

Supporting Information

Selective Long-Distance Isomerization of Terminal Alkenes via Nondissociative Chain Walking

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I. Optimization of the Reaction Conditions

Table S1 Screening of Complexes

$\text{1b} \xrightarrow[\text{CH}_2\text{ClCH}_2\text{Cl, rt, 3 h}]{\begin{matrix} 2.5 \text{ mol \% (L)PdMeCl } \mathbf{2} \\ 3 \text{ mol \% NaBARf}_4 \\ \text{MS 4A} \end{matrix}} \text{3b}$

entry	complex [L]	GC yield (%)	E/Z
1	2a [1,10-phenanthroline]	77	34/66
2	2b [3,4,7,8-tetramethylphenanthroline]	70	34/66
3	2c [2,2'-bipyridine]	63	35/65
4	2d [2,9-dimethylphenanthroline]	73	34/66

^aReaction conditions: **1b** (0.1 mmol), **2** (0.0025 mmol), NaBAR₄^f (0.003 mmol), CH₂ClCH₂Cl (5 mL), rt.

Table S2 Screening of the Reaction Conditions

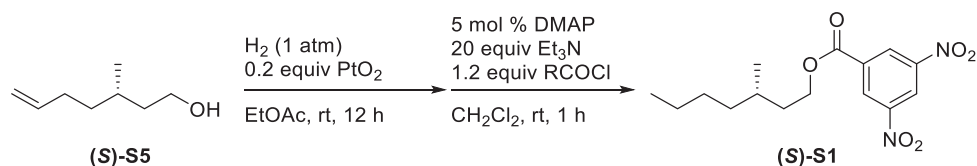
$\text{1b} \xrightarrow[\text{CH}_2\text{ClCH}_2\text{Cl, temp, 3 h}]{\begin{matrix} \text{cat. } \mathbf{2a} \\ \text{NaBARf}_4 \text{ 1.2 eq to Pd cat.} \\ \text{MS 4A} \end{matrix}} \text{3b}$

Entry	2a (mol %)	CH ₂ Cl ₂ (mL)	temp (°C)	GC yield (%)	E/Z
1	2.5	5	rt	77	34/66
2	1.0	5	rt	71	35/65
3	5.0	5	rt	65	33/67
4	2.5	3	rt	69	34/66
5	2.5	10	rt	66	35/65
6	2.5	5	40	55	36/64
7	2.5	5	0	80	27/73
8	2.5	5	-5	64	20/80
9	2.5	5	-20	20	32/68
10 ^b	2.5	5	-20	60	18/82

^aReaction conditions: **1b** (0.1 mmol). ^b24 h

II. Determination of Enantiomeric Excess of **1q** and **3q**

The enantiomeric excess for the substrate (*S*)-**1q** was determined by HPLC analysis of the derivative, dinitrobenzoate (*S*)-**S1**, which was derived in the following procedure from the esterification of the corresponding alcohol (*S*)-**S5** before the silylative protection.



To a Schlenk flask charged with (*S*)-**S5** (27.8 mg, 0.217 mmol) were added EtOAc (2 mL) and platinum oxide (9.1 mg, 0.040 mmol) to form a suspension. A balloon filled with hydrogen gas was attached to the flask, which was then briefly evacuated and backfilled with hydrogen gas three times. The mixture was stirred at room temperature for 12 h. The resulting mixture was filtered through a pad of Celite and concentrated.

The residue was dissolved in CH₂Cl₂ (15 mL), and DMAP (1.2 mg, 0.098 mmol), 3,5-dinitrobenzoyl chloride (60.6 mg, 0.260 mmol), and Et₃N (0.6 mL, 4.2 mmol) were added to the solution at room temperature. After stirring for 1 h, the mixture was diluted with dichloromethane and washed twice with brine. The combined organic portions were dried over MgSO₄, filtered, and concentrated. Silica gel column chromatography (hexane:EtOAc = 10:1) of the crude material afforded dinitrobenzoate **S1** (23.3 mg, 33% yield, 97% ee) as a colorless oil.

The enantiomeric excess was determined by chiral HPLC analysis (Daicel Chiralpak AY-H column, column temperature: 25 °C, eluent; *n*-hexane:EtOH = 98:2, flow rate: 1.0 mL/min, λ = 254 nm; t_R = 15.1 and 16.3 min).

