Supporting Information

Synthesis of (Arylalkenyl)silanes by Palladium-Catalyzed Regiospecific and Stereoselective Allyl Transfer from Silyl-Substituted Homoallyl Alcohols to Aryl Halides

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Contents

Instrumentation and Chemicals S1

Experimental Procedure S2

Characterization Data S11

Instrumentation

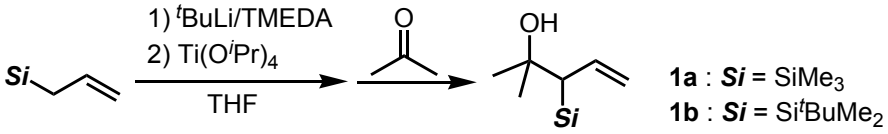
^{1}H NMR (300 MHz and 500 MHz) and ^{13}C NMR (75.3 MHz and 125.7 MHz) spectra were taken on Varian Mercury 300 and UNITY INOVA 500 spectrometers and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.23 ppm for ^{13}C unless otherwise noted. ^{19}F NMR spectra were obtained in $CDCl_3$ with fluorotrichloromethane as an external standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra (EI unless otherwise noted) were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 3.80 mL/min, RI detector). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Chemicals

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene were purchased from Wako Pure Chemical Co. and stored over slices of sodium. Tri(*p*-tolyl)phosphine, triphenylphosphine, cesium carbonate, and potassium carbonate were purchased from Wako Pure Chemical Co. Palladium acetate and tricyclohexylphosphine were obtained from TCI. The preparations of the homoallyl alcohols are described in the following section. All reactions were carried out under argon atmosphere.

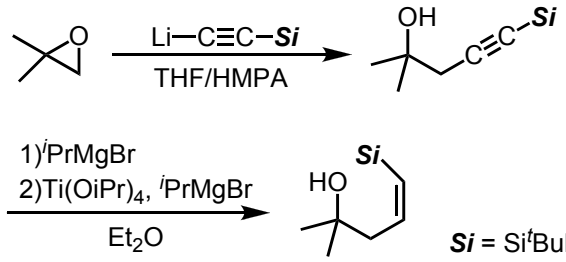
Experimental Procedure

Preparation of 1a and 1b



Under argon atmosphere, allyl(*tert*-butyl)dimethylsilane (1.80 g, 11.5 mmol), *N,N,N',N'*-tetramethylethylenediamine (1.58 mL, 10.5 mmol), and THF (30 mL) were placed in a 100-mL reaction flask. At –78 ˚C, *tert*-butyllithium (1.59 M pentane solution, 6.60 mL, 10.5 mmol) was added dropwise via a syringe to the solution. The mixture was stirred for 2 h at –30 ˚C. The reaction mixture was again cooled to –78 ˚C before titanium tetraisopropoxide (3.39 mL, 11.5 mmol) was added. After stirring for 1 h at the same temperature, acetone (0.71 mL, 9.6 mmol) was added. The resulting mixture was stirred for 3 h. The mixture was poured into 1 M hydrochloric acid (40 mL) at 0 ˚C and stirred for 10 min. Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 20:1) provided **1b** (1.14 g, 5.34 mmol, 56%). A similar procedure gave **1a**, starting from allyltrimethylsilane (45%).

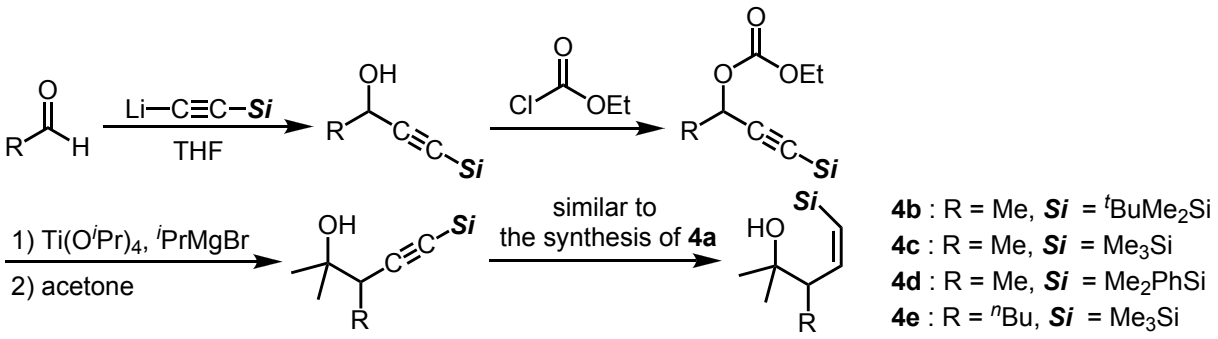
Preparation of 4a



A 100-mL reaction flask was filled with argon. THF (10 mL), *tert*-butyldimethylsilylacetylene (2.65 mL, 14.2 mmol), and *n*-butyllithium (1.60 M hexane solution, 9.37 mL, 14.9 mmol) were added at 0 ˚C. The resulting mixture was stirred for 30 min. Hexamethylphosphoramide (2.49 mL, 14.9 mmol) and isobutylene oxide (1.38 mL, 15.6 mmol) were added at 0 ˚C. The mixture was allowed to warm to room temperature and stirred for 20 h at ambient temperature. The reaction was quenched with saturated ammonium chloride solution (20 mL). Extraction, evaporation, and purification furnished 5-(*tert*-butyldimethylsilyl)-2-methyl-4-pentyn-2-ol (2.77 g, 13.0 mmol, 92%) as a white solid.

The reduction of the alkynol to yield **4a** was performed according to the literature.[1] Under an atmosphere of argon, diethyl ether (13 mL), 5-(*tert*-butyldimethylsilyl)-2-methyl-4-pentyn-2-ol (2.77 g, 13.0 mmol), and isopropylmagnesium bromide (1.00 M ethereal solution, 13.5 mL, 13.5 mmol) were sequentially added at 0 ˚C. After being stirred for 10 min at 0 ˚C, the mixture was cooled to –78 ˚C. Titanium tetraisopropoxide (7.69 mL, 26.0 mmol) and isopropylmagnesium bromide (52.0 mL, 52.0 mmol) were added. The resulting black solution was allowed to warm to –50 ˚C and stirred for 3 h at the same temperature. The mixture was carefully poured into ice-cold 1 M hydrochloric acid (100 mL). The resulting mixture was stirred for 30 min at ambient temperature. Extractive workup and silica gel column purification afforded 2.47 g of **4a** (11.5 mmol, 88%) as a colorless oil.

Preparation of 4b-4e



Preparation of **4c** is representative. Under argon atmosphere, *n*-butyllithium (1.60 M hexane solution, 22.0 mL, 36.0 mmol) was added dropwise to a solution of trimethylsilylacetylene (4.24 mL, 30.0 mmol) in THF (30 mL) at –78 ˚C. After stirring for 15 min at this temperature, acetaldehyde (3.35 mL, 60.0 mmol) was added. The reaction mixture was stirred at the same temperature for 2 h before quenching with saturated ammonium chloride solution (40 mL). Extraction and silica gel column purification provided 4-trimethylsilyl-3-butyn-2-ol (4.11 g, 28.9 mmol).

4-Dimethylaminopyridine (ca. 0.1 g) was placed in a 100-mL reaction flask under argon. A solution of 4-trimethylsilyl-3-butyn-2-ol (4.11 g, 28.9 mmol) in dichloromethane (30 mL), pyridine (3.51 mL, 43.4 mmol), and ethyl chloroformate (3.32 mL, 34.7 mmol) were sequentially added at 0 ˚C. The reaction mixture was allowed to warm to room temperature and was stirred

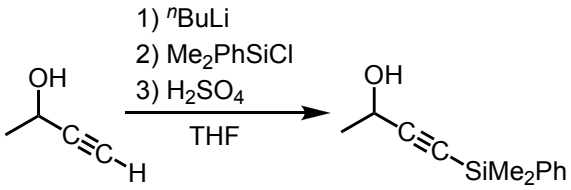
[1] Sato, F.; Urabe, H.; Okamoto, S. *Chem. Rev.* **2000**, *100*, 2789–2834.

for 1 h. The mixture was poured into saturated sodium hydrogencarbonate solution, and the product was extracted with ethyl acetate three times. The combined organic layer was dried and concentrated in vacuo. Silica gel column purification provided the carbonate (5.53 g, 25.8 mmol, 89 % in 2 steps) as a colorless oil.

Diethyl ether (50 mL) and the carbonate (4.5 g, 21 mmol) were placed in a 100-mL reaction flask under argon. The flask was cooled to –50 ˚C, and then titanium tetraisopropoxide (6.20 mL, 21.0 mmol) and isopropylmagnesium bromide (1.00 M ether solution, 40.0 mL, 40.0 mmol) were added and the whole mixture was stirred for 1 h at this temperature. After the obtained black solution was cooled to –78 ˚C, acetone (1.10 mL, 15.0 mmol) was added. The reaction mixture was warmed to –20 ˚C and stirring for 3 h at this temperature.[2] The mixture was carefully poured into ice-cold 1 M hydrochloric acid (100 mL). Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 10:1) afforded 2,3-dimethyl-5-trimethylsilyl-4-pentyn-2-ol (1.38 g, 7.49 mmol, 50%) and the starting carbonate (5.54 mmol).

The reduction of 2,3-dimethyl-5-trimethylsilyl-4-pentyn-2-ol to yield **4c** was accomplished by a similar procedure for the preparaton of **4a**. Note that 1.5 equivalent of titanium tetraisopropoxide and 3.0 equivalent of isopropylmagnesium bromide were used for the reduction of 2,3-dimethyl-5-trimethylsilyl-4-pentyn-2-ol. Alcohol **4c** was obtained in 82 % yield as colorless oil.

Preparation of **4d** is different from that of **4c** in the first step.

