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Supplementary Materials for

Directed evolution of cytochrome c for carbon–silicon bond formation: Bringing silicon to life

S. B. Jennifer Kan, Russell D. Lewis, Kai Chen, Frances H. Arnold*

*Corresponding author. E-mail: frances@cheme.caltech.edu

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I. Materials and Methods

Unless otherwise noted, all chemicals and reagents for chemical reactions were obtained from commercial suppliers (Acros, Arch Bioscience, Fisher Scientific, Sigma-Aldrich, TCI America) and used without further purification. The following proteins were all purchased from Sigma-Aldrich: bovine serum albumin (BSA), cytochrome *c* (from bovine, equine heart and *S. cerevisiae*), peroxidase II (from horseradish), and catalase (from *C. glutamicum*). Silica gel chromatography purifications were carried out using AMD Silica Gel 60, 230-400 mesh. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Prodigy 400 MHz instrument and are internally referenced to the residual solvent peak (chloroform). ^{29}Si NMR spectra were recorded on the same instrument and referenced to tetramethoxysilane (δ −78.9 ppm). Data for ^{1}H NMR are reported in the conventional form: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, br = broad, app = appears as), coupling constant (Hz), integration. Data for ^{13}C and ^{29}Si are reported in terms of chemical shift (δ ppm). High-resolution mass spectra were obtained with a JEOL JMS-600H High Resolution Mass Spectrometer at the California Institute of Technology Mass Spectral Facility. Sonication was performed using a Qsonica Q500 sonicator. Chemical reactions were monitored using thin layer chromatography (Merck 60 silica gel plates) and a UV-lamp for visualization. Gas chromatography (GC) analyses were carried out using a Shimadzu GC-17A gas chromatograph, a FID detector, and J&W HP-5 (30 m x 0.32 mm, 0.25 μm film; 90 °C hold 1 min, 90 to 110 °C at 15 °C/min, 110 to 280 °C at 60 °C/min, 280 °C hold 1 min, 6.2 min total). Analytical chiral supercritical fluid chromatography (SFC) was performed with a JACSO 2000 series instrument using *i*-PrOH and supercritical CO_2 as the mobile phase, with visualization at 210 nm. The following chiral columns were used: Daicel Chiralpak IC, Chiralpak AD-H, or Chiralcel OD-H (4.6 mm x 25 cm).

Plasmid pET22 was used as a cloning vector, and cloning was performed using Gibson assembly (*31*). The cytochrome *c* maturation plasmid pEC86 (*32*) was used as part of a two-plasmid system to express prokaryotic cytochrome *c* proteins. Cells were grown using Luria-Bertani medium or HyperBroth (AthenaES) with 100 μg/mL ampicillin and 20 μg/mL chloramphenicol ($LB_{amp/chlor}$ or $HB_{amp/chlor}$). Cells without the pEC86 plasmid were grown with 100 μg/mL ampicillin (LB_{amp} or HB_{amp}). Primer sequences are available upon request. Electrocompetent *Escherichia coli* cells were prepared following the protocol of Sambrook *et al.* (*33*). T5 exonuclease, Phusion polymerase, and *Taq* ligase were purchased from New England Biolabs (NEB, Ipswich, MA). M9-N minimal medium (abbreviated as M9-N buffer; pH 7.4) was used as a buffering system for whole cells, lysates, and purified proteins, unless otherwise specified. M9-N buffer was used without a carbon source; it contains 47.7 mM Na_2HPO_4, 22.0 mM KH_2PO_4, 8.6 mM NaCl, 2.0 mM $MgSO_4$, and 0.1 mM $CaCl_2$.

II. General Procedures

(A) Plasmid construction. All variants described in this paper were cloned and expressed using the pET22(b)+ vector (Novagen). The gene encoding *Rma* cyt *c* (UNIPROT ID B3FQS5) was obtained as a single gBlock (IDT), codon-optimized for *E. coli*, and cloned using Gibson assembly (*31*) into pET22(b)+ (Novagen) between restriction sites *Nde*I and *Xho*I in frame with an *N*-terminal pelB leader sequence (to ensure periplasmic localization and proper maturation; MKYLLPTAAAGLLLLAAQPA MA) and a *C*-terminal 6xHis-tag. This plasmid was co-transformed with the cytochrome *c* maturation plasmid pEC86 (*32*) into *E. cloni*® EXPRESS BL21(DE3) cells (Lucigen).

(B) Cytochrome *c* expression and purification. Purified cytochrome *c* proteins were prepared as follows. One liter $HB_{amp/chlor}$ in a 4 L flask was inoculated with an overnight culture (20 mL, $LB_{amp/chlor}$) of recombinant *E. cloni*® EXPRESS BL21(DE3) cells containing a pET22(b)+ plasmid encoding the cytochrome *c* variant, and the pEC86 plasmid. The culture was shaken at 37 °C and 200 rpm (no humidity control) until the OD_{600} was 0.7 (approximately 3 hours). The culture was placed on ice for 30 minutes, and isopropyl β-D-1-thiogalactopyranoside (IPTG) and 5-aminolevulinic acid (ALA) were added to final concentrations of 20 μM and 200 μM respectively.

The incubator temperature was reduced to 20 °C, and the culture was allowed to shake for 20 hours at 200 rpm. Cells were harvested by centrifugation (4 °C, 15 min, 4,000xg), and the cell pellet was stored at –20 °C until further use (at least 24 hours). The cell pellet was resuspended in buffer containing 100 mM NaCl, 20 mM imidazole, and 20 mM Tris-HCl buffer (pH 7.5 at 25 °C) and cells were lysed by sonication (2 minutes, 2 seconds on, 2 seconds off, 40% duty cycle; Qsonica Q500 sonicator). Cell lysate was placed in a 75 °C heat bath for 10 minutes, and cell debris was removed by centrifugation for 20 min (5000xg, 4 °C). Supernatant was sterile filtered through a 0.45 μm cellulose acetate filter and purified using a 1 mL Ni-NTA column (HisTrap HP, GE Healthcare, Piscataway, NJ) using an AKTA purifier FPLC system (GE healthcare). The cytochrome *c* protein was eluted from the column by running a gradient from 20 to 500 mM imidazole over 10 column volumes.

The purity of the collected cytochrome *c* fractions was analyzed using sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE). Pure fractions were pooled and concentrated using a 3 kDa molecular weight cut-off centrifugal filter and dialyzed overnight into 0.05 M phosphate buffer (pH = 7.5) using 3 kDa molecular weight cut-off dialysis tubing. The dialyzed protein was concentrated again, flash-frozen on dry ice, and stored at –20 °C.

The concentration of cytochrome *c* was determined in triplicate using the ferrous assay described in section (E).