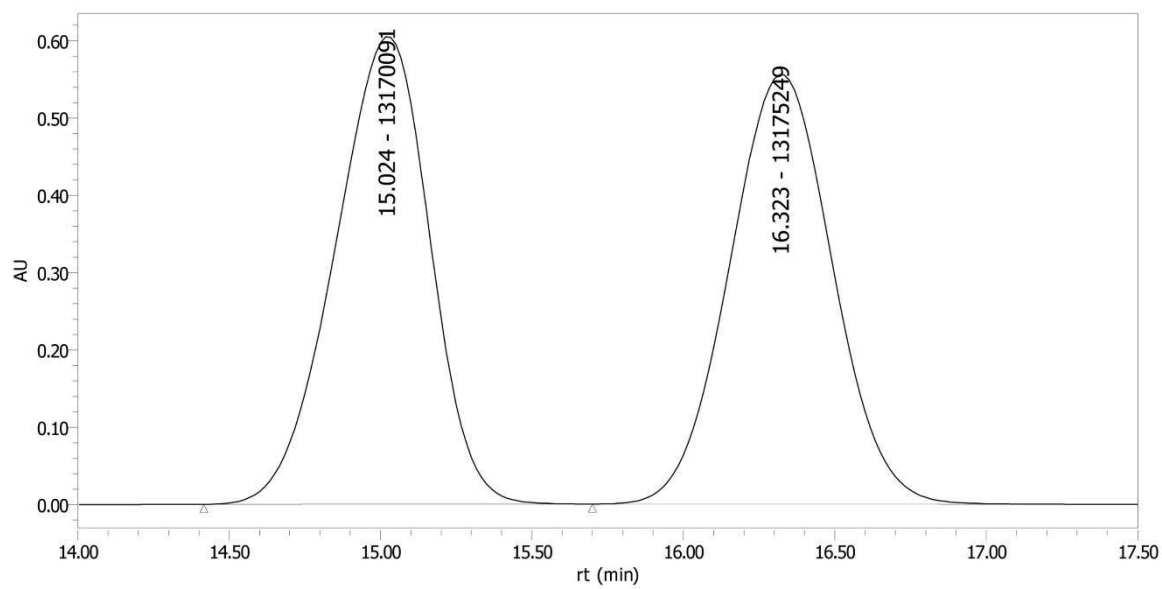
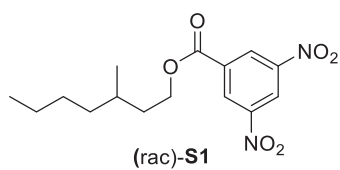


Figure S1. HPLC Analysis of (rac)-**S1**

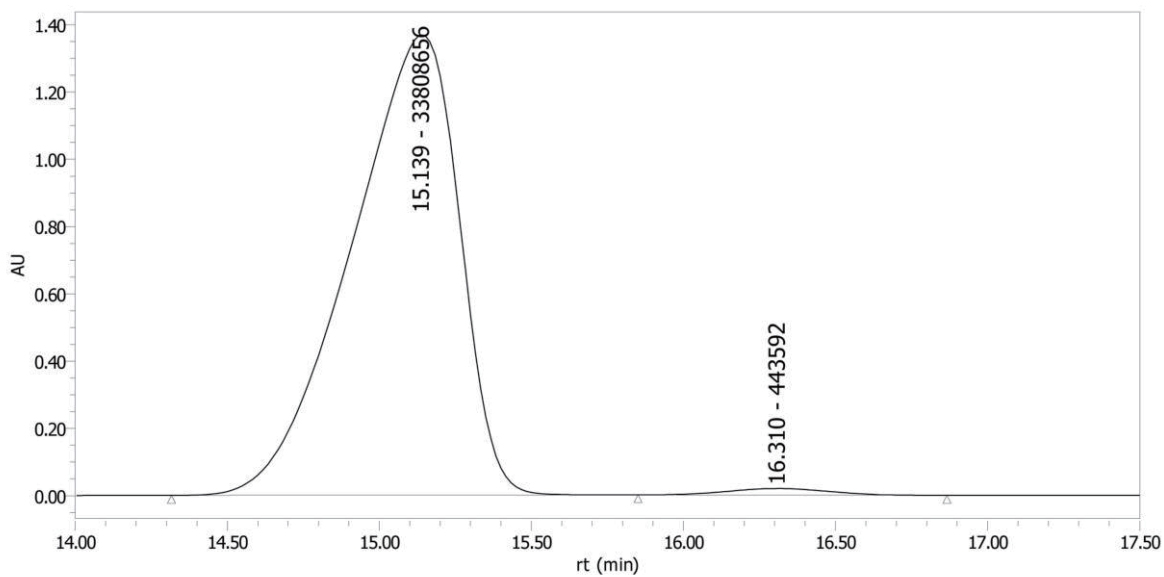
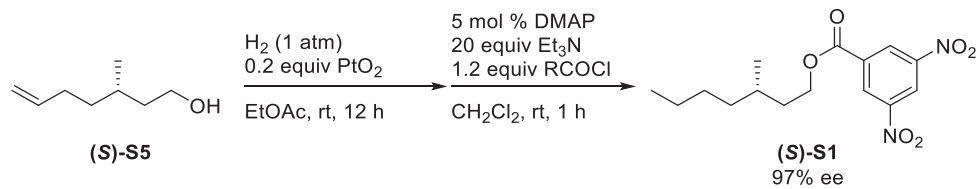
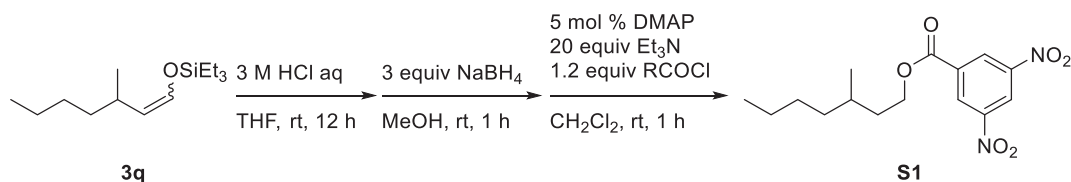


