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Supporting Information

Ru(II)-Pheox-Catalyzed Si–H Insertion Reaction: Construction of Enantioenriched Carbon and Silicon Centers

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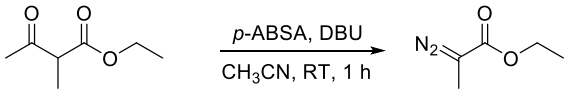
CONTENTS:

General: All reactions were performed under an atmosphere of argon unless otherwise noted. Dichloromethane (CH_2Cl_2) was purchased from Kanto Chemical Co., Inc.. All reactions were monitored by thin layer chromatography (TLC), glass plates pre-coated with silica gel Merck KGaA 60 F_{254}, layer thickness 0.2 mm. The products were visualized by irradiation with UV light or by treatment with a solution of phosphomolybdic acid or by treatment with a solution of *p*-anisaldehyde. Flash column chromatography was performed using silica gel (Merck, Art. No. 7734). ^{1}H NMR (500 MHz, 400 MHz) and ^{13}C NMR (125 MHz, 100 MHz) spectra were recorded on JEOL JNM-ECX500, JEOL JNM-ECS400 spectrometer. Chemical shifts are reported as δ values (ppm) relative to $CDCl_3$ (7.26 ppm). Elemental analyses were measured on a Yanaco CHN CORDER MT-6. Optical rotations were performed with a JASCO P-1030 polarimeter at the sodium D line (1.0 ml sample cell). Enantiomeric excesses were determined by high-performance liquid chromatography (HPLC) analyses with a JASCO GULLIVER using Daicel CHIRALPAK or CHIRALCEL columns. DART mass (positive mode) analyses were

performed on a LC-TOF JMS-T100LP.

1. Preparation of Various Functionalized Diazoesters

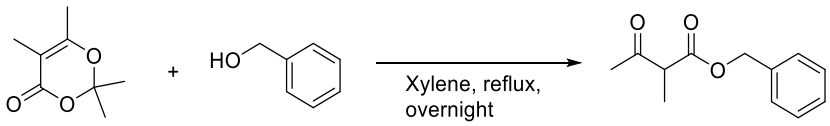
Ethyl 2-diazopropanoate (1a) [1]



To a stirred suspension of ethyl 2-methyl-3-oxobutanoate (432.5 mg, 3.0 mmol, 1 equiv.) in CH_3CN (30 mL) was added *p*-ABSA (1.08 g, 4.5 mmol, 1.5 equiv.) under argon atmosphere.

The mixture was cooled down to 0 ºC, and added DBU (0.67 mL, 4.5 mmol, 1.5 equiv.). After stirring for 2 h at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA to give ethyl 2-diazopropanoate as yellow oil (198.9 mg, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (q, J = 7.02 Hz, 2H), 1.95 (s, 3H), 1.27 (t, J = 7.32 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 60.7, 50.8, 14.4, 8.3 ppm. IR (neat) ν 2916, 2849, 2080, 1698, 1312, 1136 cm^{-1}. HRMS (DART) calcd for $C_5H_{12}N_3O_2$ $[M+NH_4]^+$: 146.09295 found: 146.09223

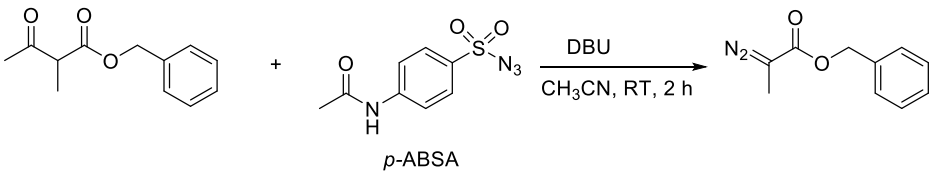
Benzyl 2-methyl-3-oxobutanoate [2]



To a stirred suspension of 2,2,5,6-Tetramethyl-4H-1,3-dioxane-4-one (0.44 mL, 3.0 mmol, 1.0 equiv.) in Xylene (5 mL) was added benzyl alcohol (0.34 mL, 3.3 mmol, 1.1 equiv.) under argon atmosphere.

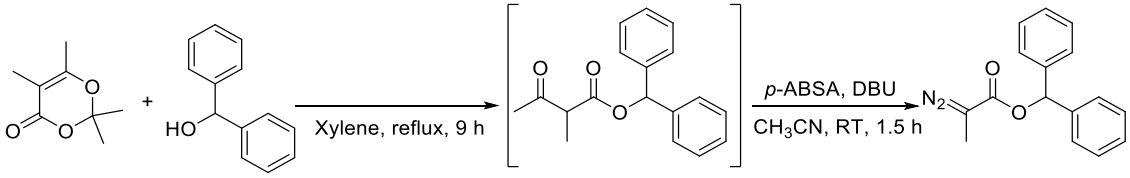
After stirring overnight at 140 ºC, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography with Hex/EA to give benzyl 2-methyl-3-oxobutanoate as colorless oil (489.6 mg, 79 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.40 (m, 5H), 5.16-5.18 (m, 2H), 3.54 (q, J = 7.26 Hz, 1H), 2.19 (s, 3H), 1.36 (d, J = 7.26 Hz, 3H) ppm.

Benzyl 2-diazopropanoate (1c)



To a stirred suspension of benzyl 2-methyl-3-oxobutanoate (471.6 mg, 2.2 mmol, 1 equiv.) in CH_3CN (12 mL) was added 4-acetoamidobenzenesulfonyl azide (*p*-ABSA) (824.0 mg, 3.4 mmol, 1.5 equiv.) under argon atmosphere.
The mixture was cooled down to 0 ºC, and added DBU (0.52 mL, 3.4 mmol, 1.5 equiv.). After stirring for 2 h at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA to give benzyl 2-diazopropanoate as yellow oil (269.2 mg, 62 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.40 (m, 5H), 5.21 (s, 2H), 1.98 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 136.0, 128.4, 128.0, 127.9, 66.2, 8.3 ppm. IR (neat) ν 3032, 2956, 2076, 1694, 1307, 1125, 730, 694 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{14}N_3O_2$ $[M+NH_4]^+$: 208.1086 found: 208.1089.

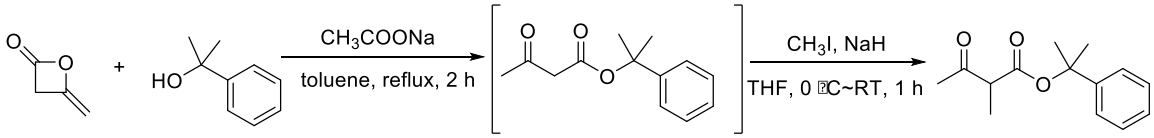
Benzhydryl 2-diazopropanoate (1e)



To a stirred suspension of 2,2,5,6-tetramethyl-4H-1,3-dioxane-4-one (0.44 mL, 3.0 mmol, 1.0 equiv.) in xylene (5 mL) was added diphenylmethanol (608.0 mg, 3.3 mmol, 1.1 equiv.) under argon atmosphere. After stirring overnight at 140 ºC, the reaction mixture was concentrated under reduced pressure.

To a stirred suspension of benzhydryl 2-methyl-3-oxobutanoate (3.0 mmol, 1 equiv.) in CH_3CN (15 mL) was added 4-acetoamidobenzenesulfonyl azide (*p*-ABSA) (1081 mg, 4.5 mmol, 1.5 equiv.) under argon atmosphere.
The mixture was cooled down to 0 ºC, and added DBU (0.68 mL, 4.5 mmol, 1.5 equiv.). After stirring for 1.5 h at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA to give benzhydryl 2-diazopropanoate as yellow oil (242.0 mg, 30 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.41 (m, 10H), 1.99 (bs, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 140.2, 128.4, 127.8, 126.9, 76.9, 8.3 ppm. IR (neat) ν 3028, 2933, 2096, 1682, 1307, 1116, 746, 699 cm^{-1}. HRMS (DART) calcd for $C_{16}H_{18}N_3O_2$ $[M+NH_4]^+$: 284.1399 found: 284.1399.

2-Phenylpropan-2-yl 2-methyl-3-oxobutanoate[3]



To a stirred solution of 1-methyl-1-phenylethyl alcohol (1.28 mL, 10.0 mmol, 1.0 equiv.) and CH_3COONa (82.0 mg, 1 mmol, 0.1 equiv.) in toluene (6 mL) was added diketene (0.85 mL, 11.0 mmol, 1.1 equiv.) at 60 ºC, and the

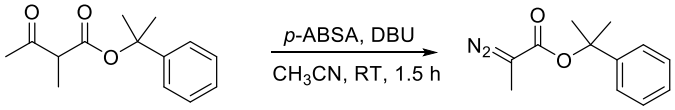
mixture was stirred at 130 ºC for 2 h.

The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL), extracted with CH_2Cl_2, the combined organic layer was washed with brine (5 mL). The crude product of 2-phenylpropan-2-yl 3-oxobutanoate was dried over Na_2SO_4 and evaporated.

To a stirred suspension of NaH (420.0 mg, 10.5 mmol, 1.05 equiv.) in THF (12 mL) at 0 ºC was added 1-methyl-1-phenylethyl 3-oxobutanoate (10.0 mmol, 1.0 equiv.) and the mixture was stirred for 5 min. MeI (0.65 mL, 10.5 mmol, 1.05 equiv.) was added slowly at 0 ºC and the solution was stirred for 1 h at 0 º to RT.

The reaction mixture was quenched with NH_4Cl aq. and the organic layer was separated and thr aqueous layer was extracted with Et_2O. The organic layer was dried over Mg_2SO_4 and the solvent was evapolated. Purification was performed by column chromatography of the crude product to give 2-phenylpropan-2-yl 2-methyl-3-oxobutanoate as colorless oil (526.1 mg, 22 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 3H), 7.29-7.23 (m, 2H), 3.48 (q, J = 7.02 Hz, 1H), 2.23 (s, 3H), 1.78 (s, 6H), 1.31 (d, J = 7.32 Hz, 3H) ppm.

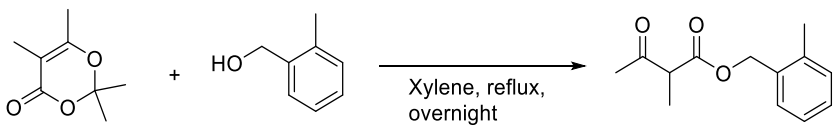
2-Phenylpropan-2-yl 2-diazopropanoate (1g)



To a stirred suspension of 2-phenylpropan-2-yl 2-methyl-3-oxobutanoate (340.0 mg, 1.45 mmol, 1 equiv.) in CH3CN (15 mL) was added 4-Acetoamidobenzenesulfonyl azide (*p*-ABSA) (523.7 mg, 2.18 mmol, 1.5 equiv.) under argon atmosphere.

The mixture was cooled down to 0 ºC, and added DBU (0.33 mL, 2.18 mmol, 1.5 equiv.). After stirring for 30 min at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA under cooling by ice to give benzhydryl 2-phenylpropan-2-yl 2-diazopropanoate as yellow oil (161.6 mg, 51 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.46 (m, 4H), 1.91 (bs, 3H), 1.80 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 145.8, 128.2, 126.9, 124.1, 82.1, 51.4, 28.8, 8.3 ppm. IR (neat) ν 2984, 2084, 1682, 1327, 1129, 766, 702 cm^{-1}.HRMS (DART) calcd for $C_{12}H_{18}N_3O_2$ $[M+NH_4]^+$: 236.13990 found: 236.13996.

2-Methylbenzyl 2-methyl-3-oxobutanoate

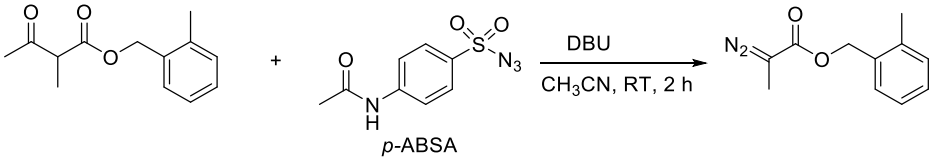


To a stirred suspension of 2,2,5,6-tetramethyl-4H-1,3-dioxane-4-one (0.58 mL, 4.0 mmol, 1.0 equiv.) in xylene (12

mL) was added 2-methylbenzyl alcohol (537.5 mg, 4.4 mmol, 1.1 equiv.) under argon atmosphere.

After stirring overnight at 140 ºC, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography with Hex/EA to give benzyl 2-methylbenzyl 2-methyl-3-oxobutanoate as colorless oil (669.0 mg, 76 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.16 (m, 5H), 5.19 (s, 2H), 3.54 (q, J = 6.88 Hz, 1H), 2.34 (s, 3H), 2.19 (s, 3H), 1.36 (d, J = 7.26 Hz, 3H) ppm.

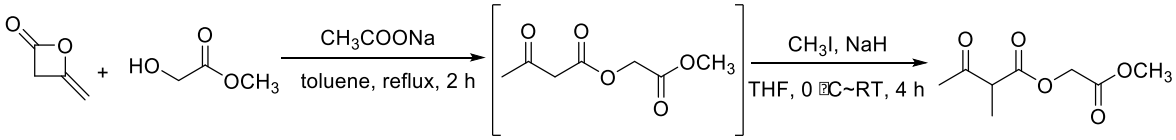
2-Methylbenzyl 2-diazopropanoate (1d)



To a stirred suspension of benzyl 2-methyl-3-oxobutanoate (669.0 mg, 3.04 mmol, 1 equiv.) in CH_3CN (20 mL) was added 4-acetoamidobenzenesulfonyl azide (1.1 g, 4.6 mmol, 1.5 equiv.) under argon atmosphere.

The mixture was cooled down to 0 ºC, and added DBU (0.69 mL, 4.6 mmol, 1.5 equiv.). After stirring overnight at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA to give 2-methylbenzyl 2-diazopropanoate as yellow oil (335.6 mg, 54 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.35 (m, 4H), 5.22 (s, 2H), 2.34 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 136.6, 133.8, 130.1, 128.8, 128.2, 125.7, 64.6, 18.6, 8.1 ppm. IR (neat) ν 3024, 2928, 2084, 1694, 1320, 1129, 742 cm^{-1}. HRMS (DART) calcd for $C_{11}H_{16}N_3O_2$ $[M+NH_4]^+$: 222.1242 found: 222.1242.

2-Methoxy-2-oxoethyl 2-methyl-3-oxobutanoate



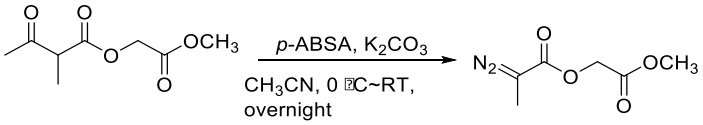
To a stirred solution of 1-methyl-1-phenylethyl alcohol (0.76 mL, 10.0 mmol, 1.0 equiv.) and CH_3COONa (82.0 mg, 1 mmol, 0.1 equiv.) in toluene (6 mL) was added diketene (0.85 mL, 11.0 mmol, 1.1 equiv.) at 60 ºC, and the mixture was stirred at 130 ºC for 2 h.

The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL), extracted with CH_2Cl_2, the combined organic layer was washed with brine (5 mL). The crude product of 2-methoxy-2-oxoethyl 3-oxobutanoate was dried over Na_2SO_4 and evaporated.

To a stirred suspension of NaH (369.9 mg, 9.24 mmol, 1.05 equiv.) in THF (10 mL) at 0 ºC was added 1-methyl-1-phenylethyl 3-oxobutanoate (1.5 g, 8.8 mmol, 1.0 equiv.) and the mixture was stirred for 5 min. MeI

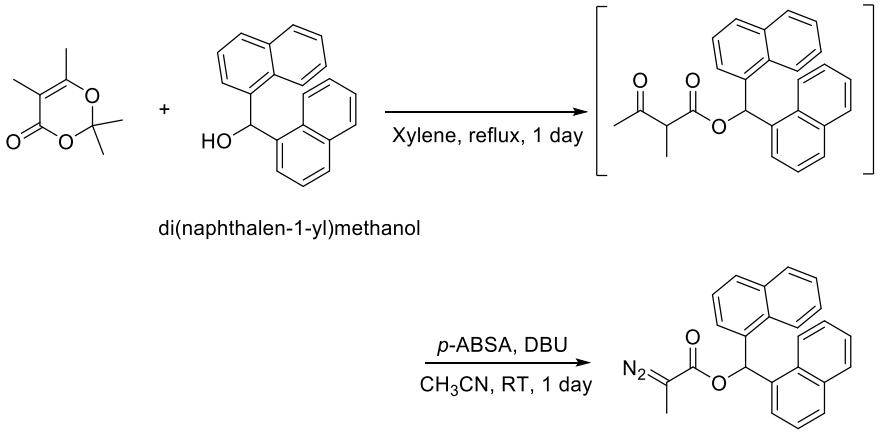
(0.58 mL, 9.24 mmol, 1.05 equiv.) was added slowly at 0 ºC and the solution was stirred for 1 h at 0 ºC to RT.
The reaction mixture was quenched with NH_4Cl aq. and the organic layer was separated and thr aqueous layer was extracted with Et_2O. The organic layer was dried over Mg_2SO_4 and the solvent was evapolated. Purification was performed by column chromatography of the crude product to give 2-methoxy-2-oxoethyl 2-methyl-3-oxobutanoate as brown oil (962.4 mg, 58 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 (s, 2H), 3.77 (s, 3H), 3.61 (q, J = 7.32 Hz, 1H), 2.31 (s, 3H), 1.39 (d, J = 7.02 Hz, 3H) ppm.

2-Methoxy-2-oxoethyl 2-diazopropanoate (1b)



To a stirred suspension of K_2CO_3 (330.3 mg, 2.4 mmol, 1.5 equiv) in CH_3CN (4 mL) was added 2-methoxy-2-oxoethyl 2-methyl-3-oxobutanoate (300.0 mg, 1.6 mmol, 1.0 equiv.) under argon atmosphere at 0 ºC. The reaction mixture was added slowly *p*-ABSA (574.2 mg, 2.4 mmol, 1.5 equiv.) in CH_3CN (4 mL) at 0 ºC.
The progress of the reaction was monited by TLC. After stirring overnight at RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic layer was dried over Na_2SO4 and evaporated to give crude product. Purification was performed by column chromatography to give 2-methoxy-2-oxoethyl 2-diazopropanoate as yellow oil (149.5 mg, 55 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.69 (s, 2H), 3.77 (s, 3H), 2.00 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.4, 168.4, 60.5, 52.1, 51.1, 8.3 ppm. IR (neat) ν 3000, 2952, 2080, 1753, 1698, 1443, 1383, 1323, 1136 cm^{-1}. HRMS (DART) calcd for $C_6H_9N_2O_4$ $[M+H]^+$: 173.0562 found: 173.0560.

Di(naphthalen-1-yl)methyl 2-diazopropanoate (1h)

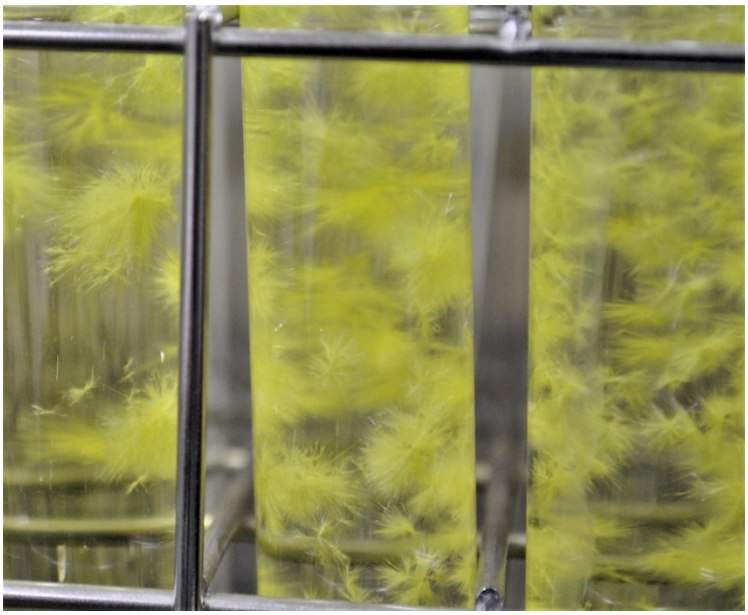


di(naphthalen-1-yl)methanol

To a stirred suspension of di-1-naphthylmethanol (3.13 g, 11.0 mmol, 1.1 equiv.) in xylene (10 mL) was added

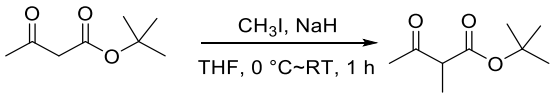
2,2,5,6-tetramethyl-4H-1,3-dioxane-4-one (1.46 mL, 10.0 mmol, 1.0 equiv.) under argon atmosphere. After stirring for 1 day at 140 ºC, the reaction mixture was concentrated under reduced pressure.

To a stirred suspension of di(naphthalen-1-yl)methyl 2-methyl-3-oxobutanoate (10.0 mmol, 1 equiv.) in CH3CN (60 mL) was added *p*-ABSA (3.6 g, 15.0 mmol, 1.5 equiv.) under argon atmosphere.
The mixture was cooled down to 0 ºC, and added DBU (2.24 mL, 15.0 mmol, 1.5 equiv.). After stirring for 1 day at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA, and directly recrystallized in the test tube after column to give di(naphthalen-1-yl)methyl 2-diazopropanoate **6h** as yellow crystal (1.91 g, 52 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.04 (d, J = 8.03 Hz, 2H), 7.90 (m, 2H), 7.84 (d, J = 7.64 Hz, 2H), 7.45-7.53 (m, 4H), 7.36-7.42 (m, 4H), 2.00 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 134.9, 133.8, 131.0, 130.8, 129.0, 128.8, 126.6, 125.8, 125.2, 123.5, 71.1, 51.4, 8.5 ppm. IR (neat) ν 3047, 2085, 1684, 1110, 760 cm^{-1}. HRMS (DART) calcd for $C_{24}H_{22}N_3O_2$ $[M+NH_4]^+$: 384.1712 found: 384.1711.



(The crystal of dinaphylenyl diazopropionate **1h** in the test tube)

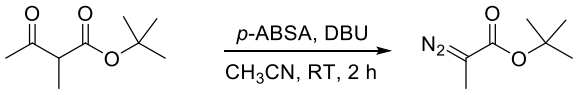
***tert*-Butyl 2-methyl-3-oxobutanoate**[4]



To a stirred suspension of NaH (420 mg, 10.5 mmol, 1.05 equiv.) in THF (12 mL) at 0 ºC was added tert-butyl acetoacetate (1.66 mL, 10.0 mmol, 1.0 equiv.) and the mixture was stirred for 5 min. MeI (0.65 mL, 10.5 mmol, 1.05 equiv.) was added slowly at 0 ºC and the solution was stirred for 1 h at 0 º to RT.

The reaction mixture was quenched with NH_4Cl aq. and the organic layer was separated and the aqueous layer was extracted with Et_2O. The organic layer was dried over Mg_2SO_4 and the solvent was evaporated. Purification was performed by column chromatography of the crude product to give *tert*-butyl 2-methyl-3-oxobutanoate as brown oil (600.0 mg, 32 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.39 (q, J = 6.88 Hz, 1H), 2.22 (s, 3H), 1.46 (s, 9H), 1.29 (t, J = 8.79 Hz, 3H) ppm.

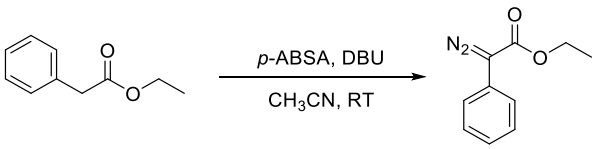
***tert*-Butyl 2-diazopropanoate (1f)**



To a stirred suspension of tert-butyl 2-methyl-3-oxobutanoate (600 mg, 3.12 mmol, 1 equiv.) in CH3CN (20 mL) was added *p*-ABSA (1.1 g, 4.7 mmol, 1.5 equiv.) under argon atmosphere.

The mixture was cooled down to 0 ºC, and added DBU (0.71 mL, 4.7 mmol, 1.5 equiv.). After stirring for 30 min at 0 ºC to RT, the reaction mixture was quenched with H_2O and extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA to give *tert*-butyl 2-diazopropanoate as yellow oil (132.3 mg, 27 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.89 (s, 3H), 1.45 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 80.9, 28.2, 27.7, 8.3 ppm. IR (neat) ν 2933, 2080, 1686, 1331, 1136 cm^{-1}. HRMS (DART) calcd for $C_7H_{13}N_2O_2$ $[M+H]^+$: 157.0977 found: 157.0974.

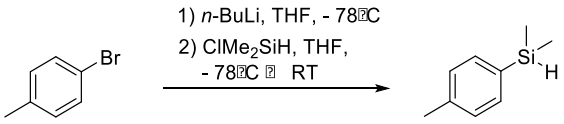
Ethyl 2-diazo-2-phenylacetate (1i)



To a stirred suspension of ethyl phenylacetate (0.8 mL, 5 mmol, 1 equiv.) in CH_3CN (25 mL) was added *p*-ABSA (1.80 g, 7.5 mmol, 1.5 equiv.) under argon atmosphere. The mixture was cooled down to 0 ºC, and added DBU (1.1 mL, 7.5 mmol, 1.5 equiv.). After stirring for 3days at RT, the reaction mixture was quenched with H_2O and

extracted with Et_2O. The organic phase was dried over Na_2SO_4 and evaporated to give crude product. Purification was performed by column chromatography with Hex/EA to give ethyl 2-diazo-phenylacetate as yellow oil (617 mg, 65 % yield, 3.24 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.03 Hz, 2H), 7.39 (t, *J* = 7.64 Hz, 2H), 7.18 (t, *J* = 7.26 Hz, 1H), 4.33 (q, *J* = 6.88 Hz, 2H), 1.34 (t, *J* = 6.88 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 128.7, 125.5, 125.5, 123.8, 63.1, 60.8, 14.3 ppm. IR (neat) ν 2987, 2083, 1703, 1600, 1250, 1345, 1168, 755 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{11}N_2O_2$ $[M+H]^+$: 191.0820 found: 191.0822.

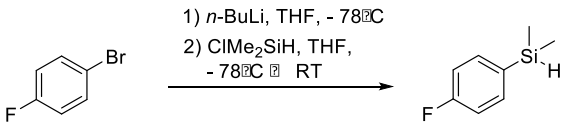
Dimethyl(*p*-tolyl)silane [6]



To a solution of *p*-bromotoluene (1.23 mL, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (7.5 mL, 12 mmol, 1.2 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.44 mL, 13 mmol, 1.3 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 100/1) to give dimethyl(*p*-tolyl)silane as colorless oil (1.397 g, 93% yield, 9.3 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.64 Hz, 2H), 7.19 (d, *J* = 7.26 Hz, 2H), 4.41 (sept, *J* = 3.82 Hz, 1H), 2.35 (s, 3H), 0.33 (d, *J* = 3.82 Hz) ppm.

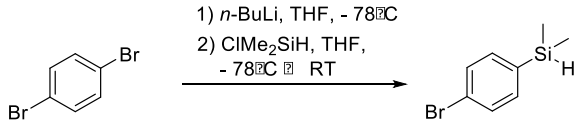
(4-Fluorophenyl)dimethylsilane



To a solution of 1-bromo-4-fluorobenzene (1.09 mL, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (7.5 mL, 12 mmol, 1.2 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.67 mL, 15 mmol, 1.5 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 100/1) to give (4-fluorophenyl)dimethylsilane as colorless oil (845.5 mg, 55% yield, 5.5 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.53 (m, 2H), 7.08-7.03 (m, 2H), 4.41 (sept, *J* = 3.82 Hz, 1H), 0.33 (d, *J* = 3.82 Hz, 6H) ppm.

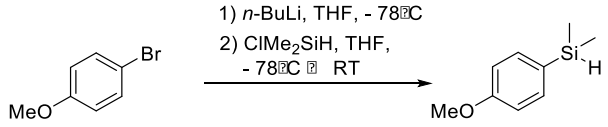
(4-Bromophenyl)dimethylsilane



To a solution of 1,4-dibromobenzene (2.35 g, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (6.9 mL, 11 mmol, 1.1 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.33 mL, 12 mmol, 1.2 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 100/1) to give (4-bromophenyl)dimethylsilane as colorless oil (1.03 g, 48% yield, 4.79 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.41 Hz, 2H), 7.39 (d, *J* = 8.03 Hz, 2H), 4.39 (sept, *J* = 3.82 Hz, 1H), 0.33 (d, *J* = 3.82 Hz, 6H) ppm.

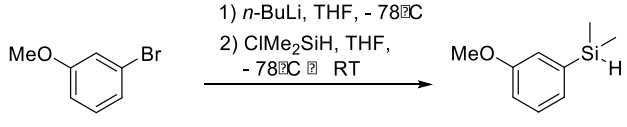
(4-Methoxyphenyl)dimethylsilane



To a solution of 4-bromoanisole (1.25 mL, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (7.5 mL, 12 mmol, 1.2 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.67 mL, 15 mmol, 1.5 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 100/1) to give (4-methoxyphenyl)dimethylsilane as colorless oil (811.9 mg, 49 % yield, 4.9 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.41 Hz, 2H), 6.92 (d, *J* = 8.79 Hz, 2H), 4.41 (sept, *J* = 3.82 Hz, 1H), 3.82 (s, 3H), 0.32 (d, *J* = 3.82 Hz, 6H) ppm.

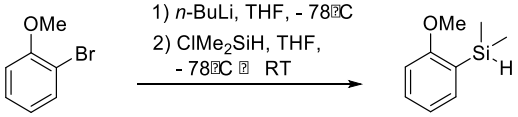
(3-Methoxyphenyl)dimethylsilane



To a solution of 3-bromoanisole (1.87 g, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (7.5 mL, 12 mmol, 1.2 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.67 mL, 15 mmol, 1.5 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 100/1) to give (3-methoxyphenyl)dimethylsilane as colorless oil (1.375 g, 83 % yield, 8.3 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.26 Hz, 1H), 7.12 (d, *J* = 7.26 Hz, 1H), 7.08 (d, *J* = 2.68 Hz, 1H), 6.91 (dd, *J* = 2.68, 8.41 Hz, 1H), 4.41 (sept, *J* = 3.82 Hz, 1H), 3.82 (s, 3H), 0.34 (d, *J* = 3.82 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 139.0, 129.0, 126.1, 119.3, 114.5, 55.0, -3.8 ppm. IR (neat) ν 2959, 2833, 2115, 1572, 1282, 1246, 889, 759 cm^{-1}.HRMS (DART) calcd for $C_9H_{15}O_1Si_1$ $[M+H]^+$: 167.0892 found:167.0894.

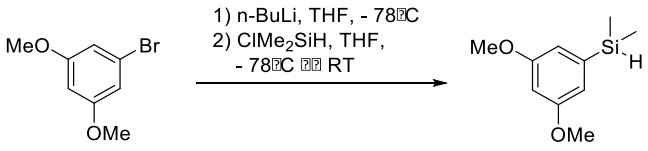
(2-Methoxyphenyl)dimethylsilane



To a solution of 2-bromoanisole (1.87 g, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (7.5 mL, 12 mmol, 1.2 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.67 mL, 15 mmol, 1.5 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 100/1) to give (2-methoxyphenyl)dimethylsilane as colorless oil (1.566 g, 94 % yield, 9.4 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 1.83, 7.02 Hz, 1H), 7.36 (dt, *J* = 1.83, 8.24 Hz, 1H), 6.95 (t, *J* = 7.02 Hz, 1H), 6.83 (d, *J* = 8.24 Hz, 1H), 4.39 (sept, *J* = 3.66 Hz, 1H), 3.82 (s, 3H), 0.33 (d, *J* = 3.66 Hz, 6H) ppm.

(3,5-Dimethoxyphenyl)dimethylsilane

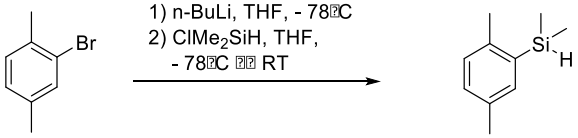


To a solution of 1-bromo-3,5-dimethoxybenzene (2.17 g, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (7.5 mL, 12 mmol, 1.2 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.67 mL, 15 mmol, 1.5 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 50/1) to give (3,5-dimethoxyphenyl)dimethylsilane as colorless oil (1.65 g, 84% yield, 8.43 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 2.68 Hz, 2H), 6.47 (t, *J* = 2.29 Hz, 1H), 4.39 (sept, *J* = 3.82 Hz,

1H), 3.81 (s, 6H), 0.33 (d, J = 3.82 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 139.7, 111.3, 101.1, 55.1, -3.8 ppm. IR (neat) ν 2954, 2837, 2123, 1581, 1285, 1152, 890 cm^{-1}.HRMS (DART) calcd for $C_{10}H_{16}O_2Si_1$ $[M]^+$: 196.0919 found: 196.0917.

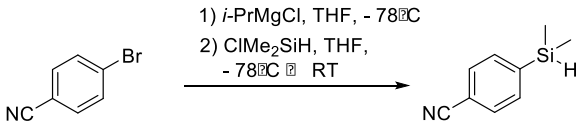
(2,5-Dimethylphenyl)dimethylsilane



To a solution of 2-bromo-1,4-dimethylbenzene (1.36 mL, 10 mmol) in THF (35 mL) was added 1.6M n-BuLi (7.5 mL, 12 mmol, 1.2 equiv.) at -78 ºC. The resulting mixture was stirred for 3 h at -78 ºC, after stirring for 3 h, the reaction mixture was added chlorodimethylsilane (1.67 mL, 15 mmol, 1.5 equiv.) and allowed to warm to RT overnight.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and washed with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Purification was performed by column chromatography (Pentane/CH_2Cl_2 = 50/1) to give (2,5-dimethylphenyl)dimethylsilane as colorless oil (1.59 g, 97% yield, 9.7 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (s, 1H), 7.09 (d, J = 16.82 Hz, 1H), 7.07 (d, J = 16.82 Hz, 1H), 4.51 (sept, J = 3.82 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H), 0.35 (d, J = 3.82 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 135.8, 135.2, 134.1, 130.1, 129.4, 21.7, 20.9, -3.3 ppm. IR (neat) ν 2997, 2954, 2880, 2123, 1476, 1249, 890 cm^{-1}.HRMS (DART) calcd for $C_{10}H_{17}Si_1$ $[M+H]^+$: 165.1099 found: 165.1092.

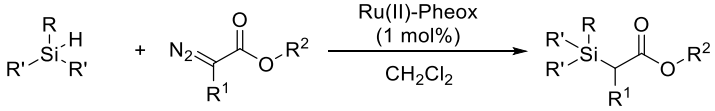
4-(Dimethylsilyl)benzonitrile



i-PrMgCl (4.26 mL of 2M solution in THF, 8.52 mmol, 1.3 equiv.) was slowly added to a cooled solution of 4-iodobenzonitrile (1.5 g, 6.55 mmol) in THF (15 mL). After 30 min, the solution was slowly added a cooled solution of chlorodimethylsilane (1.09 mL, 9.82 mmol, 1.5 equiv.) in THF (15 mL). The reaction mixture was allowed to warm to RT over 4 h.

The crude mixture was quenched with NH_4Cl aq. at 0 ºC and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to give 4-(dimethylsilyl)benzonitrile as yellow oil (1.054 g, 99.8% yield, 9.98 mmol). ^{1}H NMR (500 MHz, Acetone-D6) δ 7.77 (d, J = 16.82 Hz, 2H), 7.76 (d, J = 15.26 Hz, 2H), 4.44 (sept, J = 3.82 Hz, 1H), 0.39 (d, J = 3.82 Hz, 6H) ppm.

2. General Procedure for Catalytic Asymmetric Si-H Insertion Reaction to Construct Chiral Carbon



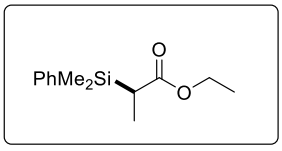
To a solution of Ru(II)-Pheox (0.001 mmol, 1.0 mol%) in CH_2Cl_2 (0.5 mL) and silane compound (0.2 mmol, 2.0 equiv.) was cooled down to 0 ºC under argon atmosphere.

The mixture was added diazo ester (0.1 mmol, 1 equiv.) in CH_2Cl_2 (0.5 mL).

After stirring for 10 min at 0 ºC, the reaction mixture was concentrated under reduced pressure to give crude product. Purification was performed by column chromatography with Hex/EA to give desired product. The *ee* value was determined by chiral HPLC analysis.

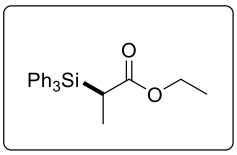
3. Analytical Data for Asymmetric Si-H Insertion Reaction Products(1)

Ethyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2a)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of ethyl 2-diazopropanoate **1a** (12.8 mg, 0.1 mmol) and dimethylphenylsilane (27.3 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ethyl (*R*)-2-(dimethyl(phenyl)silyl) propanoate **2e** as colorless oil (85 % yield, 20.2 mg, 0.085 mmol), 54% *ee*. $[\alpha]^{22}_{D}$ = +29.8 (c 0.46, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.51 (m, 2H), 7.34-7.40 (m, 3H), 3.86 (q, *J* = 7.3 Hz, 2H), 2.25 (q, *J* = 7.3 Hz, 2H), 1.12-1.15 (m, 6H), 0.37 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.9, 136.2, 133.8, 129.4, 127.7, 59.7, 29.9, 14.2, 11.2, -4.0, -4.9 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IC-3), UV detector 254 nm, eluent: Hex/IPA = 200/1, Flow late = 1.0 mL/min, tR = 10.6 min (major product), tR = 11.2 min (minor product). IR (neat) ν 3075, 2956, 1710, 1320, 1184, 822, 734, 699 cm^{-1}. HRMS (DART) calcd for $C_{13}H_{24}N_1O_2Si_1$ $[M+NH_4]^+$: 254.1576 found: 254.1570.

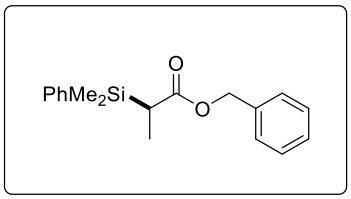
Ethyl (R)-2-(triphenylsilyl)propanoate (2t)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of ethyl 2-diazopropanoate **1a** (25.7 mg, 0.2 mmol) and triphenylsilane (104.2 mg, 0.4 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give Ethyl (R)-2-(dimethyl(phenyl)silyl) propanoate **2t** as colorless oil (84 % yield, 60.8 mg, 0.16 mmol), 91% *ee*. $[\alpha]^{22}_{D}$ = +44.1 (c 0.56, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60-7.75 (m, 6H), 7.44-7.39 (m, 3H), 7.38-7.33 (m, 6H), 3.85 (dq, *J* = 7.26, 10.70 Hz, 1H), 3.71 (dq, *J* = 7.26, 10.70 Hz, 1H), 2.96 (q, *J* = 7.26 Hz, 1H), 1.36 (d, *J* = 7.26 Hz, 3H), 0.86 (t, *J* = 7.26 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ175.8, 136.1, 132.8, 129.7, 127.7, 60.0, 28.4, 13.7, 13.0 ppm.

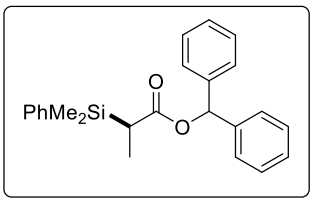
The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IC-3), UV detector 254 nm, eluent: Hex/IPA = 100/1, Flow late = 1.0 mL/min, tR = 6.5 min (major product), tR = 10.4 min (minor product). IR (neat) ν 2979, 1714, 1428, 1110, 741, 700 cm^{-1}. HRMS (DART) calcd for $C_{23}H_{28}N_1O_2Si_1$ $[M+NH_4]^+$: 378.1889 found: 378.1889.

Benzyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2c)



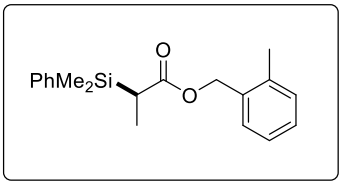
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of Benzyl 2-diazopropanoate **1c** (38.0 mg, 0.2 mmol) and dimethylphenylsilane (54.5 mg, 0.4 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give benzyl (*R*)-2-(dimethyl(phenyl)silyl) propanoate **2c** as colorless oil (88 % yield, 52.8 mg, 0.18 mmol), 50% *ee*. $[\alpha]^{30}_{D}$ = +31.9 (c 2.86, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.29-7.42 (m, 6H), 7.23-7.27 (m, 2H), 5.01 (dd, *J* = 12.23, 32.87 Hz, 2H), 2.34 (q, *J* = 7.26 Hz, 1H), 1.19 (d, *J* = 9.94 Hz, 3H), 0.35 (d, *J* = 4.20 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.7, 136.1, 136.0, 133.8, 129.4, 128.4, 127.9, 127.7, 65.8, 29.9, 11.3, -4.1, -4.8 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK OJ-H), UV detector 254 nm, eluent: Hex/IPA = 1000/1, Flow late = 1.0 mL/min, tR = 39.6 min (major product), tR = 59.2 min (minor product). IR (neat) ν 3032, 2960, 1716, 1315, 1229, 1138, 734, 699 cm^{-1}. HRMS (DART) calcd for $C_{18}H_{26}N_1O_2Si_1$ $[M+NH_4]^+$: 316.1732 found: 316.1737.

Benzhydryl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2e)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of benzhydryl 2-diazopropanoate **1e** (26.6 mg, 0.1 mmol) and dimethylphenylsilane (0.03 mL, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give benzhydryl (R)-2-(dimethyl (phenyl)silyl) propanoate **2e** as colorless oil (99% yield, 37.2 mg, 0.1 mmol), 78 %*ee*. $[\alpha]^{28}_{D}$ = -7.25 (c 0.88, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.44 (m, 15H), 6.86 (s, 1H), 2.40 (q, *J* = 7.26 Hz, 1H), 1.20 (d, *J* = 7.26 Hz, 3H), 0.26 (d, *J* = 10.70 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 140.5, 133.8, 129.4, 128.3, 123.2, 127.7, 127.7, 127.6, 126.9, 76.4, 30.0, 11.4, -4.1, -4.7 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IC-3), UV detector 254 nm, eluent: Hex/IPA = 200/1, Flow late = 1.0 mL/min, tR = 11.3 min (major product), tR = 9.2 min (minor product). IR (neat) ν 3080, 2960, 1716, 1170, 761, 699 cm^{-1}. HRMS (DART) calcd for $C_{24}H_{27}O_2Si_1$ $[M+H]^+$: 375.1780 found: 375.1781.

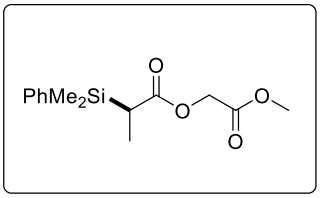
2-Methylbenzyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2d)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of 2-methylbenzyl 2-diazopropanoate **1d** (20.4 mg, 0.1 mmol) and dimethylphenylsilane (0.03 mL, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give 2-methylbenzyl (*R*)-2-(dimethyl (phenyl)silyl)propanoate **2d** as colorless oil (92% yield, 28.8 mg, 0.09 mmol), 57 %*ee*. $[\alpha]^{20}_{D}$ = +71.5 (c 1.44, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.49 (m, 2H), 7.31-7.40 (m, 4H), 7.26-7.20 (m, 2H), 7.19-7.14 (m, 2H), 5.11 (d, *J* = 12.23 Hz, 1H), 4.97 (d, *J* = 12.61

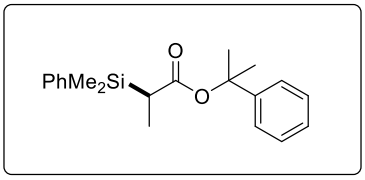
Hz, 1H), 2.33 (q, *J* = 7.26 Hz, 1H), 2.29 (s, 3H), 1.19 (d, *J* = 6.88 Hz, 3H), 0.34 (d, *J* = 5.73 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.8, 136.8, 134.2, 133.8, 130.1, 129.4, 129.2, 128.2, 127.8, 125.8, 63.9, 30.0, 18.8, 11.3, -4.1, -4.8 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK OZ-H), UV detector 254 nm, eluent: Hex/IPA = 4000/1, Flow late = 1.0 mL/min, tR = 80.1 min (major product), tR = 70.9 min (minor product). IR (neat) ν 3048, 2960, 1715, 1174, 736, 700 cm^{-1}. HRMS (DART) calcd for $C_{19}H_{25}O_2Si_1$ $[M+H]^+$: 313.1623 found: 313.1629.

2-Methoxy-2-oxoethyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2b)



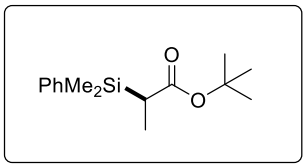
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of 2-methoxy-2-oxoethyl 2-diazopropanoate **1b** (17.2 mg, 0.1 mmol) and dimethylphenylsilane (0.03 mL, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give 2-methoxy-2-oxoethyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate **2b** as colorless oil (98% yield, 27.4 mg, 0.1 mmol), 54 %*ee*. $[\alpha]^{24}_D$ = +25.7 (c 1.34, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.54 (m, 2H), 7.33-7.41 8m, 3H), 4.52 (q, *J* = 16.05 Hz, 2H), 3.74 (s, 3H), 2.37 (q, *J* = 7.26 Hz, 1H), 1.16 (d, *J* = 7.26 Hz, 3H), 0.42 (d, *J* = 5.73 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.3, 168.6, 136.0, 133.8, 129.5, 127.8, 60.3, 52.0, 29.7, 11.2, -3.8, -5.3 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK OJ-H), UV detector 254 nm, eluent: Hex/IPA = 800/1, Flow late = 1.0 mL/min, tR = 25.7 min (major product), tR = 35.0 min (minor product). IR (neat) ν 3070, 1957, 1764, 1729, 1166, 791, 701 cm^{-1}. HRMS (DART) calcd for $C_{14}H_{24}N_1O_4Si_1$ $[M+NH_4]^+$: 298.1474 found: 298.1474.

2-Phenylpropan-2-yl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2g)



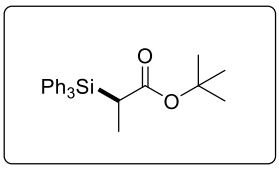
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of 2-phenylpropan-2-yl 2-diazopropanoate **1g** (15.0 mg, 0.07 mmol) and dimethylphenylsilane (0.02 mL, 0.14 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give 2-phenylpropan-2-yl (R)-2-(dimethyl(phenyl)silyl)propanoate **2g** as colorless oil (36% yield, 8.2 mg, 0.025 mmol), 90 %*ee*. $[\alpha]^{24}_D$ = +42.5 (c 0.28, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.57 (m, 2H), 7.32-7.41 (m, 3H), 7.17-7.30 (m, 5H), 2.27 (q, *J* = 7.26 Hz, 1H), 1.67 (s, 3H), 1.62 (s, 3H), 1.13 (d, *J* = 7.26 Hz, 3H), 0.38 (d, *J* = 9.17 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174. 4, 146.1, 136.6, 134.0, 129.3, 128.0, 127.7, 126.7, 124.3, 80.9, 30.5, 29.0, 27.8, 11.4, -4.0, -4.4 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK OJ-H), UV detector 254 nm, eluent: Hex/IPA = 600/1, Flow late = 1.0 mL/min, tR = 24.7 min (major product), tR = 21.8 min (minor product). IR (neat) ν 2977, 1718, 1133, 733, 698 cm^{-1}. HRMS (DART) calcd for $C_{20}H_{27}O_2Si_1$ $[M+H]^+$: 327.1780 found: 327.1781.

***tert*-Butyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2f)**



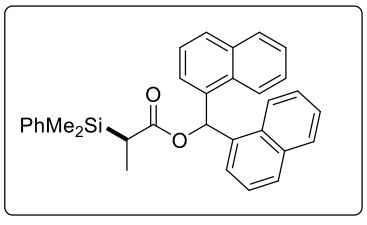
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of tert-butyl 2-diazopropanoate **1f** (15.6 mg, 0.1 mmol) and dimethylphenylsilane (0.03 mL, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give tert-butyl (*R*)-2-(dimethyl(phenyl)silyl) propanoate **2f** as colorless oil (80% yield, 21.2 mg, 0.08 mmol), 81% *ee*. $[\alpha]^{18}_{D}$ = +41.4 (c 0.925, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.54 (m, 2H), 7.32-7.38 (m, 3H), 2.17 (q, *J* = 7.26 Hz, 1H), 1.33(s, 9H), 1.10 (d, *J* = 7.26 Hz, 3H), 0.36 (d, *J* = 8.79 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 136.6, 133.9, 129.2, 127.7, 79.4, 30.5, 28.1, 11.3, -3.9, -4.6 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IC-3), UV detector 254 nm, eluent: Hex/IPA = 500/1, Flow late = 1.0 mL/min, tR = 10.1 min (major product), tR = 11.8 min (minor product). IR (neat) ν 3070, 2975, 1712, 1366, 1158, 734, 700 cm^{-1}. HRMS (DART) calcd for $C_{15}H_{25}O_2Si_1$ $[M+H]^+$: 265.1623 found: 265.1624.

***tert*-Butyl (*R*)-2-(triphenylsilyl)propanoate (2u)**



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of tert-butyl 2-diazopropanoate **1f** (15.6 mg, 0.1 mmol) and triphenylsilane (52.08 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give tert-butyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate **2u** as colorless oil (84% yield, 32.5 mg, 0.08 mmol), 99% *ee*. $[\alpha]^{23}_{D}$ = +54.9 (c 0.165, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.64 (m, 6H), 7.32-7.45(m, 9H), 2.88 (q, *J* = 7.26 Hz, 1H), 1.31 (d, *J* = 9.94 Hz, 3H), 1.09 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 136.2, 133.1, 129.6, 127.7, 80.0, 28.9, 27.6, 13.1 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IC-3), UV detector 254 nm, eluent: Hex/IPA = 100/1, Flow late = 1.0 mL/min, tR = 4.6 min (major product), tR = 5.2 min (minor product). IR (neat) ν 3049, 2976, 1709, 1428, 1141, 741, 700 cm^{-1}. HRMS (DART) calcd for $C_{25}H_{32}N_1O_2Si_1$ $[M+NH_4]^+$:406.2202 found:406.2209.

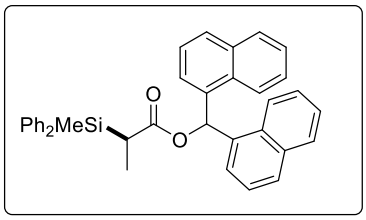
Di(naphthalen-1-yl)methyl (*R*)-2-(dimethyl(phenyl)silyl)propanoate (2h)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and dimethylphenylsilane (0.03 mL, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (R)-2-(dimethyl(phenyl)silyl)propanoate **2h** as white solid (86% yield, 40.9 mg, 0.0085 mmol), 97% *ee*. $[\alpha]^{25}_{D}$ = -44.5 (c 0.535, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.17 (d, *J* = 8.79 Hz, 1H), 7.78-7.99 (m, 5H), 7.37-7.54 (m, 6H), 7.23-7.34 (m, 5H), 7.19 (t, *J* = 7.64 Hz, 2H), 2.43 (q, *J* = 6.88 Hz, 1H), 1.20 (d, *J* = 6.88 Hz, 3H), 0.16 (d, *J* = 20.64 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 136.0,

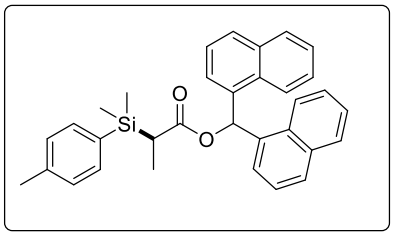
135.4, 133.8, 130.8, 129.2, 128.8, 128.7, 128.7, 128.6, 127.6, 126.6, 126.5, 126.1, 125.7, 125.7, 125.2, 123.6, 123.6, 69.8, 30.1, 11.7, -4.0, -4.9 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 400/1, Flow late = 1.0 mL/min, tR = 38.9 min (major product), tR = 54.3 min (minor product). IR (neat) ν 3050, 2961, 1714, 1170, 735, 653 cm^{-1}. HRMS (DART) calcd for $C_{32}H_{34}N_1O_2Si_1$ $[M+NH_4]^+$: 492.2358 found: 492.2354.

Di(naphthalen-1-yl)methyl (*R*)-2-(methyldiphenylsilyl)propanoate (2r)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and diphenylmethylsilane (0.04 mL, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-(methyldiphenylsilyl)propanoate **2r** as white solid (94% yield, 50.6 mg, 0.09 mmol), 99% *ee*. $[\alpha]^{23}_D$ = -18.5 (c 1.235, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.02 (d, *J* = 8.41 Hz, 1H), 7.96 (d, *J* = 8.41 Hz, 1H), 7.90 (d, *J* = 8.03 Hz, 1H), 7.87 (d, *J* = 8.41 Hz, 1H), 7.84 (d, *J* = 8.03 Hz, 1H), 7.78 (d, *J* = 8.41 Hz, 1H), 7.17-7.55 (m, 17H), 7.09 (d, *J* = 7.26 Hz, 1H), 2.84 (q, *J* = 7.26 Hz, 1H), 1.33 (d, *J* = 7.26 Hz, 3H), 0.48 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 135.5, 135.1, 134.7, 134.6, 134.2, 134.2, 133.7, 133.6, 130.8, 130.8, 129.4, 128.7, 128.6, 128.6, 127.7, 127.6, 126.5, 126.5, 125.8, 125.7, 125.6, 125.4, 125.1, 123.5, 123.4, 70.0, 28.8, 12.4, -5.5 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 400/1, Flow late = 1.0 mL/min, tR = 49.0 min (major product), tR = 58.8 min (minor product). IR (neat) ν 3049, 2935, 1714, 1428, 1174, 735, 700 cm^{-1}. HRMS (DART) calcd for $C_{37}H_{36}N_1O_2Si_1$ $[M+NH_4]^+$: 554.2515 found: 554.2519.

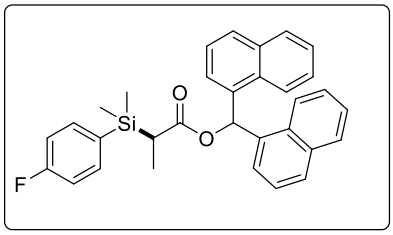
Di(naphthalen-1-yl)methyl (*R*)-2-(dimethyl(p-tolyl)silyl)propanoate (2i)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and dimethyl(p-tolyl)silane (30.1 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-(dimethyl(p-tolyl)silyl)propanoate **2i** as white solid (84 % yield, 41.3 mg, 0.08 mmol), 89% *ee*. $[\alpha]^{19}_D$ = -59.0 (c 0.835, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.15 (d, *J* = 8.41 Hz, 1H), 7.89 (q, *J* = 9.17 Hz, 3H), 7.82 (q, *J* = 8.03 Hz, 2H), 7.36-7.53 (m, 6H), 7.31 (t, J = 7.26 Hz, 1H), 7.17-7.25 (m, 3H), 6.83-6.76 (m, 2), 2.39 (q, *J* = 6.88 Hz, 1H), 1.55 (s, 2H), 1.21 (d, *J* = 7.26 Hz, 3H), 0.16 (d, *J* = 9.94 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 164.6, 162.6, 136.7, 135.6, 135.3, 133.7, 131.3, 131.3, 130.9, 130.7, 128.8, 128.8, 128.7, 128.6, 126.6, 126.4, 126.1, 125.7, 125.7, 125.1, 125.0, 123.6, 123.4, 114.8, 114.6, 69.7, 30.1, 11.6, -4.2, -4.4 ppm. The *ee* value was determined by chiral HPLC analysis.

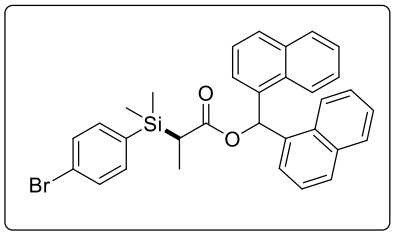
Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 400/1, Flow late = 1.0 mL/min, tR = 44.3 min (major product), tR = 62.4 min (minor product). IR (neat) ν 3055, 2960, 1713, 1313, 1165, 820, 784 cm^{-1}. HRMS (DART) calcd for $C_{33}H_{36}N_1O_2Si_1$ $[M+NH_4]^+$: 506.2515 found: 506.2513.

Di(naphthalen-1-yl)methyl (R)-2-((4-fluorophenyl)dimethylsilyl)propanoate (2j)



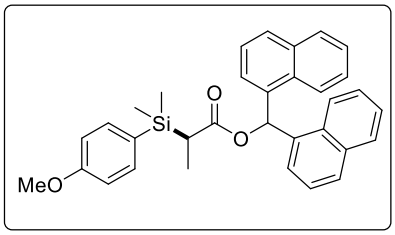
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (4-fluorophenyl)dimethylsilane (30.8 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (R)-2-((4-fluorophenyl)dimethylsilyl) propanoate **2j** as white solid (86% yield, 42.3 mg, 0.085 mmol), 94% *ee*. $[\alpha]^{17}_D$ = -58.85 (c 0.755, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.18 (d, *J* = 8.03 Hz, 1H), 7.96-7.81 (m, 5H), 7.55-7.37 (m, 6H), 7.35-7.31 (m, 1H), 7.28-7.20 (m, 3H), 6.79-6.85 (m, 2H), 2.42 (q, *J* = 6.88 Hz, 1H), 1.24 (d, *J* = 7.26 Hz, 3H), 0.19 (d, *J* = 13.0 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 164.6, 162.6, 135.7, 135.6, 135.3, 133.7, 131.3, 131.3, 130.9, 130.7, 128.8, 128.8, 128.7, 128.6, 126.6, 126.4, 126.1, 125.7, 125.7, 125.1, 125.0, 123.6, 123.4, 114.8, 114.6, 69.7, 30.1, 11.6, -4.2, -4.4 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 300/1, Flow late = 1.0 mL/min, tR = 27.2 min (major product), tR = 37.3 min (minor product). IR (neat) ν 3047, 2956, 1710, 1307, 1232, 1168, 778, 734 cm^{-1}. HRMS (DART) calcd for $C_{32}H_{33}FNO_3Si_1$ $[M+NH_4]^+$: 510.2264 found: 510.2264.

Di(naphthalen-1-yl)methyl (*R*)-2-((4-bromophenyl)dimethylsilyl)propanoate (2k)



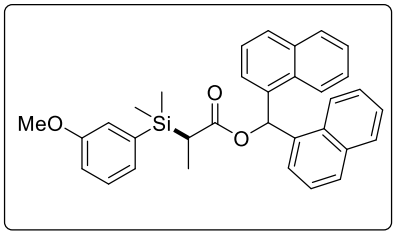
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (4-bromophenyl) dimethylsilane (43.0 mg, 0.2 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-((4-bromophenyl)dimethylsilyl) propanoate **2k** as white solid (87% yield, 48.3 mg, 0.087 mmol), 93% *ee*. $[\alpha]^{20}_D$ = -59.84 (c 2.125, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.17 (d, *J* = 8.03 Hz, 1H), 7.80-7.96 (m, 5H), 7.37-7.56 (m, 6H), 7.33 (t, *J* = 7.26 Hz, 1H), 7.21-7.27 (m, 3H), 7.06-7.12 (m, 2H), 2.42 (q, *J* = 6.88 Hz, 1H), 1.24 (d, *J* = 7.26 Hz, 3H), 0.18 (d, *J* = 8.79 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 135.6, 135.3, 135.2, 134.6, 133.7, 130.9, 130.7, 130.7, 128.9, 128.8, 128.7, 128.7, 126.6, 126.4, 126.1, 125.7, 125.7, 125.1, 125.1, 125.0, 124.1, 123.5, 123.4, 69.7, 29.8, 11.6, -4.5 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 300/1, Flow late = 1.0 mL/min, tR = 36.2 min (major product), tR = 50.3 min (minor product). IR (neat) ν 3047, 2960, 1714, 1375, 1168, 1065, 781, 727 cm^{-1}. HRMS (DART) calcd for $C_{32}H_{33}BrNO_2Si_1$ $[M+NH_4]^+$: 570.1463 found: 570.1463.

Di(naphthalen-1-yl)methyl (*R*)-2-((4-methoxyphenyl)dimethylsilyl)propanoate (2m)



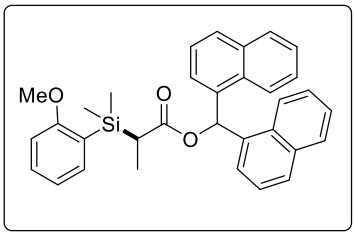
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (4-methoxyphenyl) dimethyl silane (33.2 mg, 0.2 mmol, 2 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-((4-methoxyphenyl)dimethyl silyl)propanoate **2m** as white solid (84% yield, 42.5 mg, 0.84 mmol), 95% *ee*. $[\alpha]^{22}_{D}$ = - 57.22 (c 2.066, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.22-8.17 (m, 1H), 7.98 (d, *J* = 8.41 Hz, 1H), 7.87-7.93 (m, 2H), 7.84 (d, *J* = 11.47 Hz, 1H), 7.83 (d, *J* = 11.47 Hz, 1H), 7.54-7.39 (m, 6H), 7.28-7.36 (m, 2H), 7.25-7.22 (m, 2H), 6.73 (d, *J* = 8.79 Hz, 2H), 3.78 (s, 3H), 2.42 (q, *J* = 7.26 Hz, 1H),1.23 (d, *J* = 7.2 Hz, 3H), 0.18 (d, *J* = 13.0 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1, 160.4, 135.7, 135.4, 135.2, 133.7, 131.0, 130.8, 128.7, 128.7, 128.7, 128.6, 126.7, 126.6, 126.4, 126.1, 125.7, 125.7, 125.1, 125.1, 123.6, 123.5, 113.3, 69.6, 54.8, 30.3, 11.7, -3.9, -4.6 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/CH_2Cl_2 = 300/1, Flow late = 1.0 mL/min, tR = 43.1 min (major product), tR = 65.1 min (minor product). IR (neat) ν 3059, 2958, 2833, 1709, 1592, 1503, 1245, 1167, 797, 734 cm^{-1}. HRMS (DART) calcd for $C_{33}H_{36}NO_3Si_1$ $[M+NH_4]^+$: 522.2464 found: 522.2463.

Di(naphthalen-1-yl)methyl (*R*)-2-((3-methoxyphenyl)dimethylsilyl)propanoate (2n)



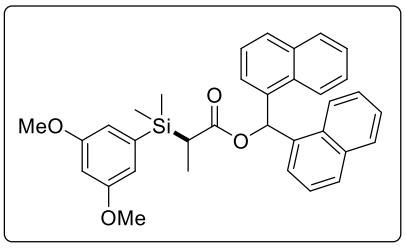
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (3-methoxyphenyl) dimethyl silane (33.2 mg, 0.2 mmol, 2 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-((3-methoxyphenyl)dimethylsilyl)propanoate **2n** as white solid (89% yield, 44.7 mg, 0.089 mmol), 96% *ee*. $[\alpha]^{25}_{D}$ = - 50.00 (c 2.235, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.17 (d, *J* = 8.79 Hz, 1H), 7,97 (d, *J* = 8.41 Hz, 1H), 7.86-7.93 (m, 2H), 7.84 (d, *J* = 11.85 Hz, 1H), 7.82 (d, *J* = 12.23 Hz, 1H), 7.38-7.54 (m, 6H), 7.36-7.69 (m, 2H), 7.17 (t, *J* = 7.26 Hz, 1H), 6.91-6.99 (m, 2H), 6.89-6.84 (m, 1H), 3.73 (s, 3H), 2.45 (q, *J* = 7.26 Hz, 1H), 1.23 (d, *J* = 7.26 Hz, 3H), 0.19 (s, 3H), 0.14 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ175.0, 158.8, 137.7, 135.6, 135.4, 133.7, 133.7, 131.0, 130.8, 128.9, 128.8, 128.7, 128.7, 128.6, 126.6, 126.4, 126.1, 126.0, 125.7, 125.7, 125.2, 125.1, 123.6, 123.5, 119.3, 114.5, 69.8, 54.9, 30.0, 11.7, -3.9, -5.0 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/CH_2Cl_2 = 300/1, Flow late = 1.0 mL/min, tR = 30.1 min (major product), tR = 43.8 min (minor product). IR (neat) ν 3063, 2954, 1833, 1709, 1573, 1234, 1171, 781 cm^{-1}. HRMS (DART) calcd for $C_{33}H_{36}NO_3Si_1$ $[M+NH_4]^+$: 522.2464 found: 522.2463.

Di(naphthalen-1-yl)methyl (*R*)-2-((2-methoxyphenyl)dimethylsilyl)propanoate (2o)



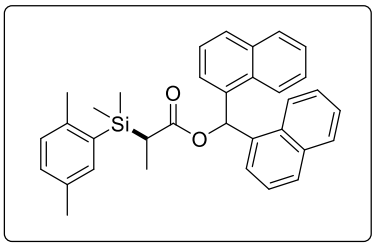
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (3-methoxyphenyl) dimethyl silane (33.2 mg, 0.2 mmol, 2 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-((2-methoxyphenyl) dimethylsilyl)propanoate **2o** as white solid (90% yield, 45.4 mg, 0.09 mmol), 95% *ee*. $[\alpha]^{24}_{D}$ = -37.23 (c 2.26, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.15 (d, *J* = 8.41 Hz, 1H), 7.97 (d, *J* = 8.41 Hz, 1H), 7.89 (d, *J* = 7.45 Hz, 2H), 7.84 (d, *J* = 7.64 Hz, 1H), 7.80 (d, *J* = 8.03 Hz, 1H), 7.53-7.39 (m, 6H), 7.34-7.23 (m, 3H), 7.18 (dd, *J* = 1.53, 7.26 Hz, 1H), 6.82 (t, *J* = 8.03 Hz, 1H), 6.73 (d, *J* = 8.41 Hz, 1H), 3.70 (s, 3H), 2.75 (q, *J* = 7.26 Hz, 1H), 1.20 (d, *J* = 7.26 Hz, 3H), 0.20 (s, 3H), 0.14 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 164.0, 135.9, 135.5, 135.4, 133.7, 131.2, 131.0, 130.9, 128.6, 128.6, 128.6, 126.5, 126.4, 126.0, 125.6, 125.2, 125.1, 124.1, 123.7, 123.6, 120.3, 109.3, 69.6, 54.8, 29.1, 11.7, -3.7, -4.6 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/CH_2Cl_2 = 300/1, Flow late = 1.0 mL/min, tR = 29.6 min (major product), tR = 42.8 min (minor product). IR (neat) ν 3055, 2954, 2833, 1718, 1581, 1507, 1234, 1163, 1023, 781 cm^{-1}. HRMS (DART) calcd for $C_{33}H_{36}N_1O_3Si_1$ $[M+NH_4]^+$: 522.2464 found: 522.2467.

Di(naphthalen-1-yl)methyl (*R*)-2-((3,5-dimethoxyphenyl)dimethylsilyl)propanoate (2p)



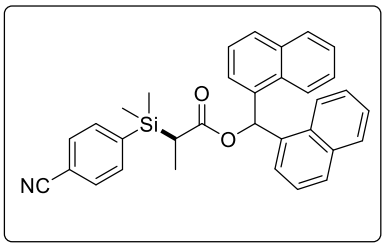
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (3-methoxyphenyl) dimethyl silane (39.26 mg, 0.2 mmol, 2 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-((3,5-dimethoxyphenyl)dimethylsilyl) propanoate **2p** as white solid (89% yield, 47.8 mg, 0.09 mmol), 96% *ee*. $[\alpha]^{24}_{D}$ = -41.81 (c 2.335, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52(s, 3H), 8.13-8.17 (m, 1H), 7.97 (d, *J* = 8.41 Hz, 1H), 7.87-7.91 (m, 2H), 7.83 (d, *J* = 14.33 Hz, 1H), 7.82 (d, *J* = 12.61 Hz, 1H), 7.53-7.39 (m, 7H), 7.33 (t, *J* = 7.26 Hz, 1H), 7.28 (d, *J* = 6.12 Hz, 1H), 6.56 (d, *J* = 2.10 Hz, 2H), 6.43 (t, *J* = 2.29 Hz, 1H), 3.77 (s, 3H), 2.45 (q, *J* = 6.88 Hz, 1H), 1.23 (d, *J* = 7.26 Hz, 3H), 0.19 (s, 3H), 0.14 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 160.2, 138.6, 135.6, 135.3, 133.7, 133.7, 130.9, 130.8, 129.0, 128.8, 128.7, 128.7, 126.6, 126.4, 126.1, 125.7, 125.7, 125.2, 125.1, 123.6, 123.5, 111.3, 101.2, 69.9, 55.1, 29.9, 11.8, -3.8, -5.0 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/CH_2Cl_2 = 80/1, Flow late = 1.0 mL/min, tR = 14.1 min (major product), tR = 20.1 min (minor product). IR (neat) ν 3055, 2958, 2837, 1709, 1577, 1159, 860, 785 cm^{-1}. HRMS (DART) calcd for $C_{34}H_{38}N_1O_4Si_1$ $[M+NH_4]^+$: 552.2570 found: 552.2574.

Di(naphthalen-1-yl)methyl (*R*)-2-((2,5-dimethylphenyl)dimethylsilyl)propanoate (2q)



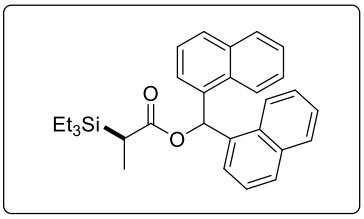
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (2,5-dimethylphenyl) dimethyl silane (32.86 mg, 0.2 mmol, 2 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-((2,5-dimethyl phenyl)dimethylsilyl) propanoate **2q** as white solid (87% yield, 43.7 mg, 0.087 mmol), 92% *ee*. $[\alpha]^{27}_{D}$ = -50.56 (c 2.17, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.14 (d, J = 8.98 Hz, 1H), 7.95 (d, J = 8.41 Hz, 1H), 7.85 (d, J = 9.17 Hz, 2H), 7.80 (d, J = 16.44 Hz, 1H), 7.78 (d, J = 16.44 Hz, 1H), 7.36-7.50 (m, 6H), 7.28 (t, J = 7.26 Hz, 1H), 7.22 (d, J = 8.03 Hz, 1H), 7.10 (s, 1H), 7.02 (d, J = 7.64 Hz, 1H), 6.96 (d, J = 7.64 Hz, 1H), 2.6 (q, J = 7.26 Hz, 1H), 2.31 (s, 3H), 2.21 (s, 3H), 1.17 (d, J = 7.26 Hz, 3H), 0.21 (s, 3H), 0.13 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.2, 140.2, 135.7, 135.6, 135.4, 134.3, 133.9, 133.7, 133.7, 130.9,130.9, 130.3, 129.9, 128.7, 128.6, 126.4, 126.1, 125.7, 125.2, 125.1, 123.6, 123.5, 69.8, 29.6, 22.6, 21.0 11.9, -2.6, -3.7 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 300/1, Flow late = 1.0 mL/min, tR = 24.6 min (major product), tR = 33.6 min (minor product). IR (neat) ν 3059, 2954, 1709, 1510, 1316, 1163, 789, 734 cm^{-1}. HRMS (DART) calcd for $C_{34}H_{38}N_1O_2Si_1$ $[M+NH_4]^+$: 520.2671 found: 520.2672.

Di(naphthalen-1-yl)methyl (*R*)-2-((4-cyanophenyl)dimethylsilyl)propanoate (2l)



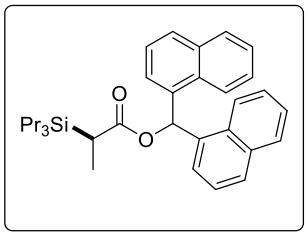
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and 4-(dimethylsilyl) benzonitrile (32.2 mg, 0.2 mmol, 2 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-((4-cyanophenyl) dimethylsilyl)propanoate **2l** as white solid (56 % yield, 29.0 mg, 0.056 mmol), 80% *ee*. $[\alpha]^{25}_{D}$ = - 61.42 (c 1.25, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.12 (d, *J* = 8.41 Hz, 1H), 7.90 (d, *J* = 8.03 Hz, 1H), 7.88-7.80 (m, 4H), 7.40-7.54 (m, 6H), 7.34 (t, *J* = 6.88 Hz, 1H), 7.29 (t, *J* = 7.45 Hz, 1H), 7.23-7.15 (m, 5H), 2.44 (q, *J* = 6.88 Hz, 1H), 1.25 (d, *J* = 7.26 Hz, 3H), 0.21 (s, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.3, 142.5, 138.3, 135.4, 135.1, 133.9, 133.8, 133.7, 130.9, 130.6, 130.4, 129.0, 128.9, 128.7, 128.7, 126.7, 126.5, 126.2, 125.8, 125.7, 125.1, 125.1, 124.8, 123.5, 123.3, 118.7, 112.6, 69.8, 29.5, 11.5, -4.2, -5.0 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 20/1, Flow late = 1.0 mL/min, tR = 14.0 min (major product), tR = 15.8 min (minor product). IR (neat) ν 3061, 2963, 2225, 1714, 1506, 1168, 1132, 783, 728 cm^{-1}. HRMS (DART) calcd for $C_{33}H_{29}N_1O_2Si_1$ $[M]^+$: 499.1967 found: 499.1966.

Di(naphthalen-1-yl)methyl (*R*)-2-(triethylsilyl)propanoate (2x)



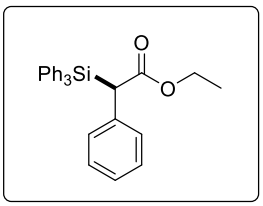
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and Triethylsilane (0.16 mL, 1 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl (*R*)-2-(triethylsilyl)propanoate **2x** as white solid (95 % yield, 43.3 mg, 0.095 mmol), 92 % *ee*. $[\alpha]^{18}_{D}$ = - 83.7 (c 2.165, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.33-8.27 (m, 1H), 7.95 (d, *J* = 8.79 Hz, 1H), 7.81-7.93 (m, 4 H), 7.61 (d, *J* = 7.26 Hz, 1H), 7.43-7.56 (m, 4H), 7.33-7.42 (m, 3H), 2.34 (q, *J* = 7.26 Hz, 1H), 1.28 (d, *J* = 7.26 Hz, 3H), 0.78 (t, *J* = 7.64 Hz, 9H), 0.42 (q, *J* = 7.64 Hz, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.6, 135.8, 135.6, 133.7, 133.7, 131.0, 130.7, 128.8, 128.7, 128.6, 128.5, 126.5, 126.3, 125.7, 125.6, 125.1, 124.8, 123.7, 123.6, 69.5, 27.2, 11.5, 7.1, 2.3, The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 400/1, Flow late = 1.0 mL/min, tR = 22.0 min (major product), tR = 31.7 min (minor product). IR (neat) ν 3064, 2948, 2877, 1714, 1320, 1168, 778, 722 cm^{-1}. HRMS (DART) calcd for $C_{30}H_{34}O_2Si_1$ $[M]^+$: 454.2328 found: 454.2328.

Di(naphthalen-1-yl)methyl (*R*)-2-(tripropylsilyl)propanoate (2y)



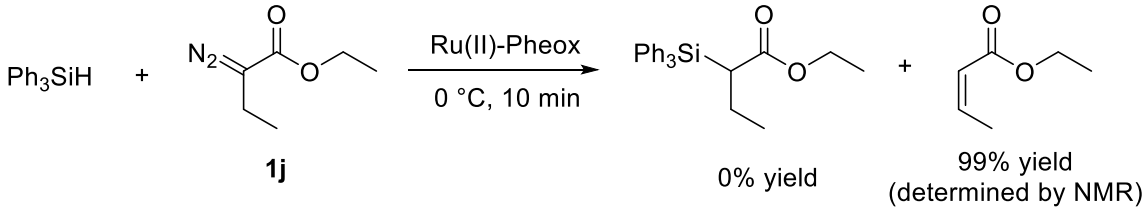
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and tripropylsilane (0.4 ml, 1.0 mmol, 10 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl) methyl (*R*)-2-(tripropylsilyl)propanoate **2y** as white solid (89% yield, 44.1 mg, 0.089 mmol), 94% *ee*. $[\alpha]^{20}_{D}$ = - 105.4 (c 2.15, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.33 (d, *J* = 7.64 Hz, 1H), 7.80-7.94 (m, 5H), 7.64 (d, *J* = 6.88 Hz, 1H), 7.58-7.41 (m, 4H), 7.32-7.40 (m, 3H), 2.31 (q, *J* = 6.88 Hz, 1H), 1.27 (d, *J* = 7.26 Hz, 3H), 1.25-1.07 (m, 6H), 0.75 (t, *J* = 9.94 Hz, 9H), 0.39 (t, *J* = 9.17 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 135.8, 135.7, 133.8, 133.7, 131.1, 130.7, 128.8, 128.7, 128.6, 128.5, 126.6, 126.4, 126.3, 125.7, 125.6, 125.1, 125.1, 124.6, 123.7, 123.5, 69.3, 27.8, 18.3, 17.0, 14.0, 11.4 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 300/1, Flow late = 1.0 mL/min, tR = 16.95 min (major product), tR = 25.72 min (minor product). IR (neat) ν 3050, 2959, 1721, 1163, 776 cm^{-1}. HRMS (DART) calcd for $C_{33}H_{41}O_2Si_1$ $[M+H]^+$: 497.2875 found: 497.2874.