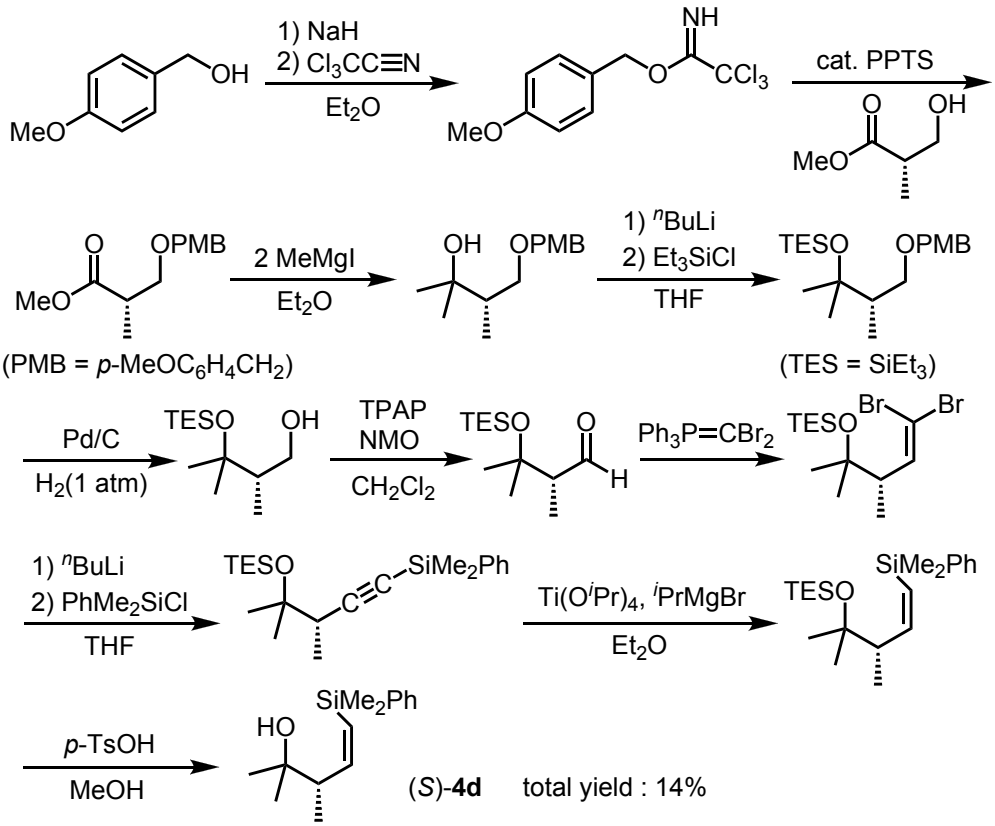


A 300-mL three-necked reaction flask equipped with a Dimroth condenser was cooled to 0 ˚C under argon atmosphere. *n*-Butyllithium (1.60 M hexane solution, 46.9 mL, 75.0 mmol) was added dropwise to the solution of 3-butyn-2-ol (2.35 mL, 30.0 mmol) in THF (60 mL) via a syringe at 0 ˚C. After stirring for 30 min at this temperature, chlorodimethylphenylsilane (12.5 mL, 75.0 mmol) was added at 0 ˚C. The reaction mixture was refluxed for 2 h. After cooling

[2] Nakagawa, T.; Kasatkin, A.; Sato, F. *Tetrahedron Lett*. **1995**, *36*, 3207–3210.

to 0 ˚C, 1.4 M sulfuric acid (33 mL, 150 mmol) was added dropwise below 45 ˚C and stirred for another 5 min. Extraction, evaporation, purification by silica gel column provided a mixture of 4-dimethylphenylsilyl-3-butyn-2-ol (21.7 mmol, 72%) and tetramethyldiphenyldisiloxane. The disiloxane was separated in the next step by silica gel column purification.

Preparation of (*S*)-4d



Preparations of 4-methoxybenzyl trichloroacetimidate and methyl (*S*)-3-[(4-methoxybenzyl)oxy]-2-methylpropanoate were performed according to the literature.[3] Sodium hydride (60 % suspension in oil, 0.56 g, 14 mmol) was placed in a 100-mL reaction flask under argon. The hydride was washed with hexane (9 mL × 3). Diethyl ether (25 mL) and 4-methoxybenzyl alcohol were slowly added at 0 ˚C. The reaction mixture was allowed to warm to room temperature, stirred for 30 min, and then cooled to 0 ˚C. Trichloroacetonitrile (5.61 mL, 56.0 mmol) was added dropwise via a syringe and the resulting mixture was allowed to warm gradually to room temperature by removing the ice bath. After stirring for 2 h, the

[3] Fürstner, A.; Kattnig, E.; Lepage, O. *J. Am. Chem. Soc*. **2006**, *128*, 9194–9204.

reaction was quenched with saturated sodium hydrogencarbonate solution. The mixture was extracted with ether three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo to afford crude 4-methoxybenzyl trichloroacetimidate.

Under argon atmosphere, pyridinium *p*-toluenesulfonate (1.01 g, 4.0 mmol) was added to a solution of methyl (*S*)-3-hydroxy-2-methylpropionate (4.73 mL, 40.0 mmol) and 4-methoxybenzyltrichloroacetimidate (ca. 56 mmol) in dichloromethane (80 mL) at room temperature. After stirring for 17 h, saturated sodium hydrogencarbonate solution (50 mL) was added. The product was extracted with hexane/ethyl acetate = 10:1 three times, and the organic layer was washed with water and brine. Evaporation followed by silica gel column purification (hexane/ethyl acetate = 10:1) provided methyl (*S*)-3-[(4-methoxybenzyl)oxy]-2-methylpropanoate (8.80 g, 36.9 mmol, 92%).

A 300-mL reaction flask was filled with argon. Methylmagnesium iodide (1.00 M ether solution, 88.6 mL, 88.6 mmol) was placed in the flask at 0 ˚C and a solution of methyl (*S*)-3-[(4-methoxybenzyl)oxy]-2-methylpropanoate (8.80 g, 36.9 mmol) in diethyl ether (30 mL) was added dropwise through a syringe. The resulting mixture was stirred for 2 h at room temperature, before quenching with saturated ammonium chloride solution (100 mL). Extractive workup followed by silica gel column purification furnished (*S*)-4-[(4-methoxybenzyl)oxy]-2,3-dimethyl-2-butanol (6.35 g, 26.6 mmol, 72%) as a colorless oil.

A solution of (*S*)-4-[(4-methoxybenzyl)oxy]-2,3-dimethyl-2-butanol (6.35 g, 26.6 mmol) in THF (27 mL) was placed in a 100-mL flask under argon. The flask was cooled to 0 ˚C, and then *n*-butyllithium (1.60 M hexane solution, 16.9 mL, 27.0 mmol) was added dropwise via a syringe. After stirring for 15 min at 0 ˚C, chlorotriethylsilane (5.36 mL, 31.9 mmol) was added at ambient temperature. The reaction mixture was heated at 50 ˚C for 12 h. After the reaction mixture was cooled to room temperature, water was added. Extraction, evaporation and silica gel column purification provided silyl-protected alcohol (8.13 g, 23.1 mmol, 87%) as a colorless oil.

Pd/C (10% Pd, 1.05 g) was placed in a 100-mL reaction flask. A solution of silyl-protected alcohol (8.13 g, 23.1 mmol) in ethanol (92 mL) was added under argon atmosphere. The flask was then flushed with hydrogen. After stirring for 12 h at atmospheric pressure of H_2, starting material was detected by TLC. The hydrogen balloon was then replaced by a new one and the reaction mixture was heated at 40 ˚C for 2 h. The reaction mixture was filtrated and the filtrate

was concentrated. Silica gel column purification afforded (*S*)-3-triethylsiloxy-2,3-dimethyl-1-butanol (3.67 g, 15.8 mmol, 68 %) as a colorless oil.

Molecular sieves 4A (powdered, 15.8 g) was placed in a reaction flask. Under argon atmosphere, a solution of (*S*)-3-triethylsiloxy-2,3-dimethyl-1-butanol (3.67 g, 15.8 mmol) in dichloromethane (100 mL), *N*-methylmorpholine *N*-oxide (5.55 g, 47.3 mmol), and tetra-*n*-propylammonium perruthenate (0.39 g, 1.1 mmol) were sequentially added. After stirring for 1 h, the mixture was concentrated in vacuo, which was followed by filtration through a pad of neutral silica gel with the aid of hexane/ethyl acetate = 5:1. (*S*)-3-Triethylsiloxy-2,3-dimethylbutanal was obtained as an oil.

Tetrabromomethane (7.46 mmol, 22.5 mmol) was placed in a 300-mL flask under argon. Dichloromethane (80 mL) and triphenylphosphine (11.8 g, 45.0 mmol) were added at 0 ˚C. The reaction mixture was turned to red brown solution. After stirring for 1 h, the mixture was cooled to –78 ˚C, a solution of crude (*S*)-3-triethylsiloxy-2,3-dimethylbutanal in dichloromethane (20 mL) was added and the resulting mixture was stirred for 1 h at ambient temperature. The mixture was concentrated in vacuo. Hexane (100 mL) was added to precipitate phosphine oxide. Filtration, evaporation, purification by neutral silica gel column (hexane) provided (*S*)-(4,4-dibromo-1,1,2-trimethyl-3-butenyloxy)triethylsilane (3.00 g, 7.8 mmol, 49 % in two steps) as a colorless oil.

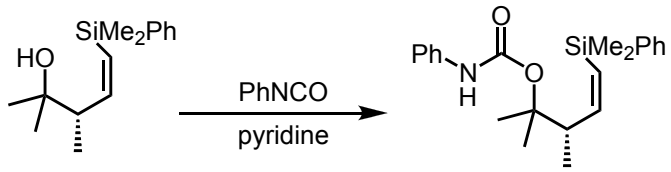
THF (25 mL) and (*S*)-(4,4-dibromo-1,1,2-trimethyl-3-butenyloxy)triethylsilane (3.00 g, 7.8 mmol) were placed in a 100-mL flask under argon. The solution was cooled to –78 ˚C, then *n*-butyllithium (1.60 M hexane solution, 12.1 mL, 19.4 mmol) was added dropwise via a syringe. The mixture was allowed to warm to –20 ˚C and stirred at ambient temperature. After 1 h, the mixture was recooled to –78 ˚C, chlorodimethylphenylsilane (3.9 mL, 23.3 mmol) was added to the mixture and the resulting mixture was stirred for 2.5 h at –20 ˚C. The reaction was quenched with saturated ammonium chloride solution. Extractive workup followed by column purification on neutral silica gel afforded (*S*)-(4-dimethylphenylsilyl-1,2,2-trimethyl-3-butynyloxy)triethylsilane (3.72 g, 7.4 mmol, 94 %) as a colorless oil.

Under argon atmosphere, diethyl ether (10 mL), (*S*)-(4-dimethylphenylsilyl-1,2,2-trimethyl-3-butynyloxy)triethylsilane (3.72 g, 7.4 mmol,), titanium tetraisopropoxide (3.29 mL, 11.1 mmol), and isopropylmagnesium bromide (1.0 M ether solution, 22.3 mL, 22.3 mmol) were added to a 100-mL flask at –78 ˚C. The resulting black

solution was stirred for 2 h at –50 ˚C, then warmed to –40 ˚C, and stirred for another 1 h. The reaction was quenched with ice-cold 1 M hydrochloric acid (40 mL). Extraction, evaporation, and purification by neutral silica gel column (hexane) provided (*Z*)-(*S*)-(4-dimethylphenylsilyl-1,2,2-trimethyl-3-butenyloxy)triethylsilane (2.26 g, 5.8 mmol, 78 %) as a colorless oil.

