Supporting Information

Enhanced Catalyst Activity and Enantioselectivity with Chirality-switchable Polymer Ligand PQXphos in Pd-catalyzed Asymmetric Silaborative Cleavage of *meso*-Methylenecyclopropanes

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1. General

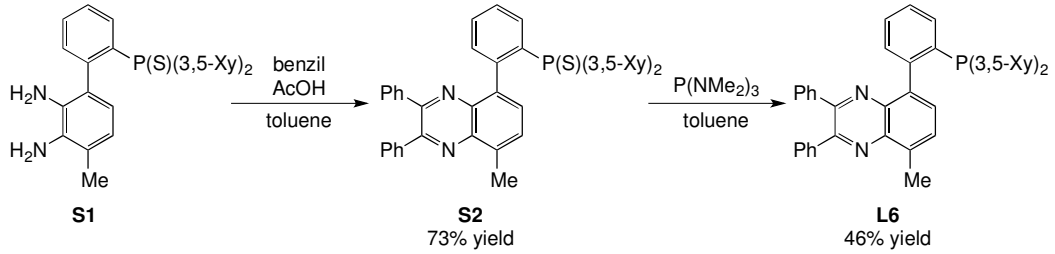
All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury vx400 or a JEOL JNM-A500 spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, sep = septet, m = multiplet, and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 (85%). All ^{13}C NMR and ^{31}P NMR spectra were obtained with complete proton decoupling. The GPC analysis was carried out with TSKgel G4000H_{HR} ($CHCl_3$, polystyrene standard).

Toluene and THF were dried and deoxygenized using an alumina/catalyst column system (GlassContour Co.). Benzil (Wako), acetic acid (Wako), tris(dimethylamino)phosphine (Wako), 0.5 M HCl/MeOH solution (Wako), 1-bromopropane (Wako), trimethylphosphine (Strem), sodium borohydride (Aldrich), tris(dibenzylideneacetone)dipalladium(0) (Strem), triphenylphosphine (Nacalai tesque), and PS-PPh_3 **L9** (Biotage) were used as received from the commercial sources. 1,1,2-trichloroethane (Wako) was purchased from the commercial sources and distilled before use. Sodium Hydride (Nacalai tesque) was purchased from the commercial sources and washed with hexane. Methylenecyclopropanes (MCPs) **2a**-**2f**[S1], Silylborane **1**[S2], PQXphos **L1-L3**[S3], **L4**[S1c], and **L5**[S1] were synthesized by the method reported previously. **L7**[S4] and **L8**[S5] were provided by Professor Yasushi Tsuji's group (Kyoto University).

2. Experimental Procedures and Spectral Data for New Compounds

2.1 Synthesis of Ligand L6

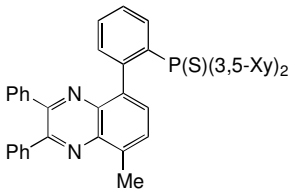
Ligand **L6** was prepared according to Scheme S1.



S1 **S2** 73% yield **L6** 46% yield

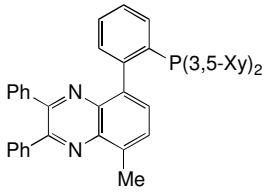
***Scheme S1*. Synthesis of Ligand L6**

2.1.1 Synthesis of S2



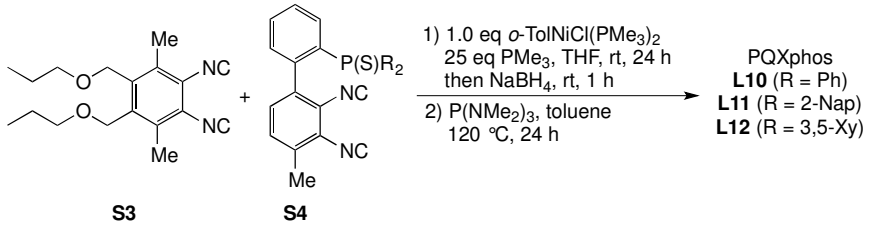
A mixture of **S1**[S3] (428 mg, 0.91 mmol), benzil (201 mg, 0.96 mmol), and acetic acid (1 mL) in toluene (15 mL) was heated for 2 h under reflux with azeotropic removal of water. After evaporation of volatile material under reduced pressure, the residual solid was dissolved in CH_2Cl_2 and subjected to silica gel column chromatography (hexane:CH_2Cl_2 = 3:5), giving the title compound **S2** (429 mg, 73%).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 1H), 7.74 (dd, J = 15.2 Hz, 8.0 Hz, 1H), 7.53-7.57 (m, 3H), 7.49 (s, 1H), 7.40-7.46 (m, 5H), 7.31-7.40 (m, 5H), 7.24-7.29 (m, 2H), 7.07 (s, 1H), 7.04 (s, 1H), 6.94 (s, 1H), 6.53 (s, 1H), 2.69 (s, 3H), 2.21 (s, 6H), 1.91 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) Due to the complexity of the spectra all the peaks are listing without take into consideration C-P couplings. δ 150.8, 150.5, 142.1, 142.0, 139.6, 139.3, 139.1, 139.0, 137.5, 137.5, 137.4, 136.6, 136.4, 136.3, 136.3, 134.5, 134.4, 134.3, 133.9, 133.7, 133.7, 133.4, 132.9, 132.7, 132.7, 132.5, 131.7, 131.6, 131.5, 130.9, 130.3, 130.3, 130.2, 129.9, 129.4, 129.3, 128.6, 128.5, 128.3, 128.2, 127.9, 127.2, 127.0, 21.3, 21.0, 17.1; ^{31}P NMR (200 MHz, $CDCl_3$) δ 42.6 (s); HRMS (ESI) *m/z* calcd for $C_{43}H_{37}N_2PS$+H (M^++H): 645.2493, found: 645.2471

2.1.2 Synthesis of L6



To a solution of **S2** (429 mg, 0.69 mmol) in toluene (5 mL) were added $P(NMe_2)_3$ (240 μL, 1.3 mmol) at room temperature. The mixture was stirred at 120 °C for 24 h, then water was added to the mixture. The mixture was washed with water and brine, and dried over Na_2SO_4. After evaporation of the volatiles, the residue was subjected to silica gel column chromatography (hexane:CH_2Cl_2 = 1:1), giving the title compound **L6** (189 mg, 31% yield).; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (ddd, J = 7.2 Hz, 2.4 Hz, 1.6 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.46-7.49 (m, 3H), 7.38-7.45 (m, 5H), 7.24-7.33 (m, 4H), 7.00 (s, 1H), 6.96 (s, 1H), 6.94 (s, 1H), 6.71-6.74 (m, 3H), 2.91 (s, 3H), 2.31 (s, 6H), 2.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) Due to the complexity of the spectra all the peaks are listing without take into consideration C-P couplings. δ 150.9, 150.6, 144.5, 144.2, 139.9, 139.7, 139.6, 139.2, 138.4, 138.3, 138.1, 138.0, 137.7, 137.6, 137.5, 137.5, 137.1, 137.0, 137.0, 133.1, 131.7, 131.7, 131.5, 131.5, 131.5, 131.4, 131.4, 130.2, 130.2, 130.0, 129.8, 129.7, 128.6, 128.5, 128.3, 128.1, 127.7, 127.6, 127.2, 21.3, 21.1, 17.2; ^{31}P NMR (160 MHz, $CDCl_3$) δ -10.7 (s); HRMS (ESI) *m/z* calcd for $C_{43}H_{37}N_2P$+H (M^++H): 613.2773, found: 613.2767

2.2 Synthesis of PQXphos L10-L12



***Scheme S2*.** Synthesis of PQXphos (**L10**-**L12**)

[Polymerization] To a THF (45 mL) solution of organonickel initiator (*o*-Tol)NiCl$(PMe_3)_2$[S6] (0.01 mM in THF, 0.20 mL, 2.0 μmol) and PMe_3 (0.1 M in THF, 0.50 mL, 50 μmol) was added a mixture of monomer **S3**[S7] (312 mg, 0.95 mmol) and **S4**[S3] (50 μmol) in THF (5 mL) at room temperature. The mixture was stirred for 24 h at room temperature. To the reaction mixture was added $NaBH_4$ (12 mg, 0.32 mmol), and the mixture was stirred for 1 h. The solvent was then evaporated until approximately half of the original volume. The mixture was poured into vigorously stirred MeOH (200 mL), and precipitated polymer was collected by centrifugation

followed by washing with MeOH × 2. After drying in vacuo, fibriform polymer was obtained. **[Reduction of Phosphine Sulfide]** A mixture of the obtained polymer and $P(NMe_2)_3$ (0.618 mL, 3.40 mmol) in toluene (6.7 mL) was stirred at 120 °C for 24 h. The mixture was diluted with THF (2.2 mL) and poured into vigorously stirred MeOH (400 mL). Precipitated material was collected by filtration. Purification by centrifugation with MeOH × 2 gave PQXphos(**L10**-**L12**) as fibriform solid. See Table S1 for the yields and the GPC data for the obtained polymers.

***Table S1*.** the yields and the GPC data for the PQXphos

entry	PQXphos	% Yield (2 steps)	M_n[a]	M_w/M_n[a]
1	**L10**	89	1.6×10^5	1.30
2	**L11**	83	1.5×10^5	1.39
3	**L12**	82	1.9×10^5	1.34

[a] Determined by GPC (polystyrene standard).

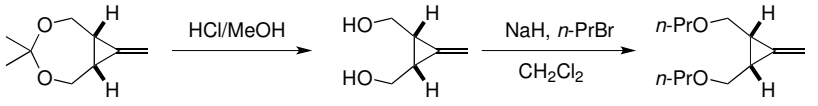
L10: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0-6.0, (brm, peak top; 0.90, 1.60, 2.35, 3.47, 4.58 (24*x*+3*y*)H), 6.4-8.4 (brm, 16*y*H); ^{31}P NMR (160 MHz, $CDCl_3$) δ -15.6 (brs)

L11: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0-6.0, (brm, peak top; 0.90, 1.60, 2.35, 3.46, 4.56 (24*x*+3*y*)H), 6.4-8.4 (brm, 20*y*H); ^{31}P NMR (160 MHz, $CDCl_3$) δ -14.3 (brs)

L12: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0-6.0, (brm, peak top; 0.90, 1.60, 2.35, 3.46, 4.58 (24*x*+15*y*)H), 6.4-8.4 (brm, 12*y*H); ^{31}P NMR (200 MHz, $CDCl_3$) δ -15.6 (brs)

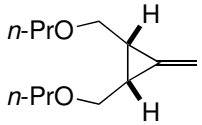
2.3 Preparation of Methylenecyclopropane 2g

Methylenecyclopropane **2g** was prepared according to *Scheme S2*.