Ethyl (*R*)-2-phenyl-2-(triphenylsilyl)acetate (2v)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of ethyl 2-diazo-2-phenylacetate **1i** (19.0 mg, 0.1 mmol) and triphenylsilane (52.1 mg, 0.2 mmol, 2 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ethyl (*R*)-2-phenyl-2 -(triphenylsilyl)acetate **2v** as colorless oil (53% yield, 22.6 mg, 0.05 mmol), 63% *ee*. $[\alpha]^{24}_{D}$ = + 17.42 (c 1.055, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.35 (m, 9H), 7.30-7.35 (m, 6H), 7.13 (s, 5H), 4.26 (s, 1H), 3.86-3.95 (m, 2H), 0.94 (t, *J* = 6.88 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 136.5, 132.2, 129.9, 129.8, 127.9, 127.6, 126.0, 60.5, 44.6, 13.7 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK OD-H), UV detector 230 nm, eluent: Hex/IPA = 100/1, Flow late = 1.0 mL/min, tR = 6.8 min (major product), tR = 17.9 min (minor product). IR (neat) ν 3069, 2978, 1714, 1424, 1274, 1109, 736, 697 cm^{-1}. HRMS (DART) calcd for $C_{28}H_{30}N_1O_2Si_1$ $[M+NH_4]^+$: 440.2045 found: 440.2041.

- **Si-H insertion of triphenylsilane with 2-diazo-2-ethylacetate (1j)**



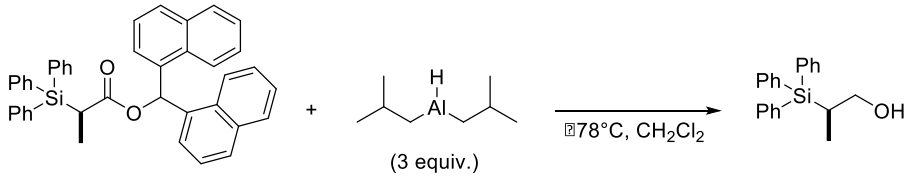
2-Diazo-2-ethylacetate **1j** was prepared following a previous report.[8] (**1j** : ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (q, *J* = 7.02 Hz, 2H), 2.34 (q, *J* = 7.63 Hz, 2H), 1.26 (t, *J* = 7.02 Hz, 3H), 1.12 (t, *J* = 7.32 Hz, 3H) ppm.)

To a solution of Ru(II)-Pheox (1 mol%, 0.002 mmol) in CH_2Cl_2 (2 mL) and triphenylsilane (2 equiv., 0.4 mmol) was cooled down to 0 °C under argon atmosphere. The mixture was added 2-Diazo-2-ethylacetate **1j** in CH_2Cl_2 (2 mL). After stirring at 0 °C for 10 min, the reaction mixture was concentrated under reduced pressure. As the result, cis-α, β-unsaturated compound was obtained in high yield (determined by crude ^{1}H NMR).

cis-α, β-unsaturated compound : ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.36-6.28 (m, 1H), 5.82-5.76 (m, 1H), 4.18 (dq, *J* = 6.88, 3.06 Hz, 2H), 2.13-2.16 (3H, m), 1.29 (dt, *J* = 3.06, 7.26 Hz, 3H) ppm.

4. Reduction of di(naphthalen-1-yl)methyl (*R*)-2-(triphenylsilyl)propanoate

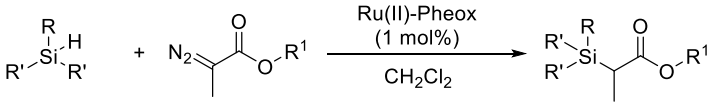
(*R*)-2-(triphenylsilyl)propan-1-ol (4)



To the solution of di(naphthalen-1-yl)methyl (*R*)-2-(triphenylsilyl)propanoate **2s** (0.05 mmol, 29.9 mg) in CH_2Cl_2 (1 mL) was cooled down to - 78 °C and stirred for 10 min. A hexane solution of diisobutylaluminum hydride (0.15 mmol, 0.15 mL, 3.0 equiv.) was added slowly to the CH_2Cl_2 solution and stirred for 90 min at – 78 °C.

The mixture was quenched with 1N HCl aq., allowed to warm to room temperature, extracted with CH_2Cl_2. Purification was performed by flush column chromatography to give corresponding alcohol; (*R*)-2-(triphenylsilyl)propan-1-ol **4** (88% yield, 14.0 mg, 0.04 mmol), 98% *ee*. $[\alpha]^{21}_{D}$ = +11.3 (c 0.395, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.58 (m, 6H), 7.34-7.43 (m, 9H), 3.99 (dd, *J* = 3.82, 10.70 Hz, 1H), 3.66 (dd, J = 9.59, 10.70 Hz, 1H), 2.06-1.97 (m, 1H), 1.24 (d, J = 726 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.9, 133.8, 129.4, 127.9, 65.7, 22.6, 12.8 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 100/1, Flow late = 1.0 mL/min, tR = 23.7 min (major product), tR = 25.5 min (minor product). IR (neat) ν 3398, 3068, 2952, 2920, 2864, 1427, 1105, 1005, 699 cm^{-1}. HRMS (DART) calcd for $C_{21}H_{26}N_1O_2Si_1$ $[M+NH_4]^+$: 336.1783 found: 336.1784.

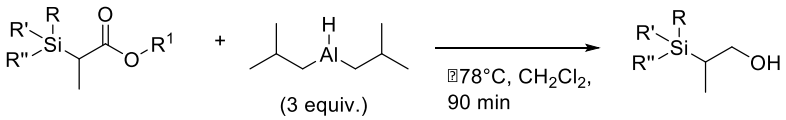
5. General Procedure for Catalytic Asymmetric Si-H Insertion Reaction to Construct Chiral Carbon and Silicon[7]



To a solution of Ru(II)-Pheox (0.001 mmol, 1.0 mol%) in CH_2Cl_2 (0.5 mL) and silane compound (0.5 mmol, 5.0 equiv.) was cooled down to -30 ºC under argon atmosphere.

The mixture was added diazo ester (0.1 mmol, 1 equiv.) in CH_2Cl_2 (0.5 mL).

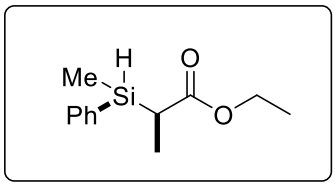
After stirring at -30 ºC, the reaction mixture was concentrated under reduced pressure to give crude product. Purification was performed by column chromatography with Hex/EA to give desired product.



The insertion product was dissolved in dichloromethane (1 mL). The solution was cooled down to -78 °C and stirred for 10 min. A hex solution of diisopropylalminum hydride (1.0 M) was added to the dichloromethane solution and stirred for 90 min at -78 °C. The mixture was quenched with 1N HCl aqu. (10 drops), allowed to warm to room temperature, extracted with dichloromethane. The combined organic layer were dried over Na_2SO_4 and concentrated. Purification was performed by column chromatography to give desired product. The *ee* value was determined by chiral HPLC analysis.

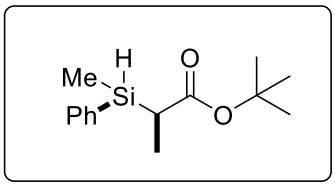
6. Analytical Data for Asymmetric Si-H Insertion Reaction Products (2)

Ethyl (*(S)*-Si, *(R)*-C)-2-(methyl(phenyl)silyl)propanoate



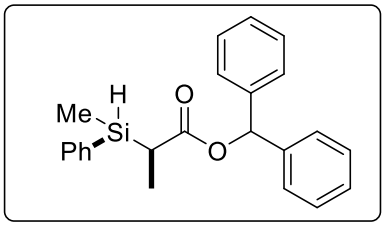
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of ethyl 2-diazopropanoate (25.6 mg, 0.2 mmol) and methylphenylsilane (0.14 mL, 1.0 mmol, 5 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ethyl ((*S*)-Si, (*R*)-C)-2-(methyl(phenyl)silyl)propanoate as colorless oil (91% yield, 40.3 mg, 0.18 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.57 (m, 2H), 7.34-7.43 (m, 3H), 4.43 (dq, *J* = 1.53, 3.82 Hz, 0.6H), 4.39 (dq, *J* = 0.76, 3.06 Hz, 0.4H), 3.99-4.08 (m, 2H), 2.88-2.31 (m, 1H), 1.22 (dd, *J* = 8.79 Hz, 3H), 1.14 (q, *J* = 15.29 Hz, 3H), 0.44 (dd, *J* = 3.44 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.5, 175.5, 134.6, 134.5, 133.3, 133.3, 129.8, 127.9, 60.0, 28.2, 28.1, 14.2, 14.2, 11.8, 11.4, -6.9, -7.1 ppm. IR (neat) ν 3072, 2960, 2924, 2128, 1718, 1427, 1256, 1120, 1065, 873, 794, 699 cm^{-1}. HRMS (DART) calcd for $C_{12}H_{22}N_1O_2Si_1$ $[M+NH_4]^+$: 240.1419 found: 240.1417.

***tert*-Butyl (*(S)*-Si, *(R)*-C)-2-(methyl(phenyl)silyl)propanoate**



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of *t*-buthyl 2-diazopropanoate # (31.2 mg, 0.2 mmol) and methylphenylsilane (0.14 mL, 1.0 mmol, 5 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give tert-butyl ((*S*)-Si, (*R*)-C)-2-(methyl(phenyl)silyl)propanoate as colorless oil (64 yield, 32 mg, 0.13 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.57 (m, 2H), 7.33-7.41 (m, 3H), 4.42 (dq, *J* = 1.53, 3.82 Hz, 06H), 4.38 (dq, *J* = 0.76, 3.82 Hz, 0.4H), 2.27 (dq, *J* = 2.10, 7.26 Hz, 1H), 1.34 (s, 3.6H), 1.33 (s, 5.4H), 1.19 (d, *J* = 7.26 Hz, 1.2H), 1.17 (d, *J* = 6.88 Hz, 1.8H), 0.44 (d, *J* = 1.53 Hz, 1.8H), 0.43 (d, *J* = 1.15 Hz, 1.2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 134.7, 134.6, 134.0, 133.7, 129.7, 129.7, 127.8, 79.8, 79.7, 28.8, 28.1, 28.0, 11.9, 11.4, -6.8, -7.0 ppm. IR (neat) ν 3065, 2970, 2939, 2873, 2130, 1718, 1428, 1365, 8, 1321, 1251, 1153, 878, 831, 725, 697 cm^{-1}. HRMS (DART) calcd for $C_{14}H_{23}O_2Si_1$ $[M+H]^+$: 251.1467 found: 251.1465.

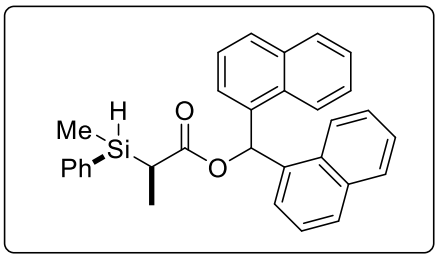
Benzhydryl (*(S)*-Si, *(R)*-C)-2-(methyl(phenyl)silyl)propanoate



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of benzhydryl 2-diazopropanoate # (26.6 mg, 0.1 mmol) and methylphenylsilane (0.07 mL, 0.5 mmol, 5 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give benzhydryl ((*S*)-Si, (*R*)-C) -2-(methyl(phenyl) silyl) propanoate as colorless oil (84 yield, 30.4 mg, 0.084 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.44 (m, 15H), 6.85 (s, 1H), 4.48 (dq, *J* = 1.91, 5.73 Hz, 0.6H), 4.42 (dq, *J* = 2.68, 6.50 Hz, 0.4H), 2.45-2.54 (m, 1H), 1.24 (dd, *J* = 7.26, 22.17 Hz, 3H), 0.30 (dd, *J* = 3.82, 17.58 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ

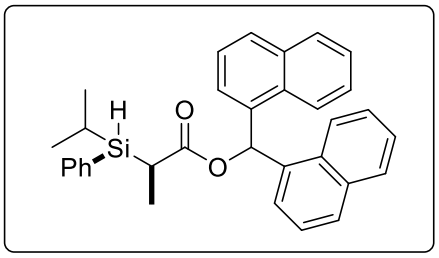
174.5, 140.5, 140.4, 140.3, 134.6, 134.6, 133.4, 133.2, 132.9, 129.8, 129.8, 128.3, 128.3, 127.9, 127.7, 127.6, 127.6, 127.4, 127.4, 127.0, 126.9, 76.6, 28.3, 28.2, 11.9, 11.3, -7.2, -7.3 ppm. IR (neat) ν 3065, 3025, 2978, 2939, 2130, 1729, 1455, 1494, 1428, 1172, 1080, 835, 736, 700 cm^{-1}. HRMS (DART) calcd for $C_{23}H_{24}O_2Si_1$ $[M]^+$: 360.1545 found: 360.1547.

Di(naphthalen-1-yl)methyl (*(S)*-Si, *(R)*-C)-2-(methyl(phenyl)silyl)propanoate (3a)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and methylphenylsilane (0.068 mL, 0.5 mmol, 5 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl ((*S*)-Si,(*R*)-C)-2-(methyl(phenyl)silyl) propanoate **3a** as white solid (93 yield, 42.6 mg, 0.093 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.12 (d, *J* = 7.64 Hz, 0.3H), 8.06 (d, *J* = 8.41 Hz, 0.7H), 7.98 (d, *J* = 8.41 Hz, 0.8H), 7.92 (d, *J* = 8.79 Hz, 0.2H), 7.78-7.91 (m, 4H), 7.27-7.53 (m, 11H), 7.15-7.21 (m, 2H), 4.45 (dq, *J* = 3.44, 3.55 Hz, 0.7H), 4.37 (dq, *J* = 3.82, 7.26 Hz, 0.3H), 2.35 (dq, *J* = 1.91, 7.26 Hz, 0.7H), 2.48 (dq, *J* = 2.29, 7,26 Hz, 0.3H), 1.26 (d, *J* = 7.26 Hz, 1H), 1.23 (d, *J* = 7.26 Hz, 2H), 3.82 (d, *J* = 3.82 Hz, 2H), 0.21 (d, *J* = 3.82 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 135.4, 135.2, 135.2, 134.5, 133.7, 133.1, 132.9, 131.0, 130.9, 130.9, 129.7, 129.7, 128.8, 128.8, 128.7, 127.8, 127.7, 126.6, 126.5, 126.5, 126.2, 125.9, 125.7, 125.6, 125.5, 125.3, 125.1, 123.6, 123.5, 70.3, 28.4, 28.1, 12.1, 11.4, -7.1, -7.6 ppm. IR (neat) ν 3060, 2968, 2937, 2128, 1710, 1312, 1172, 1136, 834, 778, 727, 694 cm^{-1}. HRMS (DART) calcd for $C_{31}H_{32}N_1O_2Si_1$ $[M+H]^+$: 478.2202 found: 478.2201.

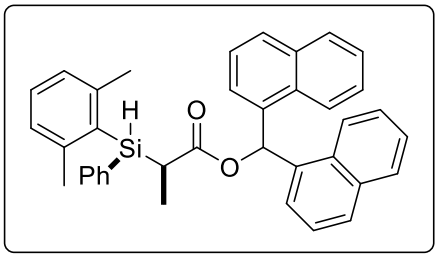
Di(naphthalen-1-yl)methyl (*(S)*-Si, *(R)*-C)-2-(isopropyl(phenyl)silyl)propanoate (3b)



This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and isopropylphenylsilane (75.15 mg, 0.5 mmol, 5 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl ((*S*)-Si, (*R*)-C)-2-(methyl(phenyl)silyl) propanoate **3b** as white solid (92% yield, 45.2 mg, 0.092 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 0.2H), 8.48 (s, 0.8H), 8.17 (d, *J* = 7.26 Hz, 0.2H), 8.13 (d, *J* = 8.03 Hz, 0.7H), 7.95-7.77 (m, 5H), 7.52-7.22 (m, 11H), 7.18 (t, *J* = 7.26 Hz, 0.4H), 7.09 (t, *J* = 8.03 Hz, 1.6H), 4.15 (t, *J* = 3.06 Hz, 0.2H), 4.10 (dd, *J* = 2.68, 3.82 Hz, 0.8H), 2.57-2.66 (m, 1H), 1.31 (d, *J* = 7.26 Hz, 2.4H), 1.25 (d. *J* = 7.26 Hz, 0.6H), 0.99-1.09 (m, 1H), 0.97 (d, *J* = 6.88 Hz, 2.4H), 0.87 (d, *J* = 7.26 Hz, 0.6H), 0.82-0.77 (m, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.9, 174.7, 135.5, 135.3, 133.7, 131.3, 130.9, 130.8, 129.6, 129.6, 128.9, 128.8, 128.7, 128.7, 127.7, 127.5, 126.5, 126.5, 126.3, 126.1, 125.7, 125.7, 125.2, 125.1, 123.6, 123.5, 70.2, 70.1, 26.8, 26.5, 18.2, 18.1, 17.9, 17.8, 12.4, 12.2, 10.7, 10.6 ppm.

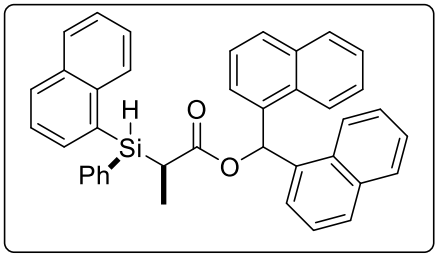
IR (neat) ν 3051, 2944, 2864, 2120, 1718, 1312, 1168, 781, 735, 699 cm^{-1}. HRMS (DART) calcd for $C_{33}H_{33}O_2Si_1$ $[M+H]^+$: 489.2249 found: 489.2247.

Di(naphthalen-1-yl)methyl (*(S)*-Si, *(R)*-C)-2-((2,6-dimethylphenyl)(phenyl)silyl)propanoate (3c)



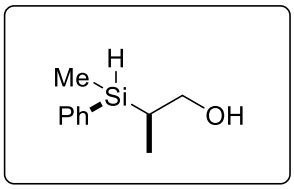
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and (2,6-dimethylphenyl) phenylsilane (106.18 mg, 0.5 mmol, 5 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl ((*S*)-Si, (*R*)-C)-2-((2,6-dimethyl phenyl)(phenyl)silyl) propanoate **3c** as white solid (87 yield, 47.9 mg, 0.87 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 0.54H), 8.36 (s, 0.46H), 8.00 (t, J = 9.59 Hz, 1H), 7.69-7.92 (m, 5H), 7.13-7.53 (m, 12H), 7.06-6.97 (m, 2H), 6.95 (d, *J* = 7.64 Hz, 1H), 6.73 (d, *J* = 7.64 Hz, 1H), 5.35 (d, *J* = 5.35 Hz, 0.5H), 5.16 (d, *J* = 4.59 Hz, 0.5H), 2.97-3.05 (m, 1H), 2.30 (s, 3H), 2.22 (m, 1H), 1.50 (d, *J* = 6.88 Hz, 1.3H), 1.24 (d, *J* = 7.26 Hz, 1.7H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.4, 175.0, 144.9, 144.7, 135.5, 135.3, 135.2, 135.0, 134.9, 133.8, 133.7, 133.6, 132.6, 132.4, 131.0, 130.9, 130.7, 130.1, 130.1, 129.9, 129.8, 129.6, 129.3, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.0, 127.8, 127.6, 127.5, 126.5, 126.5, 126.4, 125.9, 125.7, 125.6, 125.5, 125.5, 125.4, 125.1, 123.6, 123.4, 123.3, 123.3, 70.7, 70.3, 27.5, 26.9, 24.5, 24.4, 13.9, 12.8 ppm. IR (neat) ν 3057, 2963, 2928, 2873, 2161, 1718, 1451, 1310, 1168, 776, 736, 700 cm^{-1}. HRMS (DART) calcd for $C_{38}H_{38}N_1O_2Si_1$ $[M+NH_4]^+$: 568.2671 found: 568.2679.

Di(naphthalen-1-yl)methyl (*(S)*-Si, *(R)*-C)-2-(naphthalen-1-yl(phenyl)silyl)propanoate (3d)



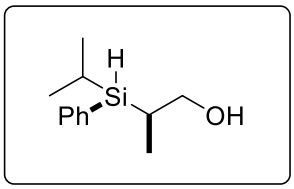
This compound was prepared according to the typical procedure for asymmetric Si-H insertion reaction of di(naphthalen-1-yl)methyl 2-diazopropanoate **1h** (36.6 mg, 0.1 mmol) and 1-Naphthylphenylsilane (117.2 mL, 0.5 mmol, 5 equiv.). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give di(naphthalen-1-yl)methyl ((*S*)-Si, (*R*)-C)-2-(naphthalen-1-yl (phenyl)silyl) propanoate **3d** as white solid (91% yield, 52.4 mg, 0.091 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ8.41 (s, 0.7H), 8.37 (s, 0.3H), 7.75-8.00 (m, 8H), 7.72 (t, *J* = 8.41 Hz, 1H), 7.64 (d, *J* = 5.73 Hz, 0.4H), 7.58 (d, *J* = 6.88 Hz, 0.6H), 7.50-7.16 (m, 13H), 7.01-7.14 (m, 3H), 5.38 (d, *J* = 3.06 Hz, 0.3H), 5.35 (d, *J* = 3.44 Hz, 0.7H), 3.10-3.00 (m, 1H), 1.38 (d, *J* = 6.88 Hz, 1H), 1.33 (d, *J* = 6.88 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.7, 137.0, 136.9, 136.3, 135.9, 135.5, 135.4, 135.3, 135.3, 134.8, 133.7, 133.7, 133.6, 133.6, 133.1, 133.1, 131.6, 131.5, 130.9, 130.8, 129.9, 129.9, 128.9, 128.8, 128.7, 128.6, 128.5, 127.9, 127.8, 127.6, 126.5, 126.4, 126.4, 126.1, 126.1, 125.9, 125.8, 125.7, 125.6, 125.6, 125.5, 125.1, 125.1, 125.1, 125.0, 125.0, 123.5, 123.4, 70.6, 27.6, 27.4, 12.9, 12.7 ppm. IR (neat) ν 3057, 2959, 2936, 2877, 2142, 1718, 1506, 1310, 1172, 776, 732, 697 cm^{-1}. HRMS (DART) calcd for $C_{40}H_{36}N_1O_2Si_1$ $[M+H]^+$: 590.2515 found: 590.2514.

((*S*)-Si, *(R)*-C)-2-(Methyl(phenyl)silyl)propan-1-ol (4a)



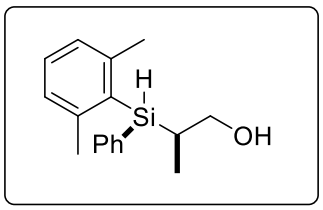
This compound was prepared according to the typical procedure for reduction of di(naphthalen-1-yl)methyl ((*S*)-Si, (*R*)-C)-2-(methyl(phenyl)silyl)propanoate **3a** (42 mg, 0.09 mmol) at -5 °C. The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ((*S*)-Si, (*R*)-C)-2-(methyl(phenyl)silyl)propan-1-ol **4a** as yellow oil (88% yield, 14.2 mg, 0.079 mmol), . ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.64 Hz, 2H), 7.33-7.41 (m, 3H), 4.29 (dq, *J* = 3.44, 7.26 Hz, 1H), 3.76 (ddd, *J* = 4.97, 10.32 Hz, 1H), 3.56-3.62 (m, 1H), 1.27-1.37 (m, 1H), 1.07 (dd, *J* = 5.35, 7.26 Hz, 3H), 0.37 (dd, *J* = 1.53, 3.82 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.9, 134.6, 134.6, 129.4, 127.9, 127.8, 66.0, 65.9, 23.0, 22.9, 12.3, 12.1, -7.3 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 220 nm, eluent: Hex/IPA = 350/1, Flow late = 1.0 mL/min, tR = 35.8 min (major product, major), tR = 43.5 min (manor product, minor), tR = 40.1 min (minor product, major), tR = 38.3 min (minor protduct, minor). IR (neat) ν 3351, 3065, 2928, 2860, 2110, 1428, 1251, 1113, 869, 831, 725, 700 cm^{-1}. HRMS (DART) calcd for $C_{10}H_{20}N_1O_1Si_1$ $[M+NH_4]^+$: 198.1314 found: 198.1317.

((*S*)-Si, *(R)*-C)-2-(Isopropyl(phenyl)silyl)propan-1-ol (4b)



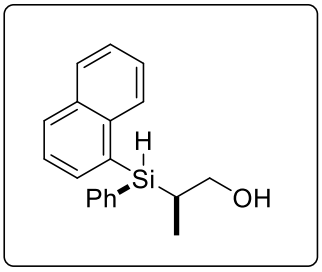
This compound was prepared according to the typical procedure for reduction of di(naphthalen-1-yl)methyl (*2R, 3S*)-2-(isopropyl(phenyl)silyl)propanoate **3b** (26.2 mg, 0.05 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ((*S*)-Si, (*R*)-C)-2-(isopropyl(phenyl) silyl)propan-1 -ol **4b** as colorless oil (47% yield, 5.3 mg, 0.025 mmol), 99% *ee* (major), 96% *ee* (minor), d.r. = 79:21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.50 (m, 2H), 7.32-7.41 (m, 3H), 4.05 (t, *J* = 2.68 Hz, 0.2H), 4.00 (t, *J* = 3.06 Hz, 0.8H), 3.83 (dd, *J* = 4.97, 10.32 Hz, 0.2H), 3.72 (dd, *J* = 4.97, 10.70 Hz, 0.8H), 3.60 (dd, *J* = 8.79, 10.70 Hz, 0.2H), 3.55 (dd, *J* = 9.17, 10.70 Hz, 0.8H), 1.43-1.51 (m, 0.2H), 1.32-1.24 (m, 0.8H), 1.14 (d, *J* = 7.26 Hz, 3H), 1.08 (d, *J* = 7.26 Hz, 2.4H), 1.06 (d, *J* = 7.26 Hz, 0.6H), 1.00 (d, *J* = 7.26 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.4, 135.3, 133.3, 133.2, 129.3, 129.3, 127.8, 66.1, 66.0, 25.3, 21.2, 18.6, 18.5, 18.4, 18.4, 12.8, 12.4, 10.6, 10.4 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IF-3), UV detector 254 nm, eluent: Hex/IPA = 350/1, Flow late = 1.0 mL/min, tR = 25.6 min (major product, major), tR = 30.0 min (major product, minor), tR = 27.5 min (minor product, major), tR = 28.9 min (minor protduct, minor). IR (neat) ν 3343, 3065, 2928, 2860, 2102, 1467, 1113, 999, 803, 780, 736, 693 cm^{-1}. HRMS (DART) calcd for $C_{12}H_{21}O_1Si_1$ $[M+H]^+$: 209.1361 found: 209.1361.

((*S*)-Si, *(R)*-C)-2-((2,6-Dimethylphenyl)(phenyl)silyl)propan-1-ol (4c)



This compound was prepared according to the typical procedure for reduction of di(naphthalen-1-yl)methyl (*2R, 3S*)-2-((2,6-dimethylphenyl)(phenyl)silyl) propanoate **3c** (33 mg, 0.06 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ((*S*)-Si, (*R*)-C)-2-(2,6-dimethyl (phenyl)silyl)propan-1-ol **4c** as colorless oil (33 % yield, 5.4 mg, 0.02 mmol), 99.9% *ee* (major), 99.7% *ee* (minor), d.r. = 58:42. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.53 (m, 2H), 7.29-7.38 (m, 3H), 7.19 (dt, *J* = 4.97, 7.26 Hz, 1H), 7.00 (t, *J* = 6.88 Hz, 2H), 5.05 (t, *J* = 4.97 Hz, 1H), 4.04 (dd, *J* = 4.97, 10.70 Hz, 0.4H), 3.81-3.72 (m, 1H), 3.61 (dd, *J* = 8.41, 10.70 Hz, 0.6H), 2.41 (s, 6H), 1.87-1.97 (m, 1H), 1.35 (d, *J* = 7.26 Hz, 1.8H), 1.08 (d, *J* = 1.3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 144.8, 135.1, 134.1, 133.8, 131.4, 131.0, 129.8, 129.7, 129.3, 129.2, 128.0, 127.9, 127.7, 127.7, 66.7, 66.2, 24.6, 24.5, 21.9, 21.7, 14.3, 12.9 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IC), UV detector 220 nm, eluent: Hex/IPA = 99.5/0.5, Flow late = 0.5 mL/min, tR = 45.0 min (major product, major), tR = 43.2 min (major product, minor), tR = 58.7 min (minor product, major), tR = 48.2 min (minor protduct, minor). IR (neat) ν 3324, 3053, 2923, 2860, 2142, 1585, 1443, 1105, 996, 783, 740 cm^{-1}. HRMS (DART) calcd for $C_{17}H_{26}N_1O_1Si_1$ $[M+NH_4]^+$:288.1783 found:288.1788.

((*S*)-Si, *(R)*-C)-2-(Naphthalen-1-yl(phenyl)silyl)propan-1-ol (4d)

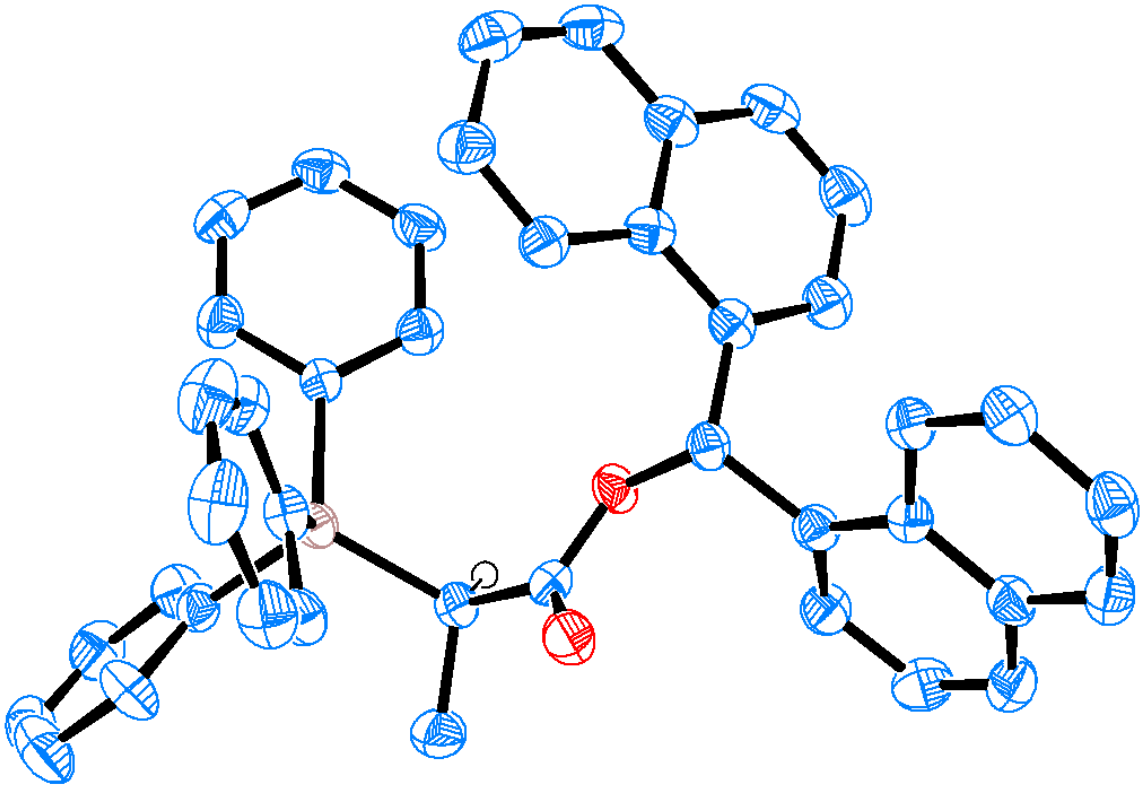


This compound was prepared according to the typical procedure for reduction of di(naphthalen-1-yl)methyl (*2R, 3S*)-2-(naphthalen-1-yl(phenyl)silyl)propanoate **3c** (31.8 mg, 0.05 mmol). The resulting mixture was purified by silica gel column chromatography with Hexane/EtOAc as an eluent to give ((*S*)-Si, (*R*)-C)-2-(naphthalene-1-yl(phenyl)silyl)propan-1-ol **4c** as colorless oil (83% yield, 13.5 mg, 0.046 mmol), 99% *ee* (major), 99% *ee* (minor), d.r. = 64:36 . ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.26 Hz, 1H), 7.91 (dd, *J* = 3.06, 8.41 Hz, 1H), 7.86 (d, *J* = 7.86 Hz, 1H), 7.81 (dt, *J* = 1.15, 6.50 Hz, 1H), 7.62 (d, *J* = 6.50 Hz, 2H), 7.50-7.41 (m, 3H), 7.41-7.32 (m, 3H), 5.20 (dd, *J* = 3.06, 6.12 Hz, 1H), 3.91 (dd, *J* = 4.97, 10.70 Hz, 0.5H), 3.82 (dd, *J* = 4.59, 10.70 Hz, 0.5H), 3.72 (dd, *J* = 8.79, 10.70 Hz, 0.5H), 3.64 (dd, *J* = 8.79, 10.70 Hz, 0.5H) 1.99-1.90 (m, 1H), 1.25 (d, *J* = 7.26 Hz, 1.5H), 1.16 (d, *J* = 7.26 Hz, 1.5H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 137.2, 135.8, 135.5, 135.4, 133.3, 133.2, 133.1, 131.5, 131.2, 130.6, 130.6, 129.7, 129.6, 128.9, 128.1, 128.0, 1287.9, 127.9, 126.1, 126.1, 125.7, 125.6, 125.1, 125.1, 66.1, 66.1, 29.6, 22.3, 13.2, 13.2 ppm. The *ee* value was determined by chiral HPLC analysis. Column (CHIRALPAK IB), UV detector 254 nm, eluent: Hex/IPA = 100/1, Flow late = 1.0 mL/min, tR = 34.6 min (major product, major), tR = 27.4 min (major product, minor), tR = 39.8 min (minor product, major), tR = 32.1 min (minor protduct, minor). IR (neat) ν 3368, 3057, 2928, 2857, 2119, 1428, 1113, 1003, 835, 791, 736, 697 cm^{-1}. HRMS (DART) calcd for $C_{19}H_{21}O_1Si_1$ $[M+H]^+$: 293.1361 found: 293.1361.

7. X-ray Crystal Structure

Di(naphthalen-1-yl)methyl (*R*)-2-(triphenylsilyl)propanoate (7s)

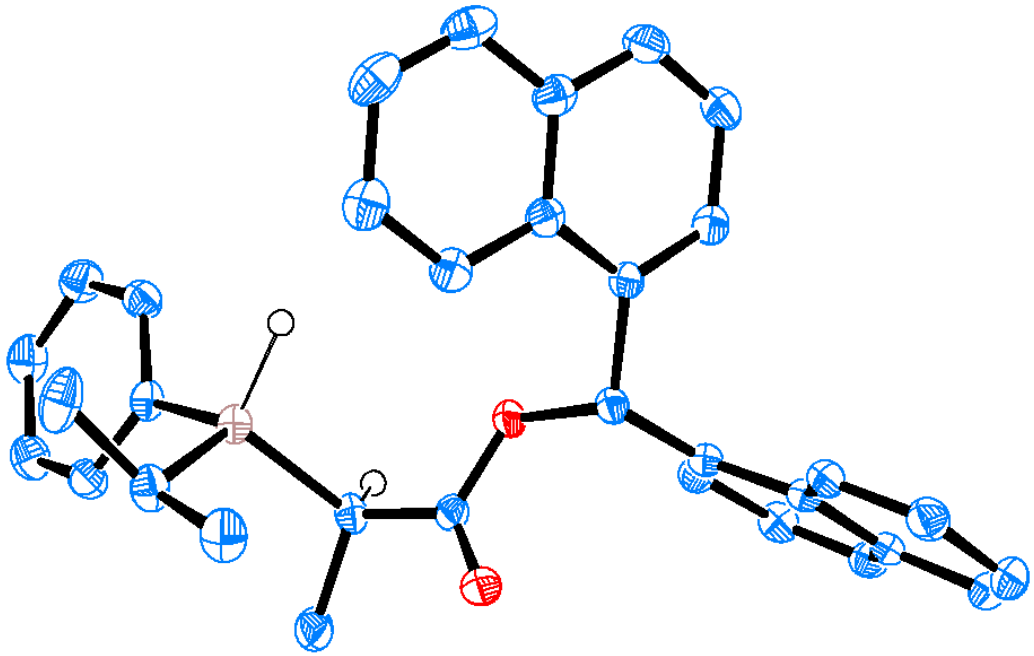
(CCDC 1520036)



Empirical formula	C42 H34 O2 Si	
Formula weight	598.78	
Temperature	150(2) K	
Wavelength	1.54187 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 10.9103(2) Å	α= 94.2055(15)°.
	b = 12.8039(3) Å	β= 104.2240(14)°.
	c = 12.8160(3) Å	γ = 112.0732(14)°.
Volume	1580.65(6) $Å^3$	
Z	2	
Density (calculated)	1.258 Mg/m^3	
Absorption coefficient	0.933 mm^{-1}	
F(000)	632	
Crystal size	0.20 x 0.20 x 0.10 mm^3	
Theta range for data collection	3.62 to 71.78°.	
Index ranges	-13<=h<=13, -15<=k<=15, -15<=l<=15	
Reflections collected	27464	
Independent reflections	10310 [R(int) = 0.0254]	
Completeness to theta = 71.78°	96.4 %	
Max. and min. transmission	0.9125 and 0.8353	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10310 / 3 / 813	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0927	
R indices (all data)	R1 = 0.0439, wR2 = 0.1058	
Absolute structure parameter	0.01(2)	
Largest diff. peak and hole	0.309 and -0.282 $e.Å^{-3}$	

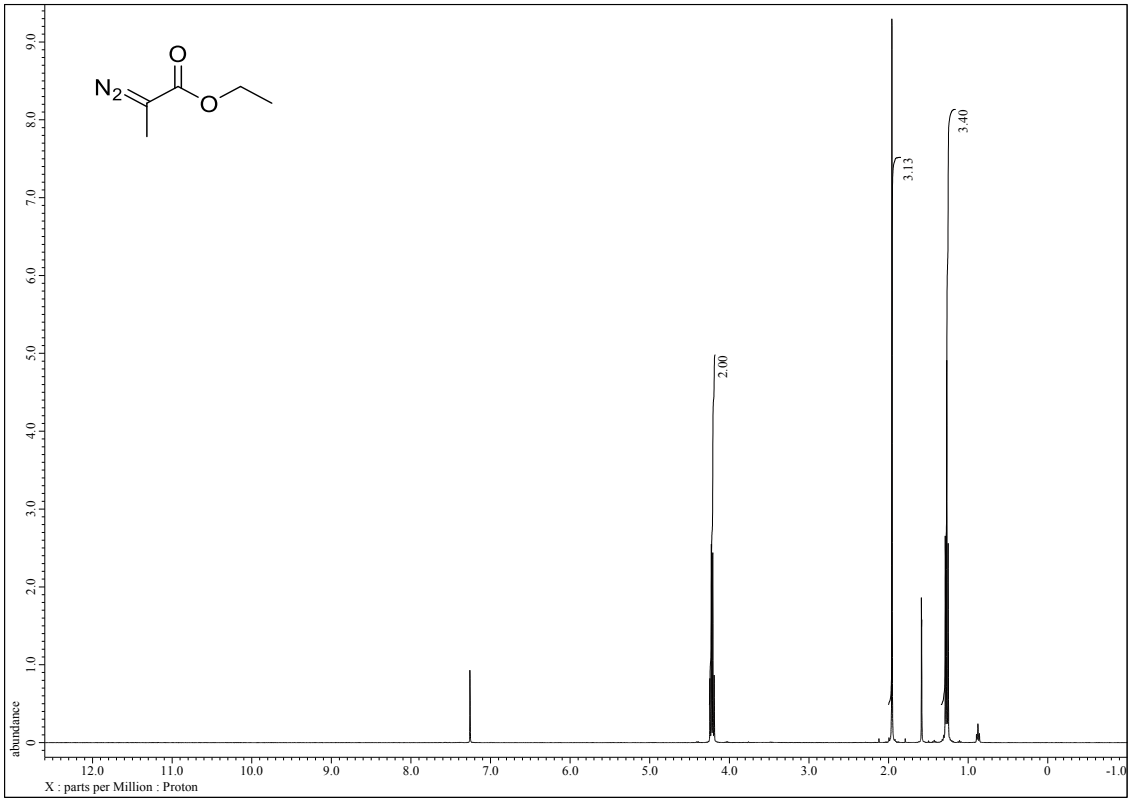
Di(naphthalen-1-yl)methyl (*(S)*-Si, *(R)*-C)-2-(isopropyl(phenyl)silyl)propanoate

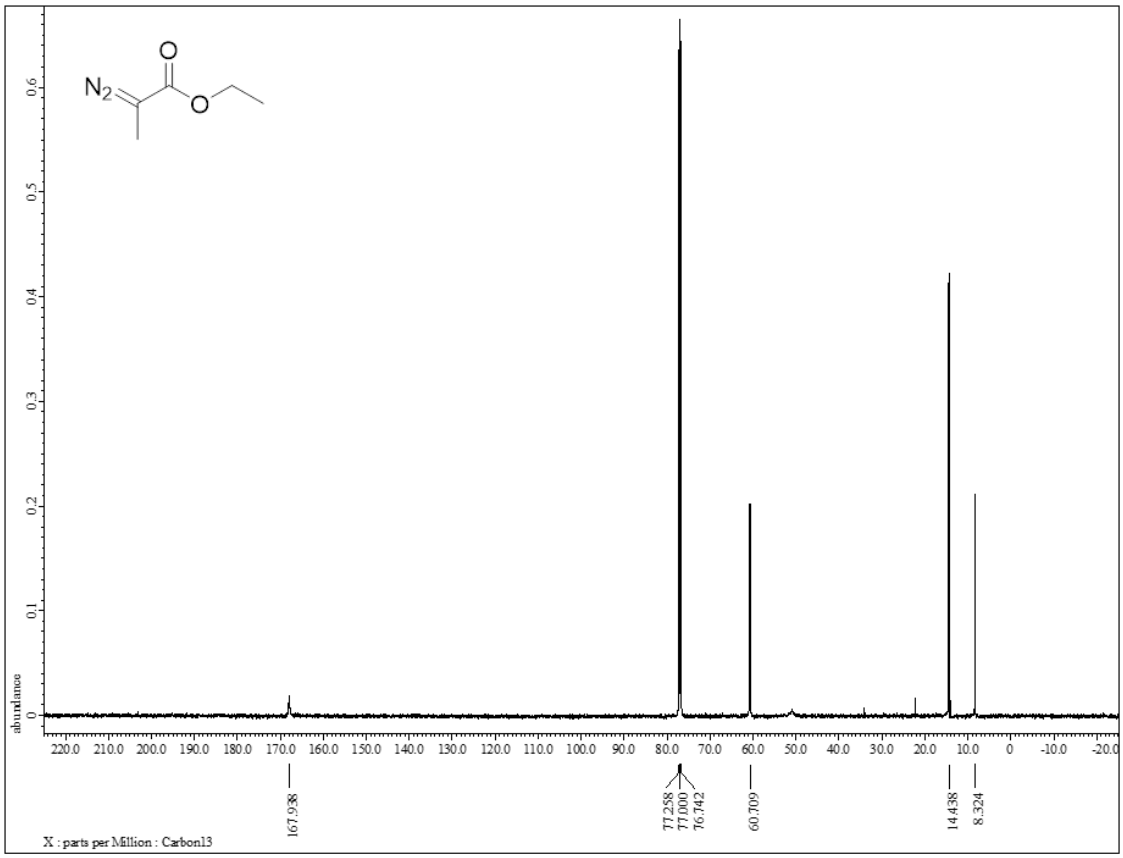
CCDC 1520048

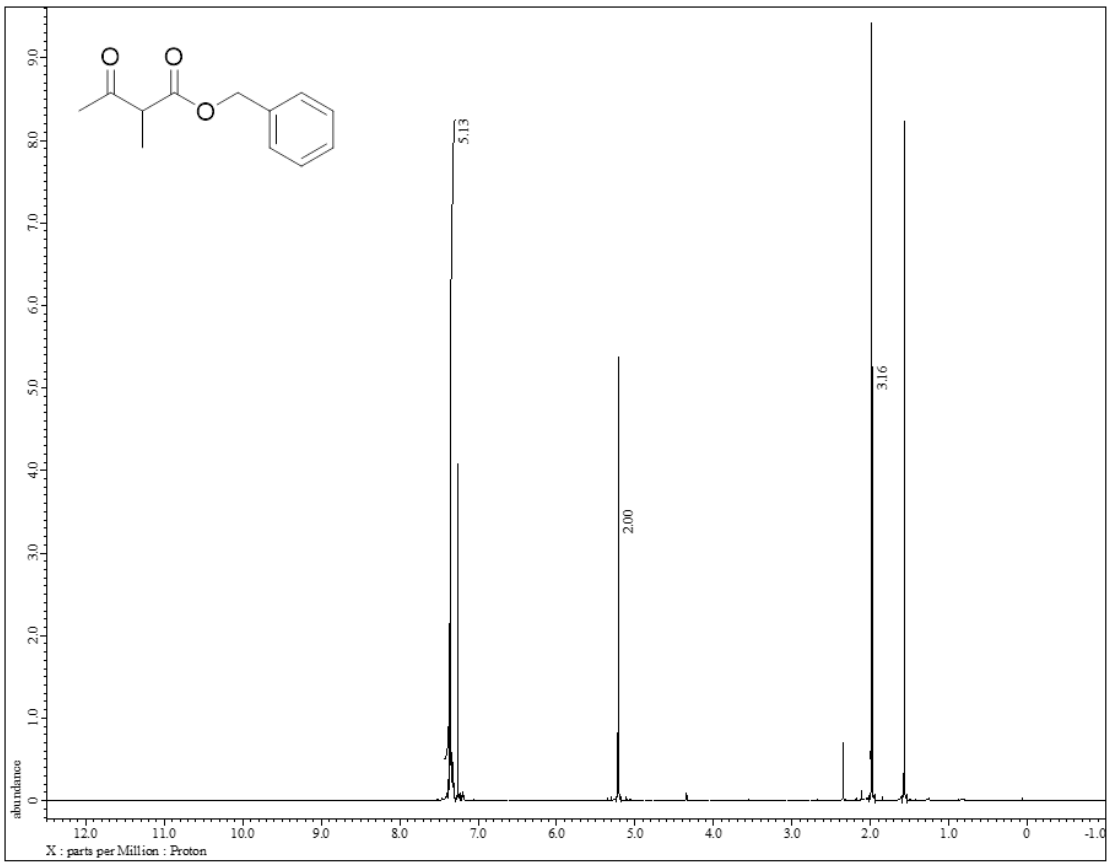


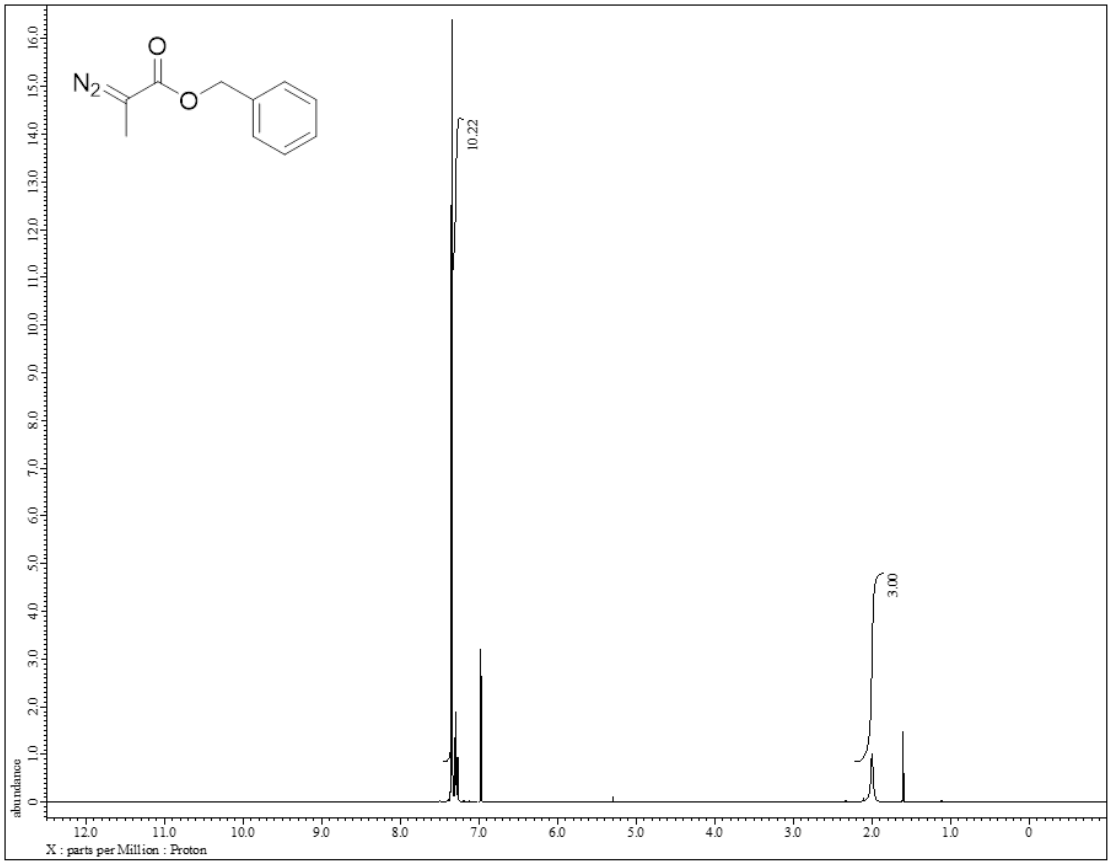
Empirical formula	C33 H32 O2 Si	
Formula weight	488.68	
Temperature	120(2) K	
Wavelength	0.71069 Å	
Crystal system	Orthorhombic	
Space group	$P\ 2_12_12_1$	
Unit cell dimensions	a = 7.8733(3) Å	α= 90°.
	b = 11.1819(4) Å	β= 90°.
	c = 29.7290(11) Å	γ = 90°.
Volume	2617.30(17) $Å^3$	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.118 mm^{-1}	
F(000)	1040	
Crystal size	0.50 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.28 to 28.50°.	
Index ranges	-10<=h<=8, -14<=k<=14, -39<=l<=39	
Reflections collected	37625	
Independent reflections	6259 [R(int) = 0.0281]	
Completeness to theta = 28.50°	96.0 %	
Max. and min. transmission	0.9883 and 0.9432	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6259 / 0 / 332	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0382, wR2 = 0.0950	
R indices (all data)	R1 = 0.0404, wR2 = 0.0969	
Absolute structure parameter	0.03(10)	
Largest diff. peak and hole	0.551 and -0.278 $e.Å^{-3}$	

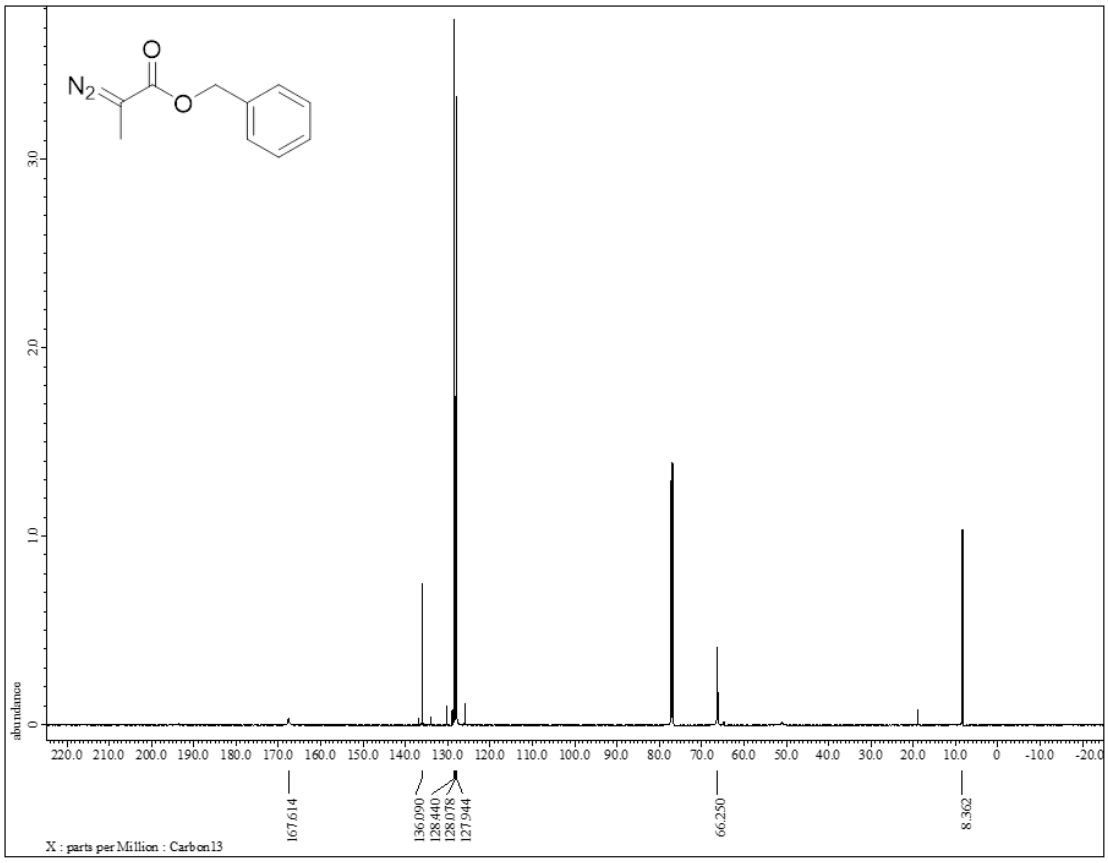
8. NMR Spectral Data






5.13
2.00
3.16
abundance
X : parts per Million : Proton


10.22
3.00
abundance
X : parts per Million : Proton


N2
O
O
abundance
167.614
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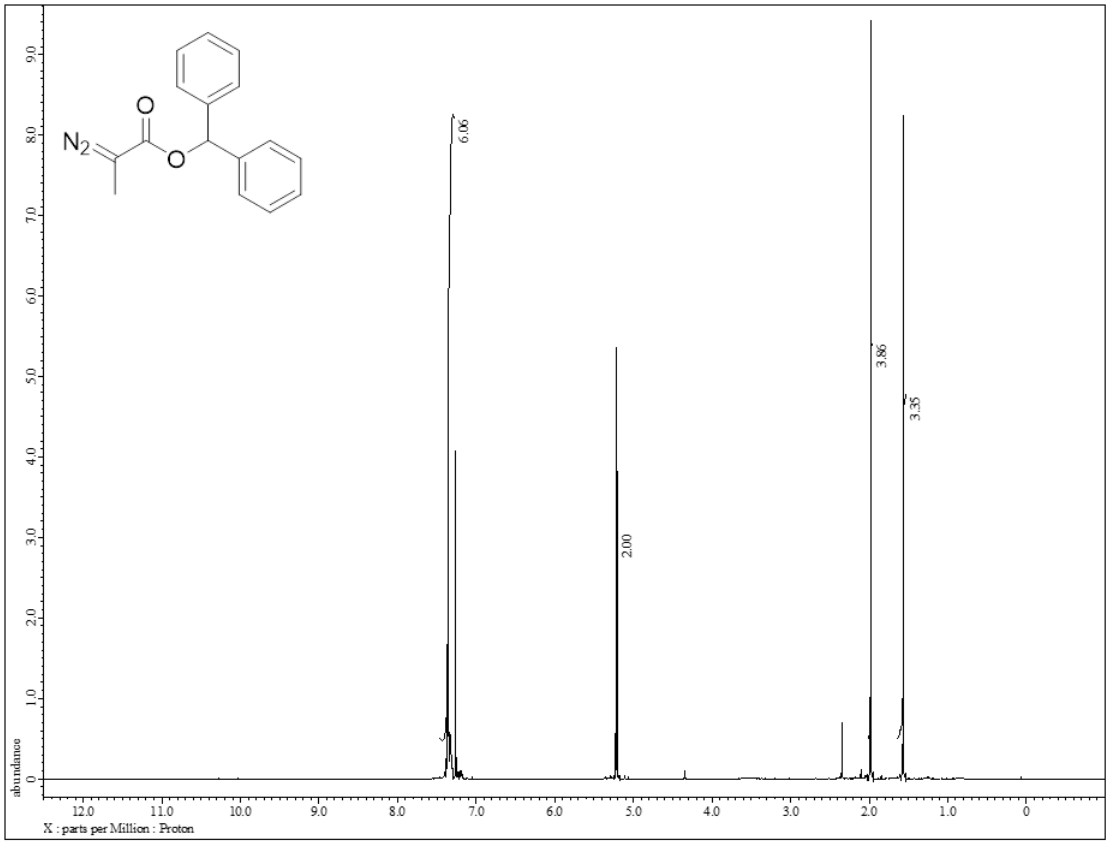
128.440
128.078
127.944
66.250
8.362
X : parts per Million : Carbon13


N2
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O
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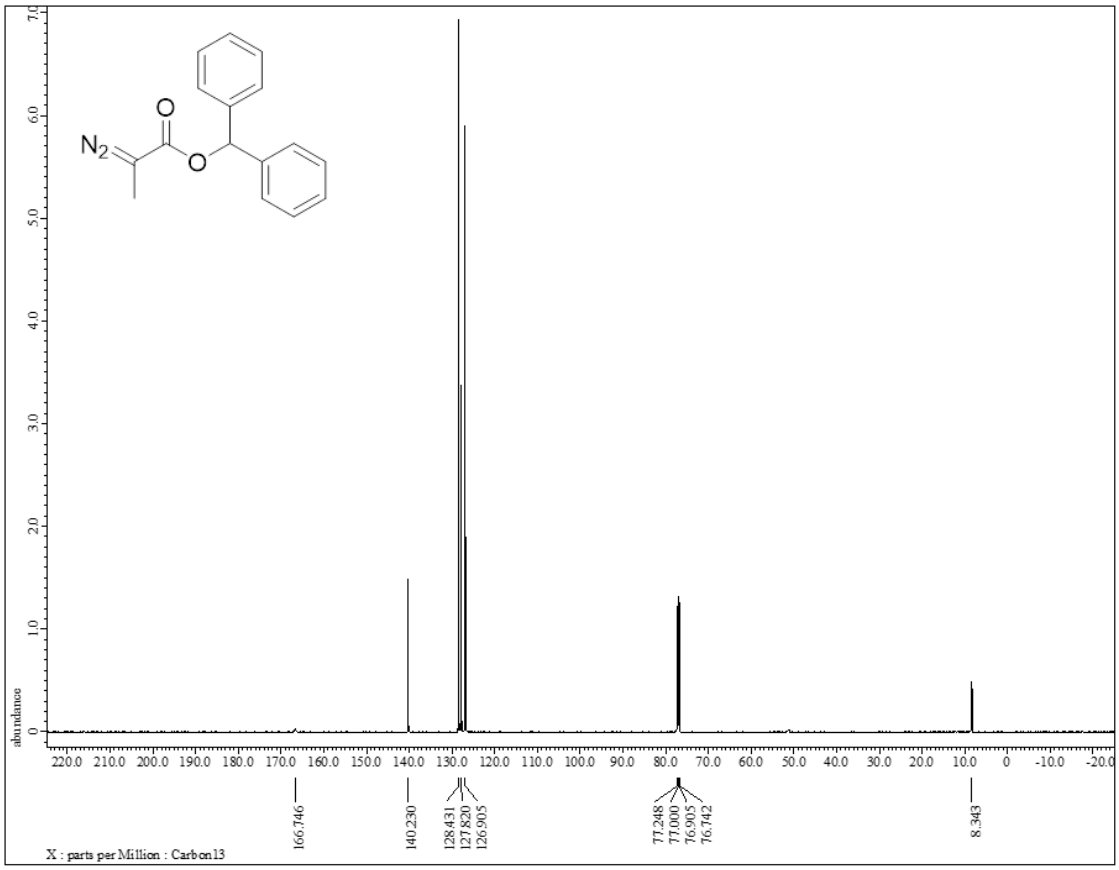
2.00
3.86
3.35
abundance
X : parts per Million : Proton


N2
O
O
abundance
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140.230
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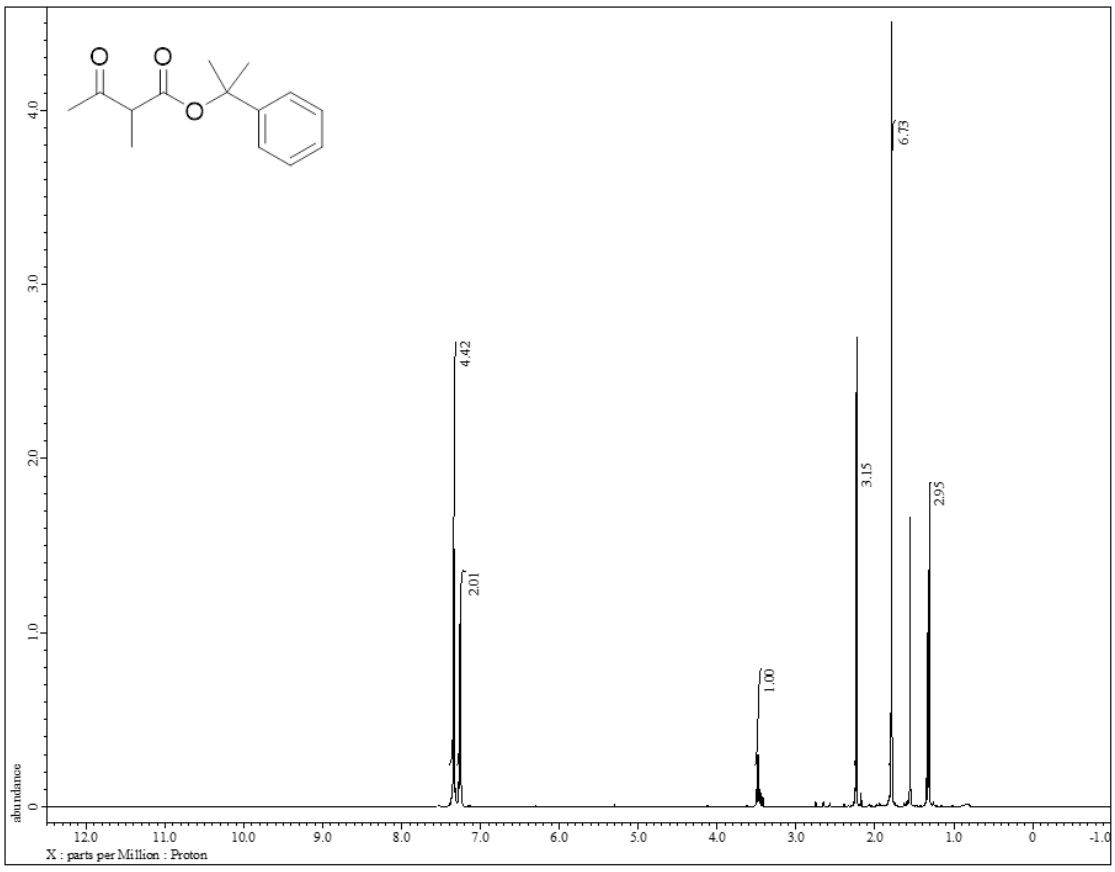
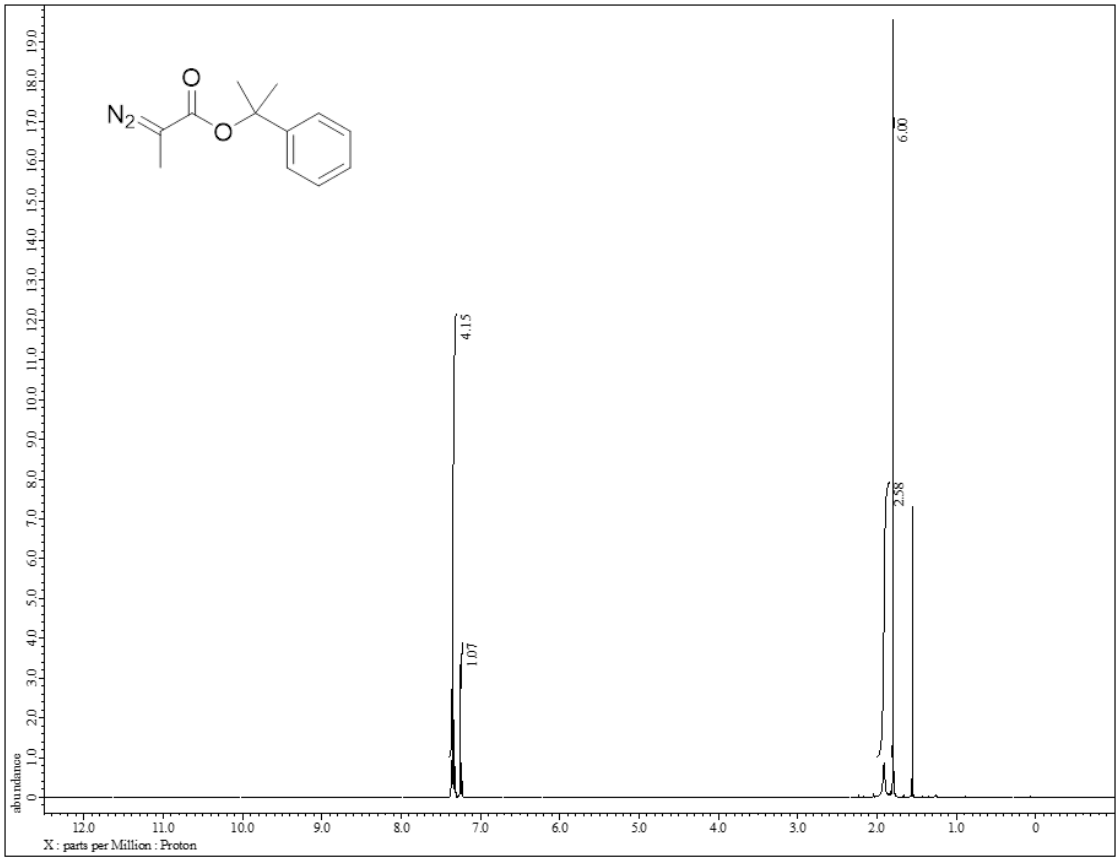
127.820
126.905
77.248
77.000
76.905
76.742
8.343
X : parts per Million : Carbon13


O
O
O
4.42
2.01
1.00
3.15
6.73
2.95
abundance
X : parts per Million : Proton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O
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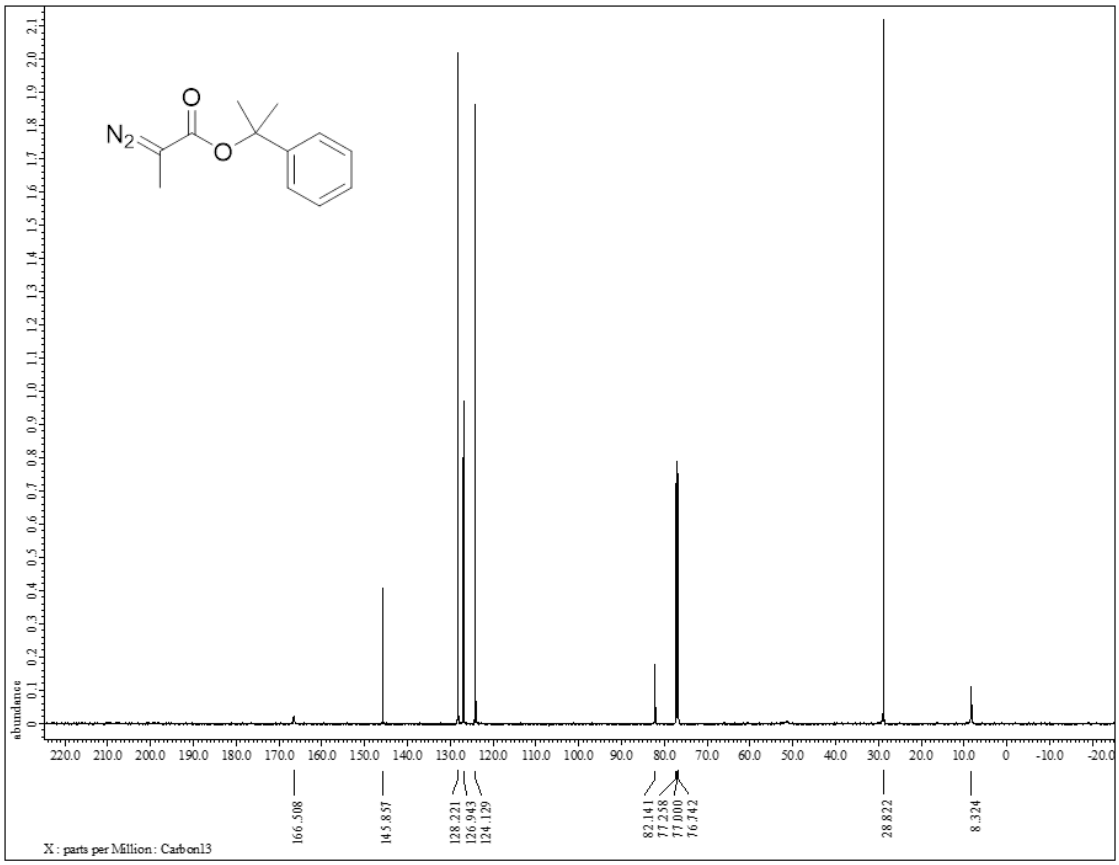
2.58
1.07
abundance
X : parts per Million : Proton


N2
O
O
abundance
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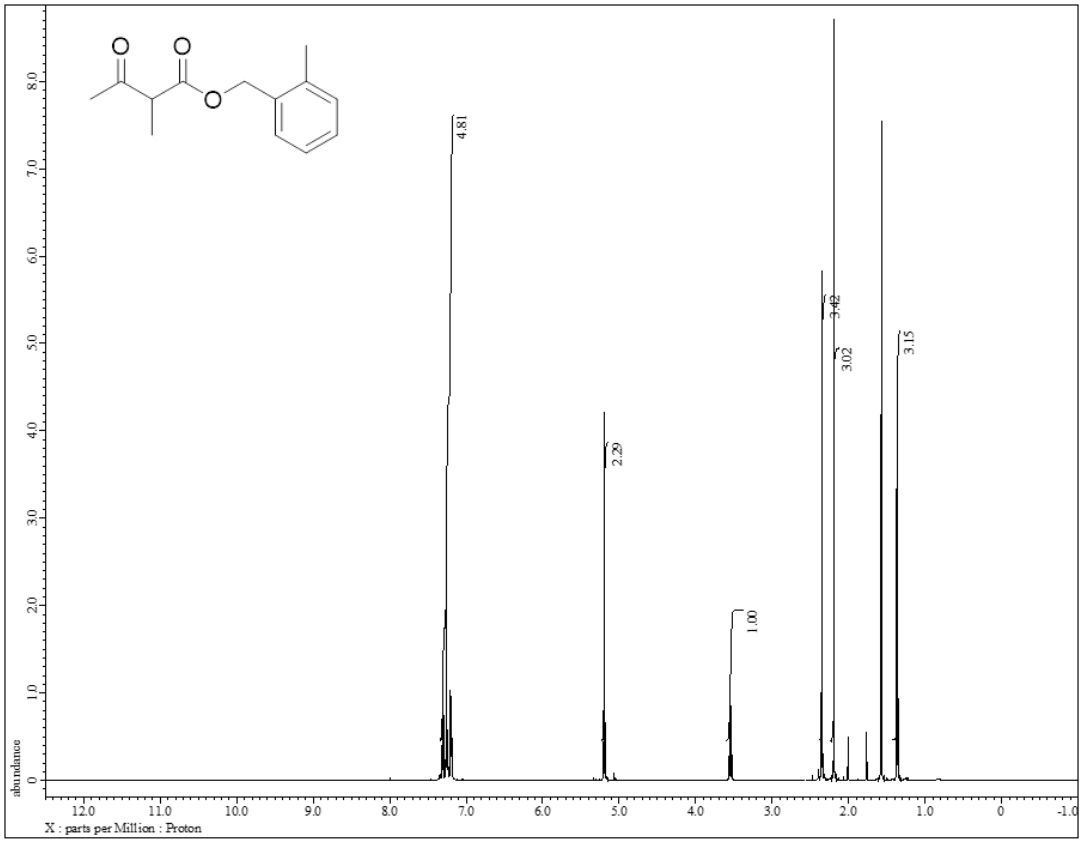
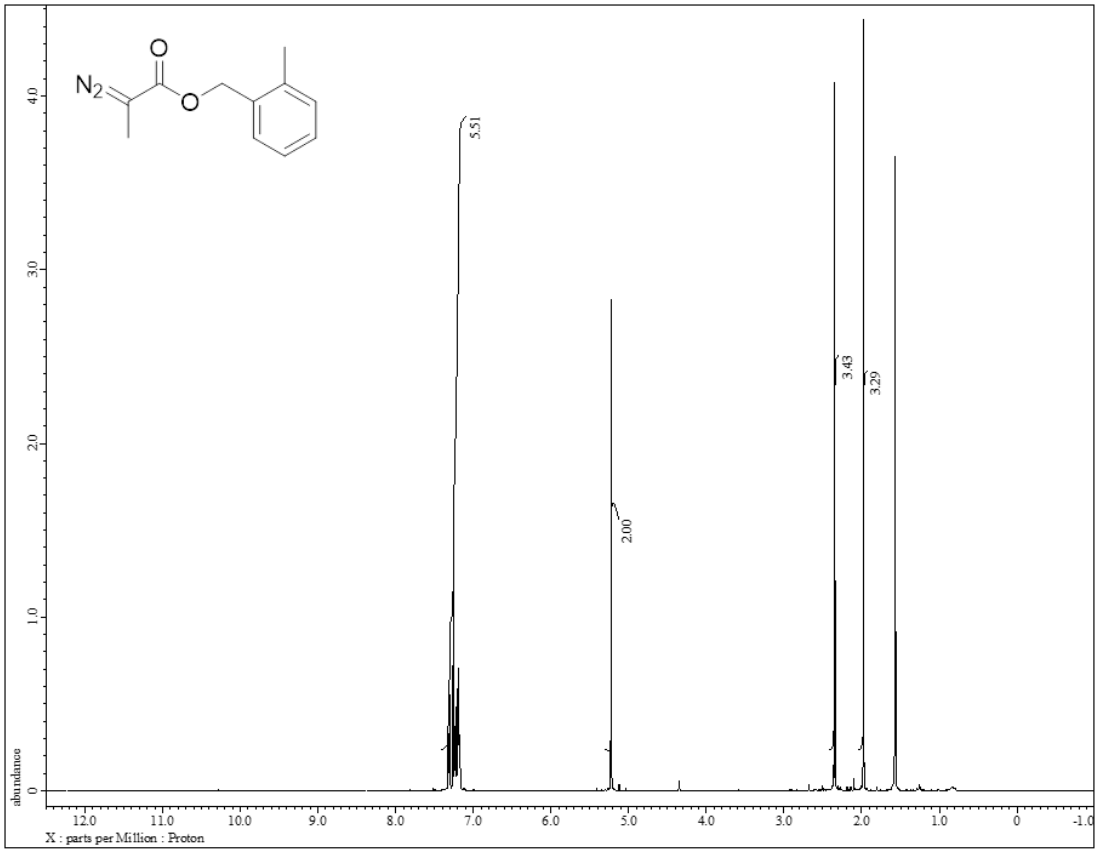
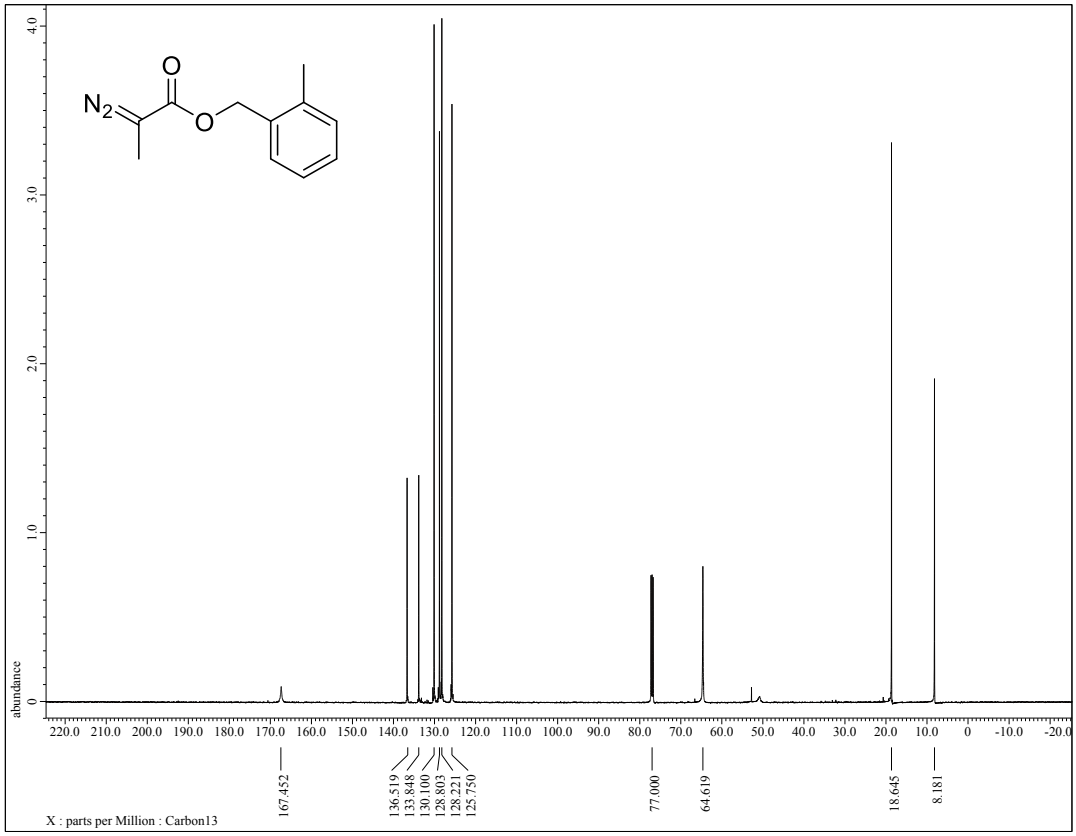
77.258
77.000
76.742
28.822
8.324
X : parts per Million : Carbon13