(*Z*)-(*S*)-(4-Dimethylphenylsilyl-1,2,2-trimethyl-3-butenyloxy)triethylsilane (2.26 g, 5.8 mmol) was placed in a 100-mL flask. Methanol (60 mL), THF (12 mL), and *p*-toluenesulfonic acid monohydrate (0.06 g, 0.3 mmol) were added and the resulting mixture was stirred for 2 h at room temperature. The mixture was then concentrated in vacuo and purified on neutral silica gel column. **(*S*)-4d** was obtained (1.35 g, 5.5 mmol, 95 %) as a colorless oil. Total yield was 14 % starting from methyl (*S*)-3-hydroxy-2-methylpropanoate.

Preparation of carbamate for determination of enantiomeric excess of (*S*)-4d



(*S*)-4d (0.075 g, 0.30 mmol) was placed in a 20-mL reaction flask under argon. Pyridine (0.30 mL) and phenylisocyanate (0.049 mL, 0.45 mmol) were added at room temperature. After the mixture was stirred for 24 h at ambient temperature, brine (15 mL) was added. Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 30:1 then 10:1) afforded the carbamate (0.067 g, 0.18 mmol, 60 %). The enantiomeric excess was determined to be 96% ee according to HPLC analysis. HPLC conditions : Daicel CHIRALPAK AD-H, hexane/2-propanol = 98/2, 1.0 mL/min, retention time : 6.19 min (*R*, minor); 6.98 min (*S*, major).

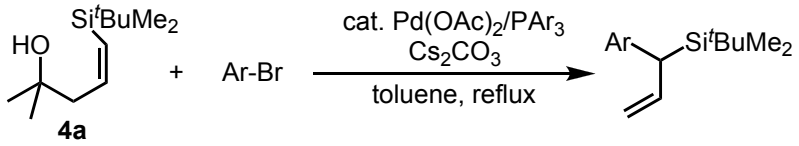
Typical procedure for the synthesis of (*E*)-3-aryl-1-propenylsilanes

Potassium carbonate (0.083 g, 0.58 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. The potassium carbonate was dried in vacuo with heating with a hair dryer for 2 min. Palladium acetate (4.5 mg, 0.020 mmol) was added in the reaction flask. The flask was filled with argon by using the standard Schlenk technique. Tricyclohexylphosphine (0.5 M toluene solution, 0.080 mL, 0.04 mmol) and toluene (0.4 mL) were then added at room temperature. After the mixture was stirred for 10 min, a solution of

homoallyl alcohol **1b** (0.10 g, 0.48 mmol) and 1-bromonaphthalene (0.083 g, 0.40 mmol) in toluene (2.0 mL) was added at ambient temperature. The resulting mixture was heated at reflux for 3 h. After the resulting mixture was cooled to room temperature, water (20 mL) was added. The product was extracted with hexane/ethyl acetate = 5:1 three times. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. Silica gel column purification provided *tert*-butyldimethyl[3-(1-naphthyl)-1-propenyl]silane (**3a**, 0.11 g, 0.37 mmol, *E*/*Z* = 95:5, 93%) as a colorless oil.

Typical procedure for the synthesis of (*E*)-1-aryl-2-alkenylsilanes

The volume of the solvent is very important in the reactions with **4a**. Reaction conditions of each aryl bromide are showed below. The reactions of **4b**-**4e** were performed with 0.17 M.



entry	Ar-Br	Pd (mol%) / Ligand (mol%)	Ligand	Conc. of Ar-Br (mmol/mL)	time(h)
1	**2a**	5 / 20	PPh_3	0.50	4
2	**2b**	2.5 / 10	P(*p*-tol)$_3$	0.50	4
3	**2c**	5 / 20	P(*p*-tol)$_3$	0.50	4
4	**2d**	5 / 20	P(*p*-tol)$_3$	0.17	15
5	**2e**	2.5 / 10	PPh_3	0.17	12
6	**2f**	5 / 10	P(*p*-tol)$_3$	0.067	12
7	**2g**	5 / 10	P(^{c}Hex)Ph$_2$	0.50	4

Cesium carbonate (0.19 g, 0.58 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. The cesium carbonate was dried by the same procedure mentioned above. Palladium acetate (4.5 mg, 0.020 mmol) and triphenylphosphine (0.021 g, 0.080 mmol) were added in the reaction flask. The flask was filled with argon by using the standard Schlenk technique. Toluene (0.2 mL) was added at room temperature and the mixture was stirred for 10 min. Toluene (0.6 mL), homoallyl alcohol **4a** (0.10 g, 0.48 mmol), and 1-bromonaphthalene (0.083 g, 0.40 mmol) were added to the yellow solution obtained at ambient temperature. The resulting mixture was then heated at reflux for 4 h. After the resulting mixture was cooled to room temperature, water (20 mL) was added. Extractive workup

followed by silica gel column purification afforded *tert*-butyldimethyl[1-(1-naphthyl)allyl]silane (**5aa**, 0.099 g, 0.35 mmol, 88 %) as a colorless oil. The product was contaminated with 2% of **3a**.

Typical procedure for chirality transfer from optically active (*S*)-4d to (*E*)-1-aryl-2-butenylsilanes

Dried cesium carbonate (0.20 g, 0.60 mmol) was placed in a 30-mL two-necked reaction flask equipped with a Dimroth condenser. Palladium acetate (5.6 mg, 0.025 mmol) and triphenylphosphine (0.026 g, 0.10 mmol) were added in the reaction flask. The flask was filled with argon by using the standard Schlenk technique. Toluene (1.0 mL) was added at room temperature and the mixture was stirred for 10 min to obtain a yellow solution. A solution of **(*S*)-4d** (0.12 g, 0.50 mmol) and 1-bromonaphthalene (0.10 g, 0.60 mmol) in toluene (2.0 mL) was added at ambient temperature. The resulting mixture was then heated at reflux for 8 h. After the resulting mixture was cooled to room temperature, water (20 mL) was added. Extraction, evaporation, column purification on neutral silica gel gave (*E*)-dimethyl[1-(1-naphthyl)-2-butenyl]phenylsilane (**5ad**, 0.15 g, 0.46 mmol, 92 %) as a colorless oil.

p-Toluenesulfonohydrazide (0.931 g, 5.00 mmol) was added to a 30-mL two-necked reaction flask equipped with a Dimroth condenser. Under argon atmosphere, (*E*)-dimethyl[1-(1-naphthyl)-2-butenyl]phenylsilane (**5ad**, 0.46 mmol), dioxane (5.55 mL), and triethylamine (0.697 mL, 5.00 mmol) were sequentially added to the reaction flask at room temperature. The resulting mixture was then refluxed for 10 h. After the mixture was cooled to room tempeature, water was added. The mixture was extracted (hexane/ethyl acetate = 30:1) three times and dried over sodium sulfate. The combined organic layer was then concentrated in vacuo. The residue was purified by gel permeation chromatography. The hydrogenated product was obtained as a colorless oil (0.13 g, 0.39 mmol, 85%).

A 20-mL two-necked reaction flask containing the reduced product (0.13 g, 0.39 mmol) was filled with argon. Trifluoroacetic acid (1.95 mL) was added at ambient temperature. After stirring for 1 h, the solvent was removed in vacuo. Methanol (0.78 mL), potassium hydrogenfluoride (0.122 g, 1.56 mmol), tetrabutylammonium fluoride (1.0 M THF solution, 0.78 mL, 0.8 mmol), aqueous 30 % hydrogen peroxide (ca. 0.47 mL, 5.8 mmol), and potassium hydrogencarbonate (0.331 g, 3.31 mmol) were sequentially added at room temperature. The resulting mixture was

then heated at 50 ˚C for 30 min. The reaction was quenched with saturated sodium thiosulfate solution (15 mL). Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 5:1) provided 1-(1-naphthyl)-1-butanol (**6ad**, 0.14 mmol, 36 %) as a colorless oil. The reaction conditions were not optimized.

Characterization Data

2-Methyl-3-trimethylsilyl-4-penten-2-ol (1a): IR (neat) 3444, 2970, 1625, 1370, 1249, 1156, 901, 857, 838 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 9H), 1.25 (s, 3H), 1.28 (s, 3H), 1.64 (s, 1H), 1.83 (d, *J* = 11.5 Hz, 1H), 4.96 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.06 (dd, *J* = 10.0 2.0 Hz, 1H), 5.76 (ddd, *J* = 17.0, 11.5, 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –0.34, 30.08, 30.24, 50.54, 72.88, 116.59, 136.96. Found: C, 62.43; H, 11.88%. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70%.

3-(*tert*-Butyldimethylsilyl)-2-methyl-4-penten-2-ol (1b): IR (neat) 3463, 3074, 2930, 2857, 1626, 1465, 1364, 1334, 1250, 1155, 1117, 1008, 904, 826, 801, 766, 663 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 1.24 (s, 3H), 1.28 (s, 3H), 1.84 (s, 1H), 2.01 (d, *J* = 11.5 Hz, 1H), 5.03 (dd, *J* = 17.0, 2.5 Hz, 1H), 5.12 (dd, *J* = 10.0, 2.5 Hz, 1H), 5.81 (ddd, *J* = 17.0, 11.5, 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –4.88, –2.79, 18.27, 27.39, 29.85, 30.01, 46.45, 72.49, 117.89, 138.64. Found: C, 67.28; H, 12.12%. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22%.

(*Z*)-5-(*tert*-Butyldimethylsilyl)-2-methyl-4-penten-2-ol (4a): IR (neat) 3351, 2955, 2928, 2884, 2857, 1607, 1472, 1463, 1249, 826, 812, 772 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6H), 0.89 (s, 9H), 1.24 (s, 6H), 1.44 (bs, 1H), 2.33 (dd, *J* = 7.5, 1.5 Hz, 2H), 5.70 (dt, *J* = 14.5, 1.5 Hz, 1H), 6.39 (dt, *J* = 14.5, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.70, 17.07, 26.62, 29.54, 47.23, 70.82, 130.17, 144.76. Found: C, 67.02; H, 12.49%. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22%.

