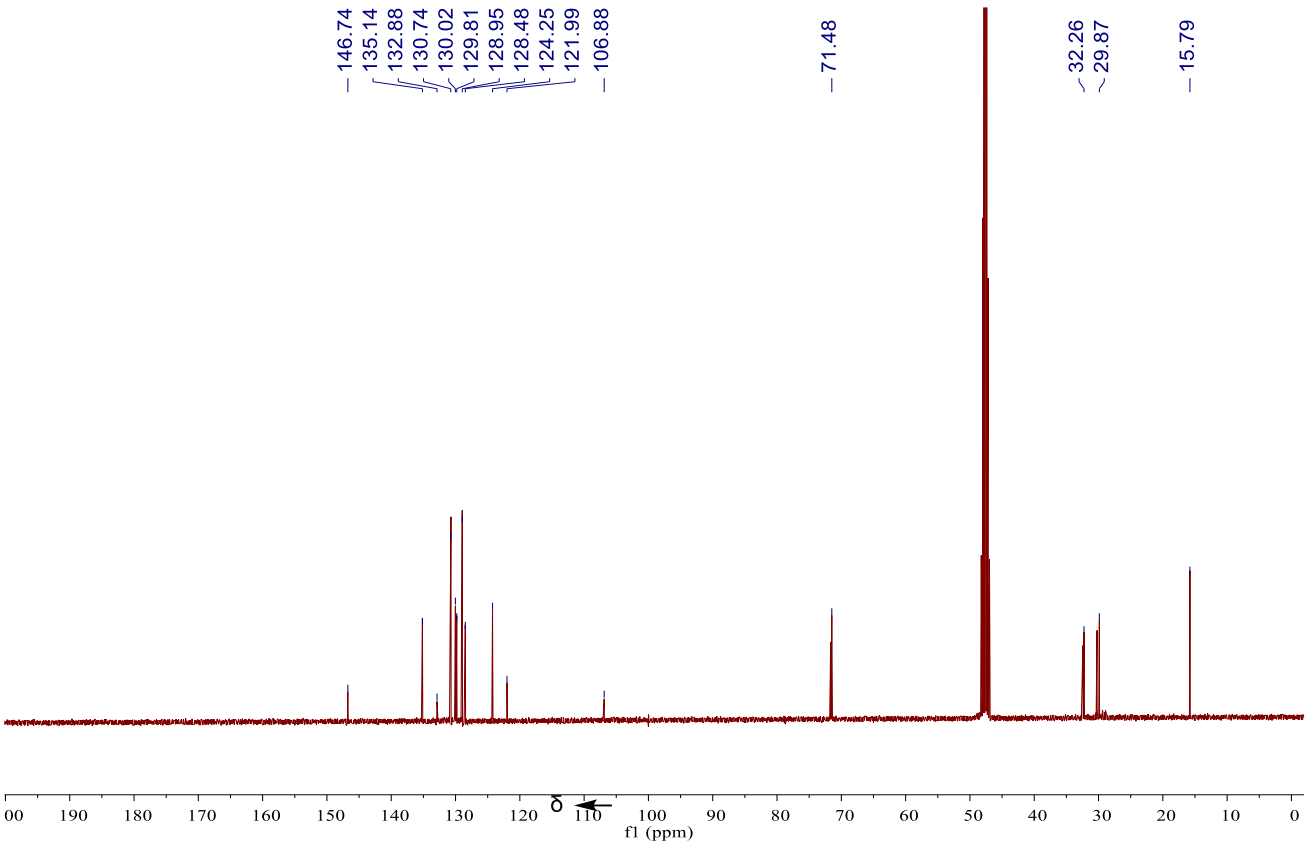
(*S,R*)-**5f:** (*1S,4R*)-1-(4-chlorophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.



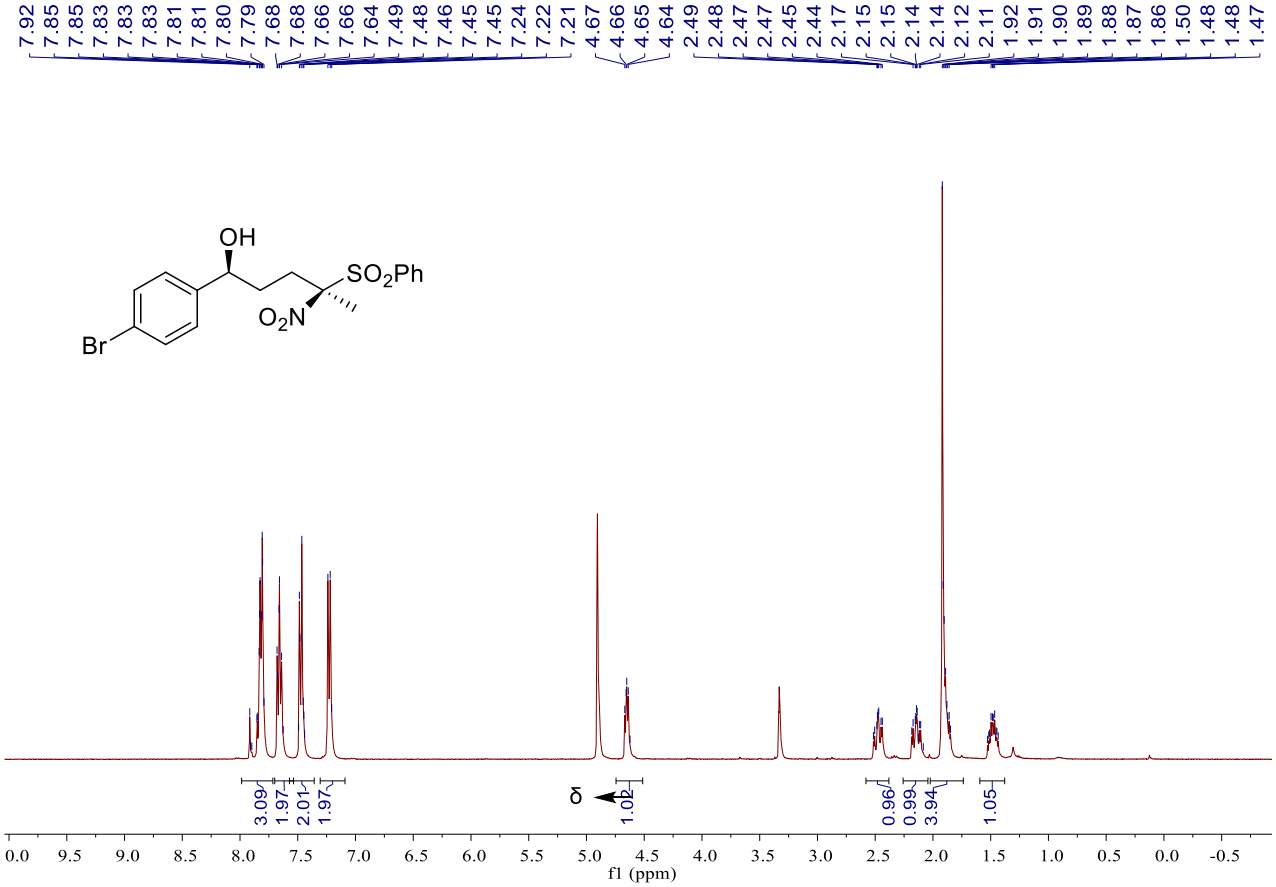


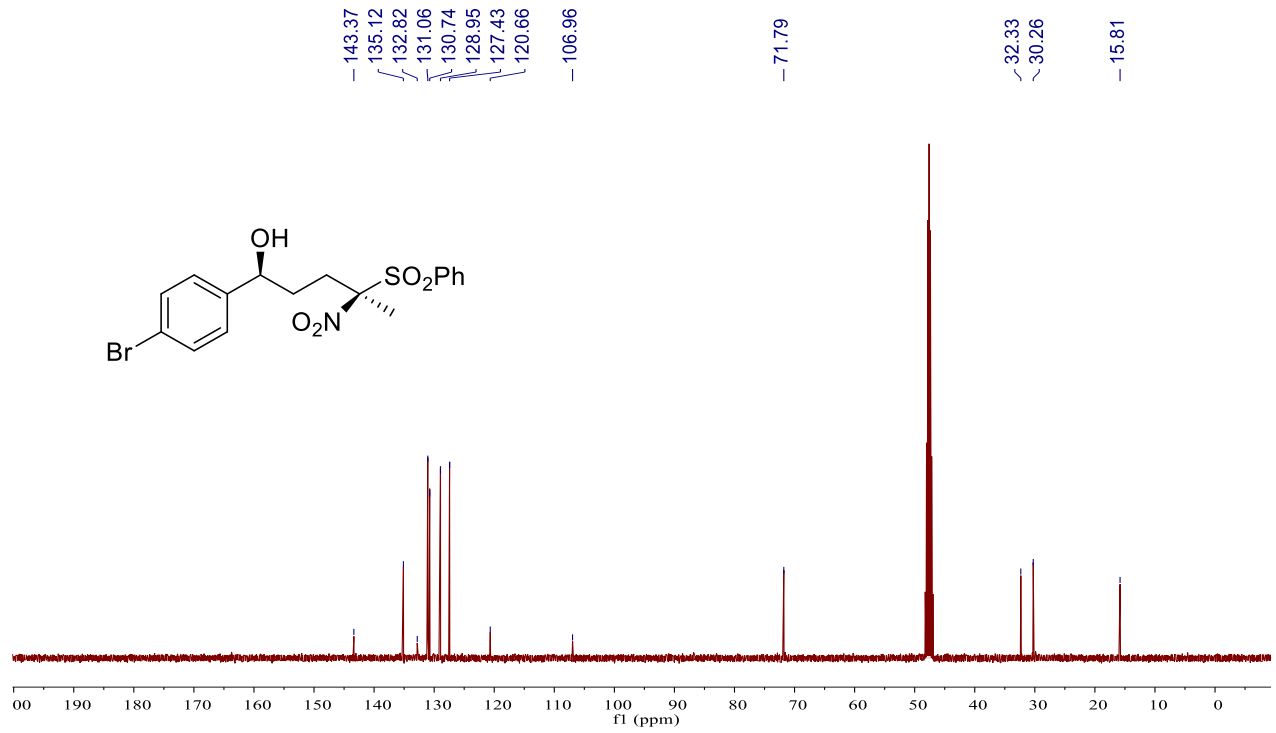
(*S*,*R*)-**5g:** (*1S*,*4R*)-1-(3-bromophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.





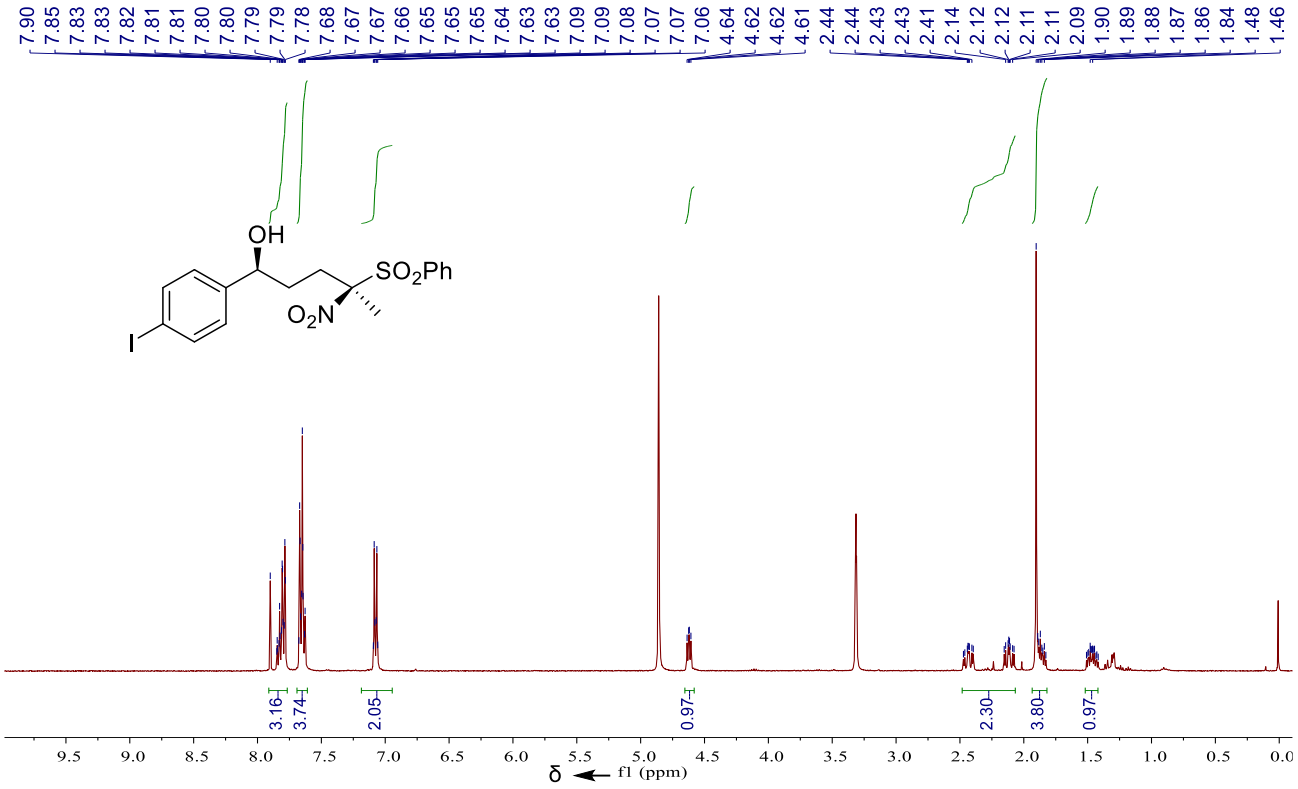
(*S*,*R*)-**5h:** (*1S*,*4R*)-1-(4-bromophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.