Figure S2. HPLC Analysis of (S)-S1 derived from (S)-S5

The enantiomeric excess for **3q** was determined by HPLC analysis of the corresponding esterification product **S1**, which was obtained through the following procedure.



To a solution of **3q** (16.2 mg, 0.067 mmol) in THF (3 mL) was added 3 M hydrochloric acid (2 mL). After stirring for 12 h at room temperature, a saturated aqueous solution of NaHCO₃ was added to the mixture, which was then extracted three times with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, and filtered. Volatile materials were removed carefully by distillation at 60 °C under ambient pressure. The residue was dissolved in MeOH (5 mL), and NaBH₄ (7.6 mg, 0.201 mmol) was added to the solution at 0 °C. The reaction mixture was stirred at room temperature for 3 h. Water and diethyl ether were added to the mixture and the organic layer was collected. The aqueous layer was extracted three times with diethyl ether. The combined organic portions were dried over MgSO₄, filtered, and concentrated. The residue was dissolved in CH₂Cl₂ (5 mL), and DMAP (0.4 mg, 0.003 mmol), 3,5-dinitrobenzoyl chloride (18.4 mg, 0.080 mmol), and Et₃N (0.2 mL, 1.3 mmol) were added to the solution at room temperature. After stirring for 1 h, the mixture was diluted with dichloromethane and washed twice with brine. The combined organic portions were dried over MgSO₄, filtered, and concentrated. Silica gel column chromatography (hexane:EtOAc = 10:1) of the crude material afforded dinitrobenzoate **S1** (6.0 mg, 0.018 mmol, 28% yield) as a colorless oil: IR (neat): 3105 w, 2960 m, 2930 m, 2872 w, 2858 w, 1740 s, 1735 m, 1731 m, 1628 w, 1550 s, 1545 s, 1544 s, 1542 s, 1541 s, 1462 w, 1344 s, 1282 s, 1170 m, 1076 w, 921 w, 730 m, 721 m cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.91 (t, *J* = 7.2 Hz, 3H), 0.98 (d, *J* = 6.0 Hz, 3H), 1.20-1.42 (m, 6H), 1.59-1.69 (m, 2H), 1.83-1.91 (m, 1H), 4.45-4.54 (m, 2H), 9.16 (d, *J* = 2.4 Hz, 2H), 9.24 (t, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 19.6, 22.9, 29.1, 29.9, 35.4, 36.5, 65.7, 122.3, 129.4, 134.1, 148.6, 162.5; HRMS (DART-TOF) *m/z*: [M+H]⁺ Calcd for C₁₅H₂₁N₂O₆ 325.1400; Found 325.1394.