(C) P450 and globin expression and purification. Purified P450s and globins were prepared differently from the cytochrome *c* proteins, and described as follows. One liter HB_{amp} in a 4 L flask was inoculated with an overnight culture (20 mL, LB_{amp}) of recombinant *E. cloni*® EXPRESS BL21(DE3) cells containing a pET22(b)+ plasmid encoding the P450 or globin variant. The culture was shaken at 37 °C and 200 rpm (no humidity control) until the OD_{600} was 0.7 (approximately 3 hours). The culture was

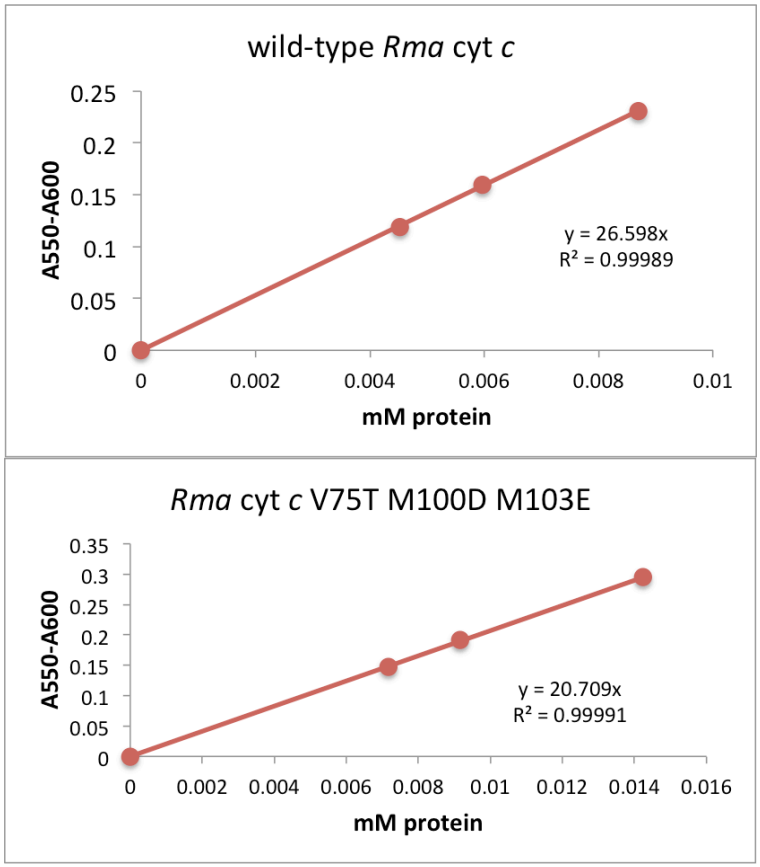
placed on ice for 30 minutes, and IPTG and 5-ALA were added to final concentrations of 0.5 mM and 1 mM, respectively. The incubator temperature was reduced to 20 °C, and the culture was allowed to shake for 20 hours at 200 rpm. Cells were harvested by centrifugation (4 °C, 15 min, 4,000xg), and the cell pellet was stored at –20 °C until further use (at least 24 hours). The cell pellet was resuspended in buffer containing 100 mM NaCl, 20 mM imidazole, and 20 mM Tris-HCl buffer (pH 7.5 at 25 °C). Hemin (30 mg/mL, 0.1 M NaOH; Frontier Scientific) was added to the resuspended cells such that 1 mg of hemin was added for every 1 gram of cell pellet. Cells were lysed by sonication (2 minutes, 1 seconds on, 2 seconds off, 40% duty cycle; Qsonica Q500 sonicator). Cell debris was removed by centrifugation for 20 min (27,000xg, 4 °C). Supernatant was sterile filtered through a 0.45 μm cellulose acetate filter, and purified using a 1 mL Ni-NTA column (HisTrap HP, GE Healthcare, Piscataway, NJ) using an AKTA purifier FPLC system (GE healthcare). The P450 and globin proteins were eluted from the column by running a gradient from 20 to 500 mM imidazole over 10 column volumes.

The purity of the collected protein fractions was analyzed using SDS-PAGE. Pure fractions were pooled and concentrated using a 10 kDa molecular weight cut-off centrifugal filter and buffer-exchanged with 0.1 M phosphate buffer (pH = 8.0). The purified protein was flash-frozen on dry ice and stored at –20 °C.

P450 and globin concentrations were determined in triplicate using the hemochrome assay described in section (D).

(D) Hemochrome assay. A solution of sodium dithionite (10 mg/mL) was prepared in M9-N buffer. Separately, a solution of 1 M NaOH (0.4 mL) was mixed with pyridine (1 mL), followed by centrifugation (10,000xg, 30 seconds) to separate the excess aqueous layer gave a pyridine-NaOH solution. To a cuvette containing 700 μL protein solution (purified protein or heat-treated lysate) in M9-N buffer, 50 μL of dithionite solution and 250 μL pyridine-NaOH solution were added. The cuvette was sealed with Parafilm, and the UV-Vis spectrum was recorded immediately. Cytochrome *c* concentration was determined using $\varepsilon_{550\text{-}535}$ = 22.1 $mM^{-1}cm^{-1}$ (*34*). Protein concentrations determined by the hemochrome assay were in agreement with that determined by the bicinchoninic acid (BCA) assay (Thermo Fisher) using bovine serum albumin (BSA) for standard curve preparation.

(E) Ferrous assay. To a cuvette containing 700 μL protein solution in M9-N buffer was added 50 μL of dithionite solution (10 mg/mL in M9-N buffer). The cuvette was sealed with Parafilm, and the UV-Vis spectrum was recorded immediately. The absorbance value for the peak at 550 nm was recorded, and background absorbance at 600 nm was subtracted. Using the protein concentration as determined by the hemochrome assay, ferrous $\varepsilon_{550\text{-}600}$ was determined to be 27 $mM^{-1}cm^{-1}$ for wild-type *Rma* cyt *c*, and 21 $mM^{-1}cm^{-1}$ for *Rma* V75T M100D M103E (see calibration curves shown on the following page). Concentrations of *Rma* M100D and V75T M100D were determined using the extinction coefficient calculated for V75T M100D M103E.



(F) Library construction. Cytochrome *c* site-saturation mutagenesis libraries were generated using a modified version of the 22-codon site-saturation method (*35*). For each site-saturation library, oligonucleotides were ordered such that the coding strand contained the degenerate codon NDT, VHG or TGG. The reverse complements of these primers were also ordered. The three forward primers were mixed together in a 12:9:1 ratio, (NDT:VHG:TGG) and the three reverse primers were mixed similarly. Two PCRs were performed, pairing the mixture of forward primers with a pET22(b)+ internal reverse primer, and the mixture of reverse primers with a pET22b internal forward primer. The two PCR products were gel purified, ligated together using Gibson assembly (*31*), and transformed into *E. cloni*® EXPRESS BL21(DE3) cells. Primer sequences are available upon request.

(G) Enzyme library screening. Single colonies were picked with toothpicks off of $LB_{amp/chlor}$ agar plates, and grown in deep-well (2 mL) 96-well plates containing $LB_{amp/chlor}$ (400 µL) at 37 °C, 250 rpm shaking, and 80% relative humidity overnight. After 16 hours, 30 µL aliquots of these overnight cultures were transferred to deep-well 96-well plates containing $HB_{amp/chlor}$ (1 mL) using a 12-channel EDP3-Plus 5-50 µL pipette (Rainin). Glycerol stocks of the libraries were prepared by mixing cells in $LB_{amp/chlor}$ (100 µL) with 50% v/v glycerol (100 µL). Glycerol stocks were stored at –78 °C in 96-well microplates. Growth plates were allowed to shake for 3 hours at 37 °C, 250 rpm shaking, and 80% relative humidity. The plates were then placed on ice for 30 min. Cultures were

induced by adding 10 μL of a solution, prepared in sterile deionized water, containing 2 mM isopropyl β-D-1-thiogalactopyranoside (IPTG) and 20 mM ALA. The incubator temperature was reduced to 20 °C, and the induced cultures were allowed to shake for 20 hours (250 rpm, no humidity control). Cells were pelleted (4,000xg, 5 min, 4 °C) and resuspended in 500 μL M9-N buffer. For cell lysis, plates were placed in a 75 °C water bath for 10 min, followed by centrifugation (4,000xg, 5 min, 4 °C) to remove cell debris. The resulting heat-treated lysates (340 μL) were then transferred to deep-well plates for biocatalytic reactions. In an anaerobic chamber, to deep-well plates of heat-treated lysates were added $Na_2S_2O_4$ (40 μL per well, 100 mM in dH_2O), $PhMe_2SiH$ (10 μL per well, 400 mM in MeCN) and Me-EDA (10 μL per well, 400 mM in MeCN). The plates were sealed with aluminum sealing tape, removed from the anaerobic chamber, and shaken at 400 rpm for 1.5 h. After quenching with cyclohexane (1 mL), internal standard was added (20 μL of 20 mM methyl 2-phenylacetate in cyclohexane) and the reaction mixtures were pipetted up and down to thoroughly mix the organic and aqueous layers. The plates were centrifuged (4,000xg, 5 min) and the organic layer (400 μL) was transferred to shallow-well 96-well plates for SFC analysis. Hits from library screening were confirmed by small-scale biocatalytic reactions, which were analyzed by GC and SFC for accurate determination of turnovers and enantioselectivities.