2d **2g** 70% yield (2 step)

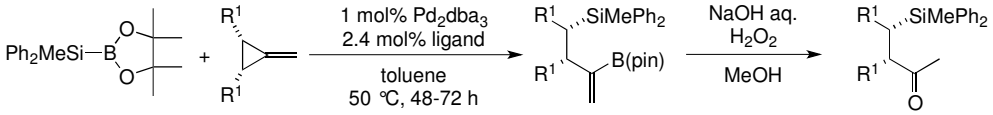
***Scheme S2*. Synthesis of Methylenecyclopropane 2g**



Synthesis of *meso*-1-methylene-2,3-bis(propoxymethyl)cyclopropane (2g): In a 30 mL of round-bottom flask, **2d**[S1] (925 mg, 6 mmol) and 0.5 M HCl/MeOH solution (10 mL) were

charged. The mixture was stirred at room temperature. After stirring for 2 h, 1 mL of Et_3N was added and the solution was diluted with Et_2O. The resulting mixture was passed through a pad of Celite® to remove the solid materials. The solution was concentrated and the residue was dissolved in DMF. NaH (432 mg, 18 mmol) was added to the solution at 0 °C. The mixture was stirred at 0 °C for 30 min, then 1-bromopropane (2.21 g, 18 mmol) was added to the mixture. The mixture was stirred at room temperature for 24 h, then water was added to the mixture. The mixture was washed with water and brine, and dried over Na_2SO_4. After evaporation of the volatiles, the residue was subjected to silica gel column chromatography (hexane:Et_2O = 20:1), giving the title compound **2g** (832 mg, 70% yield).: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (t, J = 2.4 Hz, 2H), 3.48 (dd, J = 5.2 Hz, 2.4 Hz, 4H), 3.39 (ddt, J = 7.2 Hz, 5.2 Hz, 2.4 Hz, 4H), 1.97 (sex, J = 2.4 Hz, 2H), 1.60 (sep, J = 7.2 Hz, 4H), 0.92 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 104.0, 72.3 (2C), 68.7 (2C), 22.9 (2C), 19.7 (2C), 10.6 (2C); IR (ATR) 2934, 2854, 1466, 1364, 1094, 1045, 889 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{22}O_2$+H (M+H$^+$): 199.1698, found: 199.1690

2.4 Asymmetric Silaborative C-C Cleavage of meso-MCPs using PQXphos (*P*)-L1-3 as chiral ligands (Table 1)

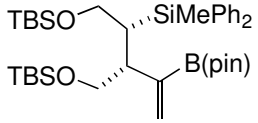


1 **2** **3** **4**

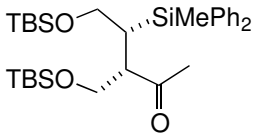
General procedure: To a solution of PQXphos (4.8 μmol phosphorous atom) in toluene (200 μL) was added Pd_2dba_3 (0.01 M in toluene, 200 μL, 2 μmol). The mixture was stirred at room temperature for 5 min. To the mixture was added **2** (0.30 mmol) and **1** (0.20 mmol) in this order, and the resulting mixture was heated at 50 °C with stirring. The reaction was monitored by GC. After the reaction was completed (48-72 h), subsequent addition of MeCN (10 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was isolated by silica gel column chromatography to give a 2-boryl-4-silyl-1-butene derivative. To determine the enantiomeric excess, the silylated alkenylborane obtained was converted to β-silyl ketone. To a methanol solution (2 mL) of the 2-boryl-4-silyl-1-butene derivative was added aqueous NaOH solution (3N, 2.5 mL) and the mixture was cooled to 0 °C. Aqueous H_2O_2 solution (30% 1.5 mL) was slowly added to the mixture. The resulting solution was stirred at room temperature for 12 h. The resulting mixture was extracted with Et_2O and the extracts were washed with water. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by PTLC to give a β-silyl ketone. Enantiomeric excess of this compound was determined by HPLC analysis.

2.5 Spectral Data for New Compounds

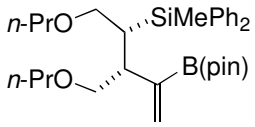
Compuonds **3a-e** were characterized by comparing their spectral data with those reported earlier[S1c].



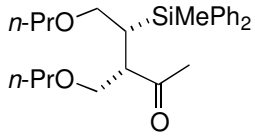
(2*R*,3*R*)-1,4-bis[(*tert*-butyldimethylsilyl)oxy]-(2-methyldiphenylsilyl)-3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]butane (3f): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.65 (m, 2H), 7.57-7.61 (m, 2H), 7.27-7.38 (m, 6H), 5.93 (d, *J* = 4.0 Hz, 1H), 5.60 (d, *J* = 3.5 Hz, 1H), 3.68 (dd, *J* = 9.5 Hz, 0.5 Hz, 1H), 3.55 (dd, *J* = 9.5 Hz, 0.5 Hz, 1H), 3.45 (dd, *J* = 10.0 Hz, 5.0 Hz, 1H), 3.41 (dd, *J* = 10.0 Hz, 10.0 Hz, 1H), 2.80 (ddd, *J* = 10.0 Hz, 5.0, 5.0 Hz, 1H), 1.84 (d, *J* = 11.0 Hz, 1H), 1.27 (s, 6H), 1.27 (s, 6H), 0.86 (d, *J* = 1.5 Hz, 1H), 0.74 (d, *J* = 1.5 Hz, 1H), 0.72 (d, *J* = 1.5 Hz, 1H), -0.12 (s, 3H), -0.16 (s, 3H), -0.21 (s, 3H), -0.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 137.9, 135.0 (2C), 134.5 (2C), 132.6, 128.6 (2C), 127.5 (2C), 127.4 (2C), 82.9 (2C), 66.2, 62.3, 48.8, 28.5, 26.0 (3C), 25.9 (3C), 24.9 (2C), 24.7 (2C), 18.3, 18.2, -4.0, -5.4, -5.5, -5.6, -5.7. The boron-bound carbon was not detected due to quadrupolar relaxation. ; HRMS (ESI) *m/z* calcd for $C_{37}H_{63}B_1O_4Si_3$+NH_4 (M^++NH_4): 684.4471, found: 684.4465; $[\alpha]^{24}_D$ +56.2 (c 0.821, CH_2Cl_2, 95% ee).



(3*S*,4*R*)-5-((*tert*-butyldimethylsilyl)oxy)-3-(((*tert*-butyldimethylsilyl)oxy)methyl)-4-(methyldiphenylsilyl)pentan-2-one (4f): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.85 (m, 4H), 7.57-7.62 (m, 6H), 3.86 (d, *J* = 3.5 Hz, 2H), 3.73 (dd, *J* = 10.0 Hz, 5.0 Hz, 1H), 3.62 (dd, *J* = 10.0 Hz, 10.0 Hz, 1H), 3.49 (ddd, *J* = 10.0 Hz, 10.0 Hz, 5.0 Hz, 1H), 2.44 (s, 3H), 2.11-2.15 (m, 1H), 1.10 (s, 9H), 0.99 (s, 9H), 0.98 (s, 3H), 0.14 (s, 3H), 0.09 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.7, 137.1, 136.0, 134.7 (2C), 134.3 (2C), 129.2 (2C), 127.9 (2C), 127.8 (2C), 66.4, 62.9, 62.0, 53.5, 32.9, 28.8, 25.9 (3C), 25.7 (3C), 18.2, 18.1, -4.6, -5.8, -5.9, -5.9; IR (ATR) 2953, 2928, 2856, 1714, 1472, 1427, 1252, 1082, 833, 775, 698 cm^{-1}; HRMS (FAB) *m/z* calcd for $C_{31}H_{53}O_3Si_3$+H (M^++H): 557.3303, found: 557.3290; $[\alpha]^{24}_D$ +33.9 (c 0.902, CH_2Cl_2, 95% ee)



(2*R*,3*R*)-1,4-dipropoxy-(2-methyldiphenylsilyl)-3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]butane (3g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.66 (m, 2H), 7.56-7.59 (m, 2H), 7.31-7.36 (m, 3H), 7.27-7.31 (m, 3H), 5.88 (d, *J* = 3.6 Hz, 1H), 5.63 (d, *J* = 3.6 Hz, 1H), 3.40 (dd, *J* = 8.8 Hz, 2.8 Hz, 1H), 3.37 (dd, *J* = 9.6 Hz, 9.6 Hz, 1H), 3.30 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 3.14 (dd, *J* = 8.8 Hz, 3.6 Hz, 1H), 3.03 (dt, *J* = 8.8 Hz, 1.2 Hz, 2H), 2.84-3.00 (m, 3H), 1.80 (dt, *J* = 10.4 Hz, 2.8 Hz, 1H), 1.50-1.56 (m, 2H), 1.30-1.35 (m, 2H), 1.27 (s, 6H), 1.27 (s, 6H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.74 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.0, 135.1 (2C), 134.6 (2C), 131.3, 128.5 (2C), 127.4 (2C), 127.3 (2C), 82.9 (2C), 73.6, 72.2, 71.8, 69.9, 46.5, 26.9, 24.8 (2C), 24.8 (2C), 23.1, 22.5, 11.0, 10.5, -3.9. The boron-bound carbon was not detected due to quadrupolar relaxation. ; IR (ATR) 2981, 2934, 2858, 1427, 1360, 1304, 1140, 1105, 788, 698 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{37}H_{63}B_1O_4Si_3$+H (M^++H): 523.3415, found: 523.3402; $[\alpha]^{24}_D$ +66.7 (c 1.1080, CH_2Cl_2, 95% ee)



(3*S*,4*R*)-4-(methyldiphenylsilyl)-5-propoxy-3-(propoxymethyl)pentan-2-one (4g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.60 (m, 4H), 7.30-7.38 (m, 6H), 3.20-3.51 (m, 5H), 2.93-3.14 (m, 4H), 2.16 (s, 3H), 1.92 (sep, *J* = 3.2 Hz, 1H), 1.52 (sex, *J* = 2.8 Hz, 2H), 1.36 (sex, *J* = 2.8 Hz, 2H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.2, 136.7, 136.1, 134.8 (2C), 134.5 (2C), 129.2, 129.1, 127.8 (2C), 127.7 (2C), 72.6, 72.5, 72.4, 70.2, 51.3, 31.9, 26.7, 22.9, 22.5, 10.8, 10.4, -4.3; IR (ATR) 2960, 2934, 2862, 1714, 1472, 1427, 1105, 790, 734, 698 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{25}H_{36}O_3Si$+H (M^++H): 413.2512, found: 413.2506; $[\alpha]^{25}_D$ +32.2 (c 0.982, CH_2Cl_2, 95% ee)