4.81
3.42
3.02
3.15
2.29
1.00
abundance
X : parts per Million : Proton


N2
5.51
3.43
3.29
2.00
abundance
X : parts per Million : Proton


N2
O
O
abundance
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.452
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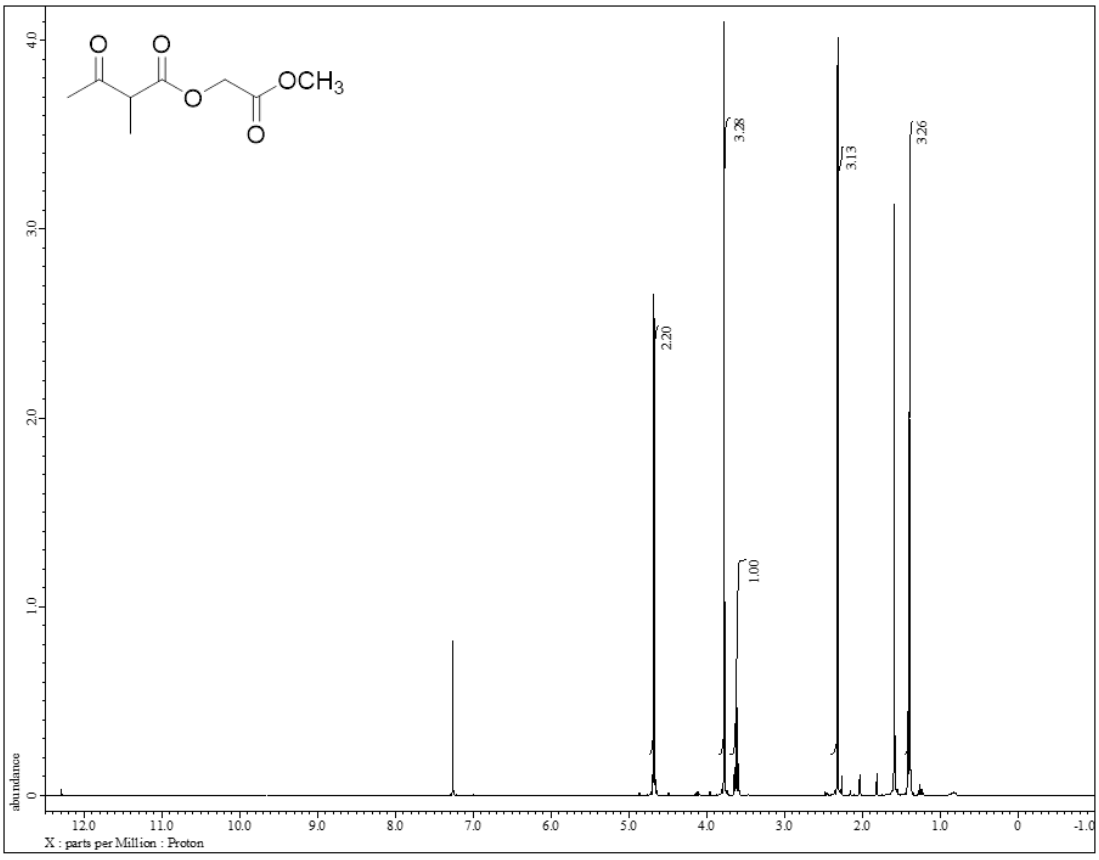
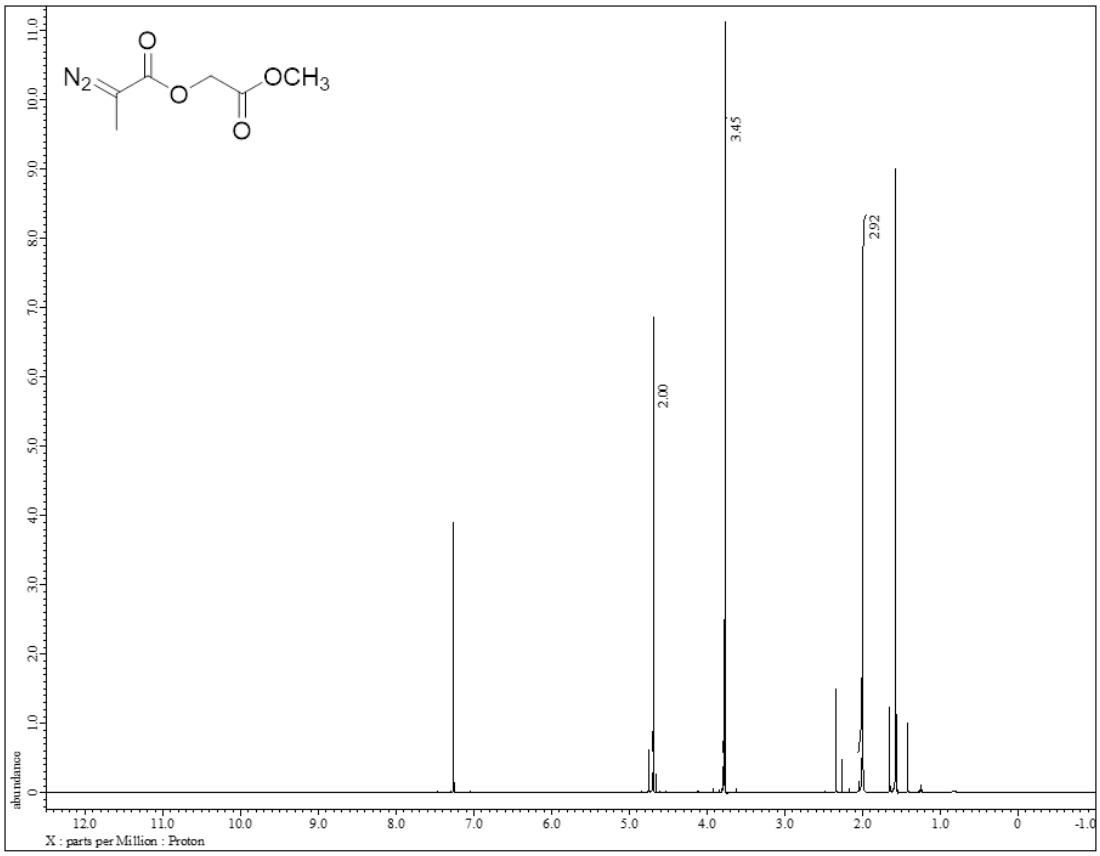
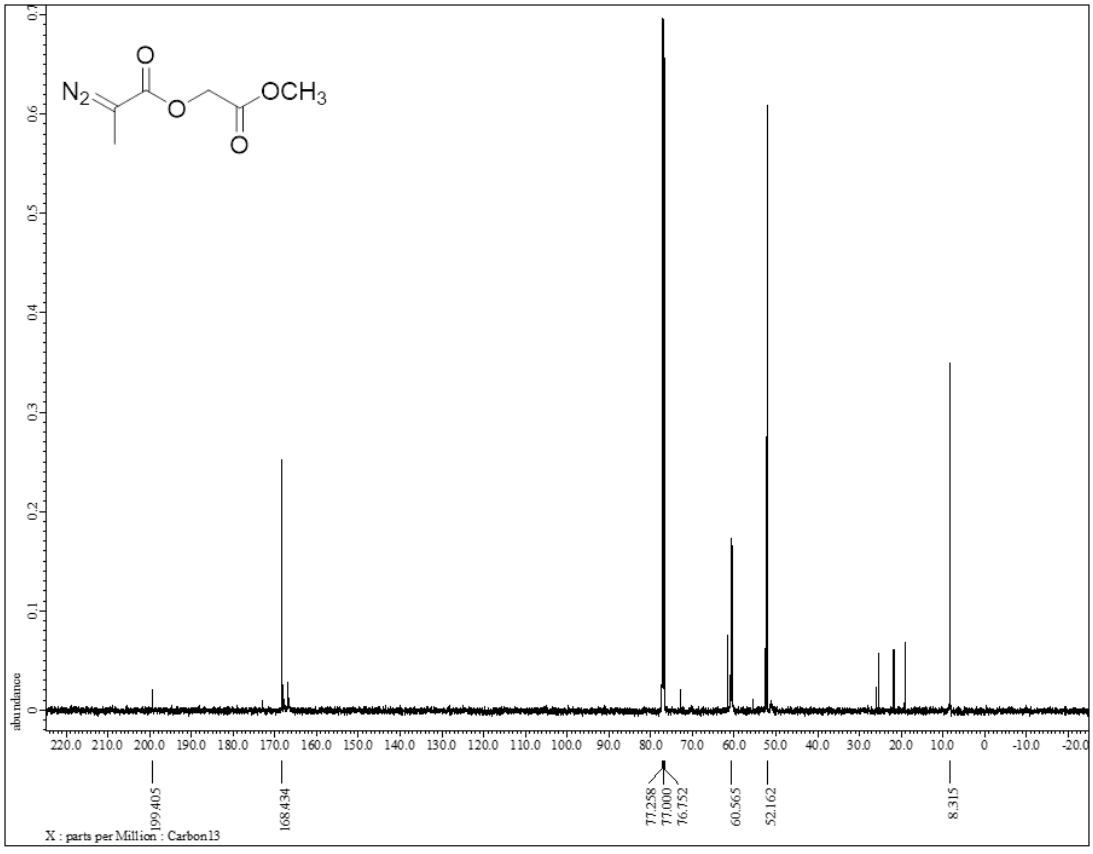
133.848
130.100
128.803
128.221
125.750
77.000
64.619
18.645
8.181
X : parts per Million : Carbon13


O
O
O
OCH3
O
abundance
4.0
3.0
2.0
1.0
0
3.28
3.13
3.26
2.20
1.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
X : parts per Million : Proton


N2
O
O
O
OCH3
3.45
2.92
2.00
abundance
X : parts per Million : Proton


N2
O
O
O
OCH3
abundance
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168.434
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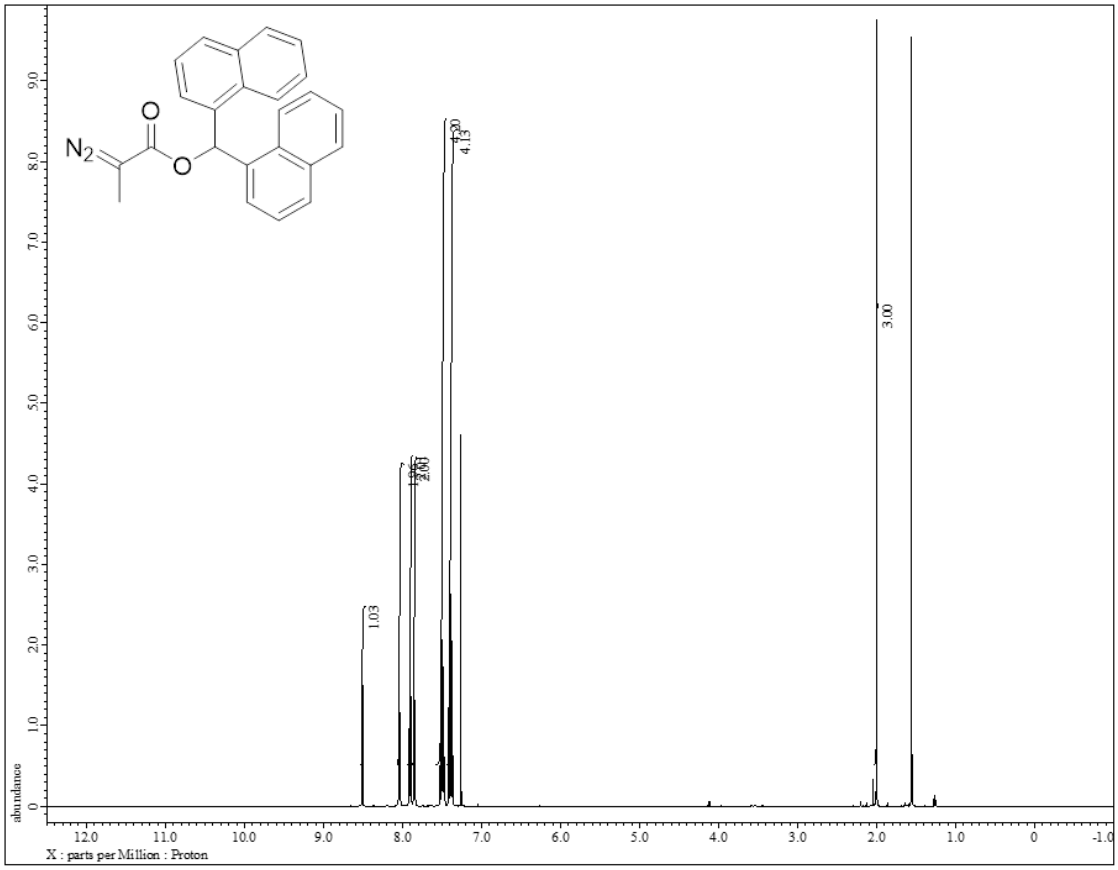
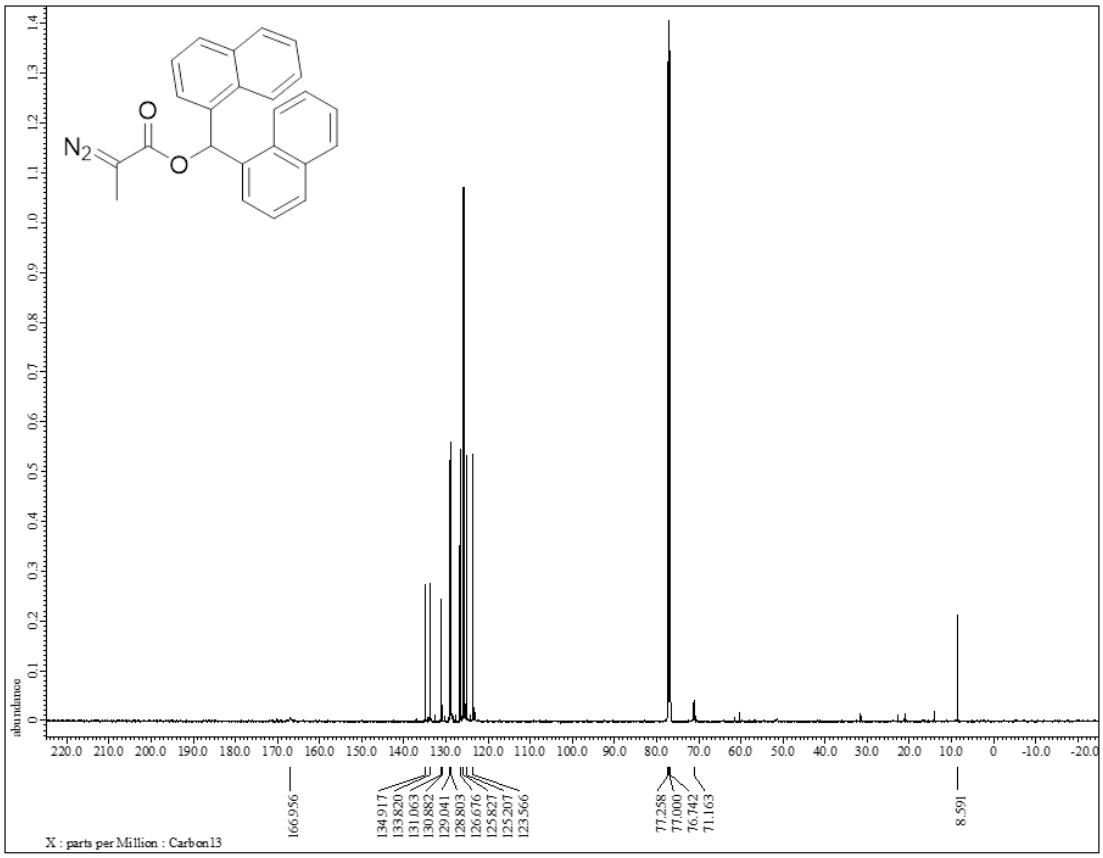
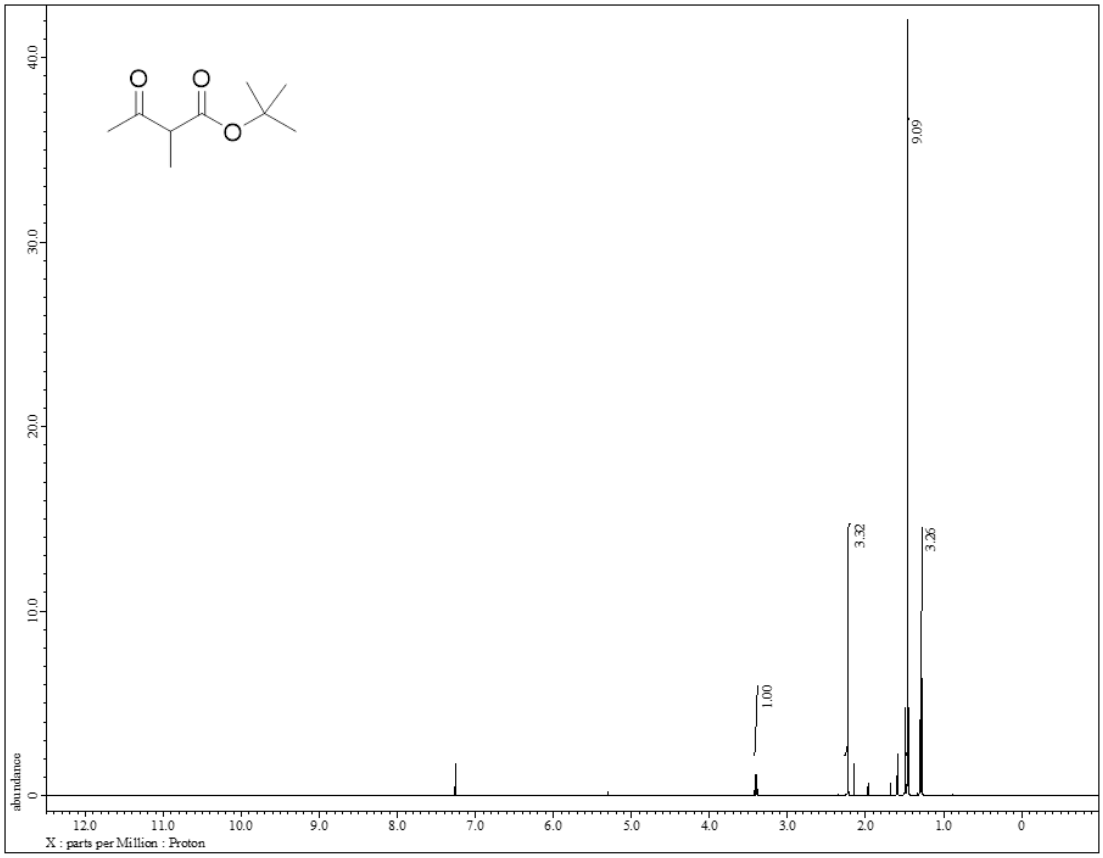
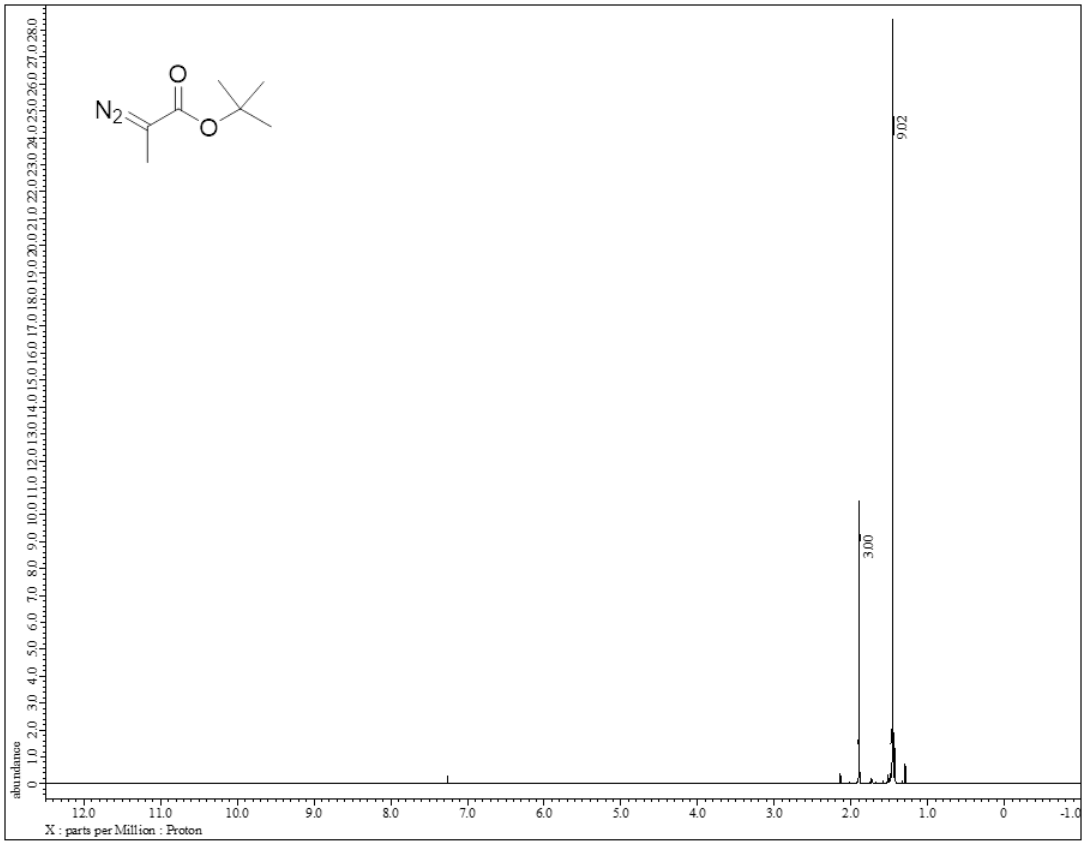
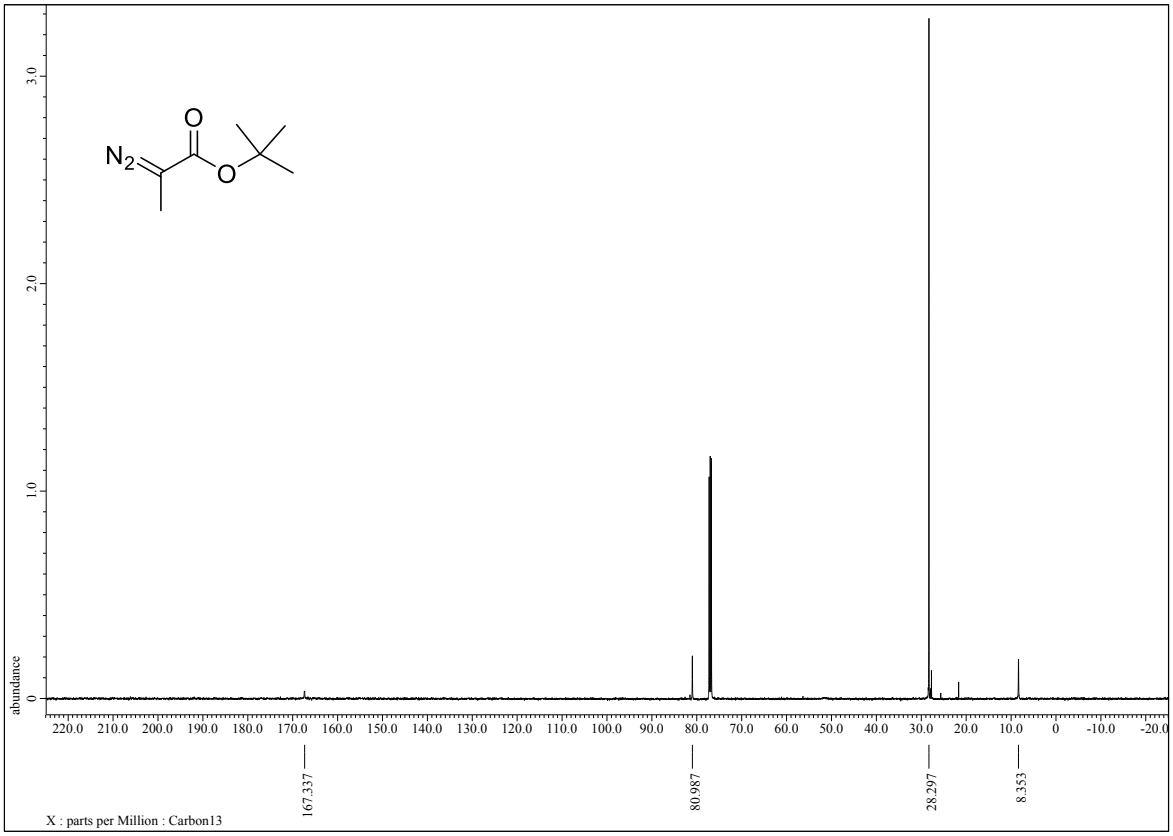
77.000
76.752
60.565
52.162
8.315
X : parts per Million : Carbon13

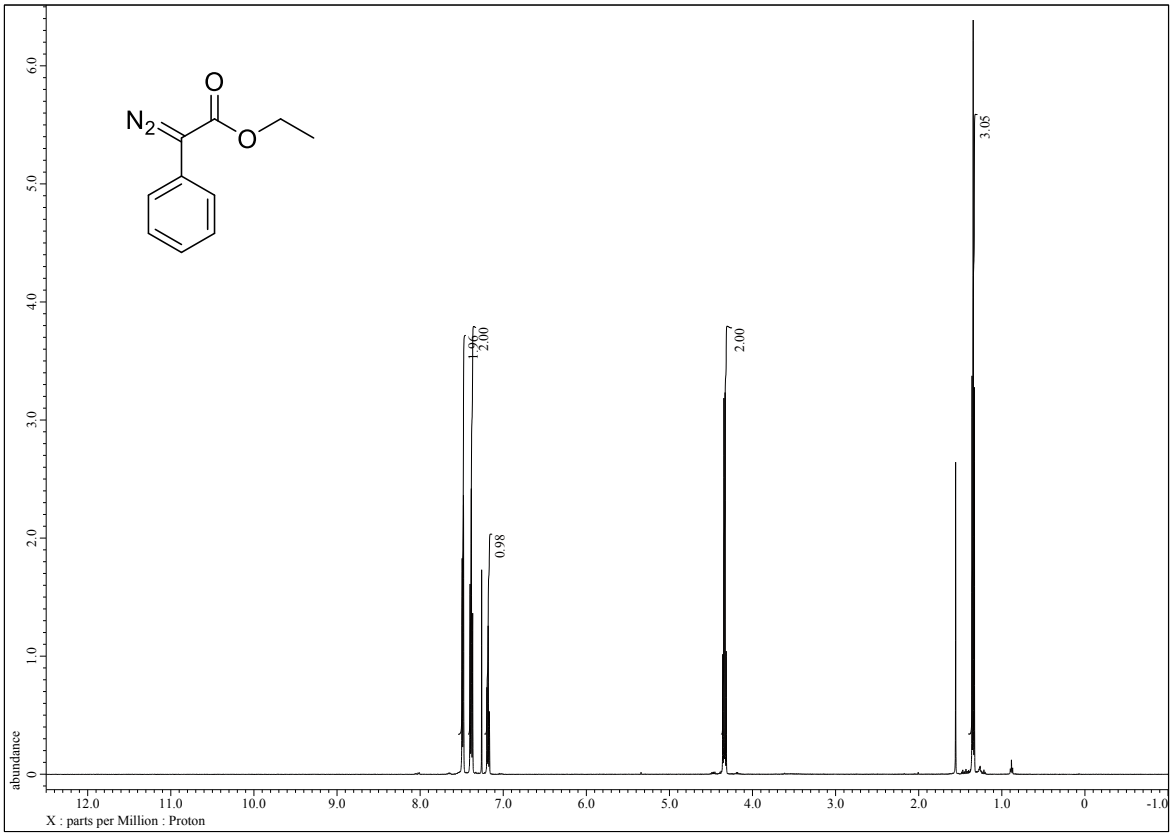

N2
O
O
1.03
2.00
4.13
3.00
abundance
X : parts per Million : Proton

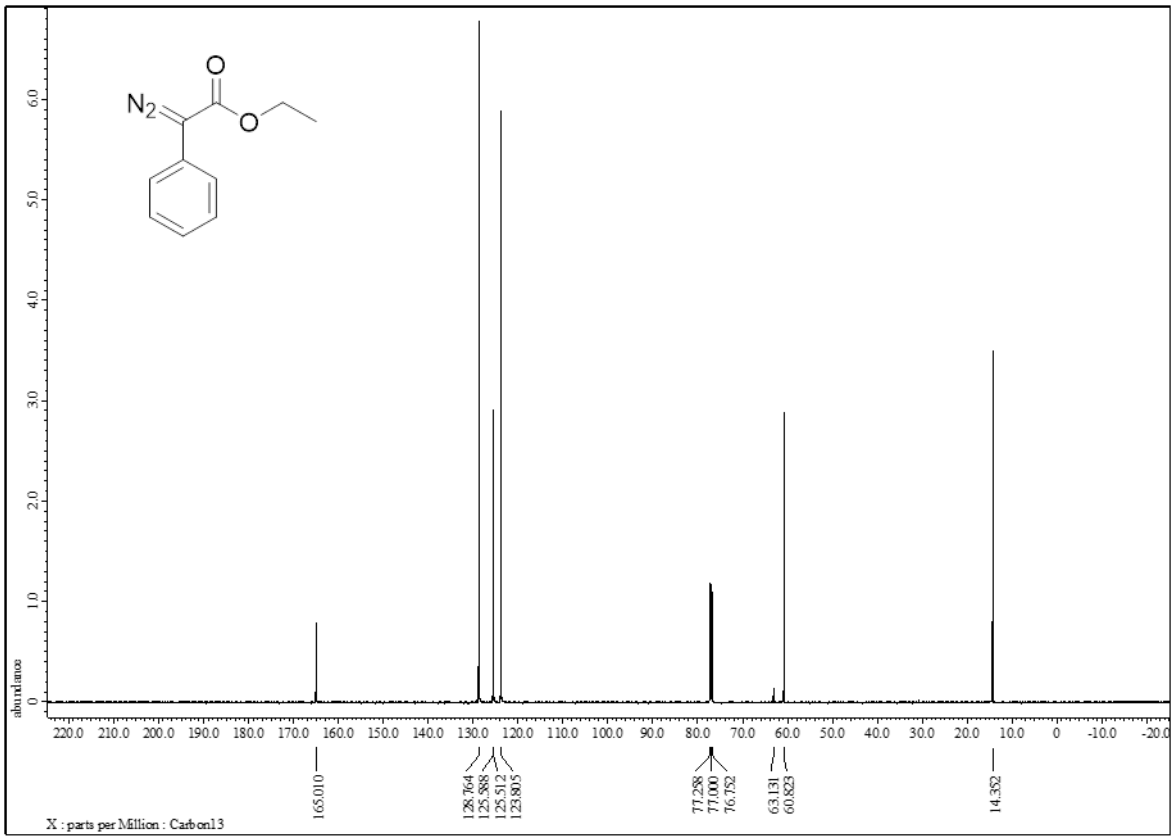

N2
O
O
abundance
166.956
134.917
133.820
131.063
130.882
129.041
128.803
126.676
125.827
125.207
123.566
77.258
77.000
76.742
71.163
8.591
X : parts per Million : Carbon13

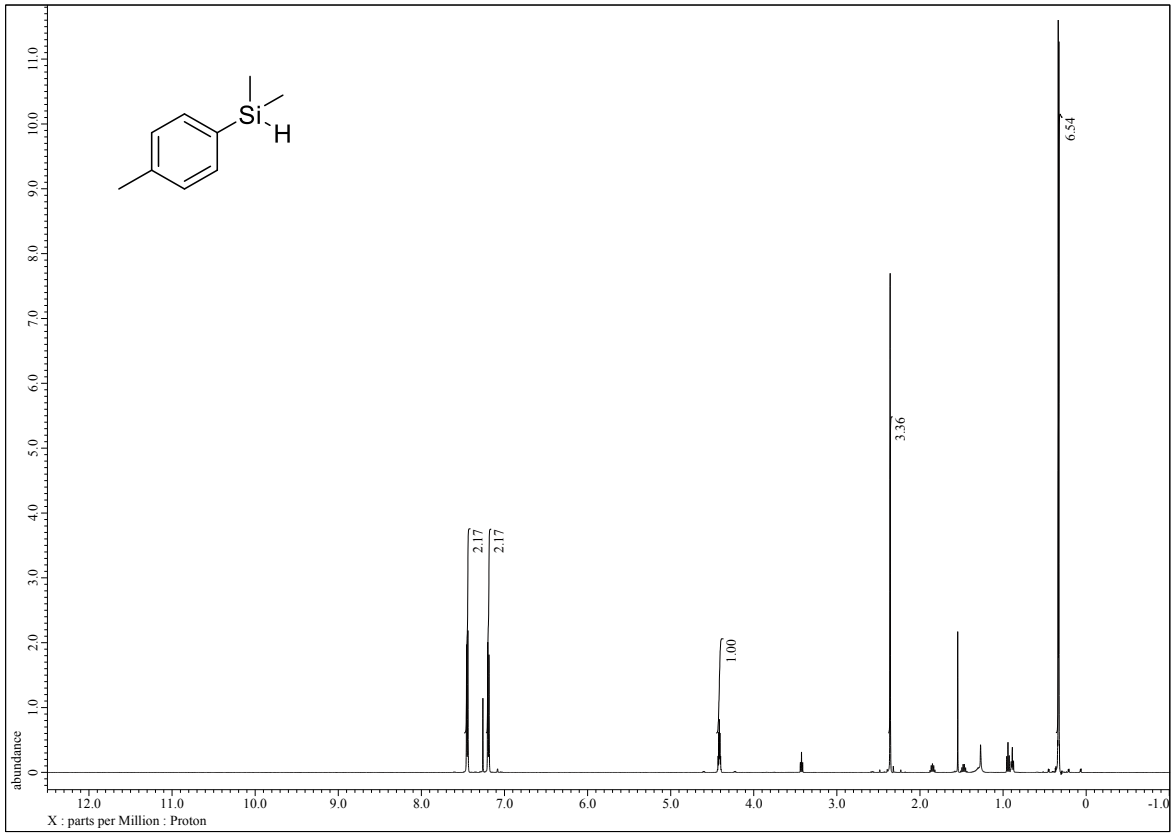

9.09
3.32
3.26
1.00
abundance
X : parts per Million : Proton

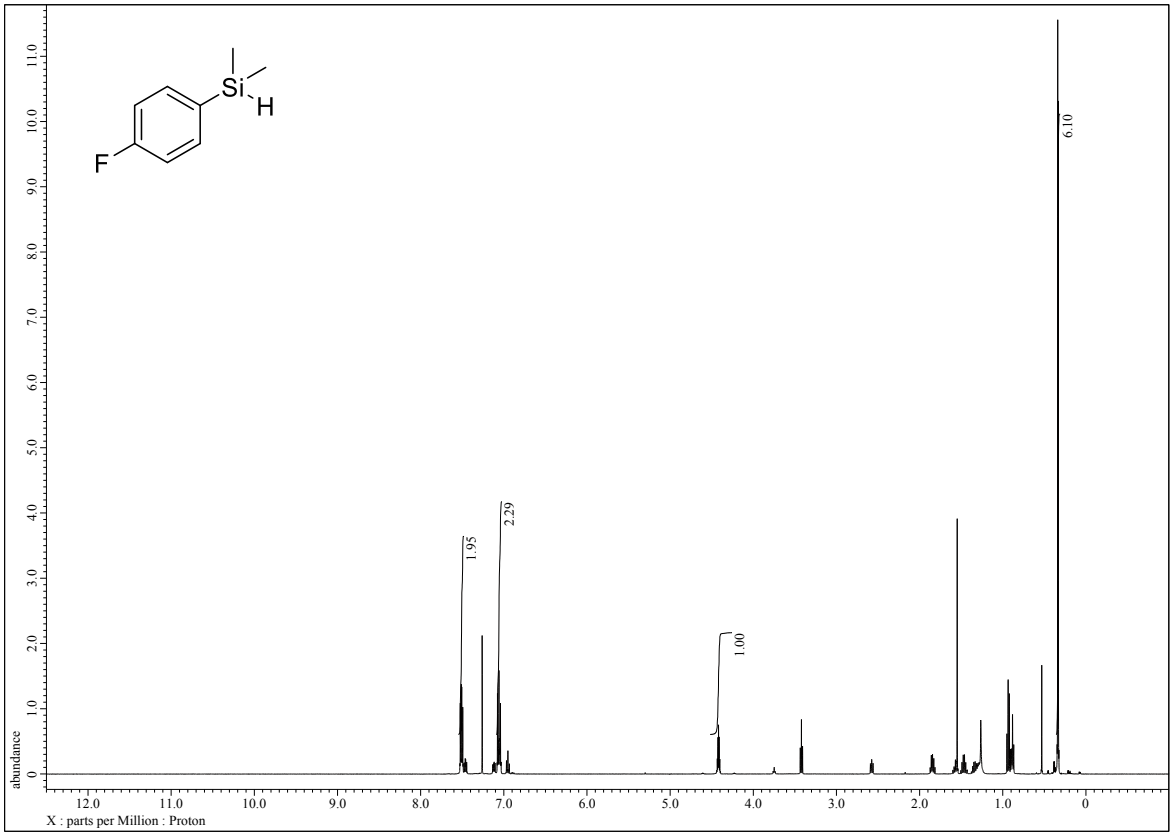

9.02
3.00
abundance
X : parts per Million : Proton

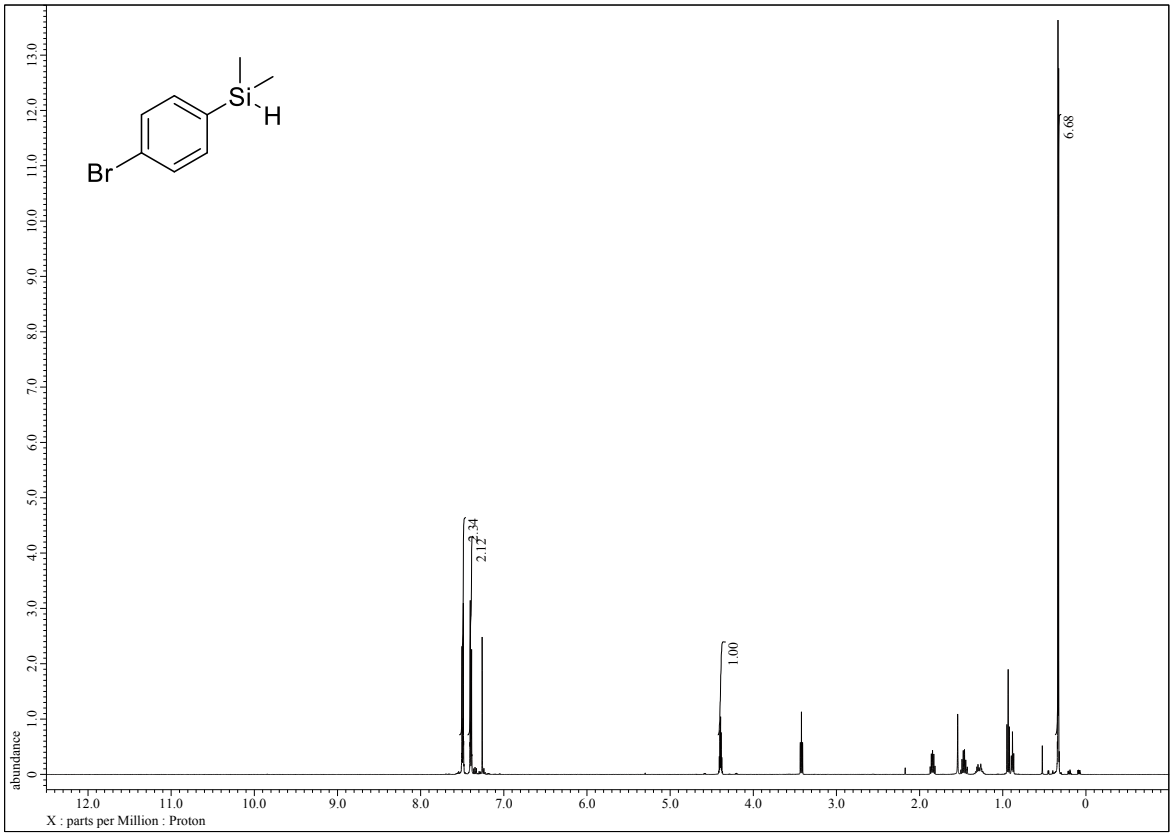

N2
O
O
abundance
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
167.337
80.987
28.297
8.353
X : parts per Million : Carbon13

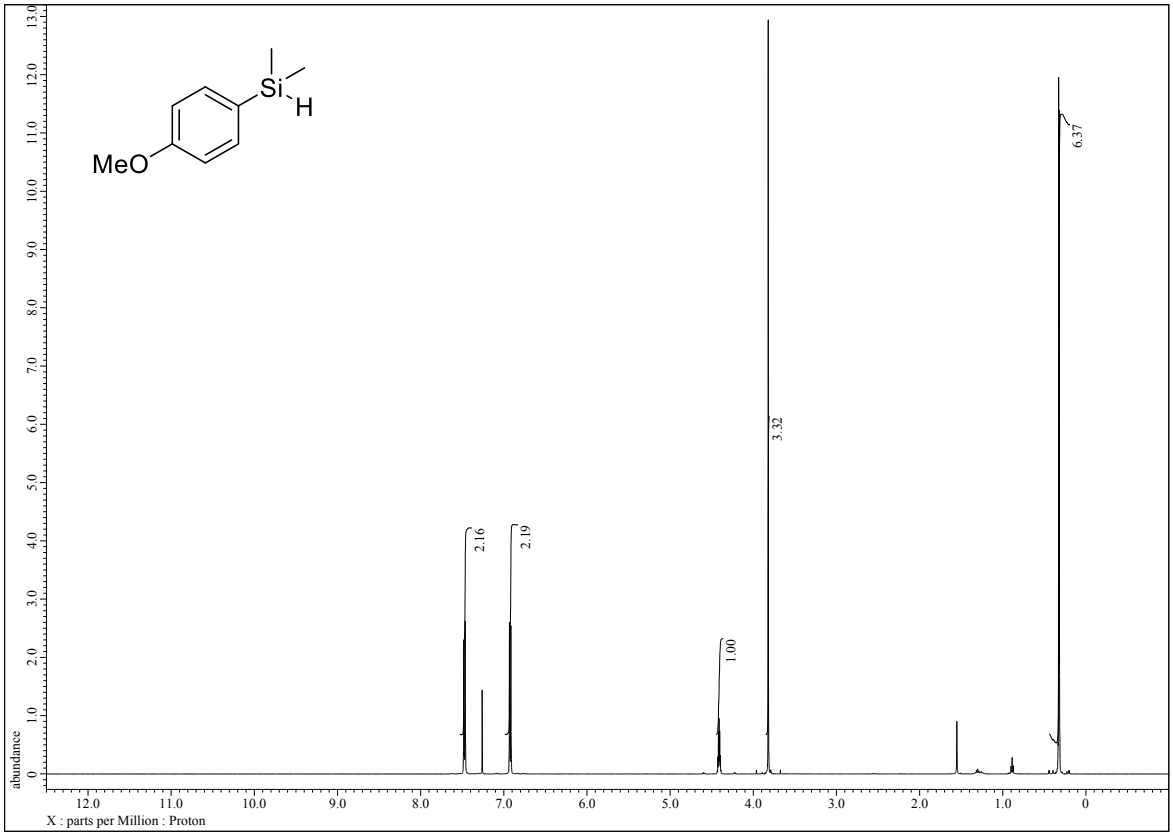

N2
O
O
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
2.00
2.00
0.98
3.05
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
X : parts per Million : Proton

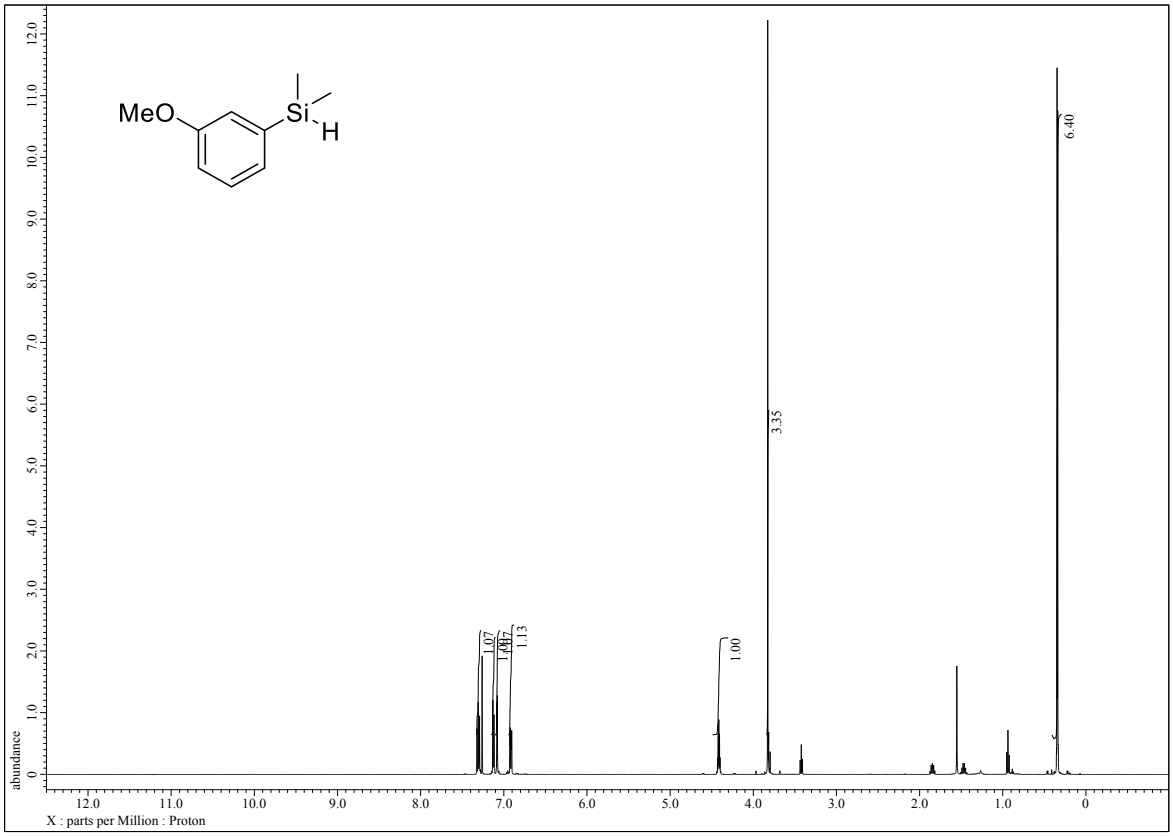

N2
O
O
abundance
165.010
128.764
125.888
125.512
123.805
77.258
77.000
76.752
63.131
60.823
14.352
X : parts per Million : Carbon13

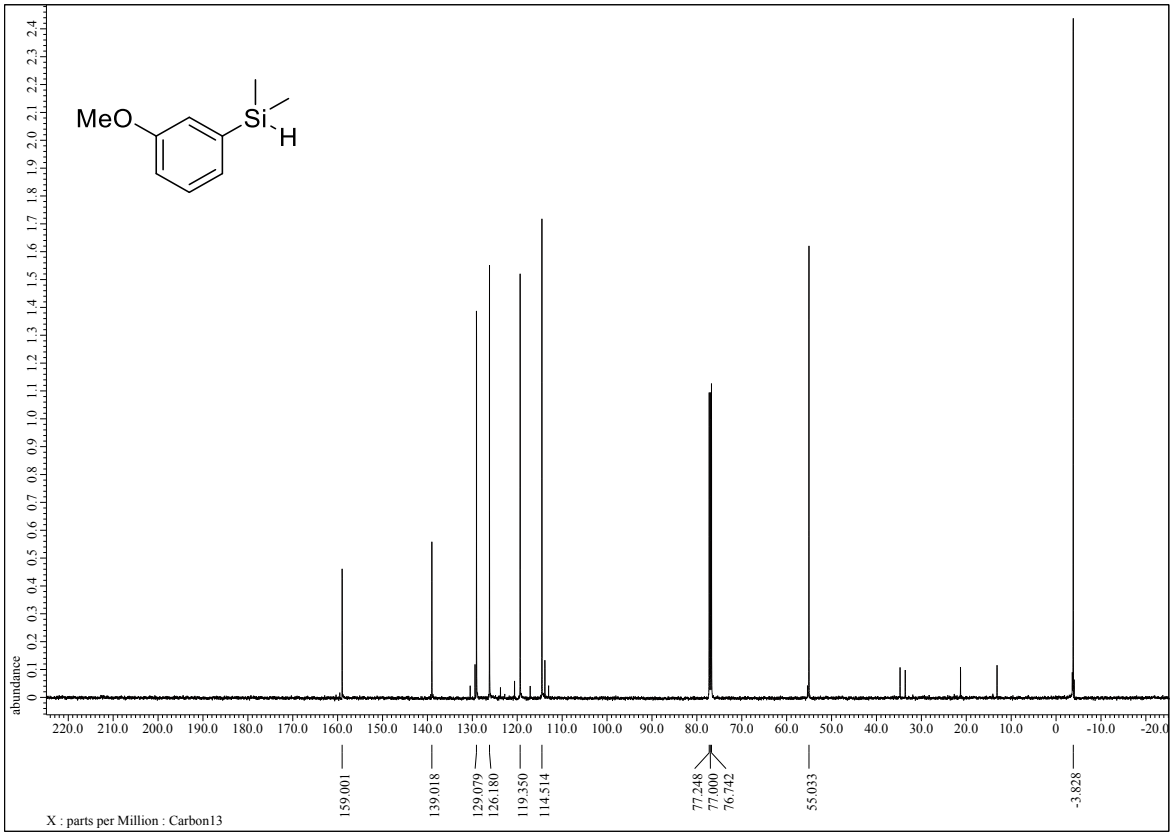

Si
H
abundance
6.54
3.36
2.17
2.17
1.00
X : parts per Million : Proton

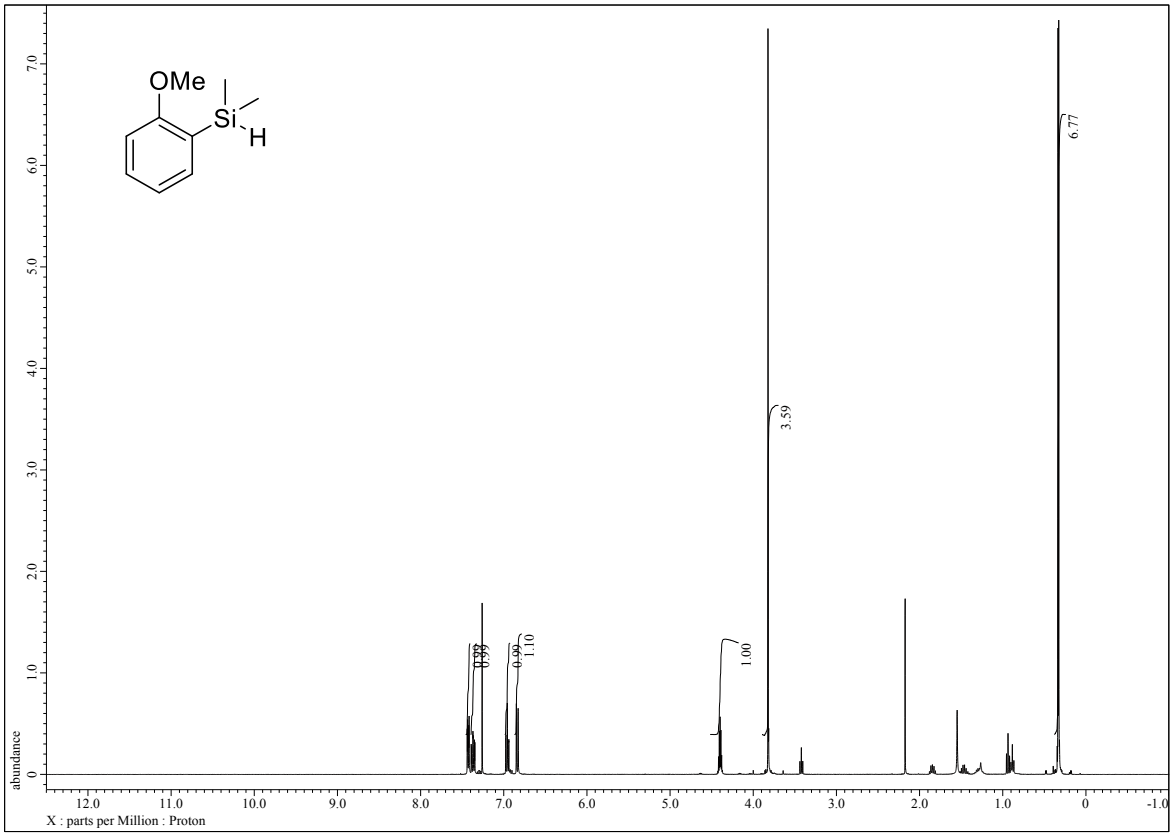

Si
H
F
6.10
2.29
1.95
1.00
abundance
X : parts per Million : Proton

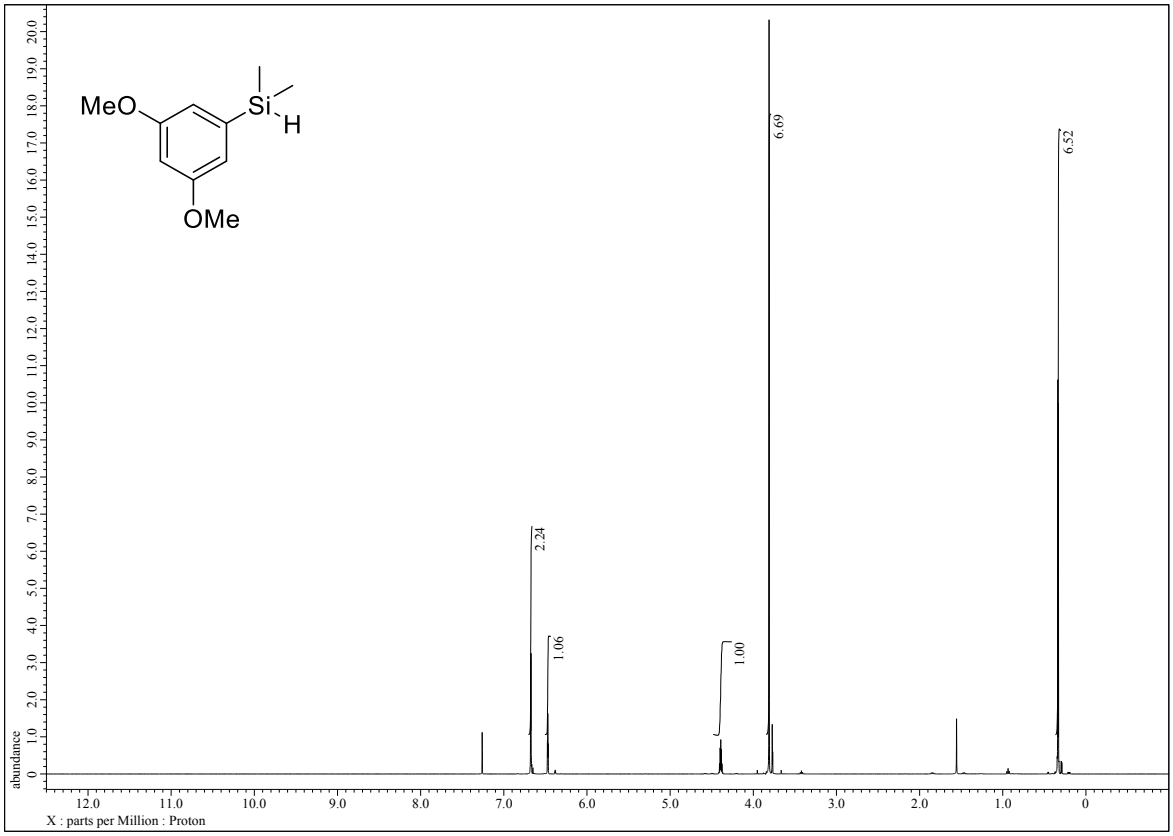

Si
H
Br
6.68
2.34
2.12
1.00
abundance
X : parts per Million : Proton

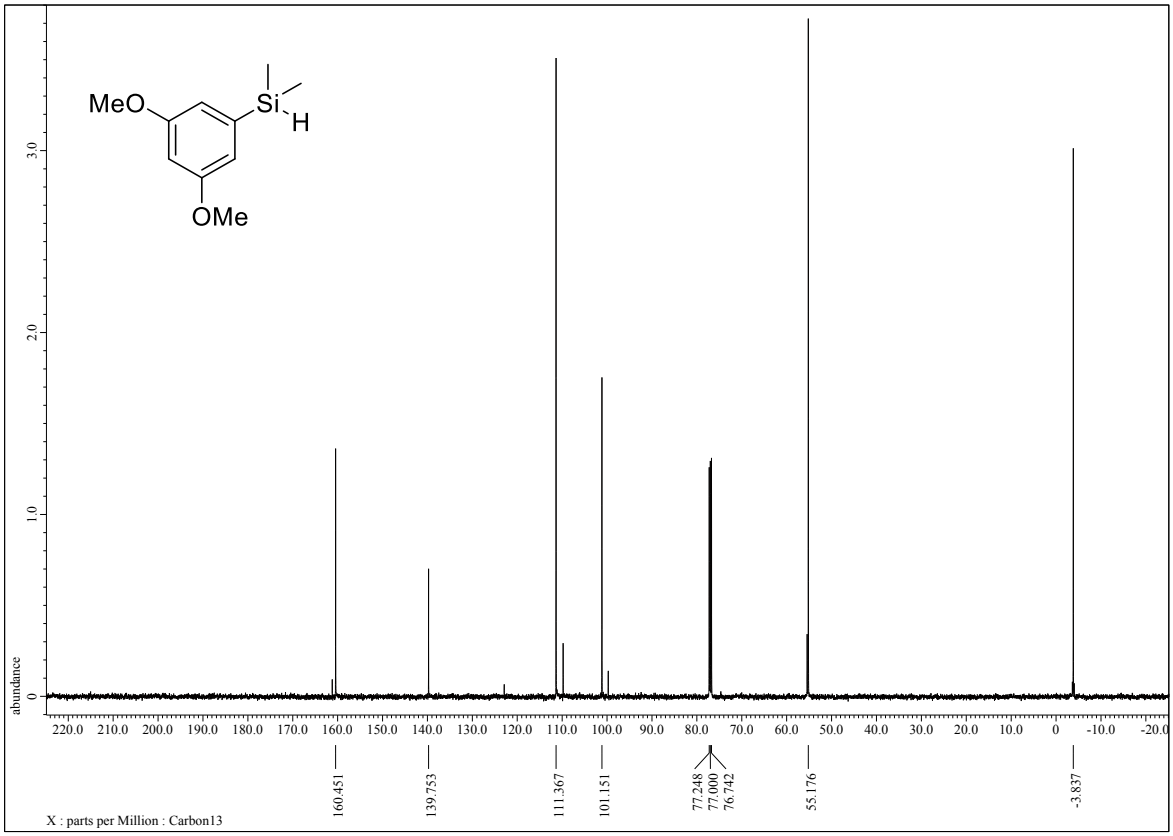

MeO
Si
H
6.37
3.32
2.16
2.19
1.00
abundance
X : parts per Million : Proton

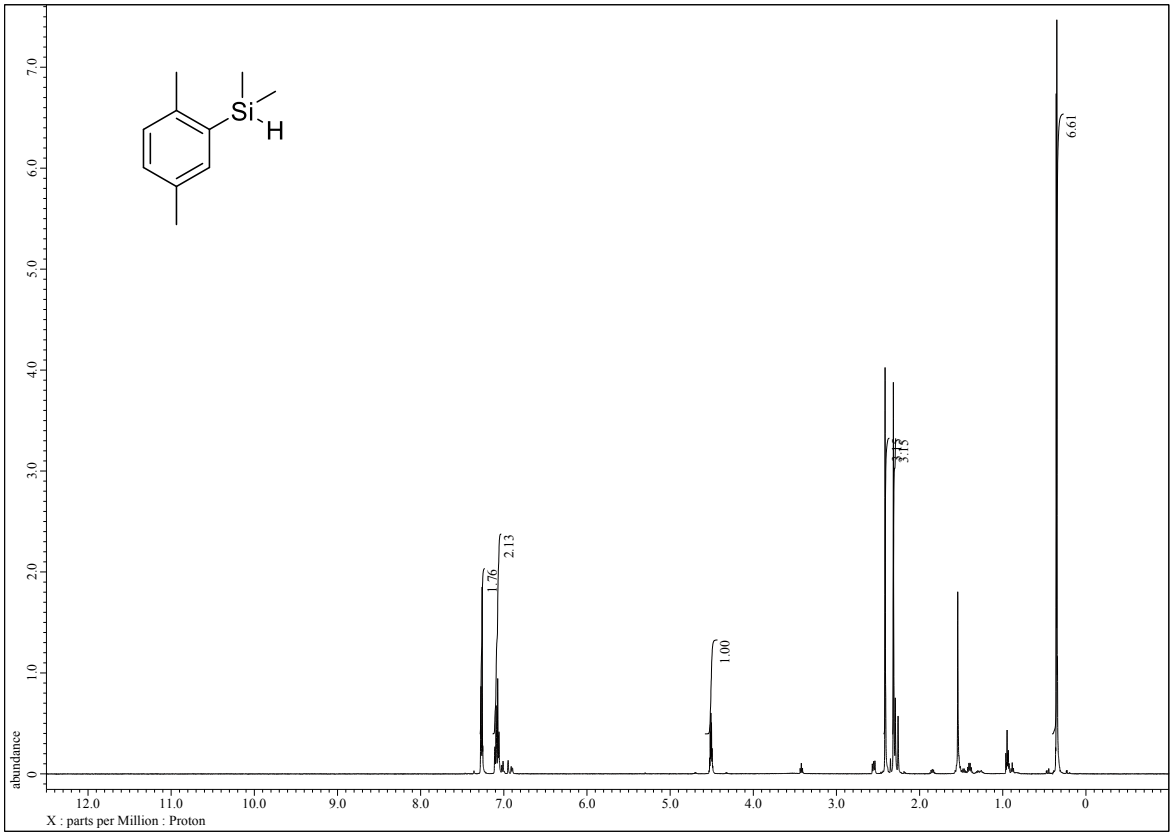

MeO
Si
H
6.40
3.35
1.00
1.13
abundance
X : parts per Million : Proton

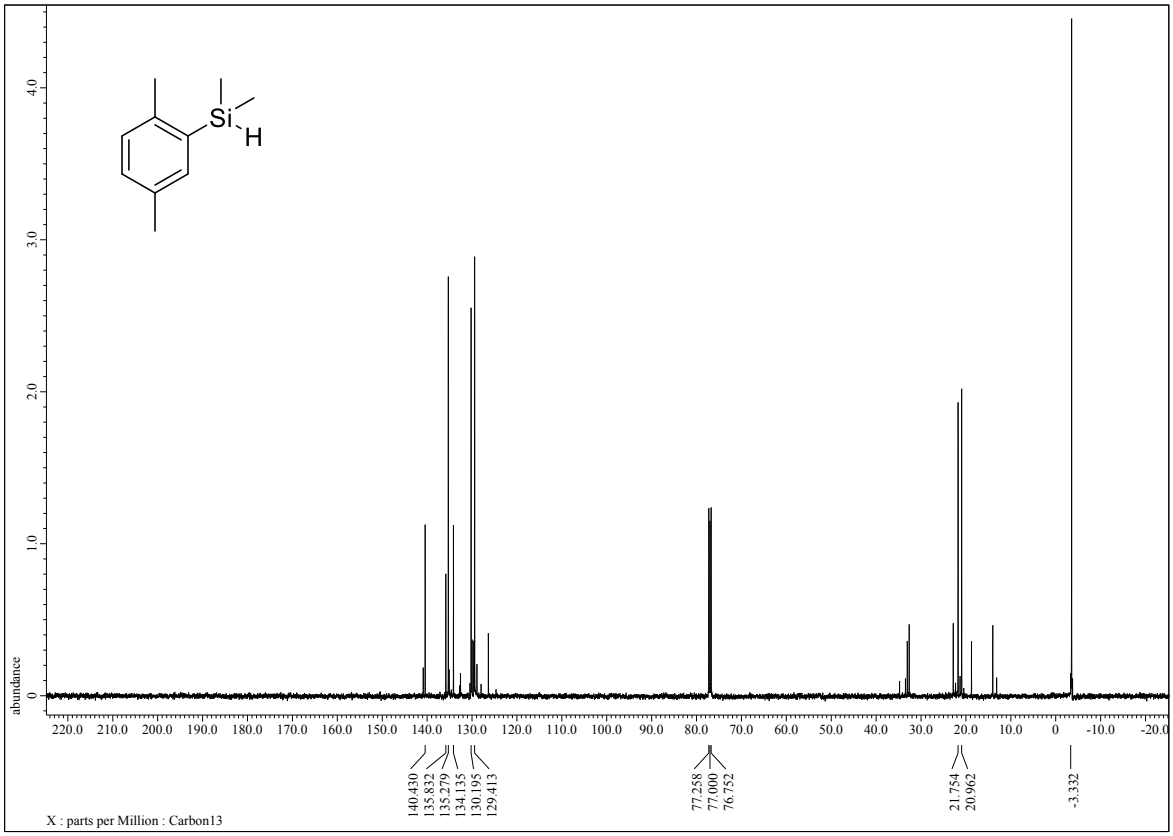

MeO
Si
H
abundance
X : parts per Million : Carbon13
159.001
139.018
129.079
126.180
119.350
114.514
77.248
77.000
76.742
55.033
-3.828

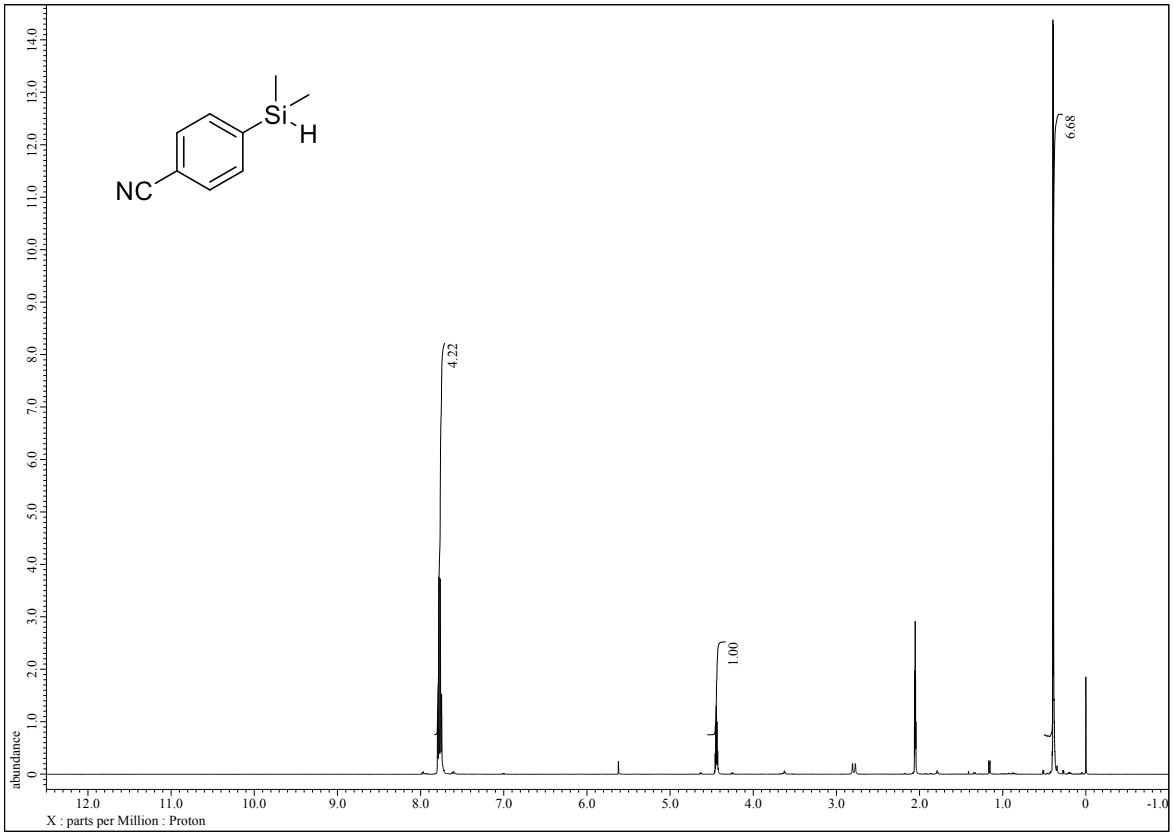

OMe
Si
H
abundance
X : parts per Million : Proton
6.77
3.59
1.10
1.00

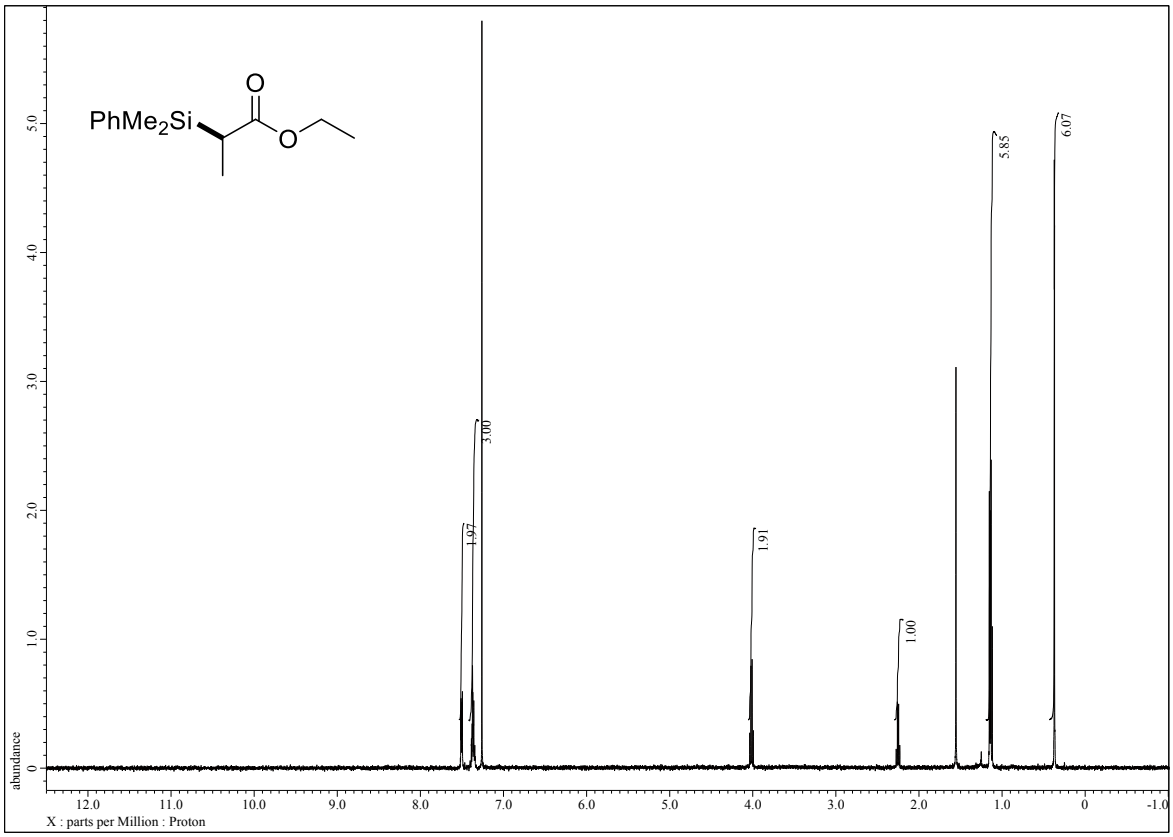

MeO
Si
H
OMe
6.69
6.52
2.24
1.06
1.00
abundance
X : parts per Million : Proton

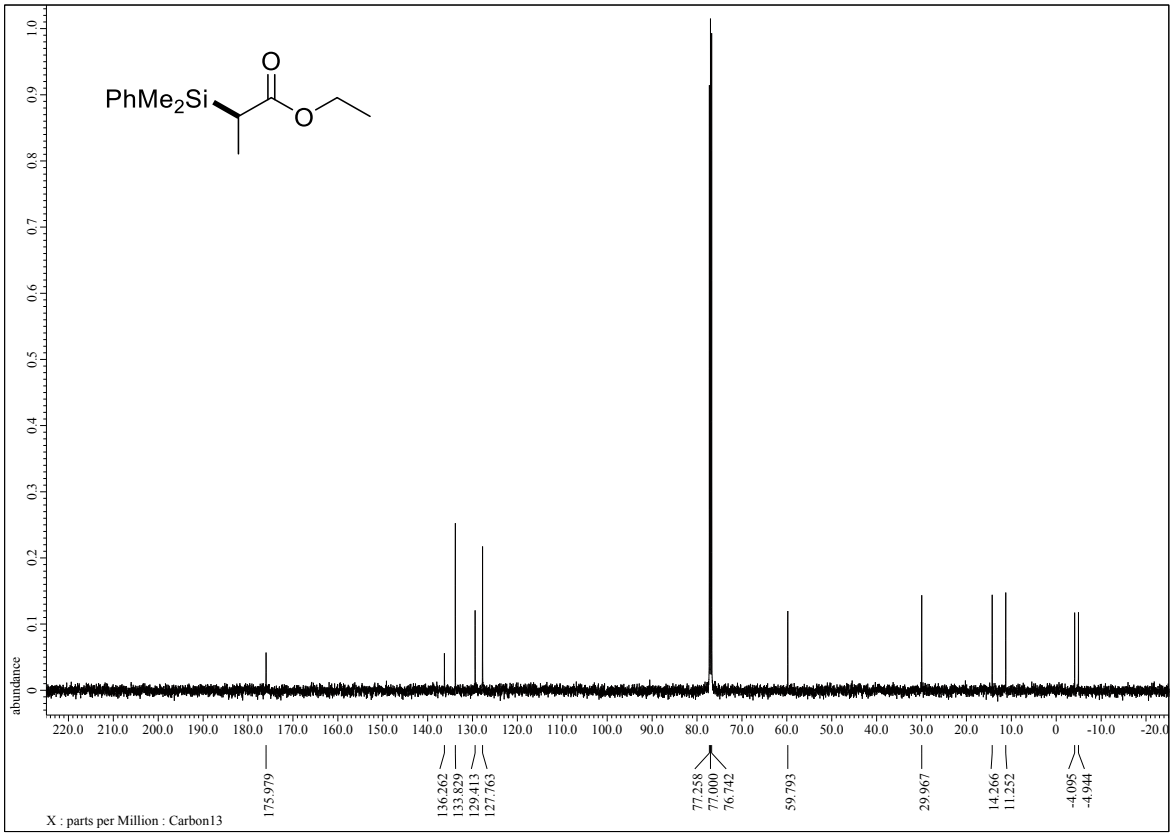

MeO
Si
H
OMe
abundance
160.451
139.753
111.367
101.151
77.248
77.000
76.742
55.176
-3.837
X : parts per Million : Carbon13

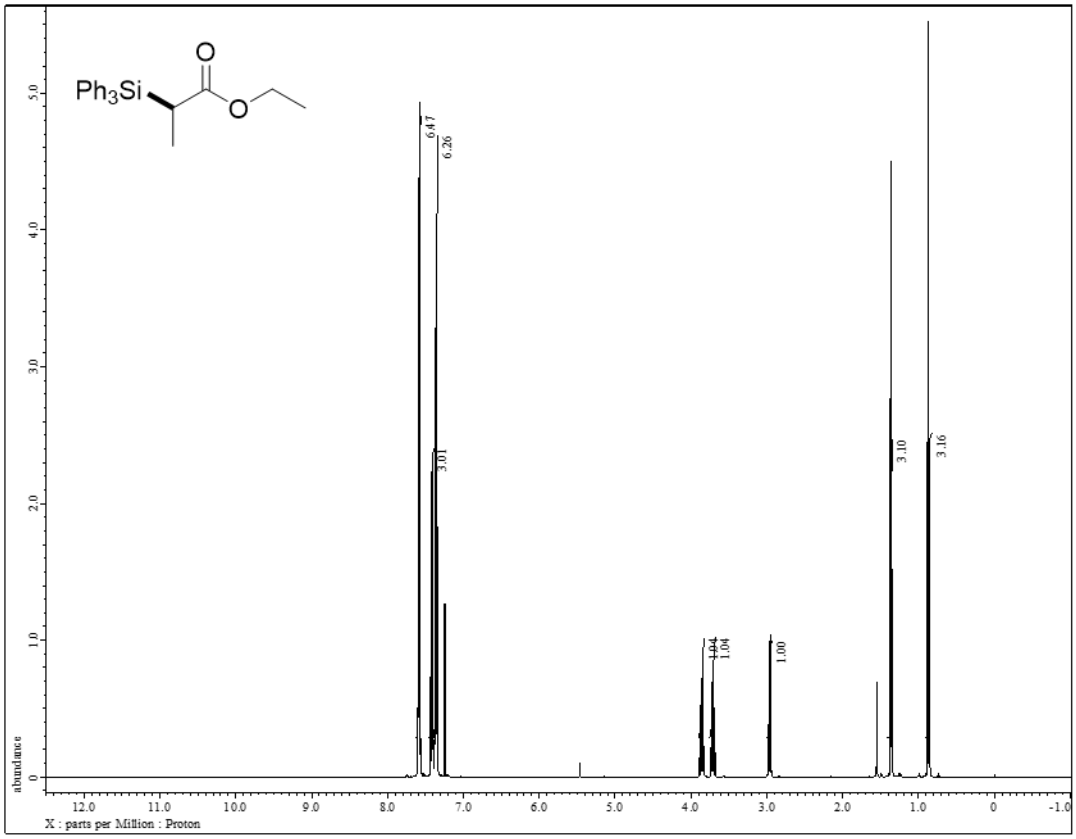

Si
H
6.61
3.15
3.13
2.13
1.76
1.00
abundance
X : parts per Million : Proton


Si
H
abundance
140.430
135.832
135.279
134.135
130.195
129.413
77.258
77.000
76.752
21.754
20.962
-3.332
X : parts per Million : Carbon13