(H) Protein lysate preparation. Protein lysates for biocatalytic reactions were prepared as follow: *E. coli* cells expressing *Rma* cyt *c* variant were pelleted (4,000xg, 5 min, 4 °C), resuspended in M9-N buffer and adjusted to the appropriate OD_{600}. The whole-cell solution was heat-treated (75 °C for 10 min) then centrifuged (14,000xg, 10 min, 4 °C) to remove cell debris. The supernatant was sterile filtered through a 0.45 μm cellulose acetate filter into a 6 mL crimp vial, crimp sealed, and the head space of the crimp vial was degassed by bubbling argon through for at least 10 min. The concentration of cytochrome *c* protein lysate was determined using the ferrous assay described in section (E). Using this protocol, the protein concentrations we typically observed for OD_{600} = 15 lysates are in the 8-15 μM range for wild-type *Rma* cyt *c* and 2-10 μM for other *Rma* cyt *c* variants.

(I) Small-scale biocatalytic reaction. In an anaerobic chamber, protein lysate (340 μL) in a 2 mL crimp vial was added 40 μL $Na_2S_2O_4$ (100 mM in dH_2O), 10 μL $PhMe_2SiH$ (400 or 800 mM in MeCN) and 10 μL Me-EDA (400 mM in MeCN). The vial was crimp sealed, removed from the anaerobic chamber, and shaken at 400 rpm at room temperature for the stated reaction time. At the end of the reaction, the crimp vial was opened and the reaction was quenched with cyclohexane (1 mL). Internal standard was added (20 μL of 20 mM 2-phenylethanol in cyclohexane) and the reaction mixture was transferred to a microcentrifuge tube, vortexed (10 seconds, 3 times), then centrifuged (14,000xg, 5 min) to completely separate the organic and aqueous layers (the vortex-centrifugation step was repeated if complete phase separation was not achieved). The organic layer (750 μL) was removed for GC and SFC analysis. All biocatalytic reactions were performed in triplicate unless otherwise stated. The total turnover numbers (TTNs) reported are calculated with respect to the protein catalyst and represent the total number of turnovers that is possible to obtain from the catalyst under the stated reaction conditions.

III. Supporting Tables and Figures

Table S1. Summary of known catalytic systems for enantioselective carbene insertion into silicon–hydrogen bonds

Chiral catalytic system	Ref	Reaction condition	Substrate scope	TTN	% *ee*
Copper					
A	(*15*)	CH_2Cl_2, rt, 18 h	4	17 to 25	17 to 98
B	(*36*)	C_6H_6, 0 °C, 13.5 h	1	8 to 10	29 to 78
C	(*14*)	CH_2Cl_2, −60 to 0 °C, 2-12 h	24	3 to 19	12 to 99
B	(*37*)	CH_2Cl_2, −40 to 0 °C, 48-72 h	8	5 to 9	49 to 88
B	(*38*)	CH_2Cl_2, −40 to −10 °C	9	5 to 8	40 to 84
Iridium					
D	(*13*)	CH_2Cl_2, −78 or −30 °C, 24 h	15	24 to 50	94 to 99
E	(*39*)	CH_2Cl_2, −78 °C, 24 h	7	75 to 94	72 to 91
Rhodium					
F	(*12*)	CH_2Cl_2, rt to 40 °C, 6-12 h	34	9 to 30	77 to 99
G	(*40*)	CH_2Cl_2, −78 °C or rt, 3-12 h	5	8 to 45	20 to 63
H	(*36*)	C_5H_{12}, −78 to −75 °C, 24 h	1	24 to 70	48 to 97
I	(*11*)	CF_3CH_2OH, −35 °C	10	51 to 97	20 to 99
H	(*41*)	CH_2Cl_2, −78 °C then rt, 23 h	6	22 to 54	77 to 94
various Rh(II)-carboxylate	(*42*) (*43*)	CH_2Cl_2, rt or −78 °C, 0.5 to 24 h to overnight	6	<1 to 23	6 to 76
J	(*44*)	CH_2Cl_2, −78 °C to rt, 23 h	2	35 to 40	38 to 58
H	(*45*)	CH_2Cl_2, −78 °C, 1 to 1.5 h	4	34 to 43	35 to 72
H	(*46*)	C_5H_{12}, −78 °C, 24 h	5	13 to 19	75 to 95
various Rh(II)-carboxylate	(*47*)	CH_2Cl_2, rt or reflux	1	8 to 17	6 to 47

Catalytic systems that could yield enantiopure products are highlighted in blue. rt = room temperature. In cases where the reaction times were not documented in the original literature, this information is not shown in the table above.

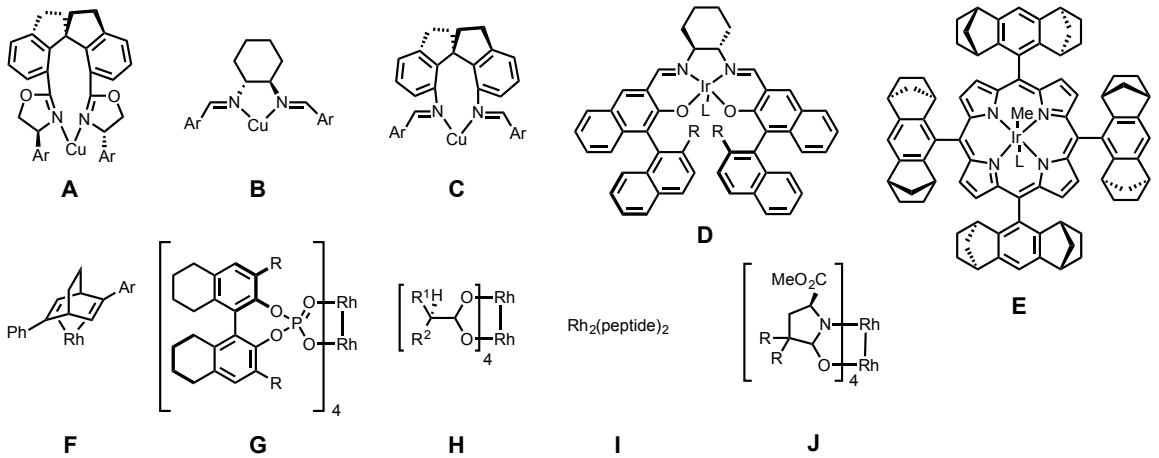


Table S2. Summary of known catalytic systems that accept α-alkyl diazo compounds as substrates for enantioselective carbene insertion into silicon–hydrogen bonds

α-Alkyl diazo compounds are challenging substrates for intermolecular carbene-transfer chemistry due to their propensity to undergo competing intramolecular β-hydride migration (*48*, *13*). As a result, only a subset of catalytic systems shown in Table S1 have been reported to accommodate these substrates, as summarized in the table below:

Chiral catalytic system	Ref	Reaction condition	Substrate scope	TTN	% *ee*
Copper					
A	(*15*)	CH_2Cl_2, rt, 18 h	4	17 to 25	17 to 98
C	(*14*)	CH_2Cl_2, −40 °C, 2-12 h	2	3 to 12	12 to 35
Iridium					
D	(*13*)	CH_2Cl_2, −78 °C, 24 h	8	24 to 44	94 to 99
Rhodium					
F	(*12*)	CH_2Cl_2, rt to 40 °C, 6-12 h	2	11 to 15	70 to 77
I	(*11*)	CF_3CH_2OH, −35 °C	1	n.d.[§]	64
H	(*41*)	CH_2Cl_2, −78 °C then rt, 23 h	5	22 to 54	77 to 94

See Table S1 for chemical structures of chiral catalysts. rt = room temperature. [§] The amount of product formed was not reported in the original literature.