2.6 Use of Inverted PQxphos (*M*)-(*R*,*R*)-L3 as a Ligand for Asymmetric Silaboration of *meso*-MCP 2a (Scheme 1)

(*P*)-(*R*,*R*)-**L3** (16.1 mg, 2.4 μmol phosphorus atom) in 1,1,2-trichloroethane (0.3 mL) and toluene (0.1 mL) was stirred at 60 °C for 24 h. To the mixture was added Pd_2dba_3 (0.01 M in 1,1,2-trichloroethane / toluene = 3/1, 100 μL, 1 μmol), and the solution was stirred at room temperature for 10 min. After evaporation of the mixture, the residue was added 1,1,2-trichloroethane (30 μL), **2a** (0.15 mmol, 16.2 mg), and **1** (0.1 mmol, 32.4 mg). The

mixture was stirred at 50 °C for 48 h. Subsequent addition of MeCN (10 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was isolated by silica gel column chromatography to give a 2-boryl-4-silyl-1-butene derivative. To determine the enantiomeric excess, the silylated alkenylborane obtained was converted to *β*-silyl ketone. To a methanol solution (2 mL) of the 2-boryl-4-silyl-1-butene derivative was added aqueous NaOH solution (3N, 2.5 mL) and the mixture was cooled to 0 °C. Aqueous H_2O_2 solution (30% 1.5 mL) was slowly added to the mixture. The resulting solution was stirred at room temperature for 12 h. The resulting mixture was extracted with Et_2O and the extracts were washed with water. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by PTLC to give a *β*-silyl ketone. The enantiomeric excess of this compound was determined by HPLC analysis.

2.7 Asymmetric Silaborative C-C Cleavage of *meso*-MCP 1f in the Presence of Various Phosphine Ligands (Table 2)

2.7.1: Silaboration of MCP using low-molecular phosphine ligands (entry 1-3, Table 2)

To a solution of ligand (2.4 *μ*mol phosphorous atom) in toluene (100 *μ*L) was added Pd_2dba_3 (0.01 M in toluene, 100 *μ*L, 1 *μ*mol). The mixture was stirred at room temperature for 5 min. To the mixture was added **2f** (0.15 mmol) and **1** (32.4 mg, 0.10 mmol) in this order, and the resulting mixture was heated at 50 °C with stirring. After 48 h, the volatile materials were evaporated. The residue was analyzed by NMR (internal standard: o-xylylene oxide).

2.7.2: Silaboration of MCP using PQXphos (entry 4-9, Table 2)

To a solution of PQXphos (2.4 *μ*mol phosphorous atom) in toluene (100 *μ*L) was added Pd_2dba_3 (0.01 M in toluene, 100 *μ*L, 1 *μ*mol). The mixture was stirred at room temperature for 5 min. To the mixture was added **2f** (0.15 mmol) and **1** (32.4 mg, 0.10 mmol) in this order, and the resulting mixture was heated at 50 °C with stirring for 48 h. Subsequent addition of MeCN (10 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. After evaporation of the volatiles, the residue was analyzed by NMR (internal standard: *o*-xylylene oxide). To determine the enantiomeric excess, the silylated alkenylborane obtained was converted to *β*-silyl ketone. To a methanol solution (2 mL) of the 2-boryl-4-silyl-1-butene derivative was added aqueous NaOH solution (3N, 2.5 mL) and the mixture was cooled to 0 °C. Aqueous H_2O_2 solution (30% 1.5 mL) was slowly added to the mixture. The resulting solution was stirred at room temperature for 12 h. The resulting mixture was extracted with Et_2O and the extracts were washed with water. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by PTLC to give a *β*-silyl ketone. The enantiomeric excess of this compound was determined by HPLC analysis.

2.8 Dependence of Time Course of Silaboration of *meso*-MCP 1a on Phosphine Ligands (Table 3)

2.8.1: Silaboration of MCP using phosphine ligands (entry 1-7, Table 3)

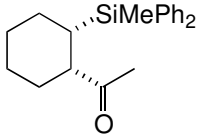
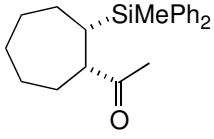
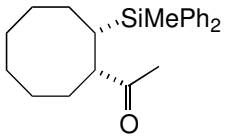
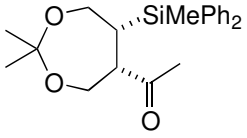
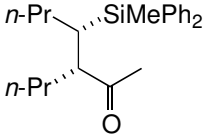
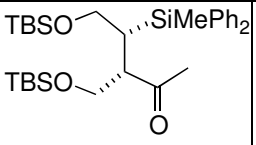
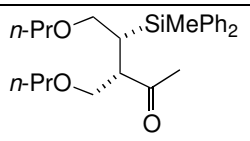
To a solution of ligand (2.4 μmol phosphorous atom) in toluene (100 μL) was added Pd_2dba_3 (0.01 M in toluene, 100 μL, 1 μmol). The mixture was stirred at room temperature for 5 min. To the mixture was added **2a** (0.15 mmol) and **1** (32.4 mg, 0.10 mmol) in this order, and the resulting mixture was heated at 50 °C with stirring. The mixture was analyzed by GC (internal standard: *n*-tetradecane 30 μL). After 120 h, the crude product was isolated by silica gel column chromatography to give a 2-boryl-4-silyl-1-butene derivative. To determine the enantiomeric excess, the silylated alkenylborane obtained was converted to β-silyl ketone. To a methanol solution (2 mL) of the 2-boryl-4-silyl-1-butene derivative was added aqueous NaOH solution (3N, 2.5 mL) and the mixture was cooled to 0 °C. Aqueous H_2O_2 solution (30% 1.5 mL) was slowly added to the mixture. The resulting solution was stirred at room temperature for 12 h. The resulting mixture was extracted with Et_2O and the extracts were washed with water. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by PTLC to give a β-silyl ketone. The enantiomeric excess of this compound was determined by HPLC analysis.

2.8.2: Silaboration of MCP using PQXphos (entry 8-13, Table 3)

To a solution of PQXphos (2.4 μmol phosphorous atom) in toluene (100 μL) was added Pd_2dba_3 (0.01 M in toluene, 100 μL, 1 μmol). The mixture was stirred at room temperature for 5 min. To the mixture was added **2** (0.15 mmol) and **1** (32.4 mg, 0.10 mmol) in this order, and the resulting mixture was heated at 50 °C with stirring. The mixture was analyzed by GC (internal standard: *n*-tetradecane 30 μL). Subsequent addition of MeCN (10 mL) resulted in precipitation of the PQXphos. The suspension was passed through a pad of Celite® using MeCN as an eluent. The crude product was isolated by silica gel column chromatography to give a 2-boryl-4-silyl-1-butene derivative. To determine the enantiomeric excess, the silylated alkenylborane obtained was converted to β-silyl ketone. To a methanol solution (2 mL) of the 2-boryl-4-silyl-1-butene derivative was added aqueous NaOH solution (3N, 2.5 mL) and the mixture was cooled to 0 °C. Aqueous H_2O_2 solution (30% 1.5 mL) was slowly added to the mixture. The resulting solution was stirred at room temperature for 12 h. The resulting mixture was extracted with Et_2O and the extracts were washed with water. After drying with anhydrous $MgSO_4$, the concentrated mixture was purified by PTLC to give a β-silyl ketone. The enantiomeric excess of this compound was determined by HPLC analysis.

3. Determination of the Enantiomeric Excesses of the Products by HPLC with a Chiral Stationary Phase

Table S2. HPLC separation conditions and retention times of β-silyl ketones

entry	Compound **4**	column	Eluent: *i*-PrOH/Hexane	Flowrate (mL/min)	t_R of (+)-isomer (min)	t_R of (-)-isomer (min)
1	 **4a**	OD-H	0.3%	0.6	15.7	13.2
2	 **4b**	OD-H	0.5%	0.6	9.0	10.1
3	 **4c**	OD-H	0.3%	0.6	23.6	17.9
4	 **4d**	OD-H	1.0%	0.6	11.5	14.1
5	 **4e**	OZ-H	0.3%	0.6	19.6	22.0
6	 **4f**	OZ-H	0.2%	0.6	10.2	9.4
7	 **4g**	OZ-H	0.3%	1.0	19.4	14.3

4. References

[S1] (a) Arora, S.; Binger, P. *Synthesis* **1974**, 801.

(b) Kitatani, K.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3288.

(c) Ohmura, T.; Taniguchi, H.; Kondo, Y.; Suginome, M. *J. Am. Soc. Chem.* **2007,** *129,* 3518.

(d) Ohmura, T.; Taniguchi, H.; Suginome, M. *J. Am. Soc. Chem.* **2009,** *131,* 11298.

[S2] Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **2000**, *19*, 4647.

[S3] Yamamoto, T.; Akai, Y.; Nagata, Y.; Suginome, M. *Angew. Chem., Int. Ed.* **2011,** *50,* 8844.