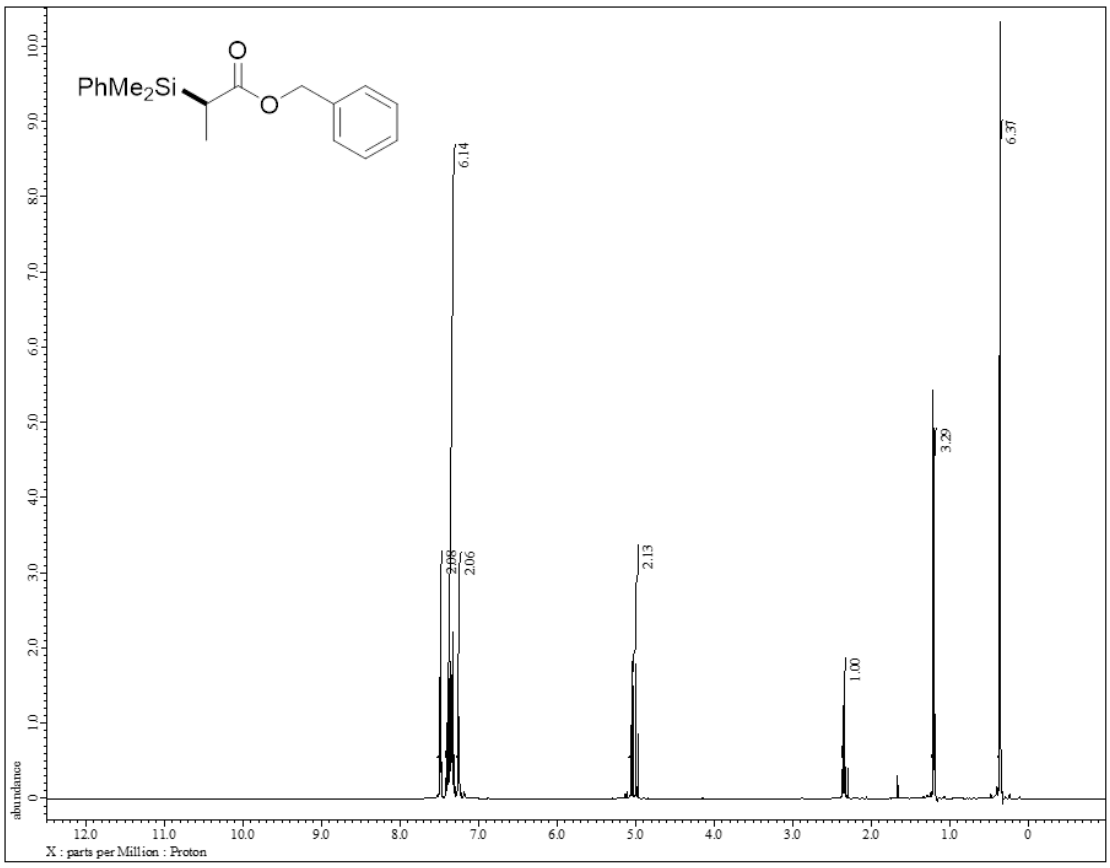

Si
H
NC
4.22
1.00
6.68
abundance
X : parts per Million : Proton

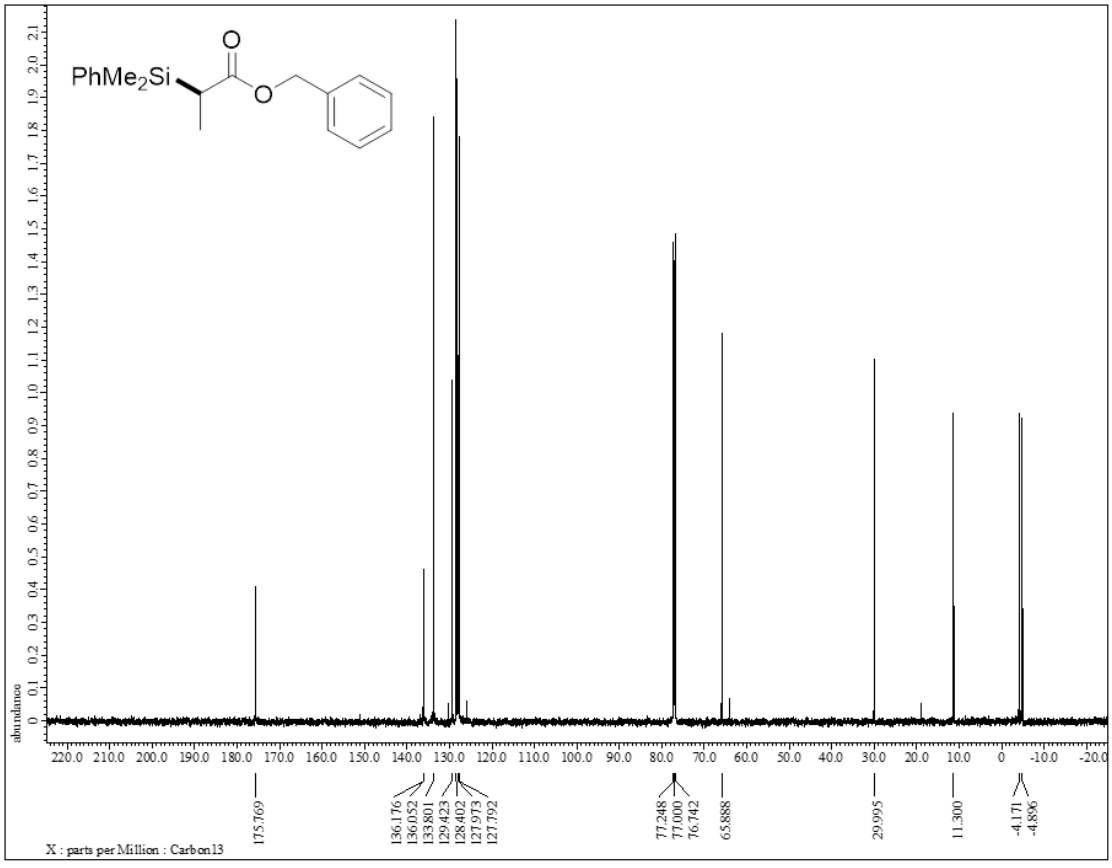

PhMe2Si
O
O
abundance
X : parts per Million : Proton
1.97
3.00
1.91
1.00
5.85
6.07

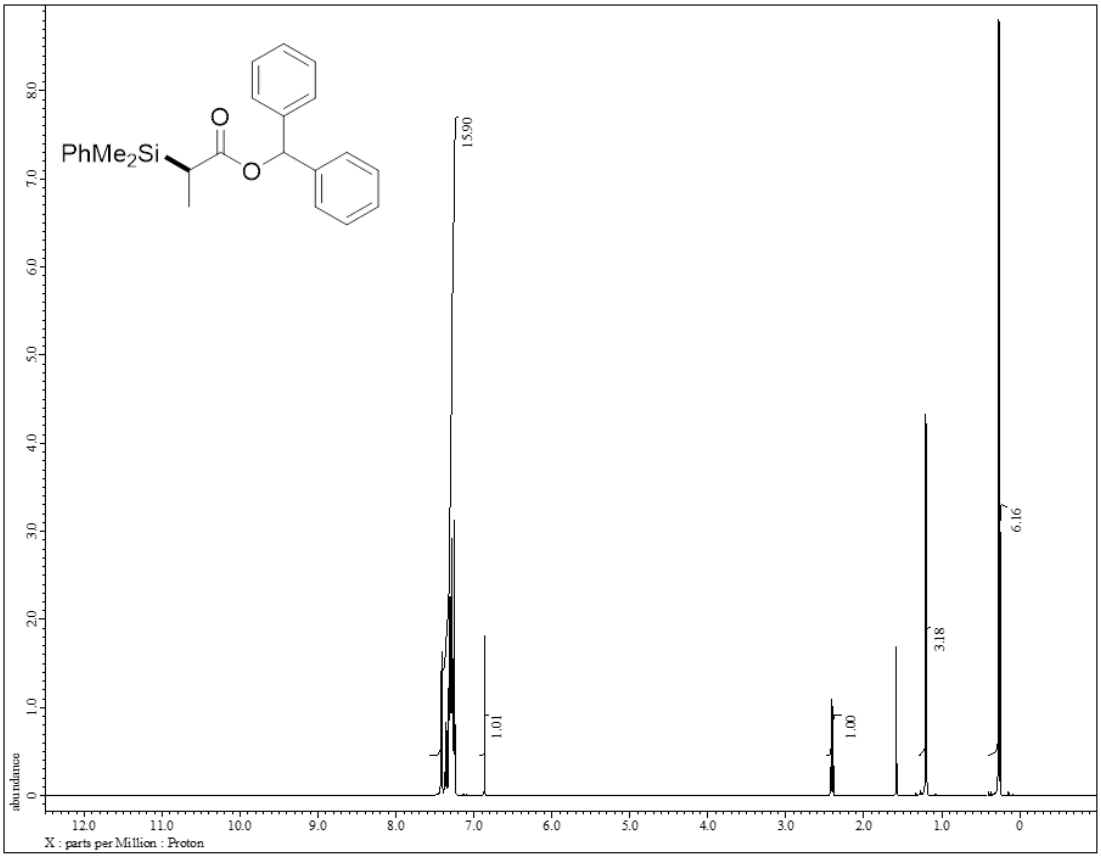

PhMe2Si
O
O
abundance
X : parts per Million : Carbon13
175.979
136.262
133.829
129.413
127.763
77.258
77.000
76.742
59.793
29.967
14.266
11.252
-4.095
-4.944

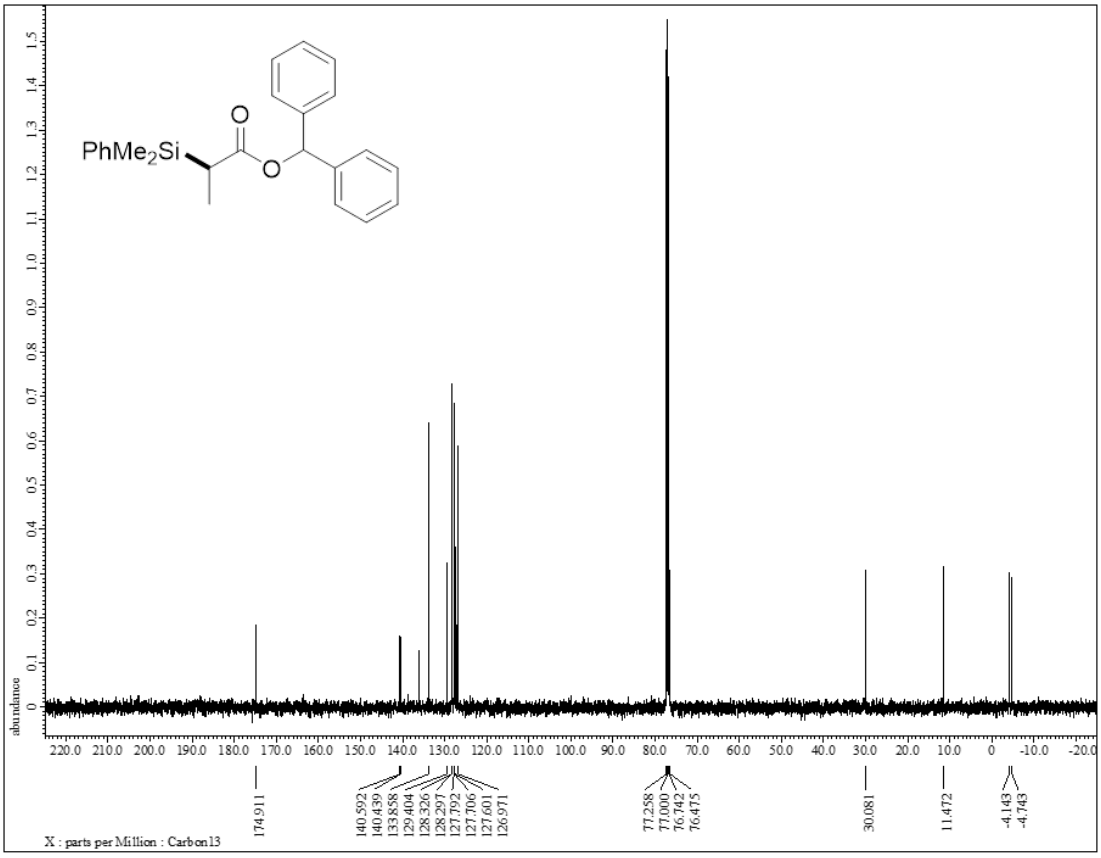

Ph3Si
O
O
6.47
6.26
3.01
1.04
1.04
1.00
3.10
3.16
abundance
X : parts per Million : Proton

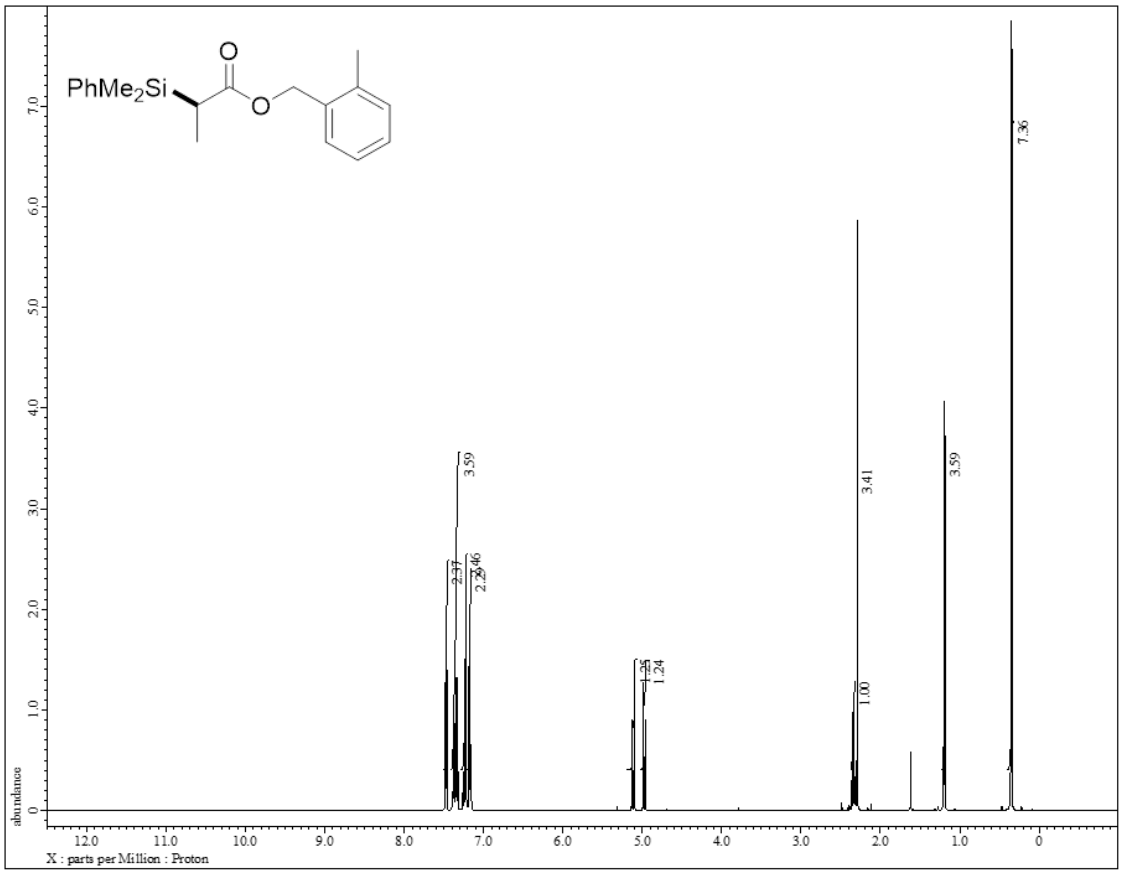

Ph3Si
O
O
abundance
175.827
136.166
132.837
129.747
127.782
60.069
28.469
13.742
13.065
X : parts per Million : Carbon13

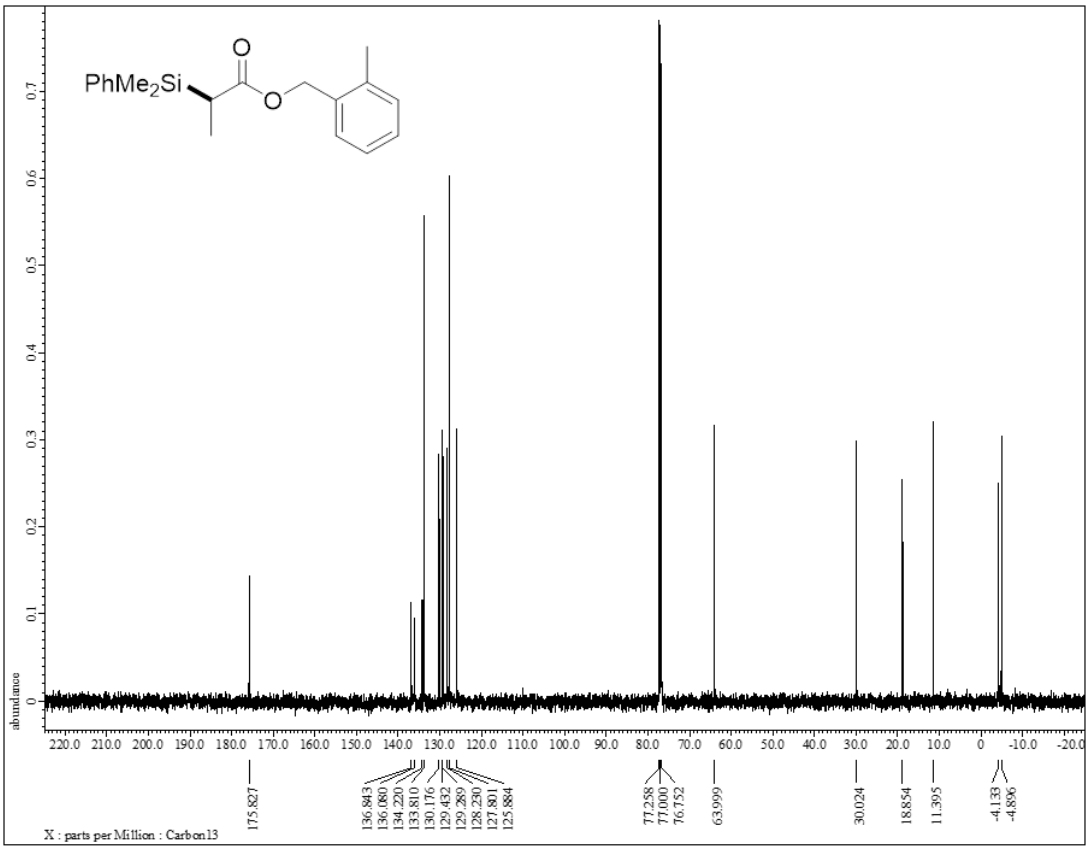

PhMe2Si
O
O
6.14
6.37
3.29
2.13
2.08
2.06
1.00
abundance
X : parts per Million : Proton

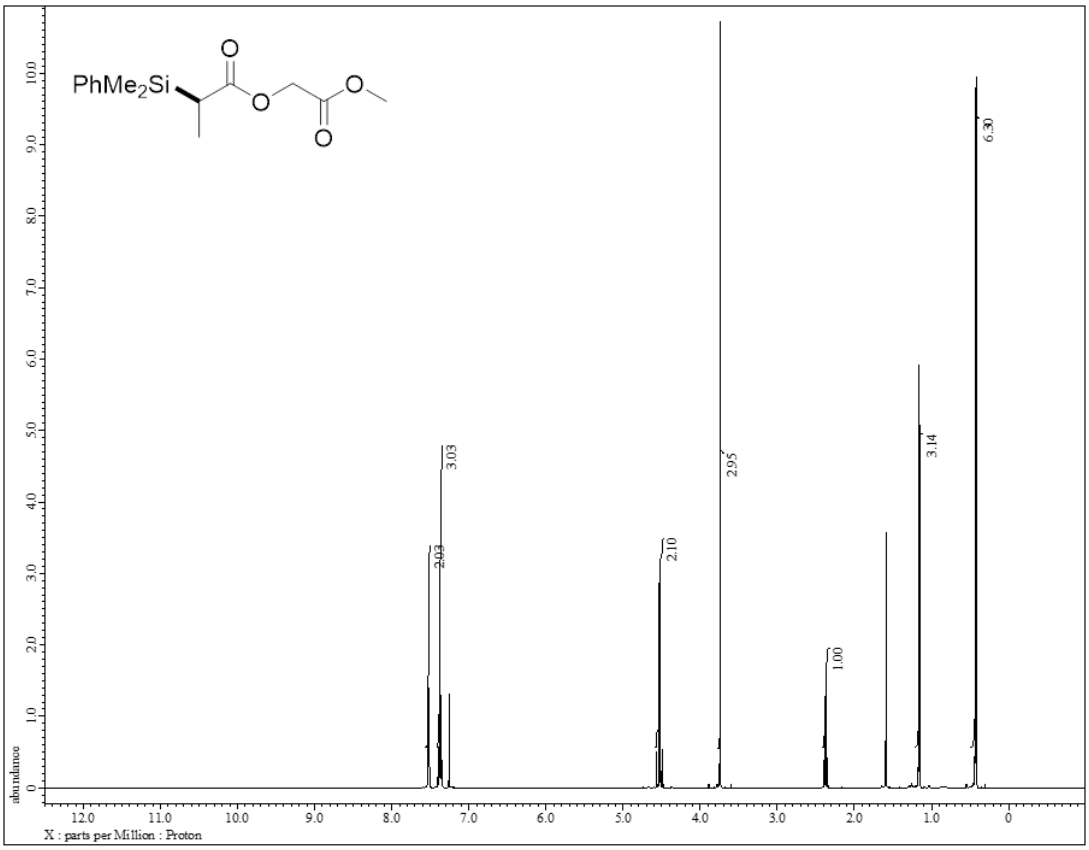

PhMe2Si
O
O
abundance
X : parts per Million : Carbon13
175.769
136.176
136.052
133.801
129.423
128.402
127.973
127.792
77.248
77.000
76.742
65.888
29.995
11.300
-4.171
-4.896

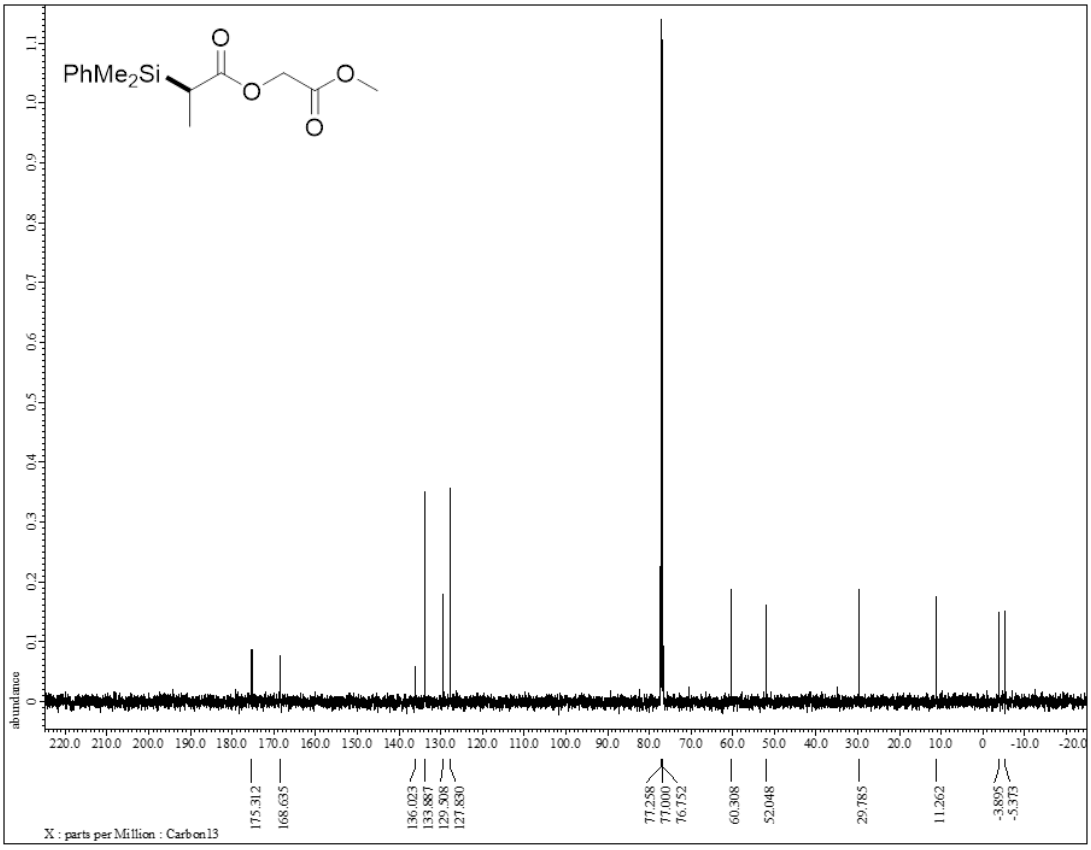

PhMe2Si
O
O
15.90
1.01
1.00
3.18
6.16
abundance
X : parts per Million : Proton

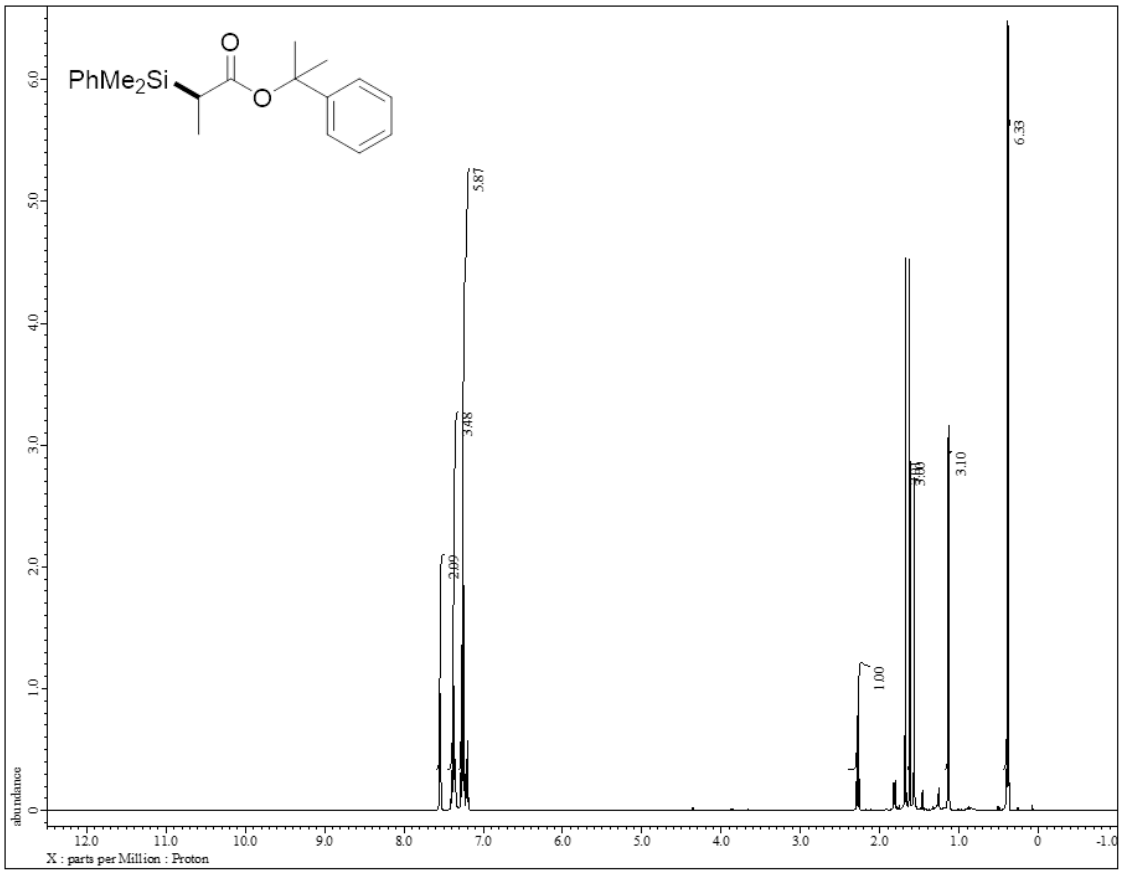

PhMe2Si
O
O
abundance
174.911
140.592
140.439
133.858
129.404
128.326
128.297
127.792
127.706
127.601
126.971
77.258
77.000
76.742
76.475
30.081
11.472
-4.143
-4.743
X : parts per Million : Carbon13

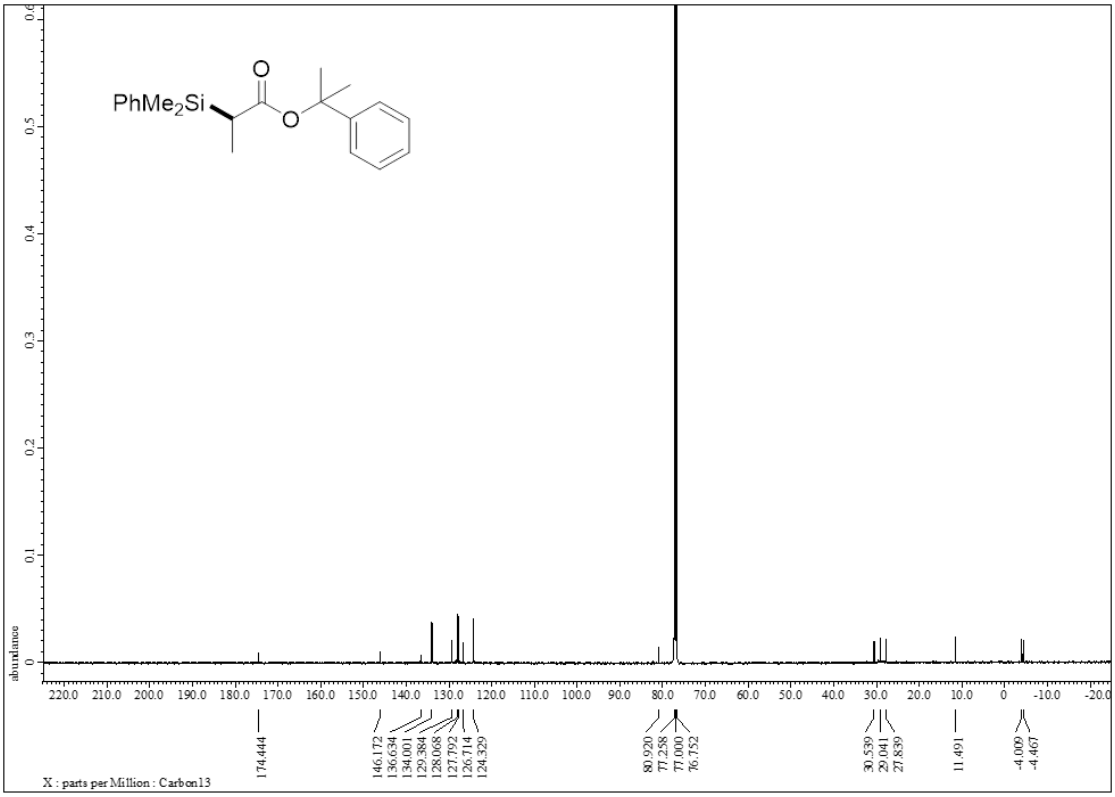

PhMe2Si
O
O
7.36
3.59
3.41
3.59
2.37
2.46
1.25
1.24
1.00
abundance
X : parts per Million : Proton

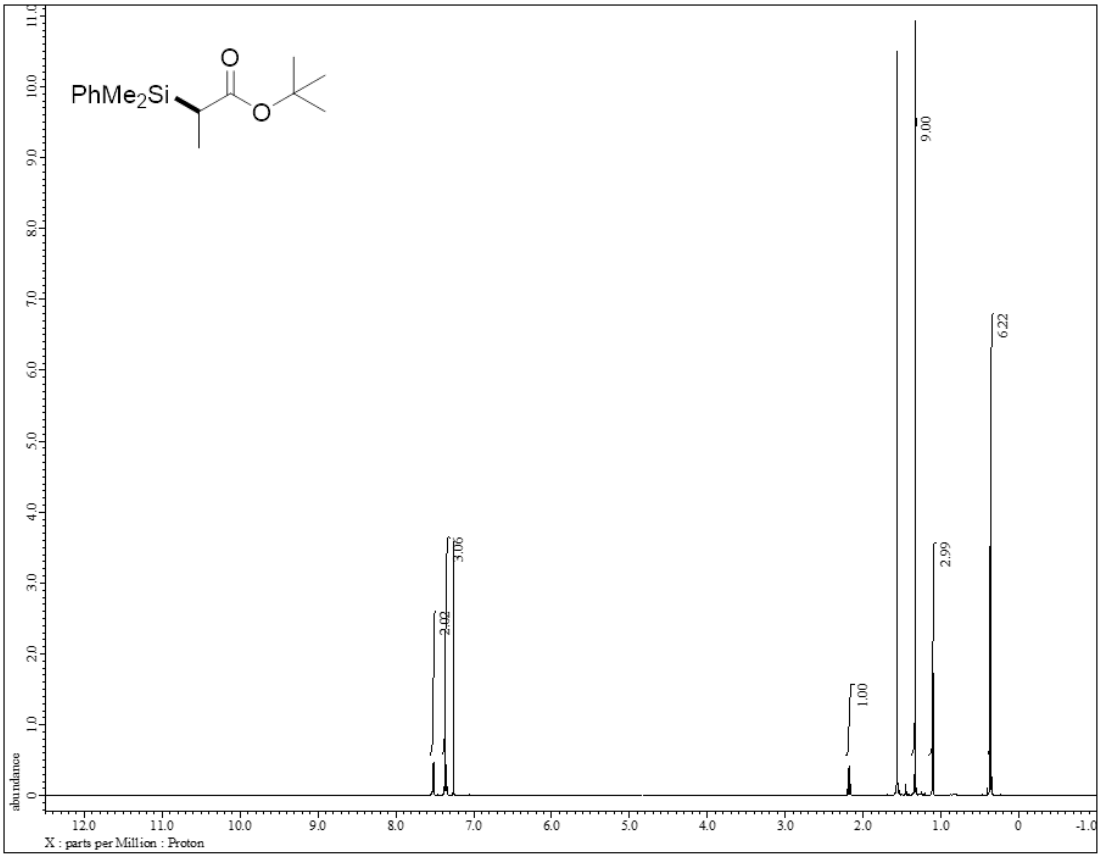

PhMe2Si
O
O
abundance
175.827
136.843
136.080
134.220
133.810
130.176
129.432
129.289
128.230
127.801
125.884
77.258
77.000
76.752
63.999
30.024
18.854
11.395
-4.133
-4.896
X : parts per Million : Carbon13

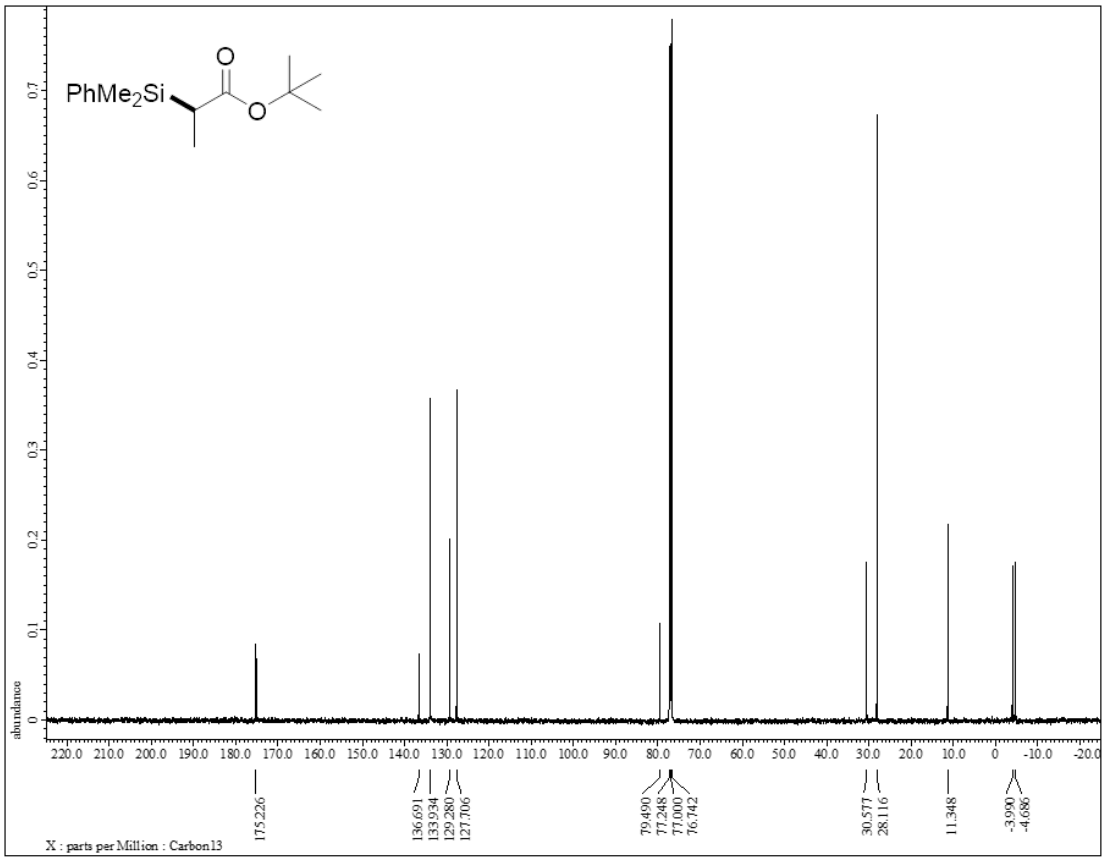

PhMe2Si
abundance
X : parts per Million : Proton
2.03
3.03
2.10
2.95
1.00
3.14
6.30

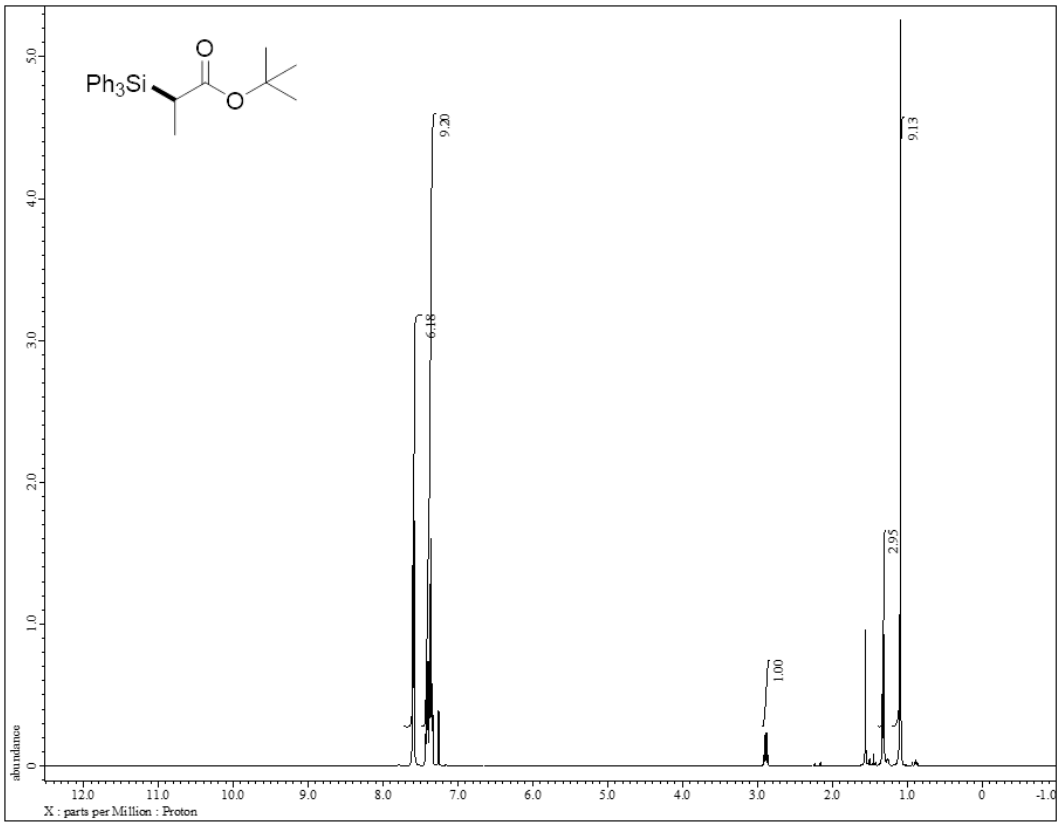

PhMe2Si
abundance
X : parts per Million : Carbon13
175.312
168.635
136.023
133.887
129.908
127.830
77.258
77.000
76.752
60.308
52.048
29.785
11.262
-3.805
-5.373

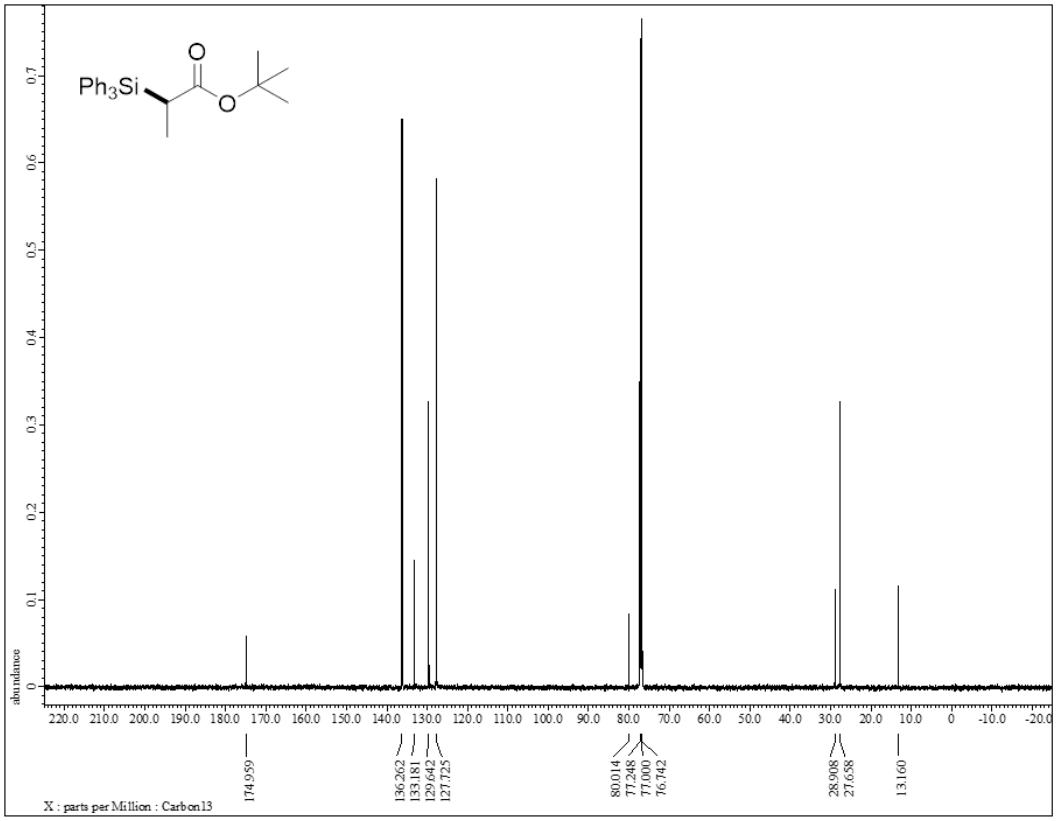

PhMe2Si
O
O
6.33
5.87
3.48
3.10
2.09
1.00
abundance
X : parts per Million : Proton

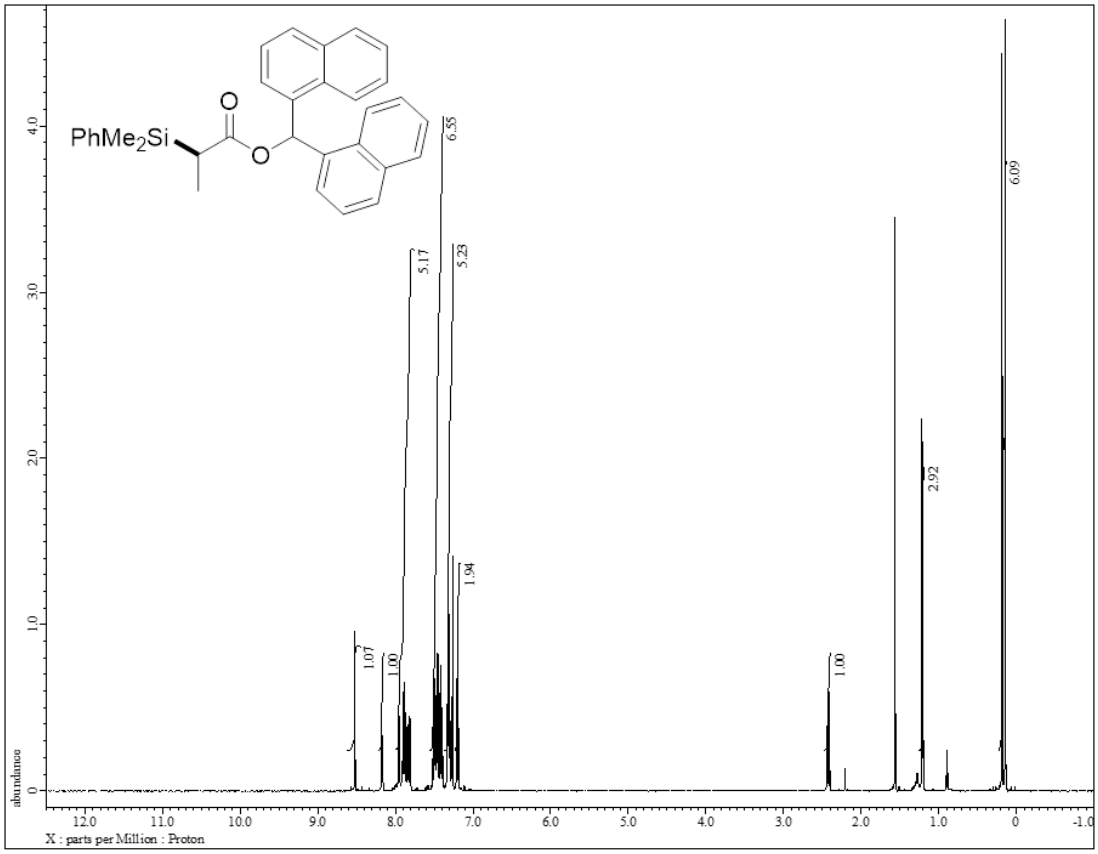

PhMe2Si
O
O
174.444
146.172
136.634
134.001
129.384
128.068
127.792
126.714
124.329
80.920
77.258
77.000
76.752
30.539
29.041
27.839
11.491
-4.009
-4.467
abundance
X : parts per Million : Carbon13

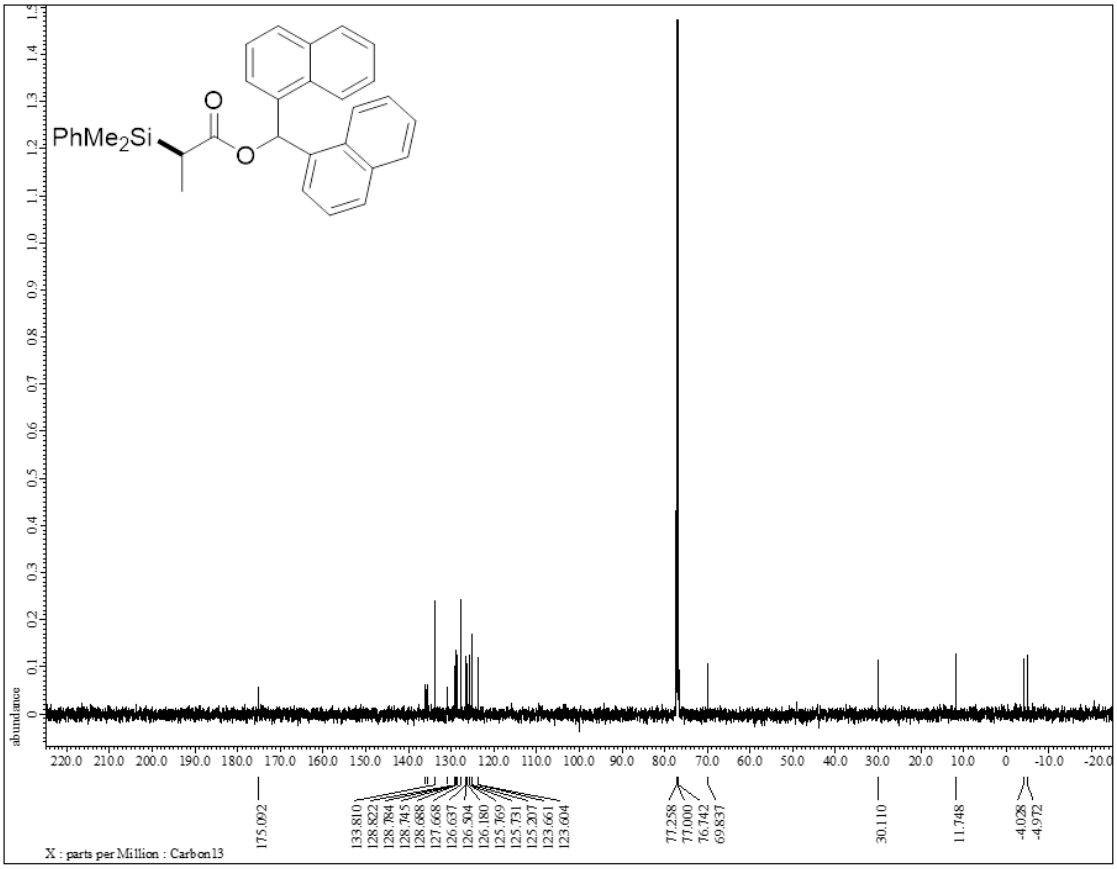

PhMe2Si
O
O
abundance
X : parts per Million : Proton
1.00
2.02
3.06
9.00
2.99
6.22

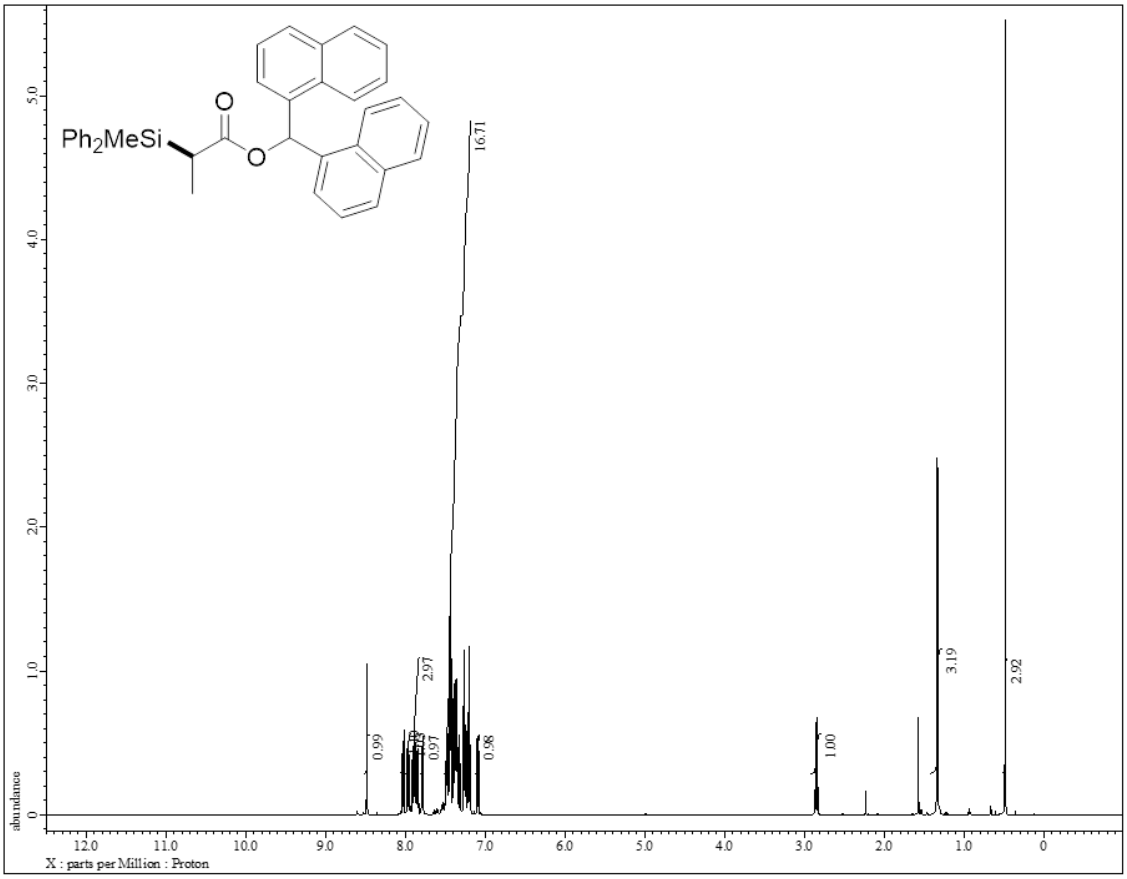

PhMe2Si
O
O
abundance
X : parts per Million : Carbon13
175.226
136.691
133.934
129.280
127.706
79.490
77.248
77.000
76.742
30.577
28.116
11.348
-3.990
-4.686

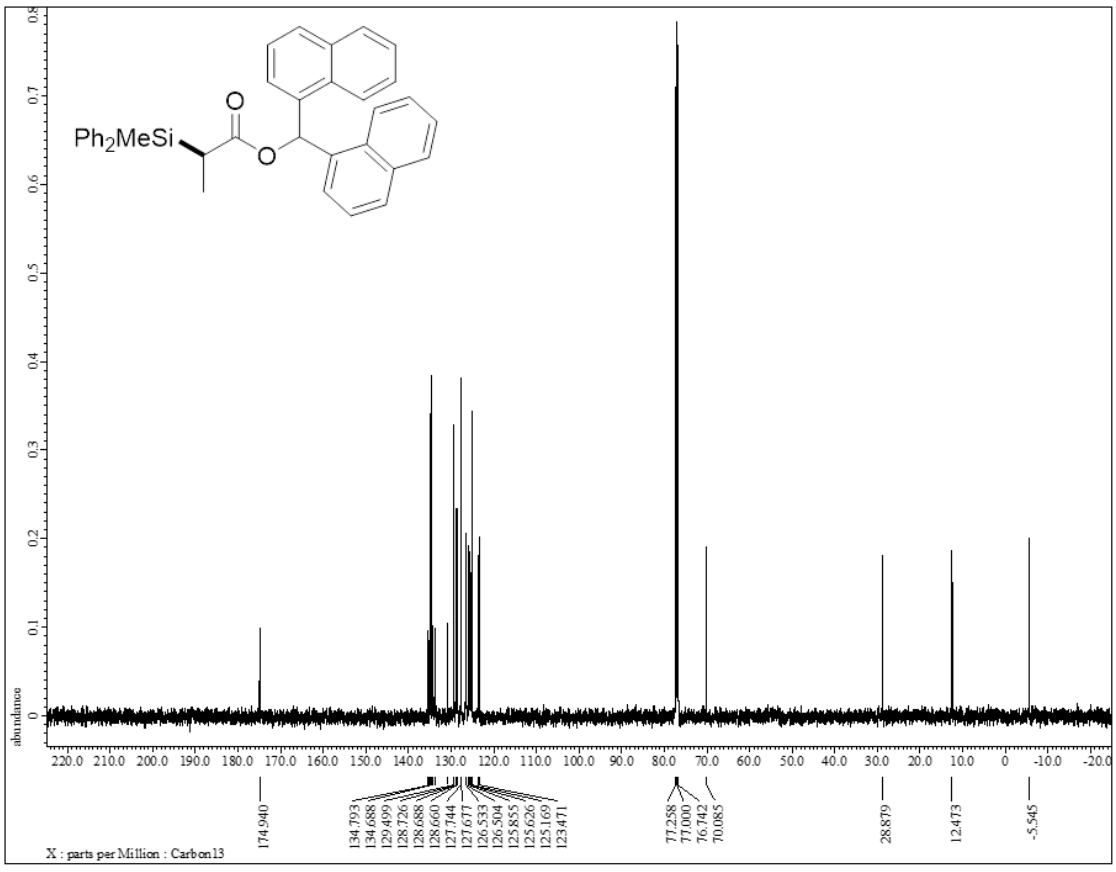

Ph3Si
O
O
9.20
9.13
6.18
2.95
1.00
abundance
X : parts per Million : Proton

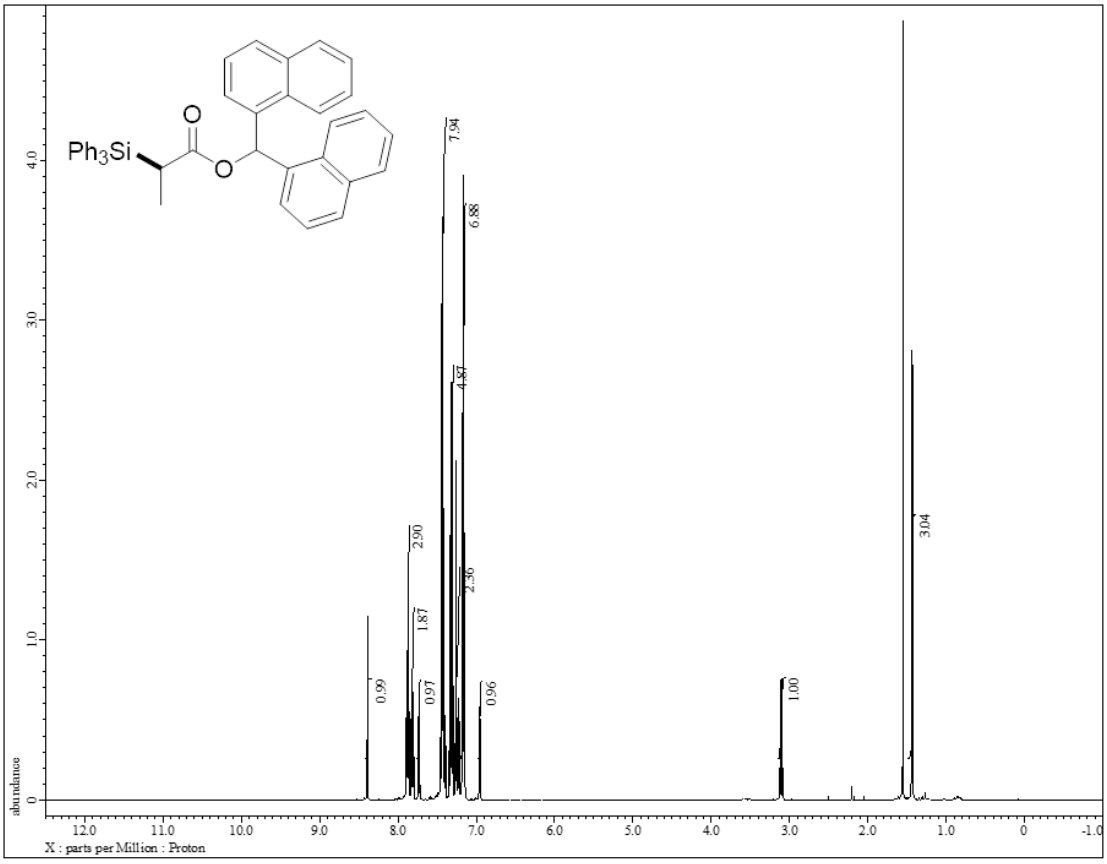

Ph3Si
O
O
abundance
174.959
136.262
133.181
129.642
127.725
80.014
77.248
77.000
76.742
28.908
27.658
13.160
X : parts per Million : Carbon13

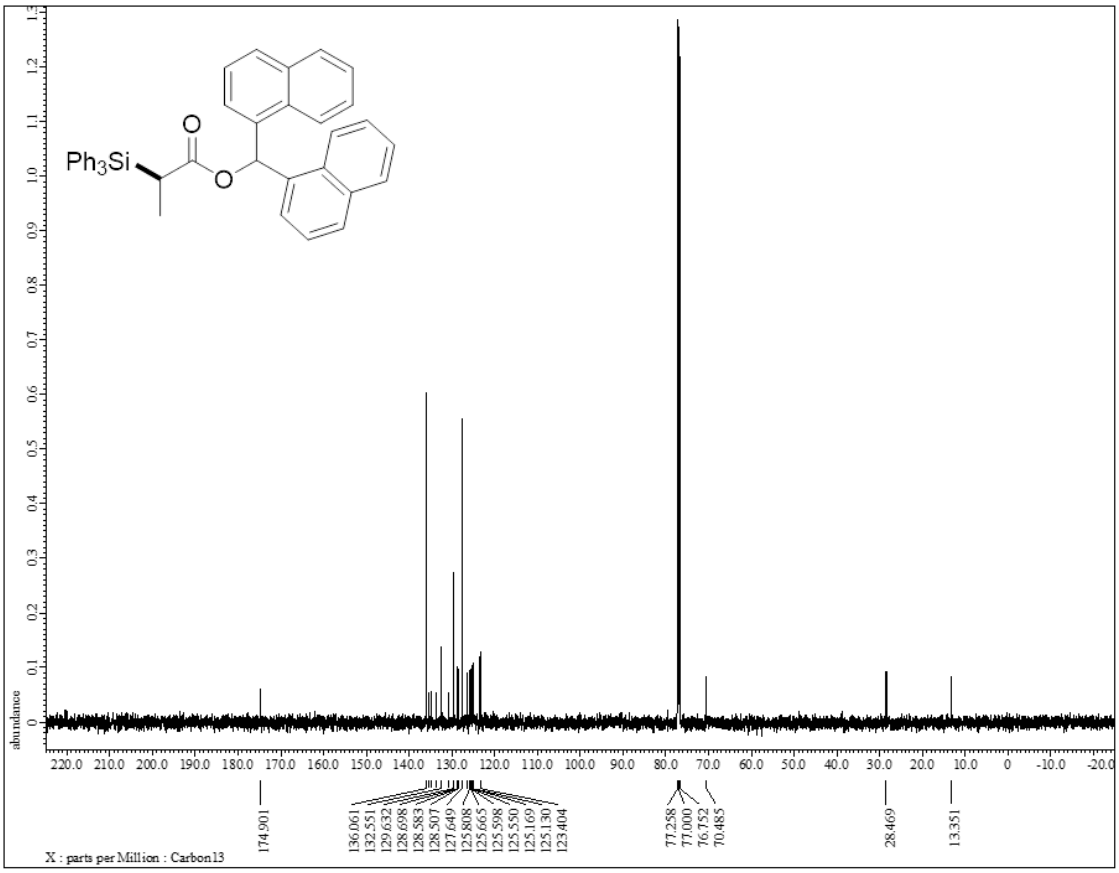

PhMe2Si
O
O
6.55
5.17
5.23
6.09
2.92
1.94
1.07
1.00
1.00
abundance
X : parts per Million : Proton

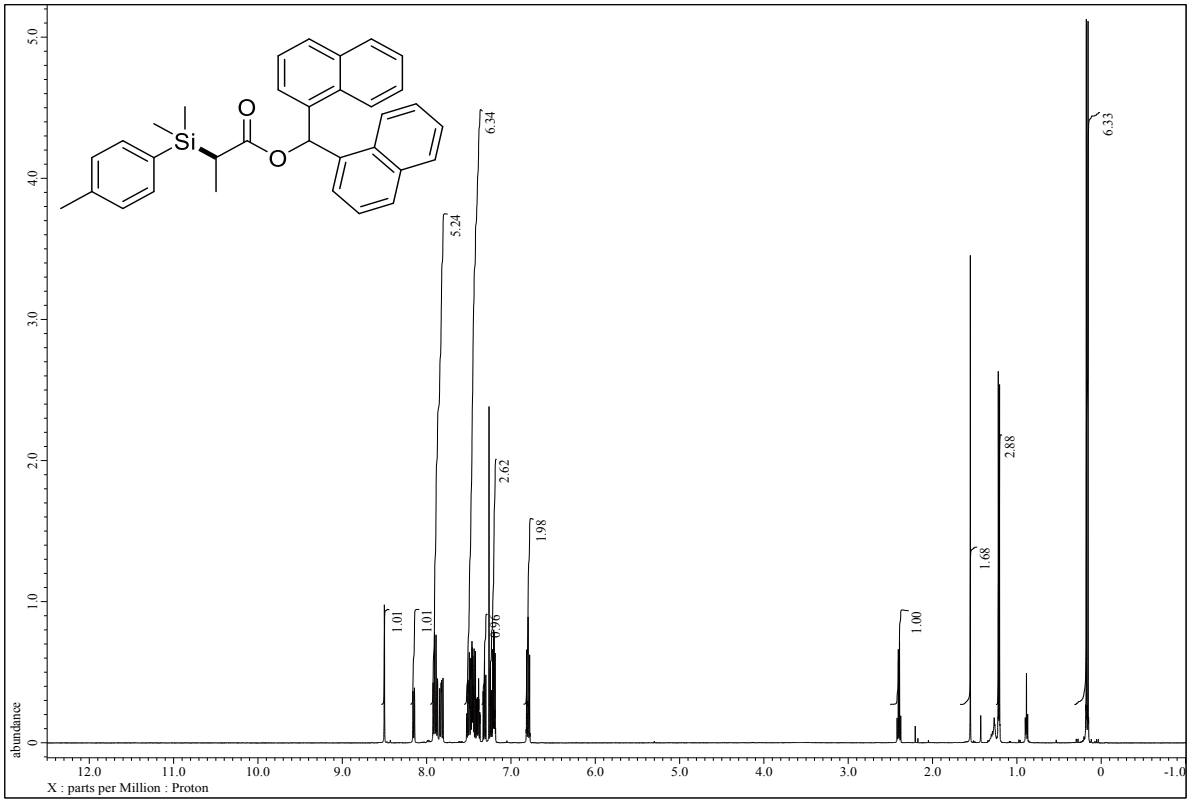

PhMe2Si
O
O
abundance
175.092
133.810
128.822
128.784
128.745
128.688
127.668
126.637
126.304
126.180
125.769
125.731
125.207
123.661
123.604
77.258
77.000
76.742
69.837
30.110
11.748
-4.028
-4.972
X : parts per Million : Carbon13

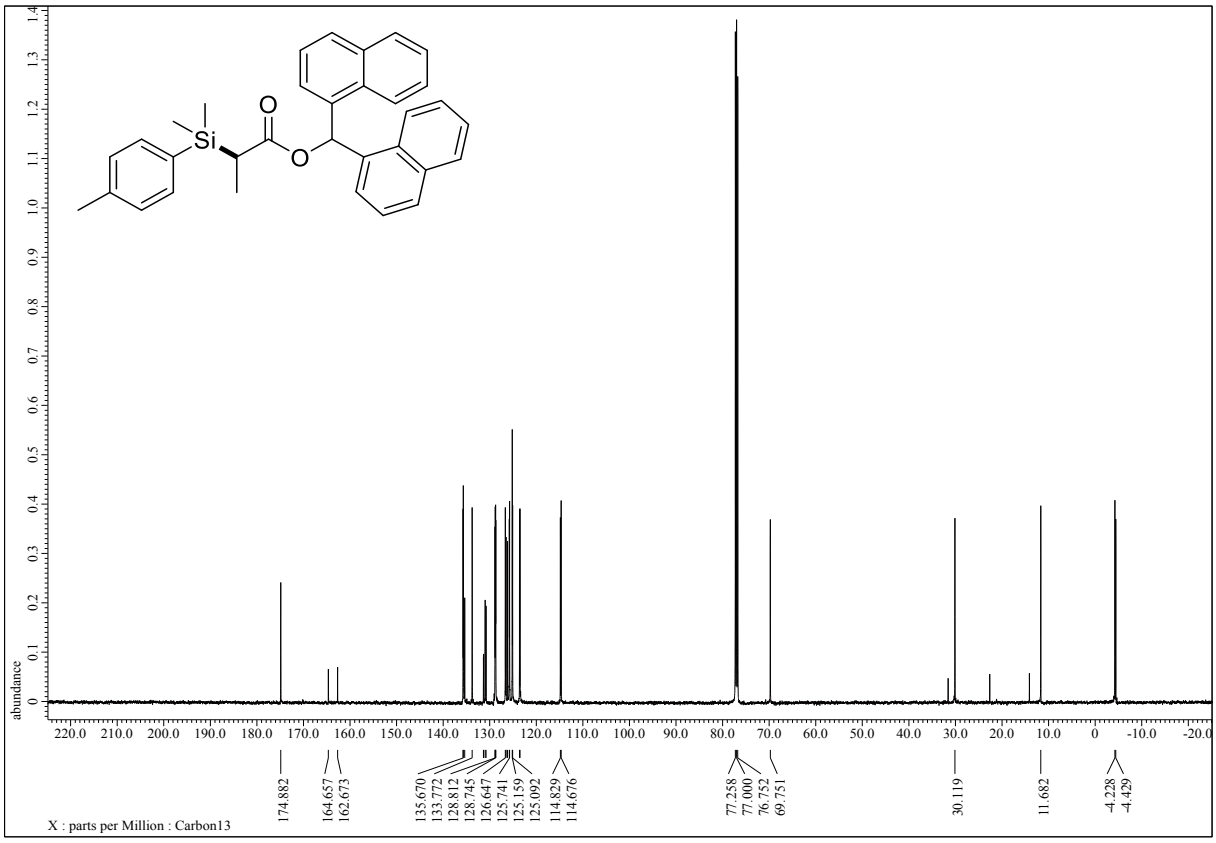

Ph2MeSi
O
O
16.71
2.97
0.99
0.97
0.98
1.00
3.19
2.92
abundance
X : parts per Million : Proton

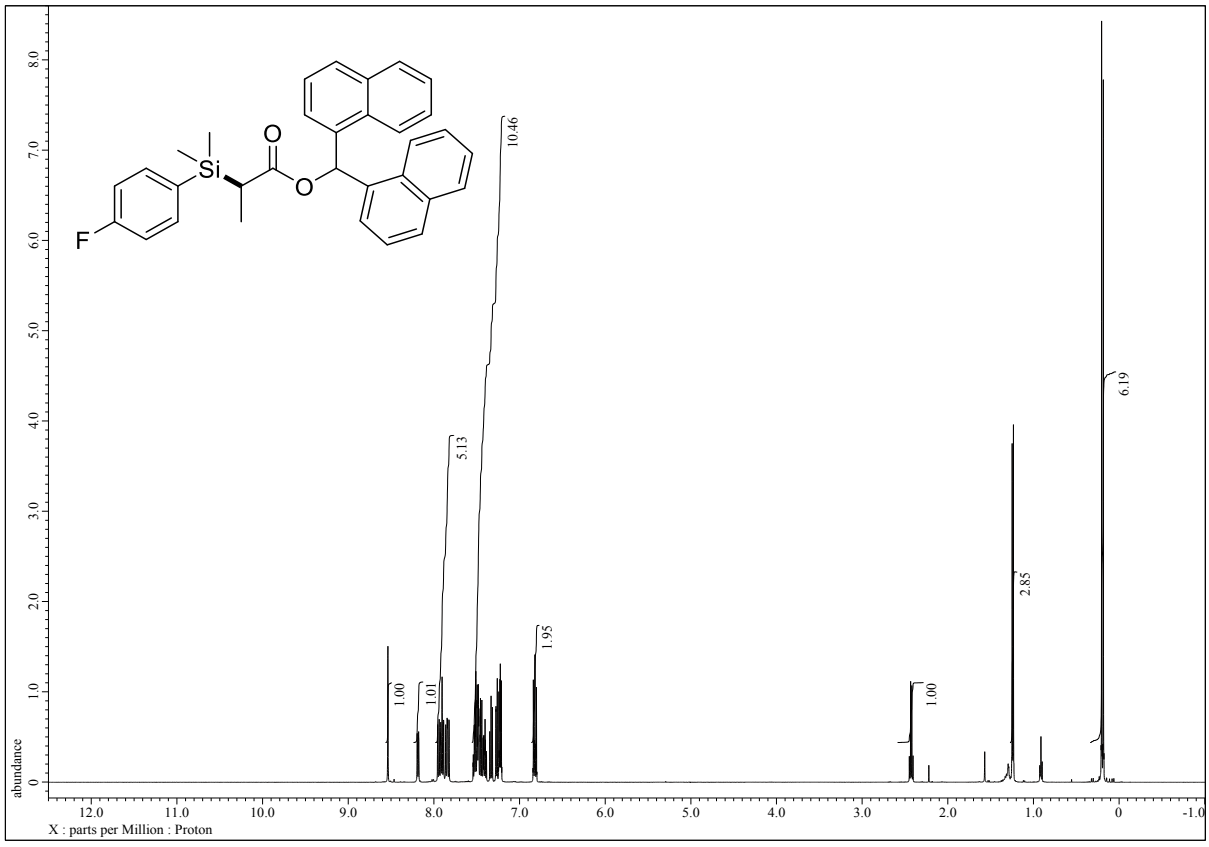

Ph2MeSi
O
O
abundance
174.940
134.793
134.688
129.499
128.726
128.688
128.660
127.744
127.677
126.533
126.504
125.855
125.626
125.169
123.471
77.258
77.000
76.742
70.085
28.879
12.473
-5.545
X : parts per Million : Carbon13

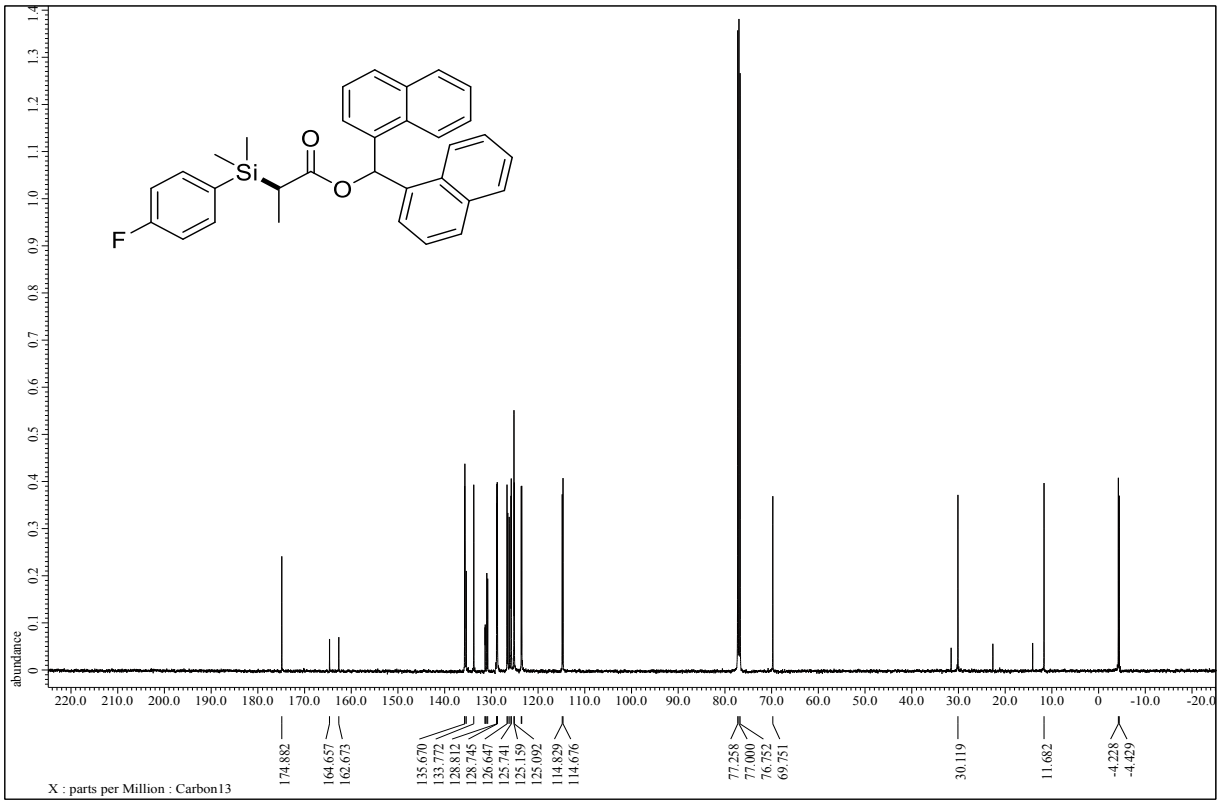

Ph3Si
O
O
7.94
6.88
4.87
2.90
2.36
1.87
3.04
0.99
0.97
0.96
1.00
abundance
X : parts per Million : Proton