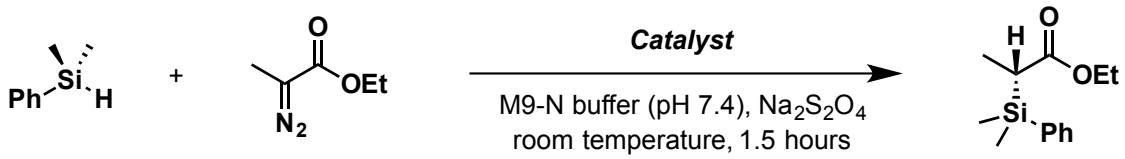
Table S3. Summary of known catalytic systems for reaction between phenyldimethylsilane and Me-EDA *via* enantioselective carbene insertion into silicon–hydrogen bond

1 **2** **3**

Chiral catalytic system	Ref	Reaction condition	TTN	% *ee*
Copper				
C	(*14*)	CH_2Cl_2, −40 °C, 2-12 h	12	35
Iridium				
D	(*13*)	CH_2Cl_2, −78 °C, 24 h	43	97
Rhodium				
F	(*12*)	CH_2Cl_2, rt to 40 °C, 6-12 h	15	77

See Table S1 for chemical structures of chiral catalysts. rt = room temperature.

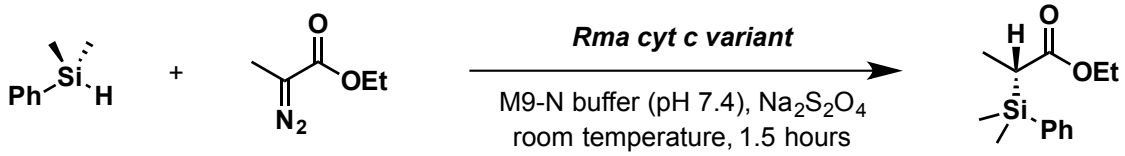
Table S4. Preliminary experiments with heme and purified heme proteins



Catalyst	TTN	% *ee*
Controls		
None	0	-
Hemin	4 ± 1	0
Hemin + BSA	1 ± 1	0
P450s		
BM3 P450 T268A (*22*)	44 ± 15	0
BM3 P450 T268A C400H (*49*)	45 ± 3	<5
BM3 P450 CIS I263F C400S T438S *(50)*	24 ± 9	<5
BM3 P450 F87A T268A C400S (*51*)	40 ± 15	<5
BM3 P450 Hstar H92N H100N (*52*)	46 ± 7	0
Myoglobins		
Sperm whale Mb	12 ± 1	0
Sperm whale Mb H64V V68A (*53*)	17 ± 1	0
Cytochromes *c*		
Horse heart cyt *c*	31 ± 10	<5
Bovine heart cyt *c*	54 ± 2	6
S. cerevisiae cyt *c*	11 ± 1	<5
R. marinus* cyt *c	**34 ± 10**	**97**
H. thermophilus cyt *c*	8 ± 2	16
R. globiformis cyt *c*	4 ± 1	<5
Others		
Horse radish peroxidase	0	-
C. glutamicum catalase	0	-

Heme proteins that are available commercially or in our laboratory inventory were screened to identify the most enantioselective protein variant as starting point for directed evolution. Experiments with heme proteins were performed using 10 μM purified heme protein, 10 mM silane, 10 mM diazo ester, 10 mM $Na_2S_2O_4$, 5 vol% MeCN, M9-N buffer at room temperature under anaerobic conditions for 1.5 h. Experiments with hemin were performed using 100 μM hemin. Experiments with hemin and BSA were performed using 100 μM hemin in the presence of BSA (0.75 mg/mL). Reactions were performed in triplicate. TTNs reported are the average of three experiments. Within instrument detection limit, variability in % *ee* was not observed. Unreacted starting materials were observed at the end of all reactions and no attempt was made to optimize these reactions.

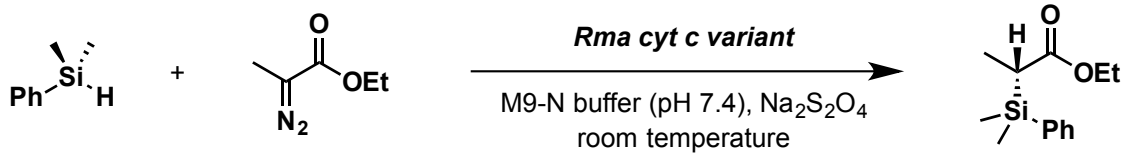
Table S5. Carbon–silicon bond formation catalyzed by *Rma* cyt *c* variants



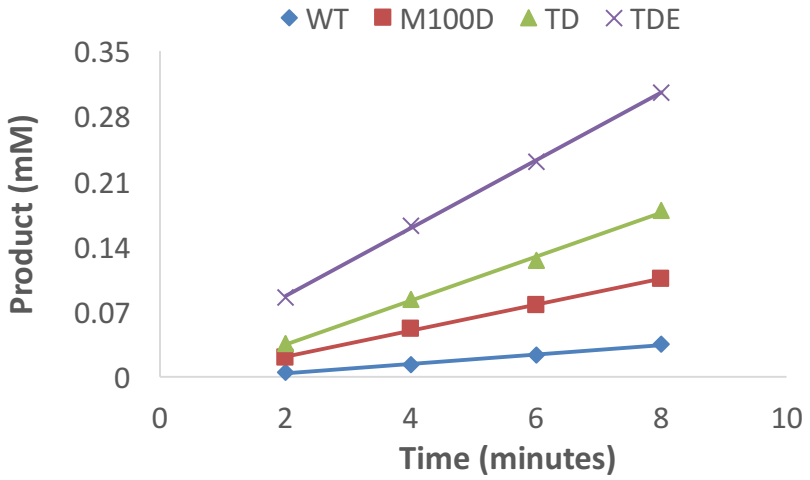
Rma cyt *c*	TTN
WT	**44 ± 27**
M100D	**549 ± 24**
V75T	150 ± 48
M103E	70 ± 21
V75T M100D	**892 ± 20**
V75T M100E	154 ± 37
M100D M103E	520 ± 88
V75T M100D M103E	**1518 ± 51**

Experiments were performed using lysates of *E. coli* expressing *Rma* cyt *c* variant (OD_{600} = 15; heat-treated at 75 °C for 10 min), 10 mM silane, 10 mM diazo ester, 10 mM $Na_2S_2O_4$, 5 vol% MeCN, M9-N buffer at room temperature under anaerobic conditions for 1.5 h. Reactions were performed in triplicate. TTNs reported are the average of three experiments.

Table S6. Comparison of carbon–silicon bond forming rates of four generations of *Rma* cyt *c*



To determine the initial reaction rate, experiments were performed using purified *Rma* cyt *c* variant (0.8 μM), 10 mM silane, 10 mM diazo ester, 10 mM $Na_2S_2O_4$, 5 vol% MeCN, M9-N buffer at room temperature under anaerobic conditions for various time intervals. See below for experimental procedure. The data used for determining the initial rate of each *Rma* cyt *c* variant is showed in the following graph:



***Rma* cyt *c* variant**	**initial rate / μM min^{-1}**	**turnover frequency (TOF) / min^{-1}**	**TOF relative to WT**
WT	5.1 ± 0.3	6.4 ± 0.3	1
M100D	14.0 ± 0.4	17.5 ± 0.5	2.8 ± 0.2
V75T M100D	23.6 ± 0.8	29.5 ± 1.0	4.6 ± 0.3
V75T M100D M103E	36.4 ± 0.5	45.5 ± 0.7	7.1 ± 0.4

Errors quoted in the table above are calculated from the standard deviations of the fitting of data in the product *vs* time plot.