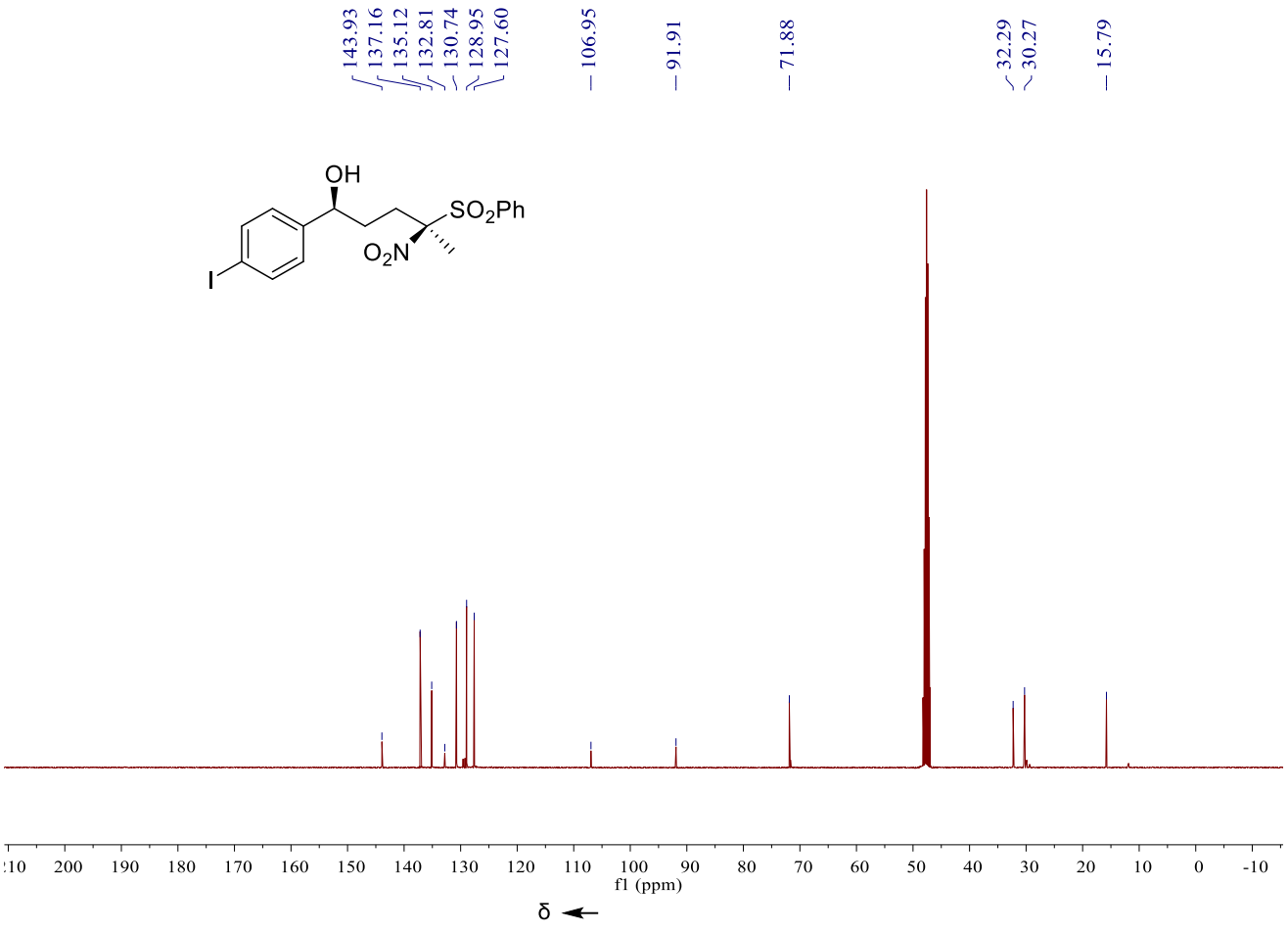




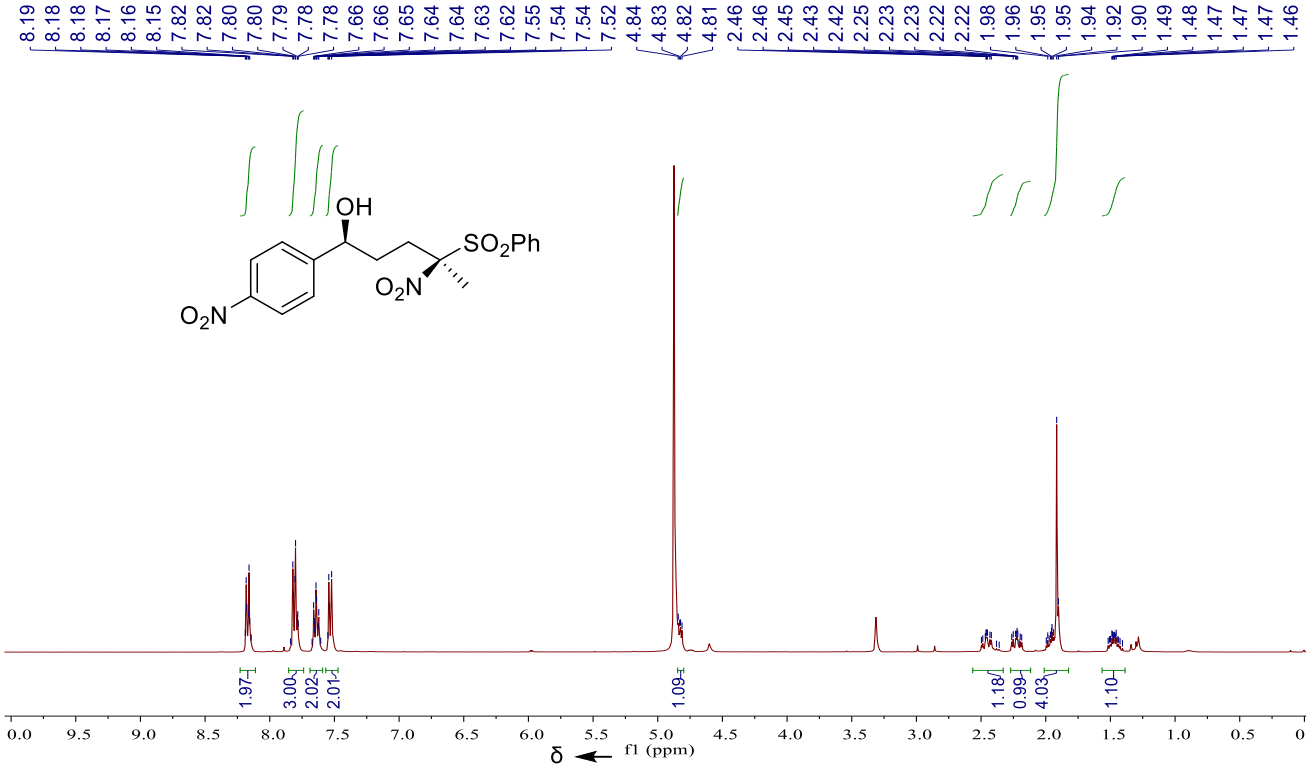
δ

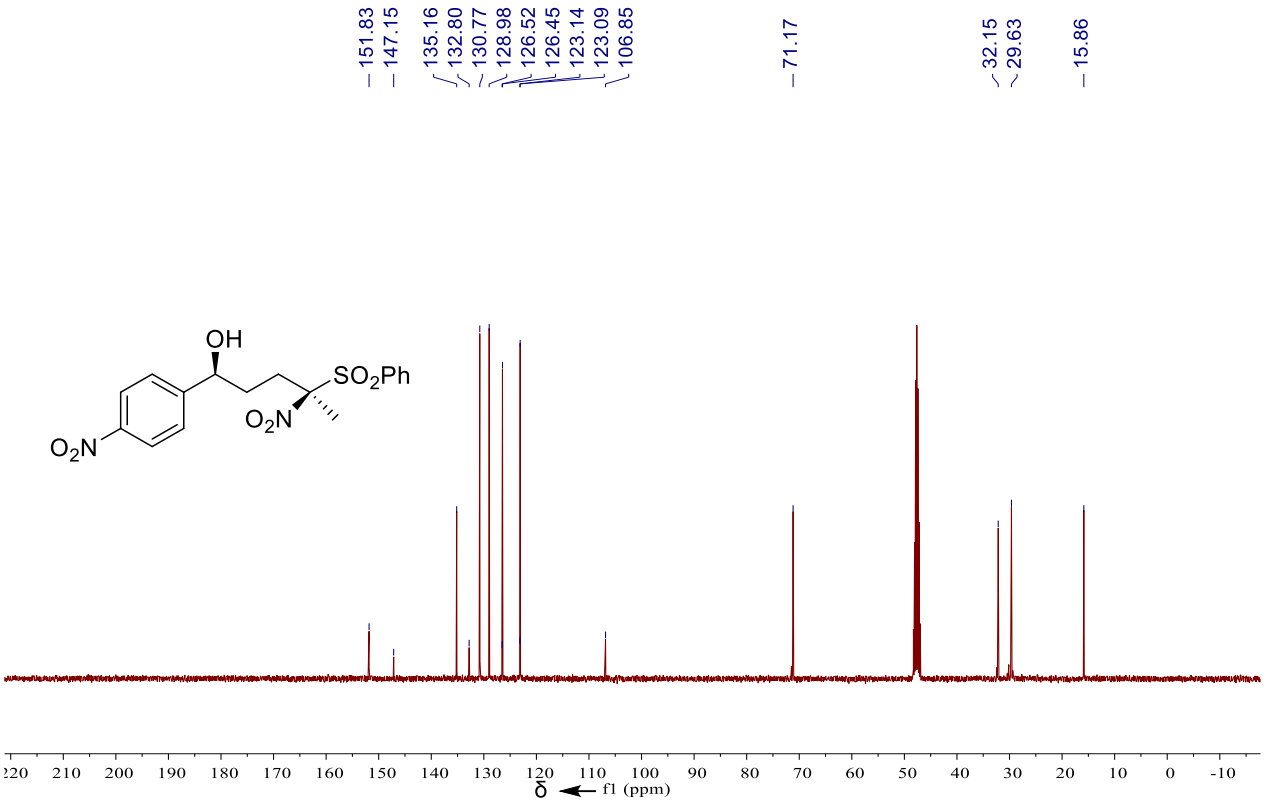
(*S,R*)-**5i:** (*1S,4R*-1-(4-iodophenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.



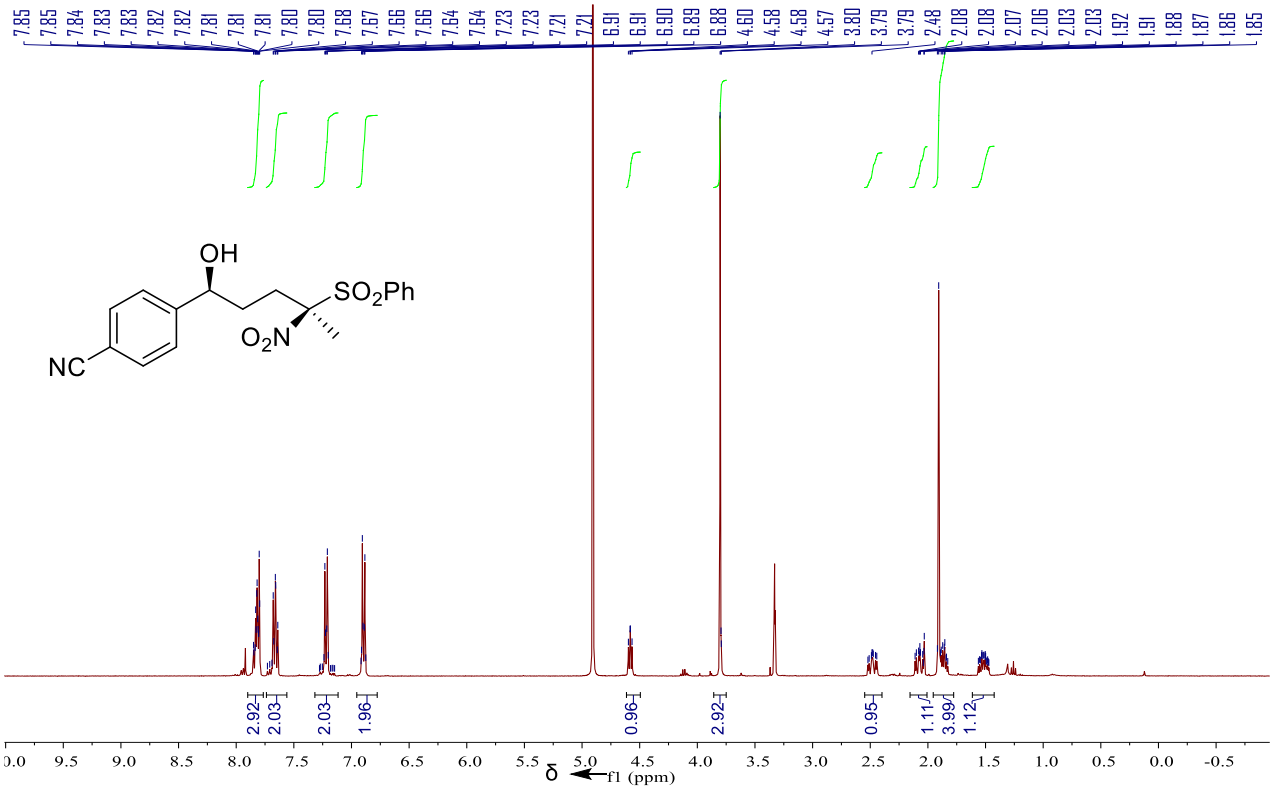


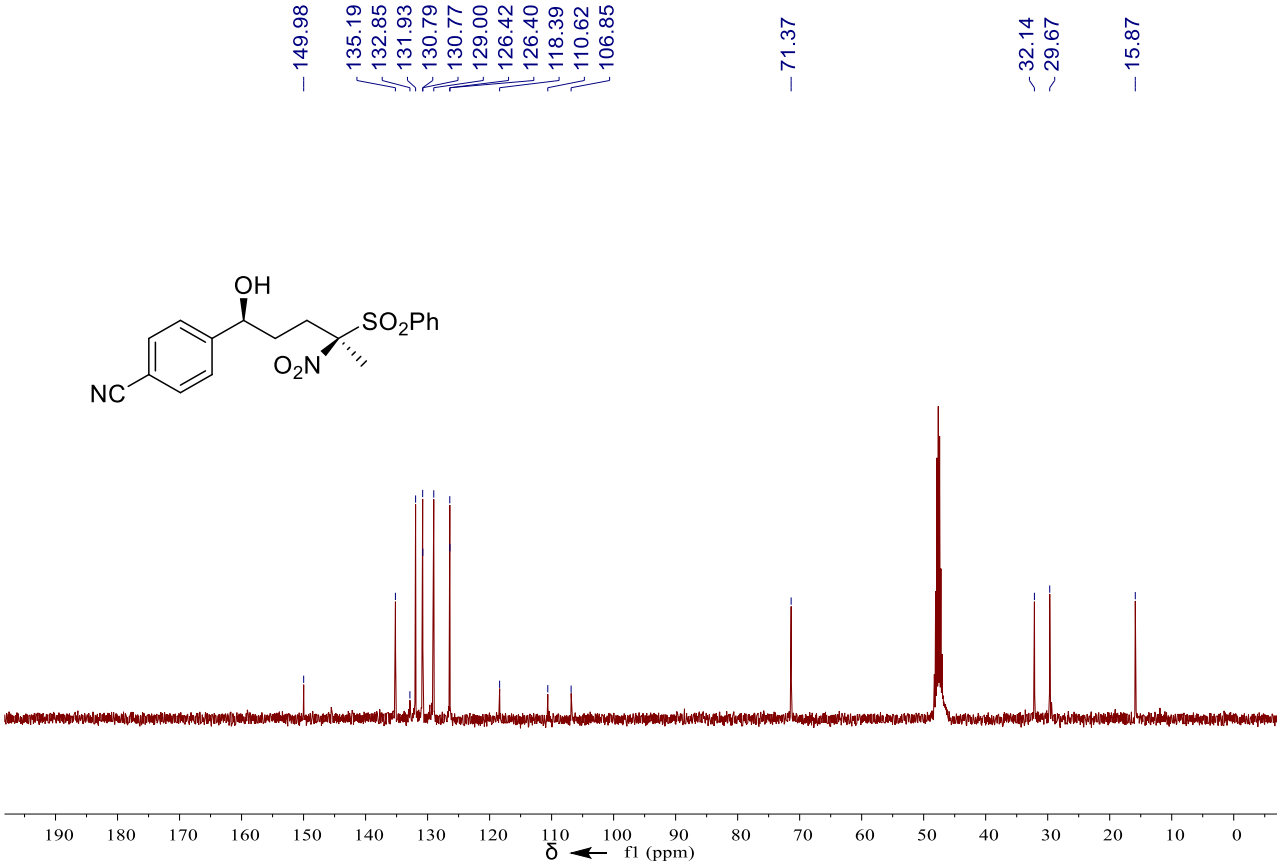
(*S,R*)-**5j:** (*1S,4R*)-4-nitro-1-(4-nitrophenyl)-4-(phenylsulfonyl)pentan-1-ol.



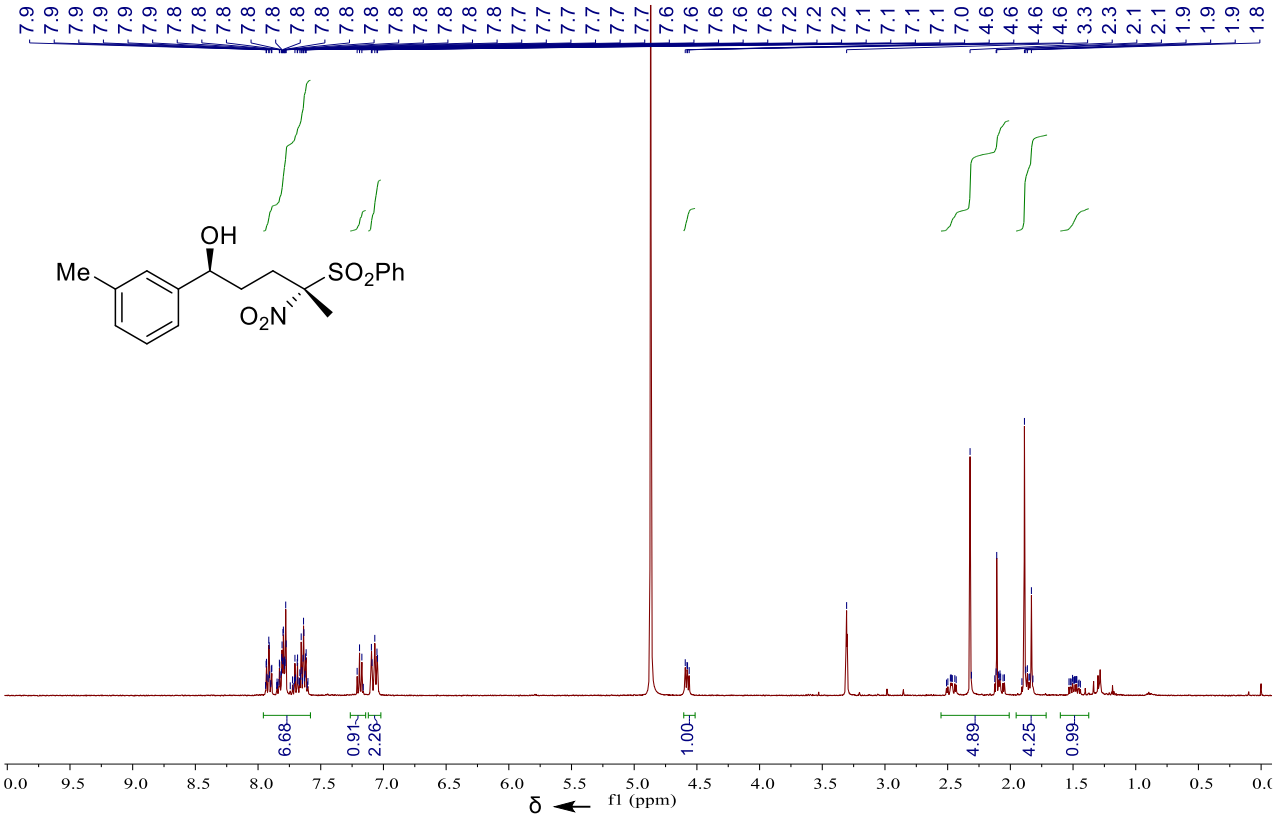


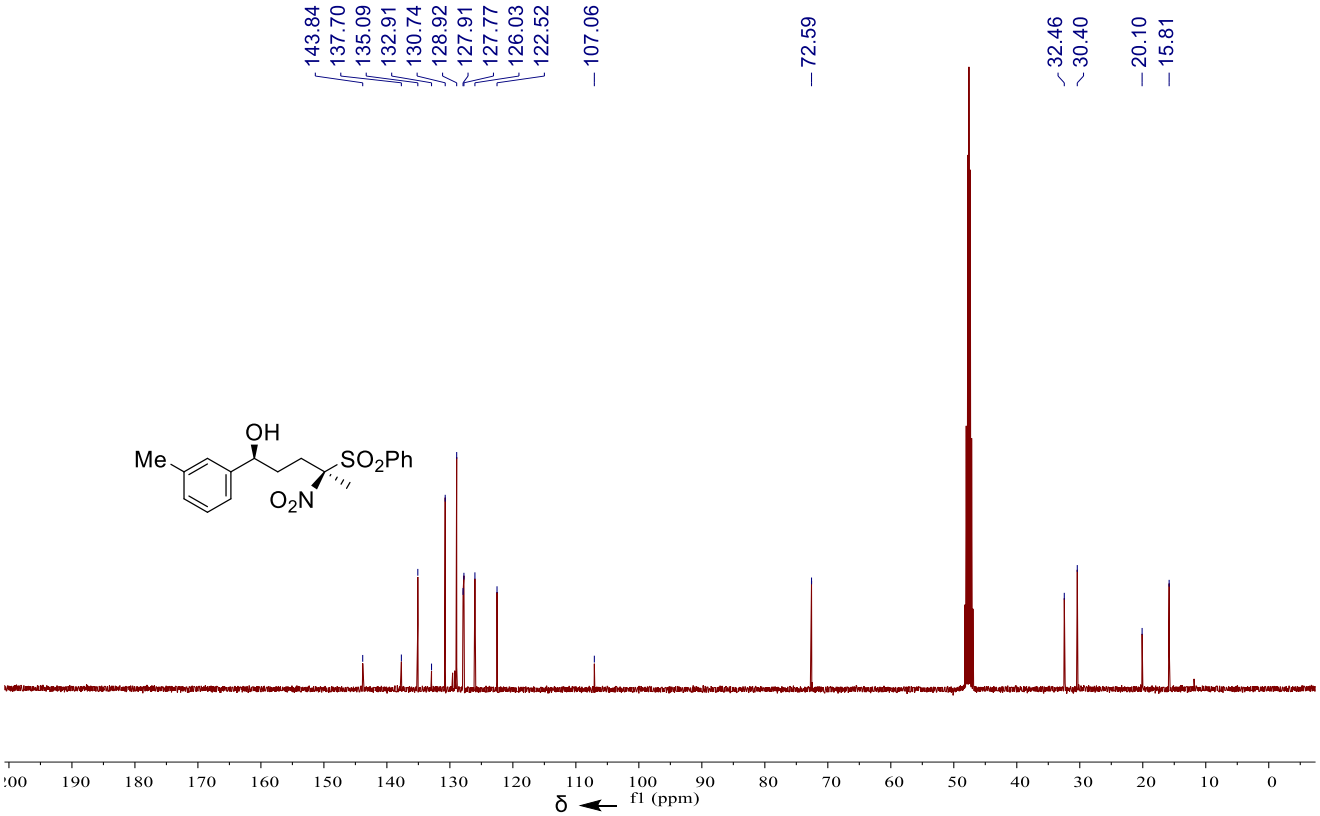
(*S,R*)-**5k:** 4-((*1S,4R*)-1-hydroxy-4-nitro-4-(phenylsulfonyl)pentyl)benzonitrile.