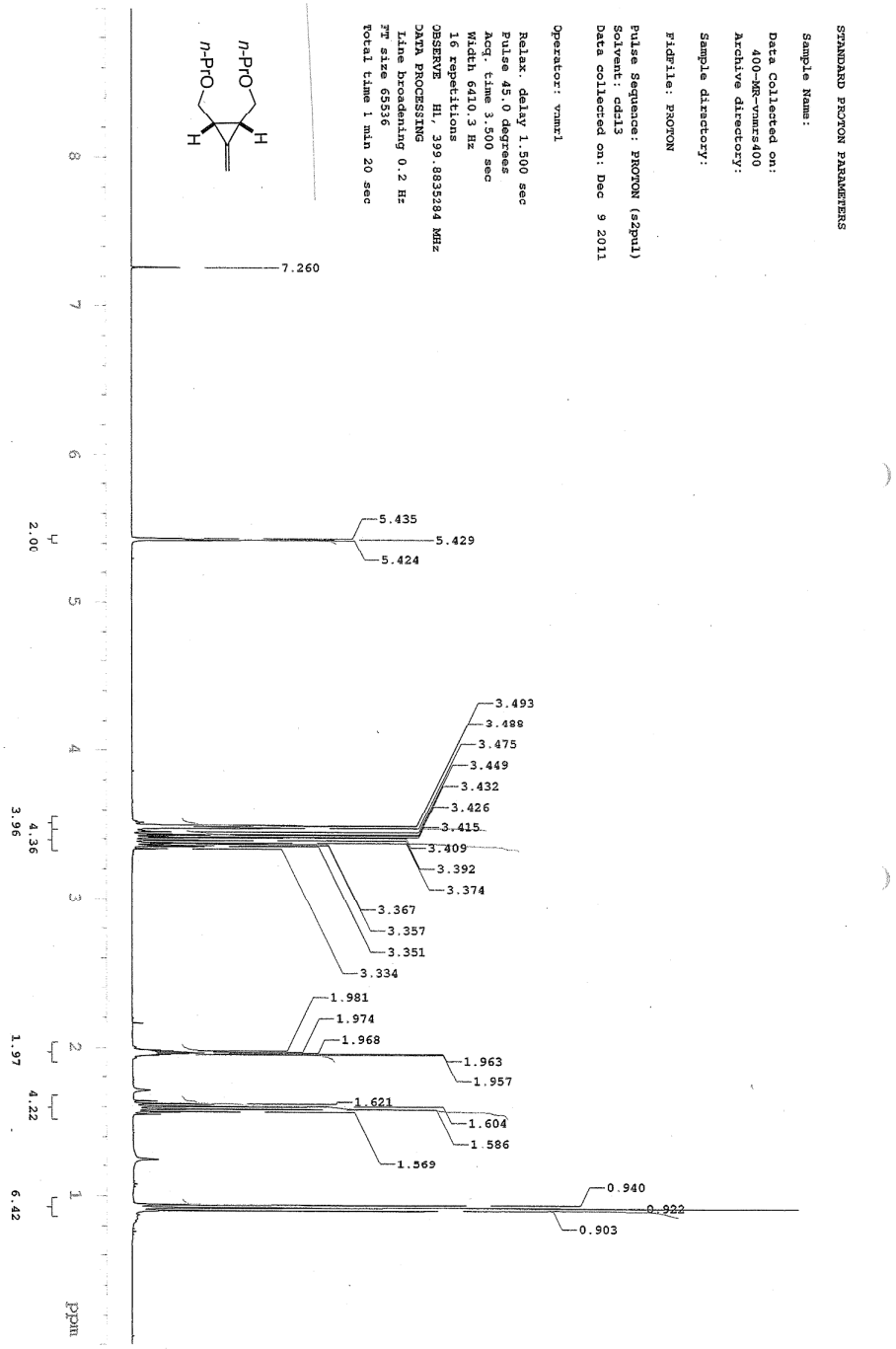
[S4] Iwasawa, T.; Komano, T.; Tajima, A.; Tokunaga, M.; Obora, Y.; Fujihara, T.; Tsuji, Y. *Organometallics* **2006**, *25*, 4665.

[S5] Ohta, H.; Tokunaga, M.; Obora, Y.; Iwai, T.; Iwasawa, T.; Fujihara, T.; Tsuji, Y. *Org. Lett.* **2007**, *9*, 89.

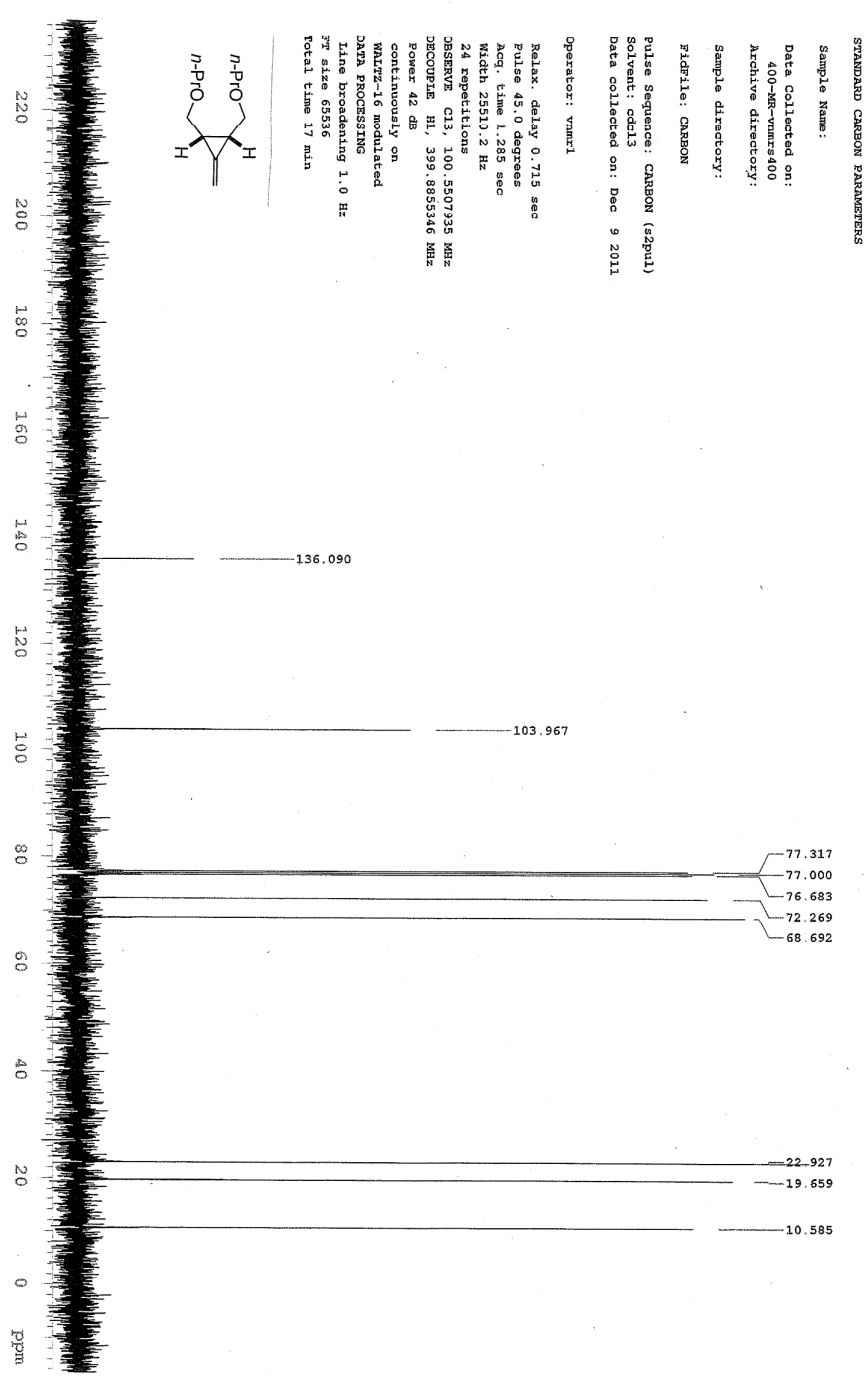
[S6] Yamada, T; Noguchi, H.; Nagata, Y.; Suginome, M. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 898.

[S7] Yamamoto, T.; Suginome, M. *Angew. Chem., Int. Ed.* **2009,** *48,* 539.