(*Z*)-5-(*tert*-Butyldimethylsilyl)-2,3-dimethyl-4-penten-2-ol (4b): IR (neat) 3389, 2955, 2929, 2857, 1608, 1463, 1363, 1251, 1140, 826, 811, 779 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.89 (s, 9H), 1.00 (d, *J* = 6.5 Hz, 3H), 1.17 (s, 3H), 1.19 (s, 3H), 1.45 (s, 1H), 2.39 (dq, *J* = 10.5, 6.5 Hz, 1H), 5.62 (d, *J* = 14.0 Hz, 1H), 6.30 (dd, *J* = 14.0, 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ –3.60, –3.53, 16.42, 16.79, 26.62, 26.93, 27.37, 48.41, 72.44, 128.13, 151.13. Found: C, 68.08; H, 12.43%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

(*Z*)-2,3-Dimethyl-5-trimethylsilyl-4-penten-2-ol (4c): IR (neat) 3394, 2968, 2900, 1601, 1374, 1248, 837, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 1.00 (d, *J* = 7.0 Hz, 3H), 1.17, (s, 3H),

1.19 (s, 3H), 1.45 (bs, 1H), 2.39, (dq, *J* = 11.0, 7.0 Hz, 1H), 5.59 (d, *J* = 14.0 Hz, 1H), 6.22 (dd, *J* = 14.0, 11.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.68, 16.27, 27.03, 27.27, 48.68, 72.43, 131.13, 150.30. Found: C, 64.27; H, 11.68%. Calcd for $C_{10}H_{22}OSi$: C, 64.45; H, 11.90%.

(*Z*)-5-(Dimethylphenylsilyl)-2,3-dimethyl-4-penten-2-ol (4d): IR (neat) 3402, 2970, 2936, 1605, 1373, 1248, 1112, 835, 821, 784, 731, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6H), 0.89 (d, *J* = 6.5 Hz, 3H, 1.06 (s, 6H), 1.20 (s, 1H), 2.29 (dq, *J* = 10.5, 6.5 Hz, 1H), 5.74 (d, *J* = 14.5 Hz, 1H), 6.33 (dd, *J* = 14.5, 10.5 Hz, 1H), 7.34–7.37 (m, 3H), 7.54–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –0.66, –0.52, 16.02, 26.62, 27.41, 48.48, 72.43, 128.06, 128.86, 129.20, 133.96, 139.86, 151.98. Found: C, 72.71; H, 10.00%. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74%.

(*Z*)-2-Methyl-3-[2-(trimethylsilyl)ethenyl]-2-heptanol (4e): IR (neat) 3404, 2957, 2933, 2900, 2861, 1610, 1462, 1378, 1247, 1135, 838, 767 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 0.89 (t, *J* = 7.0 Hz, 3H), 1.13 (s, 3H), 1.10–1.17 (m, 2H), 1.20 (s, 3H), 1.24–1.38 (m, 3H), 1.51–1.57 (m, 1H), 1.61 (bs, 1H), 2.18 (td, *J* = 10.5, 2.0 Hz, 1H), 5,72 (d, *J* = 14.5 Hz, 1H), 6.06 (dd, *J* = 14.5, 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.86, 14.23, 23.23, 26.75, 27.57, 30.03, 30.84, 54.50, 72.26, 133.89, 148.96. Found: C, 68.07; H, 12.49%. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35%.

(*E*)-Trimethyl[3-(1-naphthyl)-1-propenyl]silane (3a'): IR (neat) 3045, 2955, 2897, 1612, 1597, 1396, 1248, 991, 880 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9H), 3.91 (dd, *J* = 6.0, 1.5 Hz, 2H), 5.76 (dt, *J* = 18.0, 1.5 Hz, 1H), 6.28 (dt, *J* = 18.0, 6.0 Hz, 1H), 7.34–7.36 (m, 1H), 7.41–7.45 (m, 1H), 7.47–7.55 (m, 2H), 7.74–7.76 (m, 1H), 7.85–7.88 (m, 1H), 8.01–8.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –1.01, 40.56, 124.46, 125.71, 125.83, 125.93, 126.64, 127.11, 128.83, 132.06, 132.33, 134.03, 136.42, 144.79. Found: C, 79.67; H, 8.65%. Calcd for $C_{16}H_{20}Si$: C, 79.93; H, 8.38%.

(*E*)-*tert*-Butyldimethyl[3-(1-naphthyl)-1-propenyl]silane (3a): IR (neat) 3045, 2926, 2855, 1611, 1597, 1581, 1511, 1463, 1397, 1361, 1247, 1008, 991, 828, 776 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 6H), 0.85 (s, 9H), 3.93 (dd, *J* = 6.0, 1.5 Hz, 2H), 5.76 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.29 (dt, *J* = 18.5, 6.0 Hz, 1H), 7.33–7.35 (m, 1H), 7.42–7.45 (m, 1H), 7.47–7.52 (m, 2H), 7.75–7.76 (m, 1H), 7.86–7.88 (m, 1H), 8.03–8.05 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –5.93, 16.77, 26.64, 40.87, 124.55, 125.71, 125.81, 125.89, 126.59, 127.12, 128.79, 129.23, 132.32, 134.01, 136.42, 146.23.

Found: C, 81.07; H, 9.43%. Calcd for $C_{19}H_{26}Si$: C, 80.78; H, 9.28%.

(*E*)-*tert*-Butyl[3-(2,6-dimethylphenyl)-1-propenyl]dimethylsilane (3b): IR (neat) 2927, 2856, 1615, 1464, 1248, 989, 826, 810, 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.02 (s, 6H), 0.83 (s, 9H), 2.29 (s, 6H), 3.49 (dd, *J* = 5.5, 2.0 Hz, 2H), 5.50 (dt, *J* = 18.5, 2.0 Hz, 1H), 6.08 (dt, *J* = 18.5, 5.5 Hz, 1H), 7.02–7.07 (m, 3H); ^{13}C NMR ($CDCl_3$) δ –5.93, 16.75, 20.14, 26.66, 37.02, 126.15, 127.42, 128.13, 136.42, 137.03, 144.34. Found: C, 78.14; H, 11.07%. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83%.

(*E*)-*tert*-Butyl[3-(4-trifluoromethylphenyl)-1-propenyl]dimethylsilane (3c): IR (neat) 2954, 2929, 2856, 1326, 1165, 1127, 1106, 1069, 858, 826, 811, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.87 (s, 9H), 3.51 (d, *J* = 6.0 Hz, 2H), 5.73 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.12 (dt, *J* = 18.5, 6.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.90, 16.73, 26.65, 43,35, 124.58 (q, *J* = 272.2 Hz), 125.55 (q, *J* = 3.8 Hz), 128.65 (q, *J* = 32.2 Hz), 129.18, 130.18, 144.44 (q, *J* = 1.0 Hz), 145.32. Found: C, 63.82; H, 7.94%. Calcd for $C_{16}H_{23}F_3Si$: C, 63.97; H, 7.72%.

(*E*)-1-{4-[3-(*tert*-Butyldimethylsilyl)-2-propenyl]phenyl}ethanone (3d): IR (neat) 2953, 2927, 2855, 1687, 1606, 1360, 1267, 1248, 826, 812, 779 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.86 (s, 9H), 2.59 (s, 3H), 3.52 (dd, *J* = 6.5, 1.5 Hz, 2H), 5.72 (dt, *J* = 18.0, 1.5 Hz, 1H), 6.13 (dt, *J* = 18.0, 6.5 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.92, 16.74, 26.64, 26.80, 43.53, 128.81, 129.11, 130.04, 135.44, 145.33, 146.10, 198.11. Found: C, 74.58; H, 9.78%. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55%.

(*E*)-4-[3-(*tert*-Butyldimethylsilyl)-2-propenyl]benzaldehyde (3e): IR (neat) 2953, 2927, 2883, 2855, 1704, 1699, 1605, 1471, 1248, 1211, 1168, 827, 811, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.01 (s, 6H), 0.86 (s, 9H), 3.54 (dd, *J* = 6.0, 1.0 Hz, 2H), 5.73 (dt, *J* = 18.5, 1.0 Hz, 1H), 6.13 (dt, *J* = 18.5, 6.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 9.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –5.93, 16.73, 26.62, 43.71, 129.57, 130.23, 130.38, 134.86, 145.01, 147.74, 192.27. Found: C, 73.60; H, 9.33%. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.29%.

Ethyl (*E*)-4-[3-(*tert*-butyldimethylsilyl)-2-propenyl]benzoate (3f): IR (neat) 2928, 2855, 1721,

1609, 1275, 1100, 828, 808, 779, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 6H), 0.86 (s, 9H), 1.39 (t, *J* = 7.0 Hz, 3H), 3.51 (dd, *J* = 6.0, 1.5 Hz, 2H), 4.36 (q, *J* = 7.0 Hz, 2H), 5.71 (dt, *J* = 18.0, 1.5 Hz, 1H), 6.13 (dt, *J* = 18.0, 6.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.92, 14.57, 16.74, 26.64, 43.54, 61.03, 128.57, 128.89, 129.86, 129.94, 145.52, 145.67, 166.89. Found: C, 70.71; H, 9.22%. Calcd for $C_{18}H_{28}OSi$: C, 71.00; H, 9.27%.

(*E*)-*tert*-Butyl[3-(4-methoxyphenyl)-1-propenyl]dimethylsilane (3g): IR (neat) 2953, 2927, 2885, 2854, 1615, 1511, 1464, 1248, 1176, 1040, 857, 827, 811, 777 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 6H), 0.86 (s, 9H), 3.40 (dd, *J* = 6.5, 1.5 Hz, 2H), 3.79 (s, 3H), 5.68 (dt, *J* = 18.5, 1.5 Hz, 1H), 6.13 (dt, *J* = 18.5, 6.5 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –5.87, 16.75, 26.67, 42.77, 55.47, 114.00, 128.45, 129.81, 132.36, 147.10, 158.10. Found: C, 73.28; H, 10.08%. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98%.

***tert*-Butyldimethyl[1-(1-naphthyl)-2-propenyl]silane (5aa)**: IR (neat) 3048, 2929, 2856, 1626, 1471, 1464, 1392, 1363, 1250, 1080, 901, 824, 782, 757 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.27 (s, 3H), 0.15 (s, 3H), 0.88 (s, 9H), 4.06 (d, *J* = 10.0 Hz, 1H), 5.01 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.05 (dd, *J* = 16.5, 1.5 Hz, 1H), 6.34 (dt, *J* = 16.5, 10.0 Hz, 1H), 7.35–7.36 (m, 1H), 7.40–7.51 (m, 3H), 7.63–7.65 (m, 1H), 7.83–7.84 (m, 1H), 8.09–8.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –6.76, –6.00, 18.41, 27.44, 35.11, 113.71, 123.80, 125.08, 125.49 (overrapped 2C), 125.53, 125.64, 129.20, 131.46, 134.43, 139.76, 140.00. Found: C, 80.86; H, 9.30%. Calcd for $C_{19}H_{26}Si$: C, 80.78; H, 9.28%.