The enantiomeric excess was determined by chiral HPLC analysis (Daicel Chiralpak AY-H column, column temperature: 25 °C, eluent: *n*-hexane:EtOH = 98:2, flow rate: 1.0 mL/min, λ = 254 nm; *t*_R = 15.0 and 16.3 min).

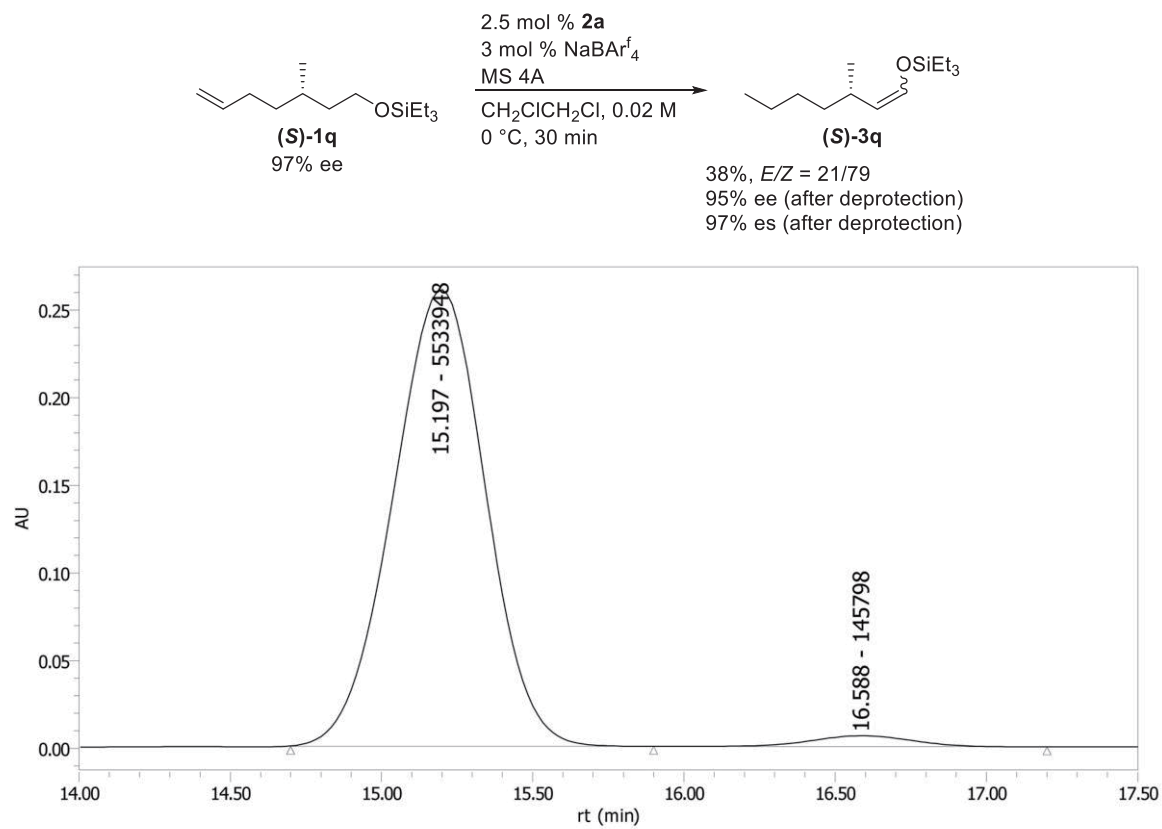


Figure S3. HPLC Analysis of (S)-3q (reaction conditions: standard)