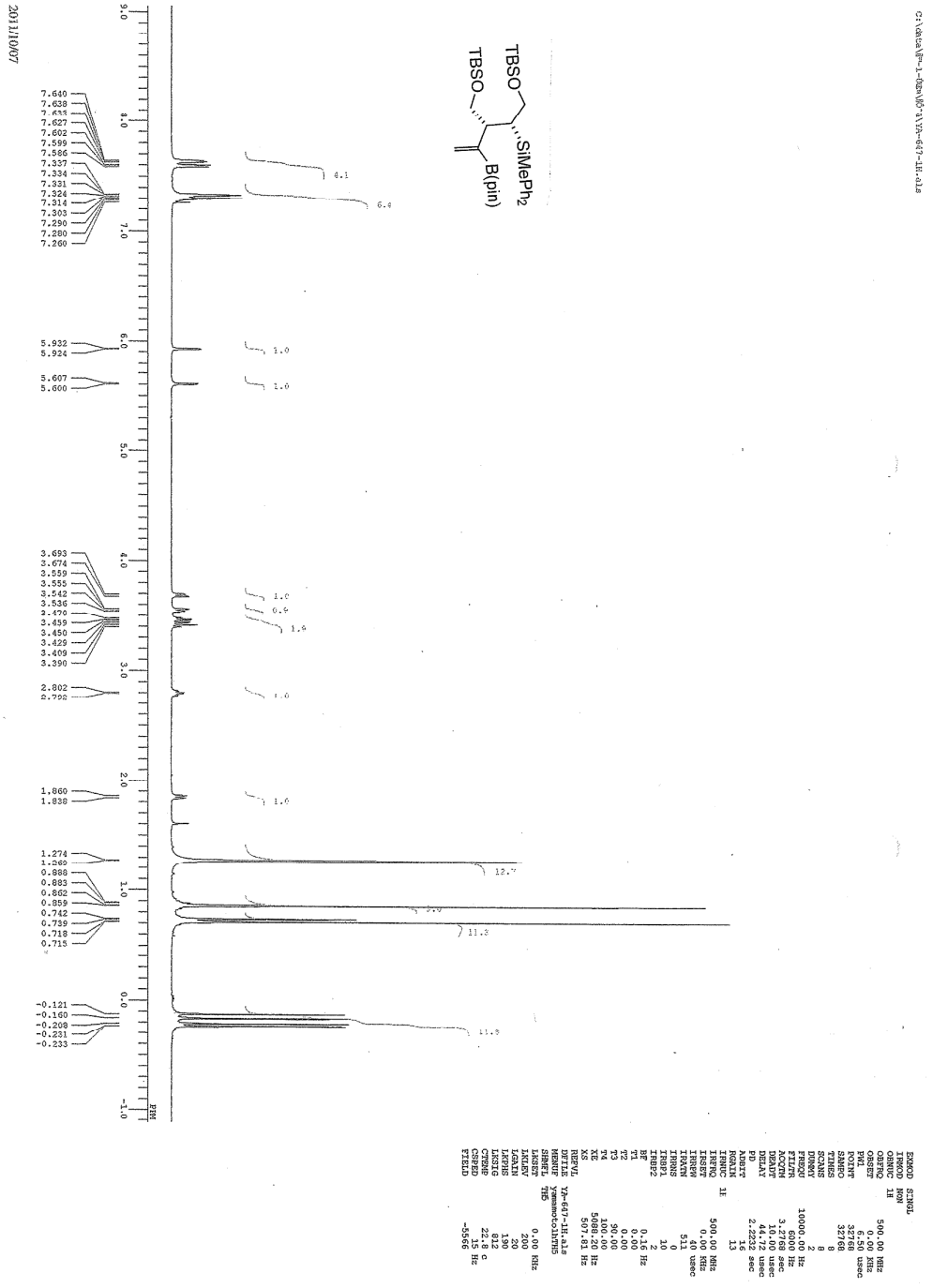
5. NMR Spectra of New Compounds



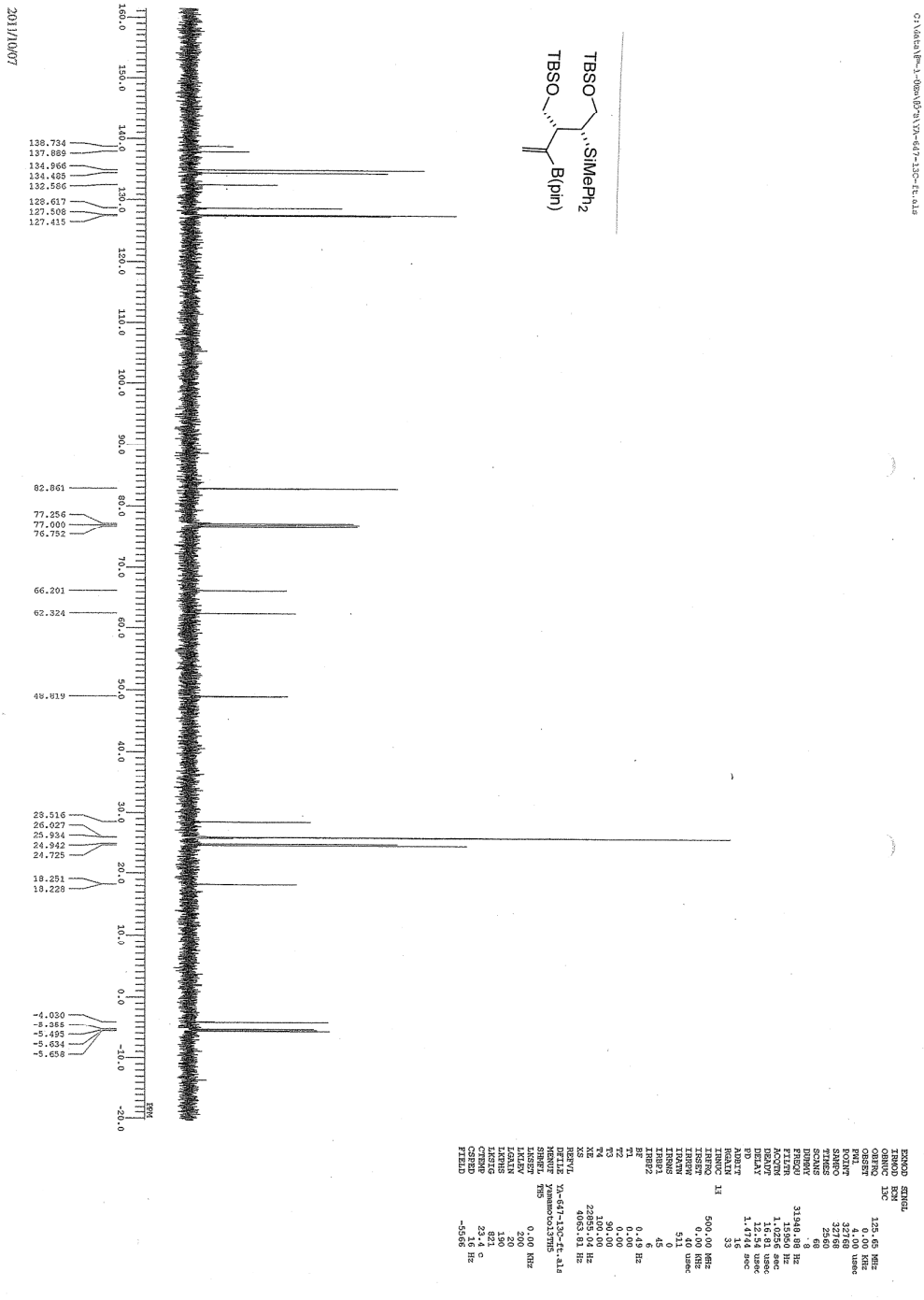
^{1}H NMR of compound **2g**



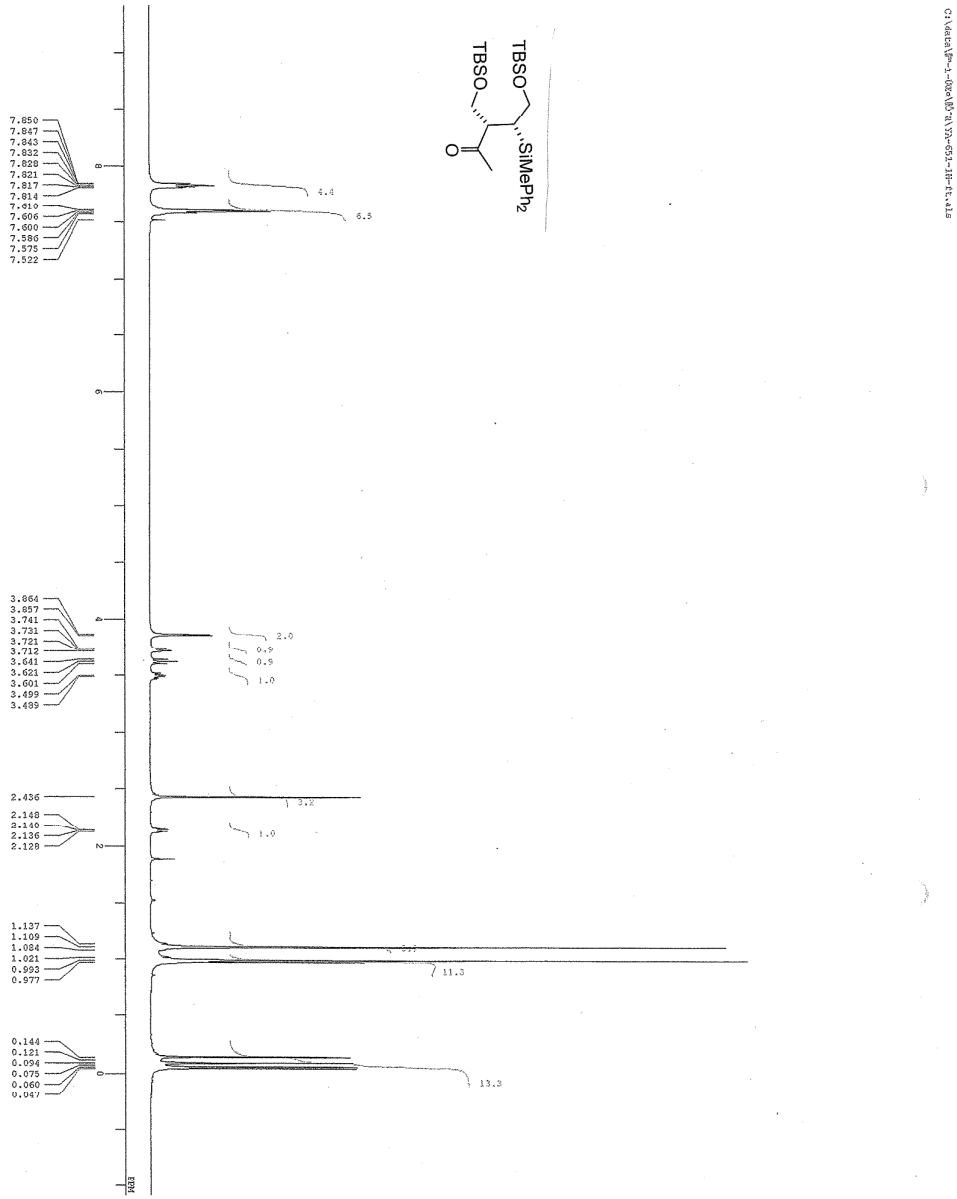
^{13}C NMR of compound **2g**



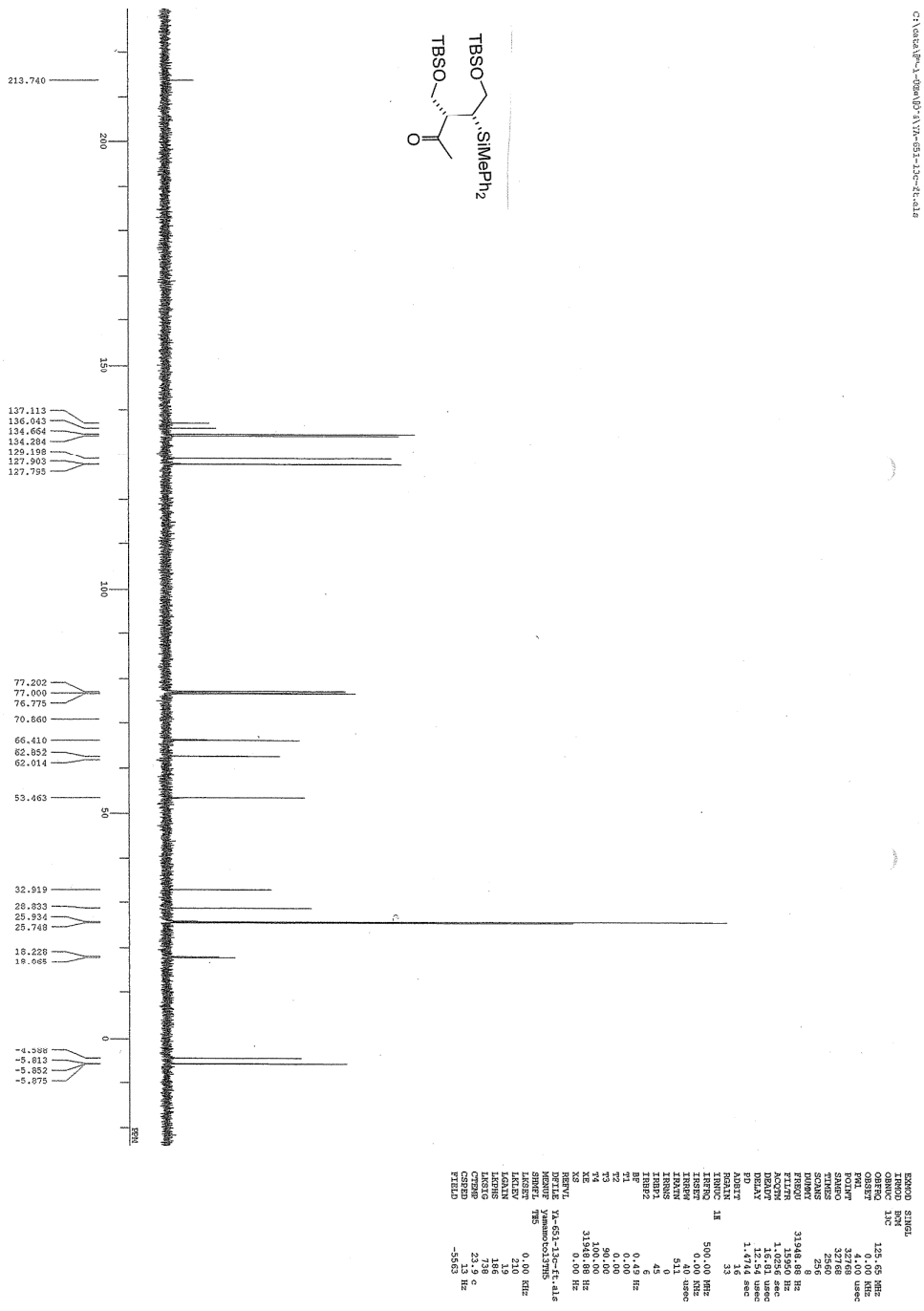
^{1}H NMR of compound **3f**



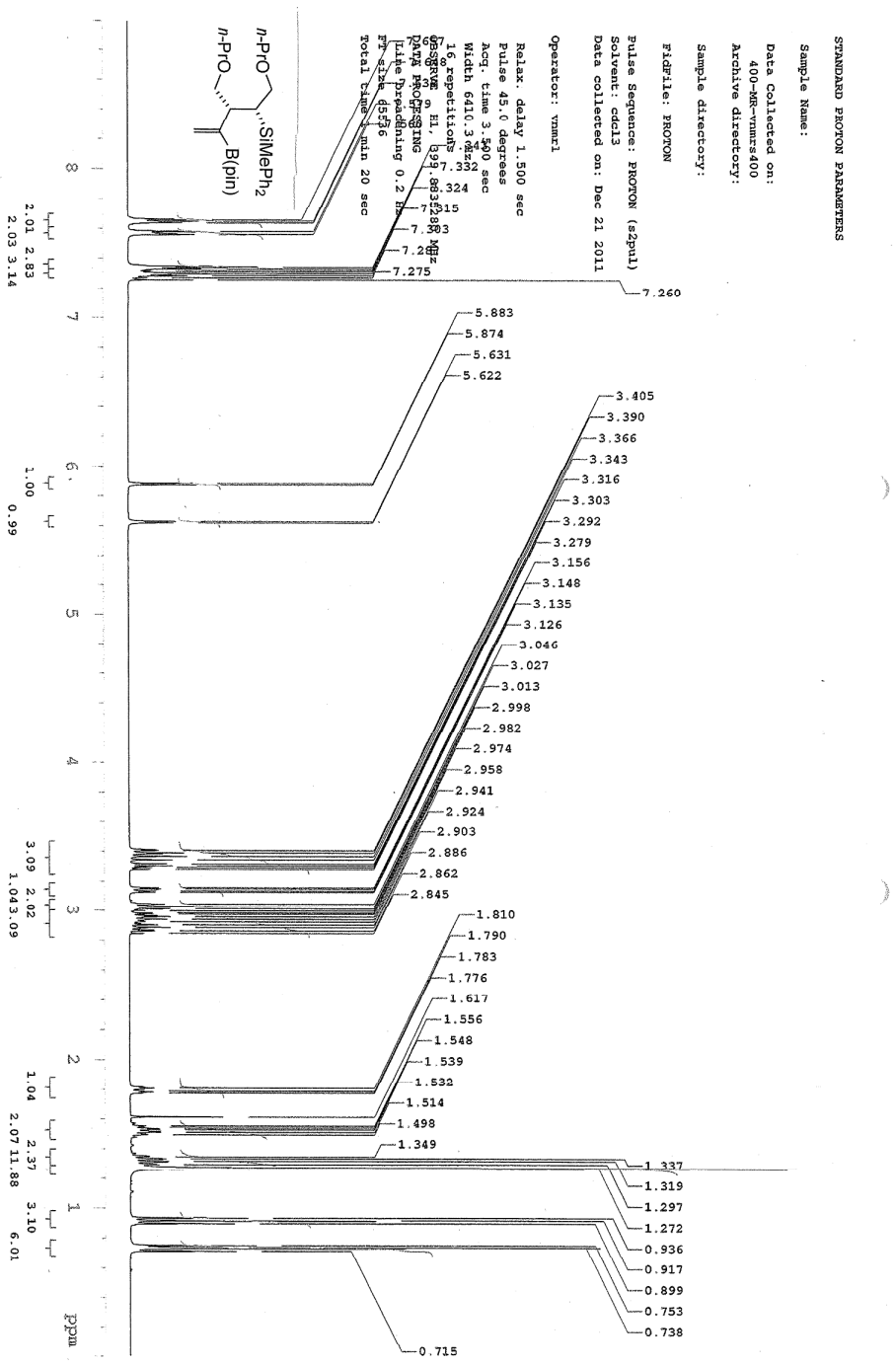
^{13}C NMR of compound **3f**



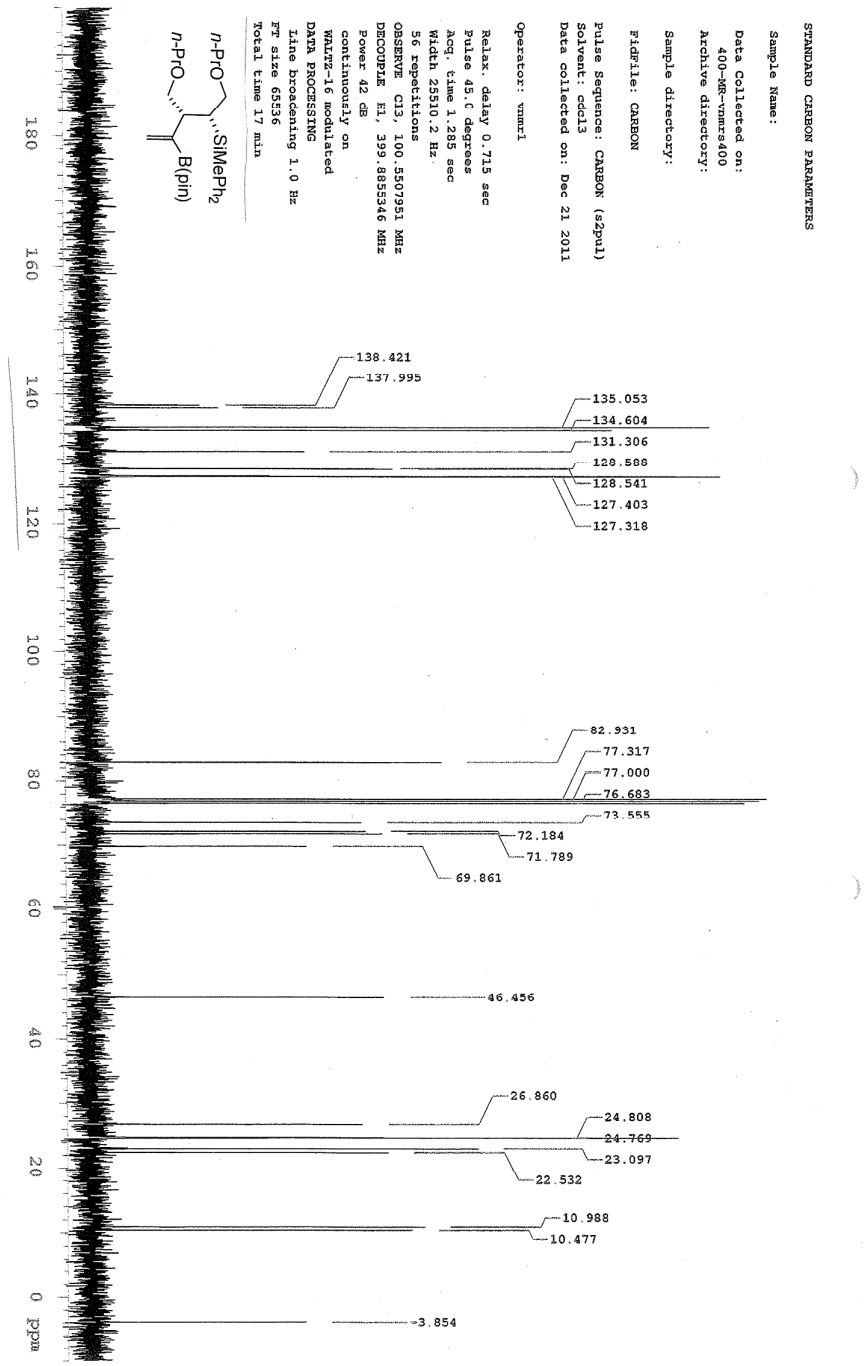
^{1}H NMR of compound **4f**



^{13}C NMR of compound **4f**



^{1}H NMR of compound **3g**



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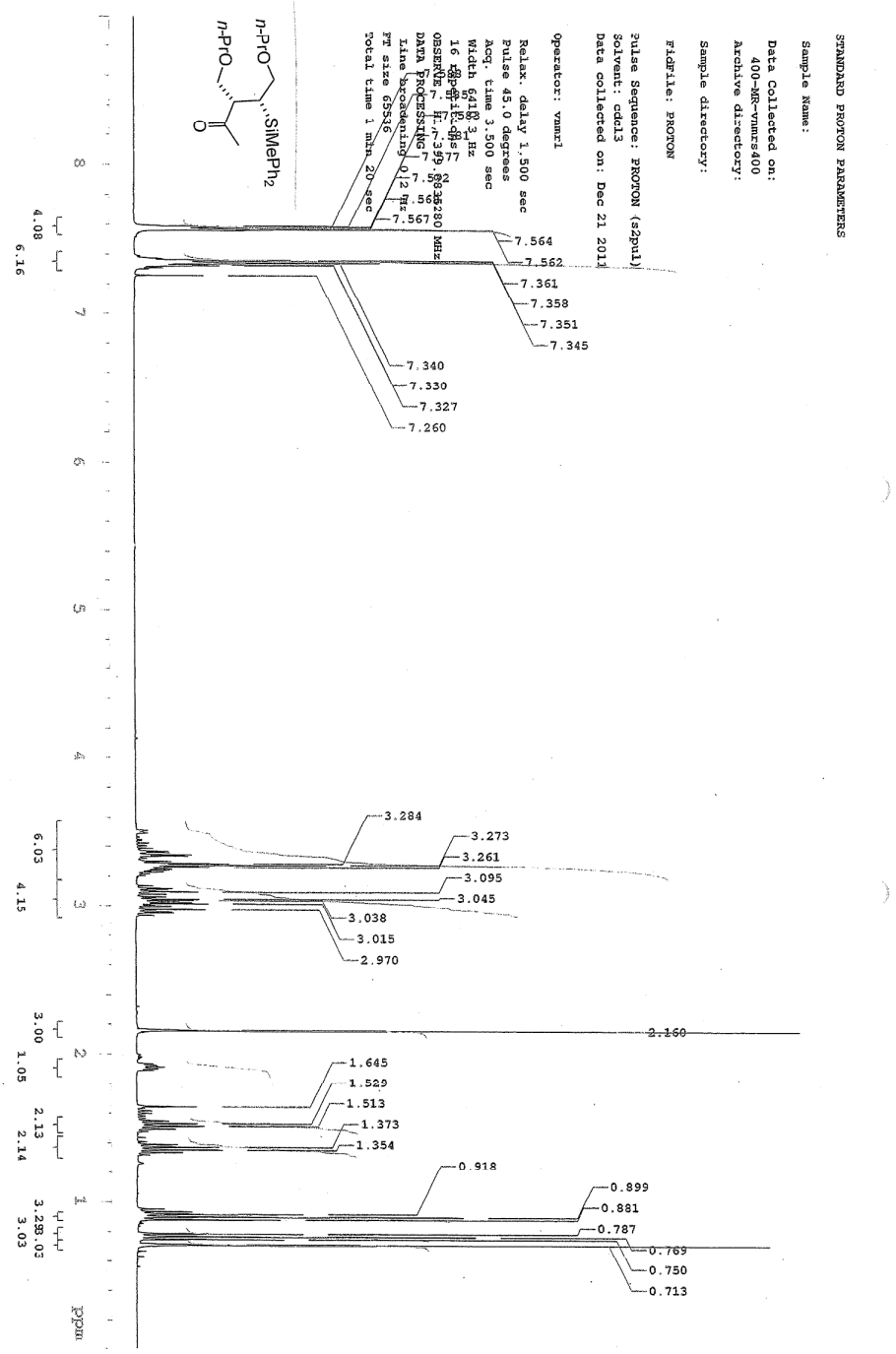
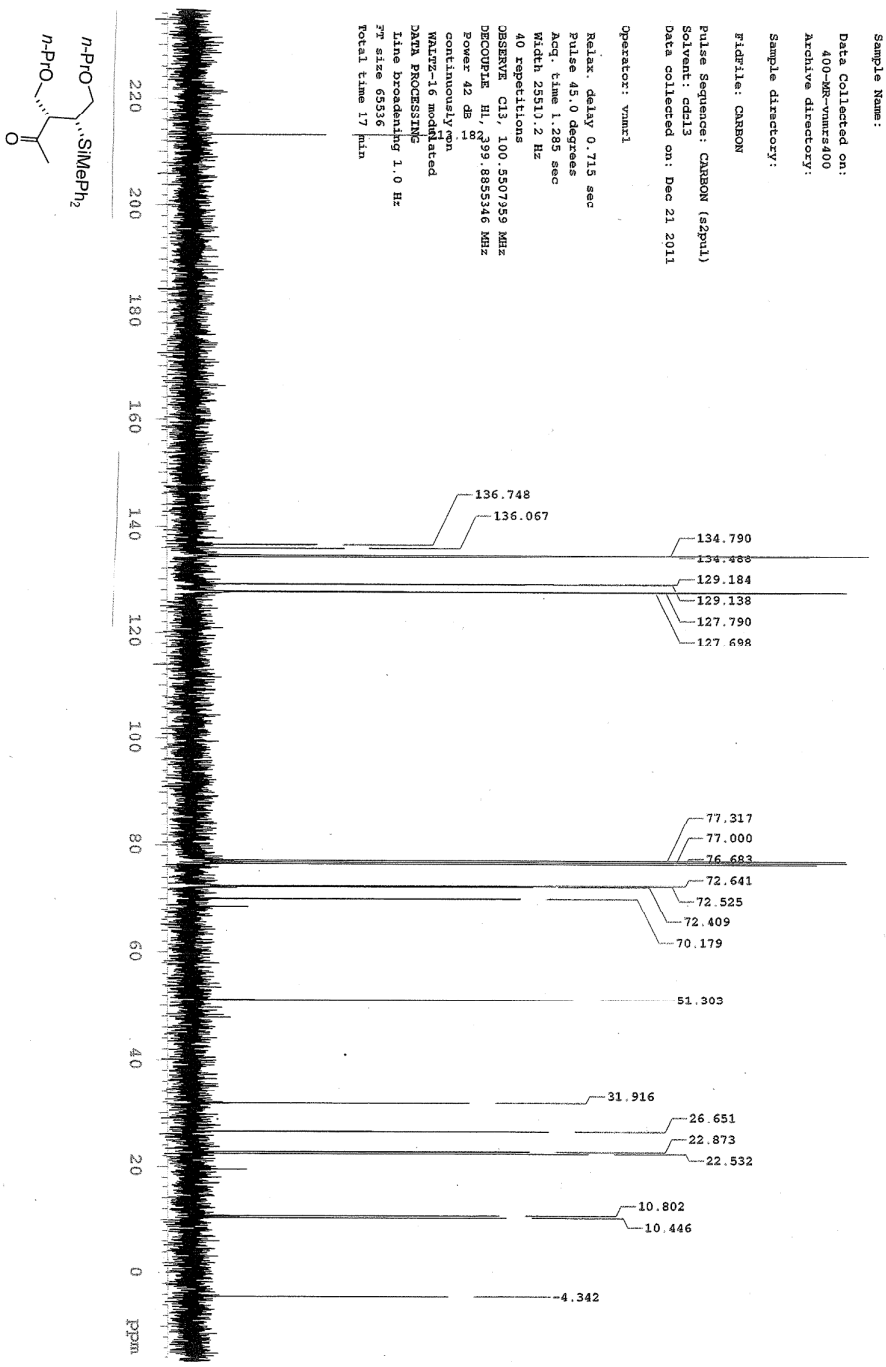


^{1}H NMR of compound **4g**