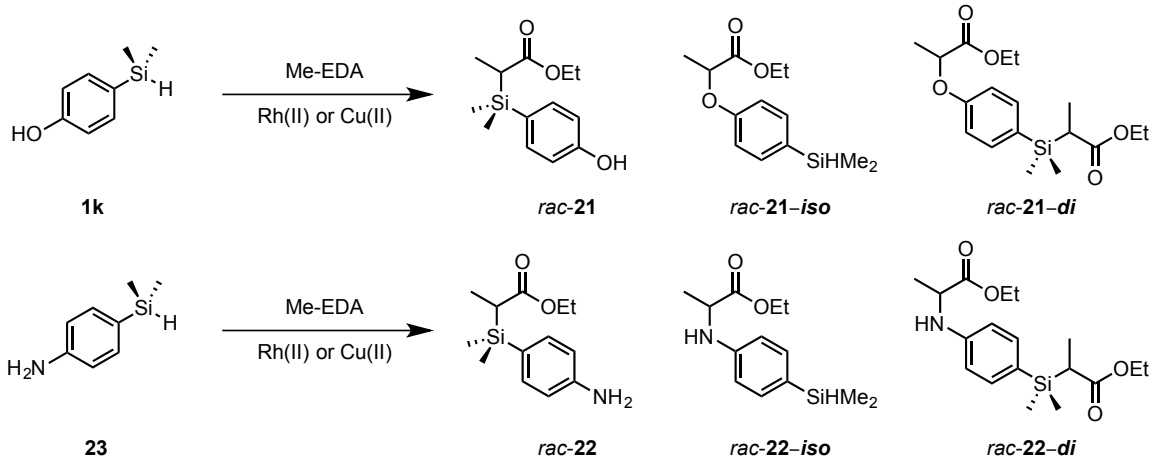
General procedure for carrying out timed experiments

In an anaerobic chamber, 1 mL $Na_2S_2O_4$ (100 mM in dH_2O) was added to 4 mL purified *Rma* cyt *c* protein (2.0 μM in M9-buffer) to give **Solution 1**. To four 2 mL microcentrifuge tubes were each added 180 μL M9-N buffer, 10 μL $PhMe_2SiH$ (400 mM in MeCN) and 10 μL Me-EDA (400 mM in MeCN), and the mixtures were mixed

thoroughly on a shaker (480 rpm for 2 min). To these mixtures were added 200 μL **Solution 1**, and the microcentrifuge tubes were closed and quickly shaken by hand for 3 seconds to ensure thorough mixing, before the tubes were returned to the shaker. The reactions were stopped at specific time points (2 min, 4 min, 6 min, and 8 min) by quick addition (within 10 seconds) of 40 μL pyridine solution (400 mM in dH_2O), 20 μL internal standard (20 mM acetophenone in toluene) and 1 mL cyclohexane. (Note: pyridine was added as a quencher to significantly slow down the reaction.) After the mixtures were vortexed for 20 seconds, 200 μL organic layer was immediately removed for GC analysis.

Table S7. Rh(II) or Cu(II)-catalyzed reactions between Me-EDA and 4-(dimethylsilyl)phenol (**1k**) or 4-(dimethylsilyl)aniline (**23**)

$Rh_2(OAc)_4$ and $Cu(OTf)_2$, which are known to catalyze carbene insertion into Si–H bonds under ligand-free conditions (*54*), were tested for their chemoselectivities towards Si–H, O–H and N–H insertions:



1k *rac*-**21** *rac*-**21**–***iso*** *rac*-**21**–***di***

23 *rac*-**22** *rac*-**22**–***iso*** *rac*-**22**–***di***

	21 (Si−H insertion)	**21-*iso*** (O−H insertion)	**21-*di*** (double insertion)
$Rh_2(OAc)_4$	×	✓	✓
$Cu(OTf)_2$	×	×	×
	22 (Si−H insertion)	**22-*iso*** (N−H insertion)	**22-*di*** (double insertion)
$Rh_2(OAc)_4$	×	✓	×
$Cu(OTf)_2$	×	×	×

Note: × = not detected; ✓ = detected. $Cu(OTf)_2$ gave complex mixtures of products in both reactions.

Experimental procedure

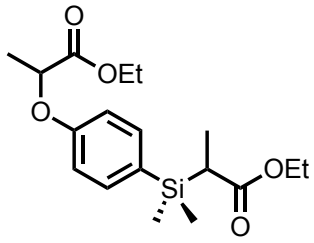
To a 5 mL vial was added silane (0.1 mmol, 1.0 equiv.), metal catalyst ($Rh_2(OAc)_4$ (0.44 mg, 1 mol%) or $Cu(OTf)_2$ (3.62 mg, 10 mol%)) and DCM (0.5 mL). The mixture was cooled to −78 °C before a solution of Me-EDA (25 μL, 2.0 equiv.) in DCM (0.3 mL) was added dropwise. After slowly warming up to room temperature in 4 hours, the reaction mixture was filtrated through a short pad of silica, diluted with DCM, and analyzed by GC-MS.

Products isolated from $Rh_2(OAc)_4$-catalyzed reactions with **1k** and **23** are shown on the next page. Both reactions generated multiple products, rendering product purification and quantitative analysis of these reactions difficult. Multiple rounds of purification by silica column chromatography were required to obtain samples suitable for characterization; yields were therefore not determined for these reactions. Notably, Si–H insertion products **21** and **22** were not observed in these reactions.

(Table S7 continued)

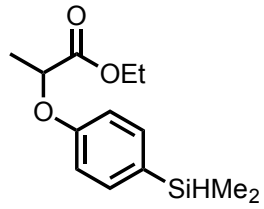
$Rh_2(OAc)_4$-catalyzed reaction with **1k** gave *rac*-**21**–***di*** and *rac*-**21**–***iso***:

rac-**21**–***di***



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.75 (q, *J* = 6.8 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.21 (q, *J* = 7.1 Hz, 1H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.17-1.10 (m, 6H), 0.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.19, 172.25, 158.86, 135.54, 128.29, 128.28, 114.65, 72.42, 61.46, 59.93, 30.30, 18.68, 14.47, 14.28, 11.43, –3.77, –4.60. HRMS (FAB) *m/z*: 352.1714 (M^+); calc. for $C_{18}H_{28}SiO_5$: 352.1706.

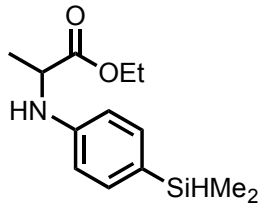
rac-**21**–***iso*** (this compound was inseparable from impurities)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.76 (q, *J* = 6.8 Hz, 1H), 4.39 (hept, *J* = 3.7 Hz, 1H), 4.22 (q, *J* = 6.9 Hz, 2H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.31 (d, *J* = 3.8 Hz, 6H).

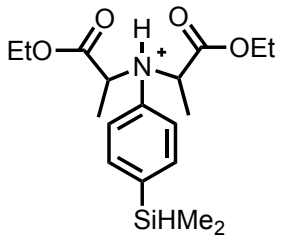
$Rh_2(OAc)_4$-catalyzed reaction with **23** gave *rac*-**22**-***iso*** and the corresponding double N–H insertion product:

rac-**22**–***iso***



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 2H), 6.88-6.68 (m, 3H), 4.68 (dq, *J* = 5.5, 2.8 Hz, 1H), 4.22-4.11 (m, 3H), 1.50 (br d, *J* = 6.4 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.19 (d, *J* = 2.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.94, 135.20, 129.50, 119.78, 114.93, 61.47, 53.20, 18.62, 14.31, 0.71. HRMS (FAB) *m/z*: 250.1253 ((M+H)–H_2^+); calc. for $C_{13}H_{20}SiNO_2$: 250.1263.