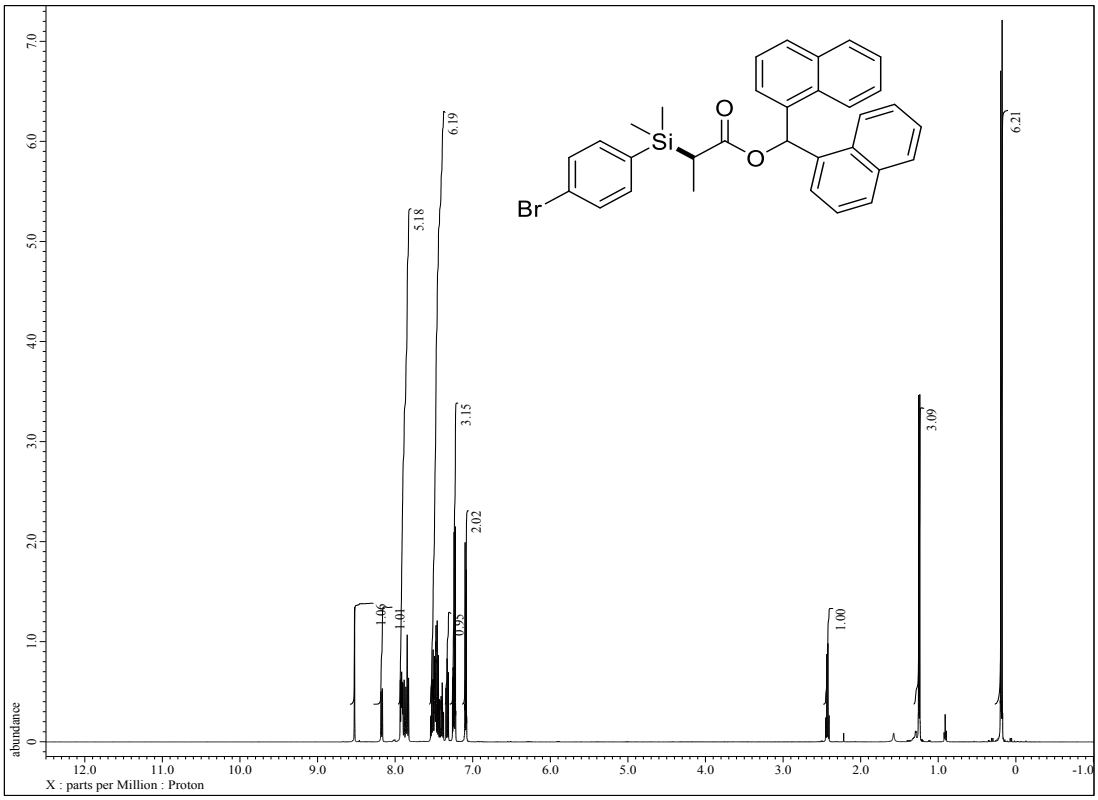

Ph3Si
O
O
abundance
174.901
136.061
132.551
129.632
128.698
128.583
128.507
127.649
125.808
125.665
125.598
125.550
125.169
125.130
123.404
77.258
77.000
76.752
70.485
28.469
13.351
X : parts per Million : Carbon13

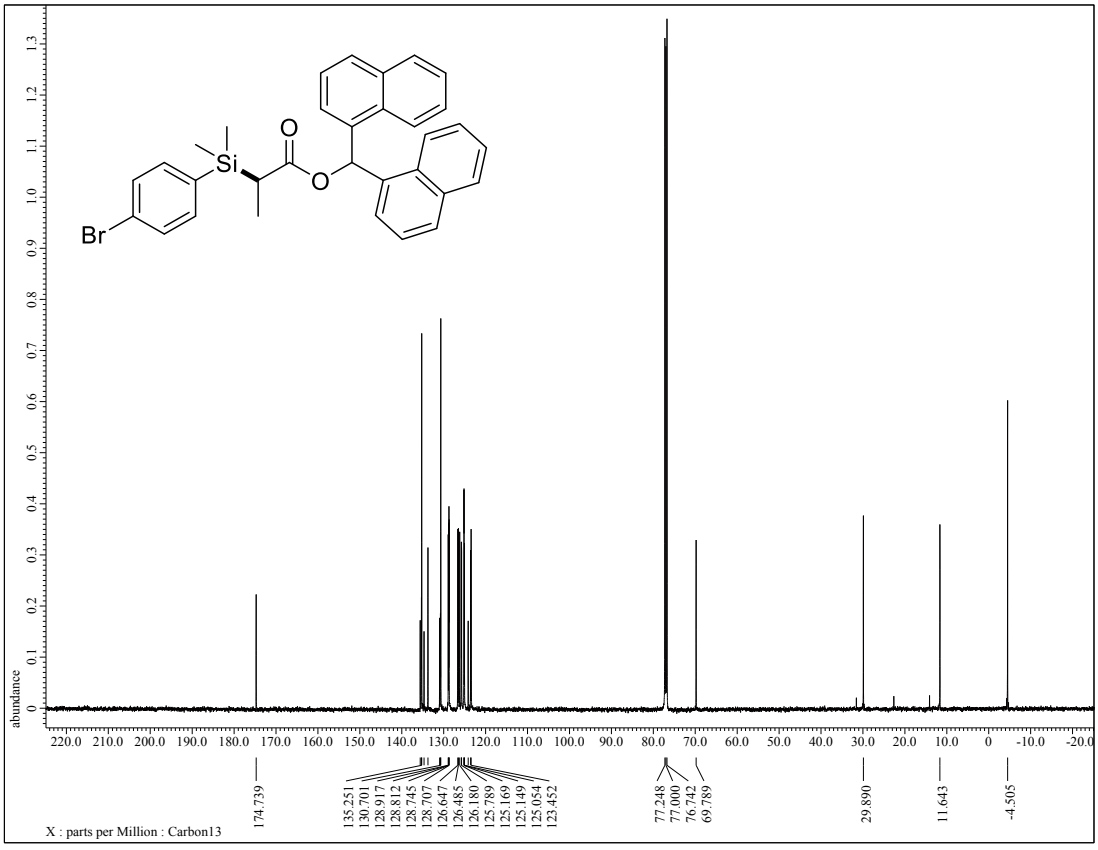

abundance
X : parts per Million : Proton
1.01
1.01
5.24
6.34
0.96
2.62
1.98
1.00
1.68
2.88
6.33

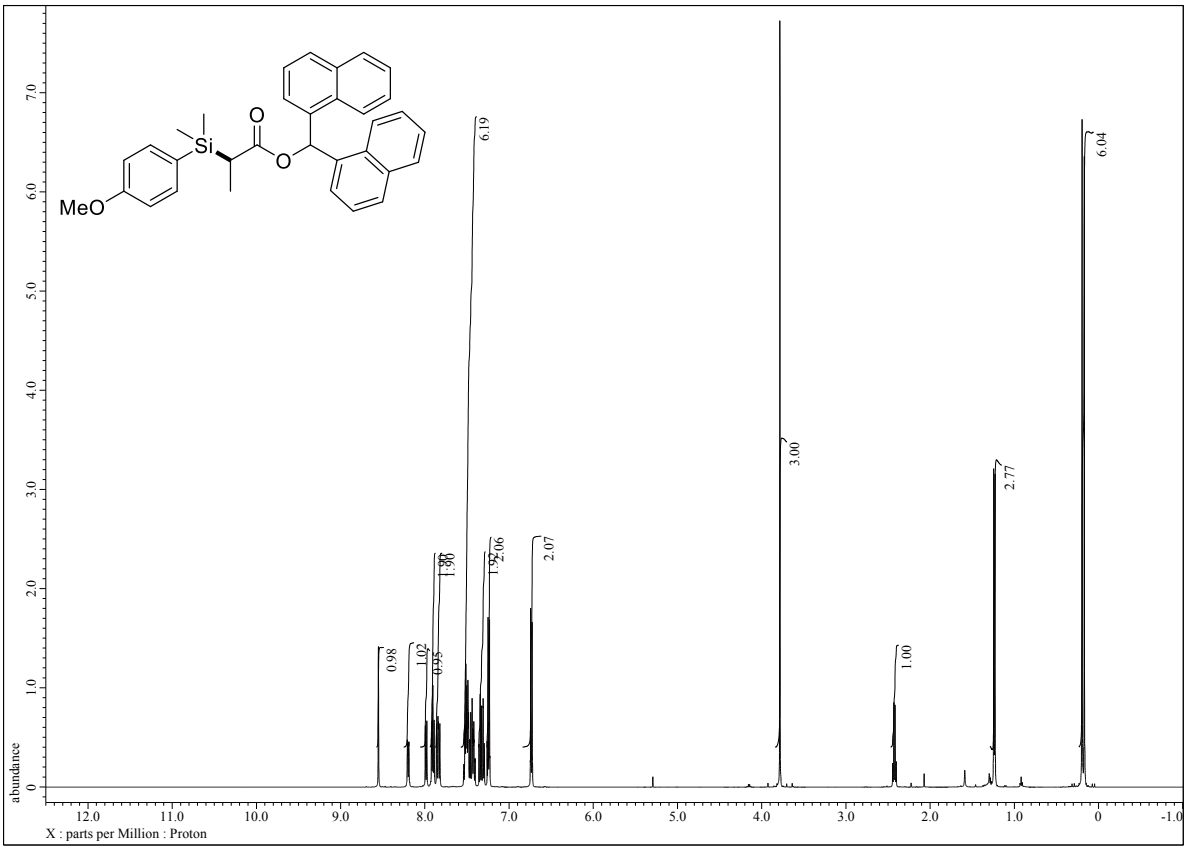

abundance
X : parts per Million : Carbon13
174.882
164.657
162.673
135.670
133.772
128.812
128.745
126.647
125.741
125.159
125.092
114.829
114.676
77.258
77.000
76.752
69.751
30.119
11.682
-4.228
-4.429

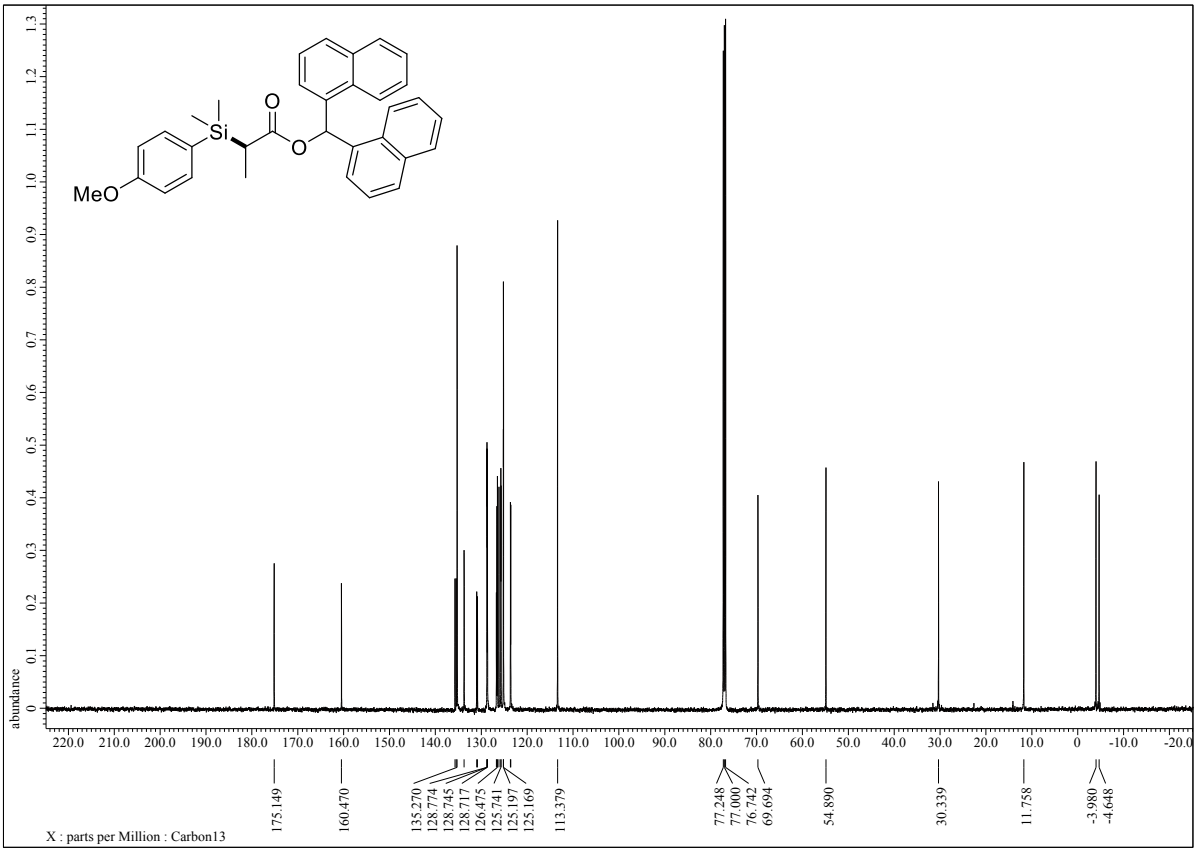

F
Si
O
O
10.46
6.19
5.13
2.85
1.95
1.00
1.01
1.00
abundance
X : parts per Million : Proton

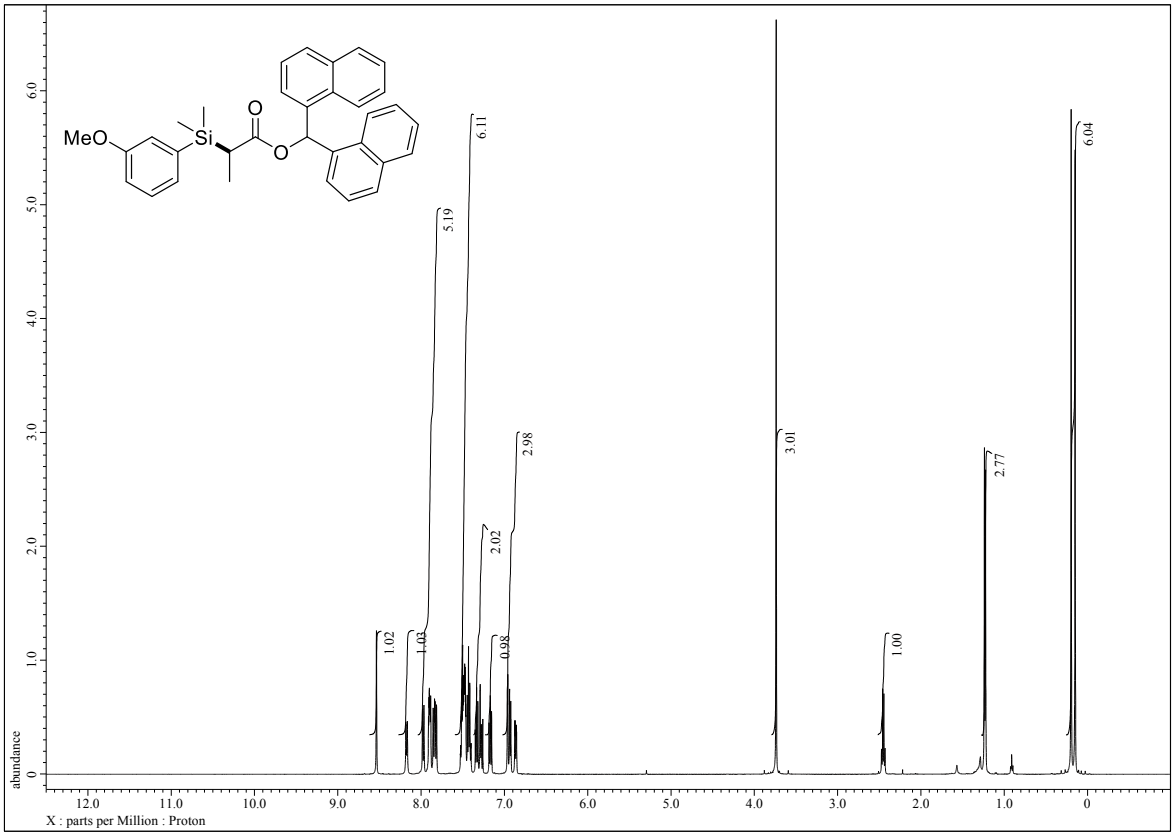

F
Si
O
O
abundance
174.882
164.657
162.673
135.670
133.772
128.812
128.745
126.647
125.741
125.159
125.092
114.829
114.676
77.258
77.000
76.752
69.751
30.119
11.682
-4.228
-4.429
X : parts per Million : Carbon13

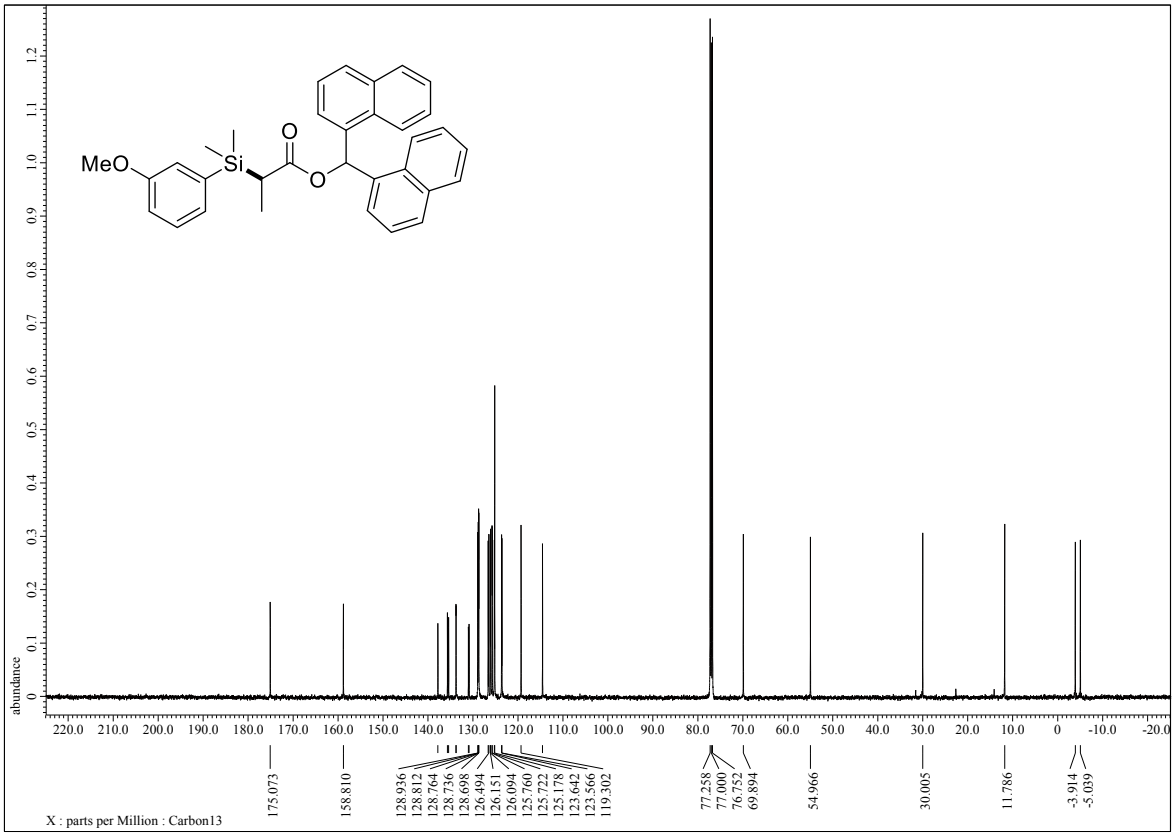

Br
Si
O
O
6.19
5.18
3.15
2.02
1.06
1.01
0.95
1.00
3.09
6.21
abundance
X : parts per Million : Proton

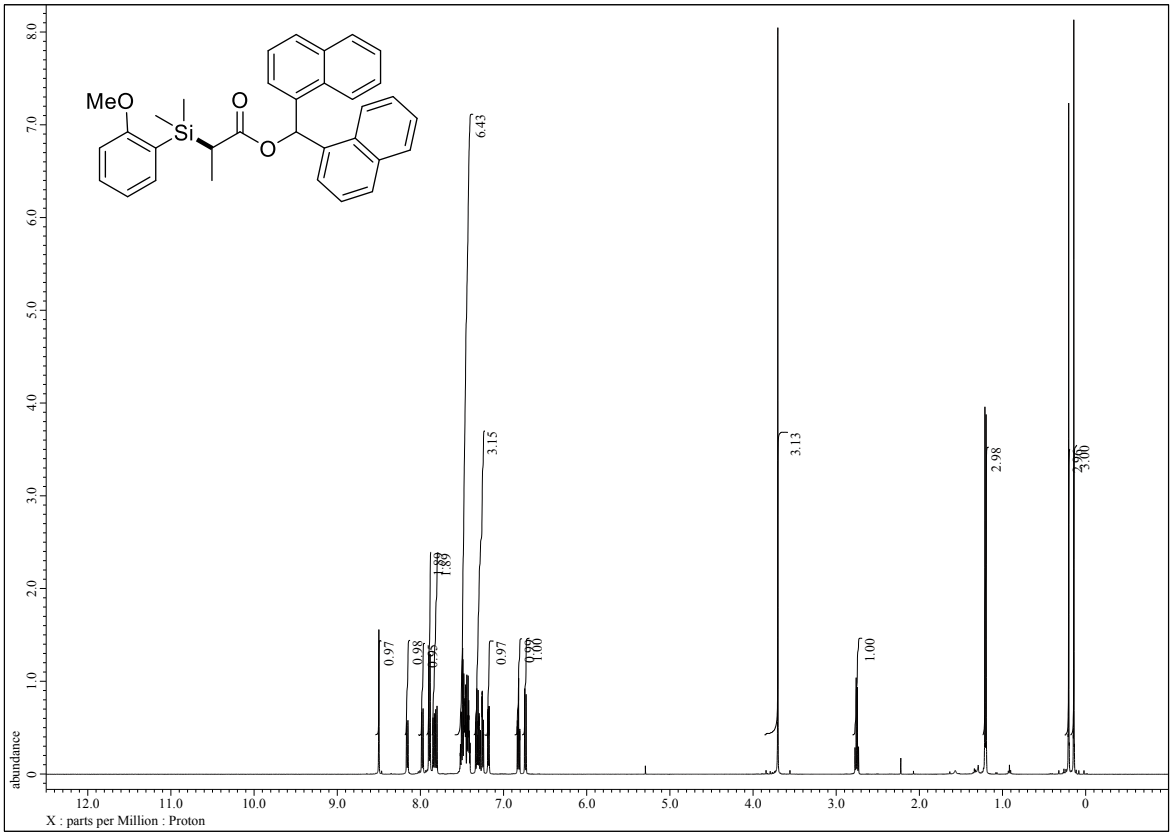

Br
Si
O
O
abundance
174.739
135.251
130.701
128.917
128.812
128.745
128.707
126.647
126.485
126.180
125.789
125.169
125.149
125.054
123.452
77.248
77.000
76.742
69.789
29.890
11.643
-4.505
X : parts per Million : Carbon13

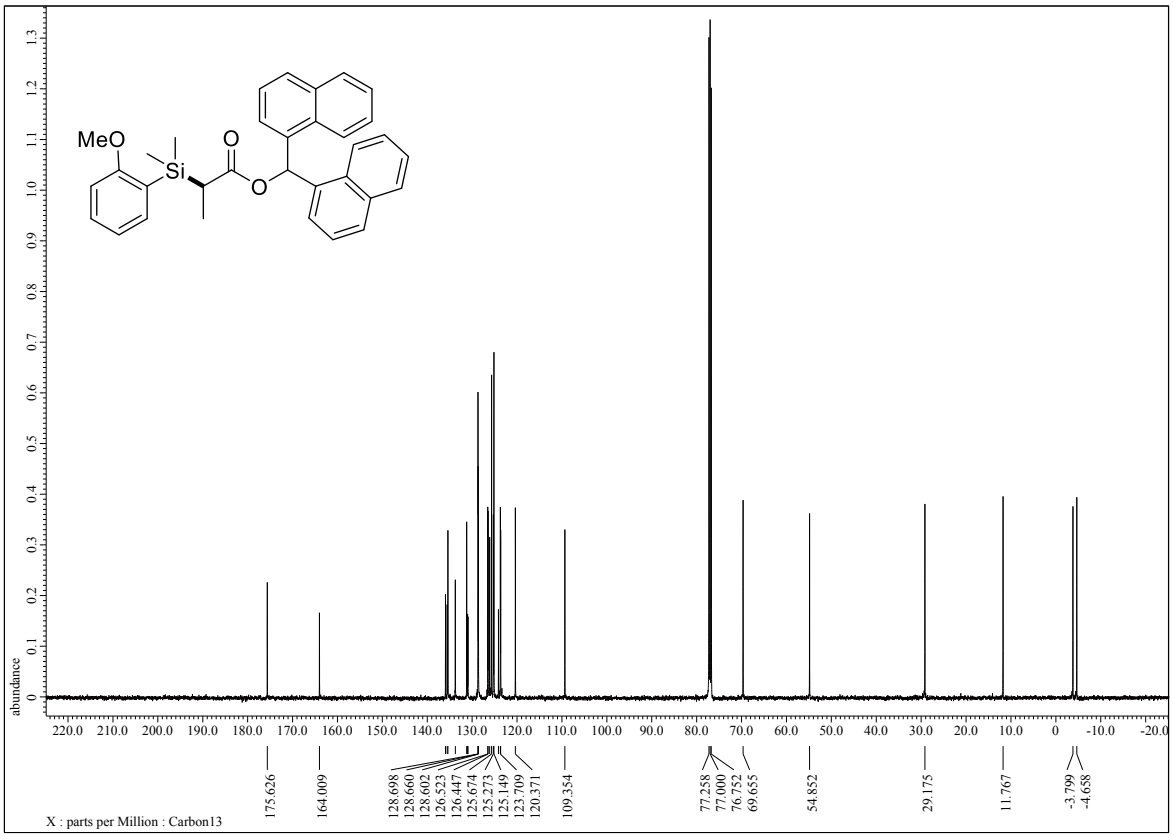

MeO
Si
O
O
6.19
6.04
3.00
2.77
2.07
2.06
1.00
0.98
1.02
0.93
abundance
X : parts per Million : Proton

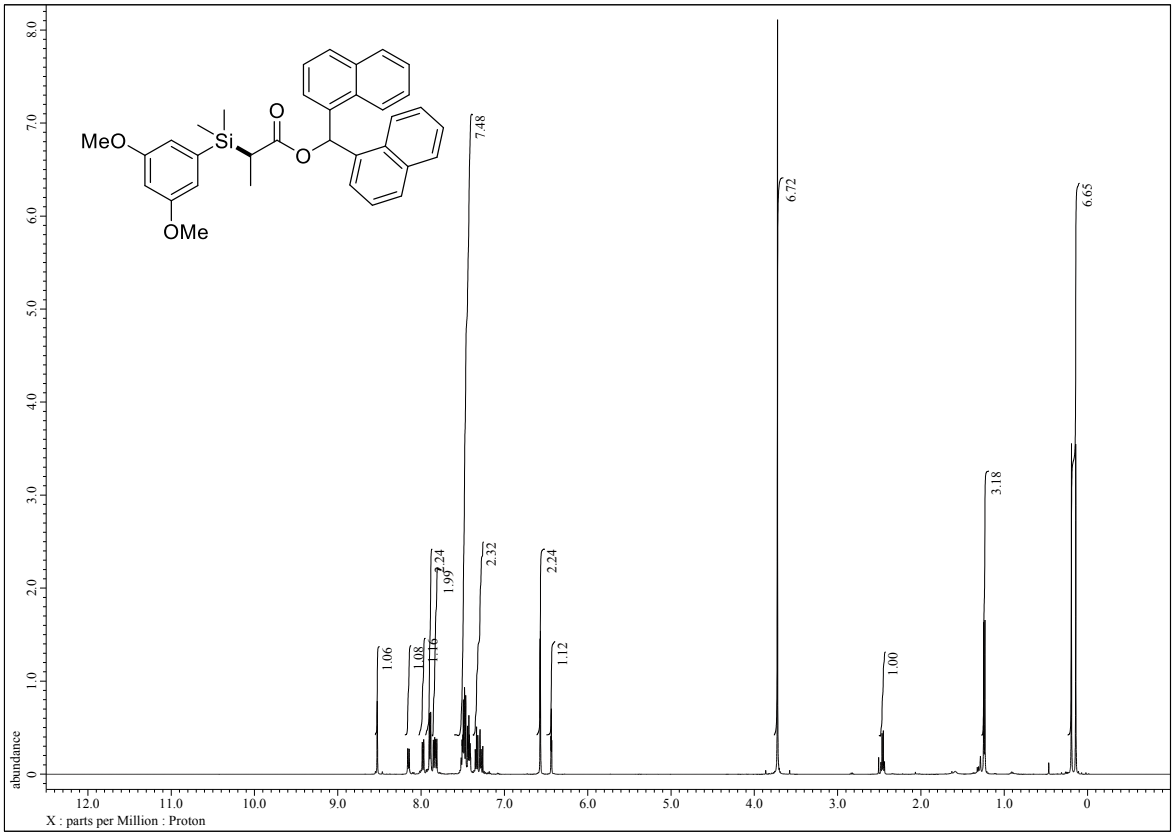

MeO
Si
O
O
175.149
160.470
135.270
128.774
128.745
128.717
126.475
125.741
125.197
125.169
113.379
77.248
77.000
76.742
69.694
54.890
30.339
11.758
-3.980
-4.648
abundance
X : parts per Million : Carbon13

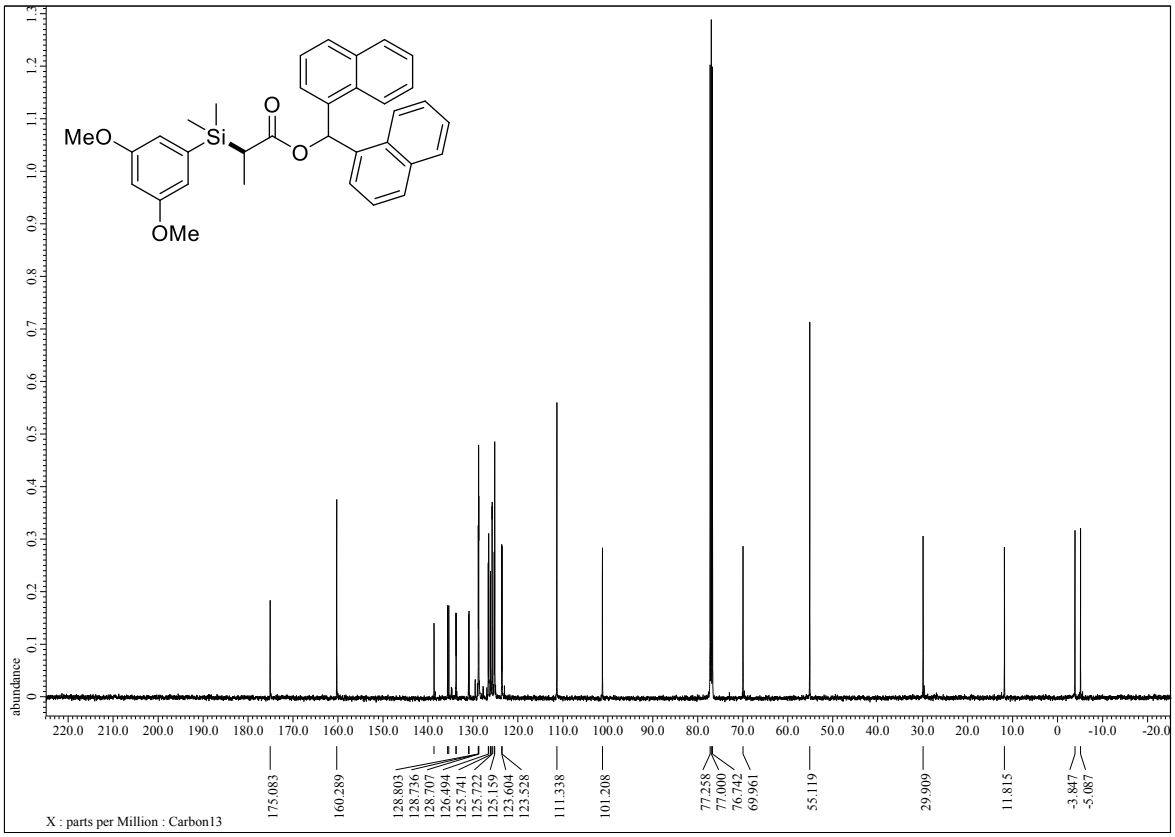

MeO
Si
O
O
6.11
5.19
2.98
2.02
1.02
1.03
0.98
3.01
1.00
2.77
6.04
abundance
X : parts per Million : Proton

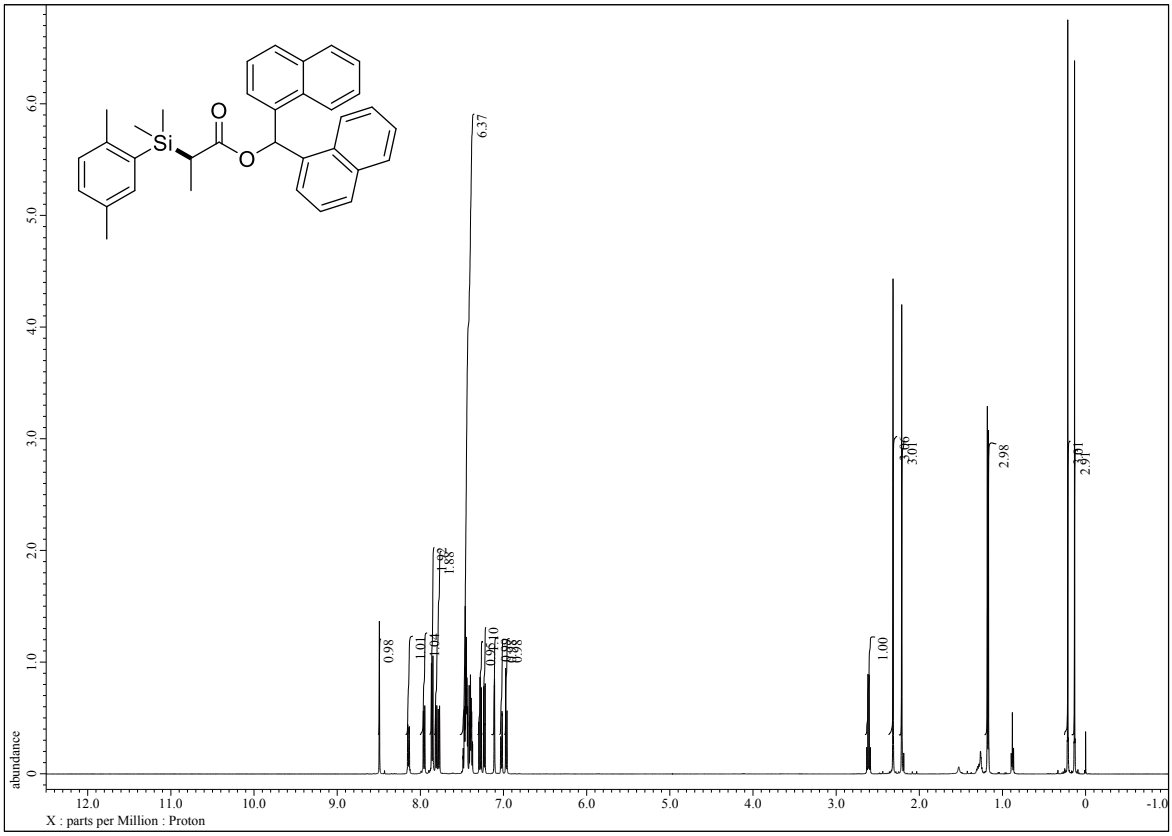

MeO
Si
O
O
abundance
X : parts per Million : Carbon13
175.073
158.810
128.936
128.812
128.764
128.736
128.698
126.494
126.151
126.094
125.760
125.722
125.178
123.642
123.566
119.302
77.258
77.000
76.752
69.894
54.966
30.005
11.786
-3.914
-5.039

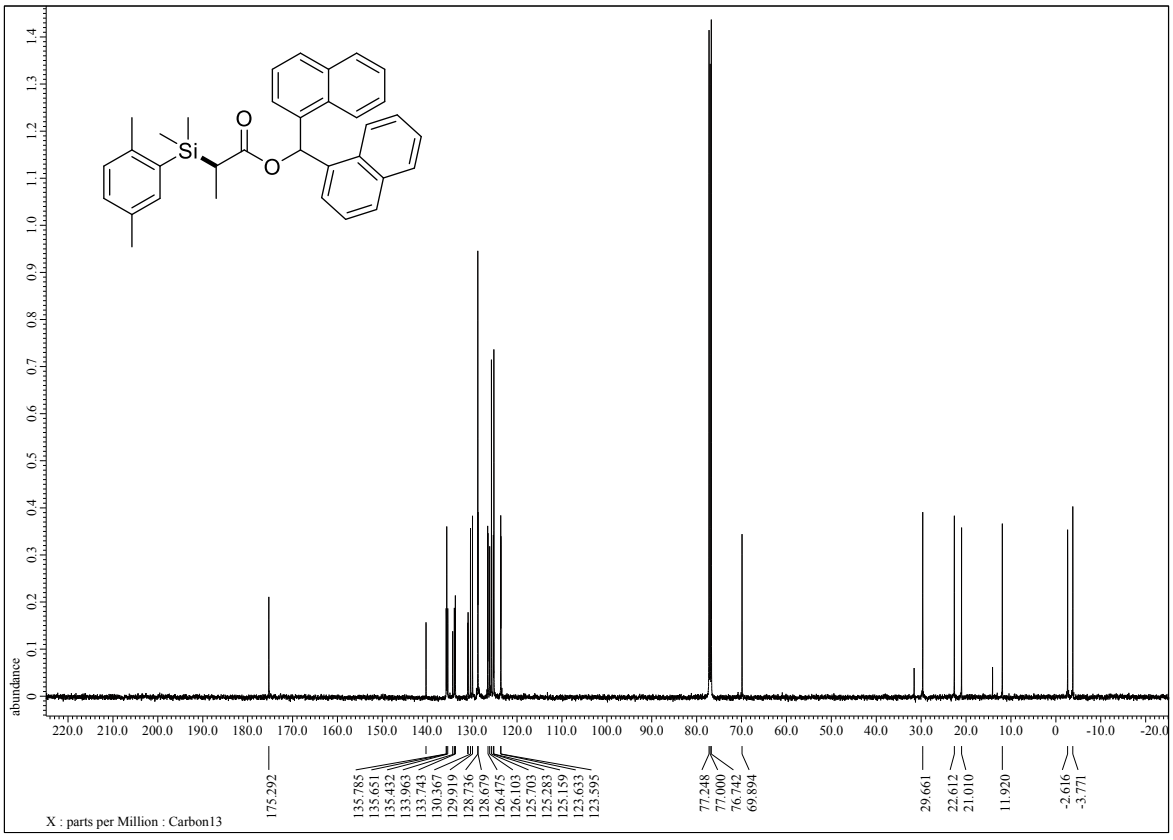

MeO
Si
O
O
6.43
3.15
3.13
2.98
3.06
3.00
1.00
0.97
0.98
0.95
0.97
0.98
1.00
abundance
X : parts per Million : Proton

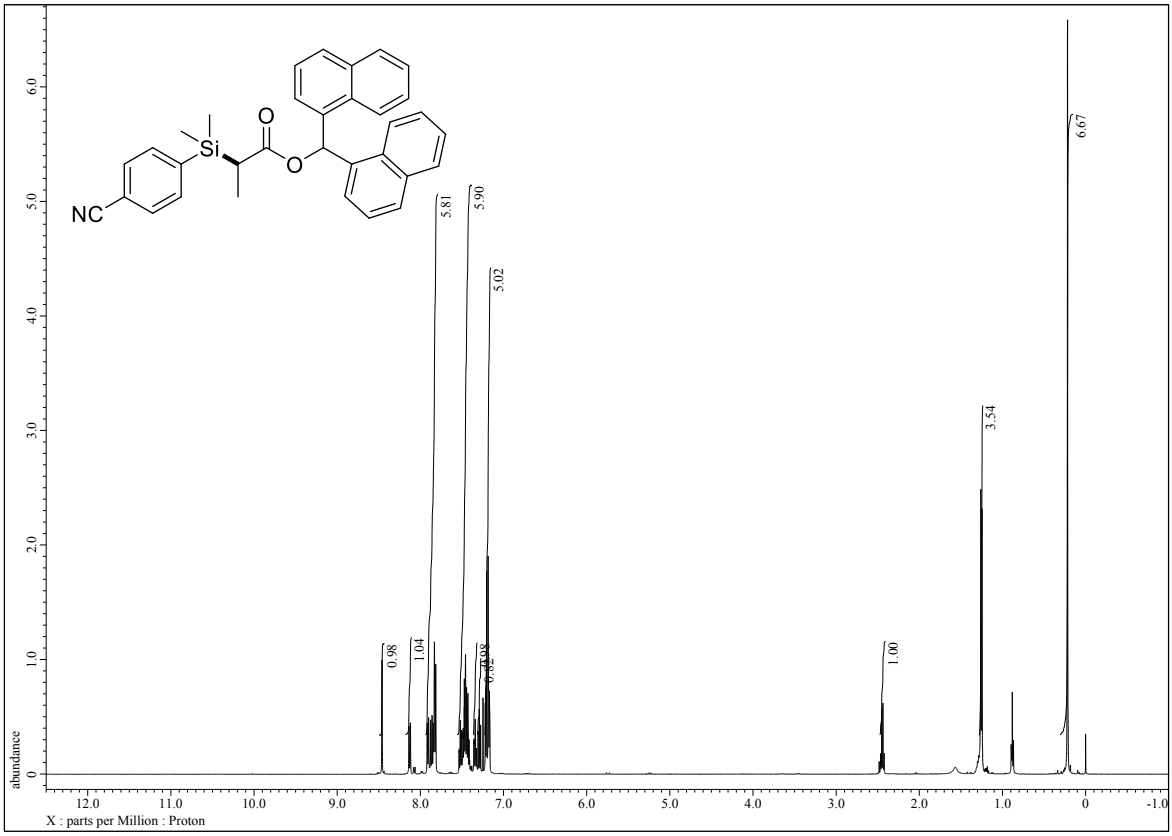

MeO
Si
O
O
abundance
175.626
164.009
128.698
128.660
128.602
126.523
126.447
125.674
125.273
125.149
123.709
120.371
109.354
77.258
77.000
76.752
69.655
54.852
29.175
11.767
-3.799
-4.658
X : parts per Million : Carbon13

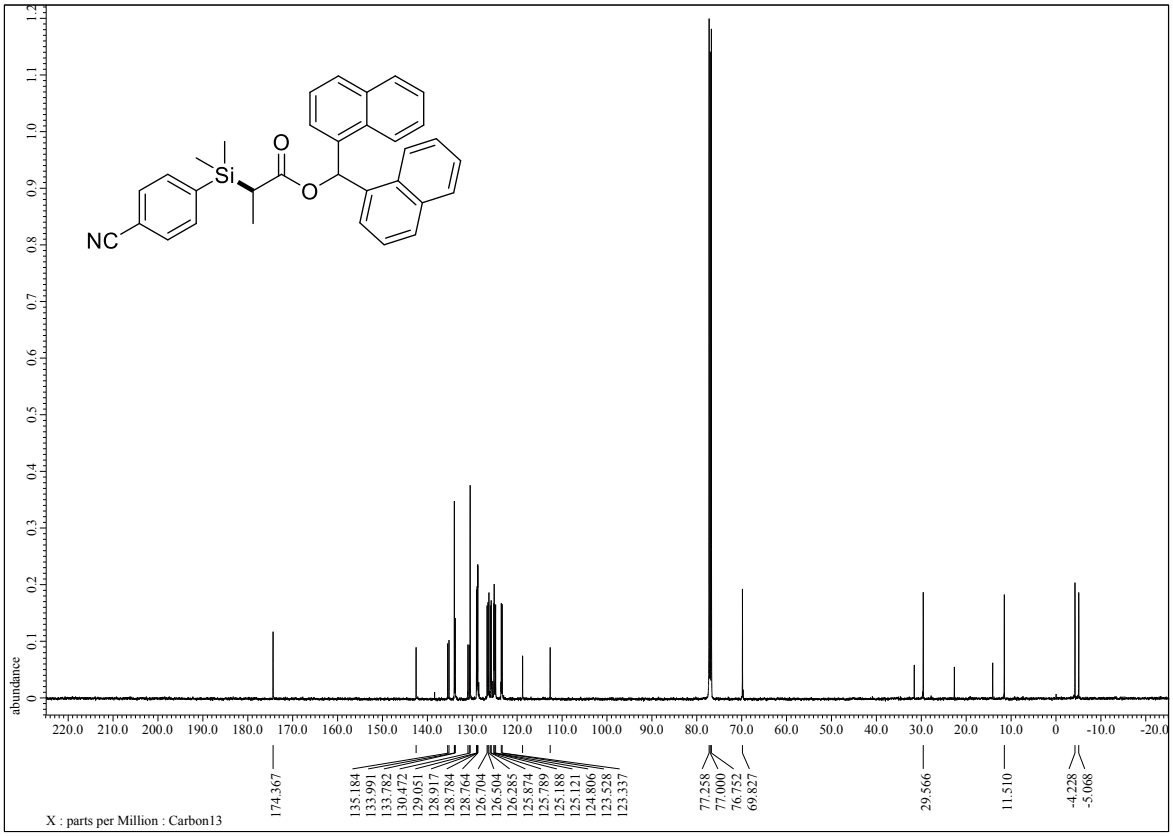

MeO
OMe
Si
O
O
7.48
6.72
6.65
3.18
2.32
2.24
2.24
1.99
1.16
1.08
1.06
1.12
1.00
abundance
X : parts per Million : Proton

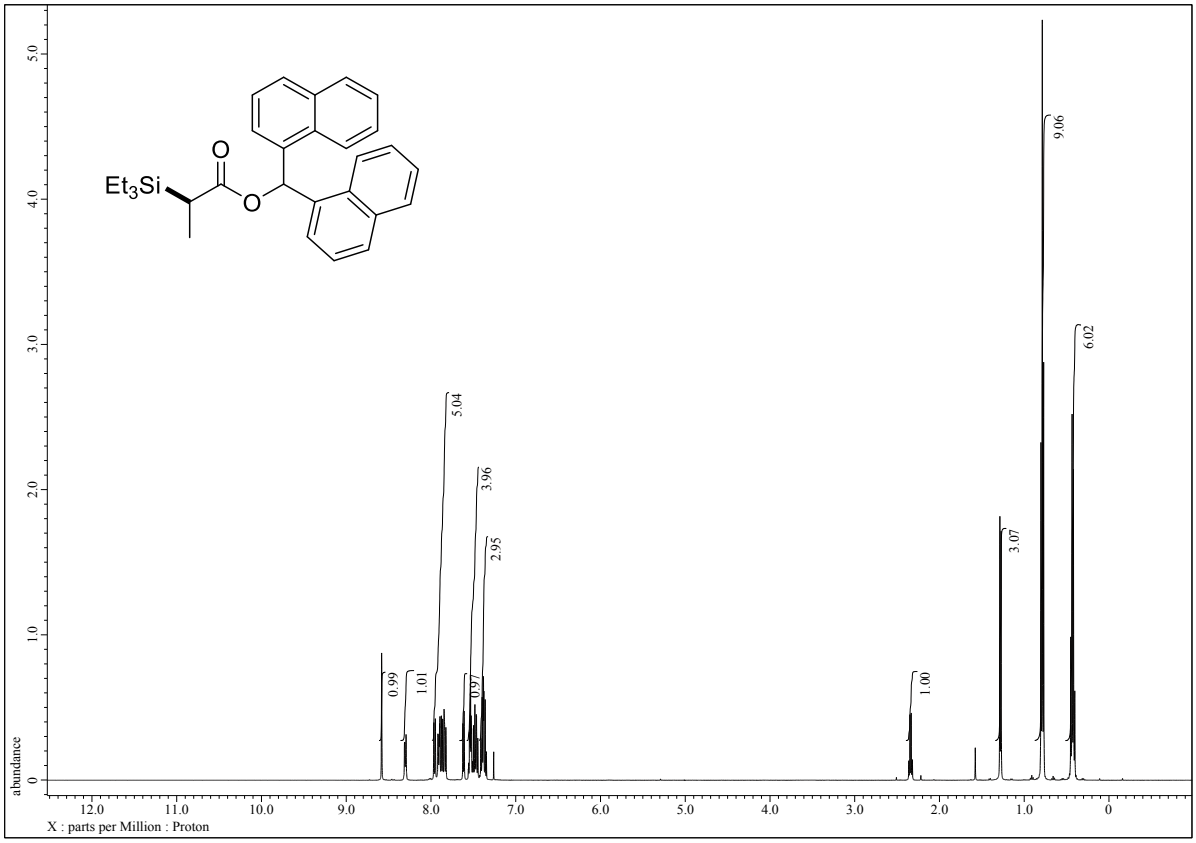

MeO
OMe
Si
O
O
abundance
175.083
160.289
128.803
128.736
128.707
126.494
125.741
125.722
125.159
123.604
123.528
111.338
101.208
77.258
77.000
76.742
69.961
55.119
29.909
11.815
-3.847
-5.087
X : parts per Million : Carbon13

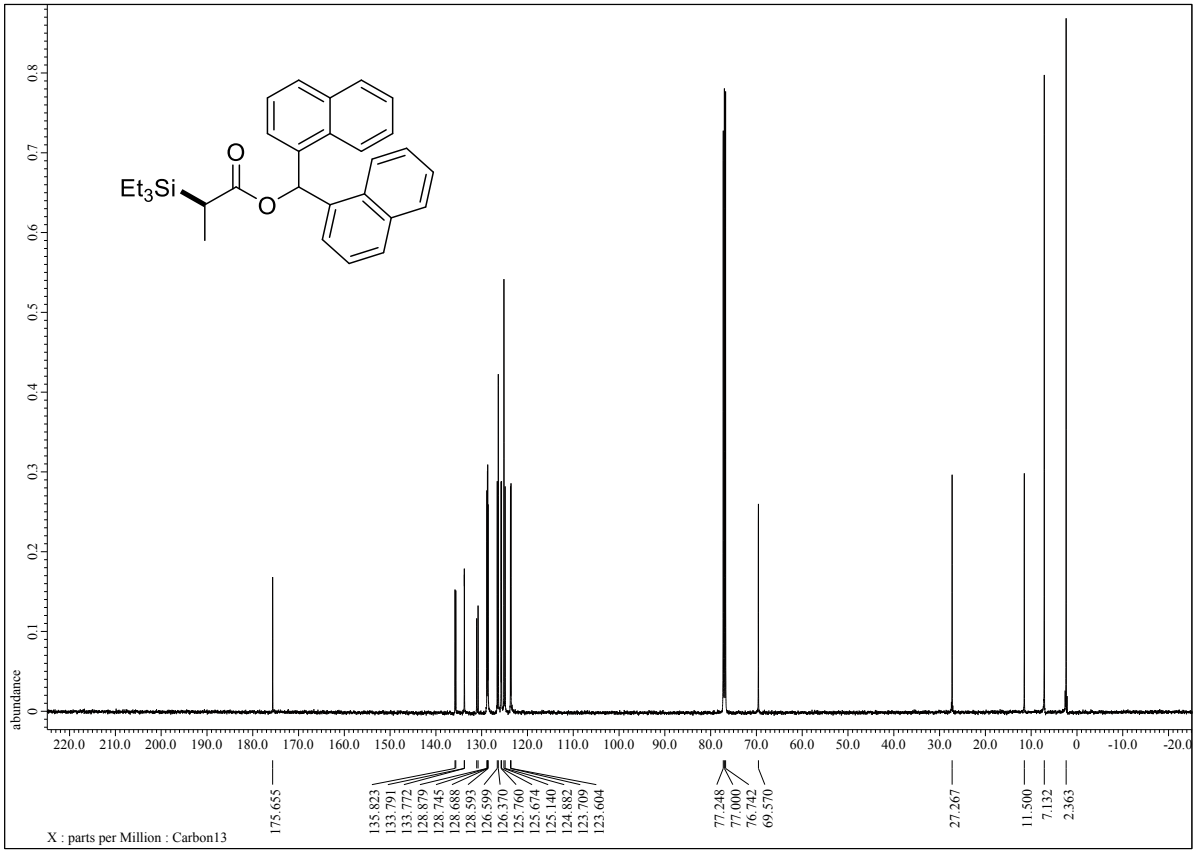

Si
O
O
6.37
0.98
1.01
1.04
1.88
0.96
1.00
3.06
3.01
2.98
2.91
abundance
X : parts per Million : Proton

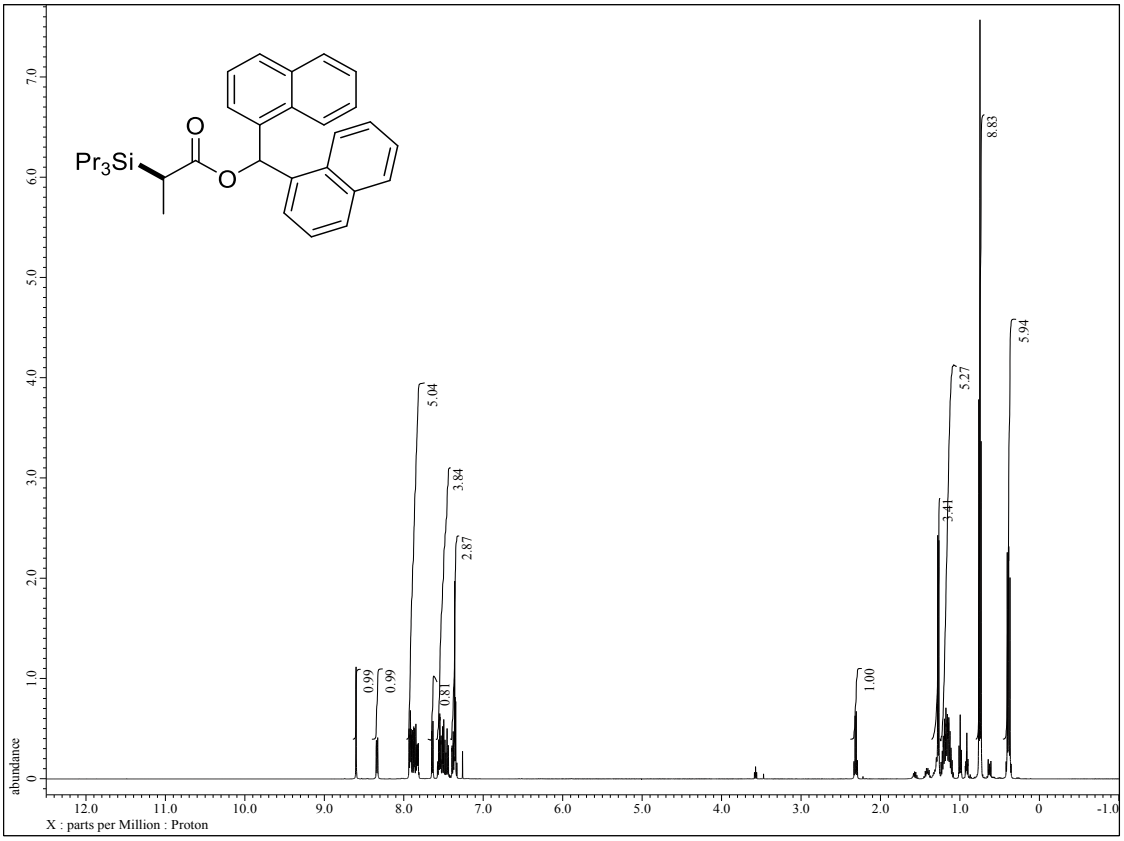

Si
O
O
abundance
175.292
135.785
135.651
135.432
133.963
133.743
130.367
129.919
128.736
128.679
126.475
126.103
125.703
125.283
125.159
123.633
123.595
77.248
77.000
76.742
69.894
29.661
22.612
21.010
11.920
-2.616
-3.771
X : parts per Million : Carbon13

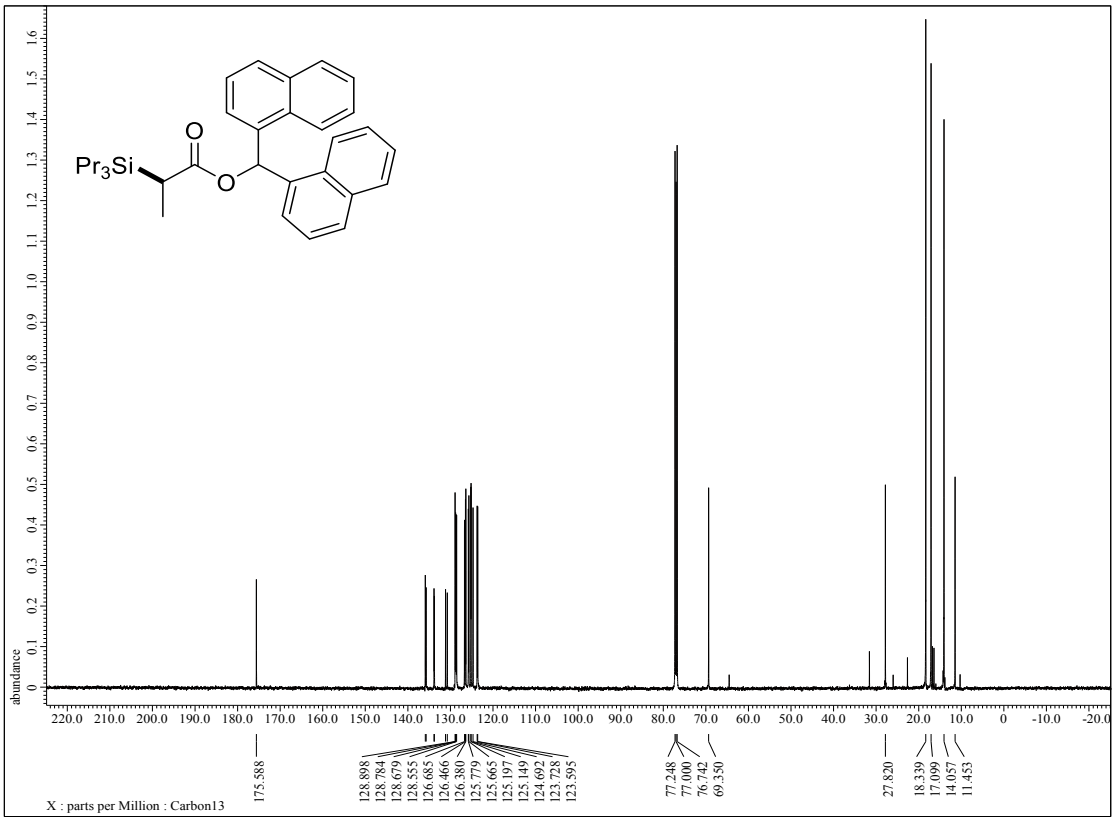

NC
Si
O
O
5.81
5.90
5.02
6.67
3.54
0.98
1.04
1.00
abundance
X : parts per Million : Proton

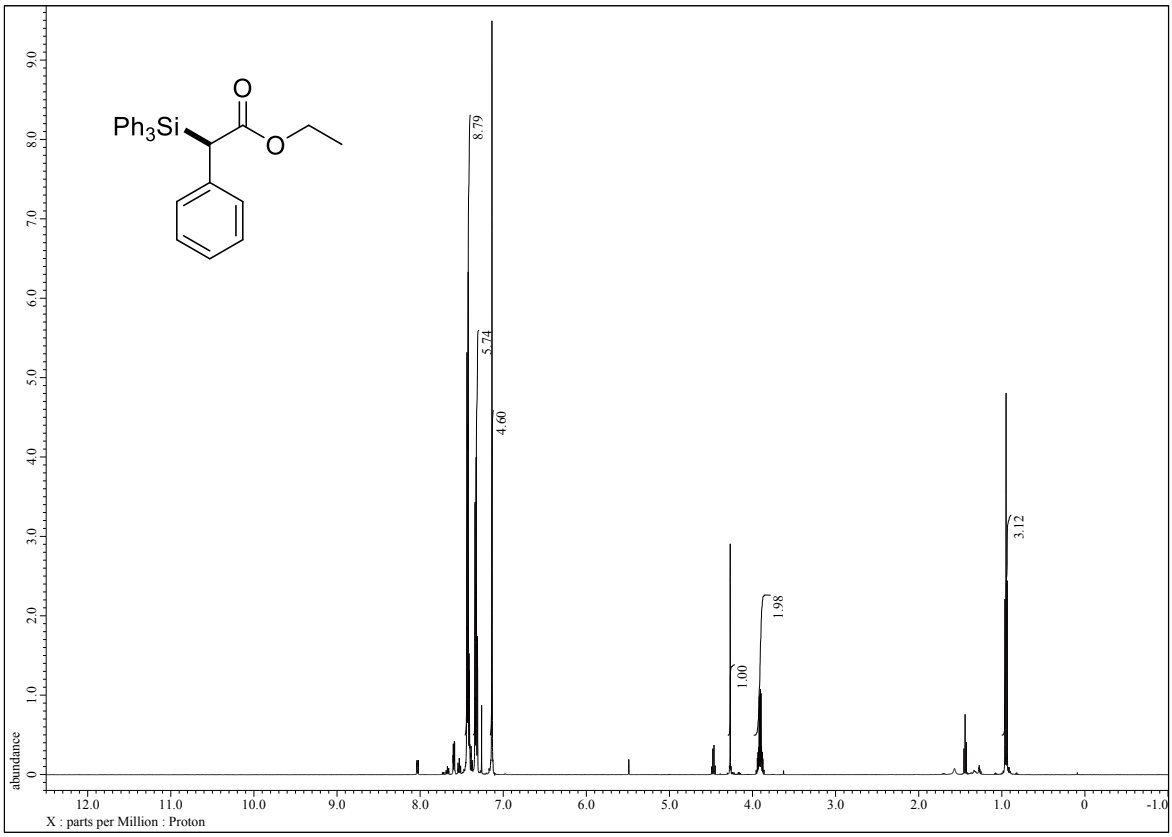

NC
Si
O
O
abundance
174.367
135.184
133.991
133.782
130.472
129.051
128.917
128.784
128.764
126.704
126.504
126.285
125.874
125.789
125.188
125.121
124.806
123.528
123.337
77.258
77.000
76.752
69.827
29.566
11.510
-4.228
-5.068
X : parts per Million : Carbon13

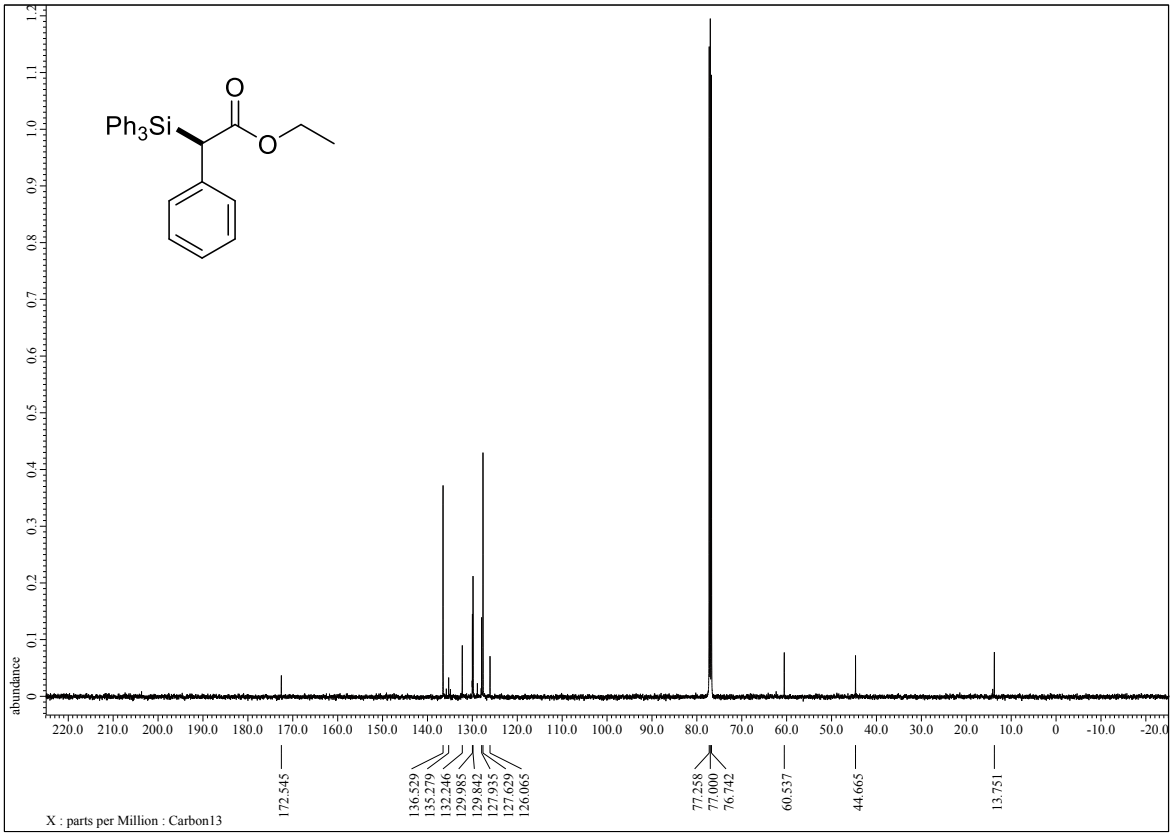

Et3Si
O
O
abundance
X : parts per Million : Proton
0.99
1.01
5.04
0.97
3.96
2.95
1.00
3.07
9.06
6.02

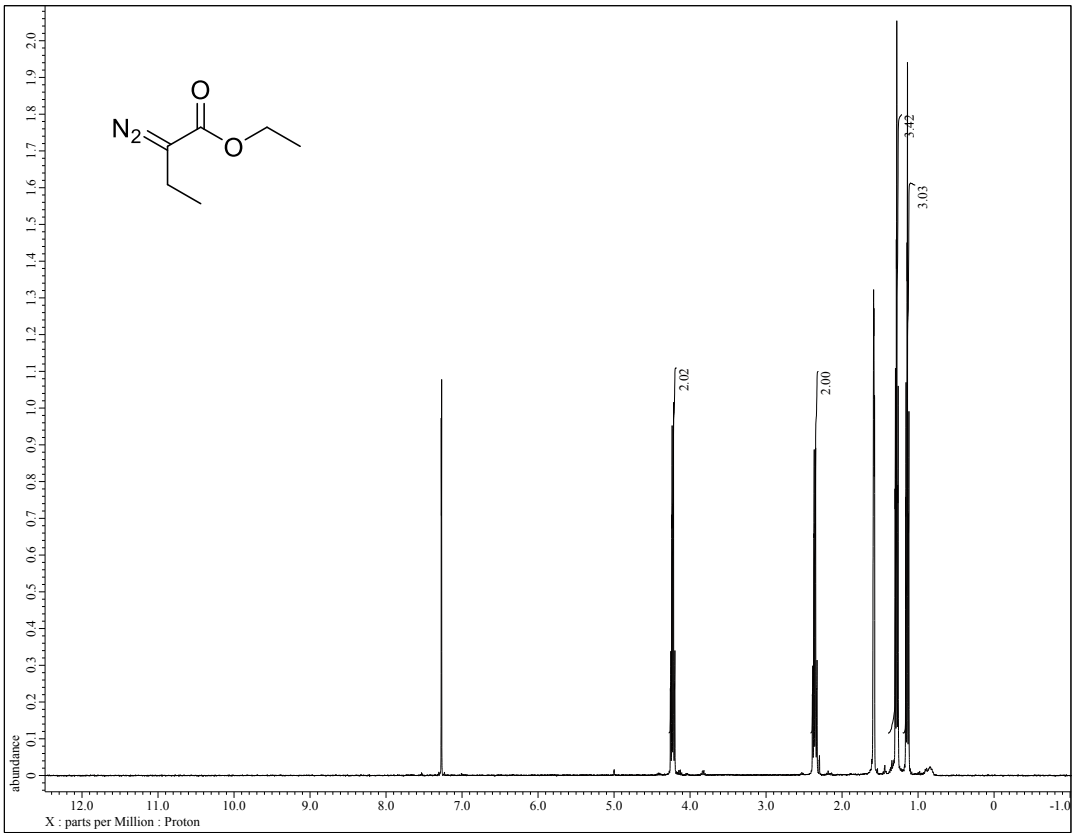

Et3Si
O
O
abundance
X : parts per Million : Carbon13
175.655
135.823
133.791
133.772
128.879
128.745
128.688
128.593
126.599
126.370
125.760
125.674
125.140
124.882
123.709
123.604
77.248
77.000
76.742
69.570
27.267
11.500
7.132
2.363

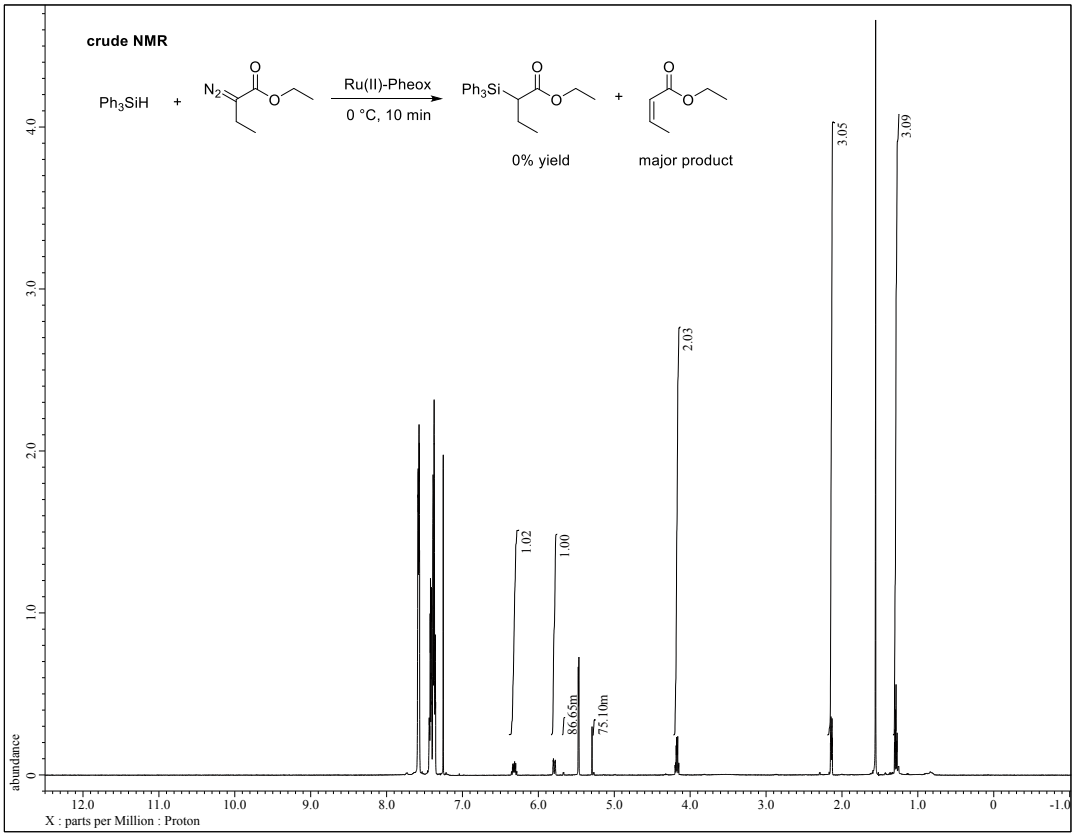

Pr3Si
O
O
abundance
X : parts per Million : Proton
0.99
0.99
0.81
5.04
3.84
2.87
1.00
3.41
5.27
8.83
5.94

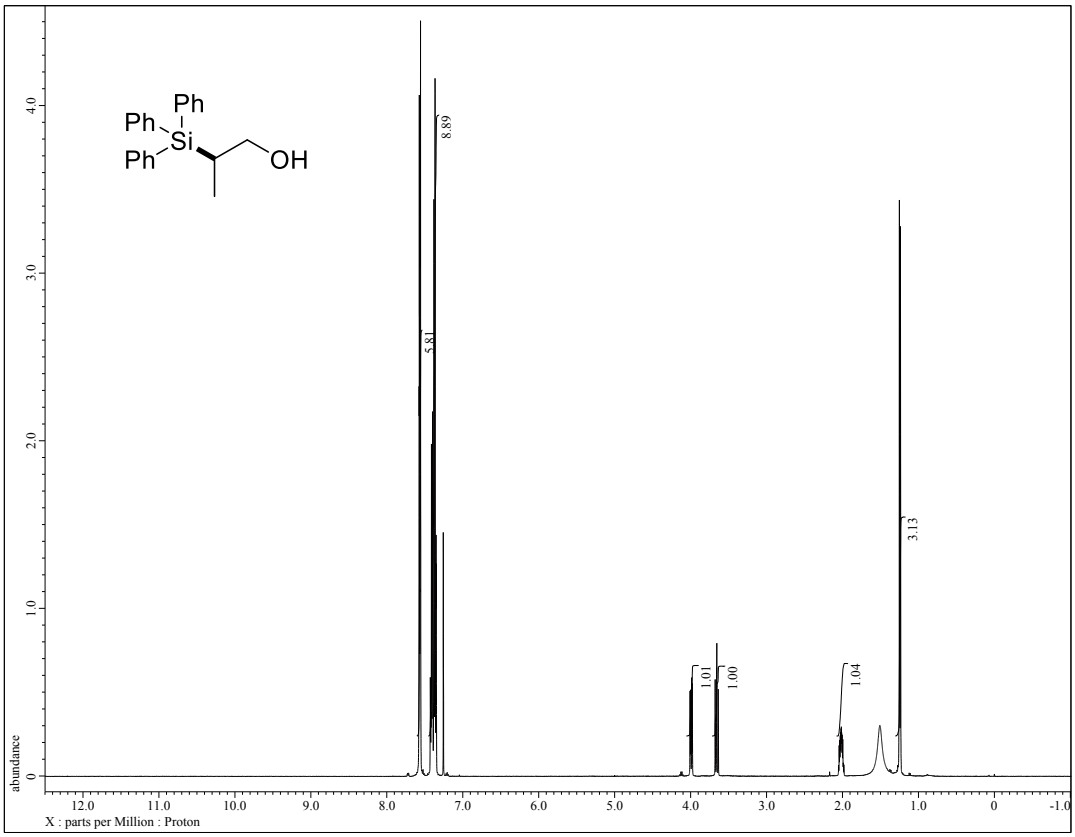

Pr3Si
O
O
abundance
X : parts per Million : Carbon13
175.588
128.898
128.784
128.679
128.555
126.685
126.466
126.380
125.779
125.665
125.197
125.149
124.692
123.728
123.595
77.248
77.000
76.742
69.350
27.820
18.339
17.099
14.057
11.453