^{13}C NMR of compound **4g**

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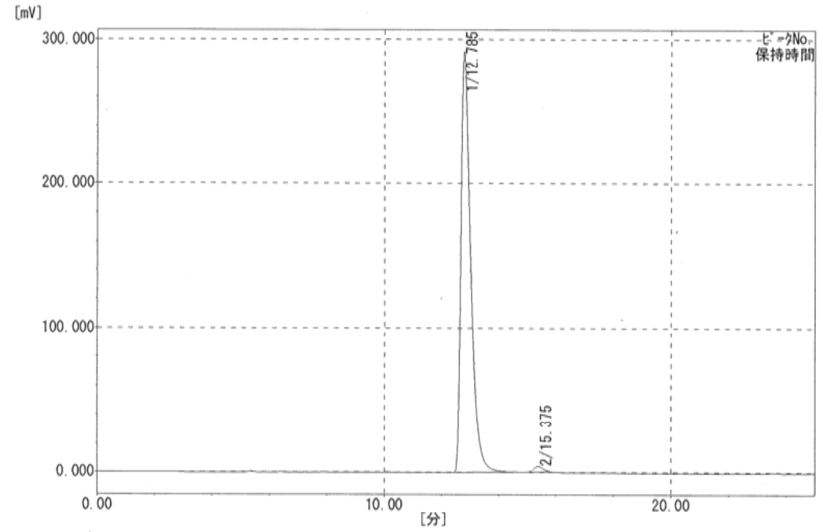
収集属性　　：独立　0.00 - 25.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	12.785	292.17	20.53	6786.22	98.68	7735	0.00	2.38
2	1	15.375	3.87	22.58	90.96	1.32	9250	4.25	1.38

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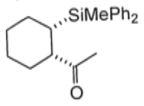

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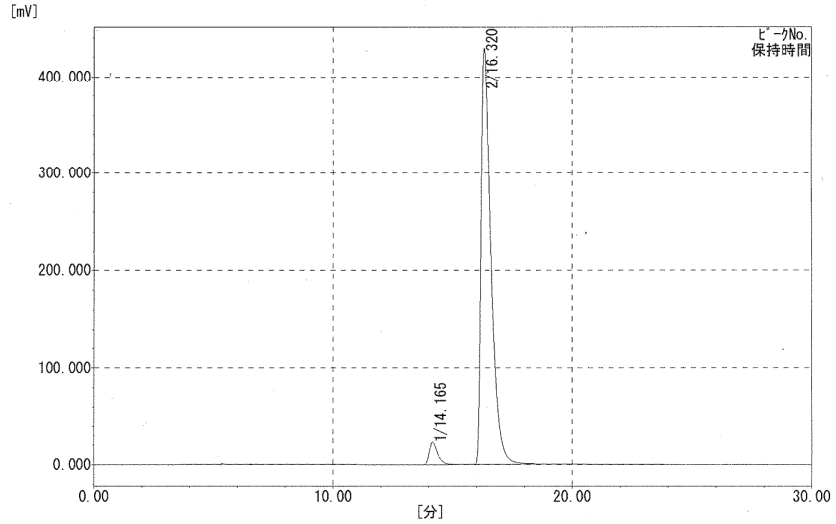
HPLC trace for **4a**

タイトル　　：
データ　　：C:¥HPLCData¥data_akai.mdb　CLC-0612　YA-801
日時　　：収集 2012/01/24 16:46:51　計算 2012/06/05 16:11:36
カップ番号　：27
収集属性　　：独立　0.00 - 30.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	14.165	22.93	21.62	566.20	4.37	8560	0.00	1.82