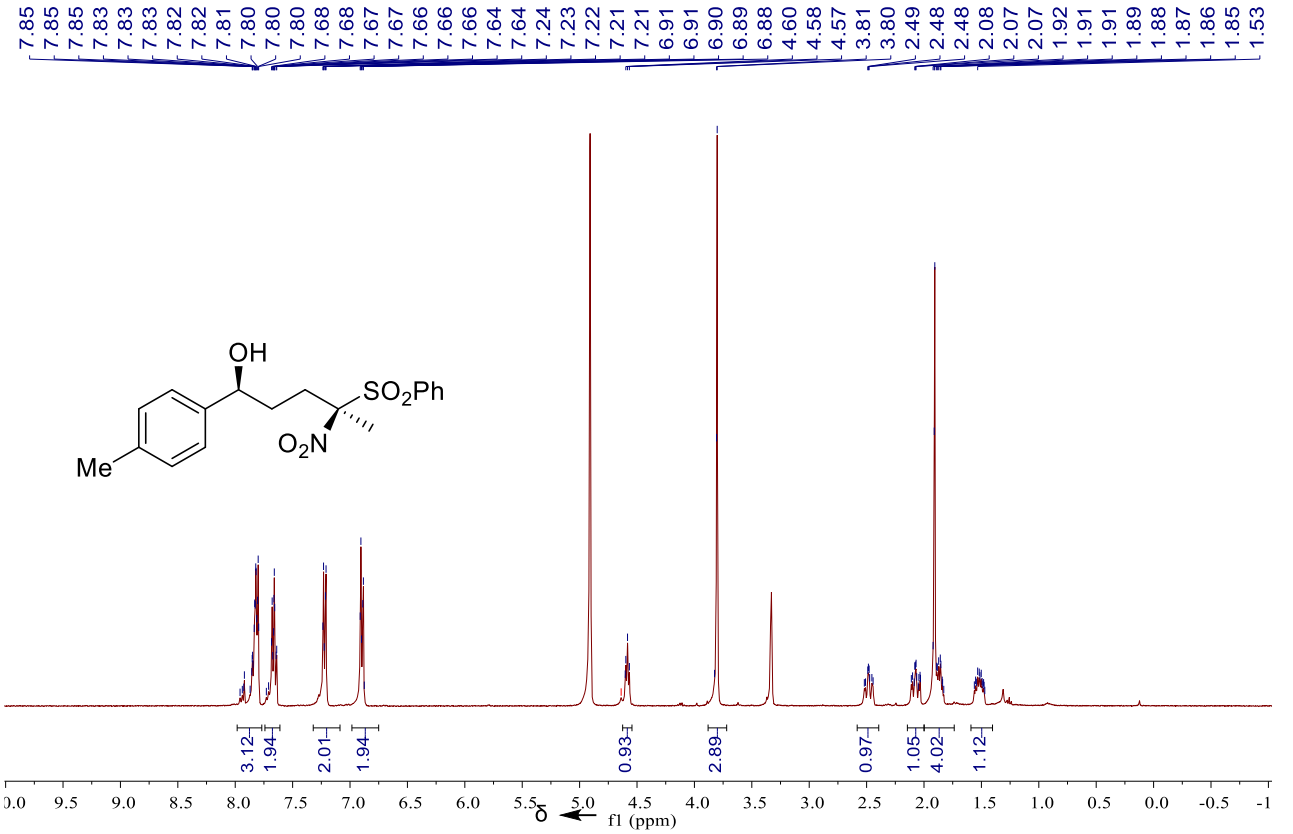


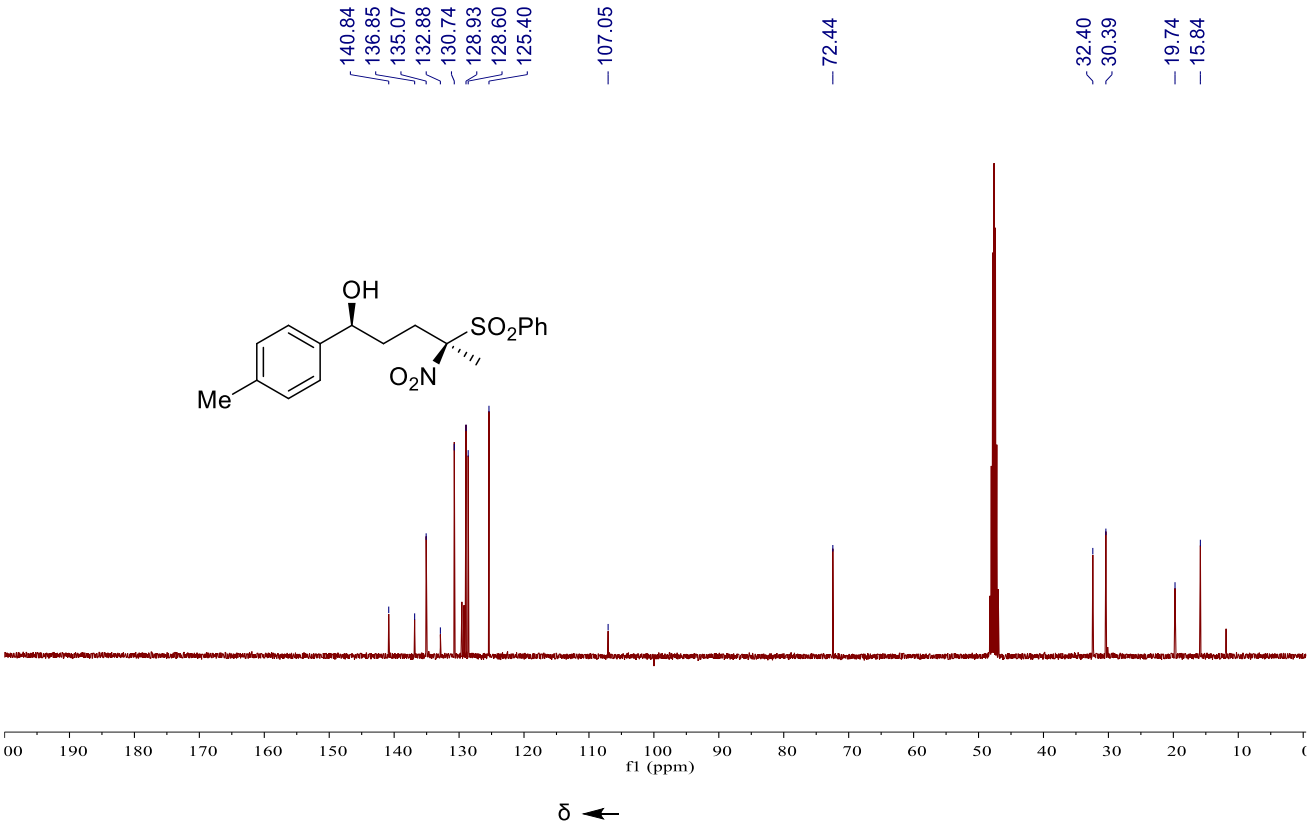
(*S,R*)-**5l:** (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(m-tolyl)pentan-1-ol.



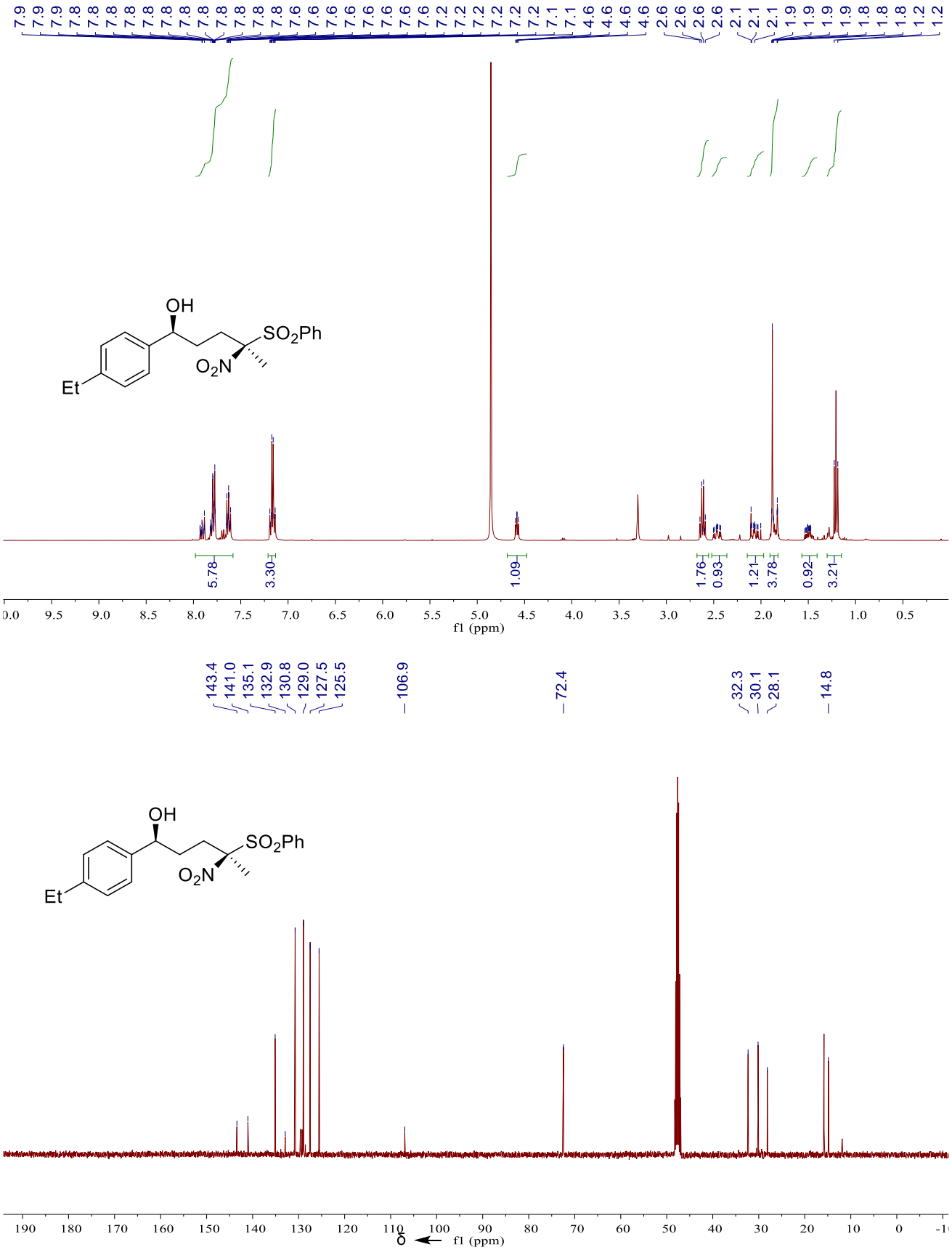


(*S,R*)-**5m:** (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(p-tolyl)pentan-1-ol.

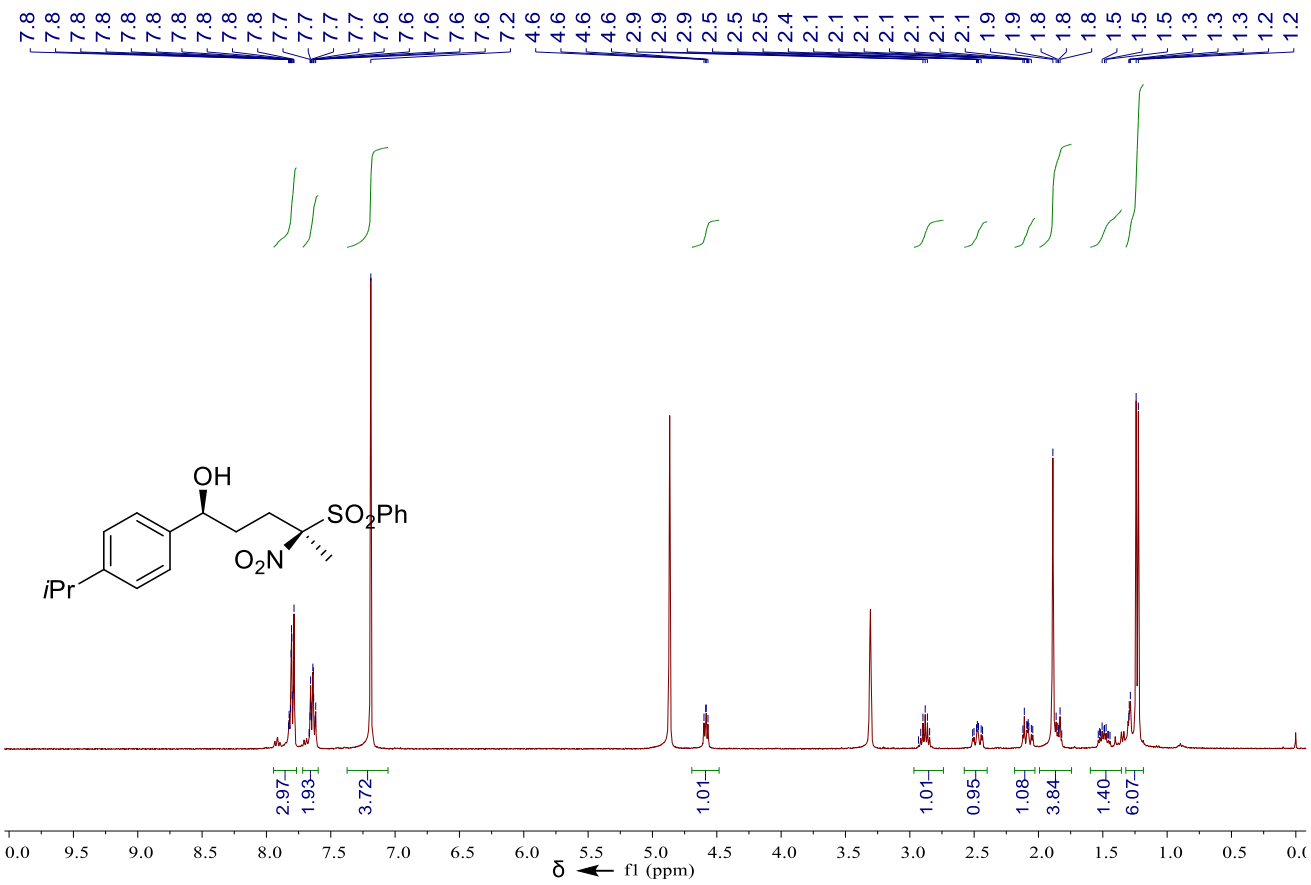


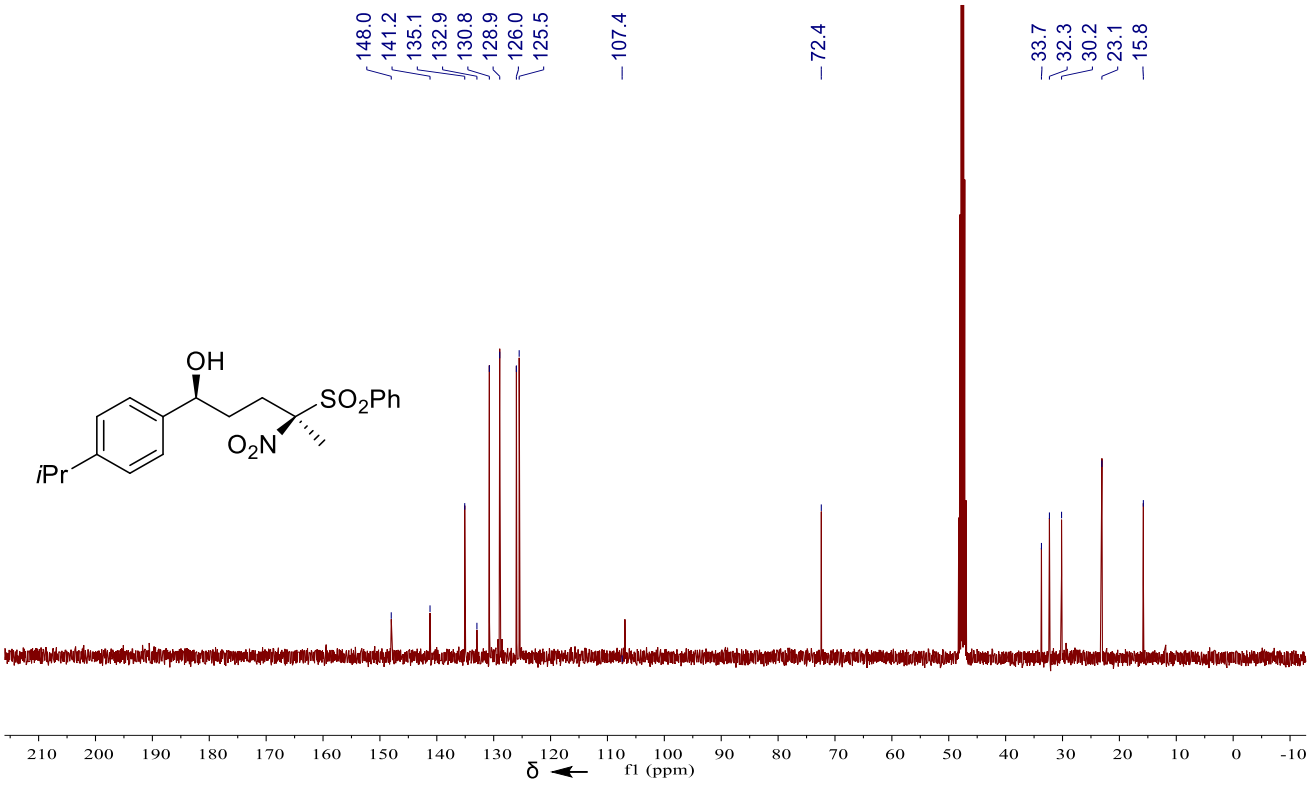


(*S*,*R*)-**5n:** (*1S*,*4R*)-1-(4-ethylphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.

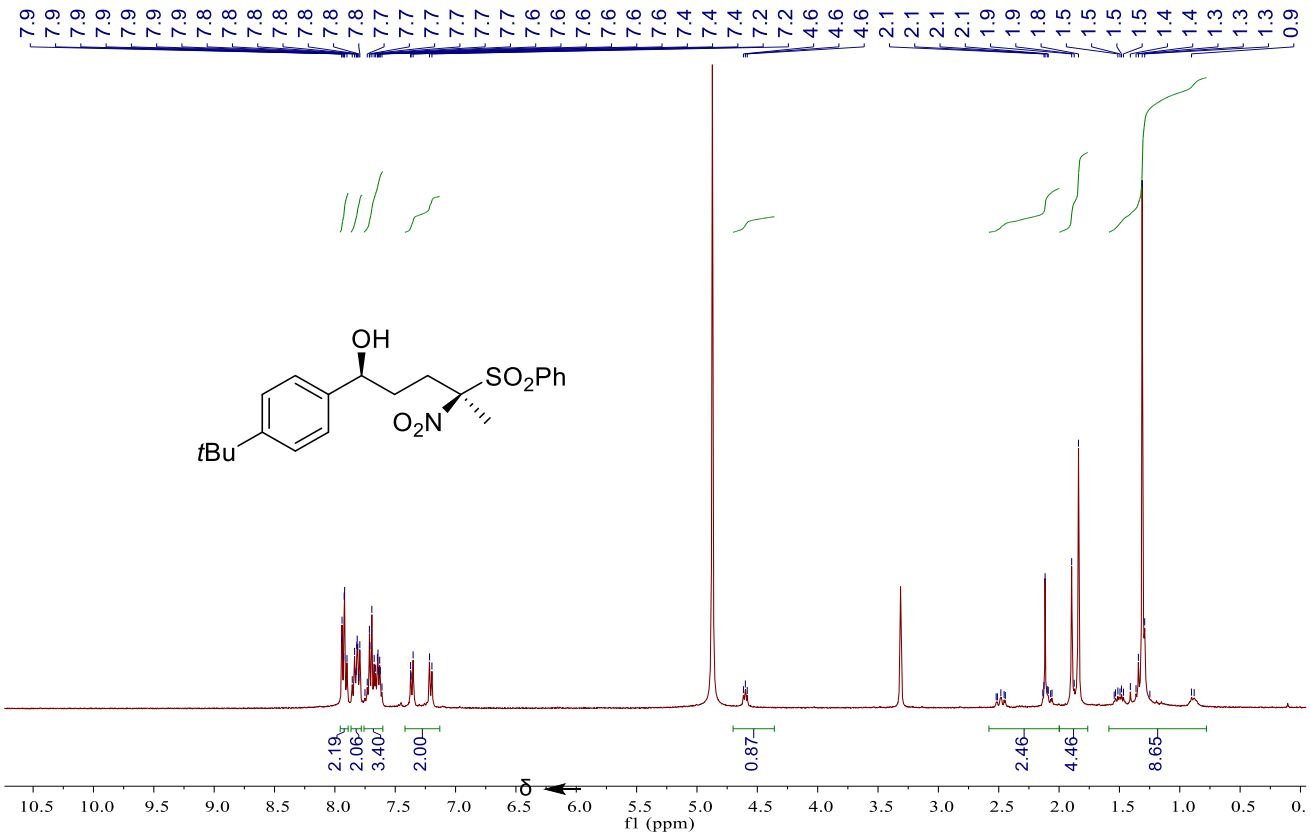


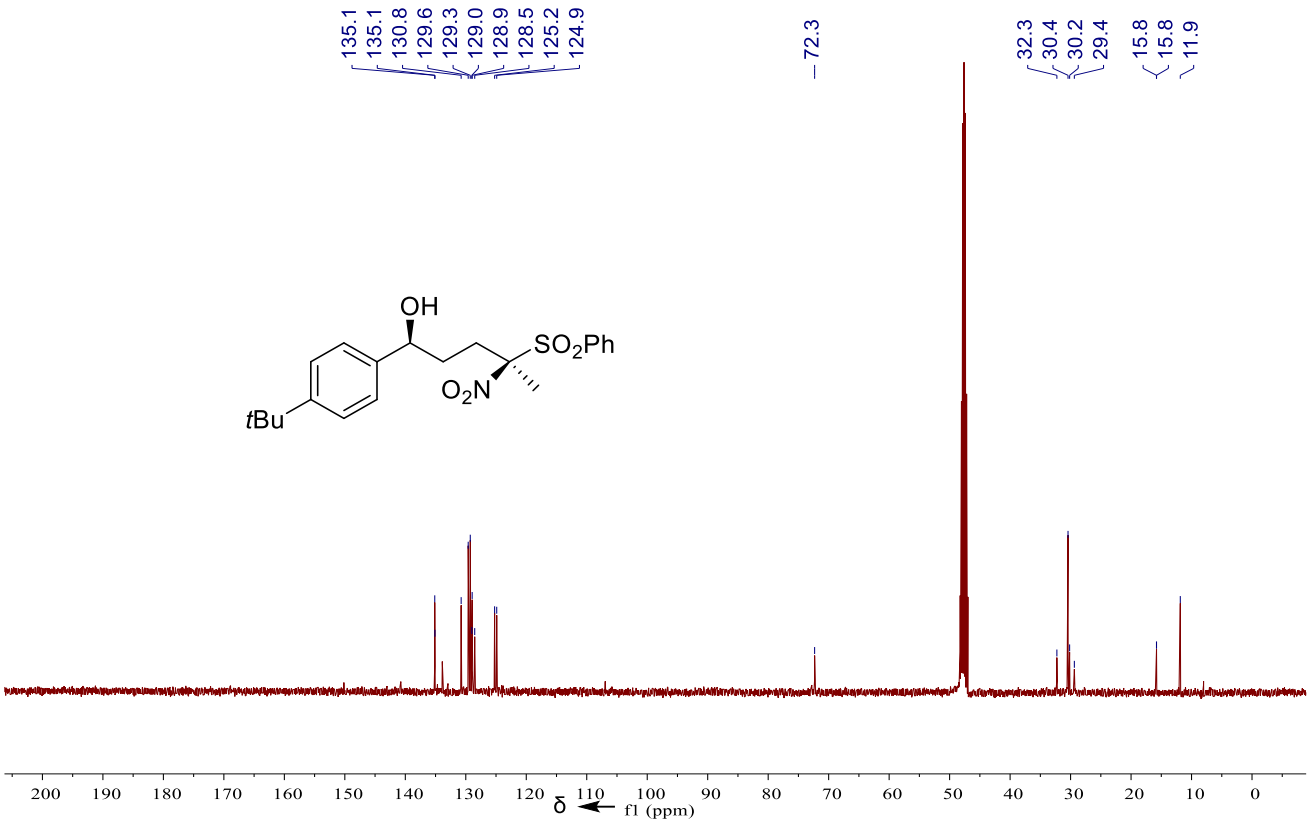
(*S,R*)-**5o:** (*1S,4R*)-1-(4-isopropylphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.