***tert*-Butyl[1-(2,6-dimethylphenyl)-2-propenyl]dimethylsilane (5ba)**: IR (neat) 3071, 2956, 2929, 2857, 1622, 1464, 1252, 902, 856, 832, 822, 807, 767 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.25 (s, 3H), 0.23 (s, 3H), 0.94 (s, 9H), 2.28 (s, 3H), 2.34 (s, 3H), 3.68 (dt, *J* = 6.5, 2.0 Hz, 1H), 4.74 (dt, *J* = 16.5, 2.0 Hz, 1H), 4.92 (dt, *J* = 10.0, 2.0 Hz, 1H), 6.17 (ddd, *J* = 16.5, 10.0, 6.5 Hz, 1H), 6.94–7.03 (m, 3H); ^{13}C NMR ($CDCl_3$) δ –5.69, –4.39 18.48, 22.21, 22.60, 27.19, 34.16, 113.35, 125.05, 128.53, 129.38, 136.16, 136.73, 137.93, 139.69. Found: C, 78.35; H, 11.07%. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83%.

***tert*-Butyl[1-(4-trifluoromethylphenyl)-2-propenyl]dimethylsilane (5ca)**: IR (neat) 2931, 2859,

1615, 1326, 1253, 1164, 1125, 1106, 1070, 1017, 905, 858, 837, 822, 803, 782 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.13 (s, 3H), 0.06 (s, 3H), 0.83 (s, 9H), 3.21 (d, *J* = 10.0 Hz, 1H), 5.00 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.00 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.17 (dt, *J* = 17.0, 10.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.96, –6.50, 18.21, 27.21, 42.50, 113.97, 124.66 (q, *J* = 271.7 Hz), 125.48 (q, *J* = 3.9 Hz), 127.28 (q, *J* = 32.1 Hz), 128.08, 138.49, 147.81 (q, *J* = 1.5 Hz); ^{19}F NMR ($CDCl_3$) δ –62.72. Found: C, 64.21; H, 7.85%. Calcd for $C_{16}H_{23}F_3Si$: C, 63.97; H, 7.72%.

1-{4-[1-(*tert*-Butyldimethylsilyl)-2-propenyl]phenyl}ethanone (5da): IR (neat) 2957, 2929, 2883, 2857, 1684, 1602, 1406, 1359, 1271, 1252, 1181, 858, 836, 823, 803, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.13 (s, 3H), 0.06 (s, 3H), 0.83 (s, 9H), 2.57 (s, 3H), 3.22 (d, *J* = 10.0 Hz, 1H), 4.90 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.91 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.19 (dt, *J* = 17.0, 10.0 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.90, –6.49, 18.28, 26.65, 27.21, 42.96, 113.92, 127.97, 128.83, 134.25, 138.39, 149.70, 197.89. Found: C, 74.15; H, 9.66%. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55%.

4-[1-(*tert*-Butyldimethylsilyl)-2-propenyl]benzaldehyde (5ea): IR (neat) 2929, 2857, 1699, 1602, 1250, 1215, 1168, 834, 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.12 (s, 3H), 0.07 (s, 3H), 0.83 (s, 9H), 3.26 (d, *J* = 10.0 Hz, 1H), 5.01 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.01 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.19 (dt, *J* = 17.0, 10.0 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 9.94 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –6.91, –6.49, 18.31, 27.19, 43.31, 114.19, 128.40, 130.21, 133.77, 138.11, 151.46, 192.01. Found: C, 73.60; H, 9.48%. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.29%.

Ethyl 4-[1-(*tert*-butyldimethylsilyl)-2-propenyl]benzoate (5fa): IR (neat) 3077, 2930, 2857, 1717, 1607, 1464, 1408, 1367, 1277, 1252, 1178, 1101, 1021, 822, 803, 767 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.13 (s, 3H), 0.05 (s, 3H), 0.82 (s, 9H), 1.38 (t, *J* = 7.5 Hz, 3H), 3.21 (d, *J* = 9.5 Hz, 1H), 4.35 (q, *J* = 7.5 Hz, 2H), 4.98–5.01 (m, 2H), 6.15–6.22 (m, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.91, –6.55, 14.58, 18.26, 27.20, 42.88, 60.92, 113.78, 127.21, 127.78, 129.92, 138.53, 149.14, 166.93. Found: C, 70.79; H, 9.39%. Calcd for $C_{18}H_{28}O_2Si$: C, 71.00; H, 9.27%.

***tert*-Butyl[1-(4-methoxyphenyl)-2-propenyl]dimethylsilane (5ga)**: IR (neat) 2955, 2929, 2883, 2856, 2835, 1626, 1511, 1464, 1298, 1248, 1178, 1040, 899, 823, 806, 785, 774 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.11 (s, 3H), 0.04 (s, 3H), 0.81 (s, 9H), 3.06 (d, *J* = 10.0 Hz, 1H), 3.78 (s, 3H), 4.93 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.94 (dd, *J* = 17.0, 2.0 Hz, 1H), 6.14 (dt, *J* = 17.0, 10.0 Hz, 1H), 6.81 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –6.74, –6.57, 18.10, 27.25, 41.08, 55.45, 112.73, 114.05, 128.88, 135.20, 139.95, 157.25. Found: C, 73.39; H, 10.10%. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98%.

(*E*)-*tert*-Butyldimethyl[1-(1-naphthyl)-2-butenyl]silane (5ab): IR (neat) 3046, 2956, 2928, 2882, 2855, 1471, 1463, 1392, 1256, 1248, 1082, 966, 835, 826, 806, 791, 775 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.35 (s, 3H), 0.11 (s, 3H), 0.88 (s, 9H), 1.68 (dd, *J* = 6.5, 1.5 Hz, 3H), 4.00 (d, *J* = 10.0 Hz, 1H), 5.49 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.95 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.32–7.34 (m, 1H), 7.40–7.50 (m, 3H), 7.61–7.62 (m, 1H), 7.81–7.83 (m, 1H), 8.08–8.10 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –6.98, –5.90, 18.26, 18.29, 27.44, 33.42, 123.89, 124.53, 124.78, 125.23, 125.42, 125.52, 125.58, 129.16, 131.39, 132.19, 134.38, 140.78. Found: C, 81.17; H, 9.69%. Calcd for $C_{20}H_{28}Si$: C, 81.01; H, 9.52%.

(*E*)-1-{4-[1-(*tert*-Butyldimethylsilyl)-2-butenyl]phenyl}ethanone (5db): IR (neat) 2958, 2929, 2882, 2856, 1682, 1602, 1359, 1270, 1249, 1179, 834, 823, 803 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.16 (s, 3H), 0.02 (s, 3H), 0.83 (s, 9H), 1.68 (dd, *J* = 7.0, 1.5 Hz, 3H), 2.56 (s, 3H), 3.16 (d, *J* = 10.0 Hz, 1H), 5.43 (dq, *J* = 15.0, 7.0 Hz, 1H), 5.80 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –7.12, –6.42, 18.17, 18.25, 26.67, 27.21, 41.27, 124.91, 127.80, 128.77, 130.51, 134.02, 150.63, 197.96. Found: C, 74.70; H, 9.52%. Calcd for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78%.

(*E*)-Trimethyl[1-(1-naphthyl)-2-butenyl]silane (5ac): IR (neat) 3046, 2959, 2898, 1511, 1393, 1249, 1086, 964, 838, 794, 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.03 (s, 9H), 1.72 (dd, *J* = 6.5, 1.5 Hz, 3H), 3.80 (d, *J* = 9.5 Hz, 1H), 5.49 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.94 (ddq, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.32–7.34 (m, 1H), 7.41–7.49 (m, 3H), 7.62–7.63 (m, 1H), 7.82–7.84 (m, 1H), 8.05–8.07 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –2.28, 18.34, 36.55, 123.96, 124.01, 124.13, 125.15, 125.40, 125.42,

125.60, 129.06, 130.07, 131.61, 134.32, 139.99. Found: C, 80.20; H, 8.66%. Calcd for $C_{17}H_{22}Si$: C, 80.25; H, 8.72%.

(*E*)-1-[4-(1-Trimethylsilyl-2-butenyl)phenyl]ethanone (5dc): IR (neat) 2959, 1683, 1603, 1414, 1358, 1271, 1249, 1179, 962, 866, 841 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.05 (s, 9H), 1.72 (dd, *J* = 6.5, 1.5 Hz, 3H), 2.57 (s, 3H), 2.99 (d, *J* = 10.0 Hz, 1H), 5.43 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.80 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.84, 18.34, 26.67, 43.82, 124.71, 127.24, 128.73, 129.12, 133.95, 149.84, 198.00. Found: C, 73.27; H, 9.19%. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00%.

(*E*)-4-(1-Trimethylsilyl-2-butenyl)benzaldehyde (5ec): IR (neat) 2959, 1700, 1602, 1570, 1249, 1213, 1168, 843, 817 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.04 (s, 9H), 1.72 (dd, *J* = 6.5, 1.5 Hz, 3H), 3.02 (d, *J* = 10.0 Hz, 1H), 5.45 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.81 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 9.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ –2.85, 18.34, 44.20, 124.98, 127.67, 128.84, 130.13, 133.49, 151.63, 192.12. Found: C, 72.07; H, 8.77%. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67%.

Ethyl (*E*)-4-(1-trimethylsilyl-2-butenyl)benzoate (5fc): IR (neat) 2960, 1718, 1607, 1367, 1276, 1249, 1178, 1101, 869, 839, 708 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.06 (s, 9H), 1.38 (t, *J* = 7.5 Hz, 3H), 1.71 (dd, *J* = 6.0, 1.5 Hz, 3H), 2.98 (d, *J* = 10.0 Hz, 1H), 4.35 (q, *J* = 7.5 Hz, 2H), 5.43 (dq, *J* = 15.0, 6.0 Hz, 1H), 5.80 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.86, 14.59, 18.34, 43.72, 60.87, 124.55, 126.88, 127.07, 129.29, 129.80, 149.28, 167.03. Found: C, 69.27; H, 8.73%. Calcd for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75%.

(*E*)-[1-(4-Methoxyphenyl)-2-butenyl]trimethylsilane (5gc): IR (neat) 2956, 2834, 1611, 1509, 1247, 1178, 1039, 868, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.06 (s, 9H), 1.69 (dd, *J* = 6.0, 1.5 Hz, 3H), 2.80 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 5.38 (dq, *J* = 15.0, 6.0 Hz, 1H), 5.74 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.74, 18.34, 41.80, 55.46, 113.94, 123.49, 128.18, 130.81, 135.41, 156.99. Found: C, 71.60; H, 9.46%. Calcd for $C_{14}H_{22}OSi$: C, 71.73; H, 9.46%.