2	1	16.320	429.16	25.74	12402.67	95.63	8019	3.22	2.68

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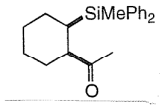

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HPLC trace for *ent*-**4a** (Scheme 1)

タイトル　　：
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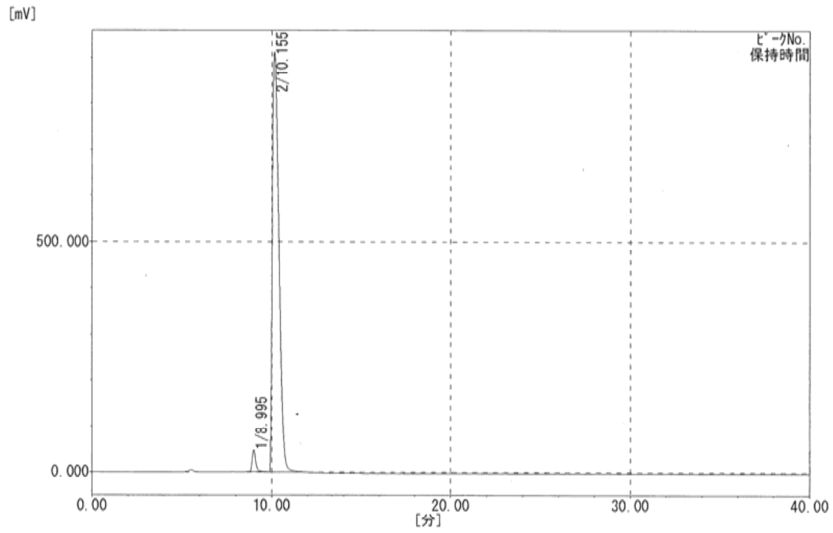
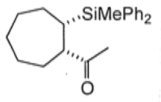
日時　　：収集 2011/07/06 18:26:11　計算 2012/06/01 16:57:51
カップ番号　：9
収集属性　　：独立　0.00 - 40.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	8.995	47.33	11.98	652.26	2.70	11237	0.00	1.48
2	1	10.155	913.50	24.71	23525.97	97.30	3368	2.23	2.53

CH.1 Peak Not Found.