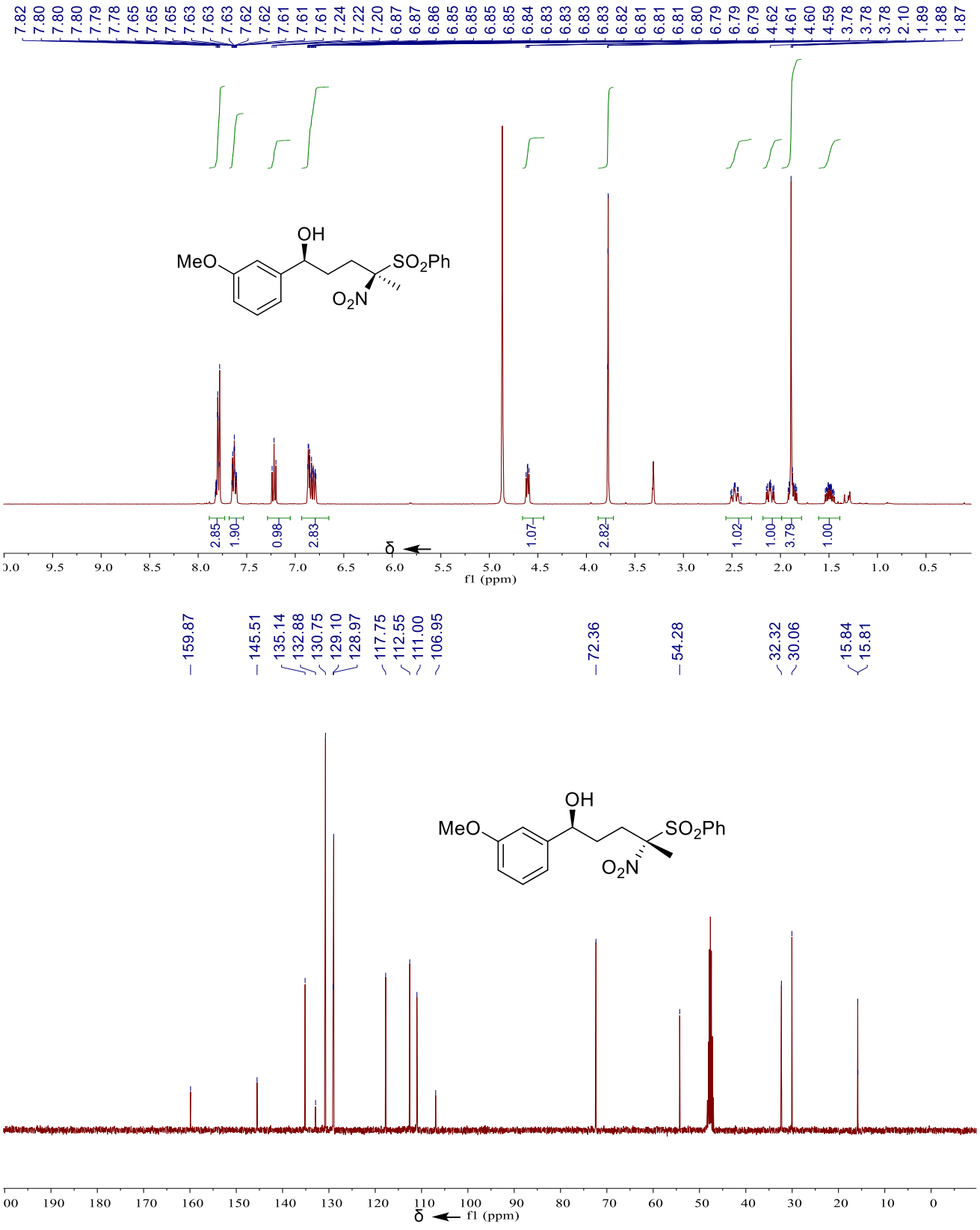


(*S,R*)-**5p:** (*1S,4R)*-1-(4-(tert-butyl)phenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.

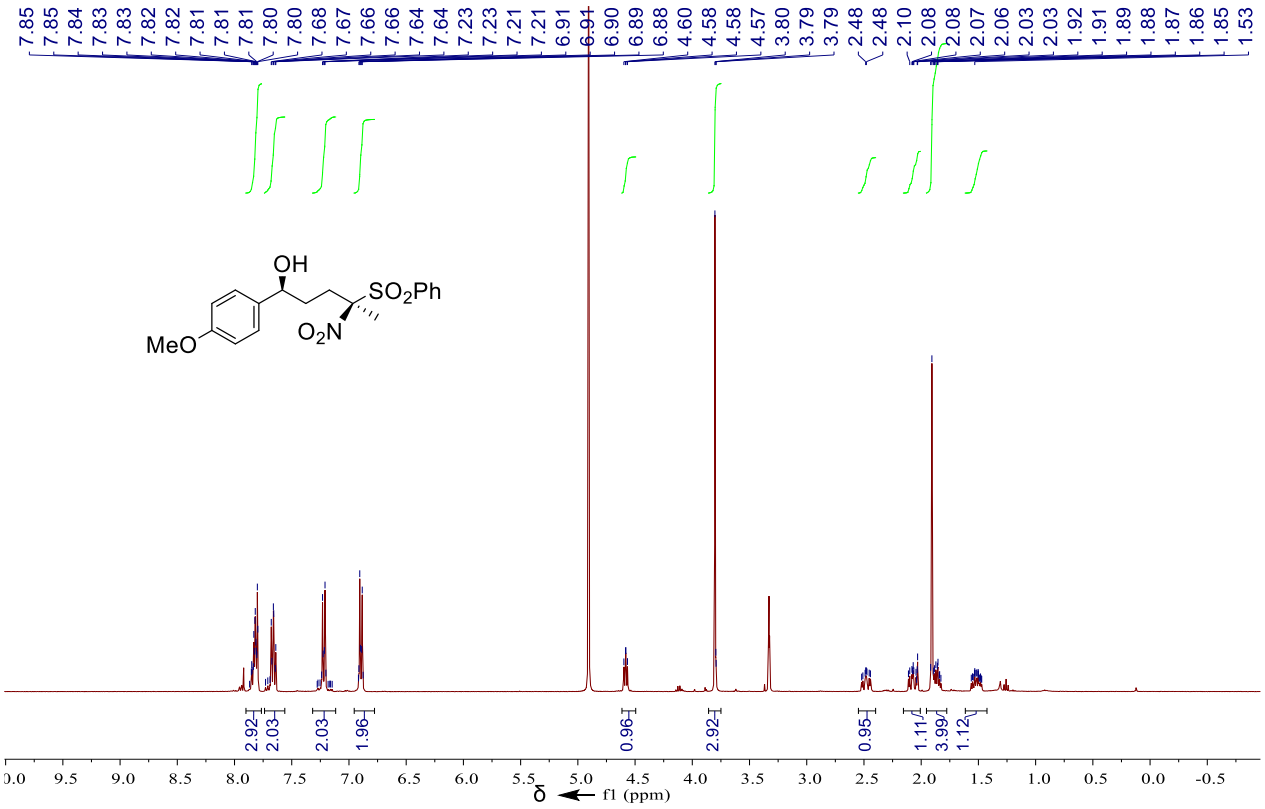


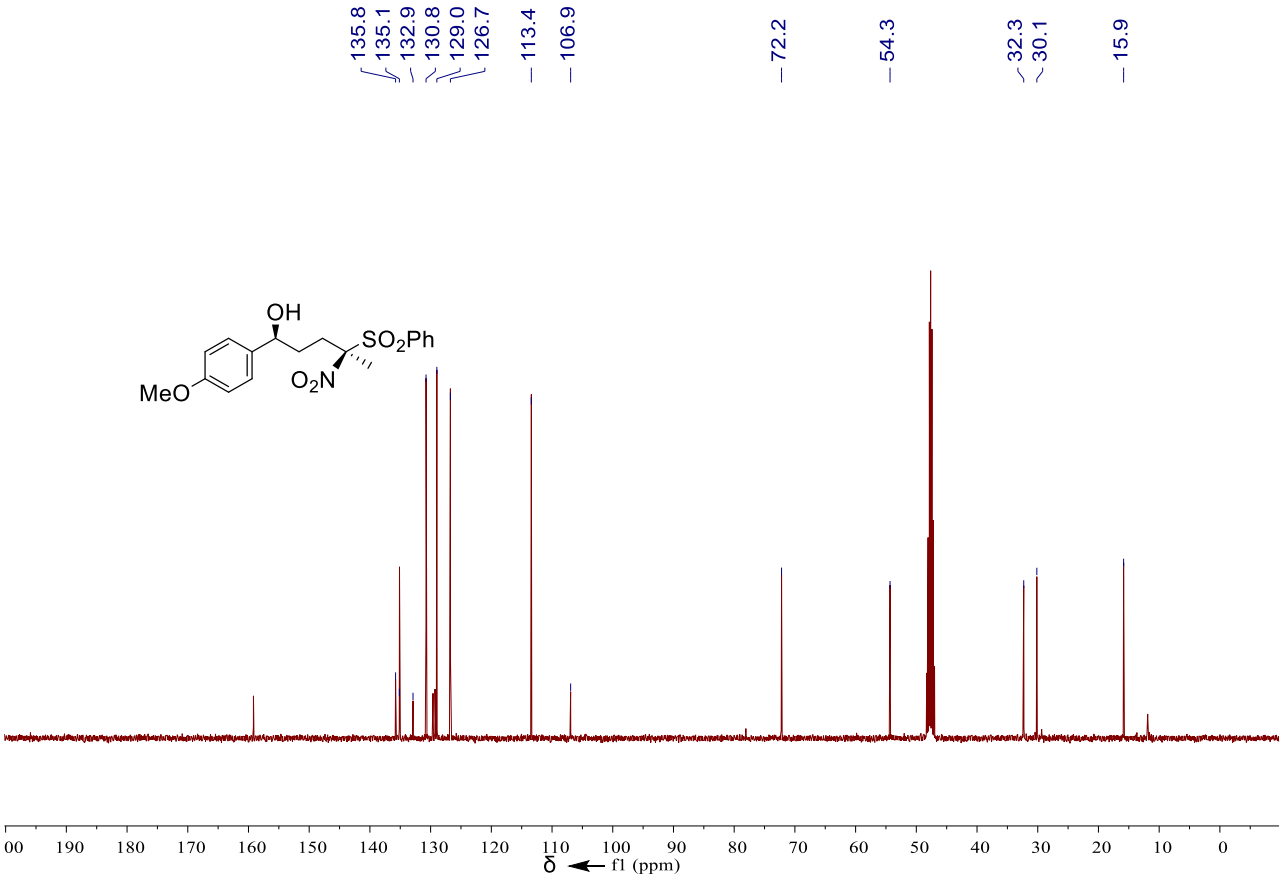


(*S*,*R*)-**5q:** (*1S*,*4R*)-1-(3-methoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.

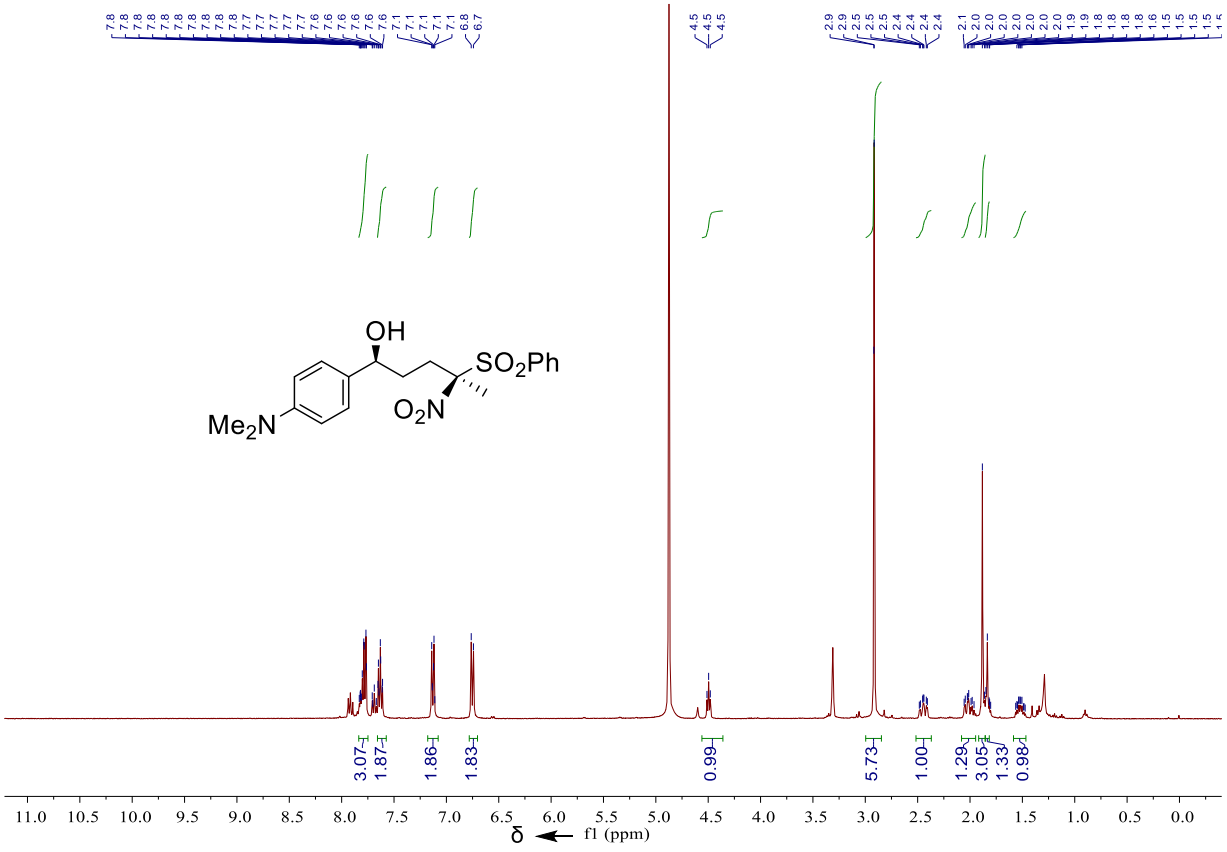


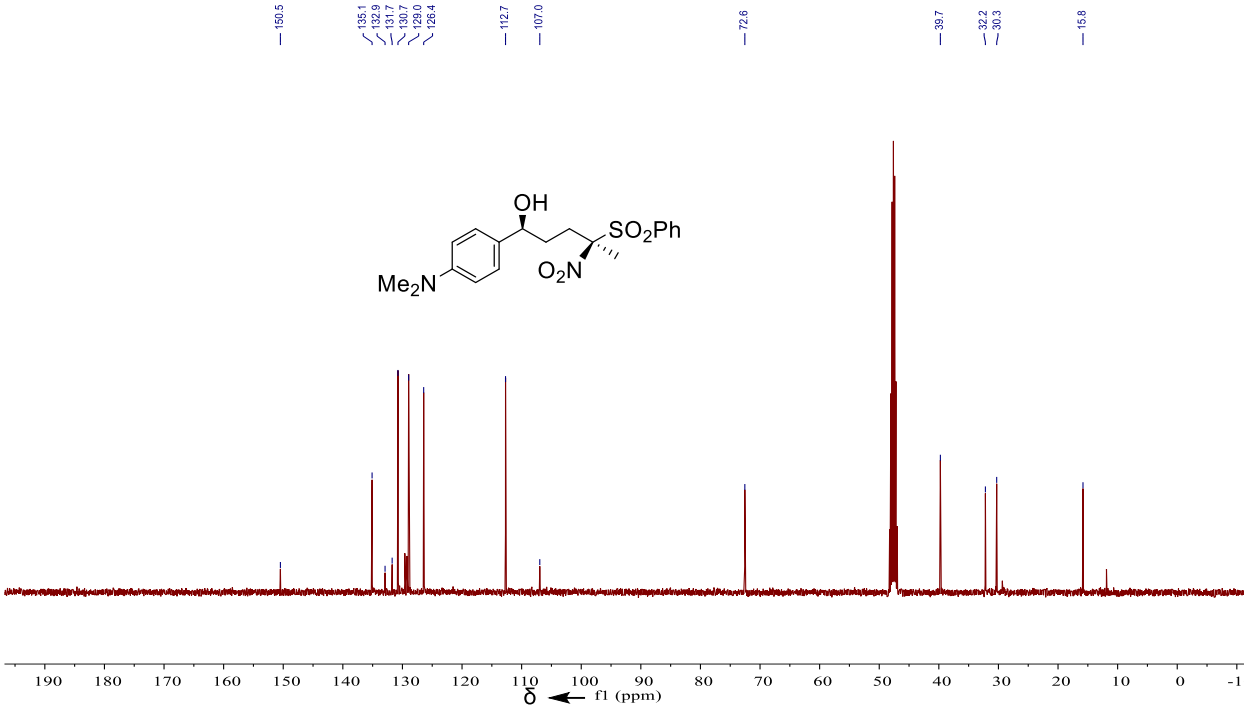
(*S,R*)-**5r:** (*1S,4R*)-1-(4-methoxyphenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.