(*E*)-Dimethyl[1-(1-naphthyl)-2-butenyl]phenylsilane (5ad): IR (neat) 3047, 3013, 2959, 2915, 2853, 1427, 1393, 1248, 1114, 833, 809, 794, 777, 732, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 3H), 0.23 (s, 3H), 1.68 (ddd, *J* = 6.5, 1.5, 1.0 Hz, 3H), 3.98 (d, *J* = 9.5 Hz, 1H), 5.39 (dqd, *J* = 15.0, 6.5, 1.0 Hz, 1H), 5.86 (ddq, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.14–7.15 (m, 1H), 7.27–7.33 (m, 2H), 7.33–7.43 (m, 6H), 7.61–7.62 (m, 1H), 7.80–7.81 (m, 1H), 7.97–7.99 (m, 1H); ^{13}C NMR ($CDCl_3$) δ –4.35, –3.38, 18.28, 36.27, 123.88, 124.44, 124.57, 125.34, 125.35, 125.38, 125.48, 127.64, 128.98, 129.23, 130.74, 131.62, 134.24, 134.55, 137.55, 139.27. Found: C, 83.21; H, 7.57%. Calcd for $C_{22}H_{24}Si$: C, 83.48; H, 7.64%.

Ethyl (*E*)-4-[1-(dimethylphenylsilyl)-2-butenyl]benzoate (5fd): IR (neat) 2960, 1715, 1607, 1276, 1249, 1178, 1101, 831, 809, 736, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.24 (s, 3H), 1.38 (t, *J* = 7.0 Hz 3H), 1.68 (dd, *J* = 6.5, 1.5 Hz, 3H), 3.15 (d, *J* = 10.0 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 5.37 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.73 (ddq, *J* = 15.0, 10.0, 1.5 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 7.30–7.31 (m, 4H), 7.34–7.38 (m, 1H), 7.85 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –4.52, –4.29, 14.58, 18.29, 43.43, 60.88, 125.02, 126.96, 127.36, 127.73, 129.04, 129.45, 129.63, 134.50, 136.59, 148.53, 167.04. Found: C, 74.25; H, 7.73%. Calcd for $C_{21}H_{26}O_2Si$: C, 74.51; H, 7.74%.

Ethyl (*E*)-4-[1-(trimethylsilyl)-2-heptenyl]benzoate (5fe): IR (neat) 2958, 2929, 2859, 1718, 1608, 1276, 1249, 1177, 1104, 837 cm^{-1}; ^1H NMR ($CDCl_3$) δ –0.05 (s, 9H), 0.89 (t, *J* = 7.5 Hz, 3H), 1.28–1.37 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 3H), 2.05 (td, *J* = 7.0, 6.5 Hz, 2H), 2.89 (d, *J* = 9.5 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 5.41 (dt, *J* = 15.0, 6.5 Hz, 1H), 5.77 (ddt, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ –2.86, 14.15, 14.59, 22.41, 32.21, 32.71, 43.68, 60.86, 126.86, 127.06, 128.10, 129.79, 130.25, 149.34, 167.03. Found: C, 71.59; H, 9.34%. Calcd for $C_{19}H_{30}O_2Si$: C, 71.64; H, 9.49%.

(*E*)-[1-(2,6-Dimethylphenyl)-2-butenyl]dimethylphenylsilane (5bd): IR (neat) 3069, 3017, 2957, 2915, 1427, 1249, 1112, 830, 813, 767, 735, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 3H), 0.35 (s, 3H), 1.65 (dt, *J* = 6.5, 1.5 Hz, 3H), 2.15 (s, 3H), 2.22 (s, 3H), 3.72 (d, *J* = 8.0 Hz, 1H), 5.27 (dqd, *J* = 15.0, 6.5, 1.5 Hz, 1H), 5.83 (ddq, *J* = 15.0, 8.0, 1.5 Hz, 1H), 6.90–6.94 (m, 3H),

7.30–7.37 (m, 3H), 7.43–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –2.33, –2.00, 18.20, 22.29, 22.64, 36.88, 124.76, 124.83, 127.84, 128.33, 129.11, 129.46, 129.54, 134.06, 135.88, 136.13, 139.61, 140.02. Found: C, 81.53; H, 9.00%. Calcd for $C_{20}H_{26}Si$: C, 81.56; H, 8.90%.

(*E*)-[1-(2-Phenylphenyl)-2-butenyl]dimethylphenylsilane (5hd): IR (neat) 3056, 3020, 2958, 2915, 1476, 1427, 1245, 831, 748, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 3H), 0.15 (s, 3H), 1.67 (dd, *J* = 6.0, 1.5 Hz, 3H), 3.33 (d, *J* = 9.5 Hz, 1H), 5.22 (dq, *J* = 15.0, 6.0 Hz, 1H), 5.71 (ddq, *J* = 15.0, 9.5, 1.5 Hz, 1H), 7.04–7.09 (m, 2H), 7.10–7.13 (m, 3H), 7.17–7.18 (m, 2H), 7.20–7.26 (m, 3H), 7.29–7.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ –4.42, –3.50, 18.27, 37.88, 123.56, 124.60, 126.73, 127.23, 127.60, 128.13 (overrapped, 2C), 129.09, 129.70, 130.47, 131.59, 134.44, 137.71, 140.20, 141.53, 142.25. Found: C, 84.35; H, 7.89%. Calcd for $C_{24}H_{26}Si$: C, 84.15; H, 7.65%.

(*E*)-[1-(4-Methoxy-2-methylphenyl)-2-butenyl]dimethylphenylsilane (5id): IR (neat) 2956, 2914, 1608, 1500, 1427, 1253, 1196, 1113, 1049, 849, 830, 818, 737, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 3H), 0.28 (s, 3H), 1.65 (ddd, *J* = 6.5, 1.5, 1.0 Hz, 3H), 2.05 (s, 3H), 3.22 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 5.28 (dqd, *J* = 15.0, 6.5, 1.0 Hz, 1H), 5.66 (ddq, *J* = 15.0, 9.0, 1.5 Hz, 1H), 6.63–6.66 (m, 2H), 6.87–6.89 (m, 1H), 7.28–7.31 (m, 2H), 7.34–7.37 (m, 3H); ^{13}C NMR ($CDCl_3$) δ –4.50, –3.74, 18.26, 20.62, 26.35, 55.36, 111.24, 116.08, 123.85, 127.63, 128.19, 129.17, 131.17, 133.15, 134.47, 136.34, 137.92, 156.65. Found: C, 77.42; H, 8.68%. Calcd for $C_{20}H_{26}OSi$: C, 77.36; H, 8.44%.

Methyl (*E*)-4-(1-dimethylphenysilyl-2-butenyl)-3-methylbenzoate (5jd): IR (neat) 2953, 2916, 1720, 1608, 1436, 1428, 1292, 1270, 1249, 1211, 1143, 1113, 831, 812, 768, 737, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 3H), 0.29 (s, 3H), 1.68 (dd, *J* = 6.0, 1.5 Hz, 3H), 2.08 (s, 3H), 3.37 (d, *J* = 9.0 Hz, 1H), 3.89 (s, 3H), 5.35 (dq, *J* = 6.0, 1.5 Hz, 1H), 5.72 (ddq, *J* = 15.0, 9.0, 1.5 Hz, 1H), 7.01–7.03 (m, 1H), 7.28–7.31 (m, 4H), 7.33–7.37 (m, 1H), 7.74–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ –4.66, –4.08, 18.26, 20.34, 38.33, 52.05, 124.88, 126.20, 126.99, 127.18, 127.74, 129.46, 129.86, 131.63, 134.39, 135.02, 136.90, 147.16, 167.65. Found: C, 74.58; H, 7.60%. Calcd for $C_{21}H_{26}O_2Si$: C, 74.51; H, 7.74%.