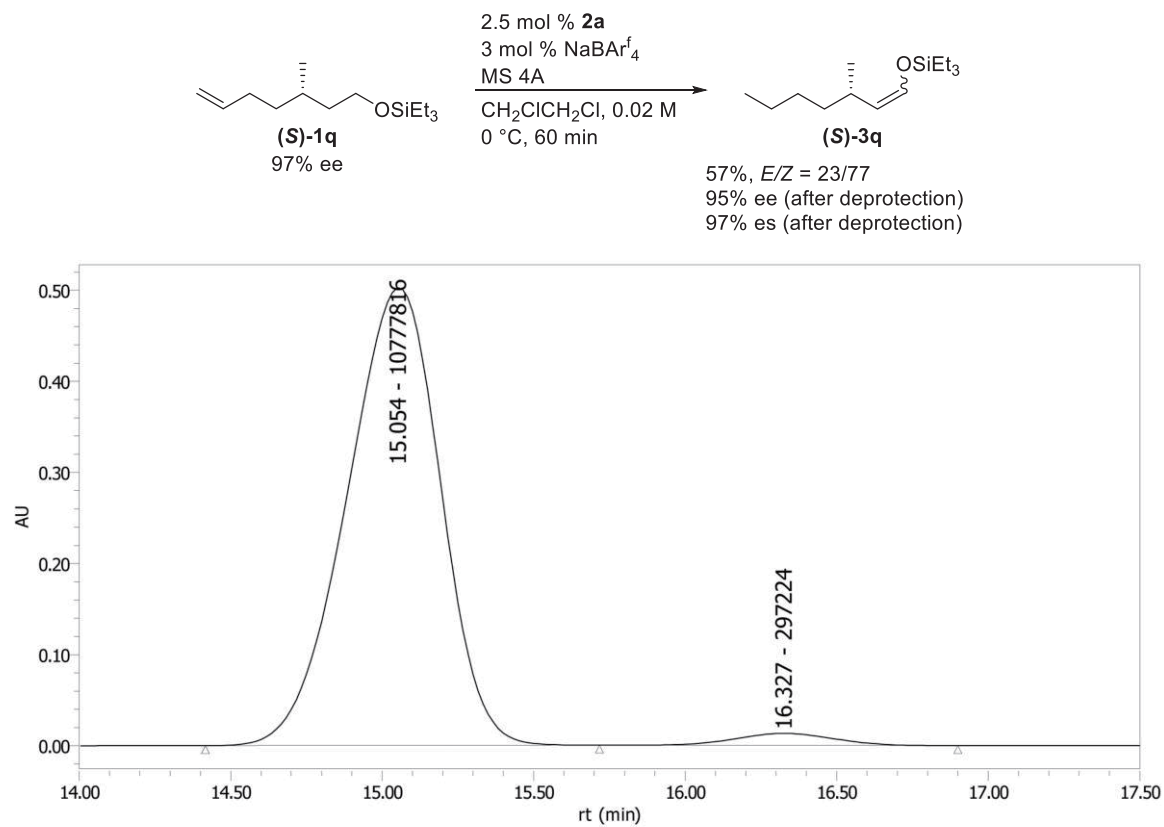


Figure S4. HPLC Analysis of **(S)-3q** (reaction conditions: standard except that the reaction time was 60 min)

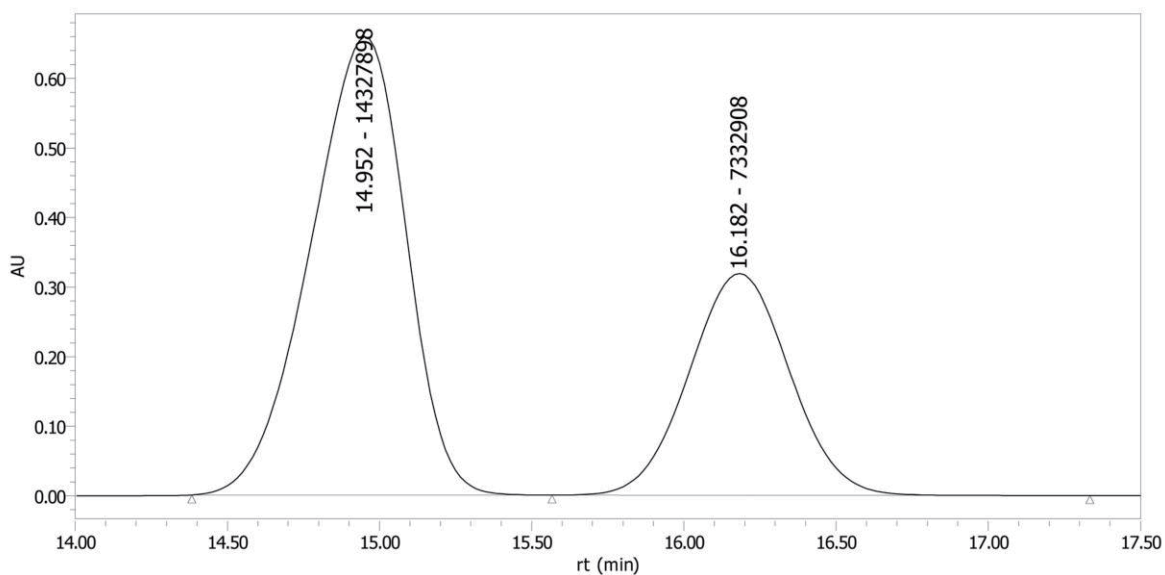
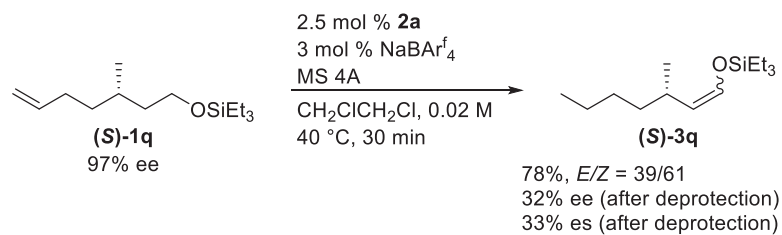