Interestingly, the following compound was also isolated as a mixture of diastereomers. The counter anion of the ammonium salt was not determined.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (overlapping doublets, *J* = 8.8, 7.3 Hz, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.78 (br d, *J* = 7.9 Hz, 2H), 4.99-4.55 (m, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.23 (app qd, *J* = 7.2, 2.0 Hz, 4H), 1.55 (d, *J* = 7.2 Hz, 6H), 1.29 (t, *J* = 7.1 Hz, 6H), 0.30-0.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.40, 146.38, 128.89, 119.30, 117.17, 61.24, 56.24, 15.95, 14.34, 0.71. HRMS (FAB) *m/z*: 352.1958 (M^+); calc. for $C_{18}H_{30}SiNO_4$: 352.1944.

Fig. S1 Representative SDS-PAGE gel of purified wild-type *Rma* cyt *c* and its V75T M100D M103E variant (TDE) in comparison to a standard protein ladder. The second and third lanes from the left are the same samples loaded at lower protein concentration.

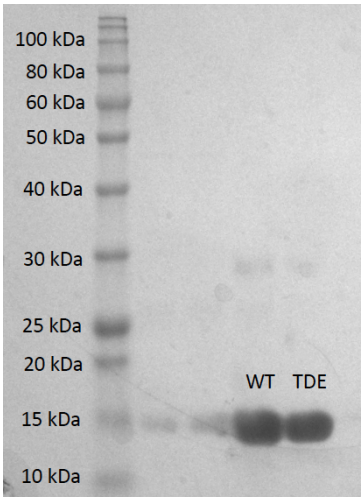


Fig. S2 Circular dichroism (CD) spectra of purified *Rma* cyt *c* V75T M100D M103E (Rma TDE).

Rma cyt *c* V75T M100D M103E was purified without performing the heat treatment step. Two identical samples were prepared in M9-N buffer, and one was heat treated at 75 °C for 10 minutes. After cooling to room temperature, the samples were analyzed by CD. The CD spectra of heat-treated and untreated *Rma* cyt *c* V75T M100D M103E are identical, suggesting that heat treatment at 75 °C for 10 minutes does not cause irreversible denaturation of the protein. The $\Delta\varepsilon_{MRW}$ values shown here are similar to previously published values for wild-type *Rma* cyt *c* (*26*), which suggests mutations V75T, M100D, and M103E are not highly disruptive to the protein secondary structure.

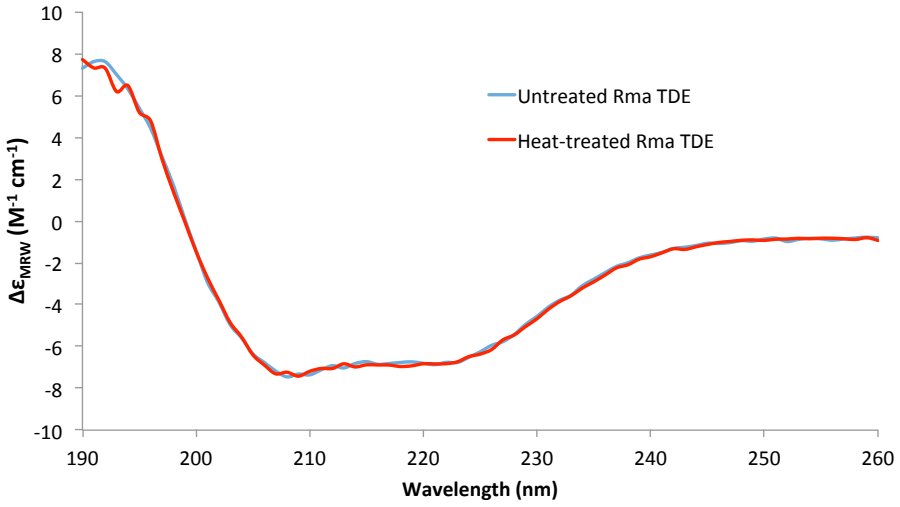
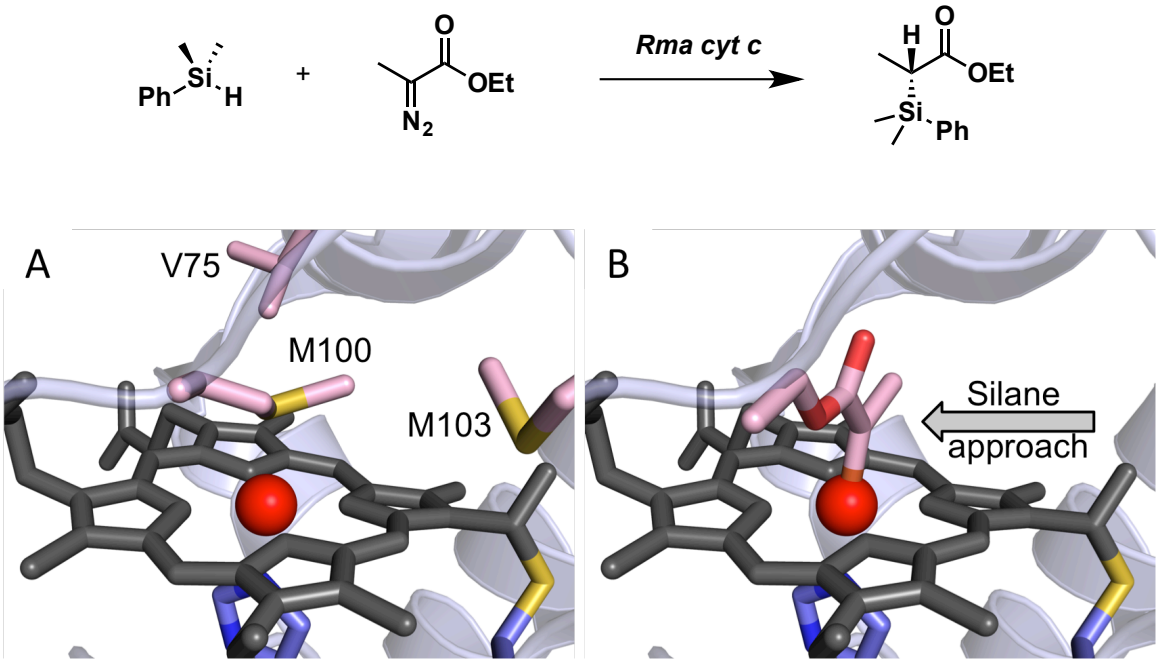
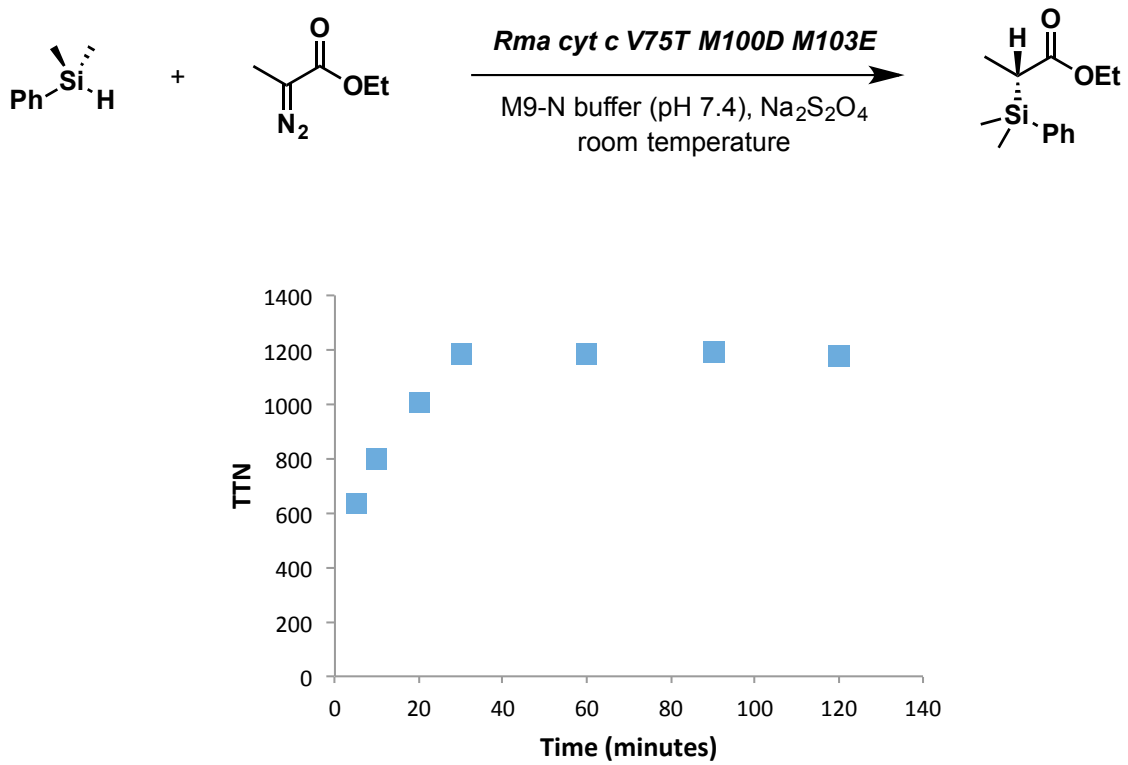