Figure S1. ^{1}H NMR Spectrum of **6ad**

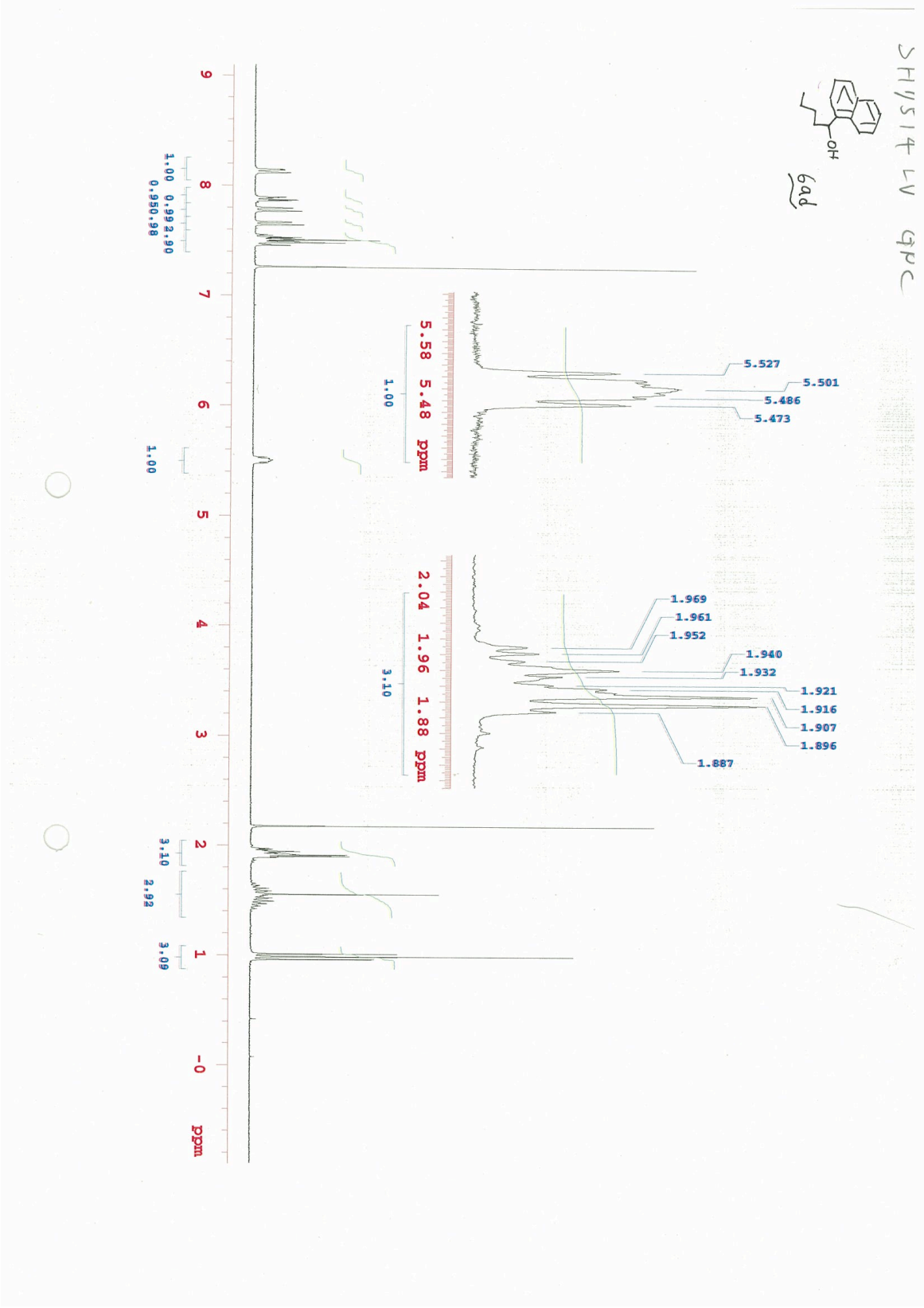


Figure S2. ^{1}H NMR Spectrum of **6bd**

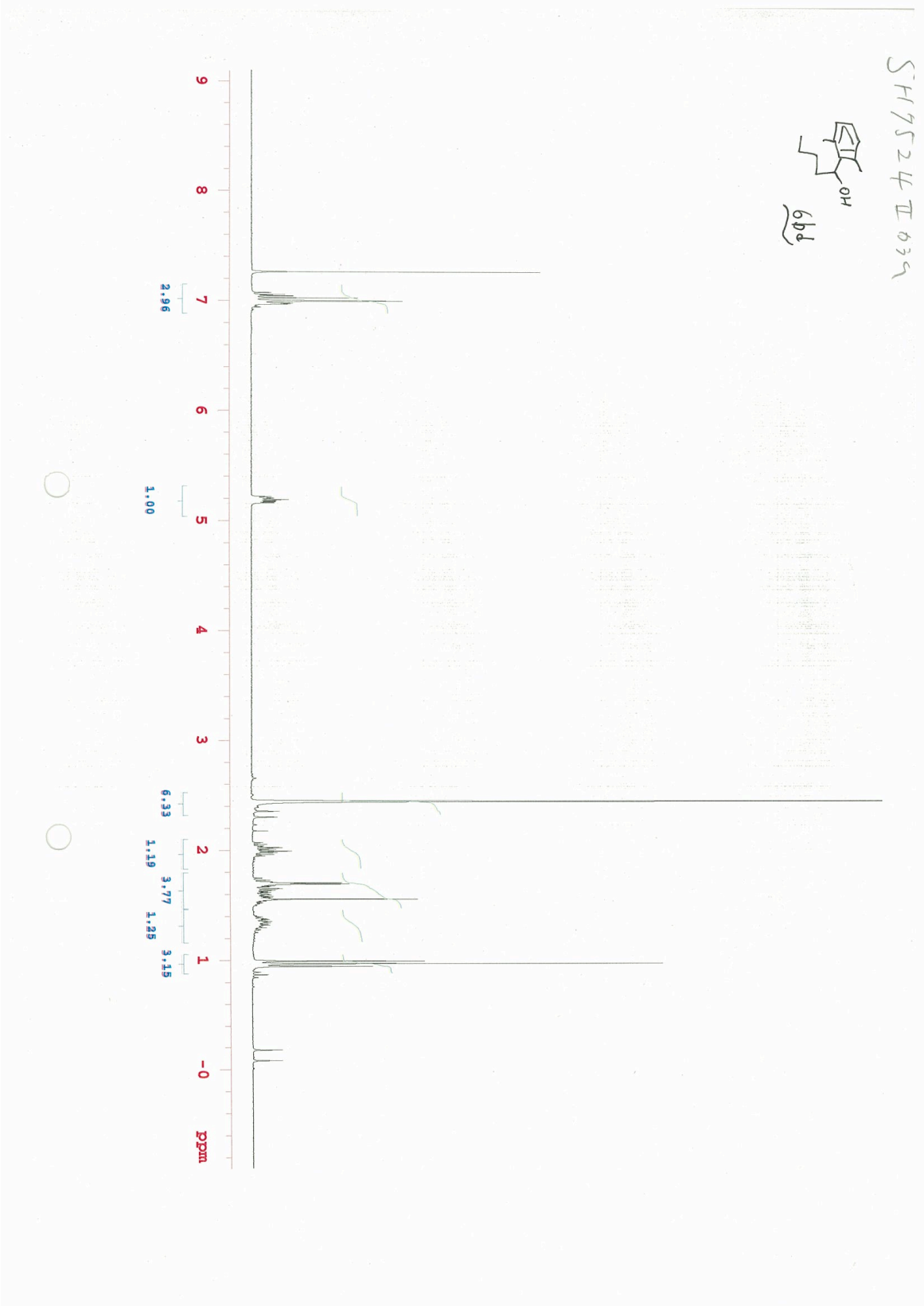


Figure S3. ^{1}H NMR Spectrum of **6hd**

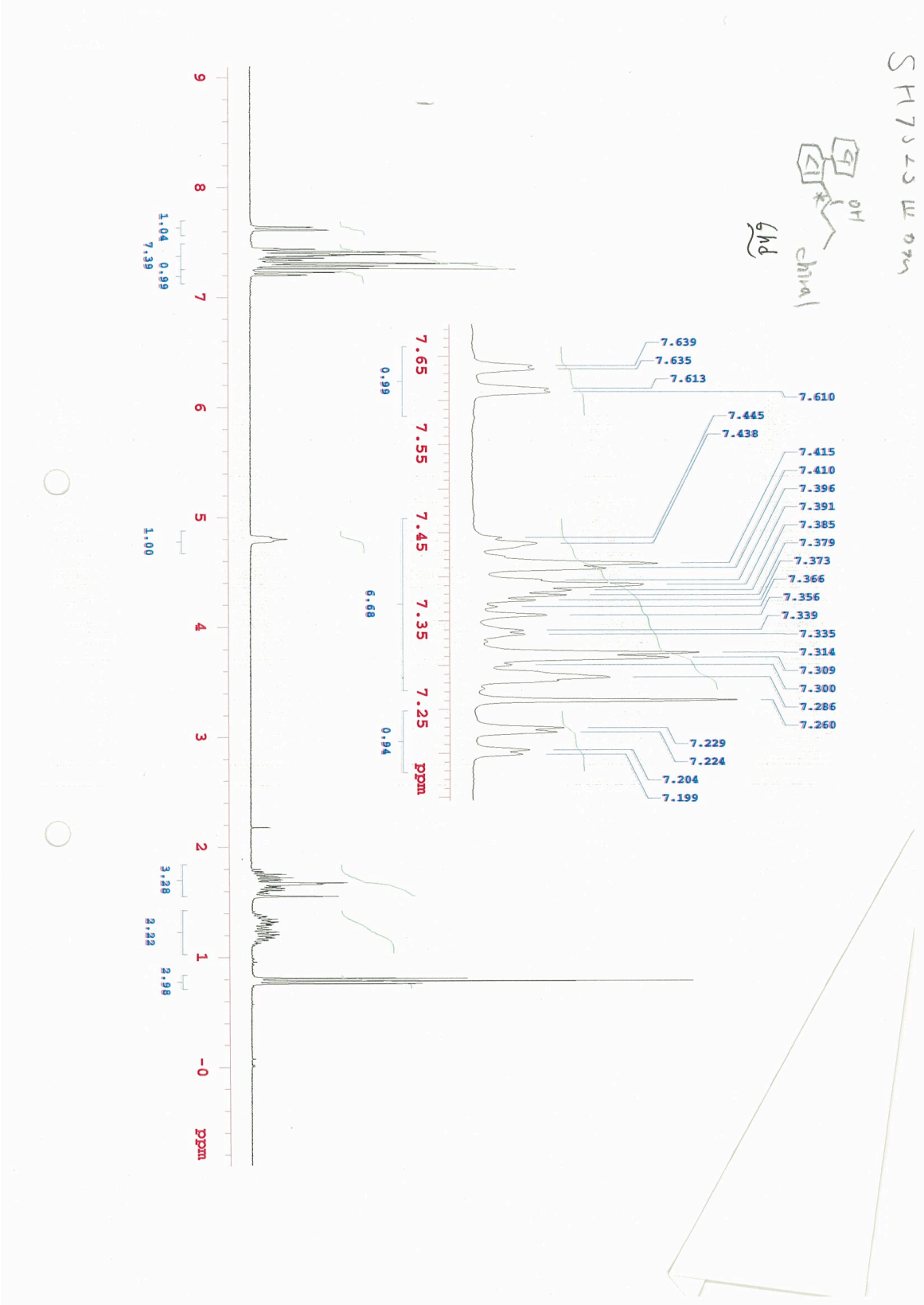


Figure S4. ^{1}H NMR Spectrum of **6id**

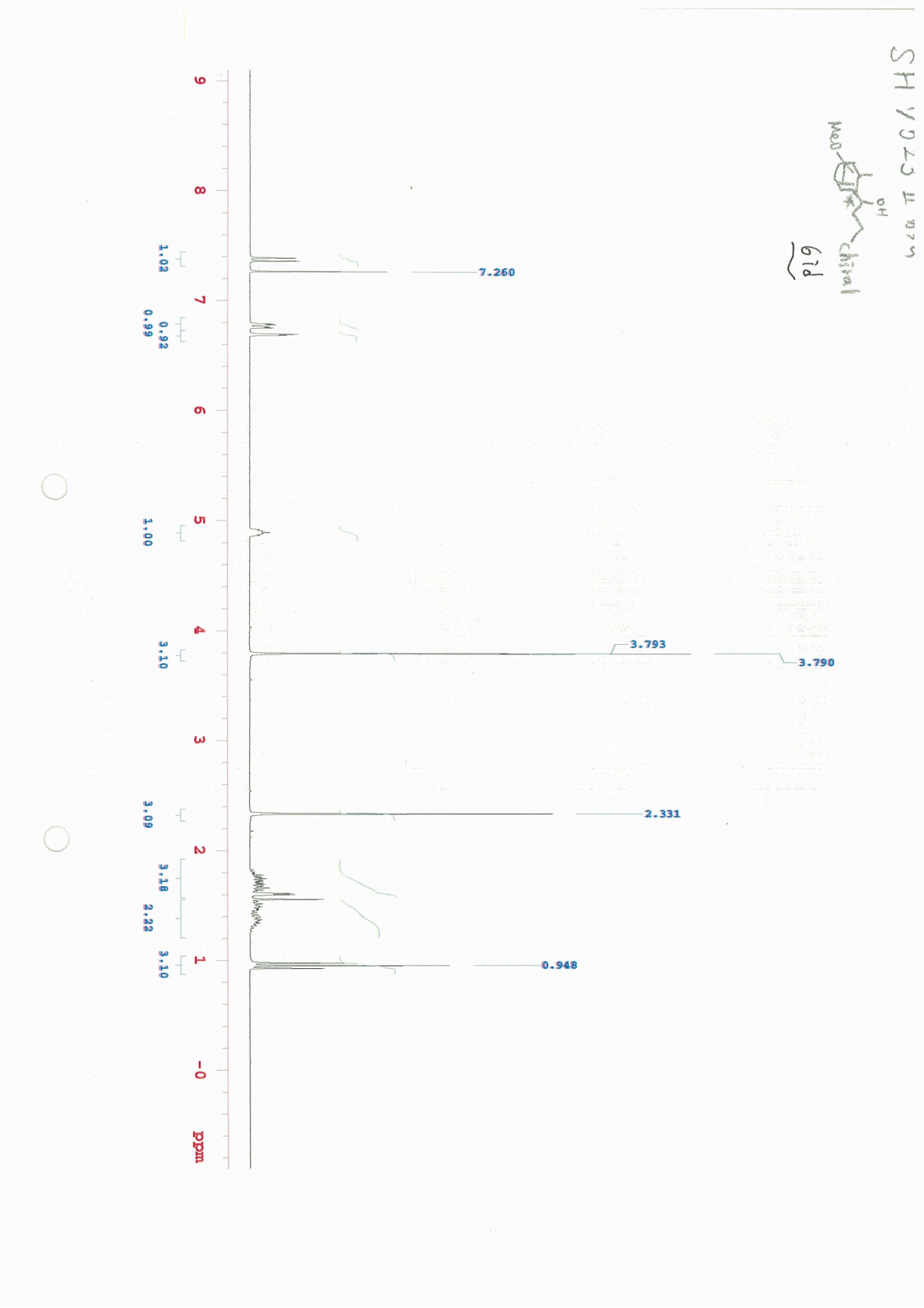


Figure S5. ^{1}H NMR Spectrum of **6jd**

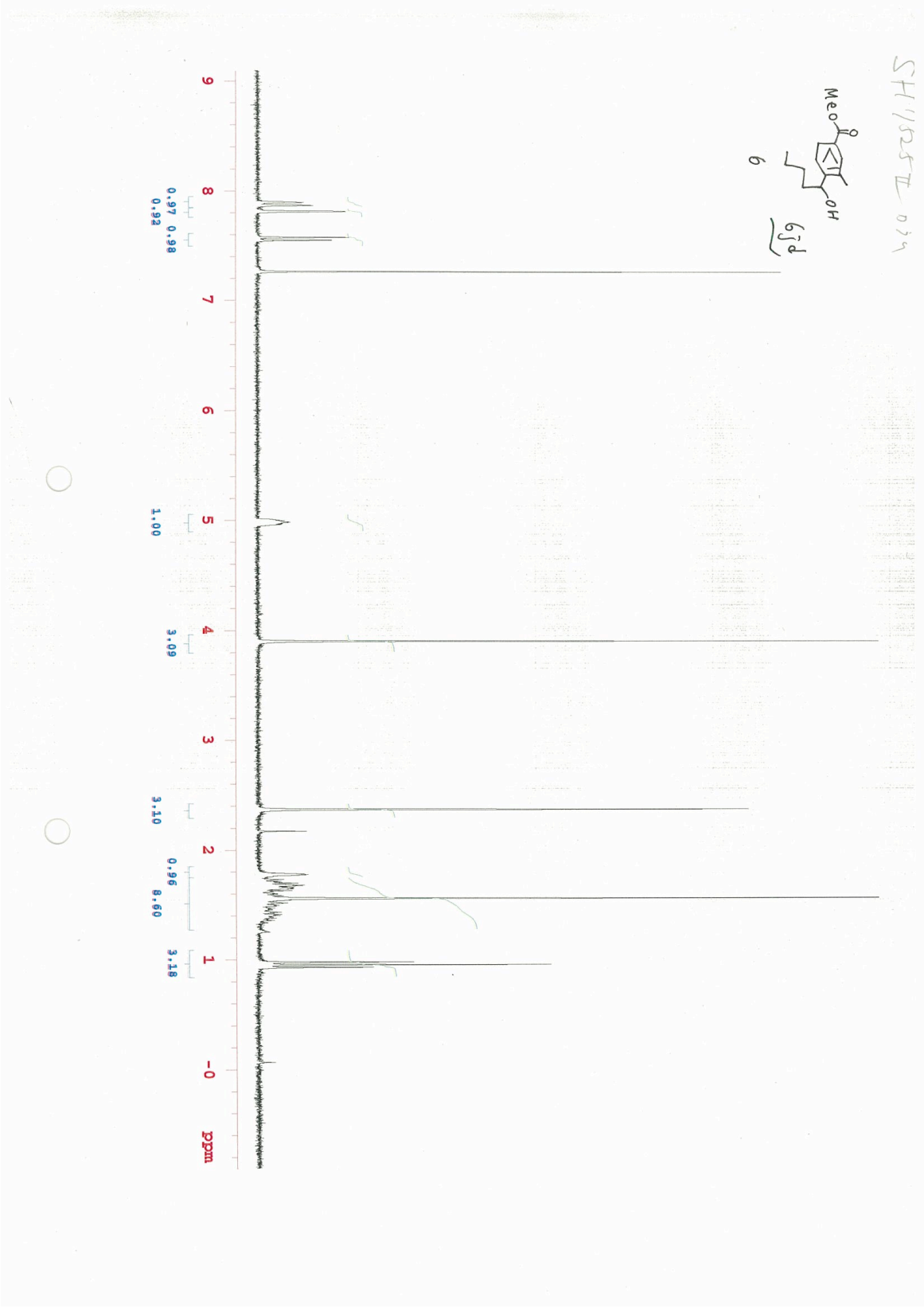