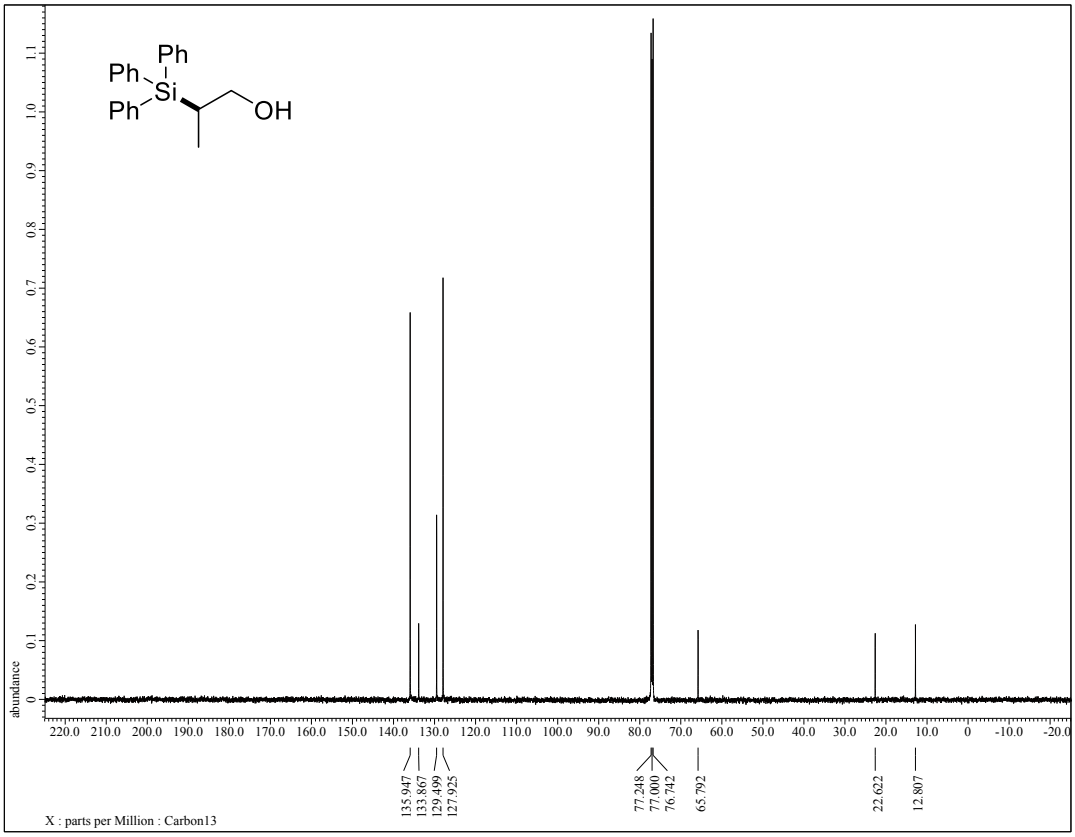

Ph3Si
O
O
8.79
5.74
4.60
3.12
1.98
1.00
abundance
X : parts per Million : Proton

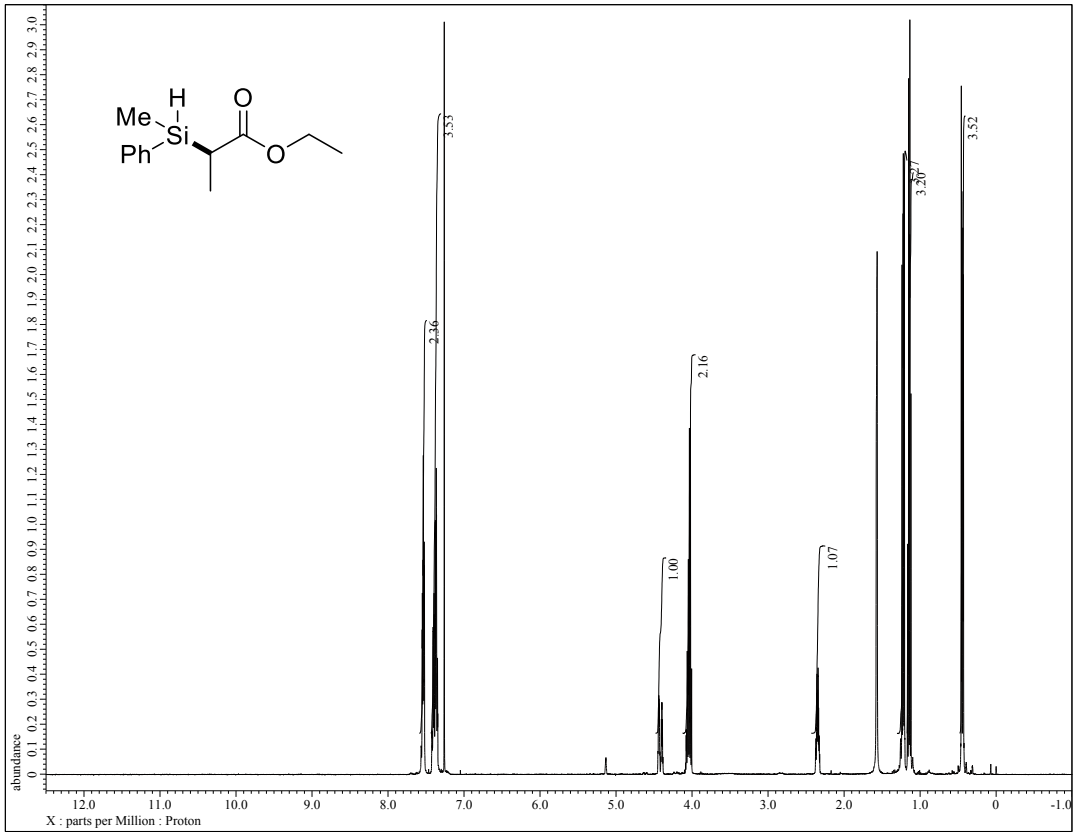

Ph3Si
O
O
abundance
172.545
136.529
135.279
132.246
129.985
129.842
127.935
127.629
126.065
77.258
77.000
76.742
60.537
44.665
13.751
X : parts per Million : Carbon13

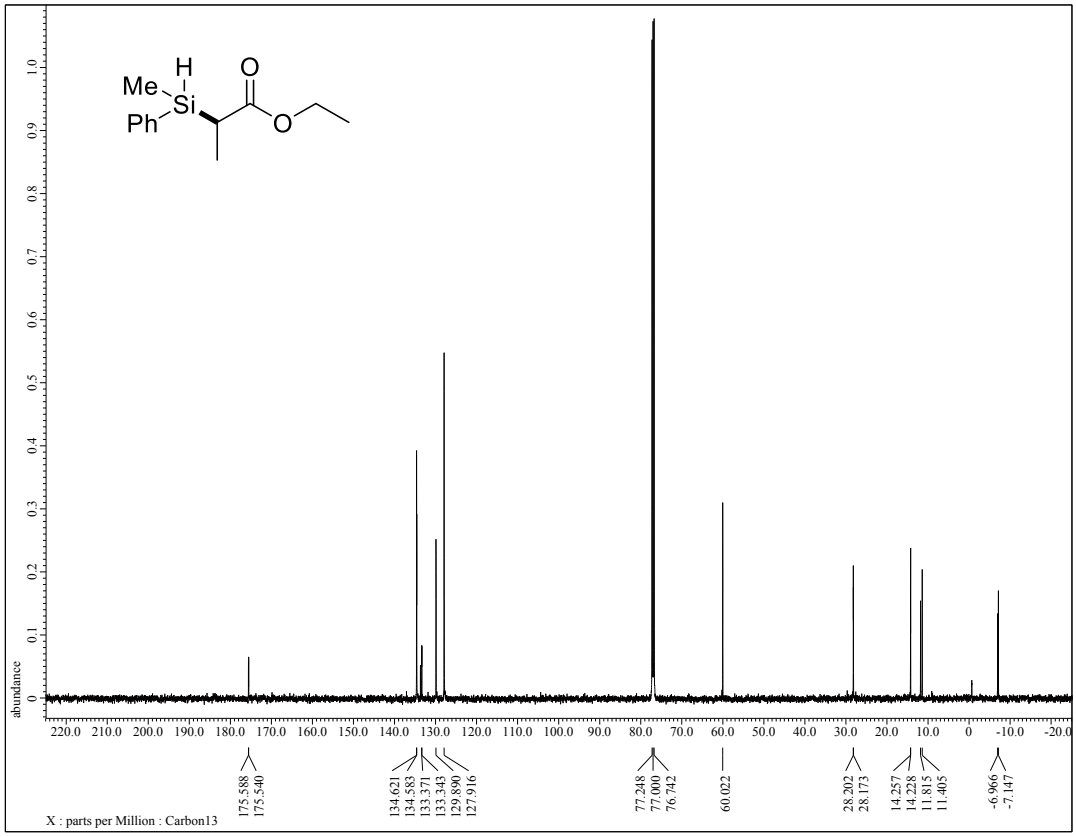

abundance
X : parts per Million : Proton
2.02
2.00
3.42
3.03

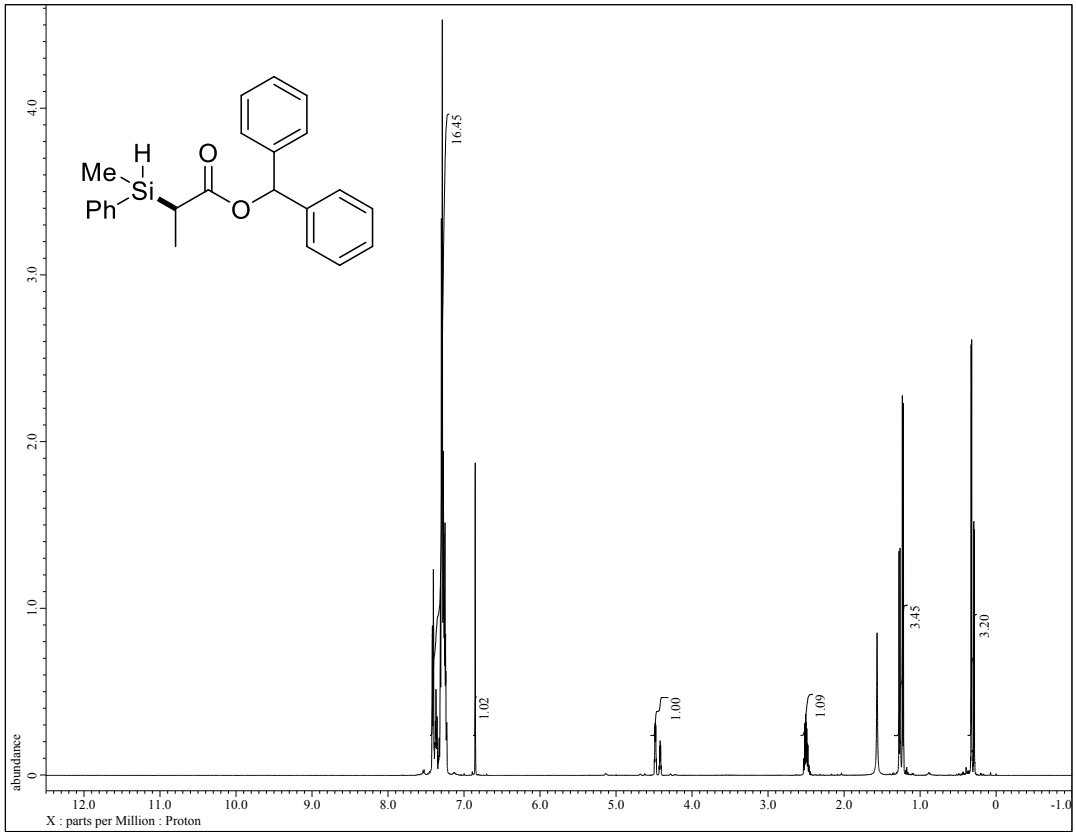

crude NMR
Ph3SiH
Ru(II)-Pheox
0 °C, 10 min
0% yield
major product
abundance
X : parts per Million : Proton
1.02
1.00
86.65m
75.10m
2.03
3.05
3.09

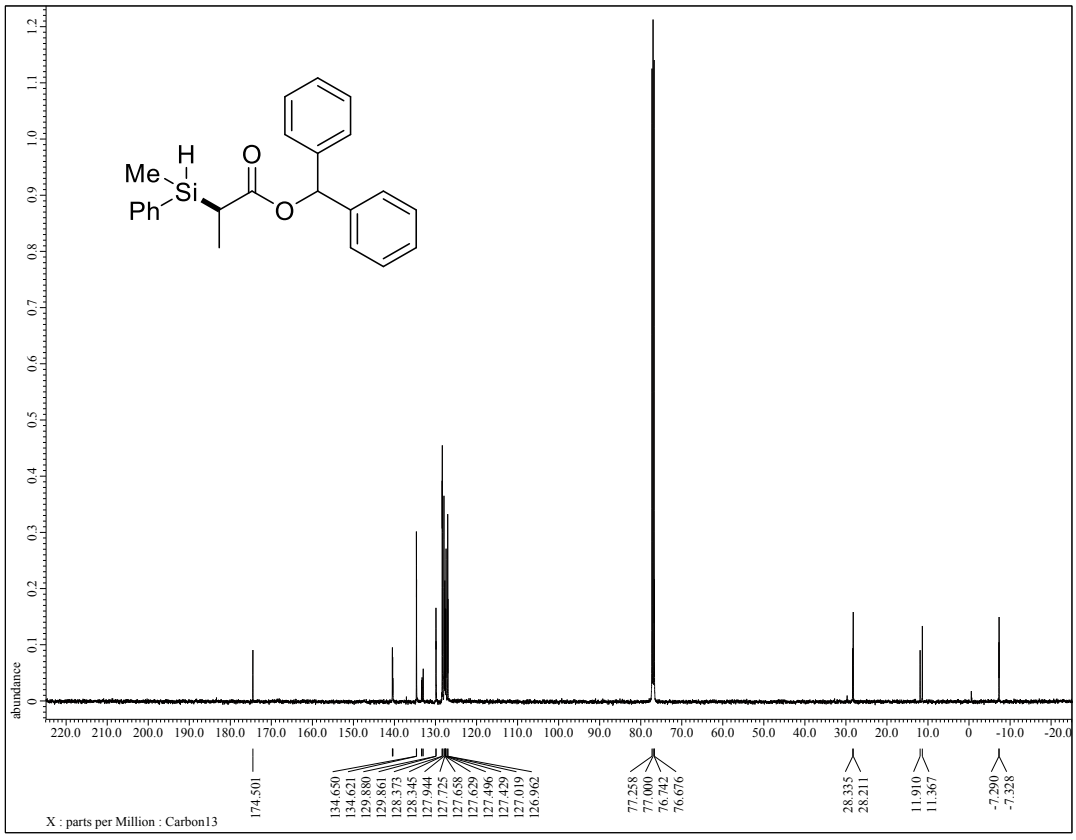

Ph
Ph
Si
Ph
OH
8.89
5.81
1.01
1.00
1.04
3.13
abundance
X : parts per Million : Proton

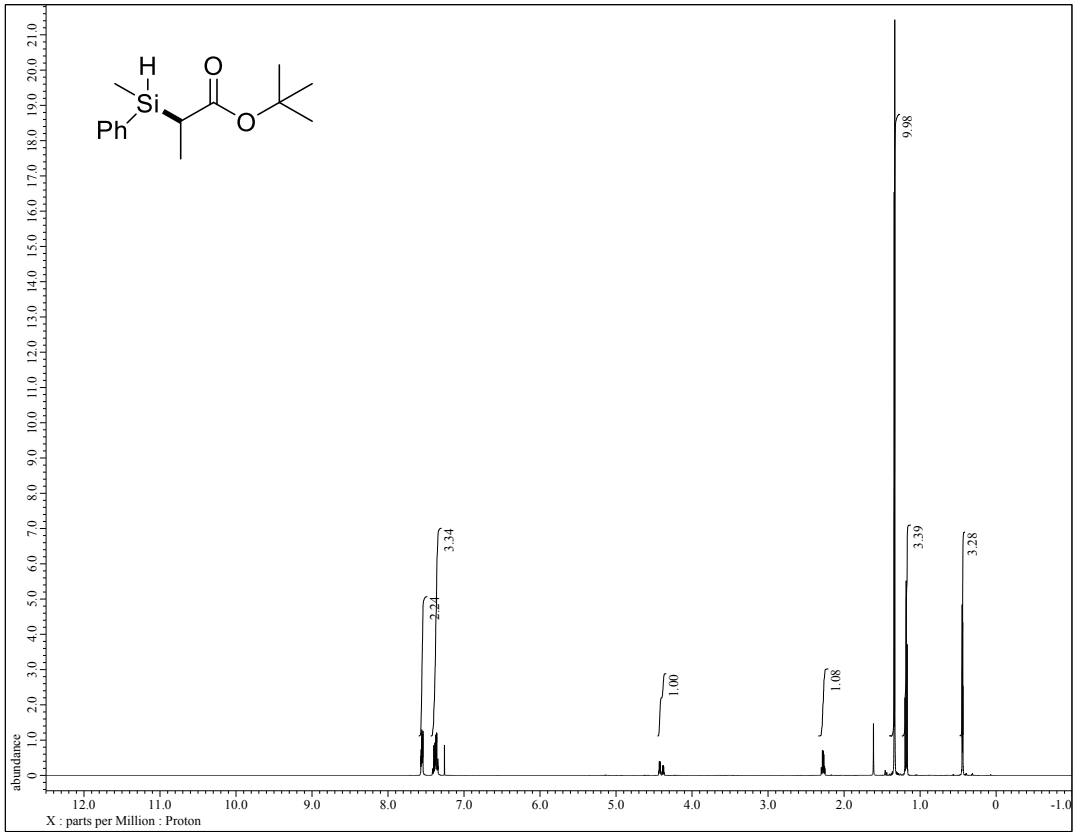

Ph
Ph
Si
Ph
OH
abundance
135.947
133.867
129.499
127.925
77.248
77.000
76.742
65.792
22.622
12.807
X : parts per Million : Carbon13

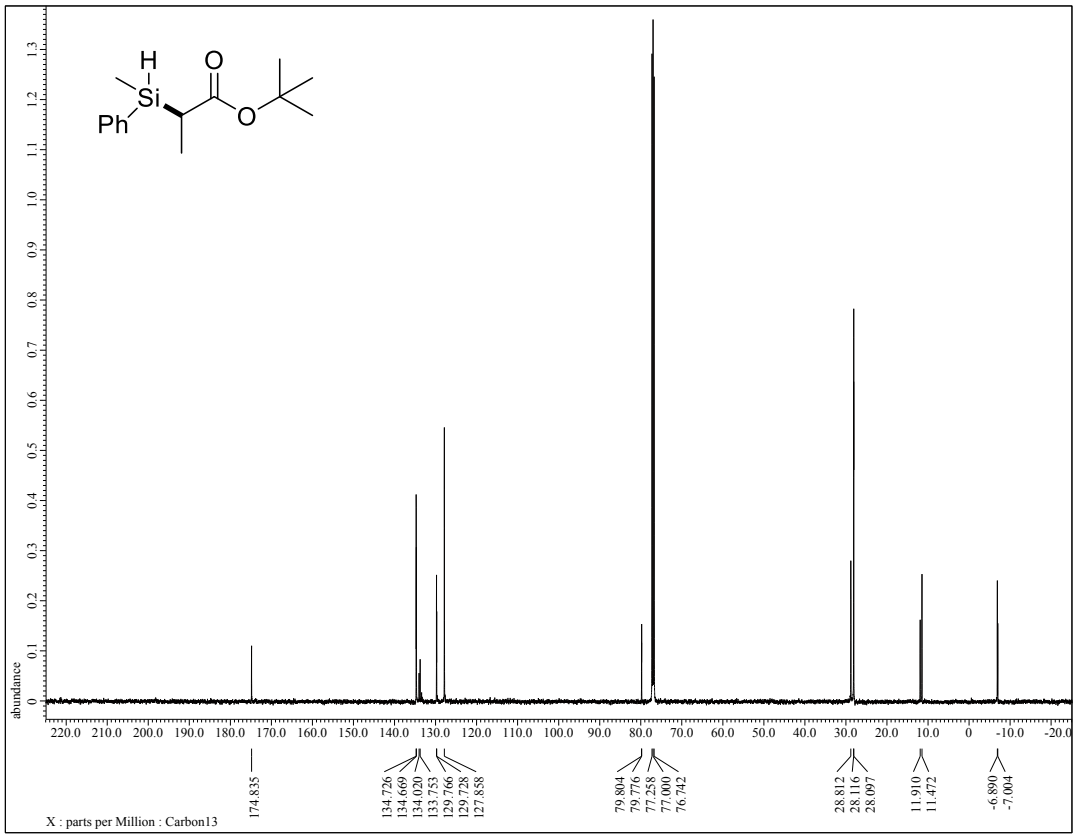

Me
H
Si
Ph
O
O
3.53
2.36
2.16
1.00
1.07
3.52
3.20
abundance
X : parts per Million : Proton

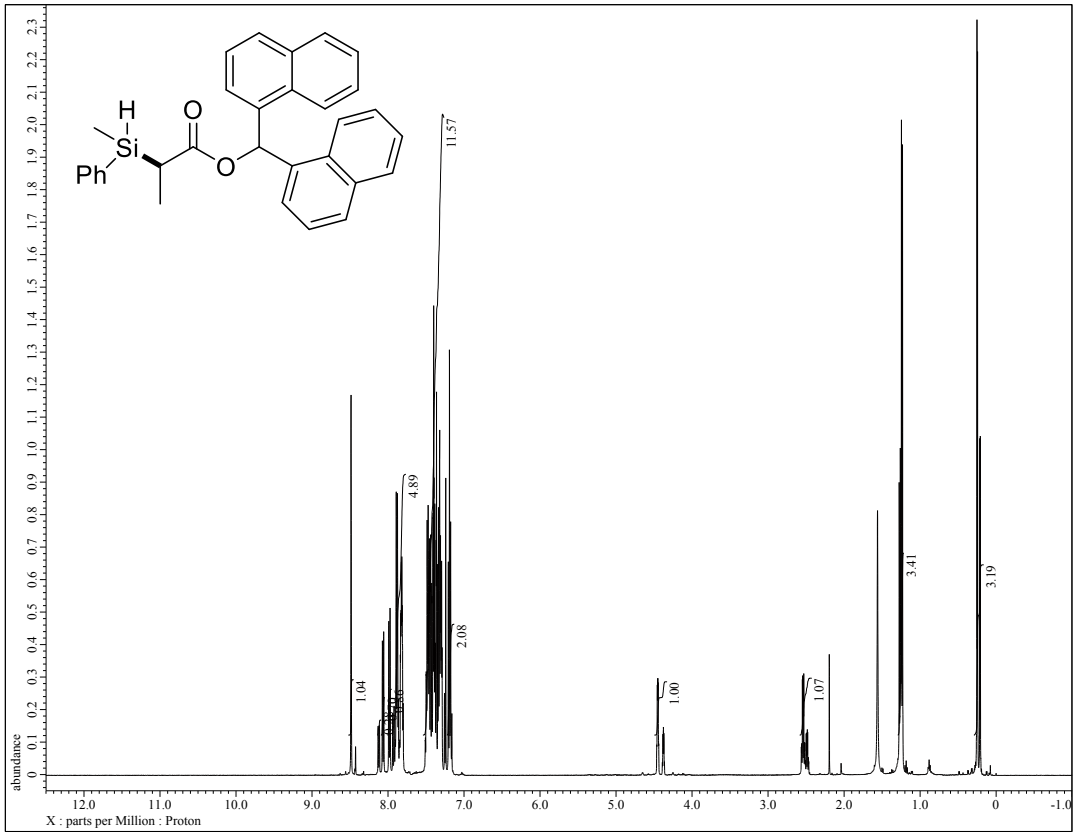

Me
H
Si
Ph
O
O
abundance
175.588
175.540
134.621
134.583
133.371
133.343
129.890
127.916
77.248
77.000
76.742
60.022
28.202
28.173
14.257
14.228
11.815
11.405
-6.966
-7.147
X : parts per Million : Carbon13

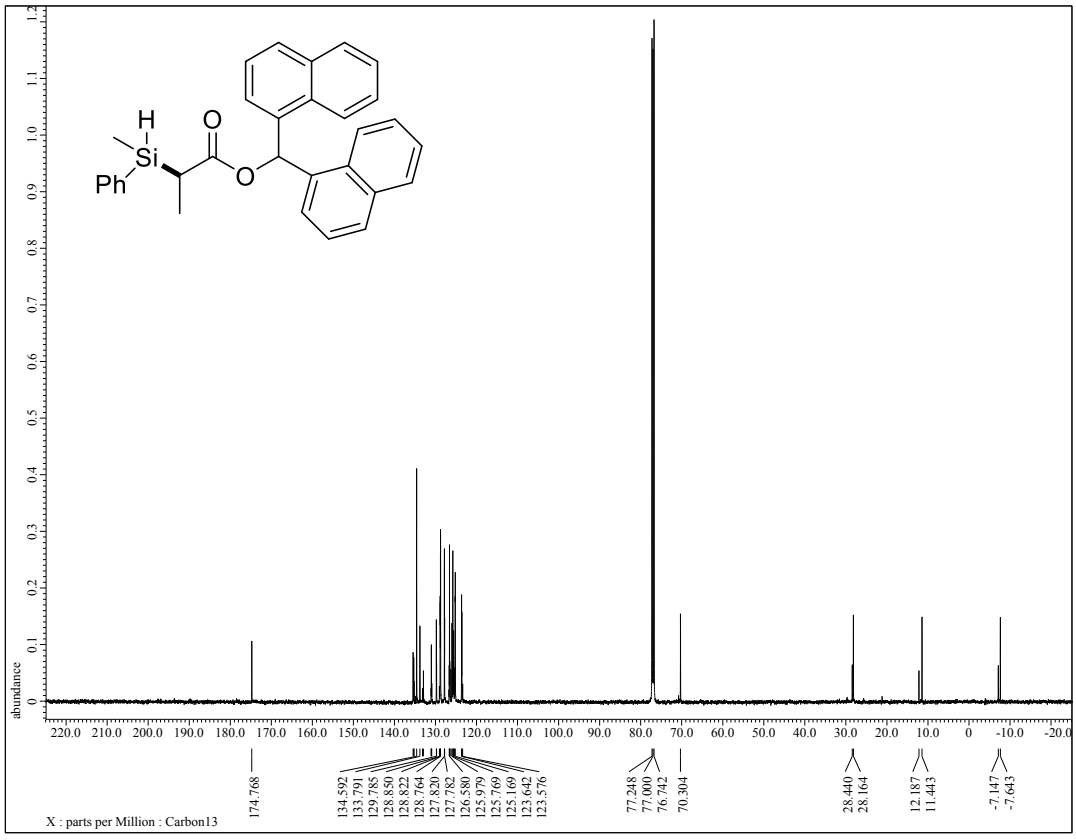

Me
H
Si
Ph
O
O
16.45
1.02
1.00
1.09
3.45
3.20
abundance
X : parts per Million : Proton

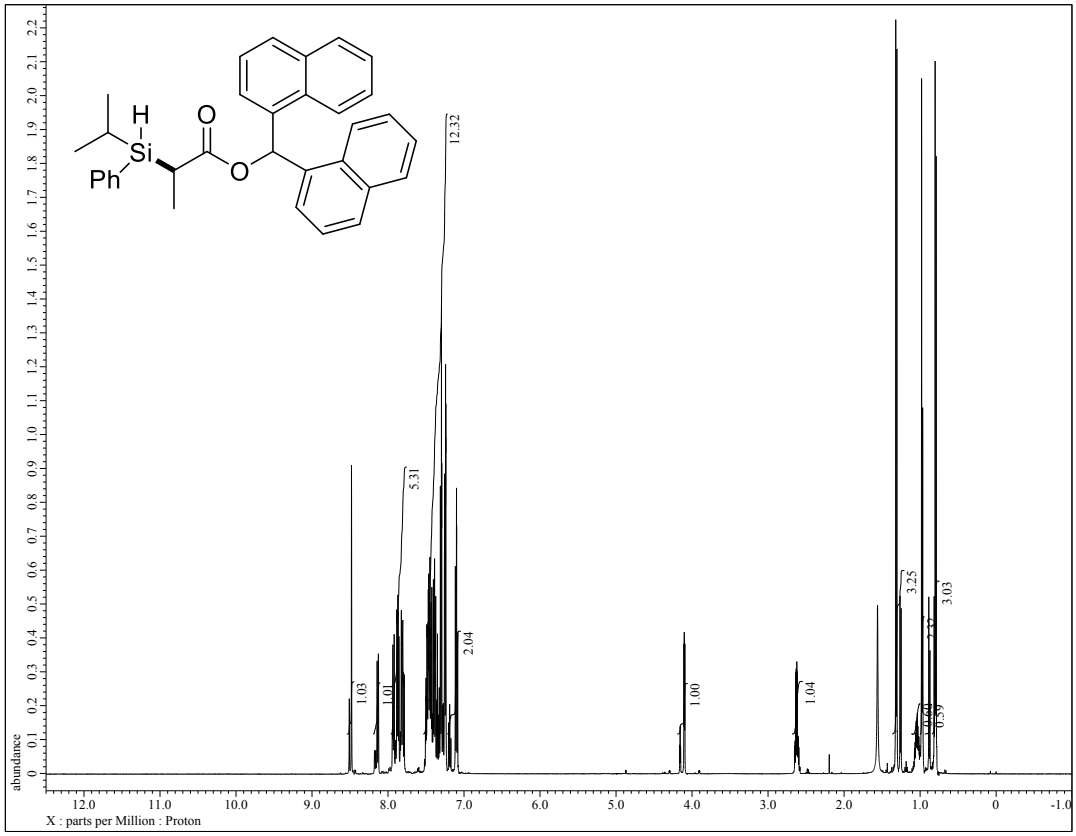

Me
H
Si
Ph
O
O
abundance
174.501
134.650
134.621
129.880
129.861
128.373
128.345
127.944
127.725
127.658
127.629
127.496
127.429
127.019
126.962
77.258
77.000
76.742
76.676
28.335
28.211
11.910
11.367
-7.290
-7.328
X : parts per Million : Carbon13

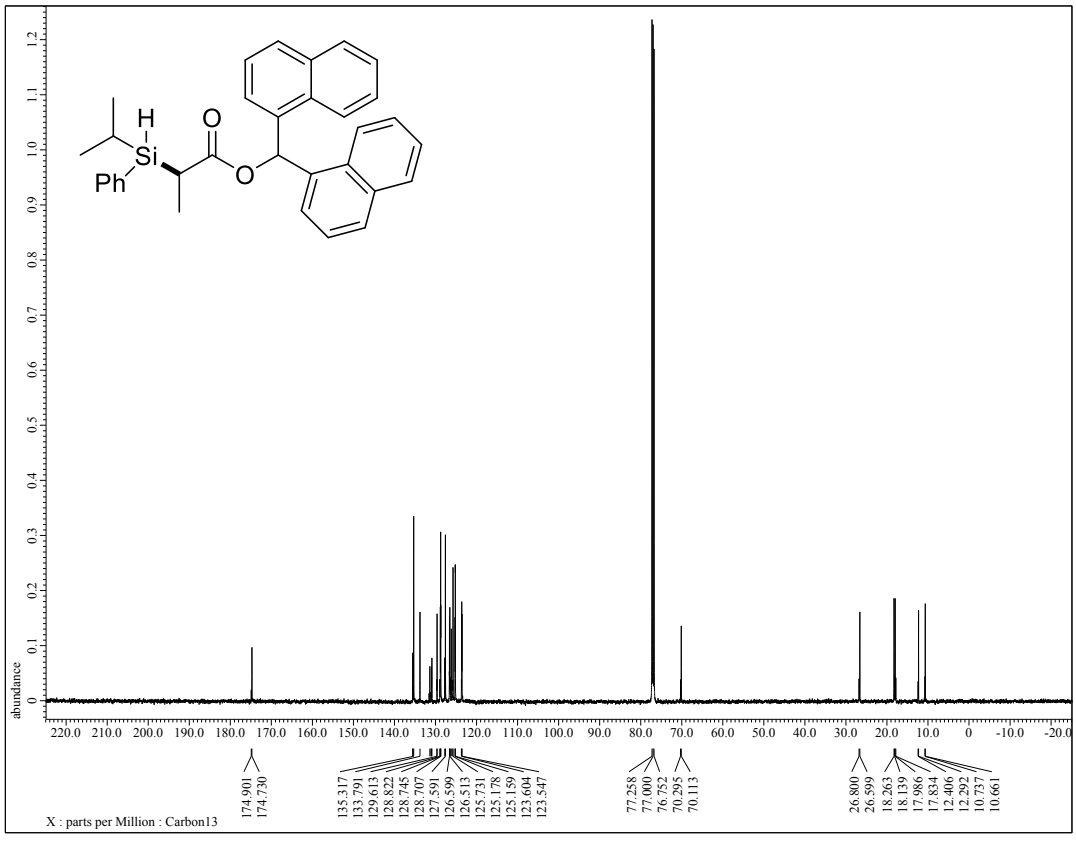

H
Si
Ph
O
O
9.98
3.34
3.39
3.28
2.24
1.00
1.08
abundance
X : parts per Million : Proton

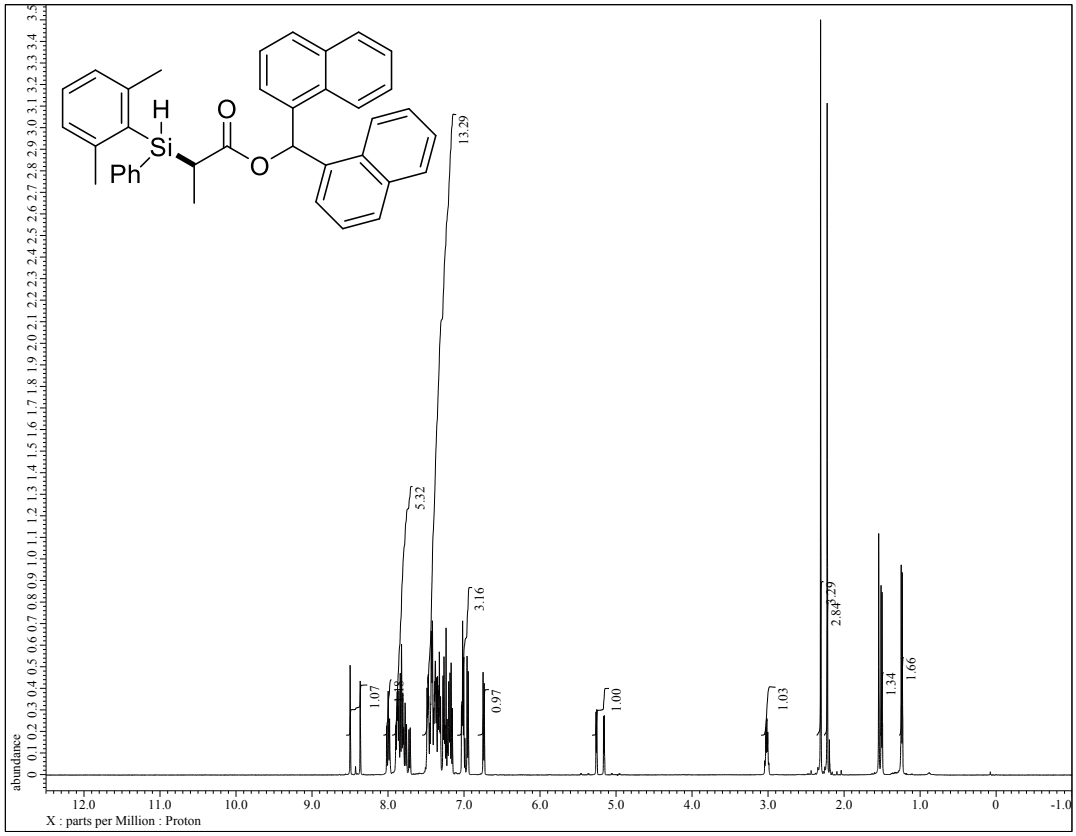

H
Si
Ph
O
O
abundance
174.835
134.726
134.669
134.020
133.753
129.766
129.728
127.858
79.804
79.776
77.258
77.000
76.742
28.812
28.116
28.097
11.910
11.472
-6.890
-7.004
X : parts per Million : Carbon13

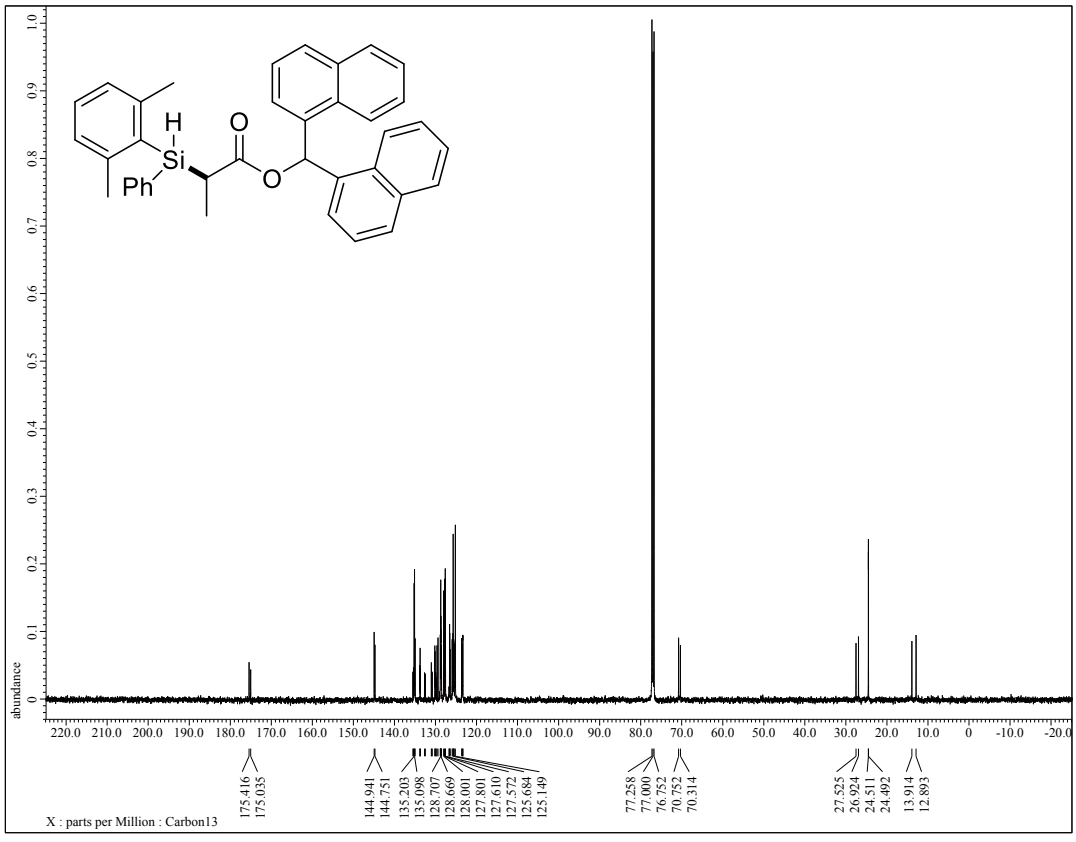

H
Si
Ph
O
O
11.57
4.89
2.08
1.04
1.00
1.07
3.41
3.19
abundance
X : parts per Million : Proton

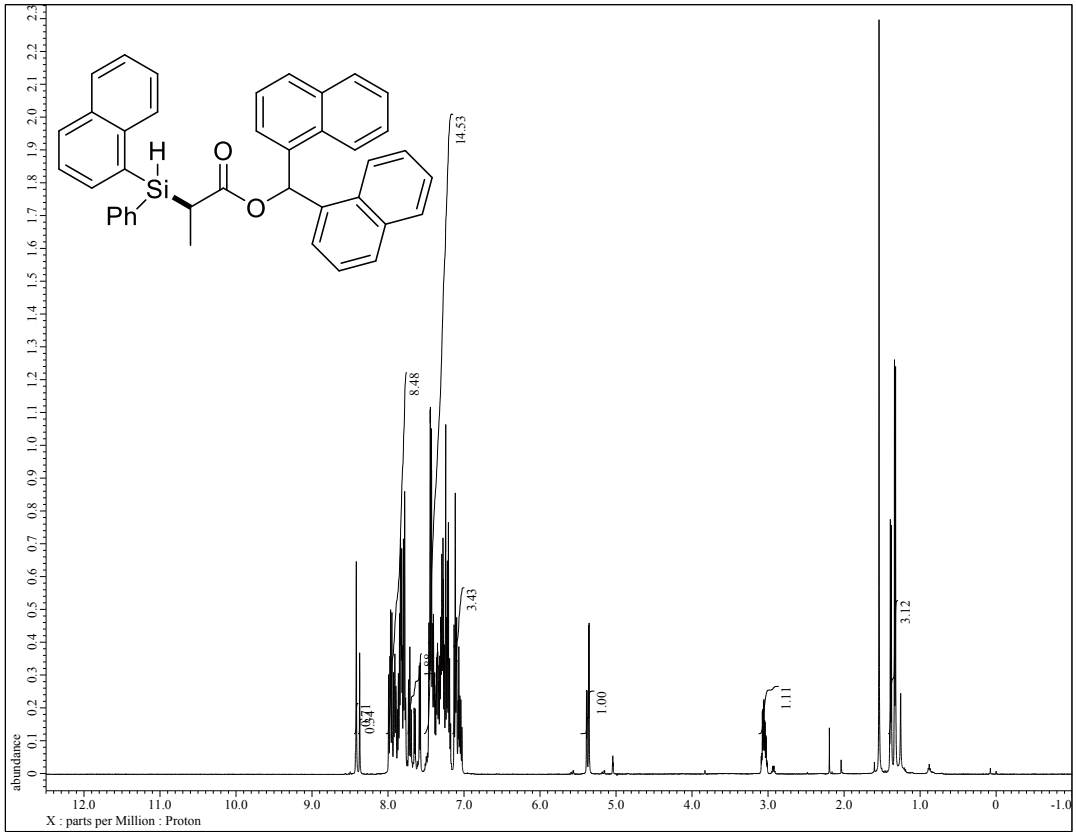

H
Si
Ph
O
O
abundance
174.768
134.592
133.791
129.785
128.850
128.822
128.764
127.820
127.782
126.580
125.979
125.769
125.169
123.642
123.576
77.248
77.000
76.742
70.304
28.440
28.164
12.187
11.443
-7.147
-7.643
X : parts per Million : Carbon13

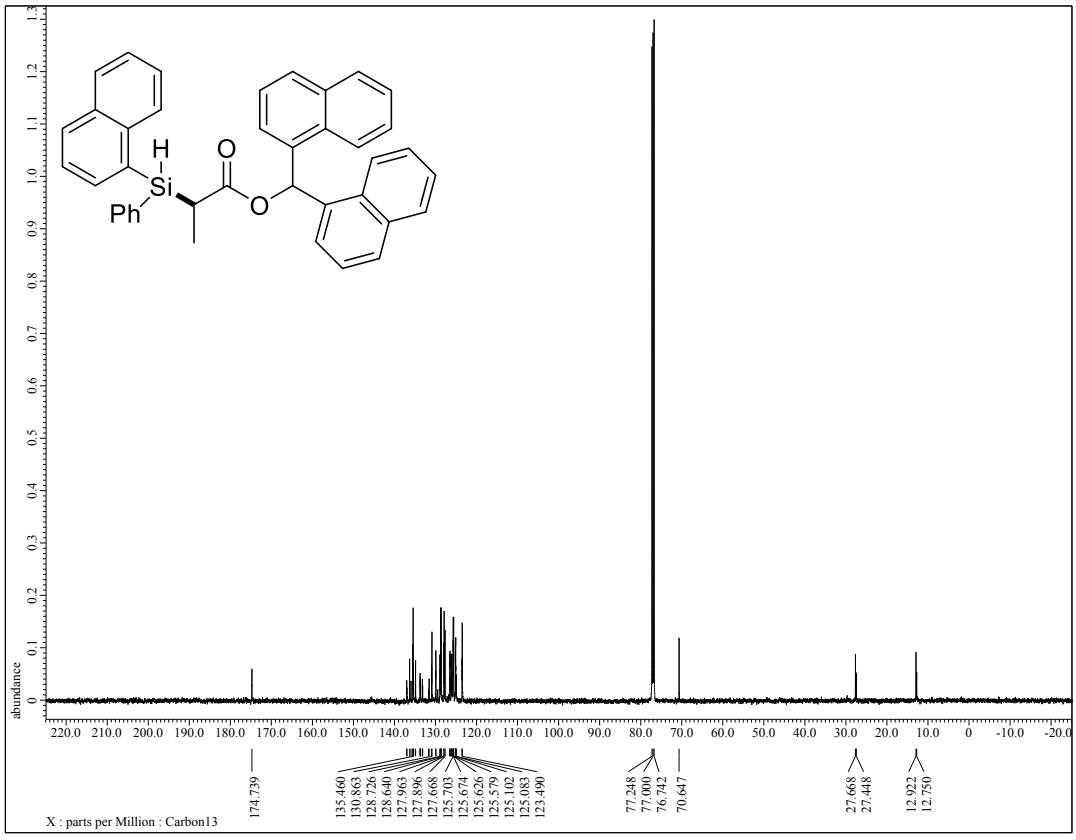

H
Si
Ph
O
O
12.32
5.31
2.04
1.03
1.01
1.00
1.04
3.25
3.03
abundance
X : parts per Million : Proton

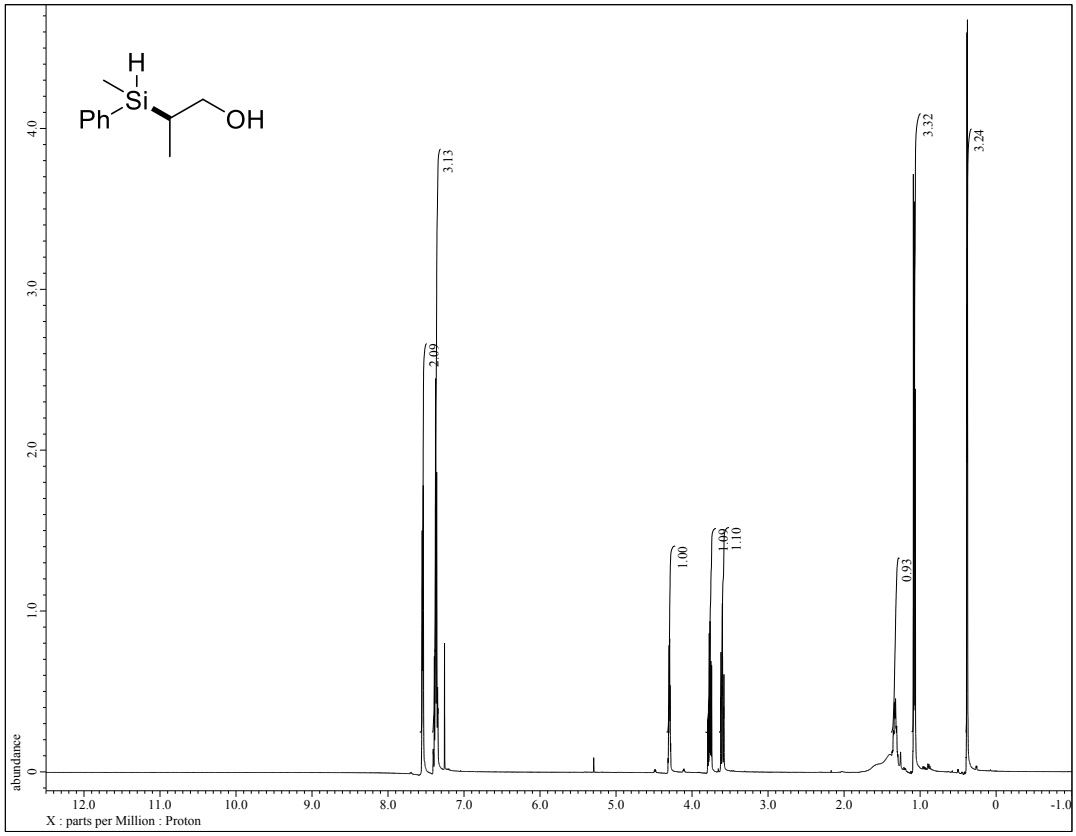

H
Si
Ph
O
O
abundance
174.901
174.730
135.317
133.791
129.613
128.822
128.745
128.707
127.591
126.599
126.513
125.731
125.178
125.159
123.604
123.547
77.258
77.000
76.752
70.295
70.113
26.800
26.599
18.263
18.139
17.986
17.834
12.406
12.292
10.737
10.661
X : parts per Million : Carbon13

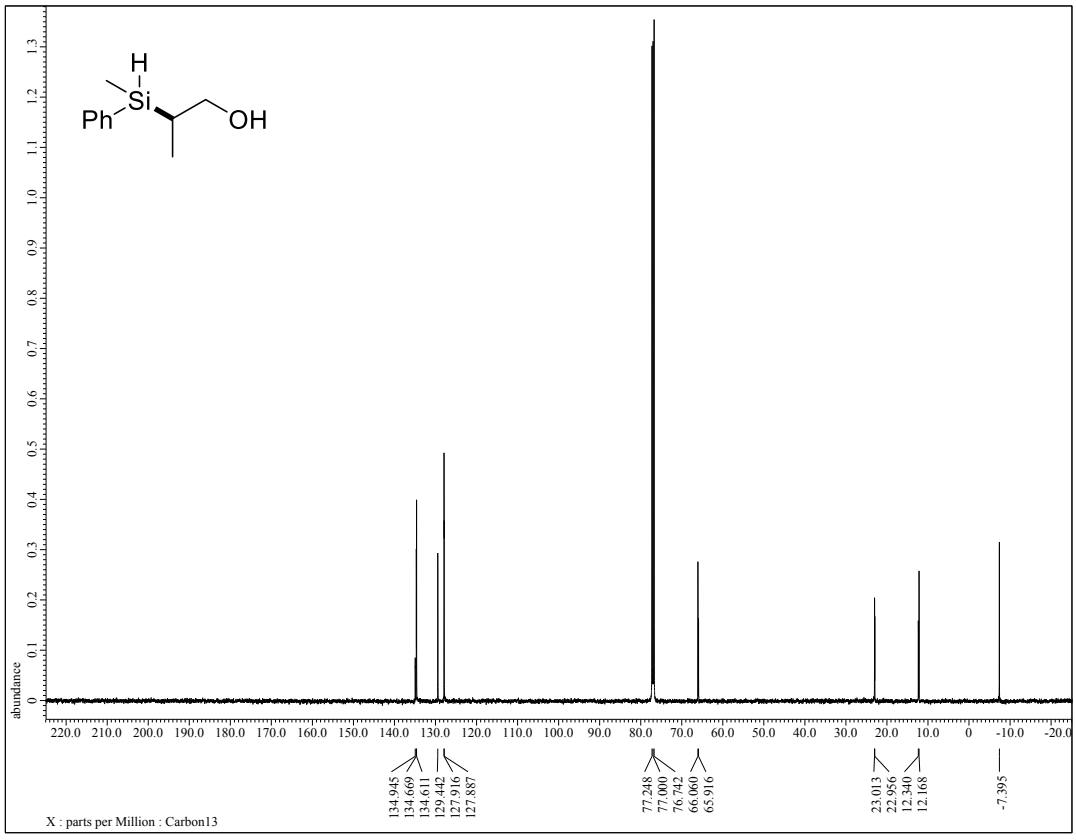

H
Si
Ph
O
O
13.29
5.32
3.16
1.07
1.18
0.97
1.00
1.03
2.84
2.89
1.34
1.66
abundance
X : parts per Million : Proton

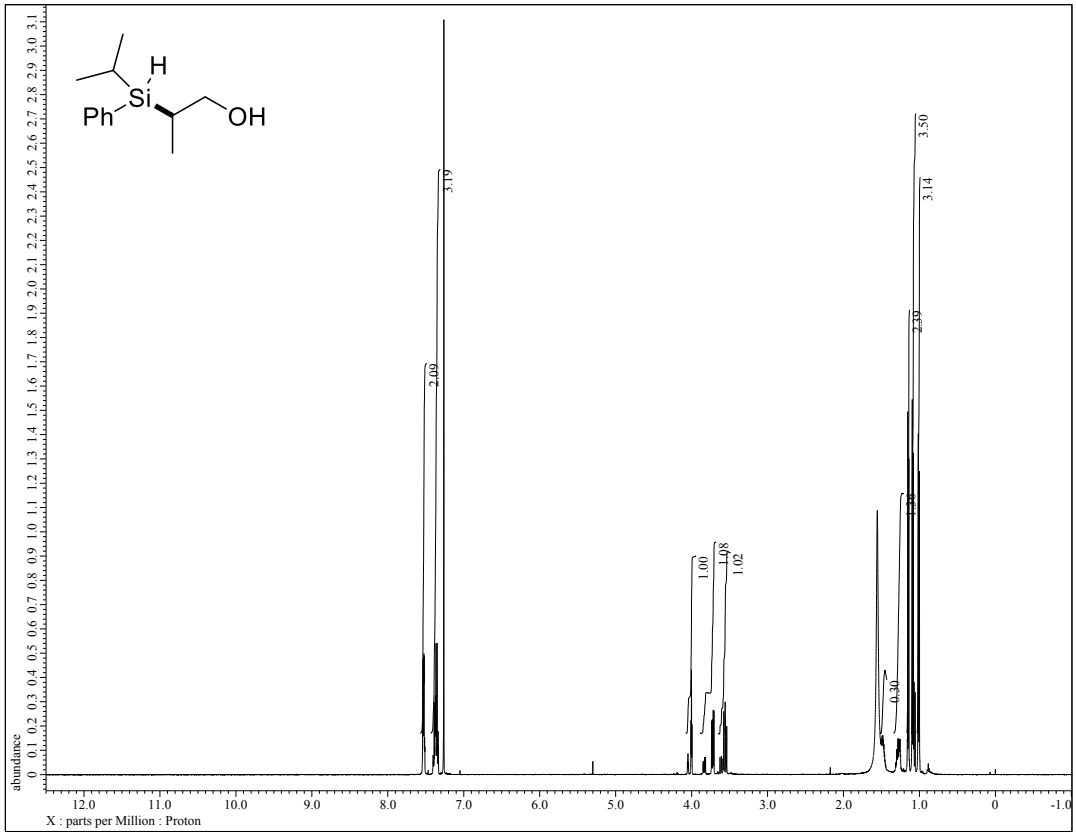

H
Si
Ph
O
O
abundance
175.416
175.035
144.941
144.751
135.203
135.098
128.707
128.669
128.001
127.801
127.610
127.572
125.684
125.149
77.258
77.000
76.752
70.752
70.314
27.525
26.924
24.511
24.492
13.914
12.893
X : parts per Million : Carbon13

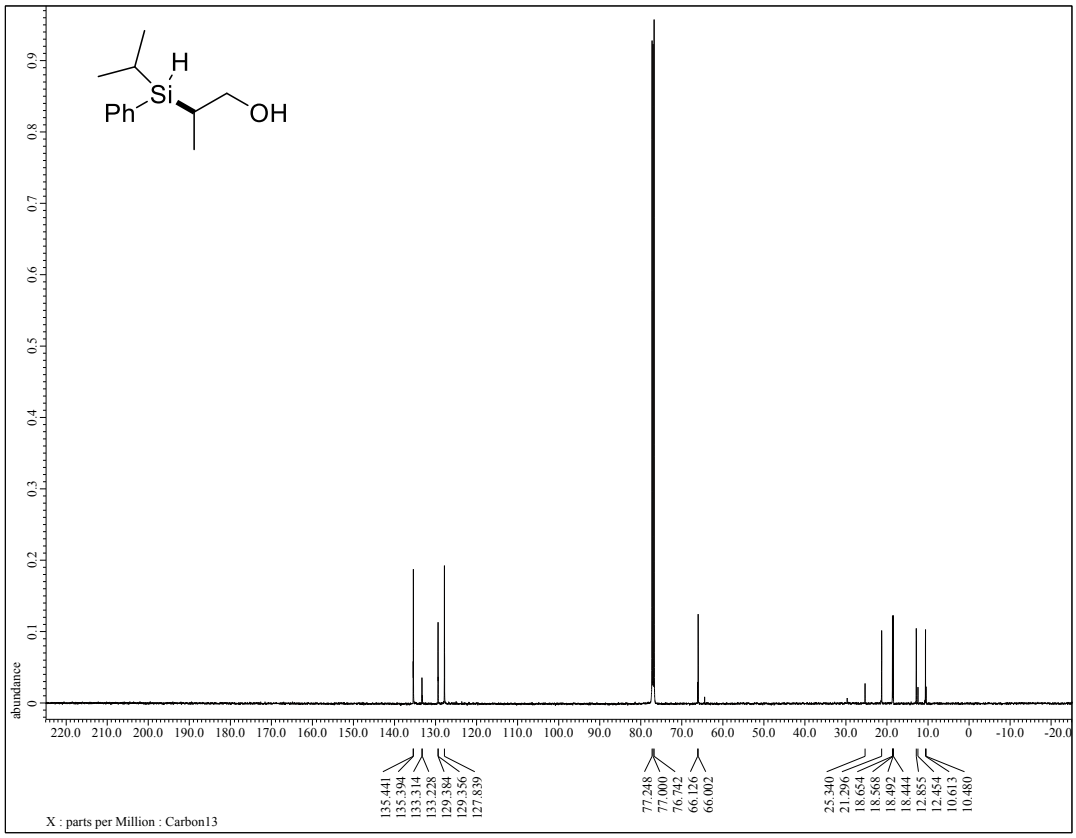

H
Si
Ph
O
O
14.53
8.48
3.43
3.12
1.11
1.00
0.41
abundance
X : parts per Million : Proton


H
Si
Ph
O
O
abundance
174.739
135.460
130.863
128.726
128.640
127.963
127.896
127.668
125.703
125.674
125.626
125.579
125.102
125.083
123.490
77.248
77.000
76.742
70.647
27.668
27.448
12.922
12.750
X : parts per Million : Carbon13


H
Si
Ph
OH
3.13
2.09
3.32
3.24
1.00
1.08
1.10
0.93
abundance
X : parts per Million : Proton


H
Si
Ph
OH
abundance
134.945
134.669
134.611
129.442
127.916
127.887
77.248
77.000
76.742
66.060
65.916
23.013
22.956
12.340
12.168
-7.395
X : parts per Million : Carbon13


H
Si
Ph
OH
abundance
X : parts per Million : Proton
2.09
3.19
1.00
1.08
1.02
0.30
2.39
3.14
3.50


H
Si
Ph
OH
abundance
X : parts per Million : Carbon13
135.441
135.394
133.314
133.228
129.384
129.356
127.839
77.248
77.000
76.742
66.126
66.002
25.340
21.296
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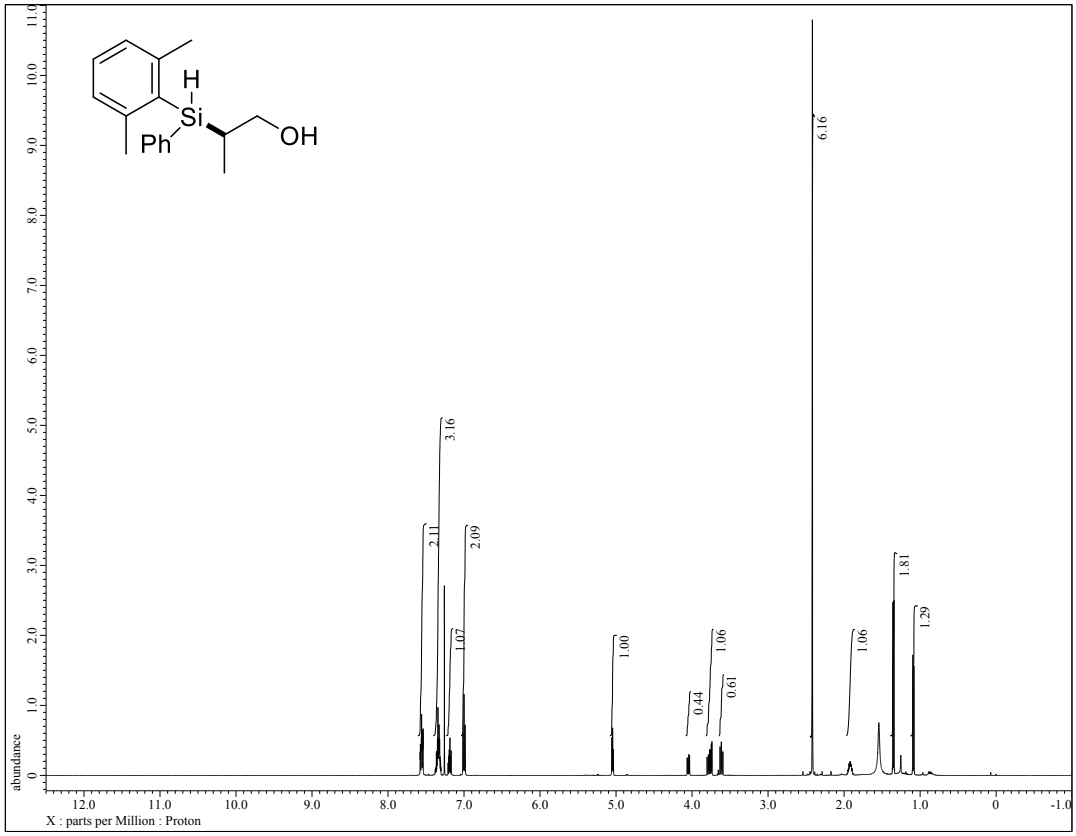
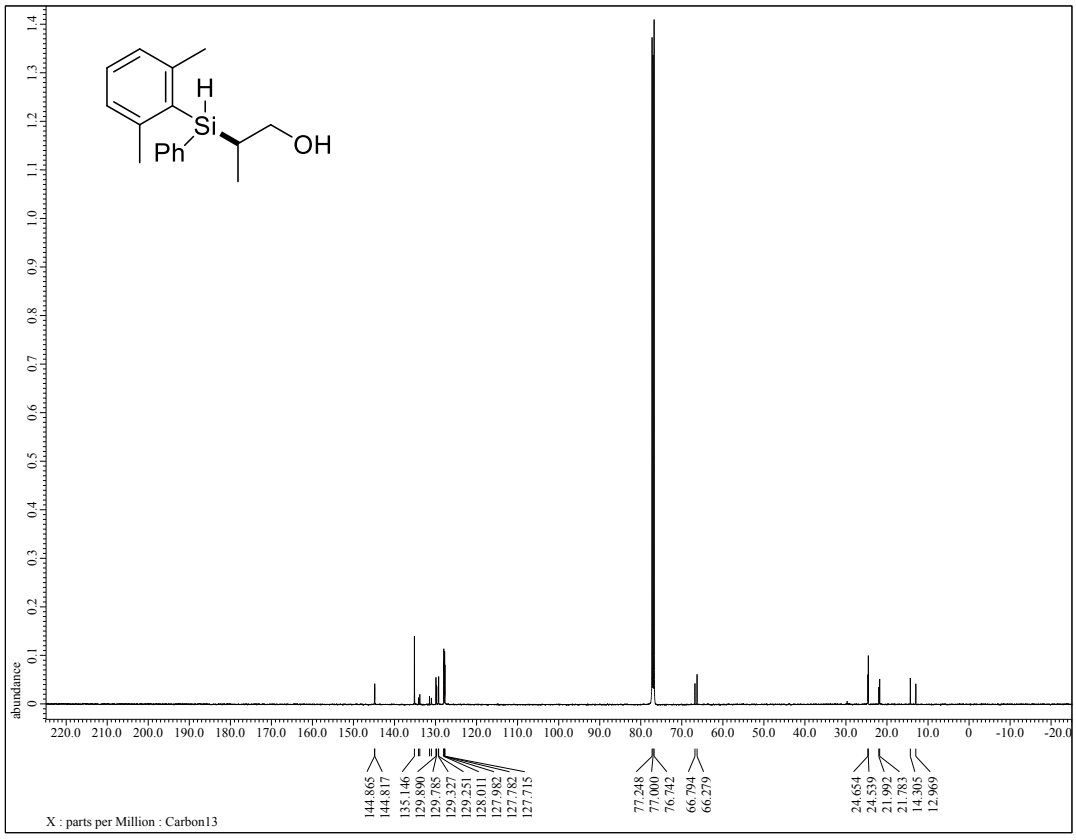
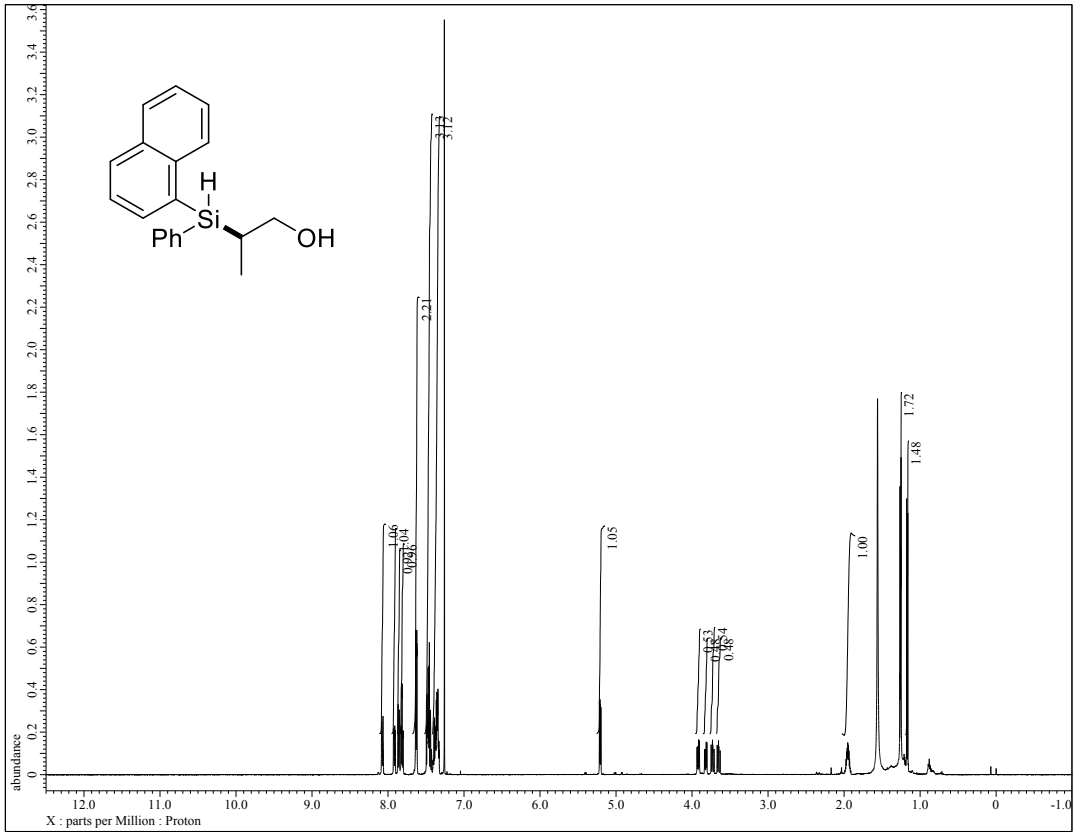
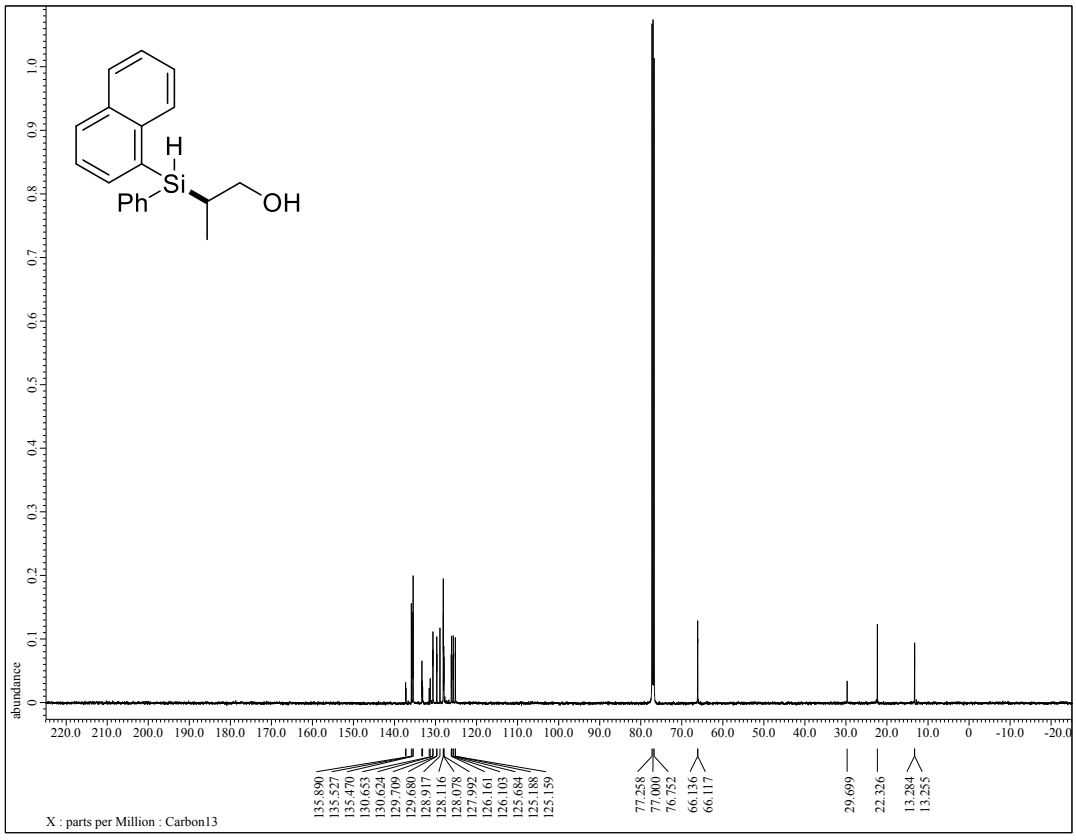
18.568
18.492
18.444
12.855
12.454
10.613
10.480

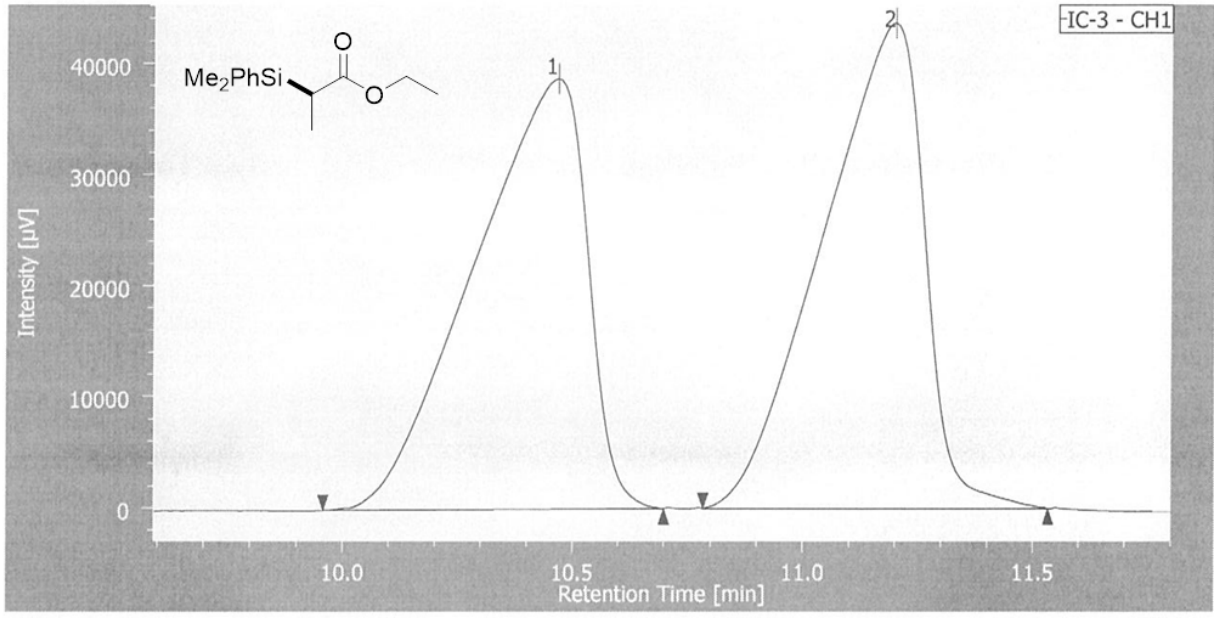

H
Si
Ph
OH
6.16
3.16
2.11
2.09
1.07
1.00
1.06
0.61
0.44
1.06
1.81
1.29
abundance
X : parts per Million : Proton


H
Si
Ph
OH
abundance
144.865
144.817
135.146
129.890
129.785
129.327
129.251
128.011
127.982
127.782
127.715
77.248
77.000
76.742
66.794
66.279
24.654
24.539
21.992
21.783
14.305
12.969
X : parts per Million : Carbon13

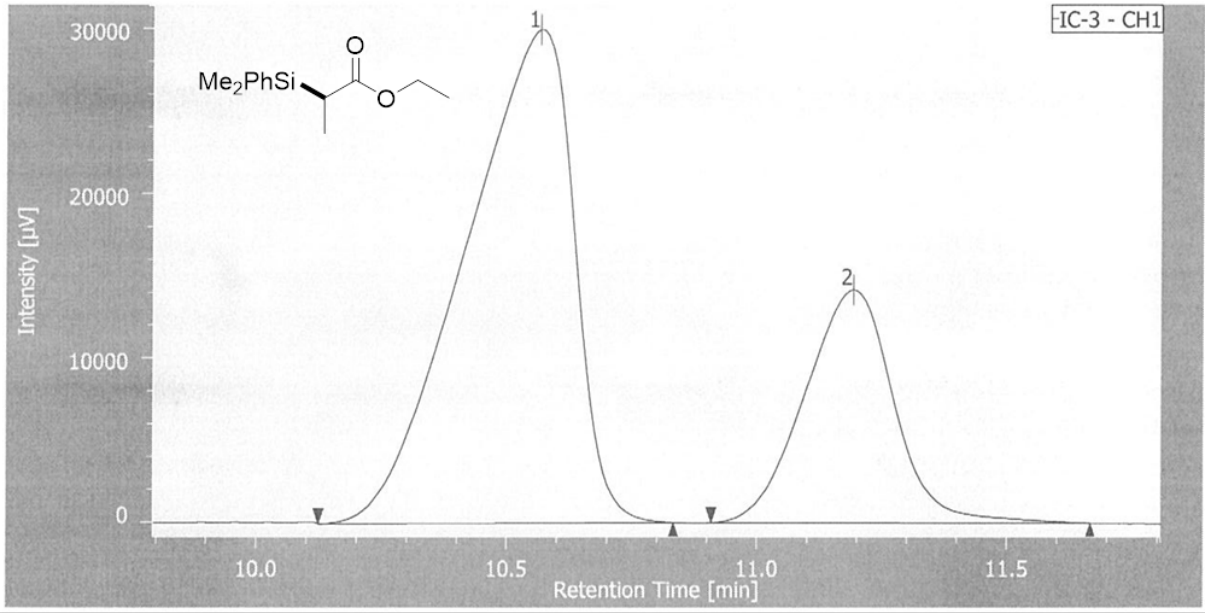

H
Si
Ph
OH
abundance
X : parts per Million : Proton


H
Si
Ph
OH
abundance
X : parts per Million : Carbon13

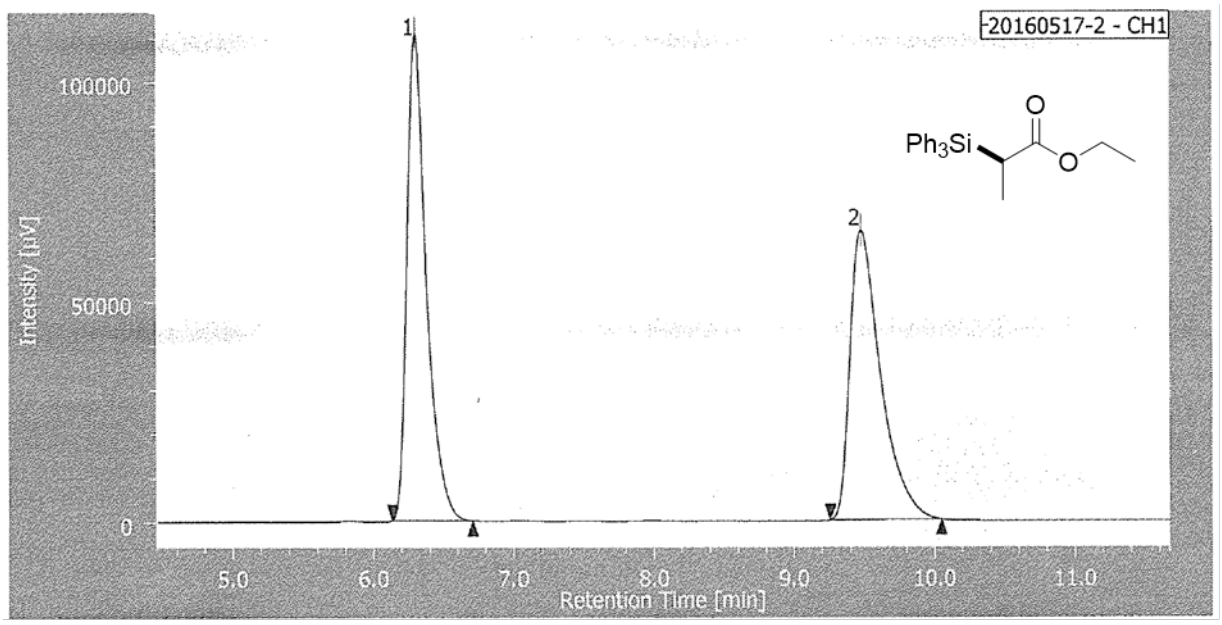
9. HPLC Spectral Data



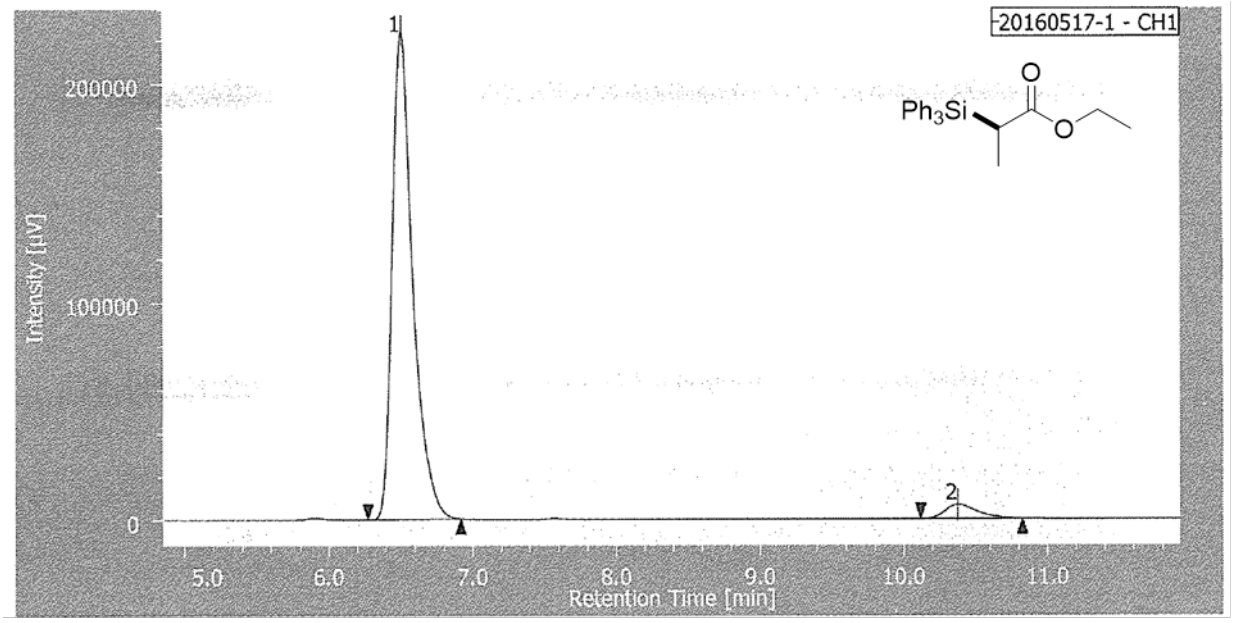
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	10.467	664692	38730	49.637	47.004
2	11.200	674425	43667	50.363	52.996