Fig. S3 Working hypothesis of binding mode for the iron carbenoid in wild-type *Rma* cyt *c* and speculated reaction trajectory for carbon–silicon bond formation.



(A) Putative active site structure of wild-type *Rma* cyt *c* showing residues V75, M100, and M103 (PDB ID: 3CP5). (B) Proposed binding mode for the iron-carbenoid, where the carbenoid forms in a way that takes the place of the axial methionine. The silane is proposed to approach from the more solvent-exposed side in the wild-type protein, which explains the observed stereochemistry of the organosilicon product. The V75T, M100D, and M103E mutations may promote reactivity by improving solvent and substrate access to the iron center. It should be noted that the working hypothesis proposed here is highly speculative as structural data about the ability of bacterial cytochrome *c* proteins to bind organic molecules is practically non-existent.

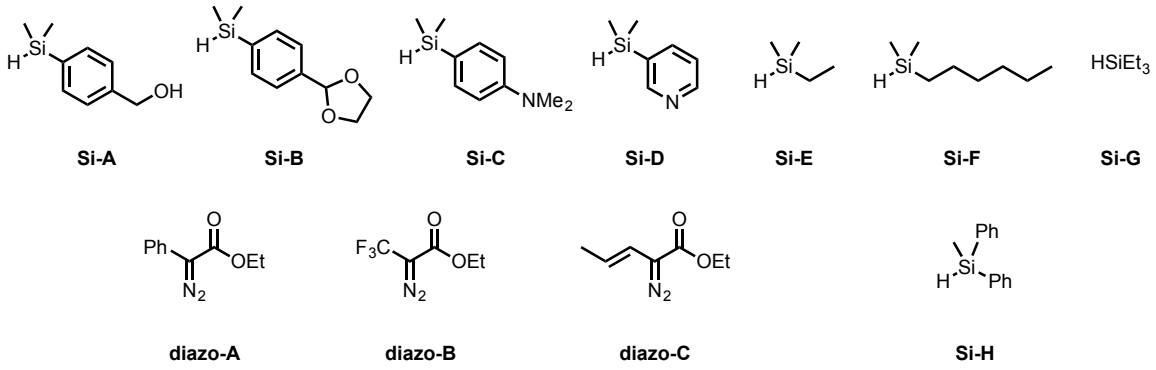
Fig. S4 Example of reaction time course of purified *Rma* cyt *c* M100D V75T M103E-catalyzed reaction between phenyldimethylsilane and Me-EDA.



Experiments were performed using 3 μM purified *Rma* cyt *c* V75T M100D M103E, 10 mM silane, 10 mM diazo ester, 10 mM $Na_2S_2O_4$, 5 vol% MeCN, M9-N buffer at room temperature under anaerobic conditions. Reactions were performed in duplicate. TTNs shown are the average of two experiments.

It is possible that catalysis slows down and ultimately stops due to catalyst inactivation by carbene transfer to the protein, an inactivation mechanism we recently analyzed in detail in another carbene-transfer enzyme (*52*). The activity and lifetime of *Rma* cyt *c* would likely improve by identifying the protein residues affected by mechanism-based inhibitors and further mutagenesis studies. Furthermore, inactivation of whole-cell catalyst was previously found to be slower than purified enzyme (*52*); this might also be applicable to *Rma* cyt *c* in whole bacterial cell.

Fig. S5 Additional substrates tested for *Rma* cyt *c* V75T M100D M103E-catalyzed carbon–silicon bond formation.



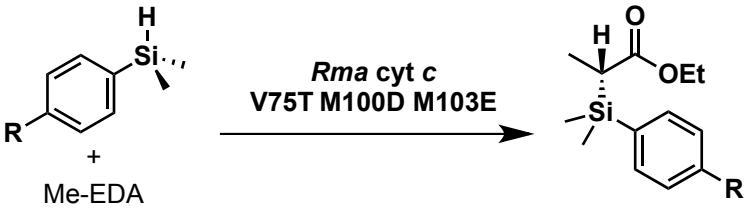
Rma cyt *c* V75T M100D M103E-catalyzed reactions of silanes **Si-A-H** were tested with Me-EDA and that of diazo compounds **diazo-A-C** were tested with phenyldimethylsilane under standard *in vitro* biocatalytic reaction conditions. Product formation was analyzed by GC-MS only, and comparison with chemically synthesized reference standards was not made. These preliminary results should be interpreted with caution and should not be used alone for drawing conclusions.

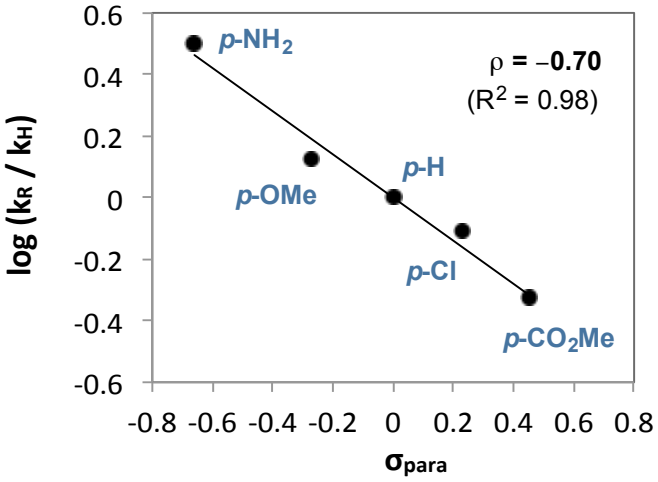
Si-A-D and **diazo-A**: formation of organosilicon product was detected by GC-MS.

Si-E-H and **diazo-B-C**: formation of organosilicon product was not detected by GC-MS.

Because biocatalysts that are fully genetically encoded can be readily optimized by directed evolution, the *Rma* cyt *c* V75T M100D M103E variant presented in this report is not the end point, but rather a parent to hundreds and thousands of future enzyme variants, some of which will most certainly surpass the scope and activity of the parent enzyme. For substrate scope expansion or other future applications, we suggest using the substrate of interest for directed evolution, and carrying out reaction screening under condition that suits individual substrate.