Figure S6. ^{1}H NMR Spectrum of **6kd**

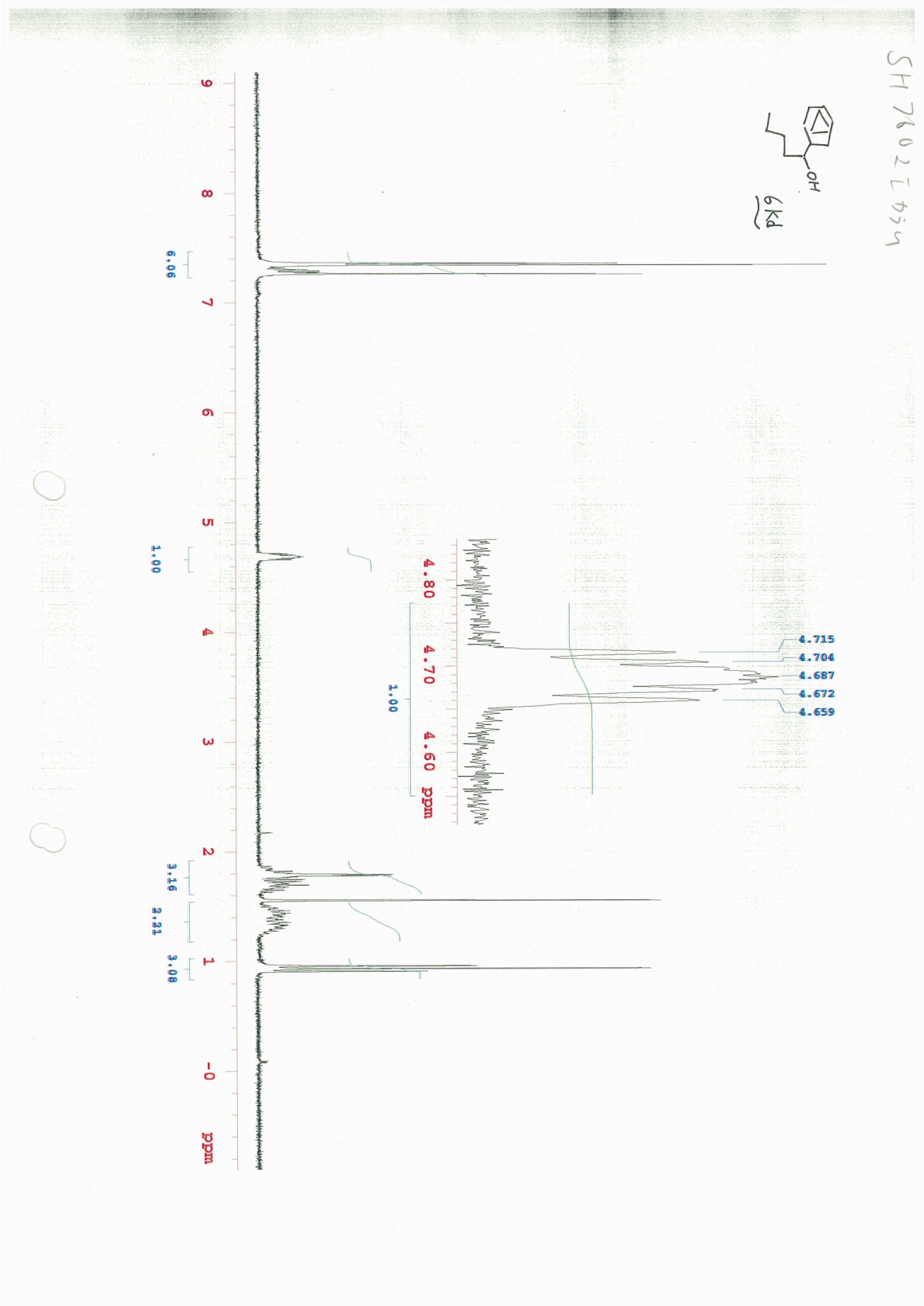


Table S1. Conditions for determining the enantiomeric excesses of **6**

6	column	eluent hexane/^{i}PrOH	Flow /mL•min^{-1}	Retention time /min	
				S, major	*R*, minor
6ad	AD-H	95/5	1.5	6.62	7.62
6bd	OD-H	95/5	1.0	5.14	6.00
6hd	OD-H	95/5	1.0	5.19	5.83
6id	OD-H	95/5	1.0	7.61	8.79
6jd	AD-H	95/5	1.5	9.58	8.78
6kd	OD-H	98/2	1.2	9.74	8.72