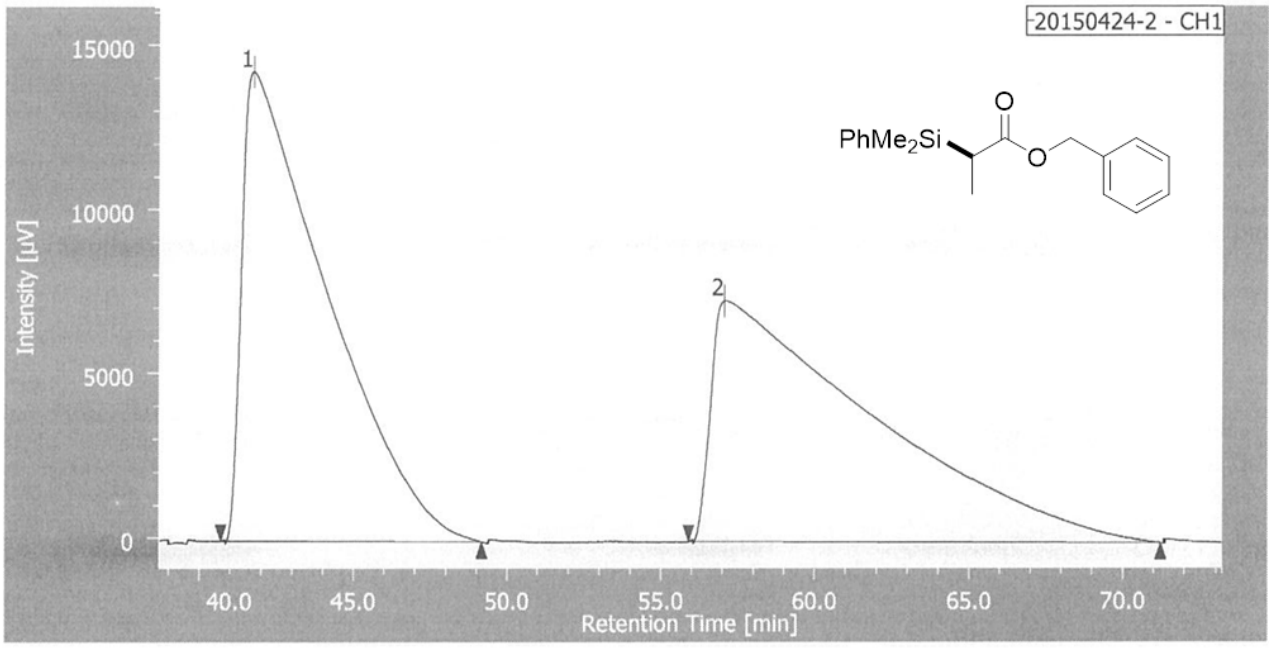
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	10.567	451522	29940	72.066	67.872
2	11.192	175015	14172	27.934	32.128



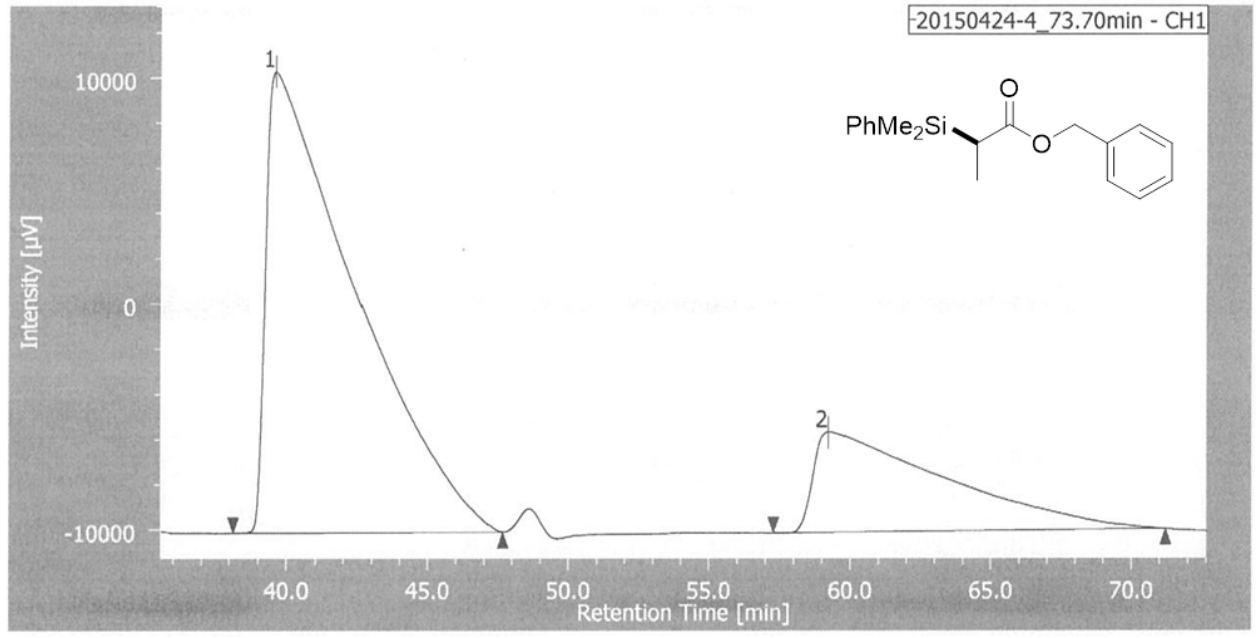
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	6.300	1048419	110743	51.175	62.774
2	9.475	1000276	65671	48.825	37.226



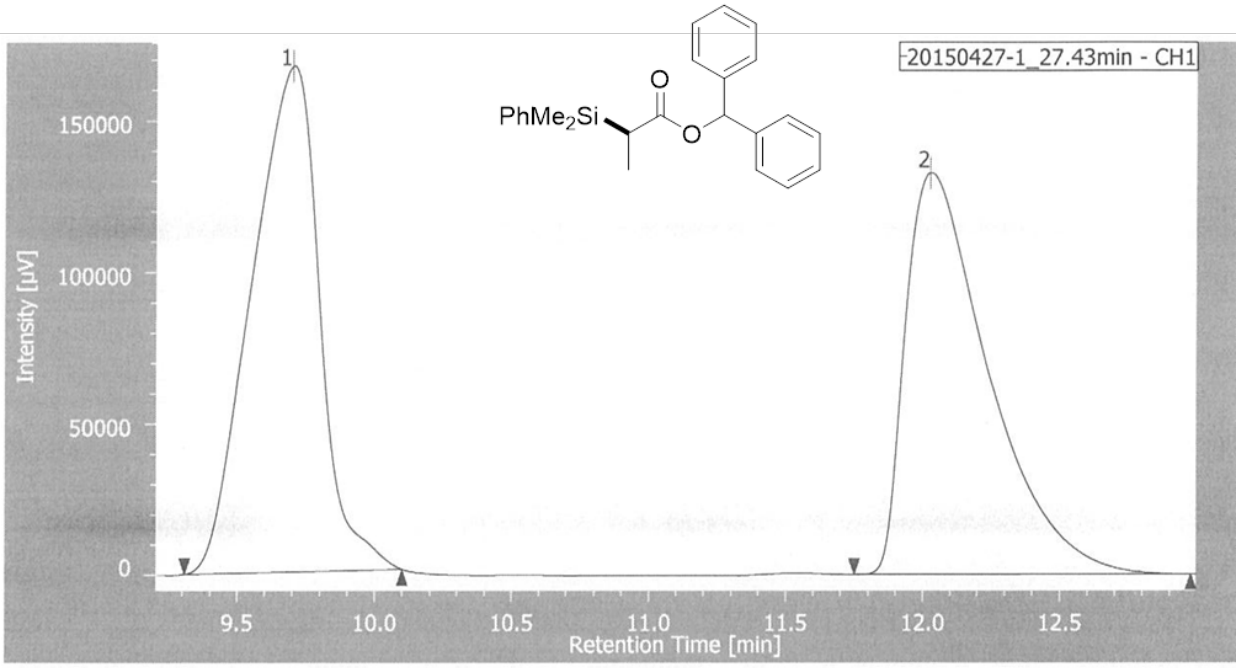
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	6.508	2202440	223826	95.722	97.238
2	10.375	98443	6359	4.278	2.762



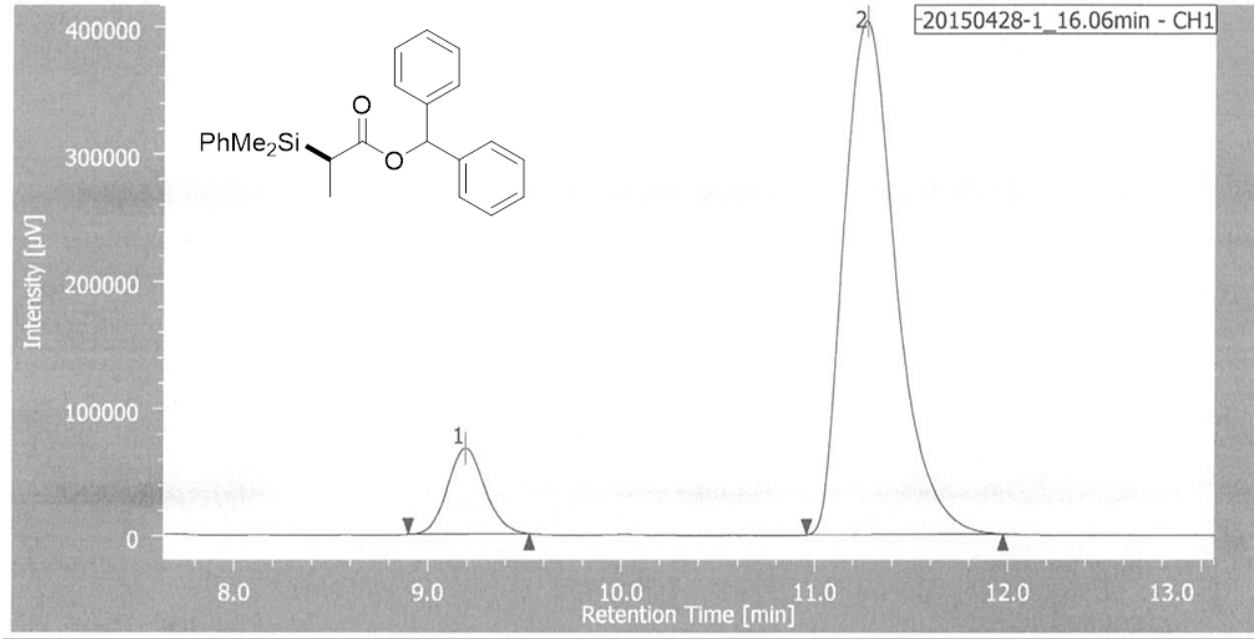
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	41.750	2739150	14298	50.703	66.145
2	57.050	2663231	7318	49.297	33.855



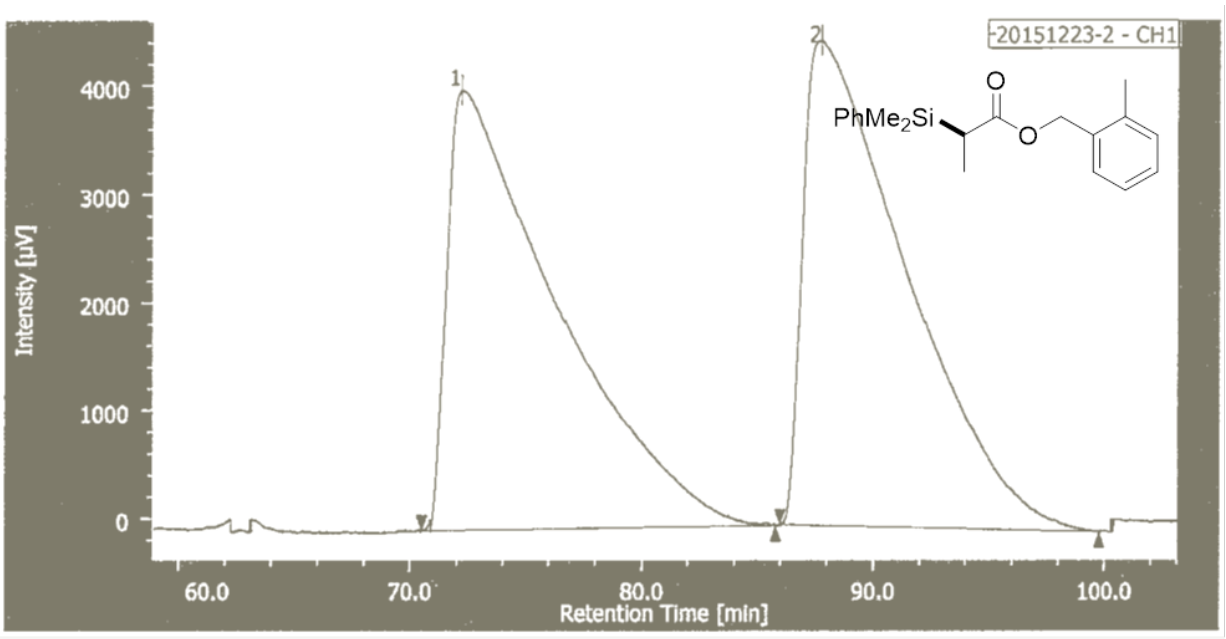
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	39.617	4459275	20431	75.449	82.086
2	59.217	1451077	4459	24.551	17.914



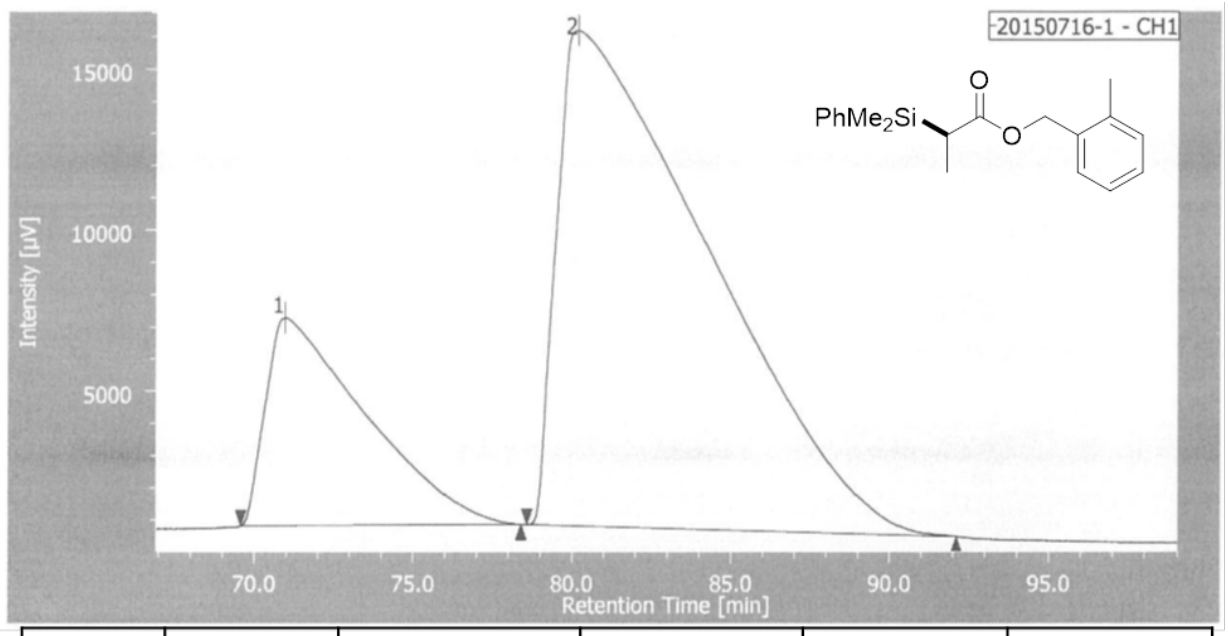
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	9.700	2856347	166932	50.510	55.740
2	12.025	2798716	132551	49.490	44.260



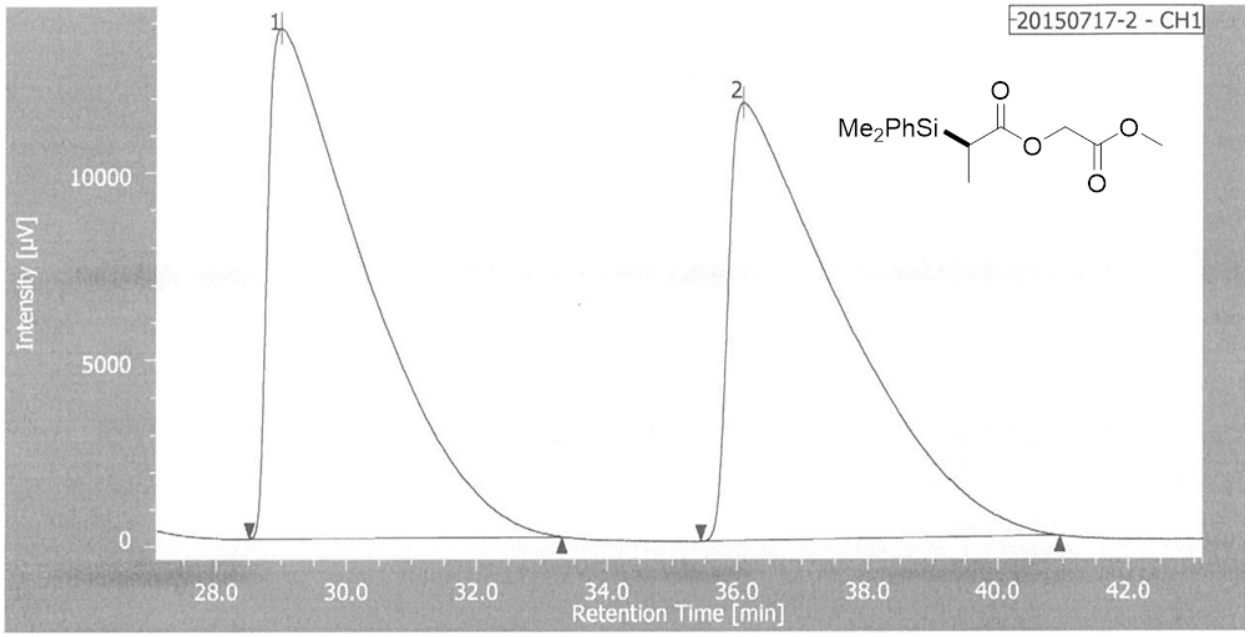
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	9.192	905090	67685	10.731	14.366
2	11.267	7529180	403446	89.269	85.634



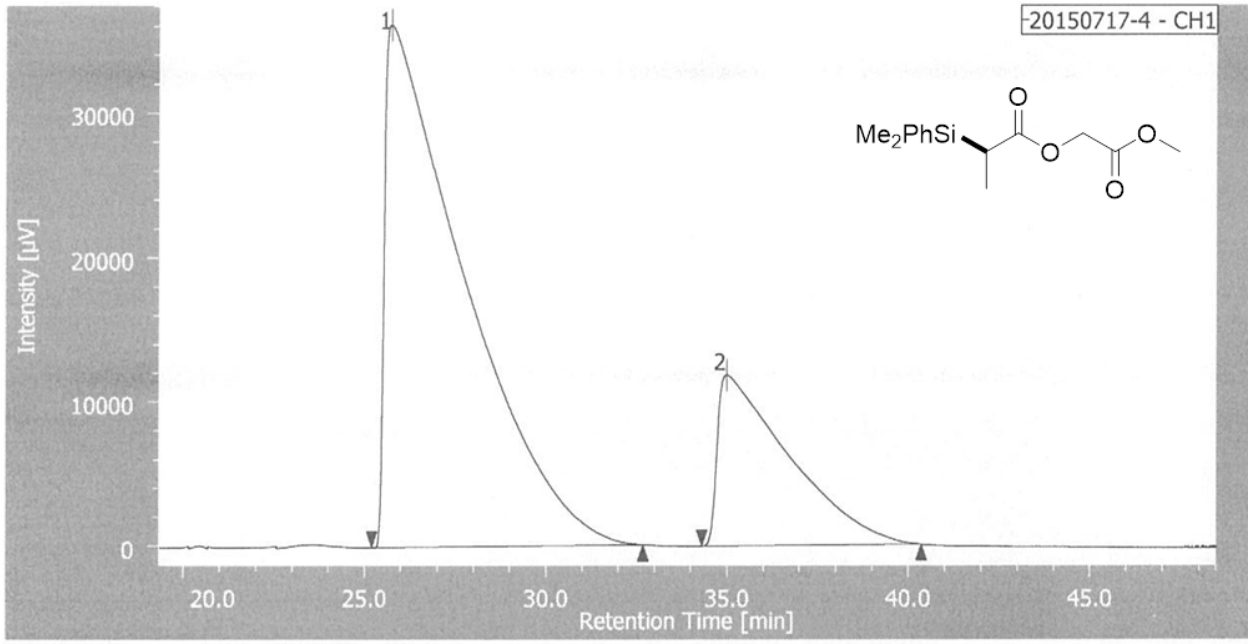
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	72.192	1340033	4071	49.145	47.578
2	87.733	1386649	4485	50.855	52.422



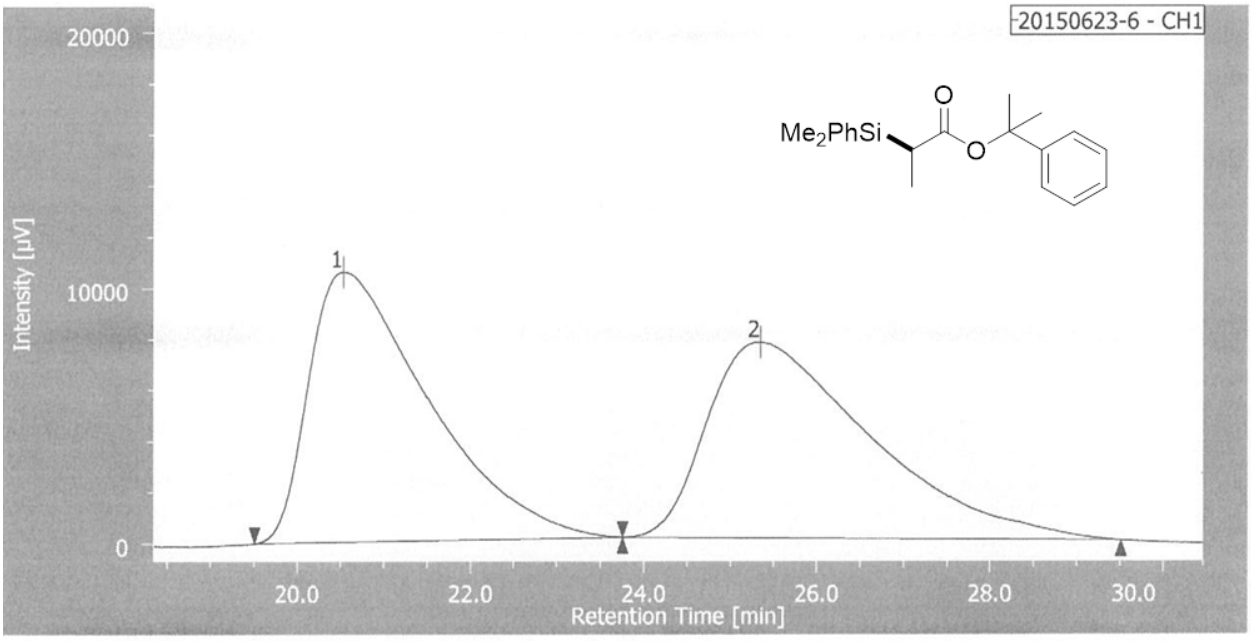
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	70.958	1400201	6453	21.479	29.560
2	80.167	5118755	15377	78.521	70.440



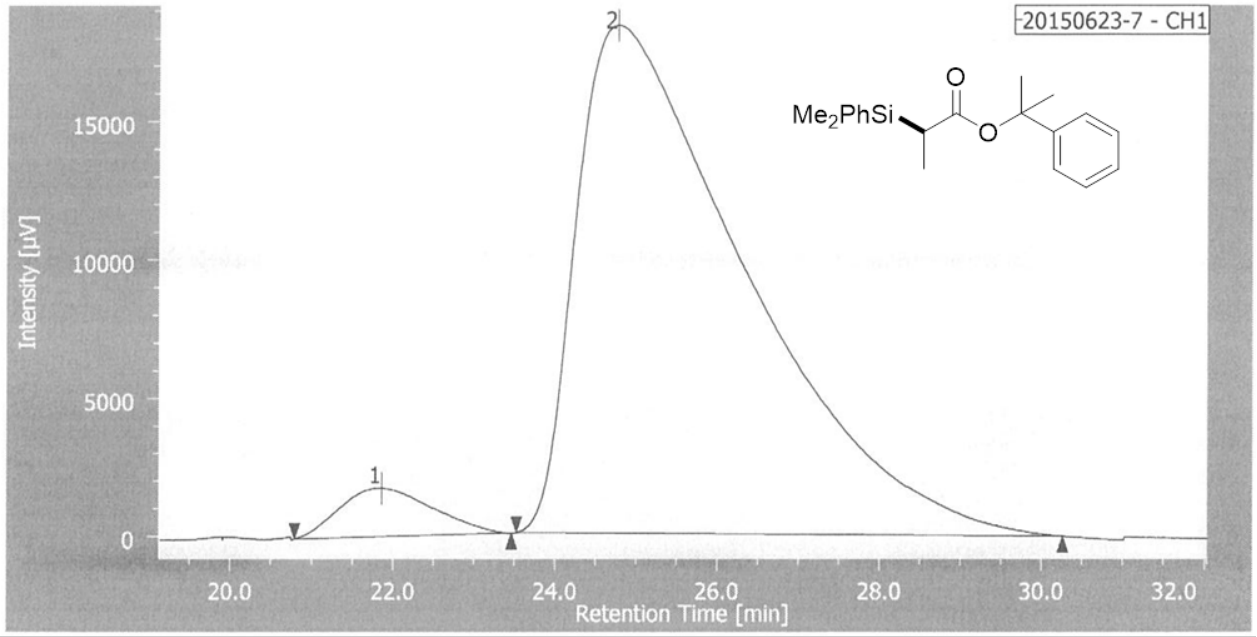
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	28.992	1427104	13655	50.112	53.822
2	36.083	1420709	11715	49.888	46.178



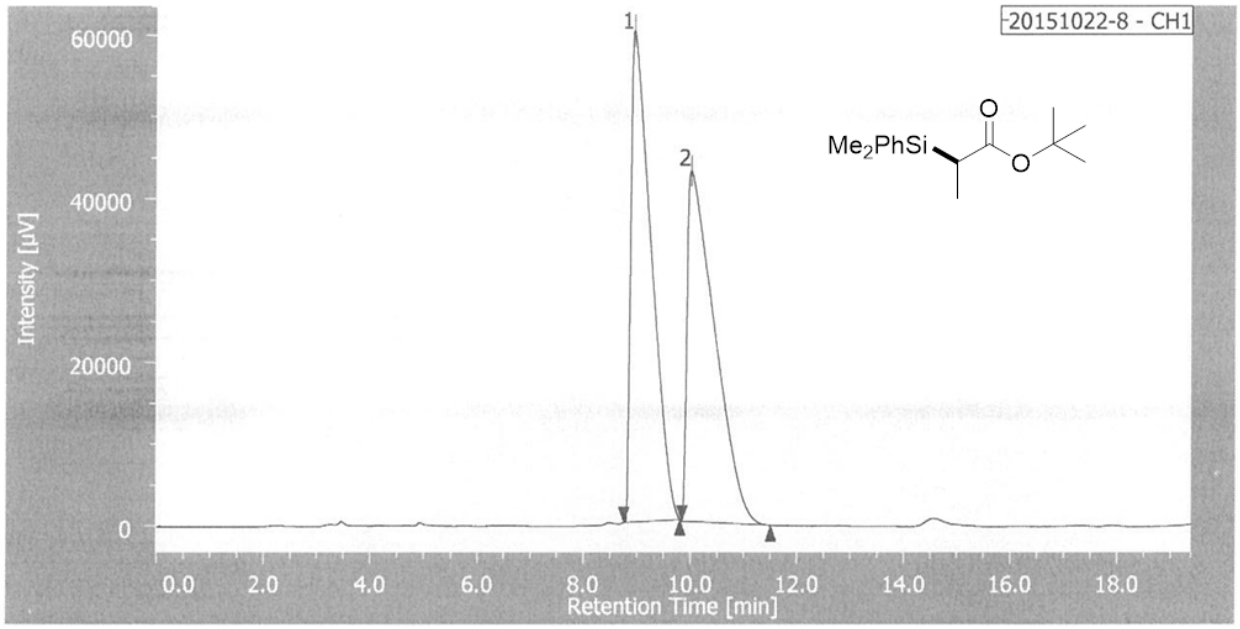
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	25.733	5503167	36163	77.188	75.320
2	34.975	1626383	11849	22.812	24.680



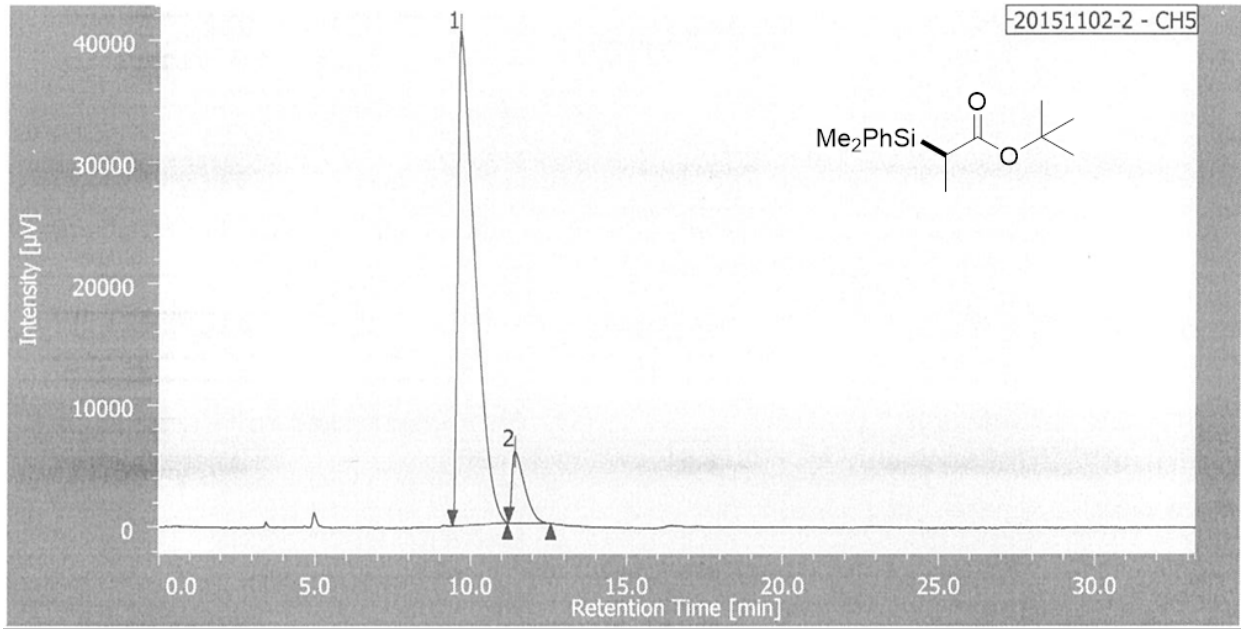
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	20.533	1015901	10588	50.347	58.002
2	25.350	1001915	7666	49.653	41.998



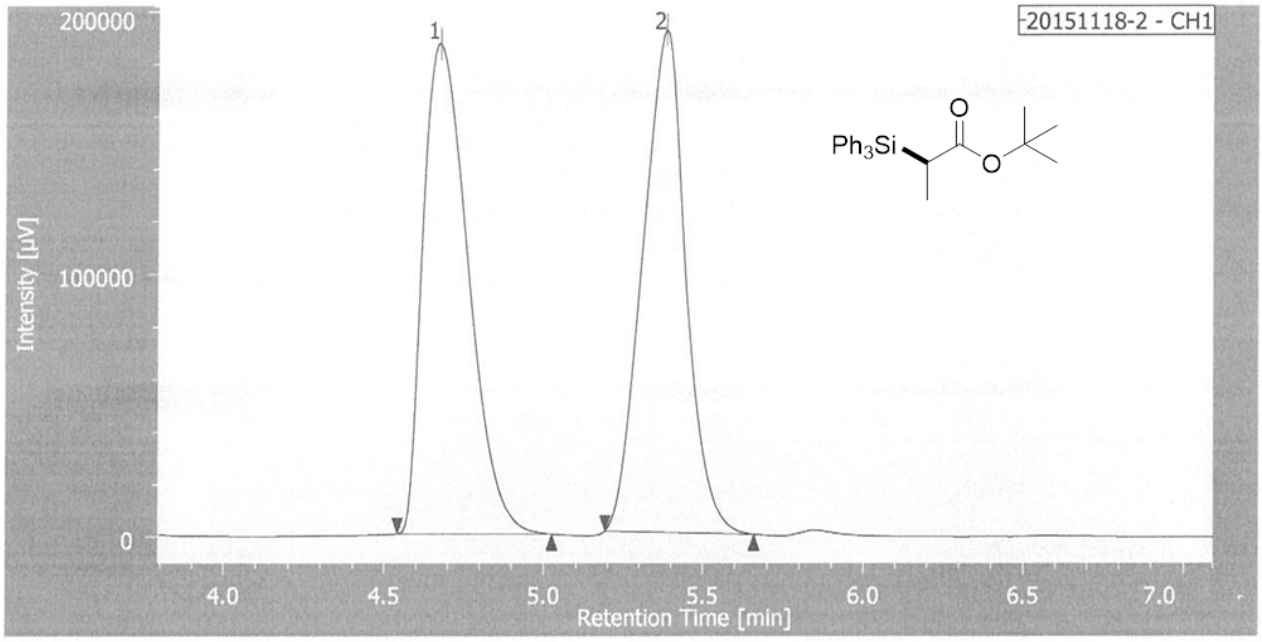
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	21.858	140007	1760	4.971	8.745
2	24.767	2676577	18362	95.029	91.255



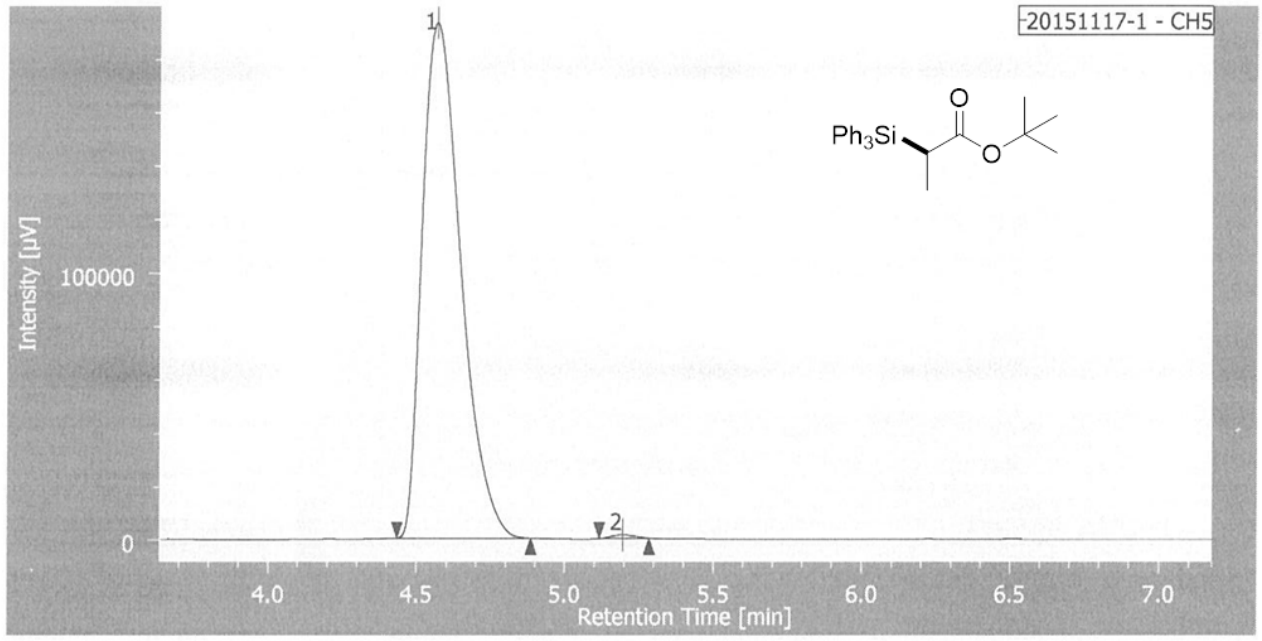
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	8.942	1584158	60034	50.702	58.342
2	10.008	1540267	42866	49.866	41.658



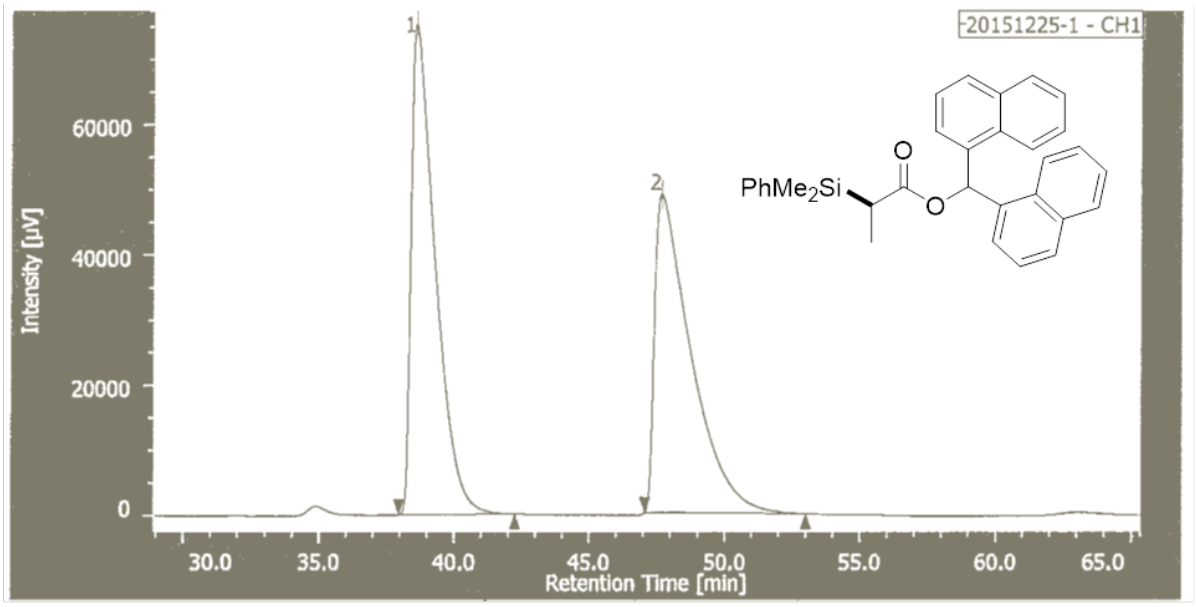
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	9.627	1553053	40689	90.367	87.305
2	11.422	165562	5917	9.633	12.695



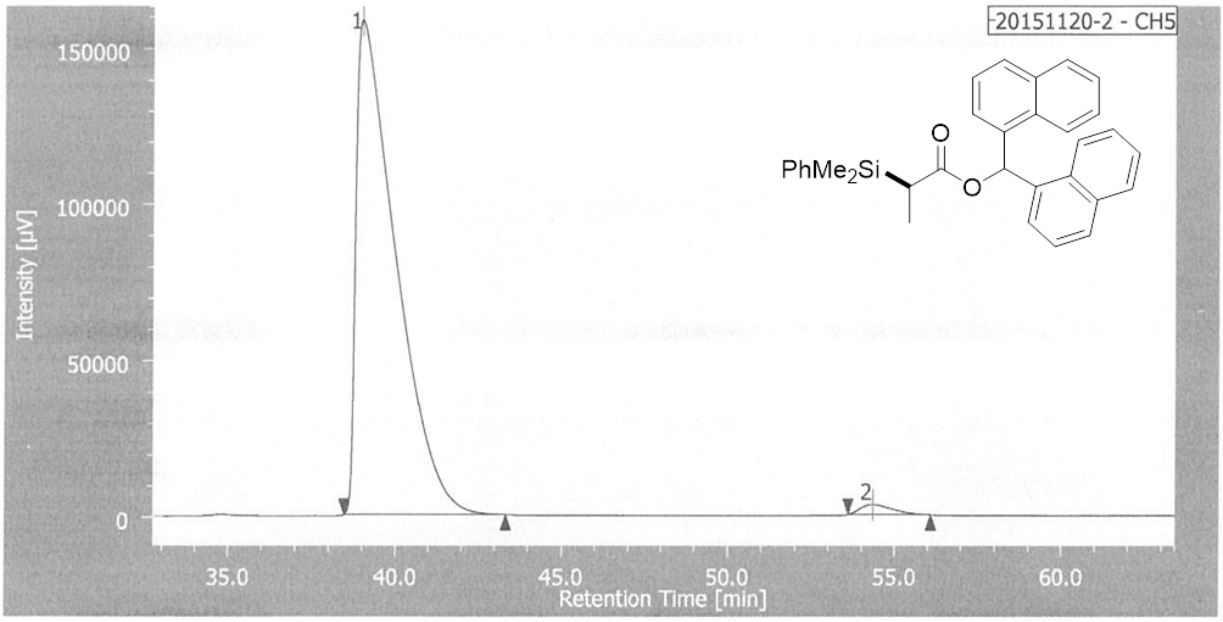
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	4.675	1839614	186745	50.306	49.379
2	5.383	1817262	191445	49.694	50.621



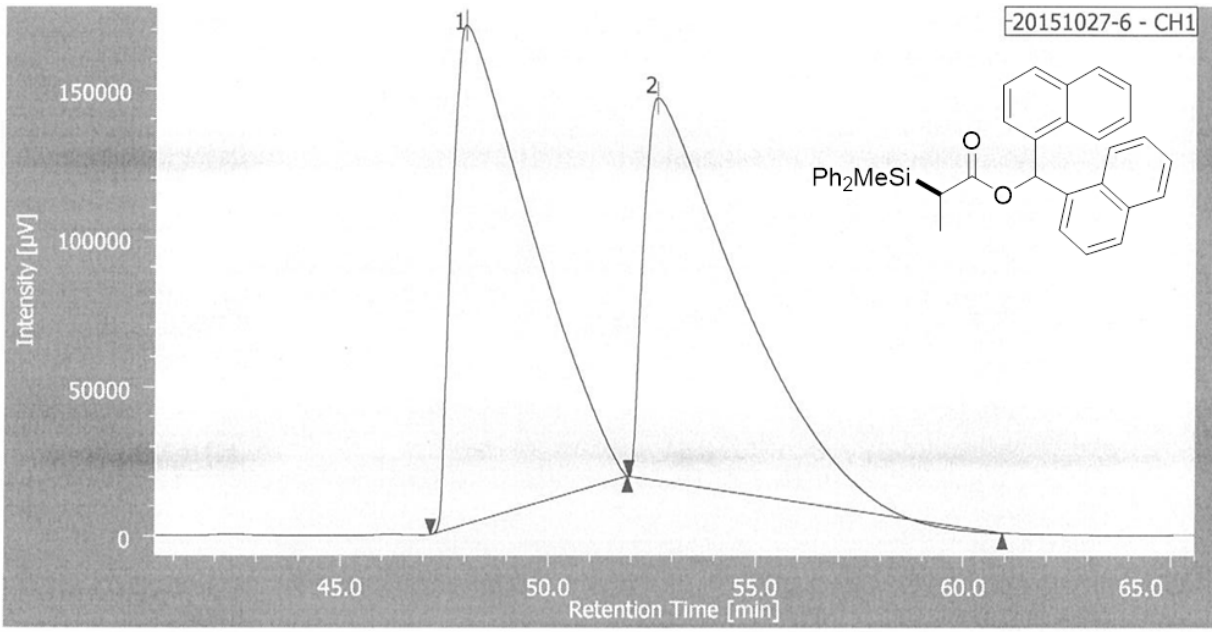
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	4.567	1731039	193023	99.589	99.313
2	5.195	7140	1336	0.411	0.687



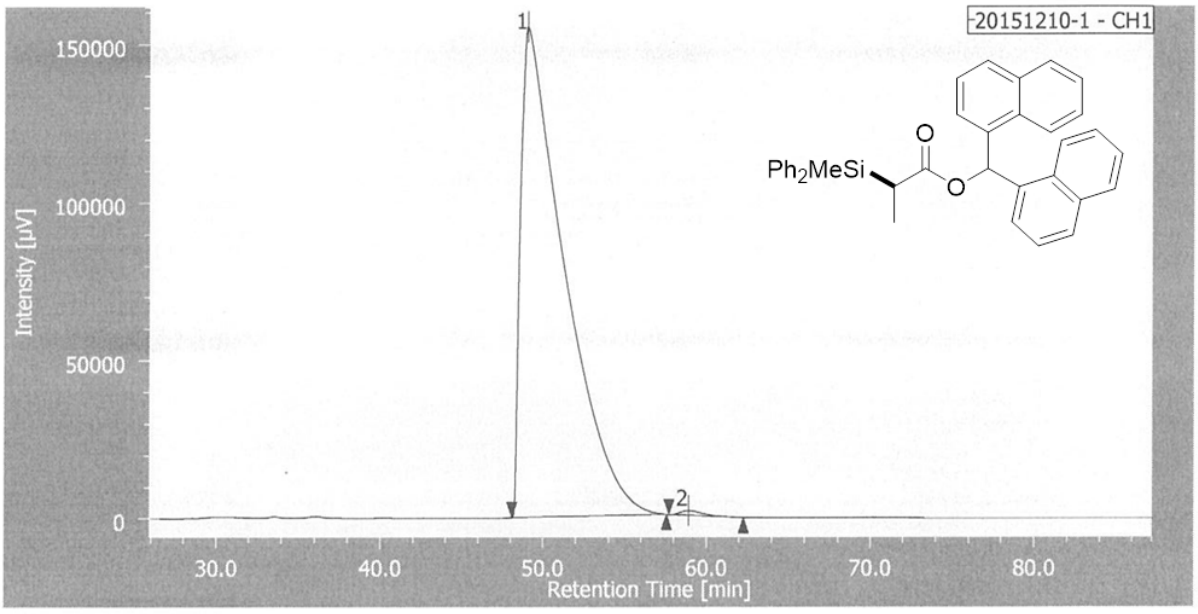
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	38.575	4613146	75145	50.595	60.625
2	47.667	4504718	48805	49.405	39.375



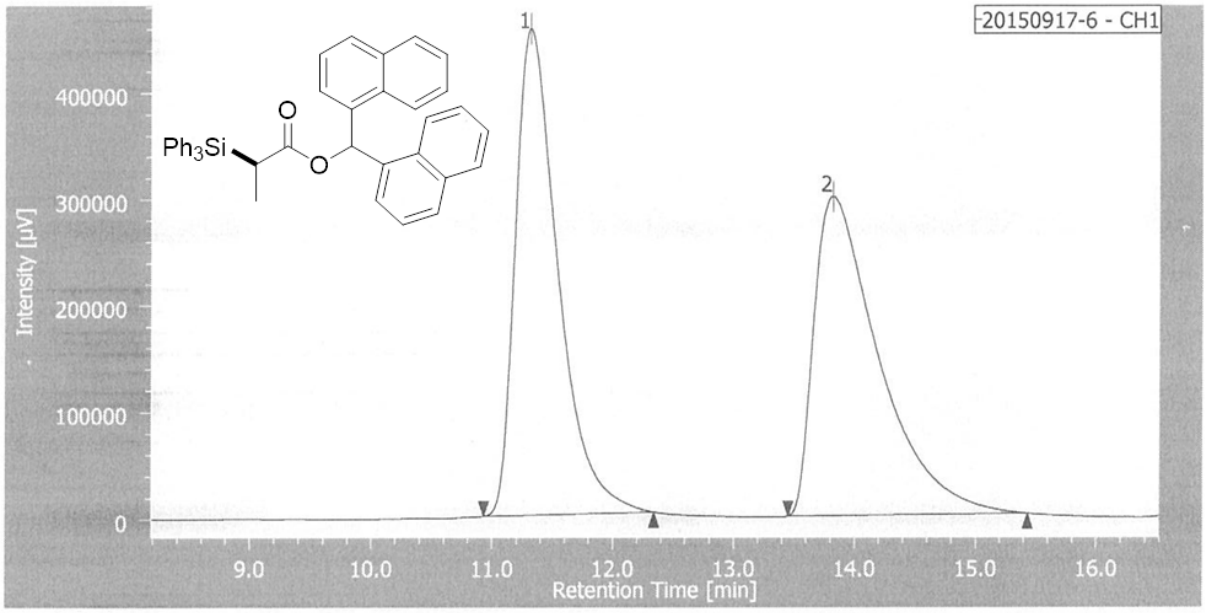
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	38.985	13163666	158099	98.367	98.013
2	54.348	218597	3205	1.633	1.987



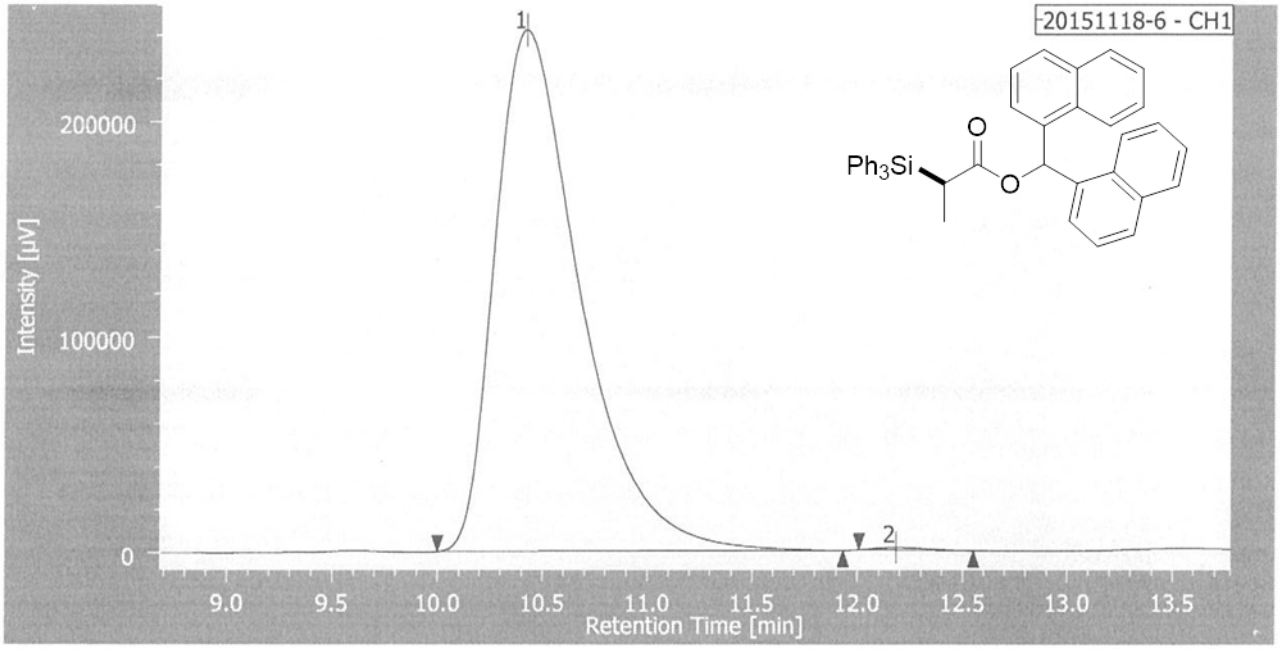
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	48.000	22098728	167352	51.635	56.628
2	52.617	20699596	128179	48.365	43.372



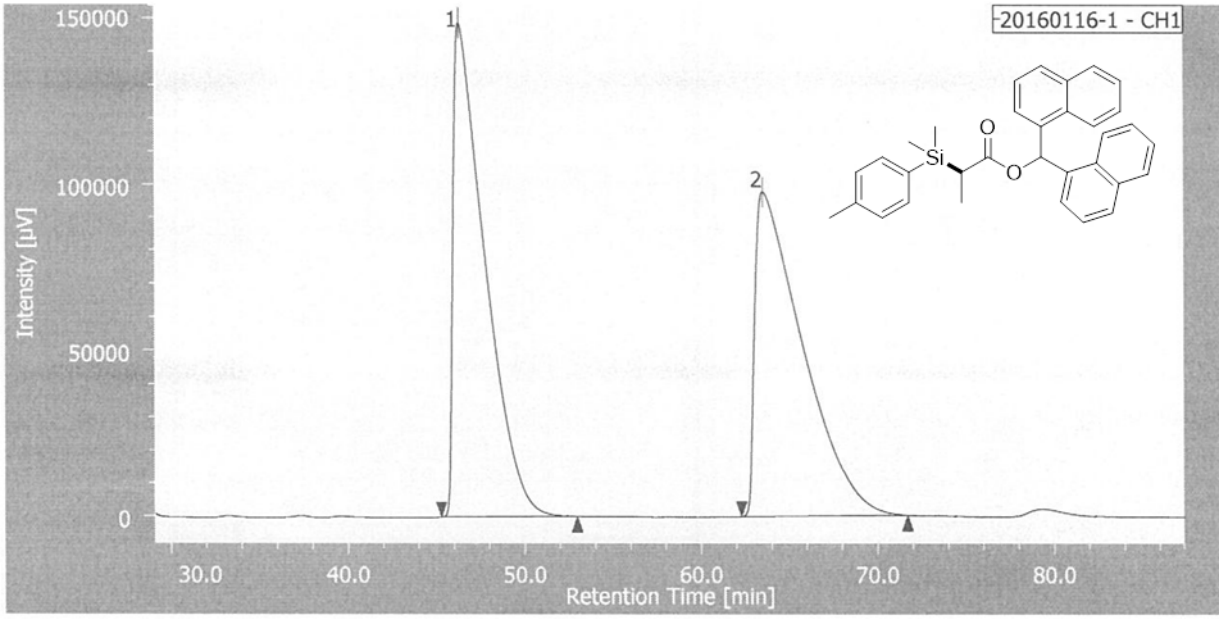
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	49.025	28718024	154990	99.545	99.056
2	58.892	131284	1477	0.455	0.994



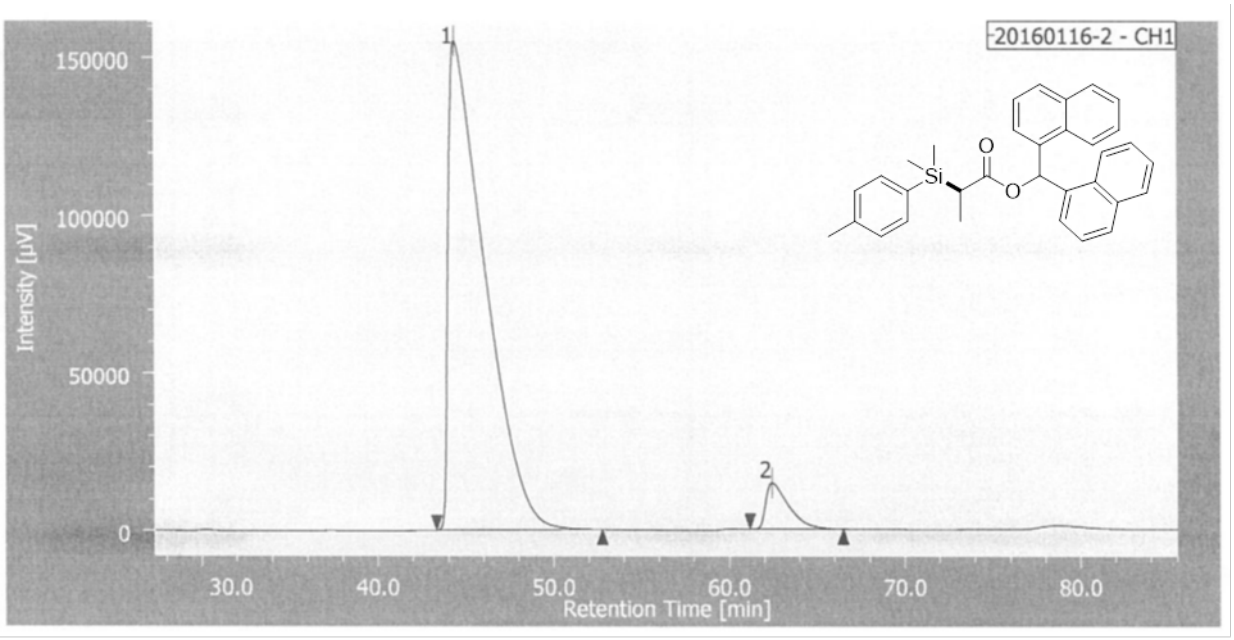
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	11.317	11183505	455993	50.120	60.383
2	13.817	11130094	299175	49.880	39.617



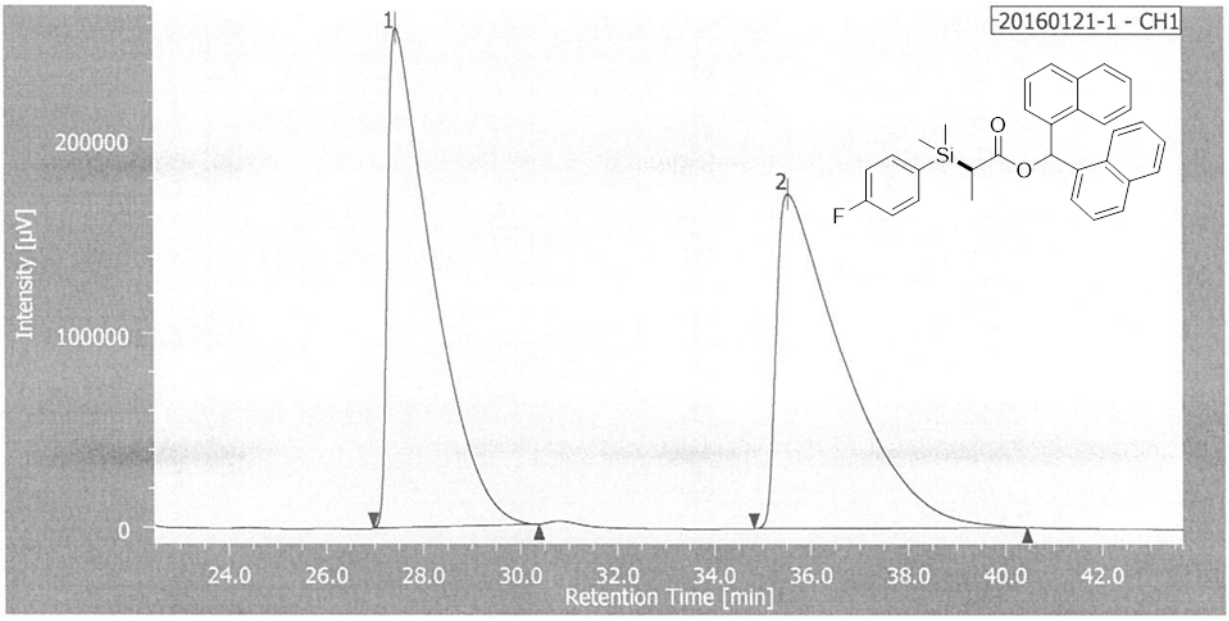
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	10.417	6845550	241709	99.707	99.466
2	12.183	20100	1298	0.293	0.534



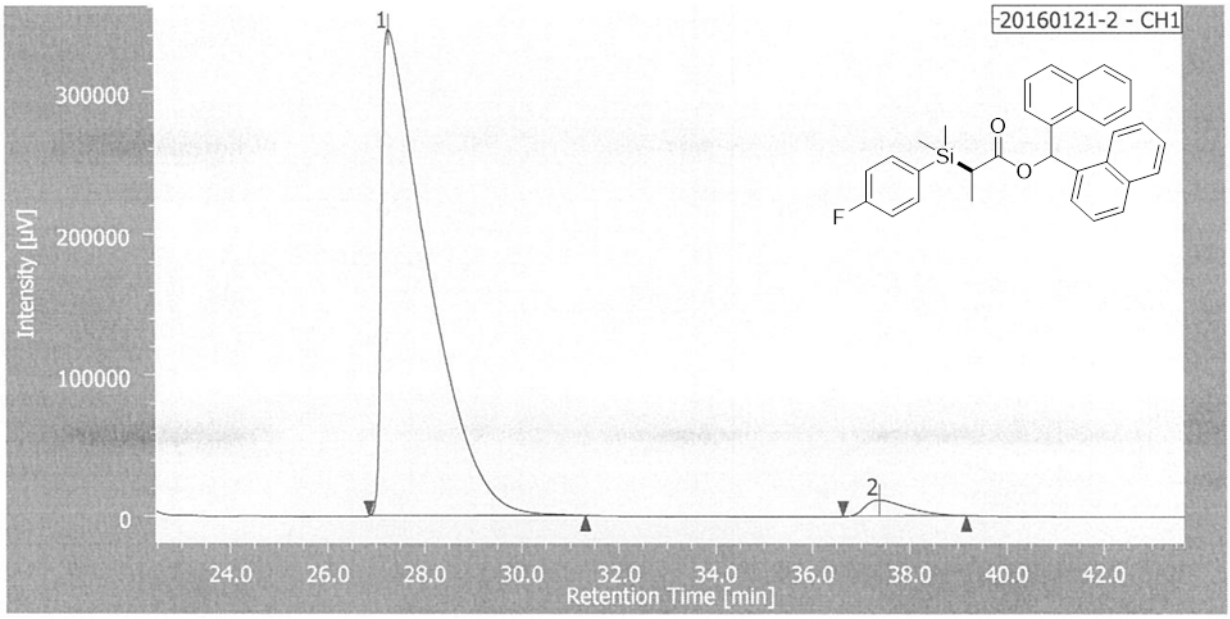
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	46.283	18623992	148896	50.188	60.366
2	63.517	18484712	97759	49.812	39.634



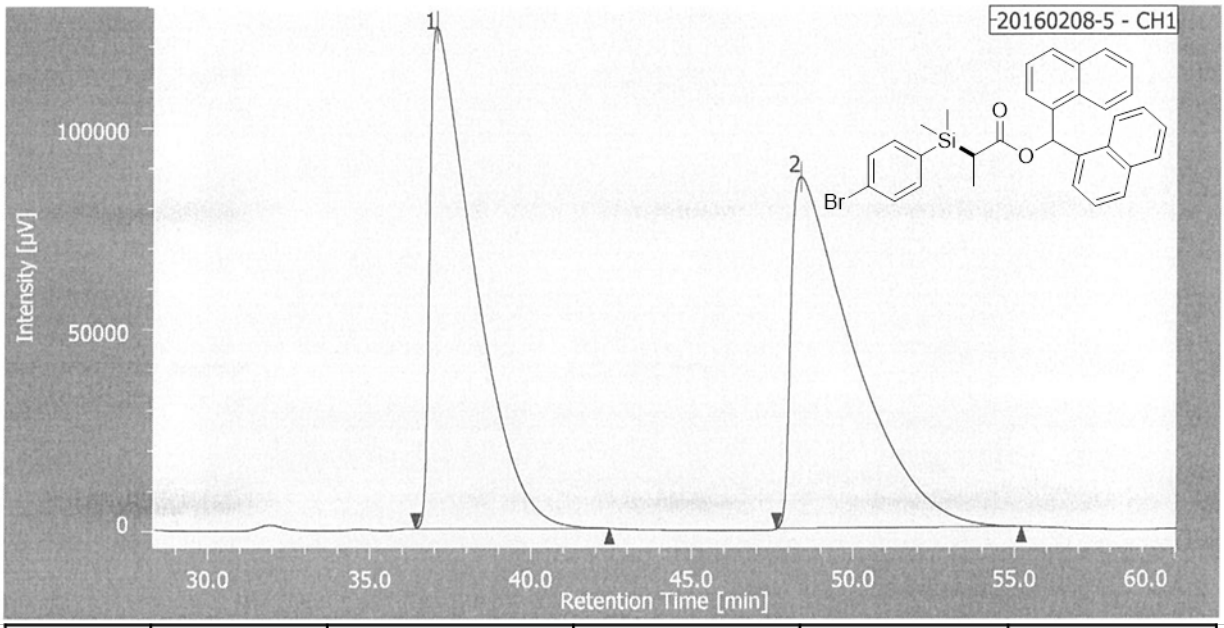
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	44.367	22484327	154947	94.399	91.365
2	62.417	1334044	14644	5.601	8.635



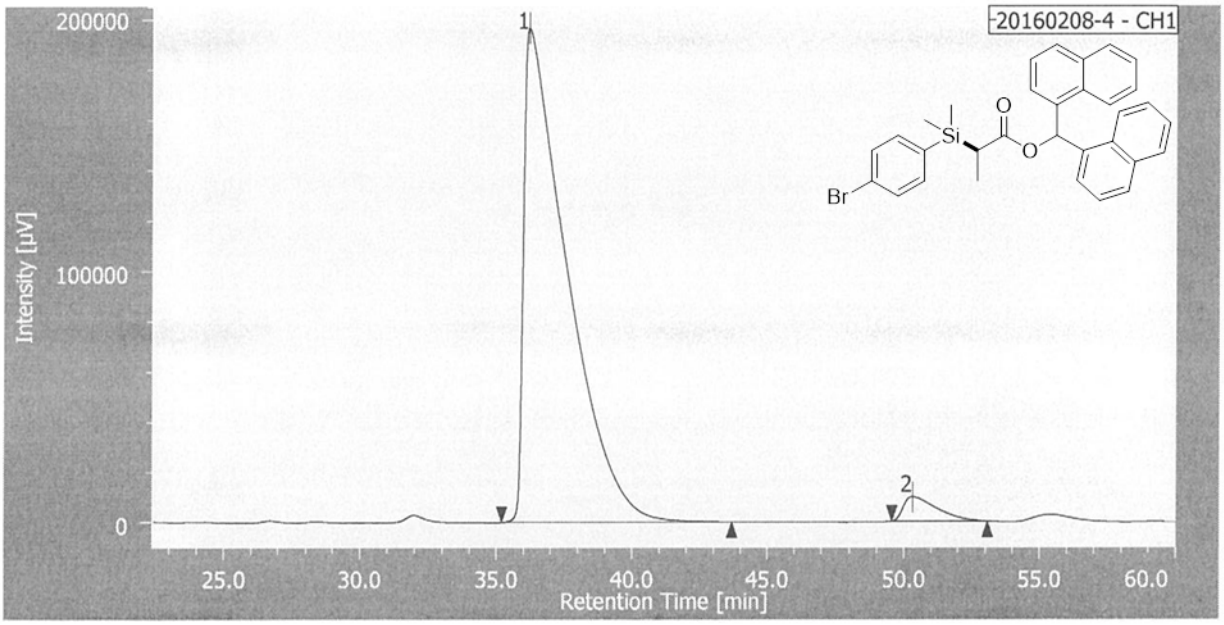
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	27.458	16506491	257847	49.766	59.905
2	35.533	16661700	172580	50.234	40.095



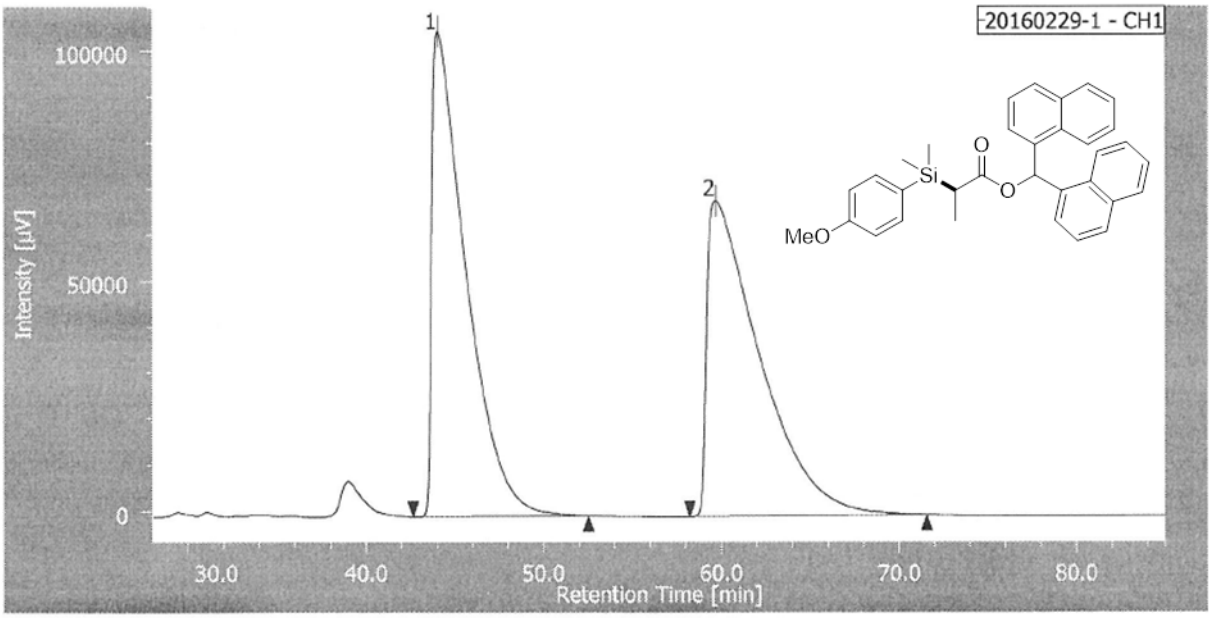
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	27.292	22749793	343584	96.953	96.697
2	37.367	715078	11735	3.047	3.303



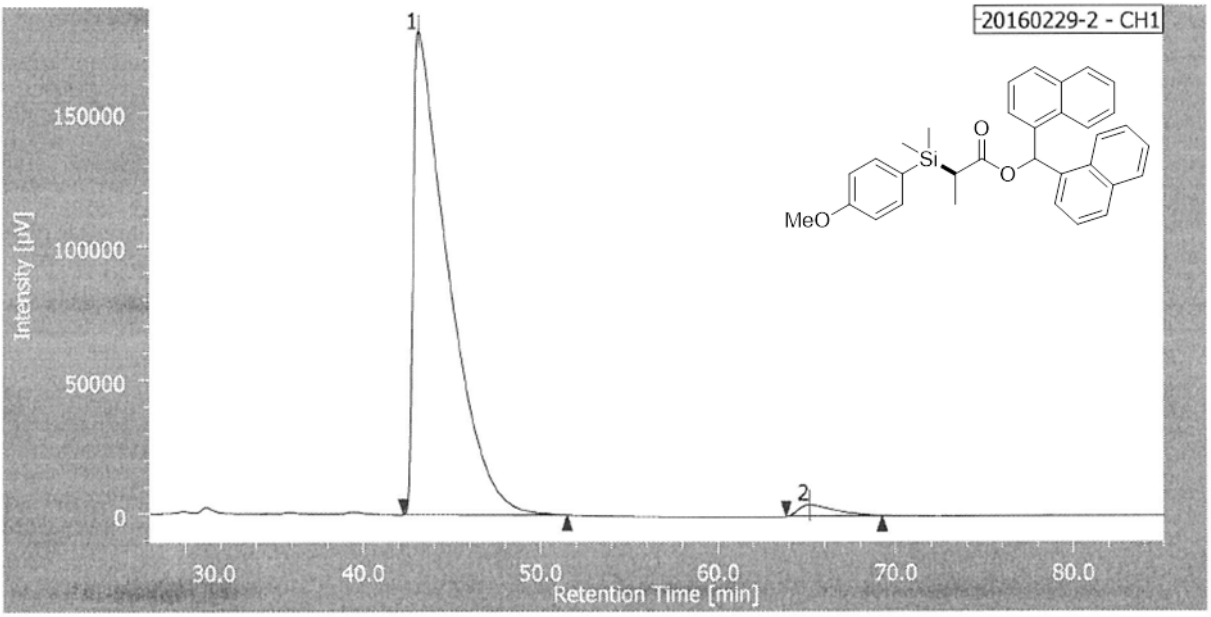
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	37.050	11942922	123947	50.377	58.776
2	48.350	11763938	86932	49.623	41.224



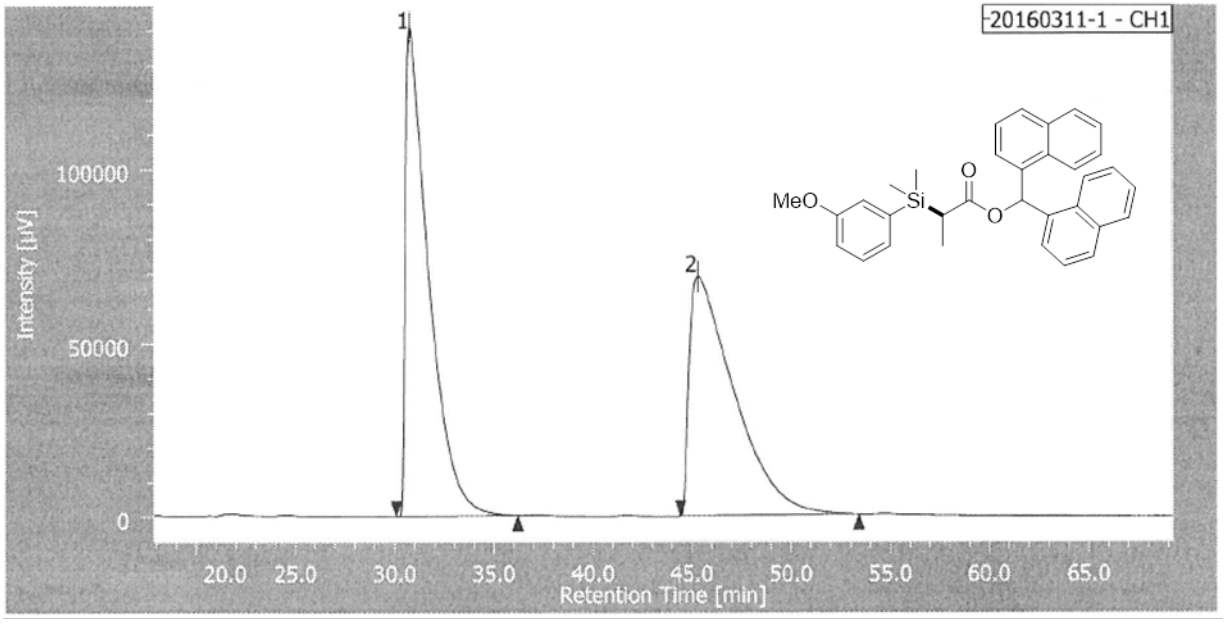
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.200	21852146	196529	96.336	95.244
2	50.317	831130	9814	3.664	4.756



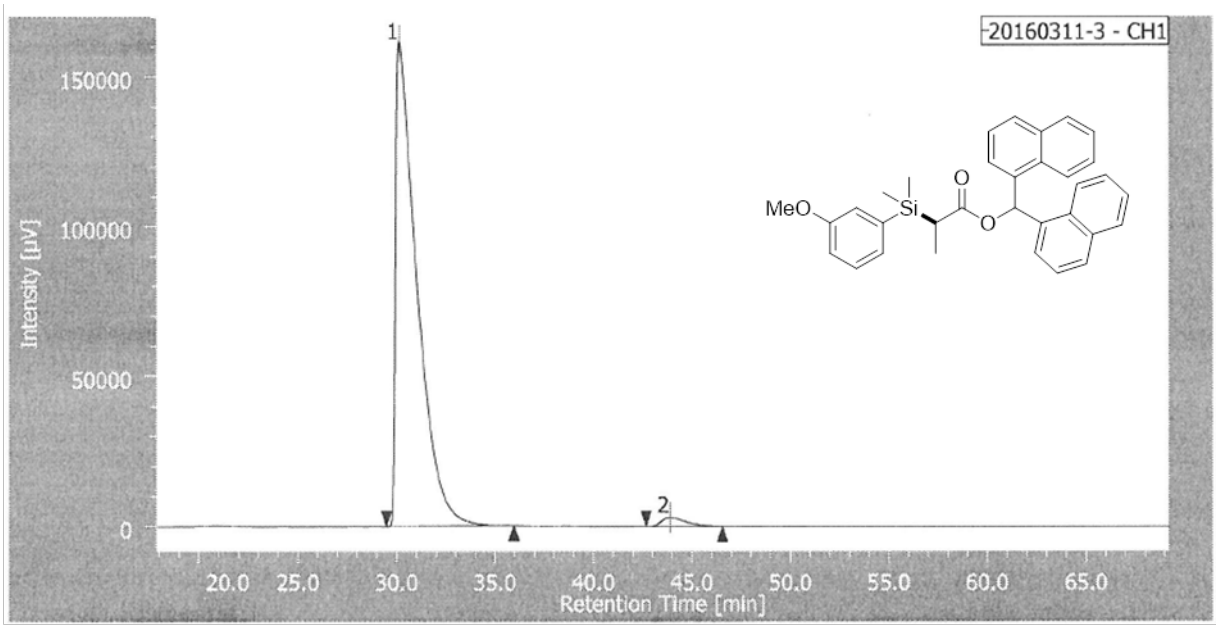
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	44.017	14161549	105247	50.113	60.597
2	59.683	14097438	68438	49.887	39.403