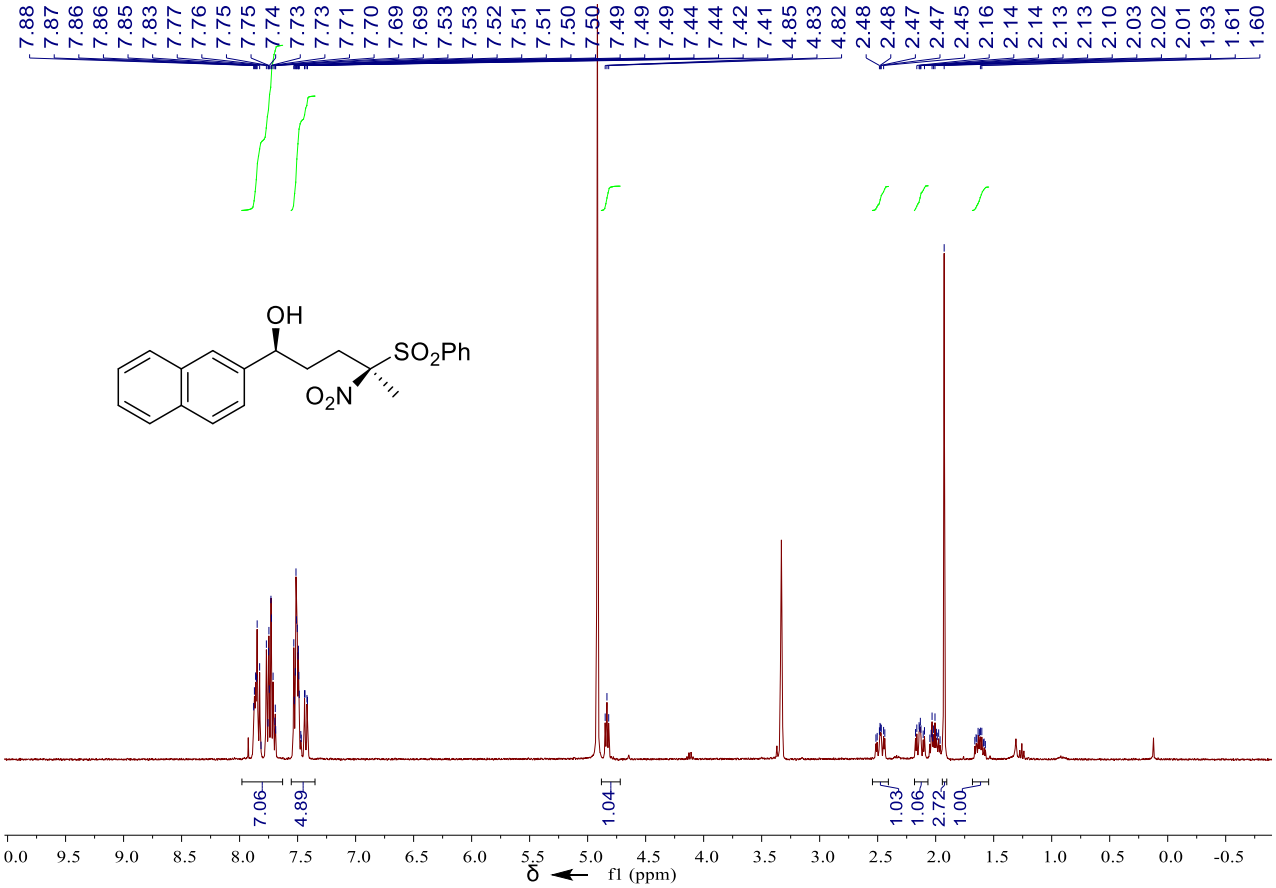


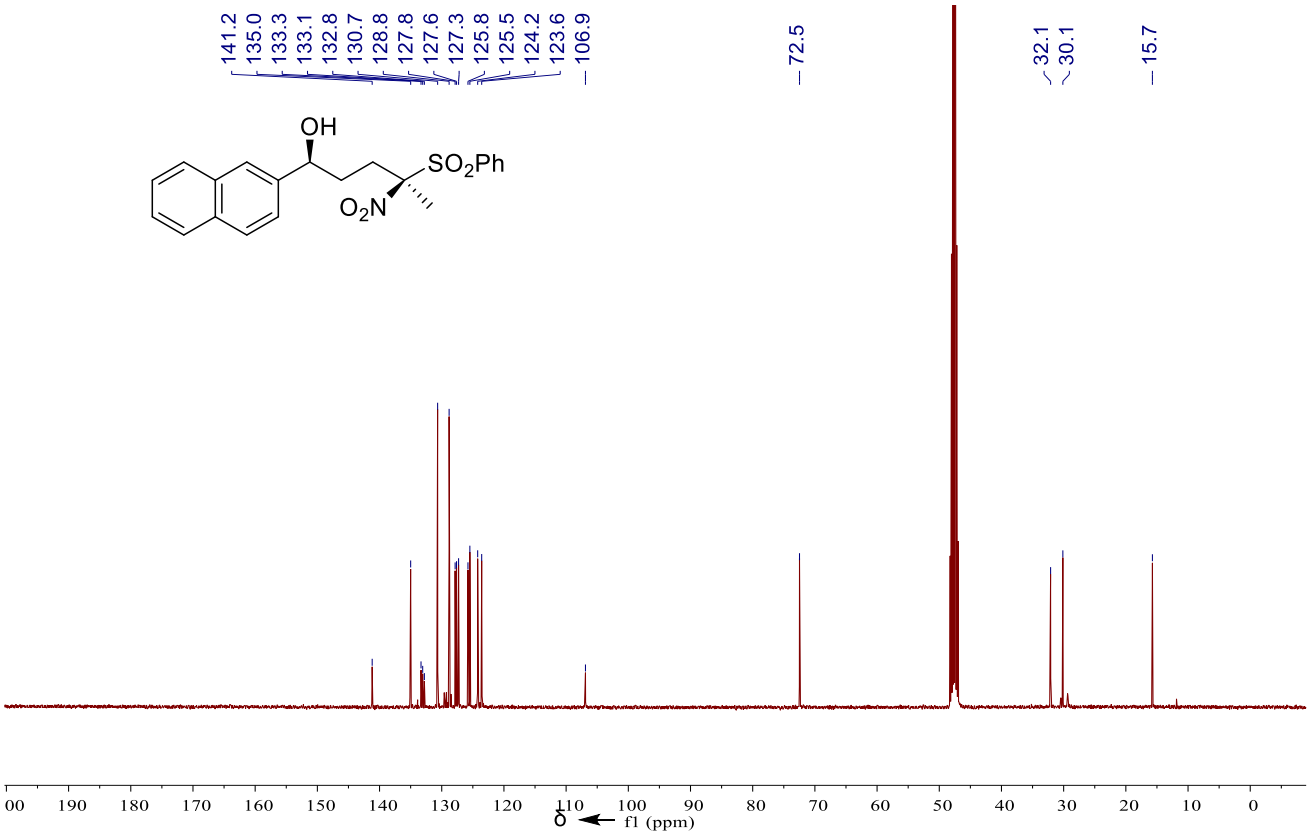
(*S*,*R*)-**5s**: (*1S*,*4R*)-1-(4-(dimethylamino)phenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol



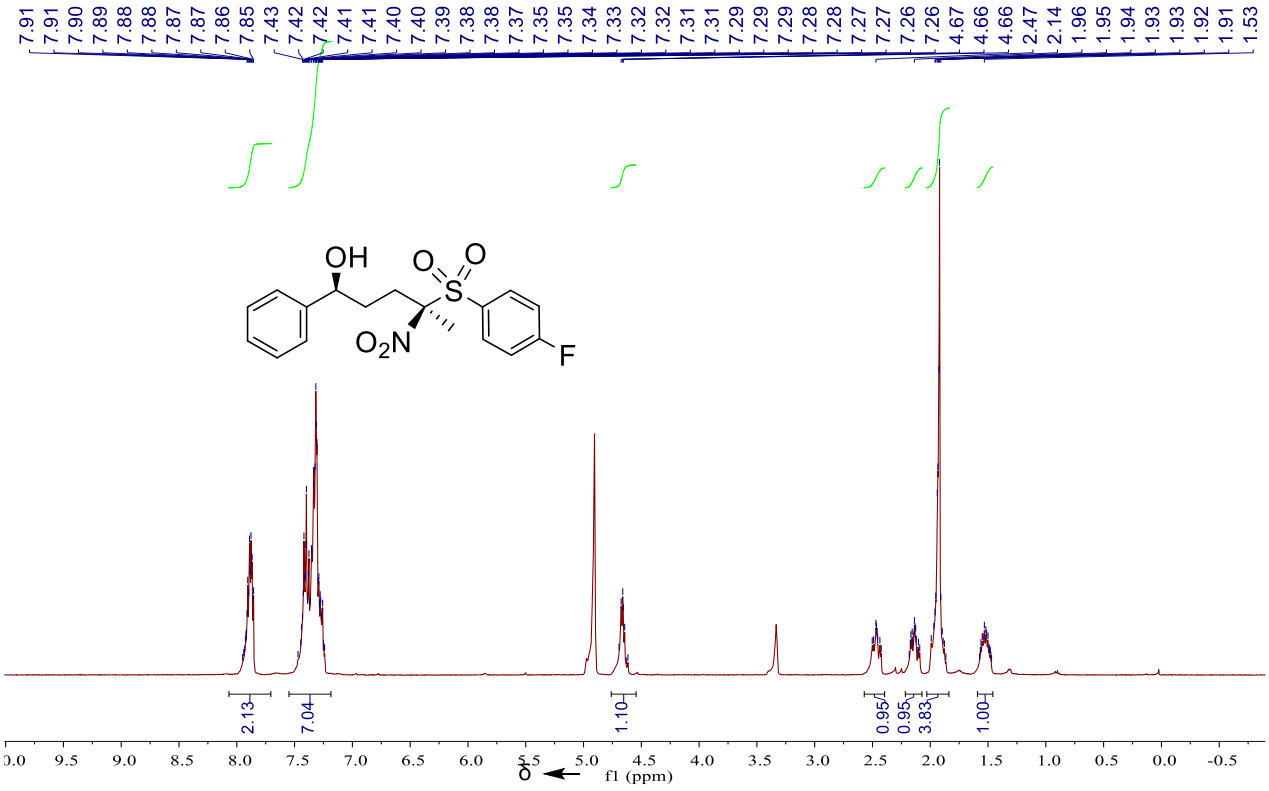


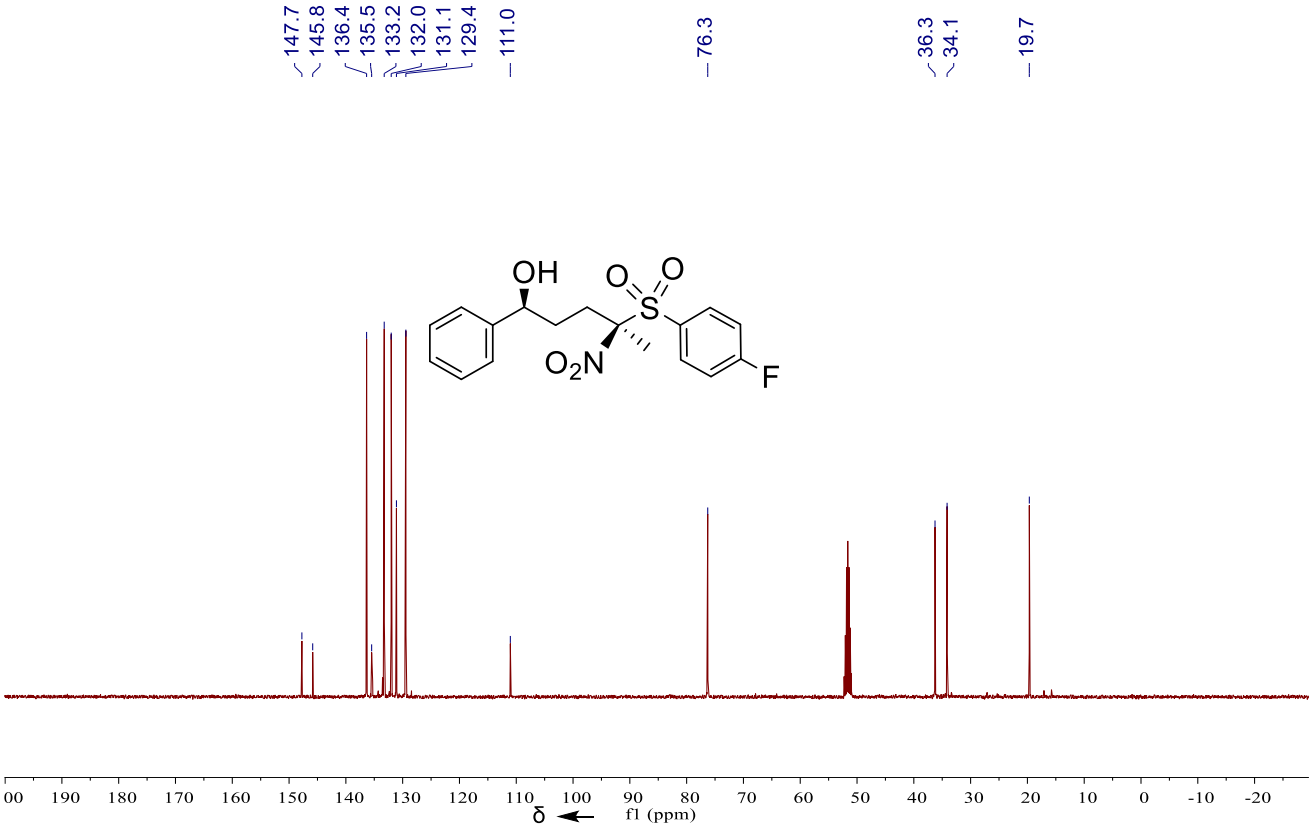
(*S,R*)-**5t:** (*1S,4R*)-1-(naphthalen-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.

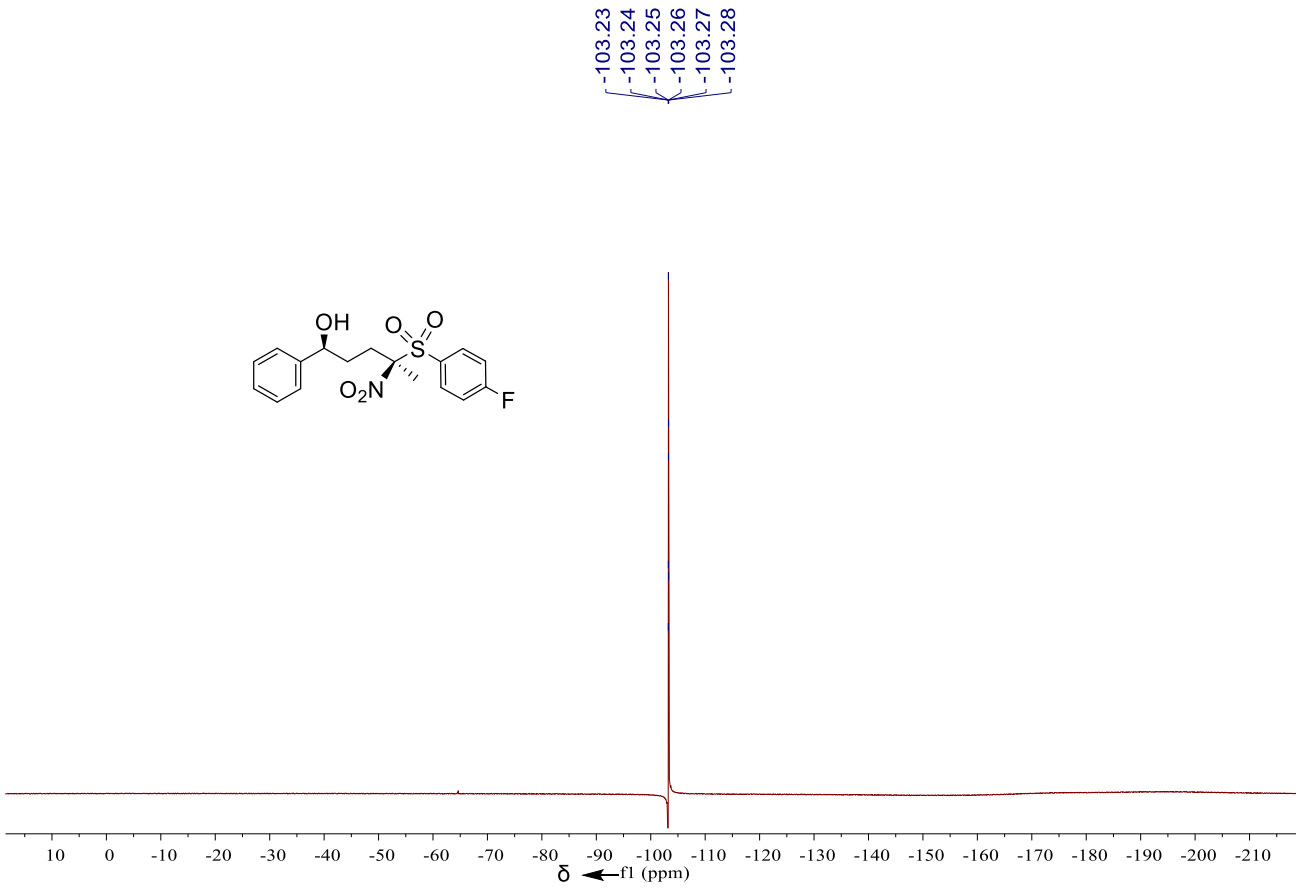




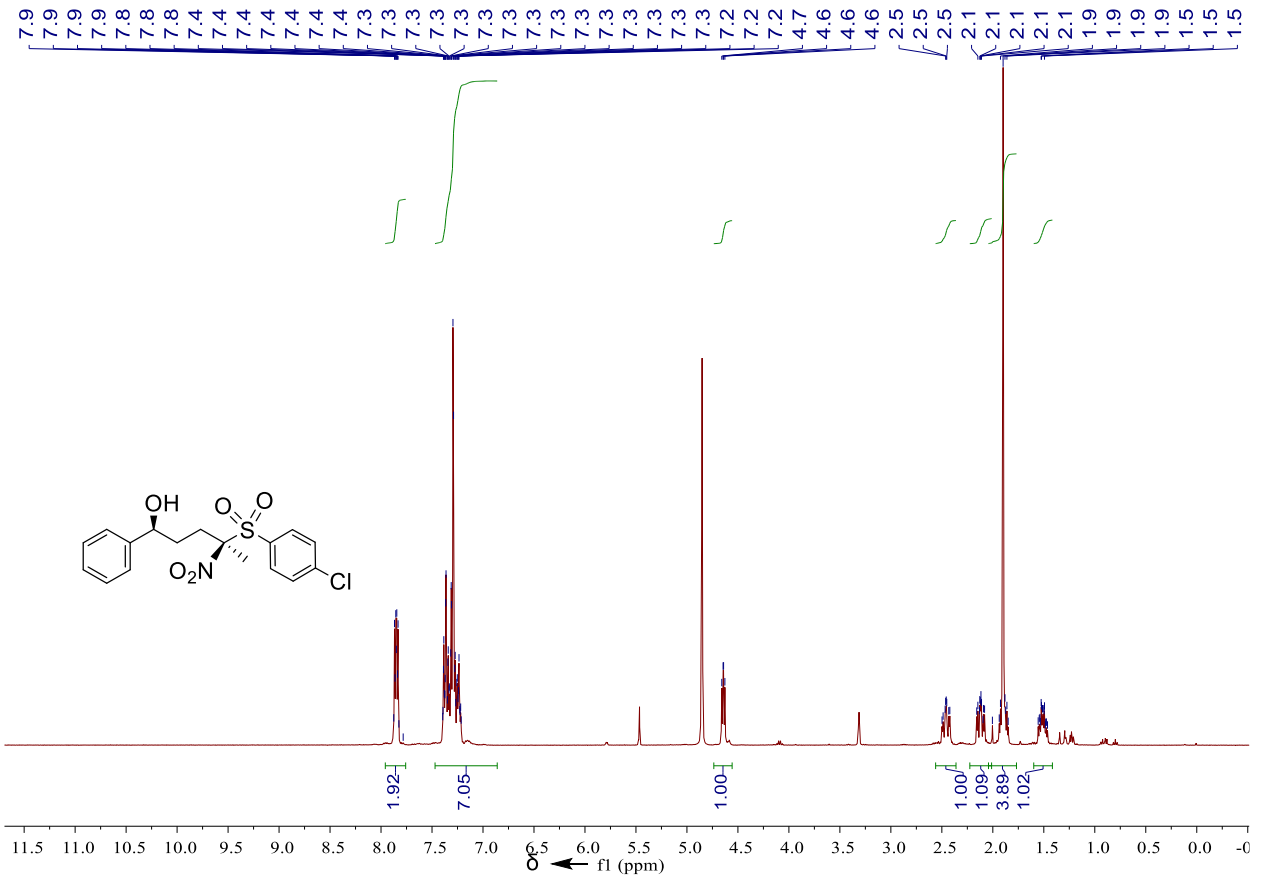
(*S,R*)-**5u:** (*1S,4R*)-4-((4-fluorophenyl)sulfonyl)-4-nitro-1-phenylpentan-1-ol.