Figure S5. HPLC Analysis of (S)-3q (reaction conditions: standard except that the reaction temperature was 40 °C)

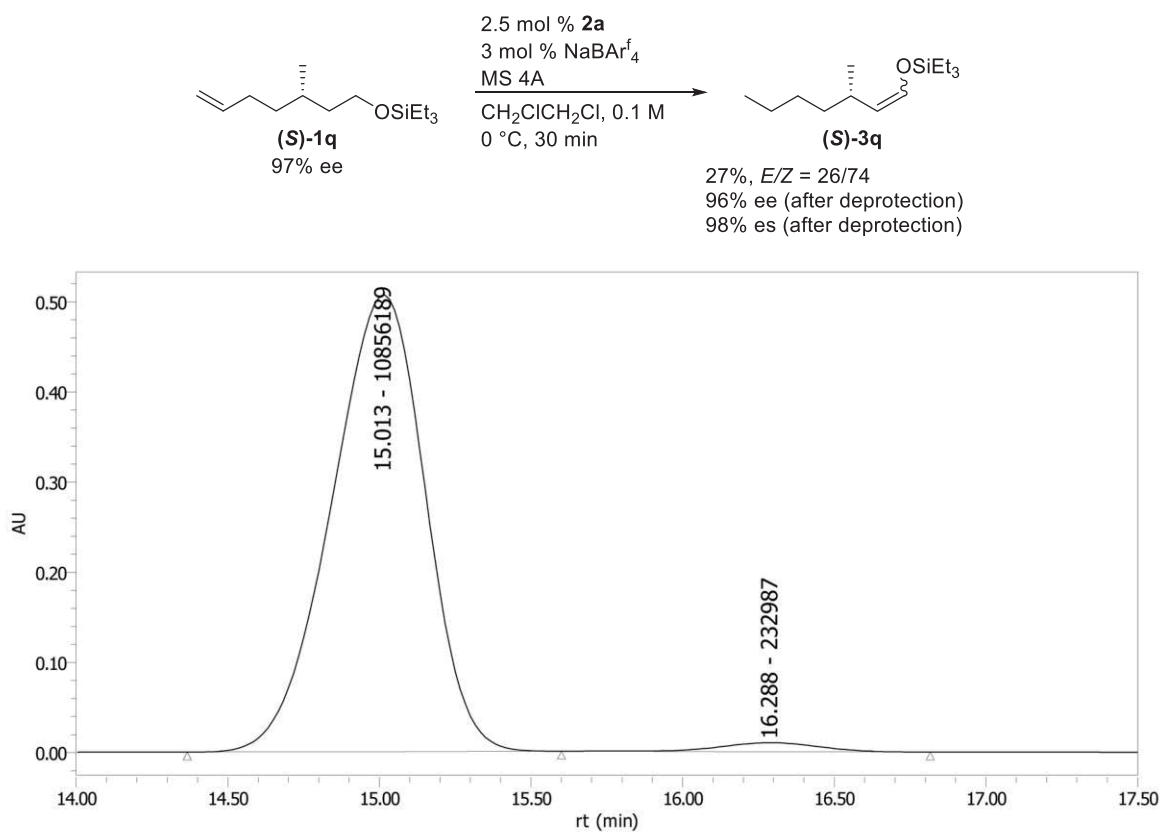


Figure S6. HPLC Analysis of (*S*)-**3q** (reaction conditions: standard except that the concentration was 0.1 M)