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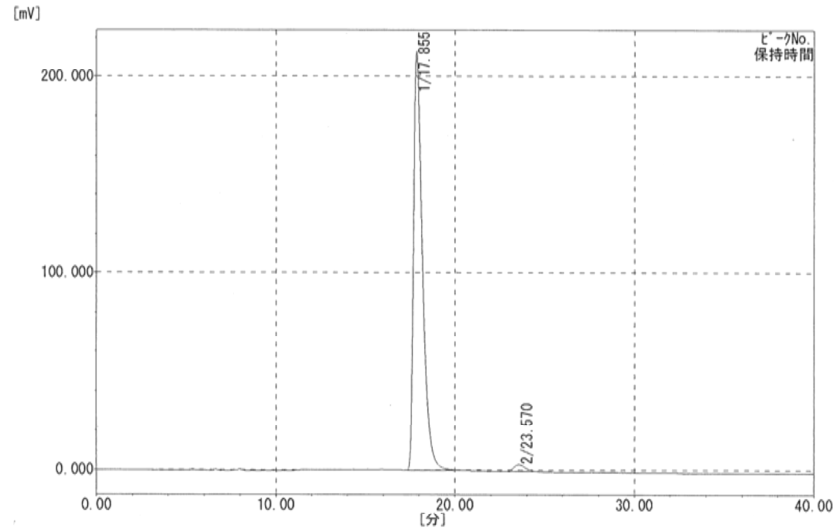
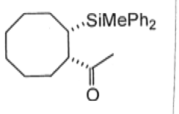
HPLC trace for **4b**

タイトル　　：
データ　　：C:¥HPLCData¥data_akai.mdb　YN03970383　YA-560
日時　　：収集 2011/06/26 18:21:33　計算 2012/06/01 17:00:26
カップ番号　：59
収集属性　　：独立　0.00 - 40.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	17.855	213.34	30.85	7396.49	97.92	6680	0.00	2.29
2	1	23.570	3.53	41.87	157.22	2.08	6319	5.55	1.30

CH.1 Peak Not Found.



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HPLC trace for **4c**

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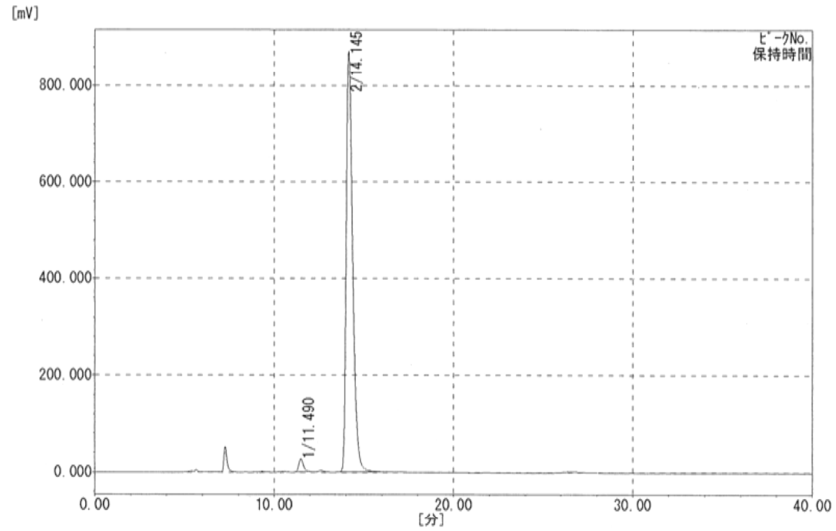
データ　　：C:¥HPLCData¥data_akai.mdb　YN03970400　YA-566
日時　　：収集 2011/07/06 21:45:56　計算 2012/06/01 16:56:21
カップ番号　：8
収集属性　　：独立　0.00 - 40.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	11.490	26.43	16.05	460.76	2.10	10216	0.00	1.32
2	1	14.145	872.52	22.25	21497.25	97.90	8060	4.90	1.84

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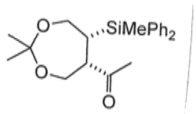

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HPLC trace for **4d**

タイトル　　：
データ　　：C:¥HPLCData¥data_akai.mdb　YN03970385　YA-559
日時　　：収集 2011/06/26 20:54:46　計算 2012/06/01 16:59:10
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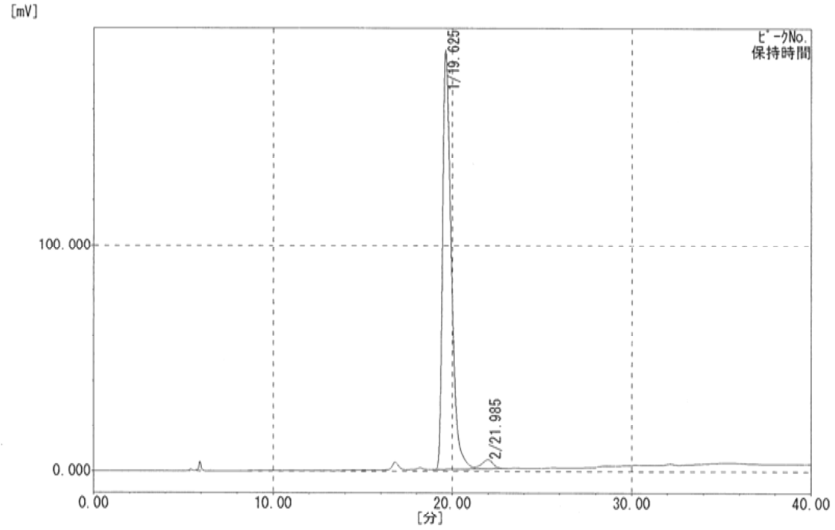
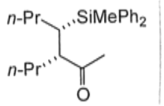
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	19.625	185.95	30.35	6262.46	97.26	8336	0.00	2.04
2	1	21.985	3.95	40.85	176.32	2.74	5777	2.34	0.00

CH.1 Peak Not Found.



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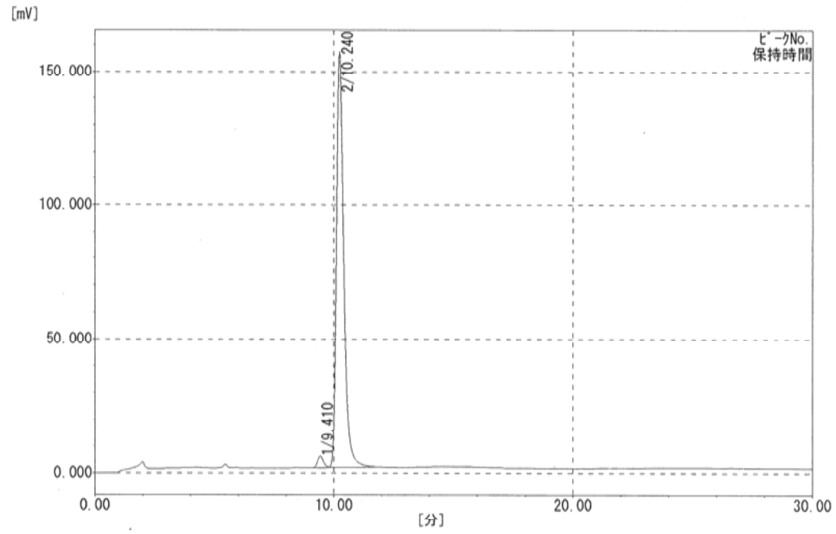
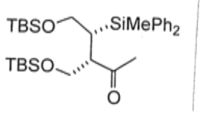
HPLC trace for **4e**

タイトル　　：
データ　　：C:¥HPLCData¥data_akai.mdb　YN03970565　b-silylketone
日時　　：収集 2011/12/05 14:41:45　計算 2012/06/01 17:07:52
カップ番号　：86
収集属性　　：独立　0.00 - 30.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	9.410	4.28	15.84	73.81	2.18	7037	0.00	1.49
2	1	10.240	155.48	18.92	3317.14	97.82	5841	1.69	1.52

CH.1 Peak Not Found.



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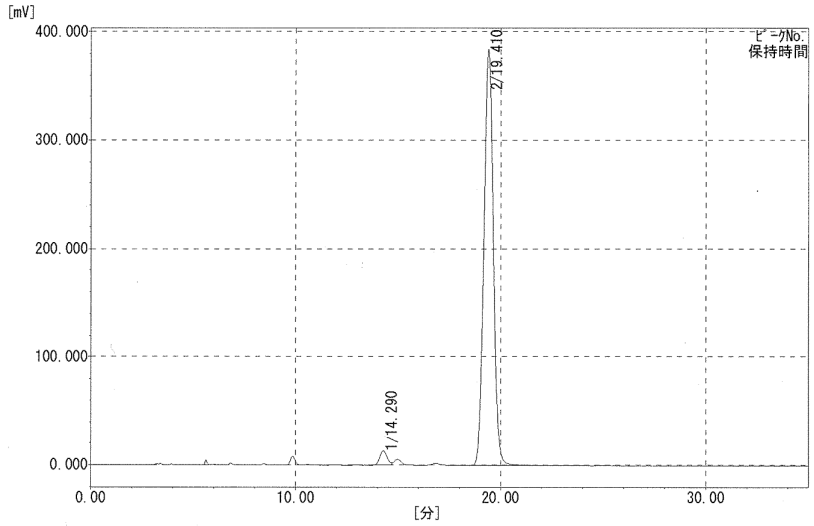
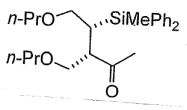
HPLC trace for **4f**

タイトル　　：
データ　　：C:¥HPLCData¥data_akai.mdb　CLC-0692　YA
日時　　：収集 2012/06/05 14:08:33　計算 2012/06/05 15:21:32
カップ番号　：96
収集属性　　：独立　0.00 - 35.00 min
計算方法　　：百分率法



No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	14.290	12.92	23.24	319.32	2.54	7538	0.00	0.00
2	1	19.410	384.39	29.49	12236.53	97.46	8638	6.86	1.05

CH.1 Peak Not Found.



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HPLC trace for **4g**