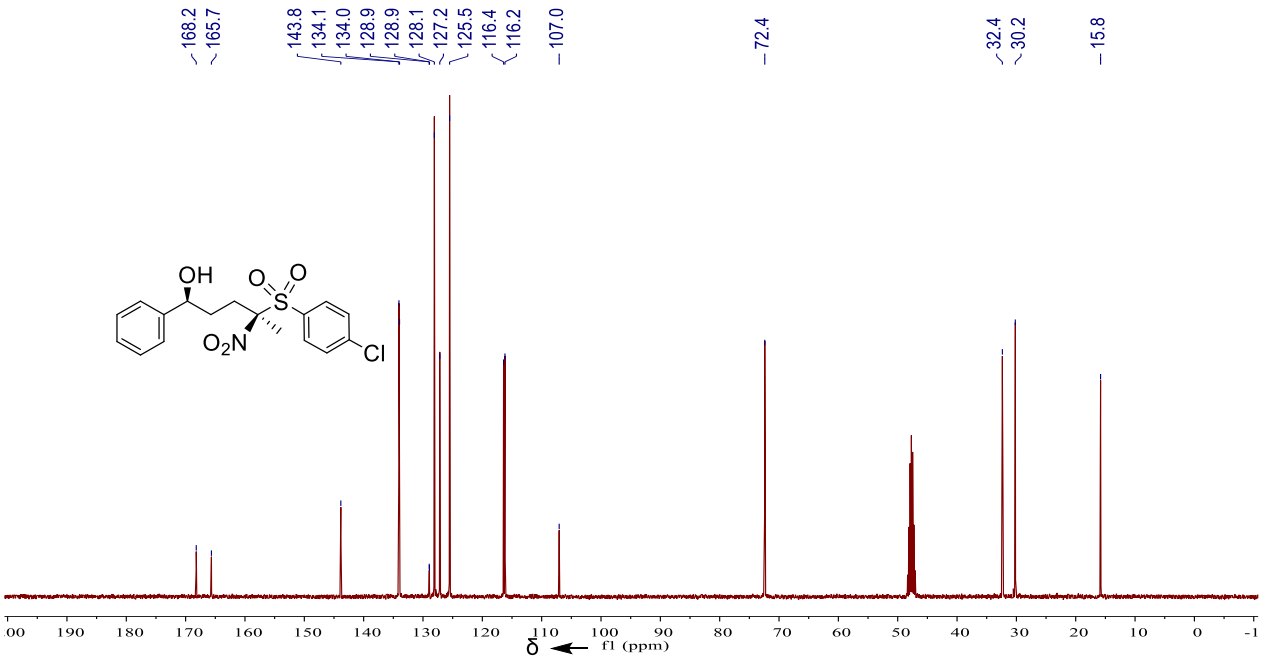




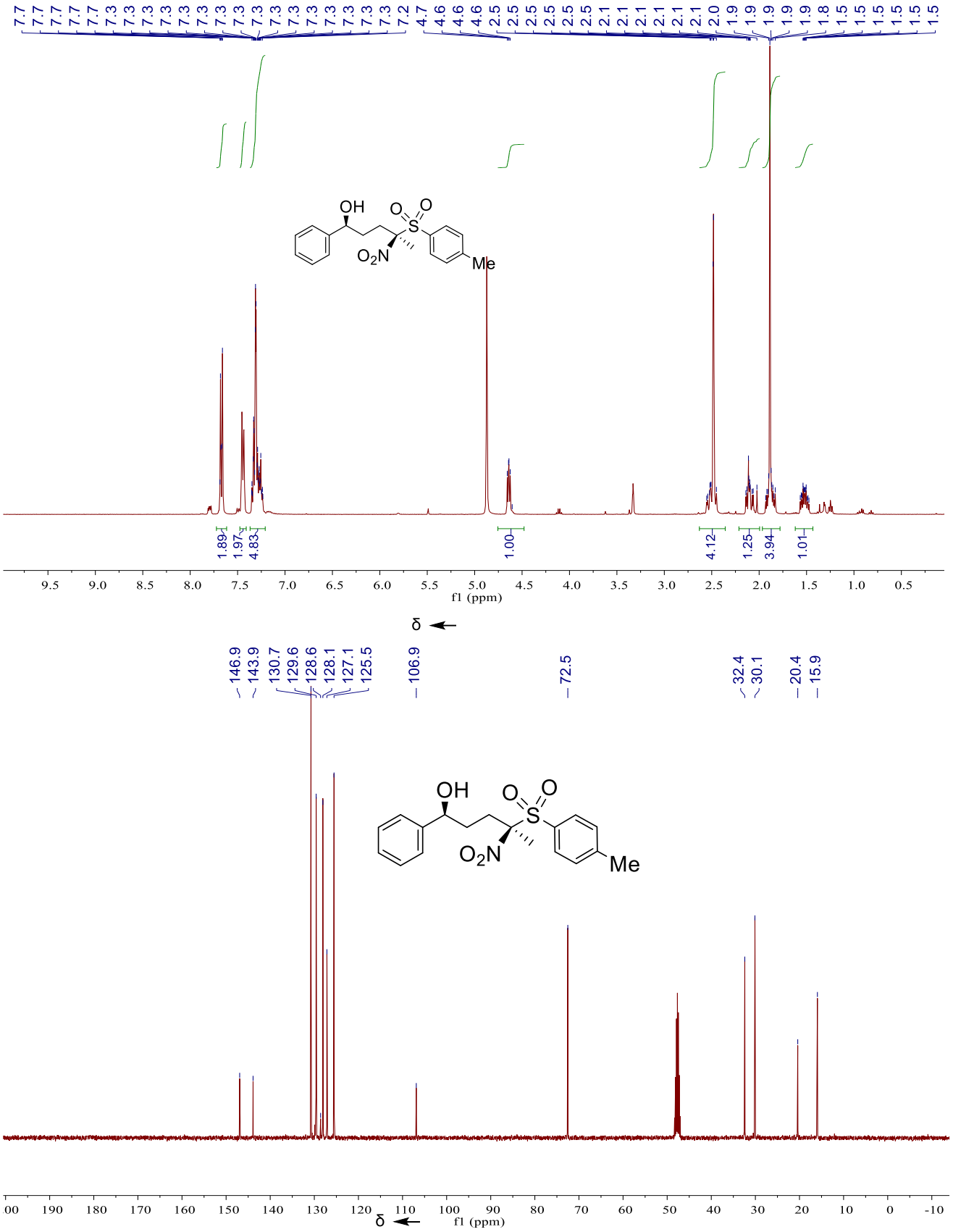

-103.23
-103.24
-103.25
-103.26
-103.27
-103.28
OH
O
O
S
O2N
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
δ f1 (ppm)

(*S,R*)-**5v:** (*1S,4R*)-4-((4-chlorophenyl)sulfonyl)-4-nitro-1-phenylpentan-1-ol.

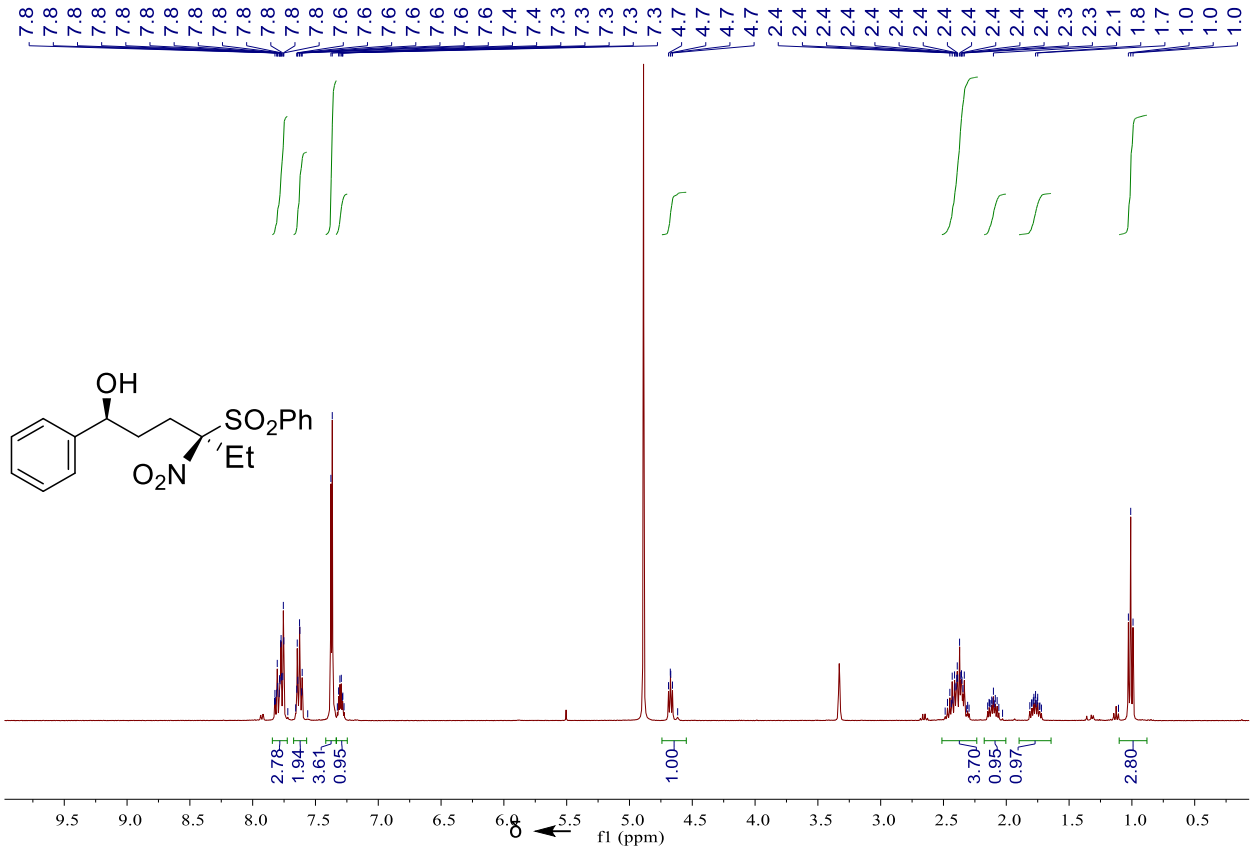


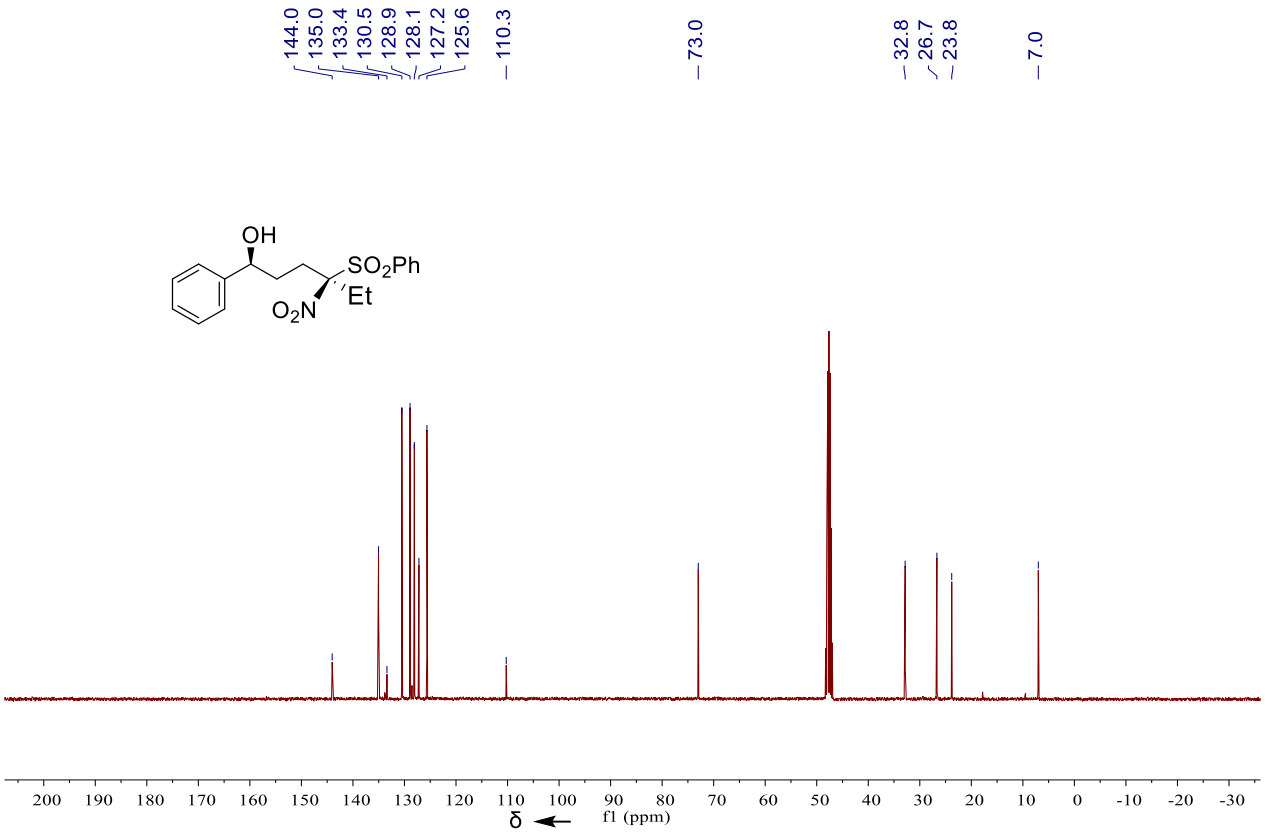


(*S,R*)-**5w:** (*1S,4R*)-4-nitro-1-phenyl-4-tosylpentan-1-ol.

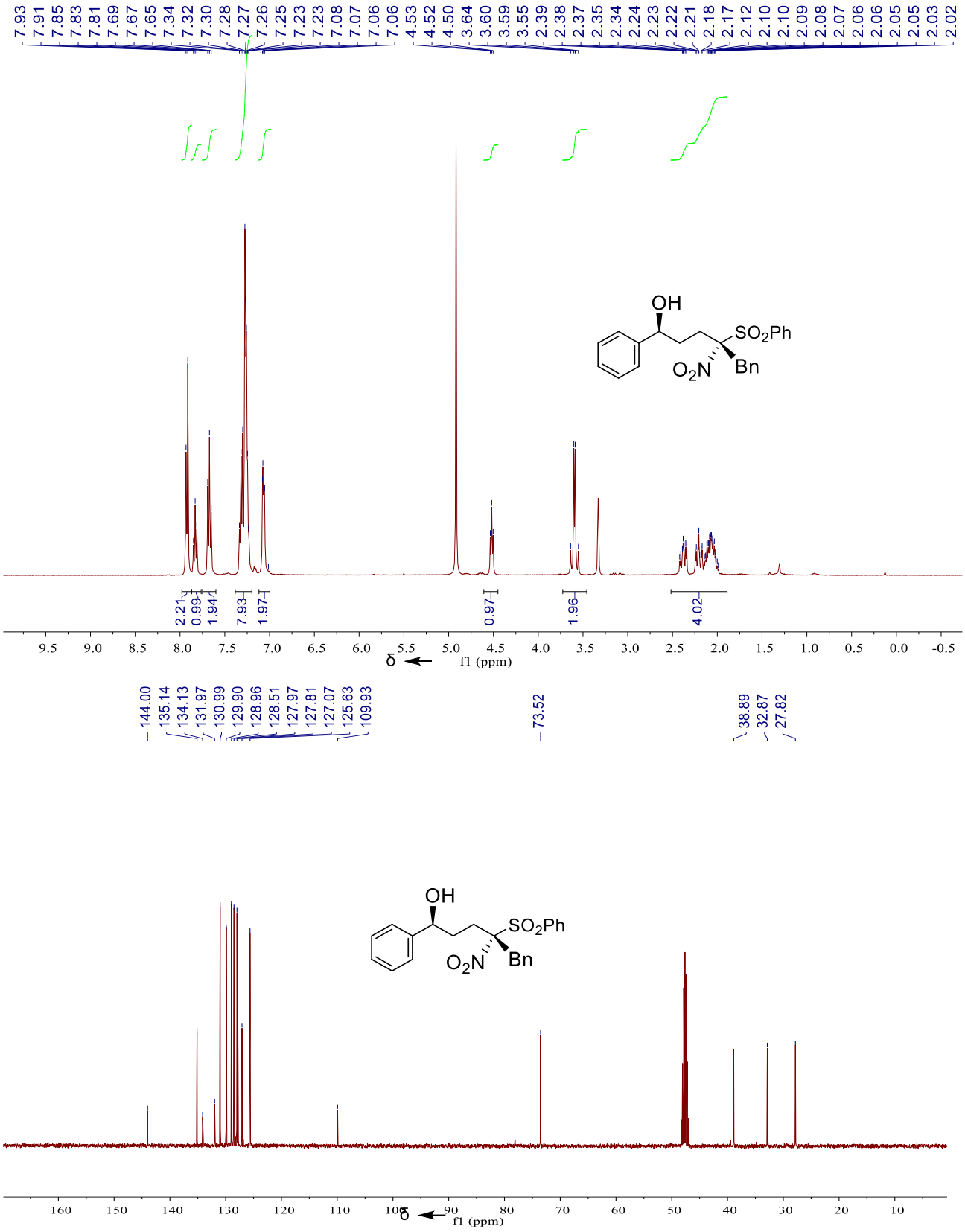


(*S,R*)-**5x:** (*1S,4R*)-4-nitro-1-phenyl-4-(phenylsulfonyl)hexan-1-ol.