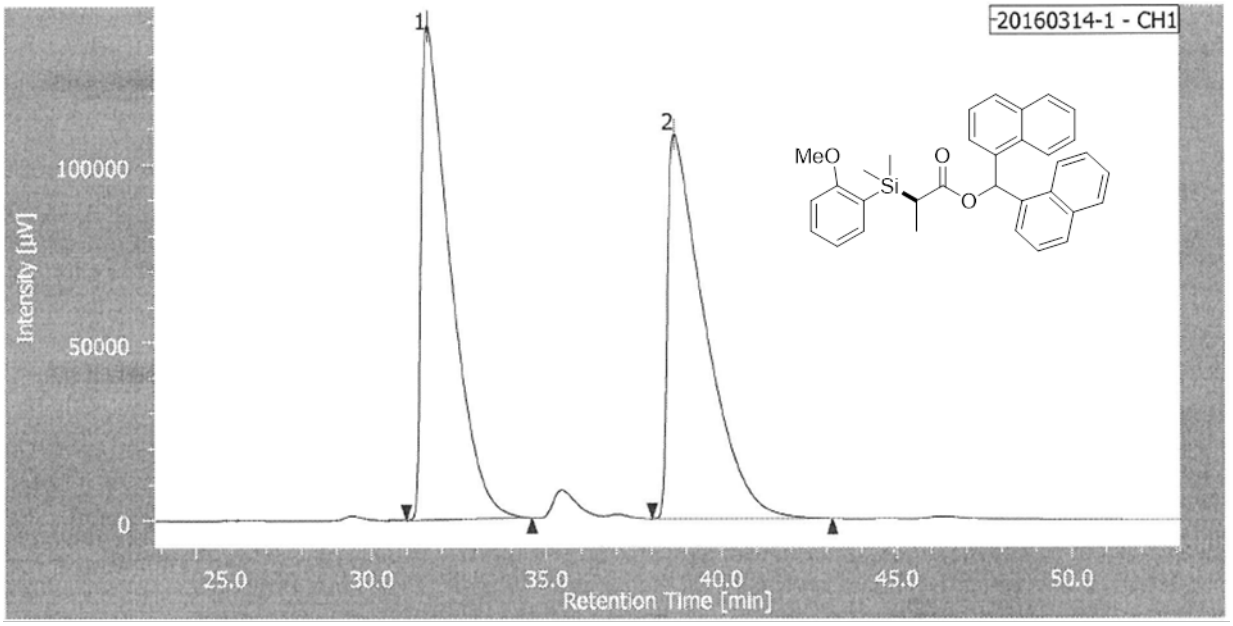
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	43.142	24746209	179914	97.679	97.750
2	65.175	588015	4141	2.321	2.250



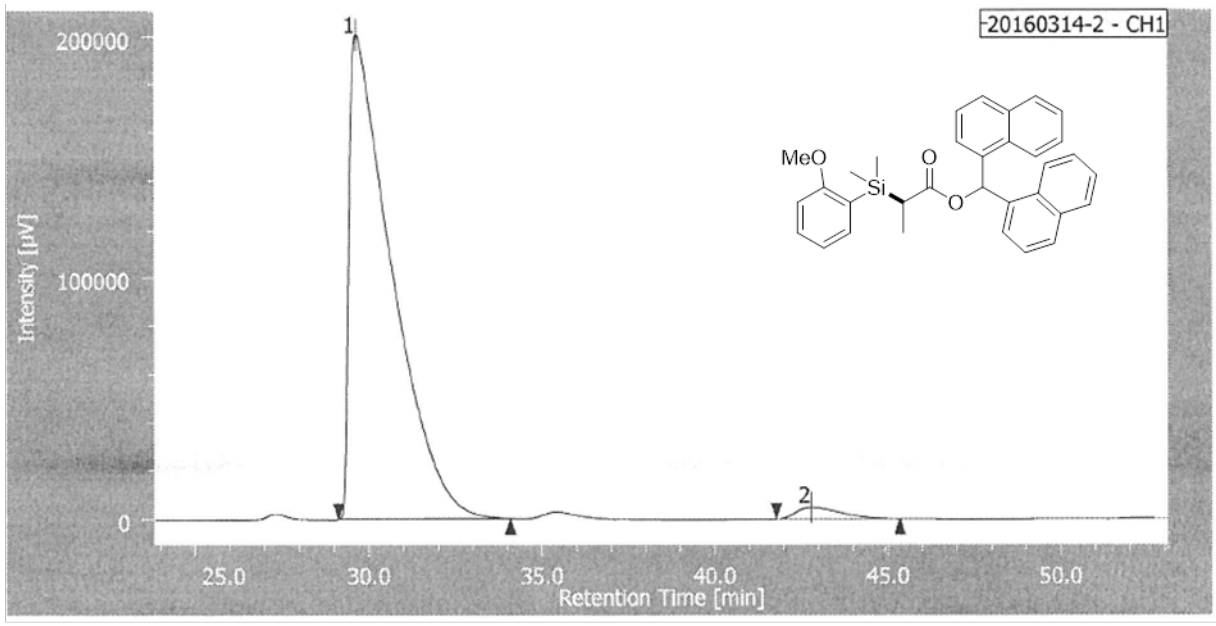
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	30.775	11430656	140554	51.332	67.162
2	45.300	10837645	68724	48.668	32.838



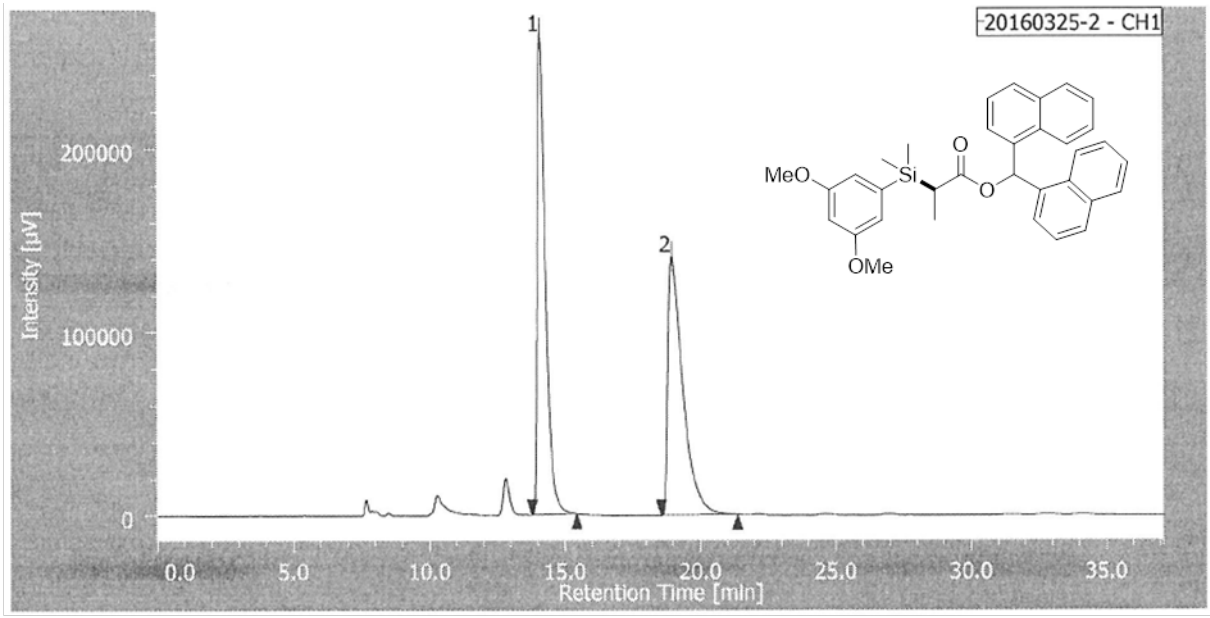
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	30.150	12016097	161655	97.985	98.210
2	43.875	247084	2947	2.015	2.015



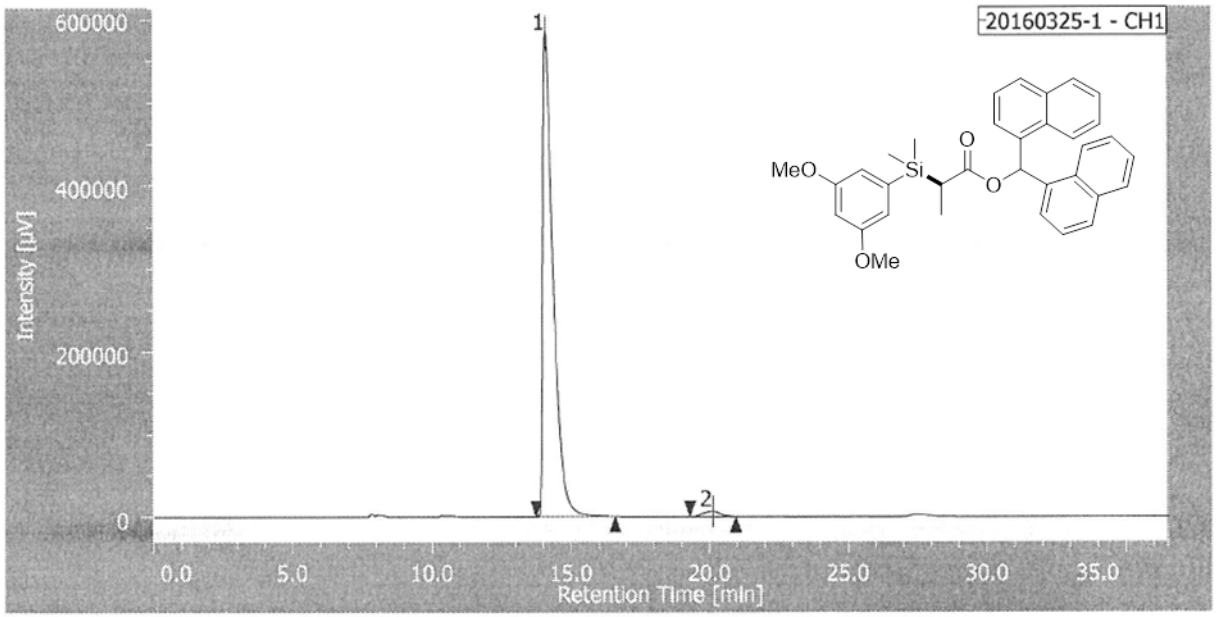
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	31.600	8036730	138511	49.824	56.218
2	38.658	8093594	107871	50.176	43.782



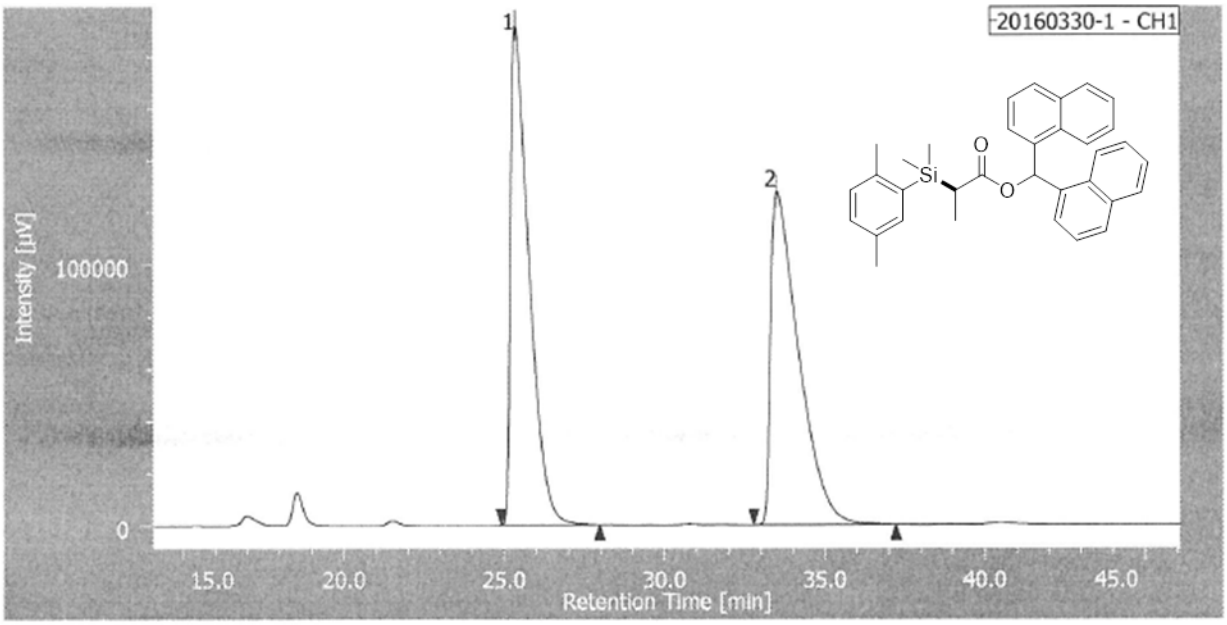
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	29.642	17122402	200642	97.681	97.743
2	42.775	406421	406421	2.319	2.257



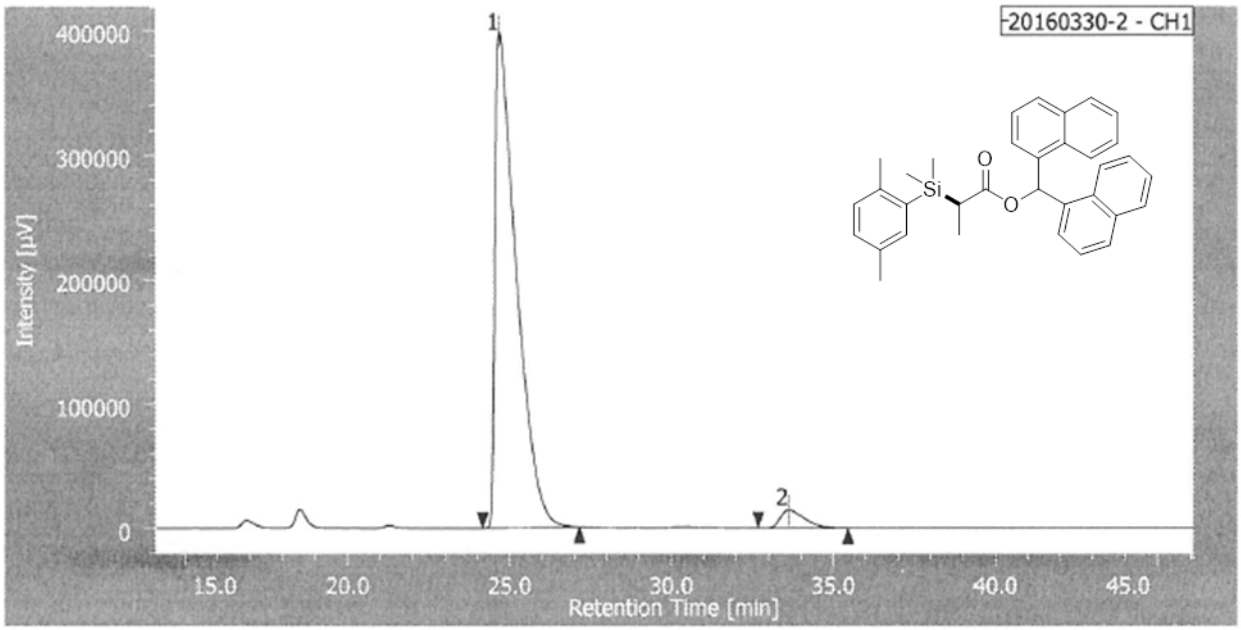
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	14.100	5481137	262192	50.509	65.031
2	18.958	5370721	140986	49.491	34.969



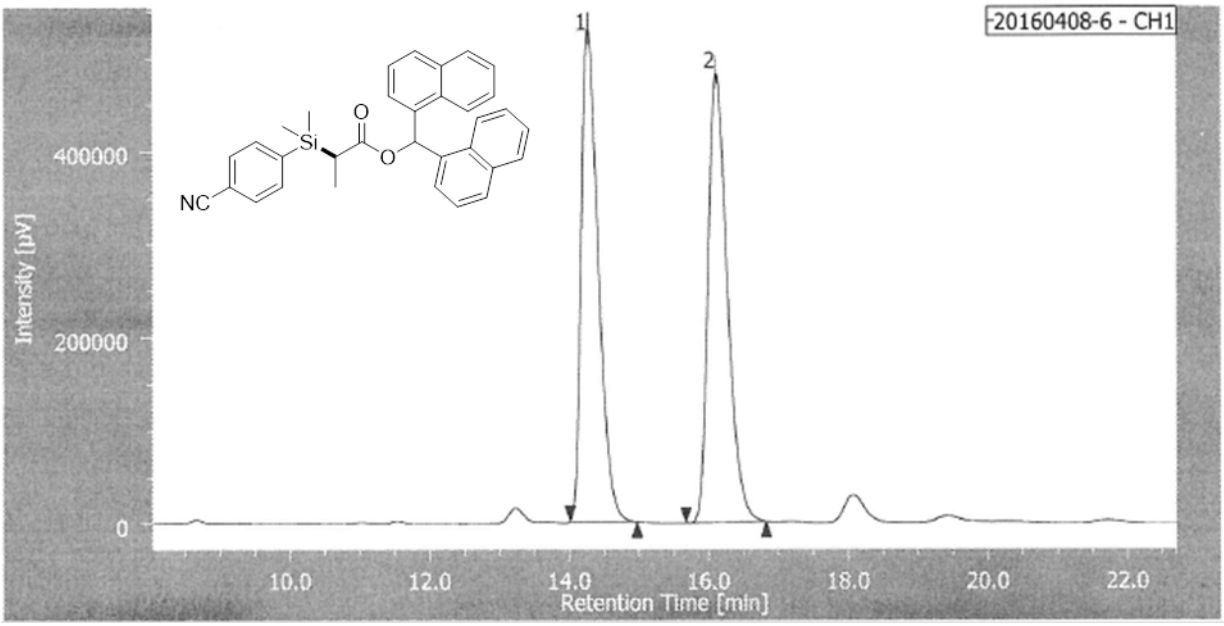
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	14.108	14746886	584786	98.158	98.861
2	20.108	276746	6740	1.842	1.139



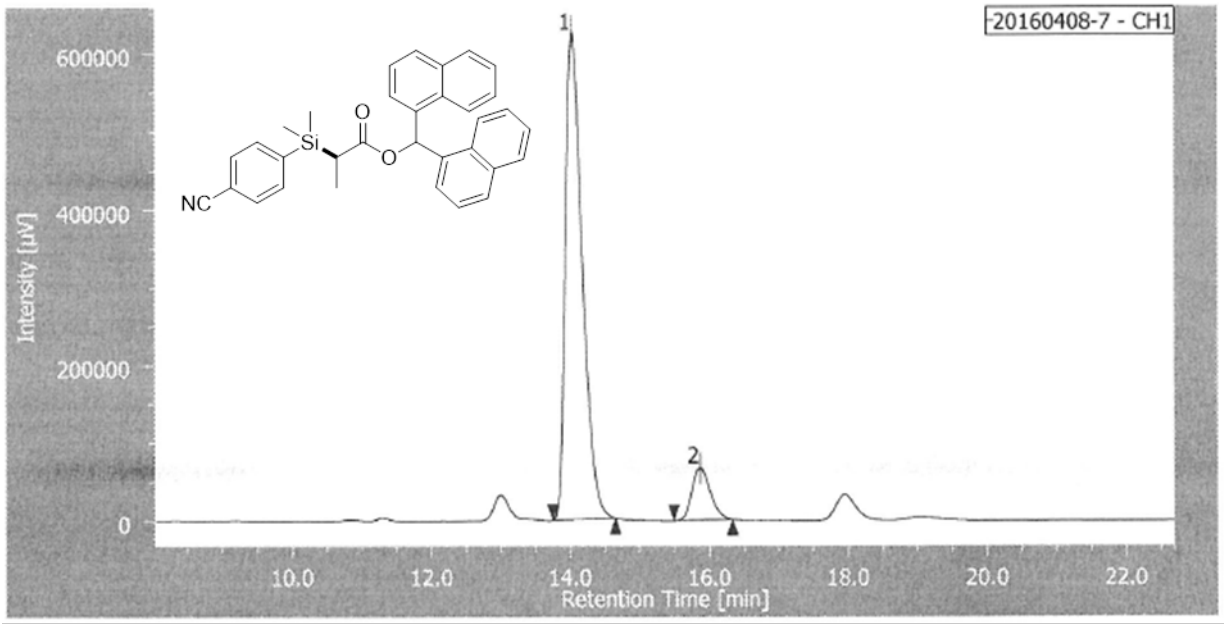
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	25.367	7683508	191412	49.755	59.971
2	33.525	7759058	127764	50.245	40.029



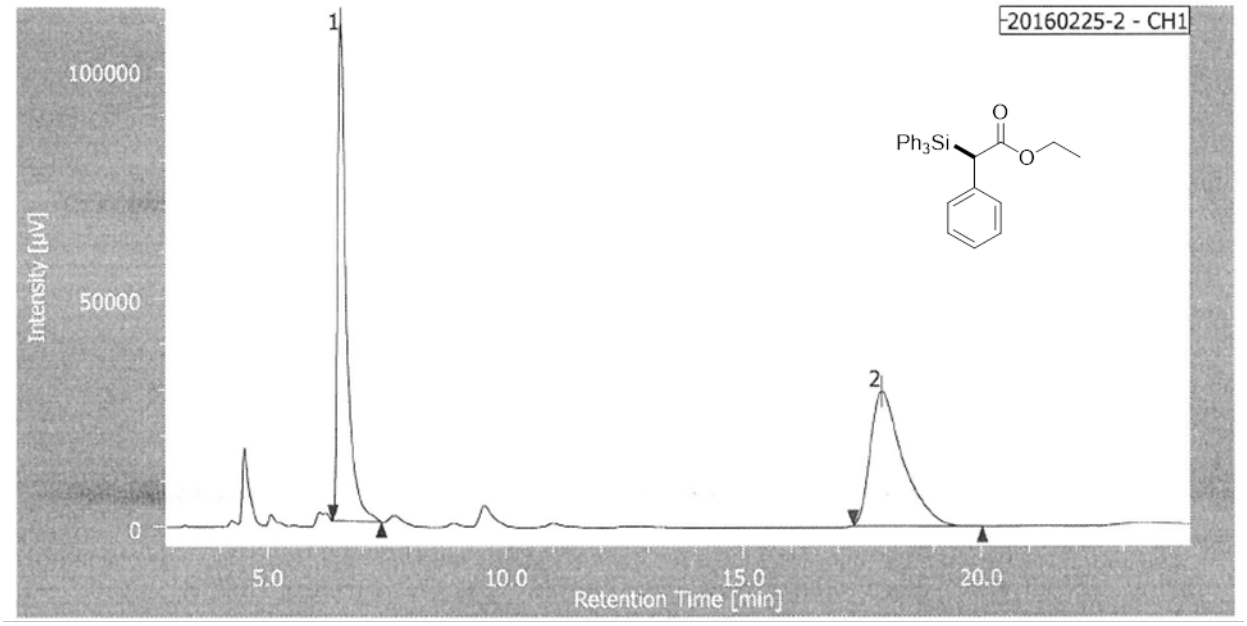
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	24.692	18363996	398575	96.192	96.483
2	33.617	727015	14528	3.808	3.517



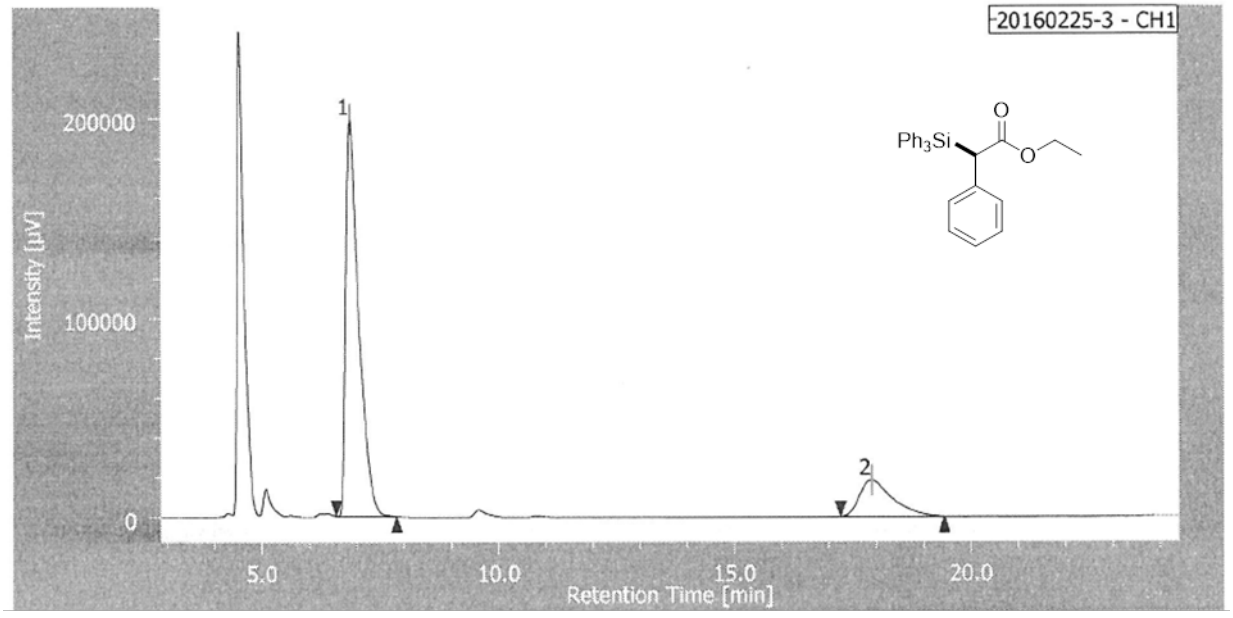
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	14.267	8999624	528932	49.224	52.290
2	16.108	9283309	482607	50.776	47.710



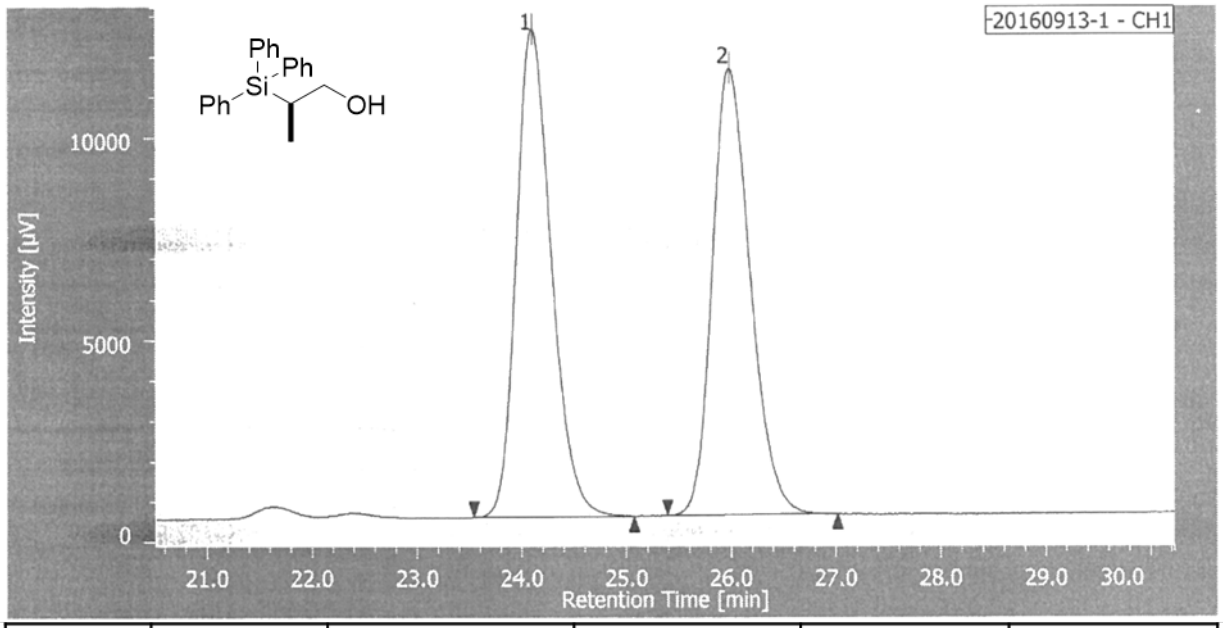
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	14.025	10536798	625347	89.819	90.358
2	15.867	1194375	66727	10.181	9.642



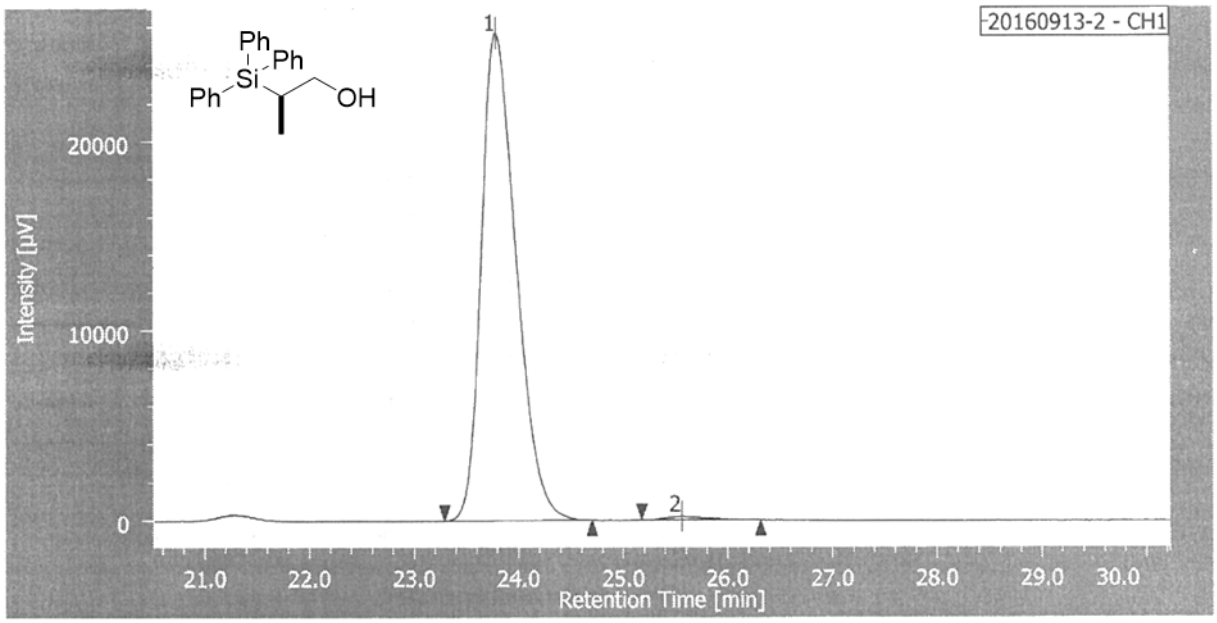
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	6.533	1401680	108716	49.819	78.734
2	17.917	1411887	29364	50.181	21.266



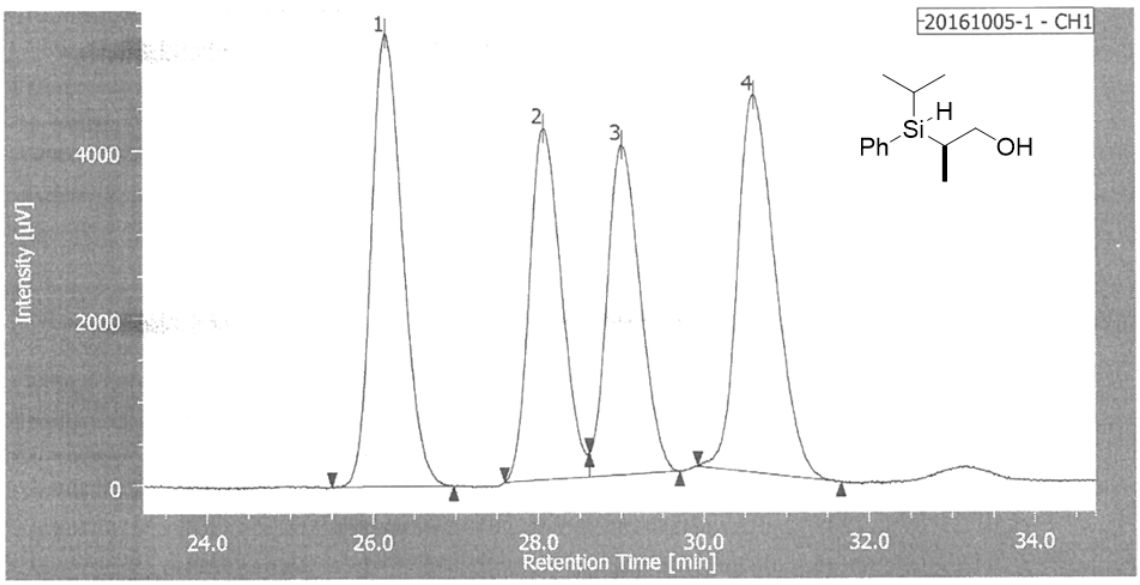
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	6.867	3799493	198828	81.300	91.548
2	17.900	873949	18356	18.700	18.700



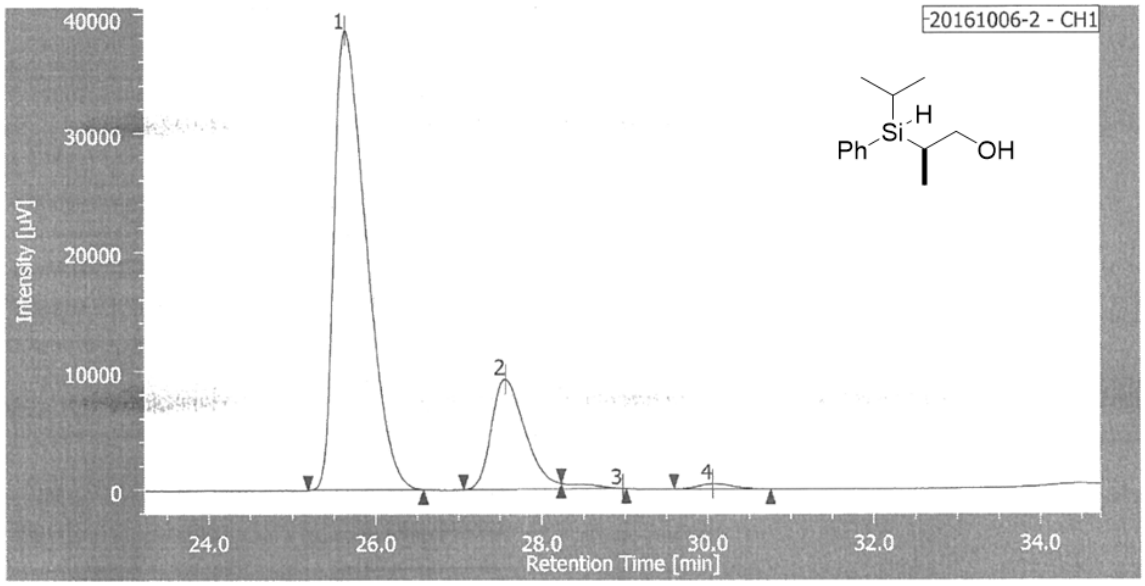
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	24.100	280826	12053	50.119	52.193
2	25.983	279498	11040	49.881	49.807



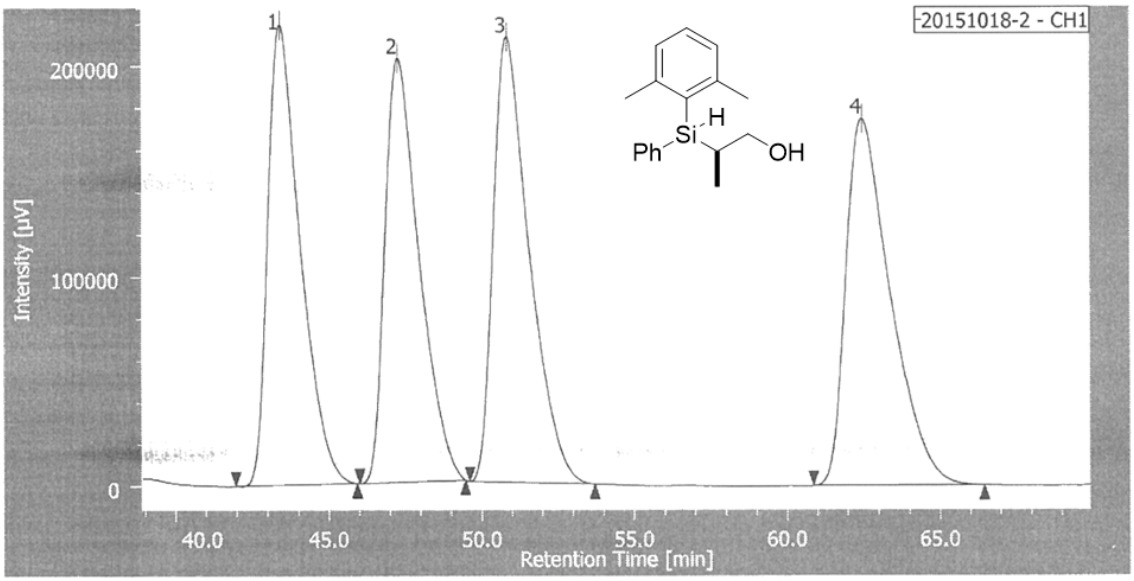
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	23.792	594905	25718	99.187	99.306
2	25.558	4875	180	0.813	0.694



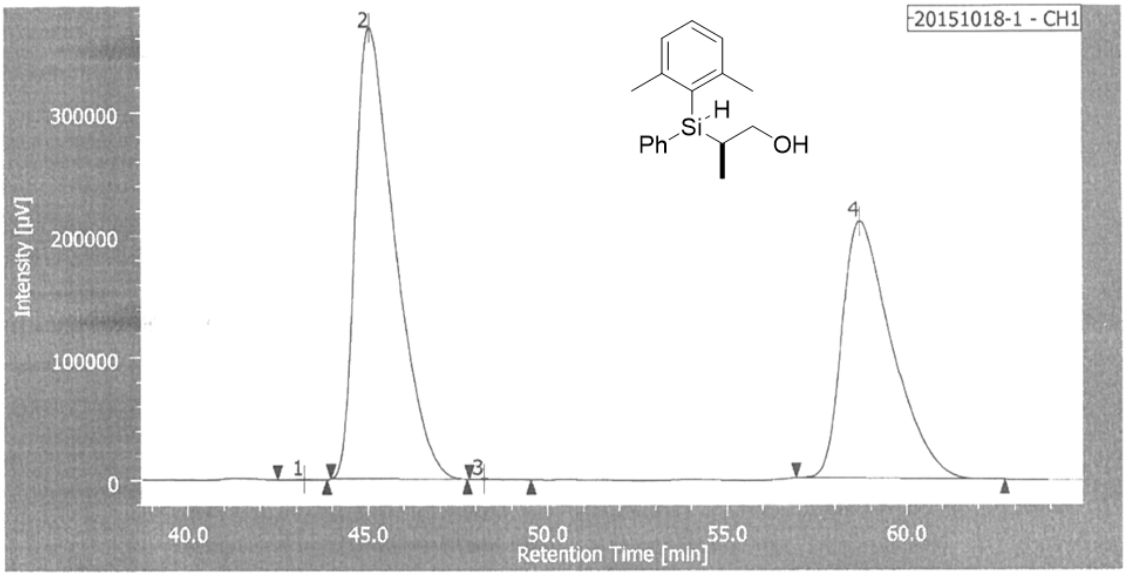
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	26.158	141373	5420	27.822	29.980
2	28.067	113492	4204	22.335	23.254
3	29.017	110044	3947	21.831	21.831
4	30.608	143223	4508	24.936	24.936



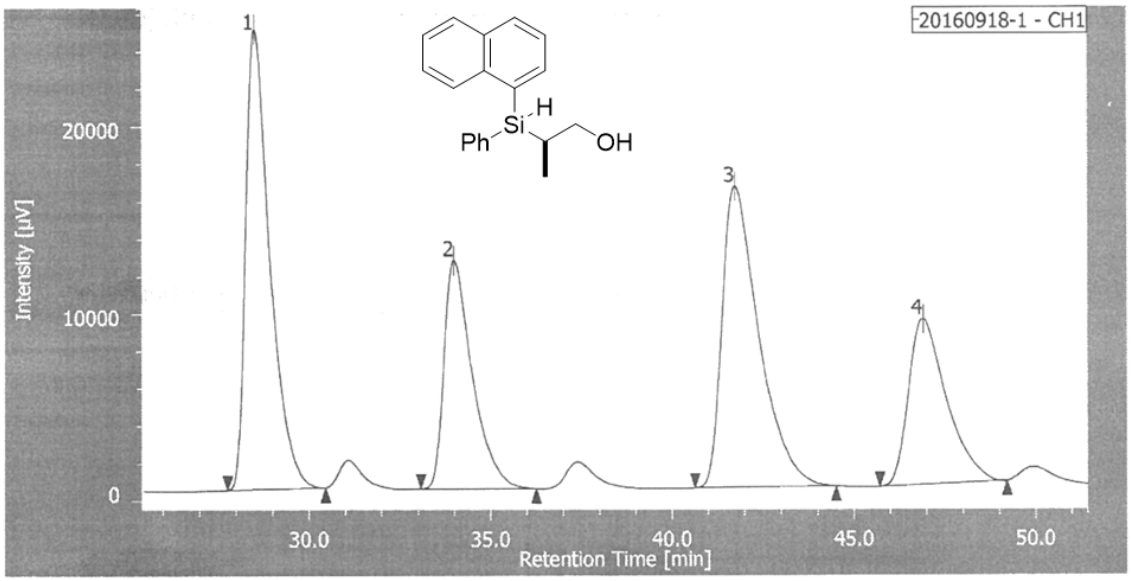
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	25.624	1035084	38648	78.306	79.888
2	27.567	262373	9292	19.850	19.207
3	28.975	11743	1	0.888	0.001
4	30.058	12602	437	0.953	0.904



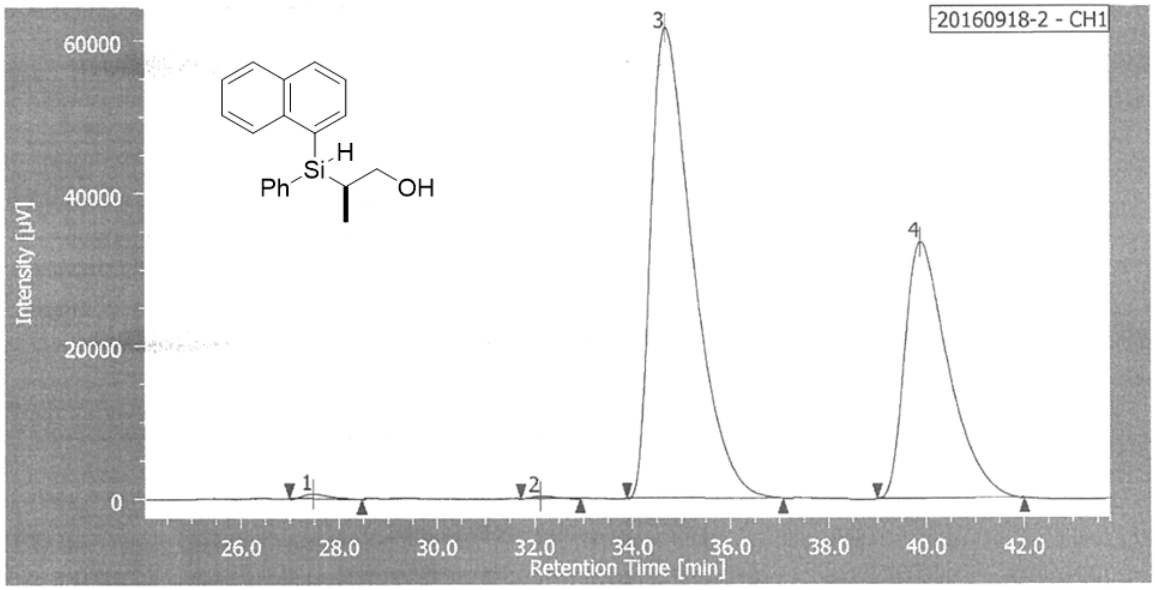
PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	43.408	16137621	218937	24.104	27.121
2	47.250	15743903	201863	23.516	25.006
3	50.825	17363421	211889	25.935	26.248
4	62.458	17703811	174567	26.444	21.625



PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	43.225	12448	397	0.026	0.069
2	45.050	28245553	367478	58.029	63.544
3	48.233	28957	458	0.059	0.079
4	58.700	20387557	209974	41.885	36.308

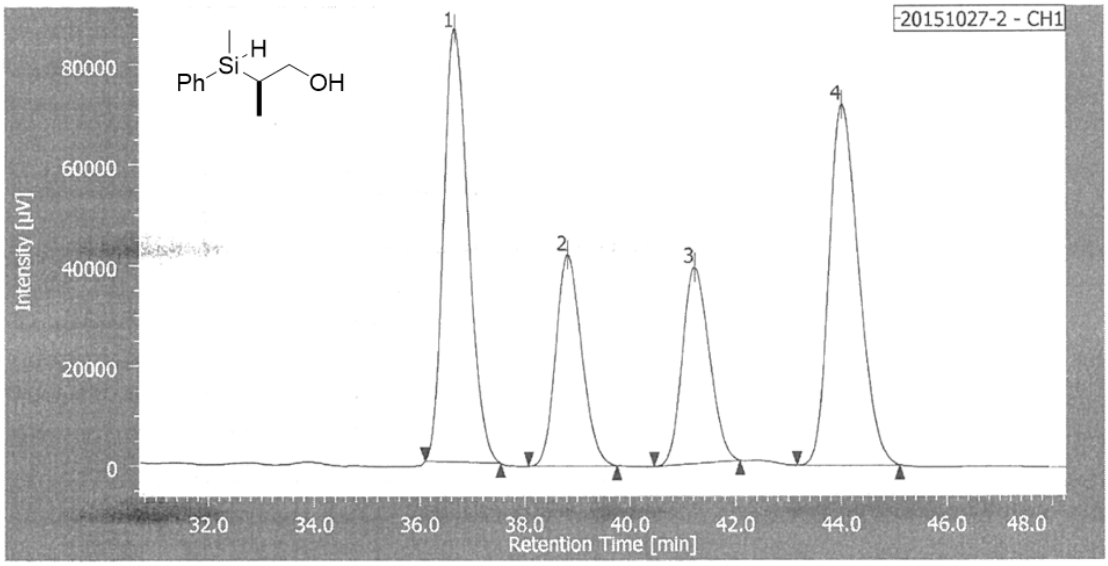


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	28.525	1125041	24584	31.546	39.819
2	34.000	664590	12204	18.635	19.768
3	41.742	1133145	16099	31.773	26.075
4	46.900	643578	8852	18.046	14.338

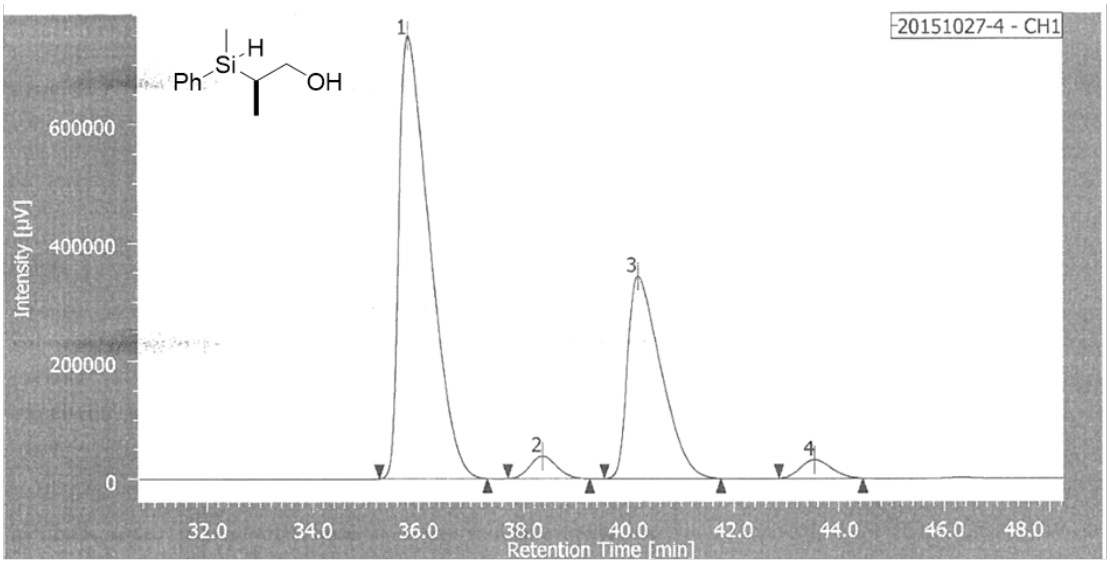


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	27.475	21333	608	0.371	0.633
2	32.108	8974	309	0.156	0.321
3	34.675	3647355	61553	63.468	64.084
4	39.883	2069089	33581	36.005	34.962

Temperature effect (-5 °C)

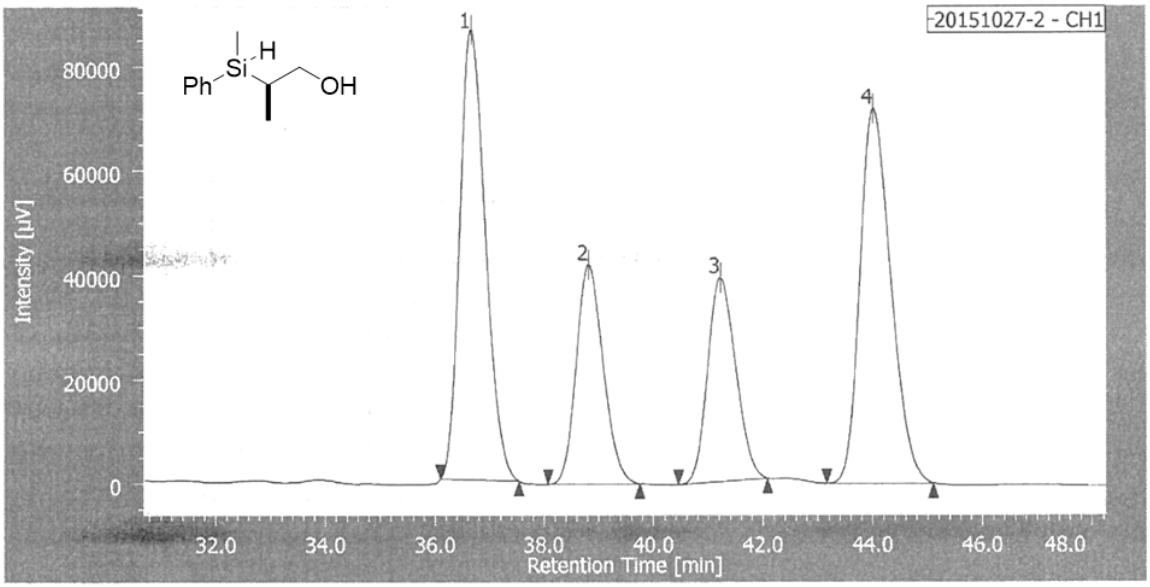


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.667	2813400	86285	33.184	36.038
2	38.817	1447198	42115	17.070	17.590
3	41.225	1400186	39211	16.515	16.377
4	44.008	2817317	71816	33.231	29.995

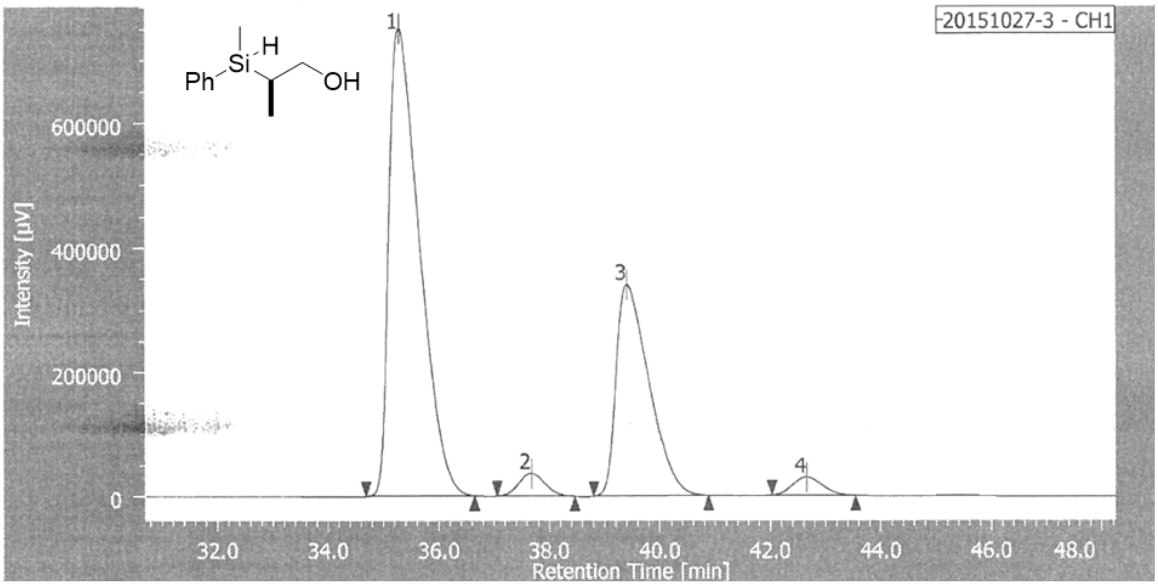


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	35.817	30195384	747198	63.182	64.510
2	38.358	1334580	37858	2.793	3.269
3	40.183	15024010	342304	31.437	29.553
4	43.533	1237039	30908	2.588	2.668

Temperature effect (-10 °C)

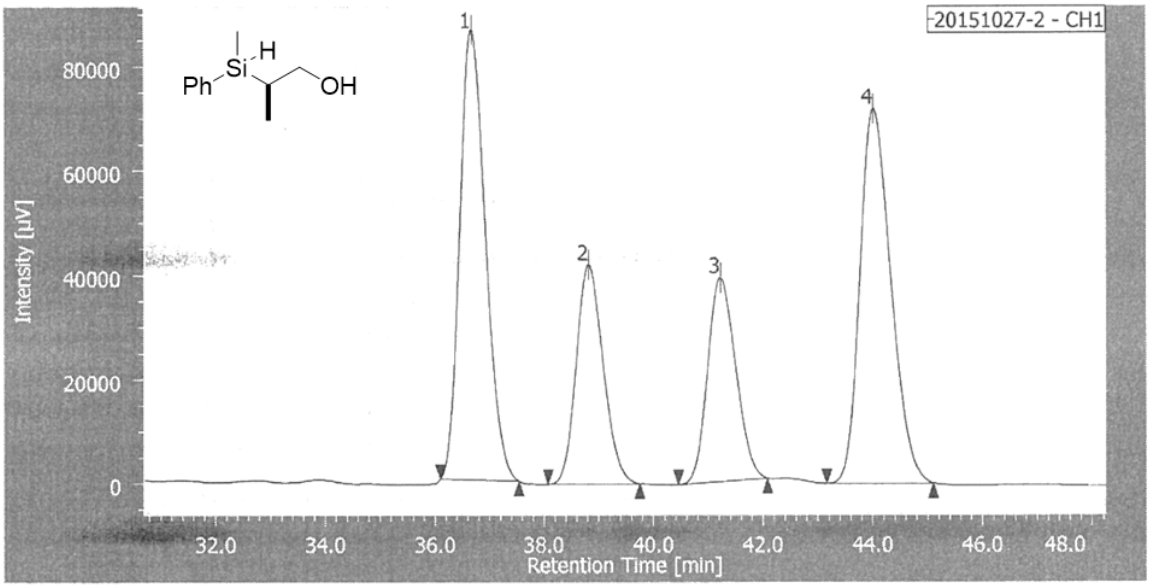


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.667	2813400	86285	33.184	36.038
2	38.817	1447198	42115	17.070	17.590
3	41.225	1400186	39211	16.515	16.377
4	44.008	2817317	71816	33.231	29.995

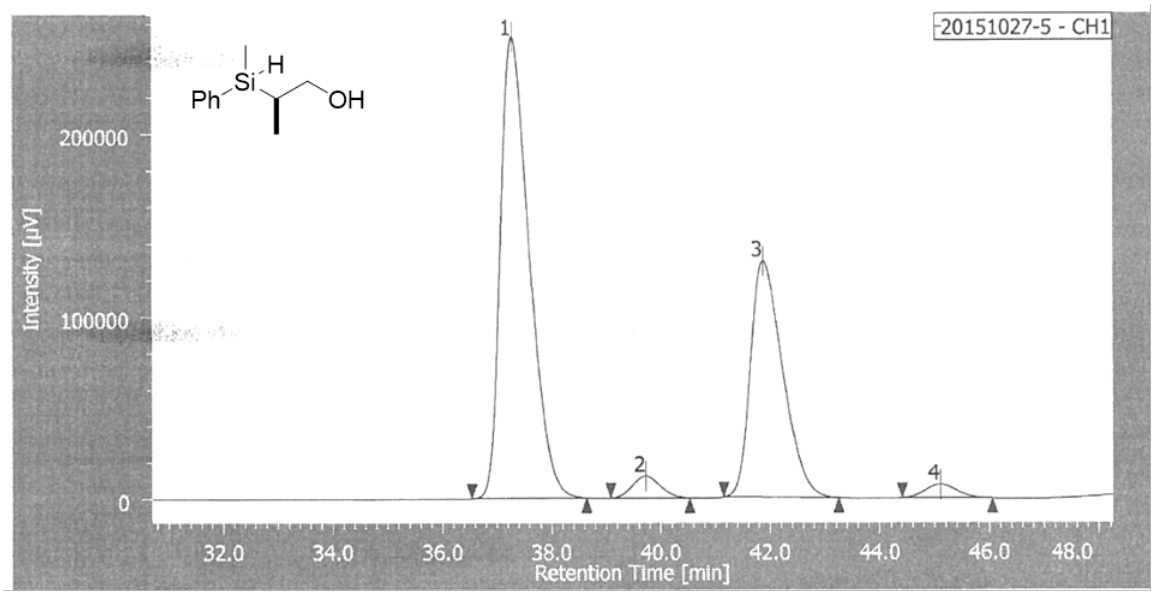


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	35.275	28672984	750944	63.712	64.888
2	37.667	1196990	36476	2.660	3.152
3	39.408	14038291	340673	31.193	29.437
4	42.650	1095925	29197	2.435	2.523

Temperature effect (-30 °C)

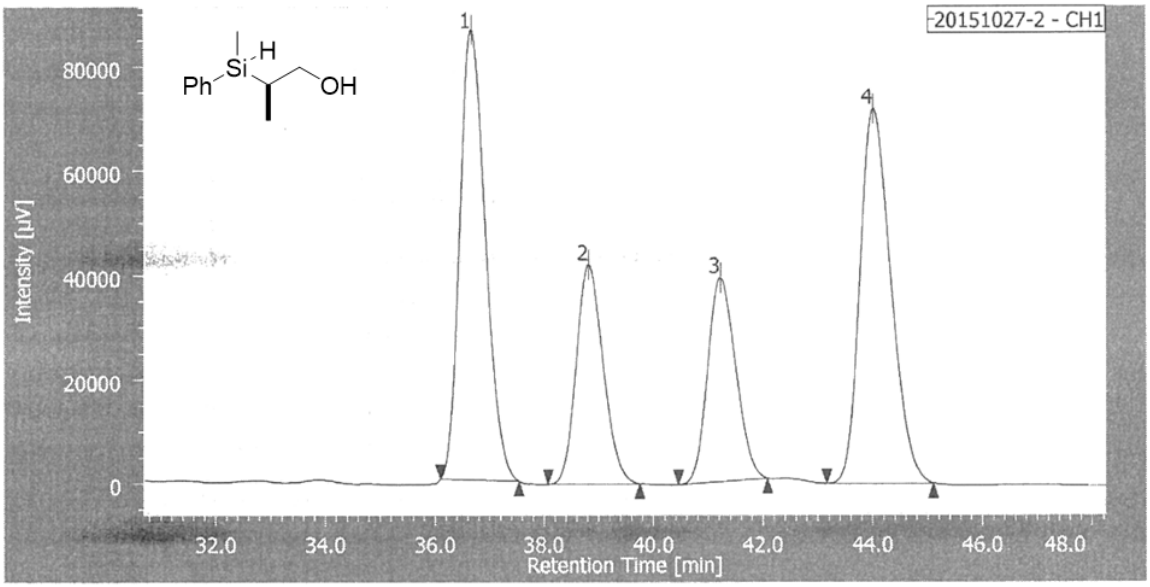


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.667	2813400	86285	33.184	36.038
2	38.817	1447198	42115	17.070	17.590
3	41.225	1400186	39211	16.515	16.377
4	44.008	2817317	71816	33.231	29.995

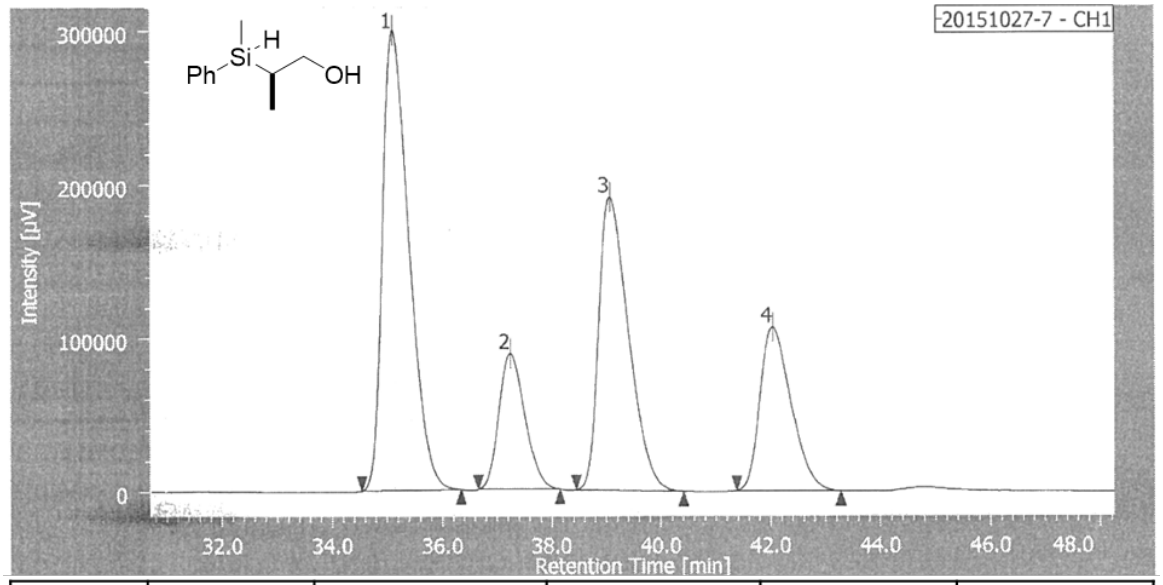


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	37.275	9224996	252308	60.500	62.892
2	39.717	421033	11909	2.761	2.969
3	41.867	5304038	129535	34.785	32.289
4	45.092	297931	7422	1.954	1.850

Substrate screening (from ethyl (2R, 3S)-2-(methyl(phenyl)silyl)propanoate)

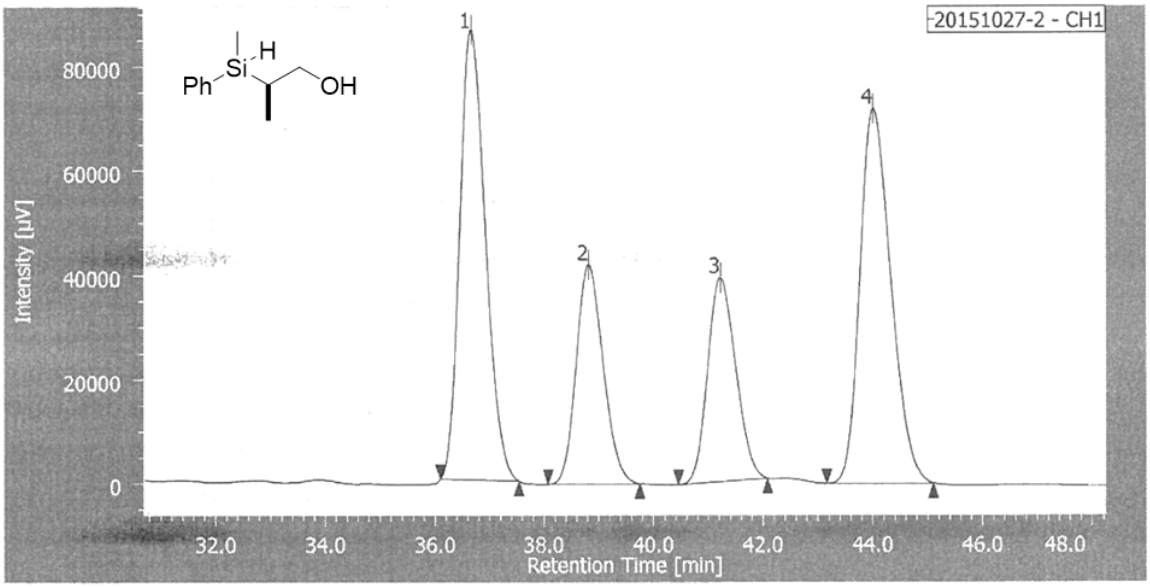


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.667	2813400	86285	33.184	36.038
2	38.817	1447198	42115	17.070	17.590
3	41.225	1400186	39211	16.515	16.377
4	44.008	2817317	71816	33.231	29.995

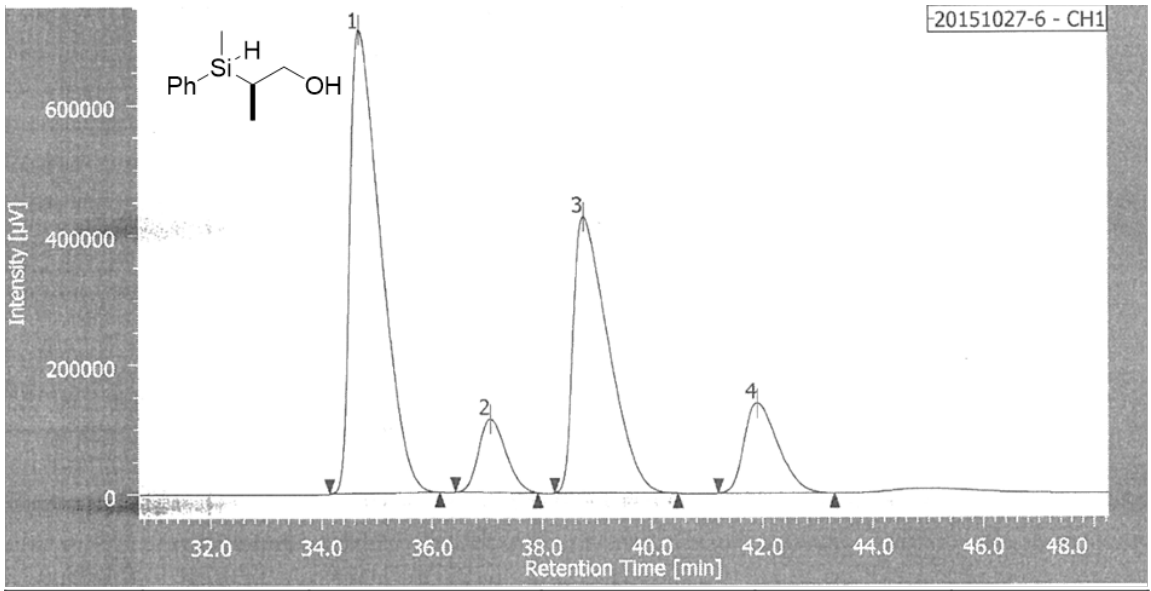


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	35.108	9973805	299491	41.013	43.685
2	37.242	2920294	88391	12.009	12.893
3	39.067	7227860	191035	29.722	27.865
4	42.033	4196426	106656	17.256	15.557

Substrate screening (from tert-butyl (2R, 3S)-2-(methyl(phenyl)silyl)propanoate)

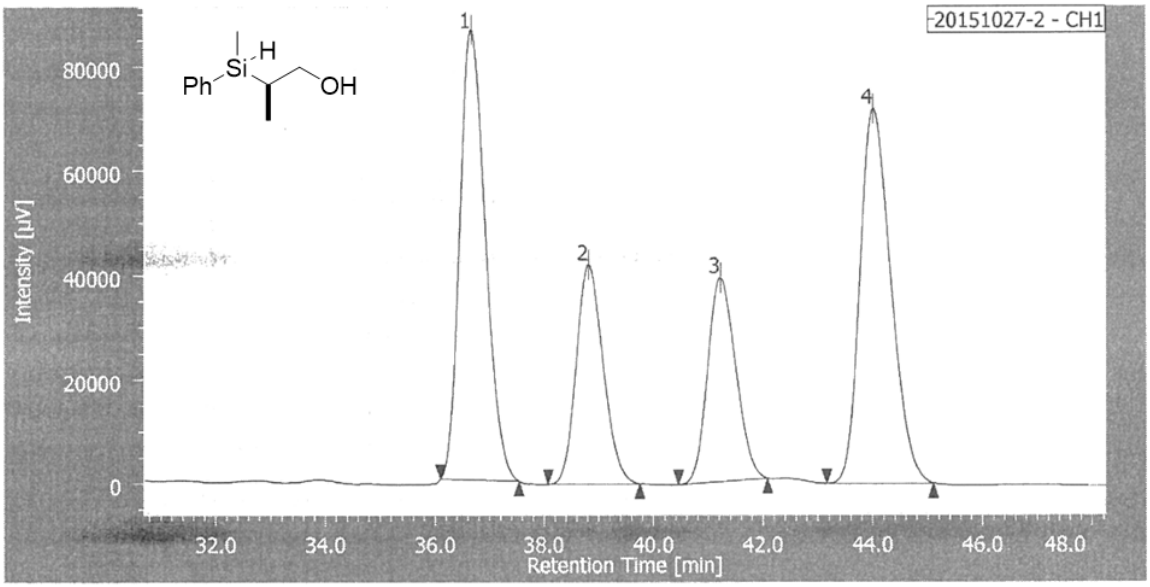


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.667	2813400	86285	33.184	36.038
2	38.817	1447198	42115	17.070	17.590
3	41.225	1400186	39211	16.515	16.377
4	44.008	2817317	71816	33.231	29.995

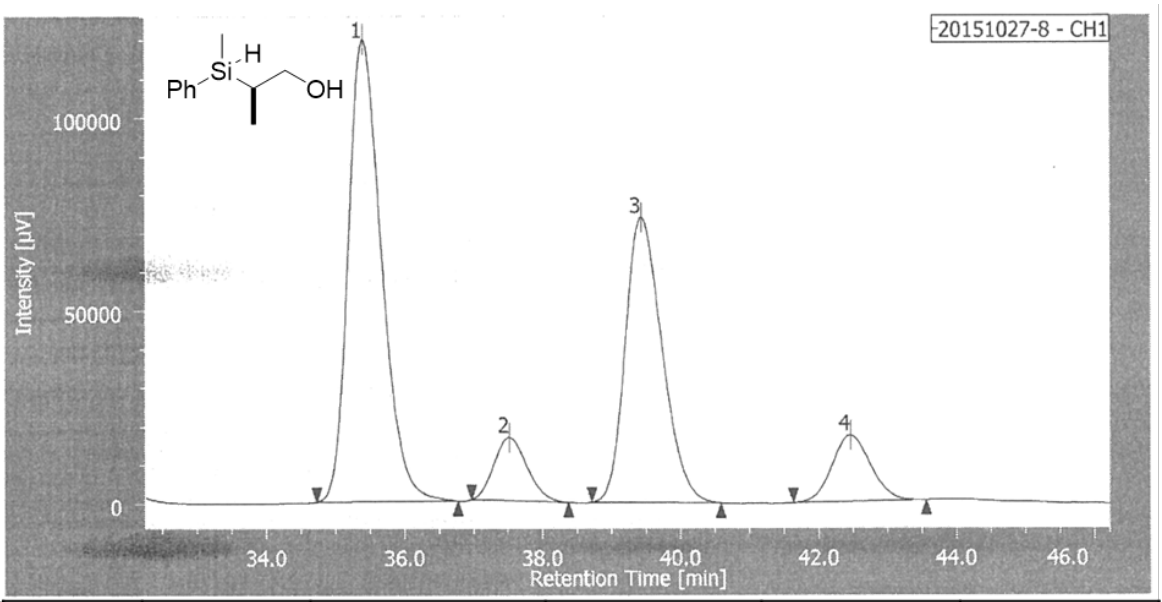


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	34.692	27759104	714719	49.012	51.225
2	37.067	3945322	114016	6.966	8.172
3	38.750	19017697	426683	33.578	30.581
4	41.900	5914687	139836	10.443	10.022

Substrate screening (from benzhydryl (2R, 3S)-2-(methyl(phenyl)silyl)propanoate)

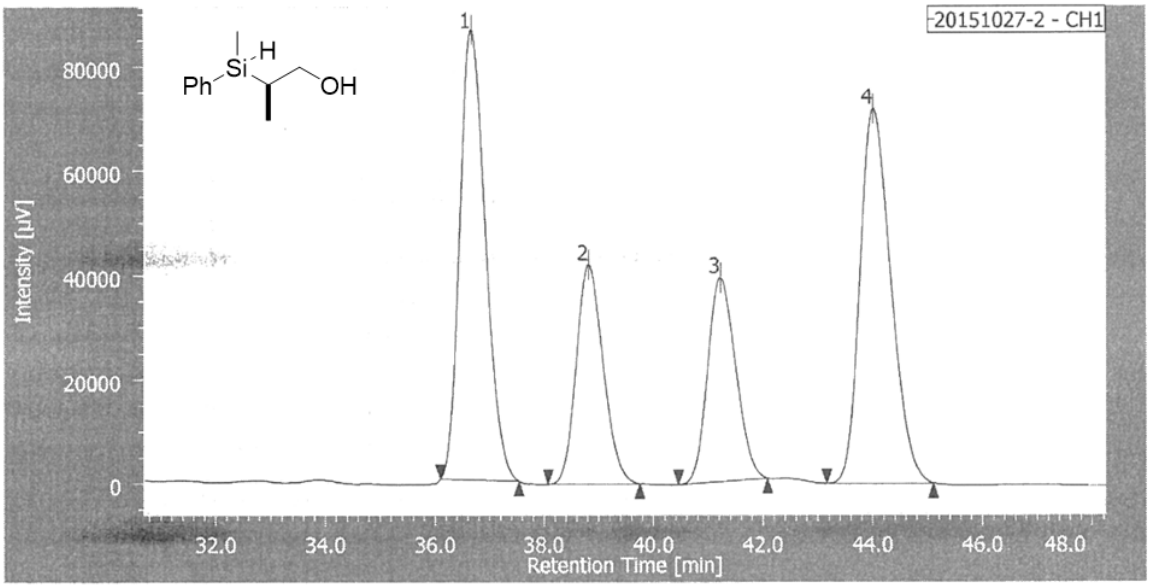


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.667	2813400	86285	33.184	36.038
2	38.817	1447198	42115	17.070	17.590
3	41.225	1400186	39211	16.515	16.377
4	44.008	2817317	71816	33.231	29.995

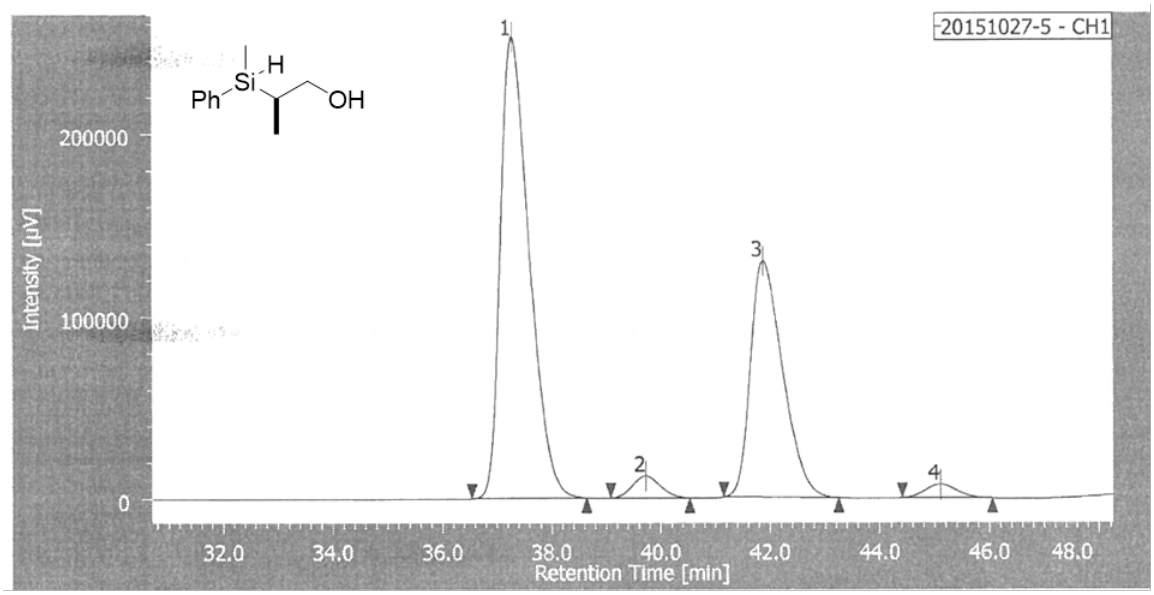


PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	35.400	4009382	119645	50.387	52.651
2	37.525	548814	16450	6.897	7.239
3	39.433	2729895	73880	34.307	32.512
4	42.458	669049	17265	8.408	7.598

Substrate screening (from di(naphthalen-1-yl)methyl (2R, 3S)-2-(methyl(phenyl)silyl)propanoate)



PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	36.667	2813400	86285	33.184	36.038
2	38.817	1447198	42115	17.070	17.590
3	41.225	1400186	39211	16.515	16.377
4	44.008	2817317	71816	33.231	29.995



PEAK	RT [min]	AREA [μV·sec]	HEIGHT [μV]	AREA%	HEIGHT%
1	37.275	9224996	252308	60.500	62.892
2	39.717	421033	11909	2.761	2.969
3	41.867	5304038	129535	34.785	32.289
4	45.092	297931	7422	1.954	1.850

10. References

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