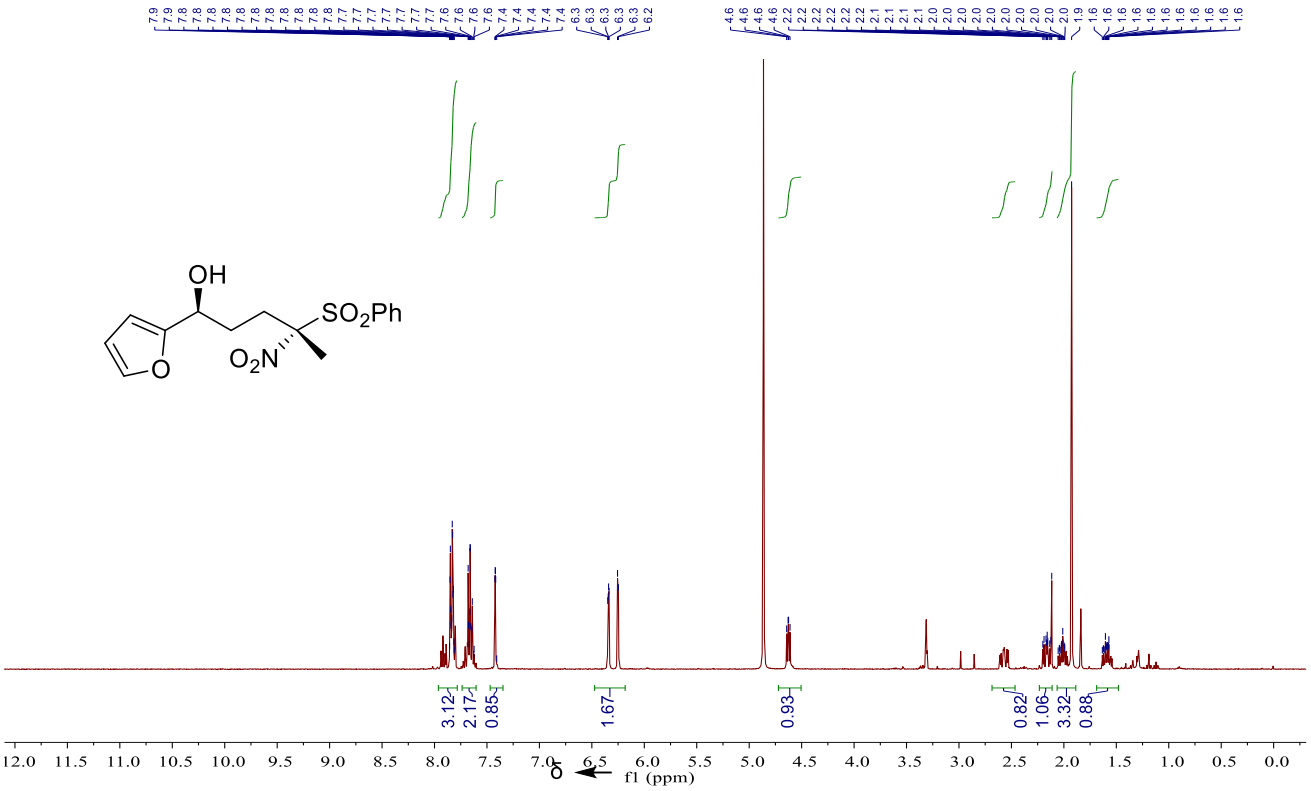


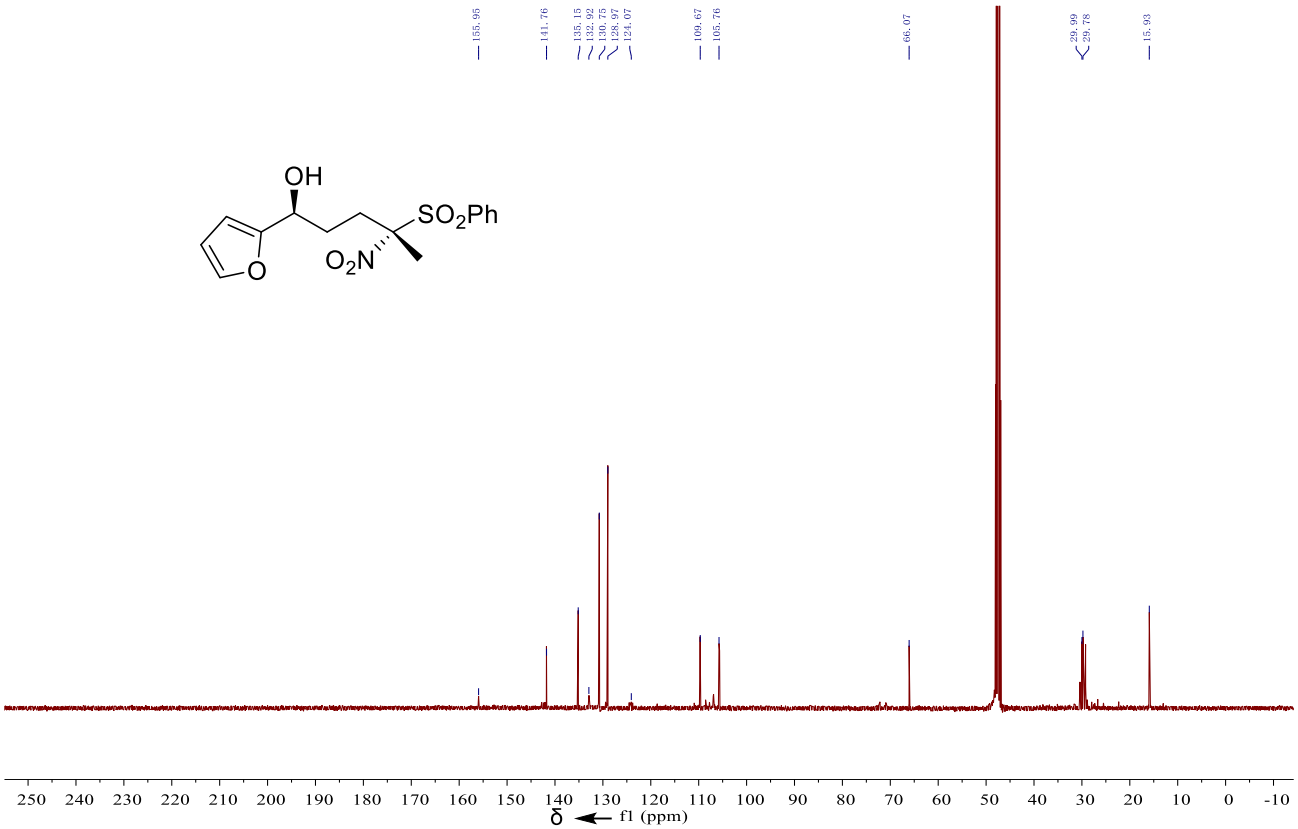


(*S,R*)-**5y:** (*1S,4R*)-4-nitro-1,5-diphenyl-4-(phenylsulfonyl)pentan-1-ol.

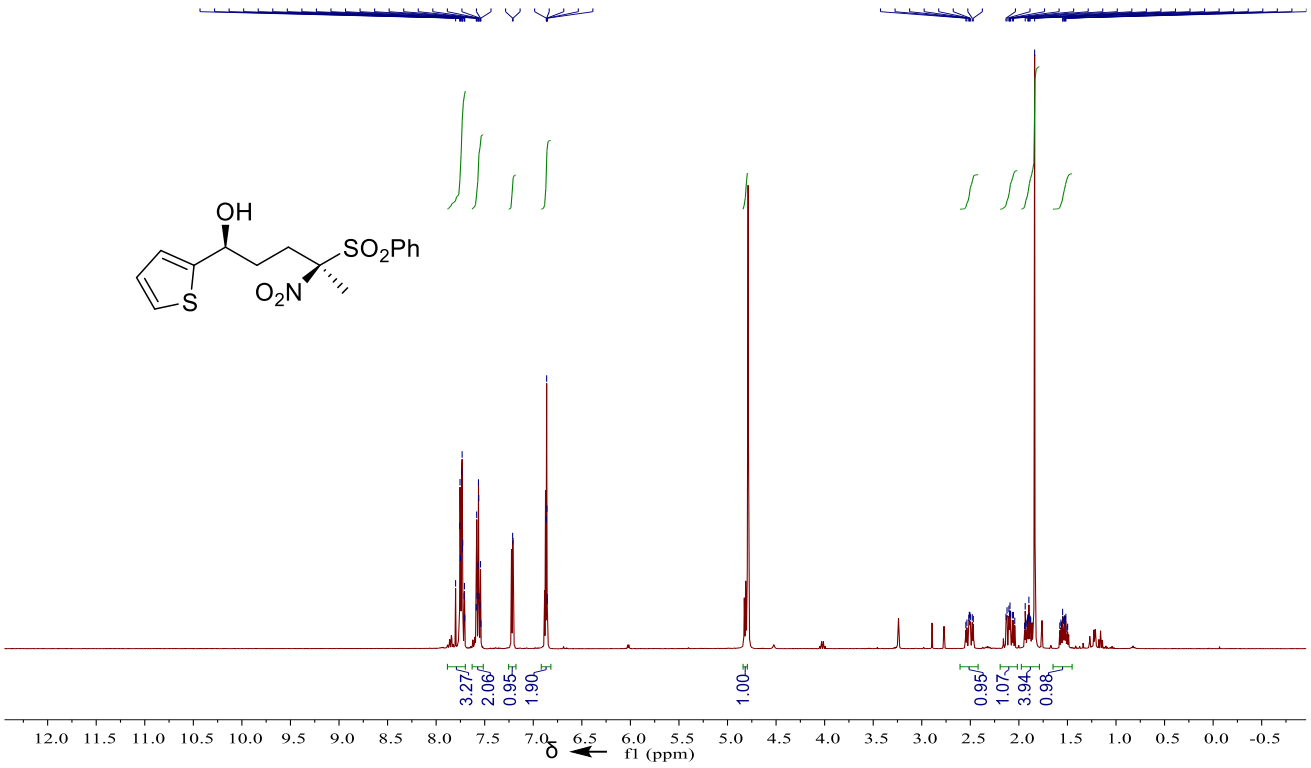


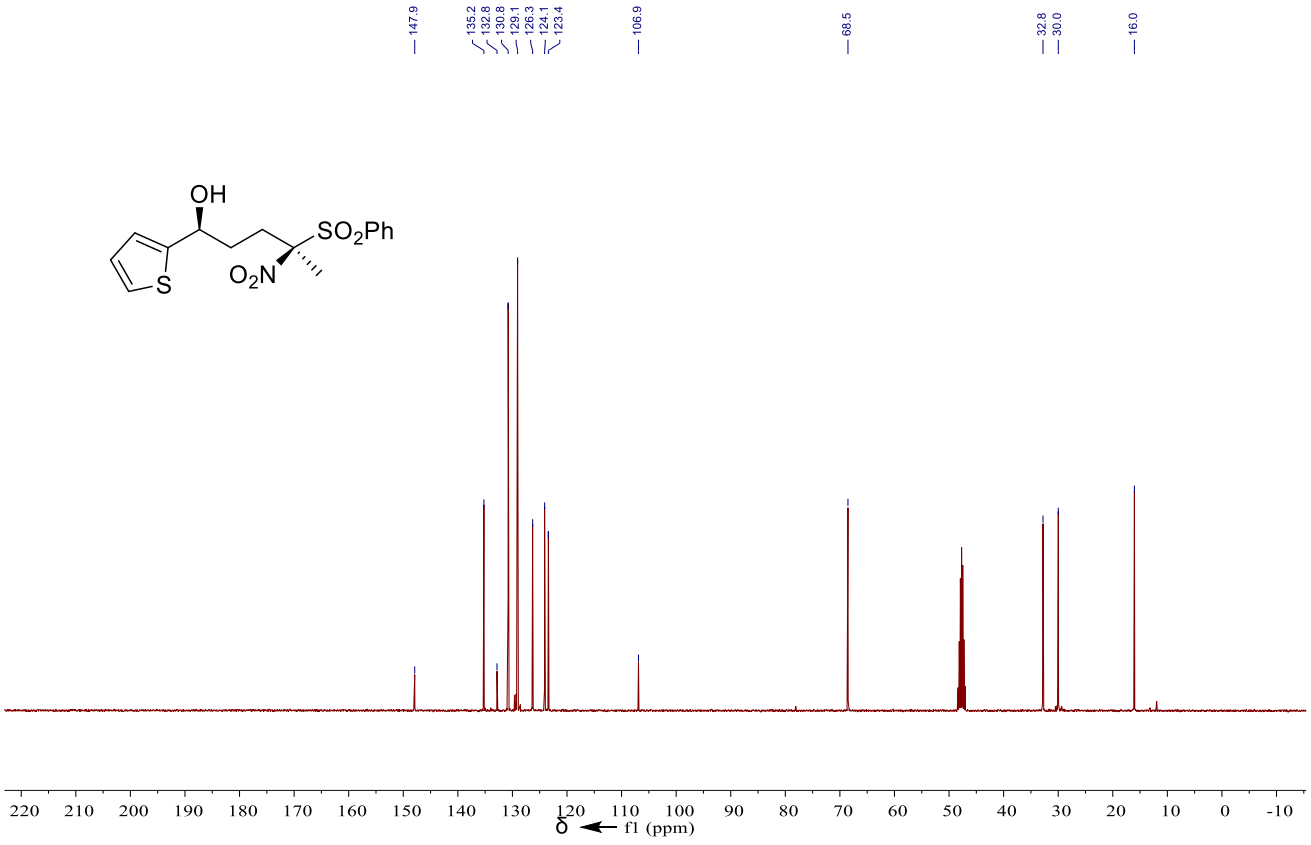
(*S*,*R*)-**5z:** (*1S*,*4S*)-1-(furan-2-yl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.



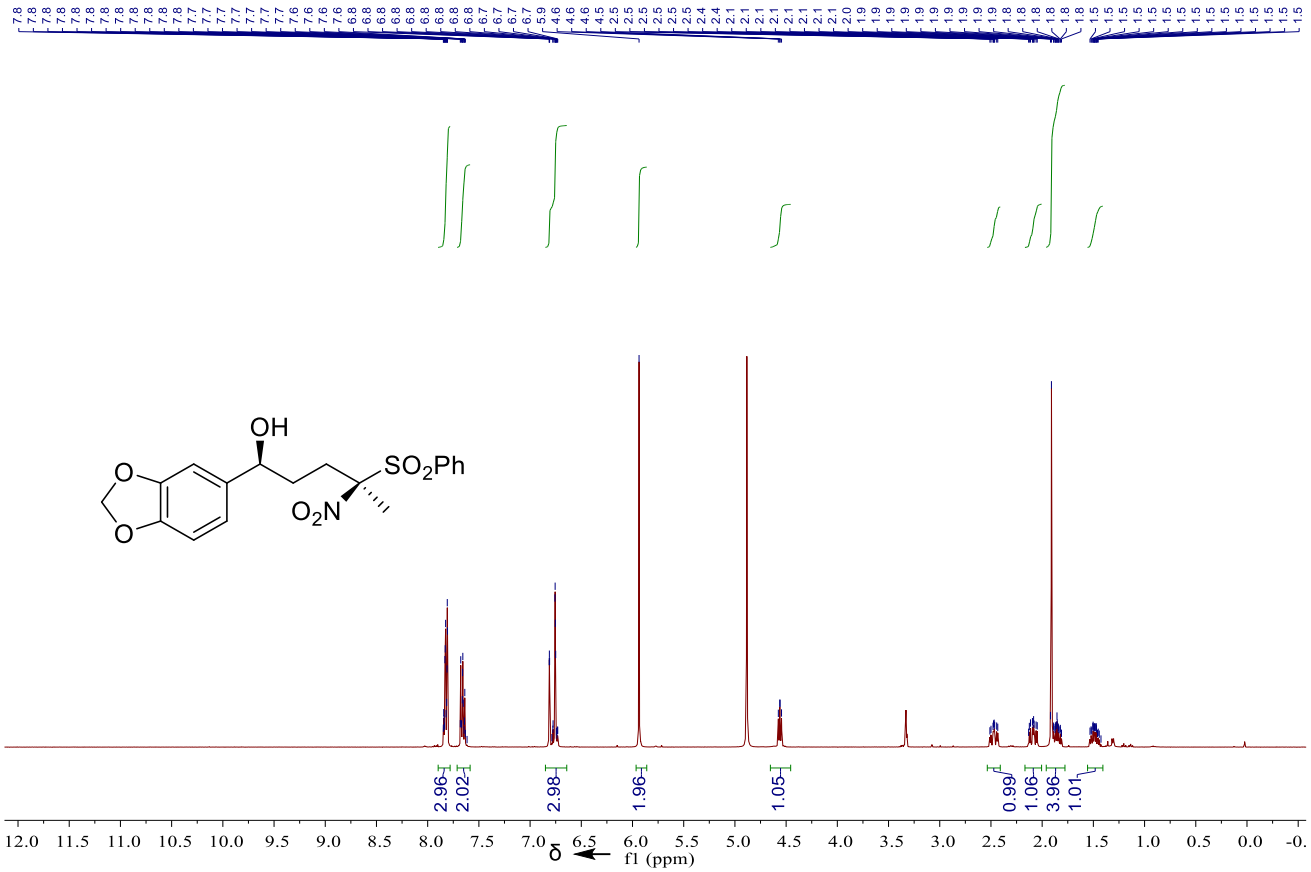


(*S,R*)-**5z':** (*1S,4R*)-4-nitro-4-(phenylsulfonyl)-1-(thiophen-2-yl)pentan-1-ol.





(*S,R*)-**5z'':** (*1S,4R*)-1-(4-(dimethylamino)phenyl)-4-nitro-4-(phenylsulfonyl)pentan-1-ol.



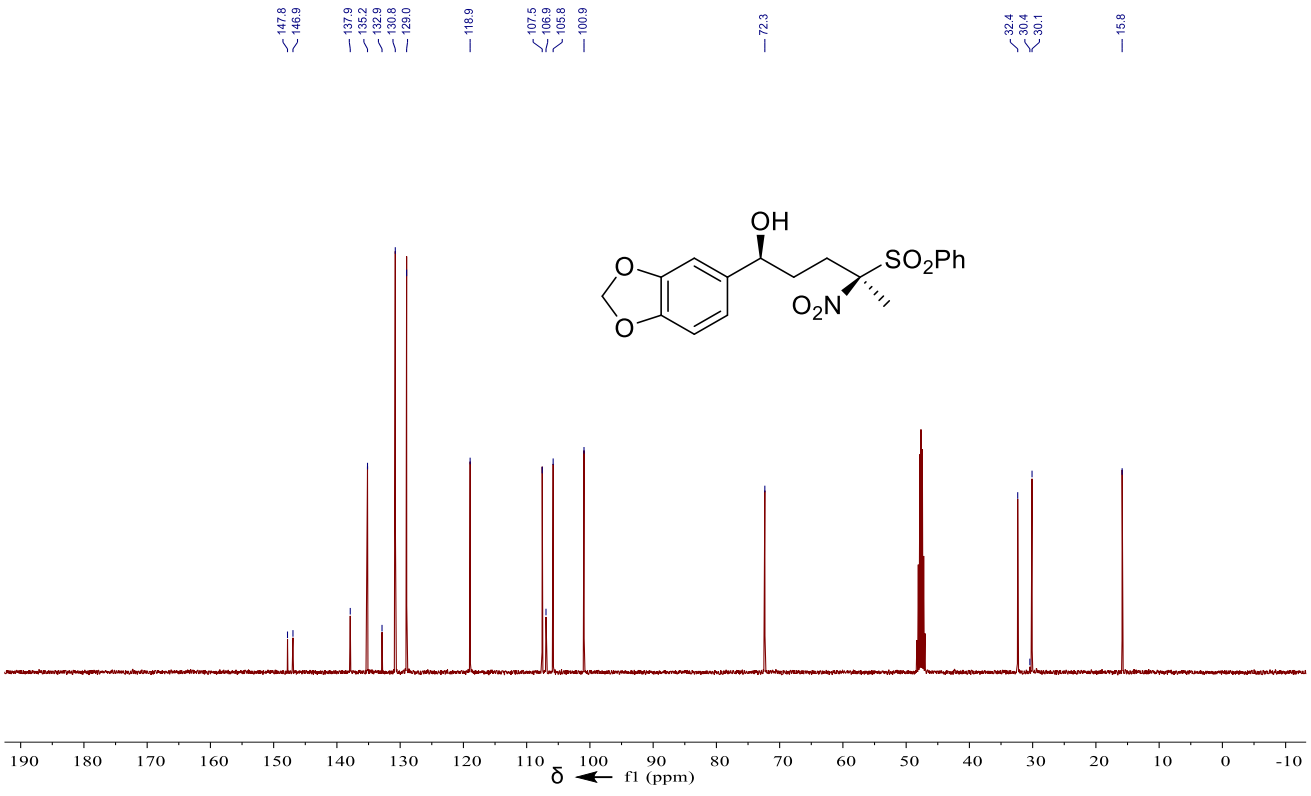
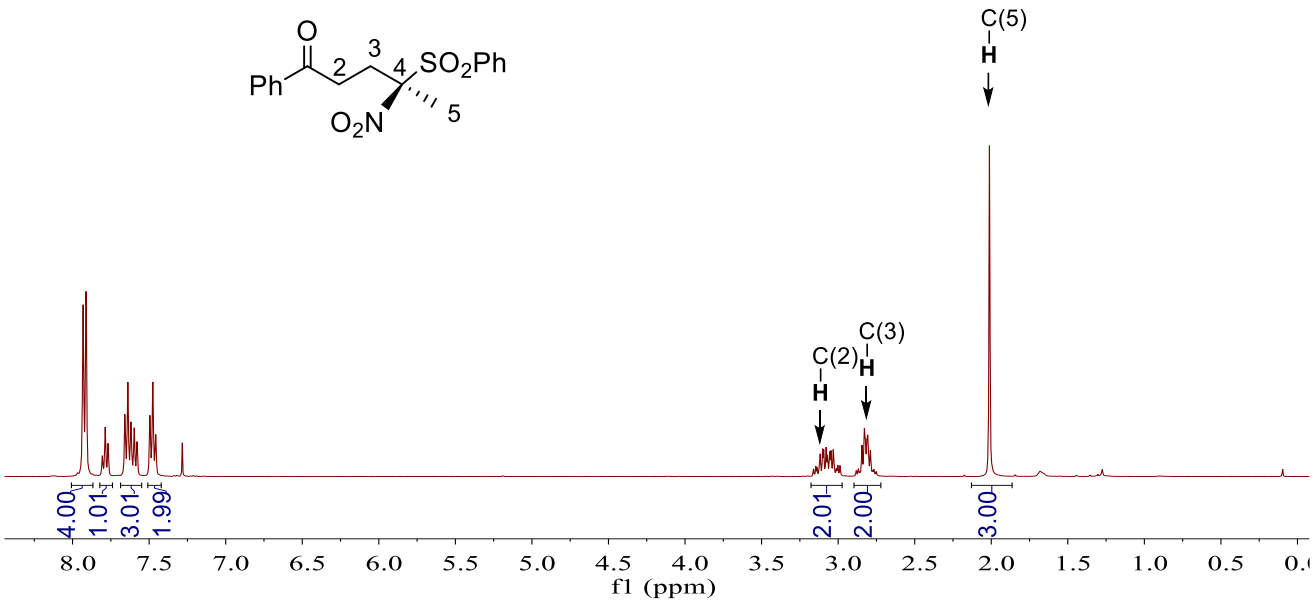


Table S3. Crystal data and structure refinement for (*S*,*R*)-**5o** (d8v23543)

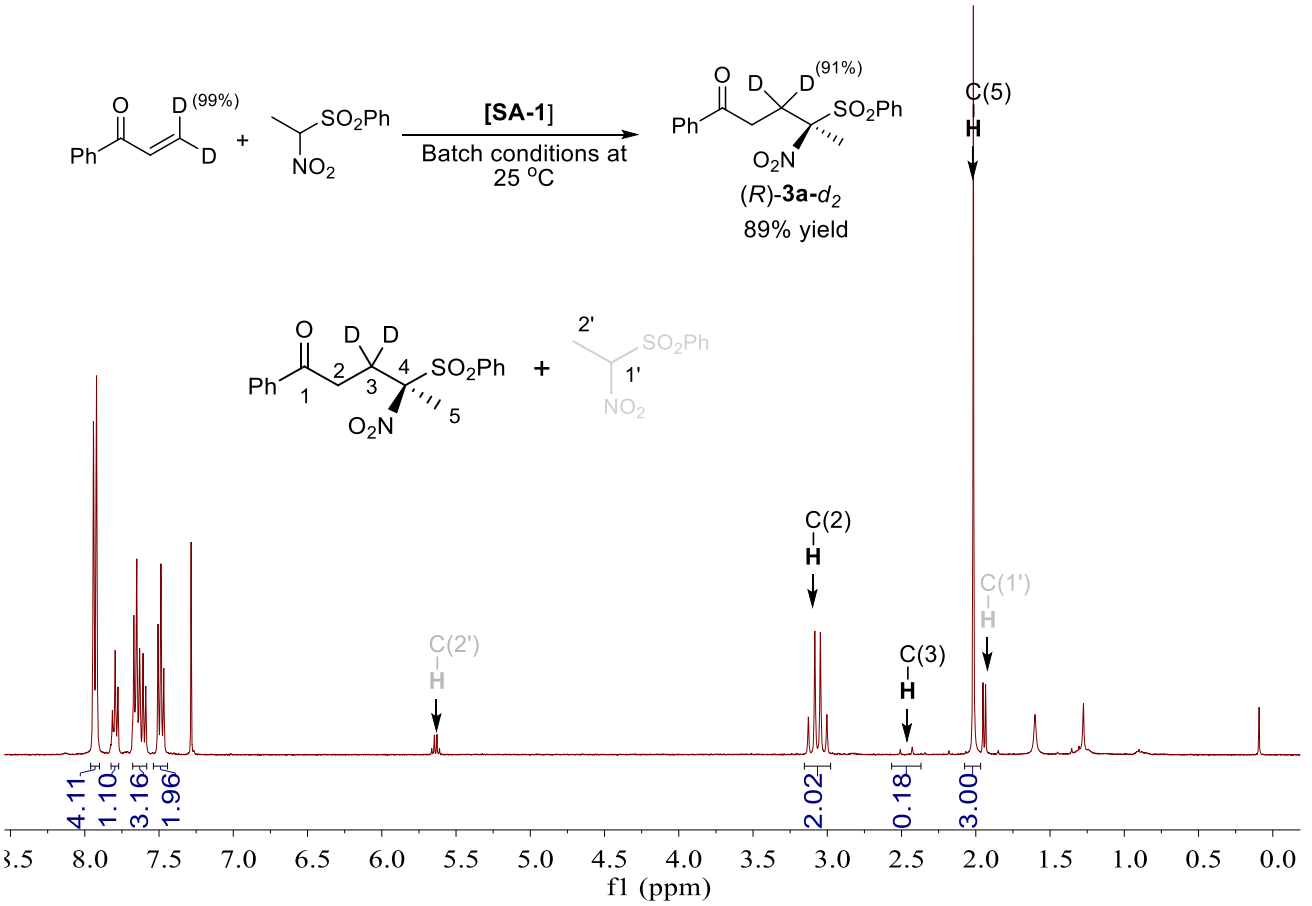
Identification code	d8v23543	
Empirical formula	C20 H25 N O5 S	
Formula weight	391.47	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.0512(3) Å	α= 90°.
	b = 10.9727(6) Å	β= 90°.
	c = 29.9353(15) Å	γ = 90°.
Volume	1987.64(18) $Å^3$	
Z	4	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	0.193 mm^{-1}	
F(000)	832	
Crystal size	0.190 x 0.150 x 0.070 mm^3	
Theta range for data collection	2.722 to 25.997°.	
Index ranges	-7<=h<=7, -13<=k<=12, -36<=l<=36	
Reflections collected	26178	
Independent reflections	3914 [R(int) = 0.1159]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.3567	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3914 / 0 / 248	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0463, wR2 = 0.0979	
R indices (all data)	R1 = 0.0565, wR2 = 0.1042	
Absolute structure parameter	0.12(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.248 and -0.330 $e.Å^{-3}$	

Figure S4. Contrastive ^{1}H-NMR spectra for the deuterium labeling experiments.

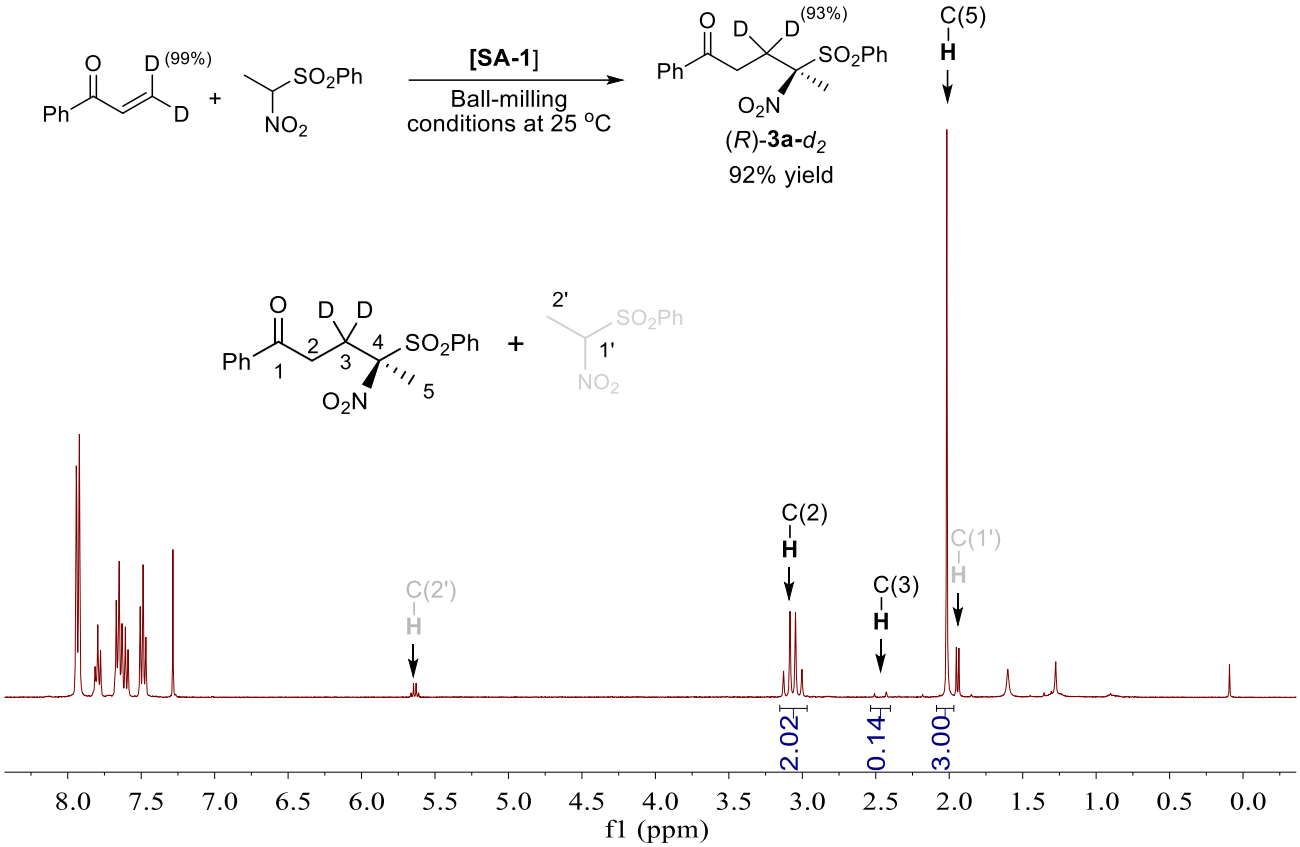
(a) The standard ^{1}H-NMR spectra of (*R*)-**3a.**



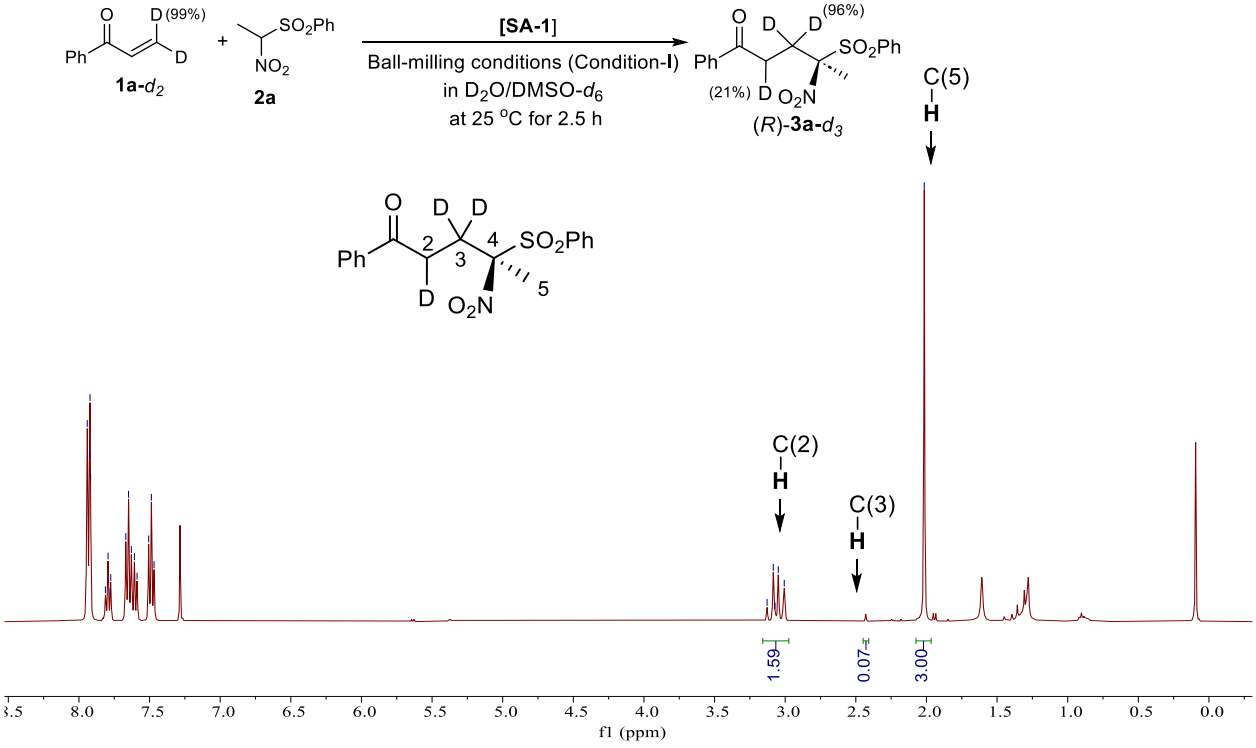
(b) The obtained ^{1}H-NMR spectra of (*R*)-**3a**-d_2 under the batch conditions.



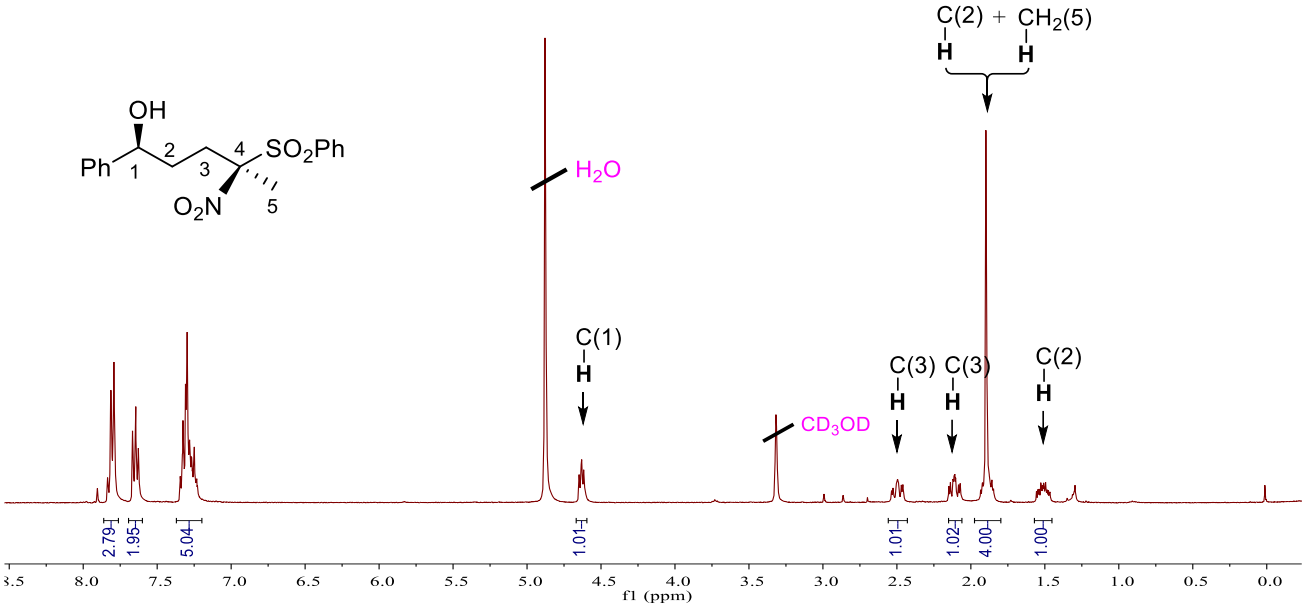
(c) The obtained ^{1}H-NMR spectra of (*R*)-**3a**-d_2 under the ball-milling conditions.



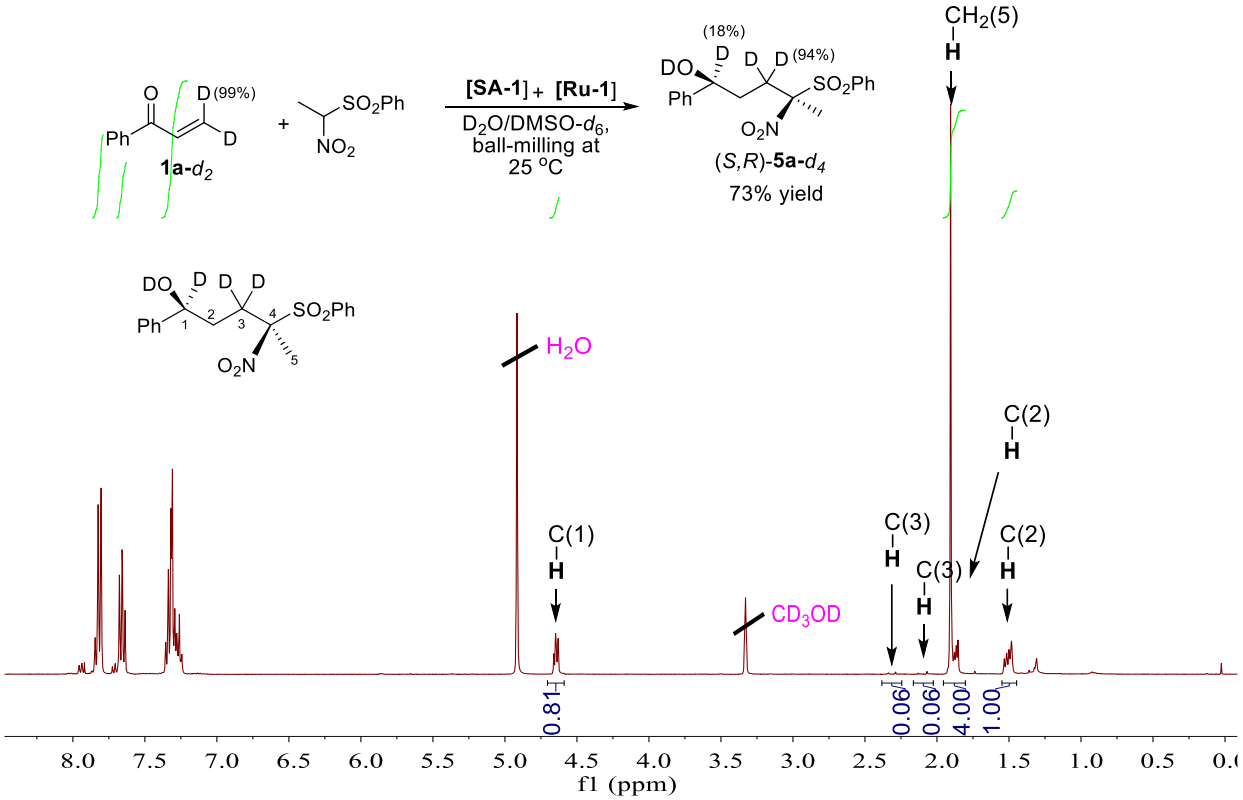
(d) The obtained ^{1}H-NMR spectra of (*R*)-**3a**-d_3 under the ball-milling conditions with D_2O/DMSO-d_6 co-solvents.



(e) The standard ^{1}H-NMR spectra of (*S*,*R*)-**5a.**



(f) The obtained ^{1}H-NMR spectra of (*S*,*R*)-**5a**-*d*$_4$ under the ball-milling conditions.



(g) The obtained ^{1}H-NMR spectra of (*S*,*R*)-**5a**-d_2 under the batch conditions.