Fig. S6 Hammett analysis of *Rma* cyt *c* V75T M100D M103E-catalyzed carbon–silicon bond formation





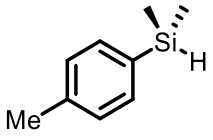
R	k_R / k_H	$\log(k_R / k_H)$	σ
H	1	0	0
MeO	1.3	0.13	−0.27
NH_2	3.2	0.50	−0.66
Cl	0.78	−0.11	0.23
CO_2Me	0.47	−0.32	0.45

The Hammett plot suggests a small build-up of positive charge on the silane in the reaction transition state. This observation is similar to that reported for carbene insertion into Si–H bond catalyzed by copper (ρ = –0.54) (*37*) and rhodium (ρ = –0.31) (*55*).

IV. Substrate Synthesis and Characterization

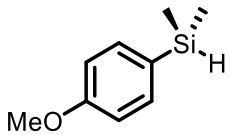
Commercially available substrates were used as received: phenyldimethylsilane (Sigma-Aldrich), benzyldimethylsilane (Sigma-Aldrich), ethyl 2-diazopropanoate (Arch Bioscience). The following diazo compounds are known and prepared according to literature procedures: isopropyl 2-diazopropanoate (*56*), ethyl 2-diazobutanoate (*57*).

Dimethyl(*p*-tolyl)silane (1b)



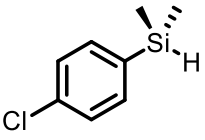
In a 100 mL round-bottom flask, chlorodimethylsilane (1.11 mL, 10.0 mmol) in THF (6 mL) was cooled to 0 °C. A solution of 4-methylphenylmagnesium bromide (24 mL, 0.5 M in THF) was added dropwise slowly over 15 min. Then reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (200 torr). The crude product was purified by silica column chromatography with pentane to afford **1b** (1.27 g, 8.44 mmol, 84%). This compound is known (*58*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 2H), 4.46 (hept, *J* = 3.7 Hz, 1H), 2.39 (s, 3H), 0.37 (d, *J* = 3.7 Hz, 6H).

(4-Methoxyphenyl)dimethylsilane (1c)



In a 100 mL round-bottom flask, chlorodimethylsilane (1.11 mL, 10.0 mmol) in THF (6 mL) was cooled to 0 °C. A solution of 4-methoxyphenylmagnesium bromide (24 mL, 0.5 M in THF) was added dropwise slowly over 15 min. Then reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (200 torr). The crude product was purified by silica column chromatography with pentane / Et_2O (10: 1) to afford **1c** (1.60 g, 9.62 mmol, 96%). This compound is known (*58*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.75-4.19 (m, 1H), 3.85 (s, 3H), 0.37 (d, *J* = 3.8 Hz, 6H).

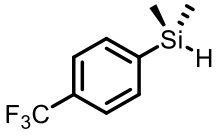
(4-Chlorophenyl)dimethylsilane (1d)



In a 100 mL round-bottom flask, chlorodimethylsilane (1.11 mL, 10.0 mmol) in THF (6 mL) was cooled to 0 °C. A solution of 4-chlorophenylmagnesium bromide (24 mL, 0.5 M in THF) was added dropwise slowly over 15 min. Then reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with

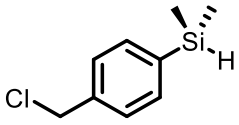
NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (200 torr). The crude product was purified by silica column chromatography with pentane to afford **1d** (1.27 g, 7.45 mmol, 75%). This compound is known (*58*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.41 (hept, *J* = 3.8 Hz, 1H), 0.34 (d, *J* = 3.7 Hz, 6H).

(4-(Trifluoromethyl)phenyl)dimethylsilane (1e)



In a 100 mL round-bottom flask, 1-bromo-4-(trifluoromethyl)benzene (1.4 mL, 10.0 mmol) in THF (15 mL) was cooled to −78 °C. *n*-BuLi (7.5 mL, 1.6 M in hexane) was added dropwise slowly over 15 min. The resulting mixture was stirred at −78 °C for 2 hours before the dropwise addition of chlorodimethylsilane (1.0 mL, 9.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (200 torr). The crude product was purified by silica column chromatography with pentane to afford **1e** (0.81 g, 3.97 mmol, 40%). This compound is known (*58*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 4.46 (hept, *J* = 3.8 Hz, 1H), 0.38 (d, *J* = 3.8 Hz, 6H).

(4-(Chloromethyl)phenyl)dimethylsilane (1f)

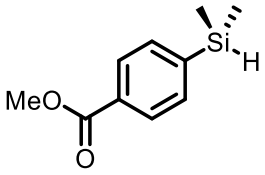


In a 250 mL round-bottom flask, (4-bromophenyl)methanol (5.61 g, 30.0 mmol) in THF (100 mL) was cooled to −78 °C. *n*-BuLi (30.0 mL, 2.5 M in hexane) was added dropwise slowly over 30 min. The resulting mixture was stirred at −78 °C for 2 hours before the dropwise addition of chlorodimethylsilane (4.5 mL, 40.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (50 mL, sat. aq.) and the product was extracted with DCM (50 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (100 torr). The crude product was purified by silica column chromatography with EtOAc / hexane (1:3) to afford (4-(dimethylsilyl)phenyl)methanol (2.96 g, 17.8 mmol, 59%). This compound is known (*59*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 4.70 (s, 2H), 4.43 (hept, *J* = 3.7 Hz, 1H), 0.35 (d, *J* = 3.8 Hz, 6H).

To a solution of (4-(dimethylsilyl)phenyl)methanol (498.9 mg, 3.0 mmol) in DCM (4 mL) were added triethylamine (0.5 mL, 3.6 mmol) and 4-methylbenzenesulfonyl chloride (629.1 mg, 3.3 mmol). The reaction mixture was stirred at room temperature for 8 hours. The reaction was then diluted with DCM (10 mL) and washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and the organic layer was concentrated under reduced pressure (100 torr). The crude product was purified by silica column chromatography with pentane to afford **1f** (0.22 g, 1.19 mmol, 40%). ^{1}H NMR (400

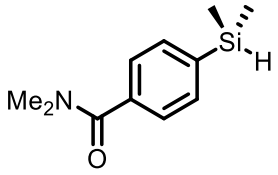
MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 4.59 (s, 2H), 4.43 (hept, *J* = 3.8 Hz, 1H), 0.35 (d, *J* = 3.8 Hz, 6H). HRMS (FAB) *m/z*: 183.0399 ((M+H)–H_2^+); calc. for $C_9H_{12}SiCl$: 183.0397.

Methyl 4-(dimethylsilyl)benzoate (1g)



In a 100 mL round-bottom flask, methyl 4-iodobenzoate (2.62 g, 10.0 mmol) in THF (15 mL) was cooled to –78 °C. *i*-PrMgCl (6 mL, 2.0 M in Et_2O) was added dropwise slowly over 5 min. The resulting mixture was allowed to warm to –40 °C in 2 hours and maintained at –40 °C for another 2 hours before the dropwise addition of chlorodimethylsilane (1.2 mL, 11.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with DCM (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (100 torr). The mixture was dissolved in Et_2O (5 mL) and treated with hexane (25 mL). This crashed out most of the starting material, which was removed by filtration. The filtrate was collected, concentrated under reduced pressure, and purified by silica column chromatography with EtOAc / hexane (1:20) to afford **1g** (0.88 g, 4.53 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 4.45 (hept, *J* = 3.8 Hz, 1H), 3.92 (s, 3H), 0.37 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.35, 143.92, 134.13, 130.78, 128.72, 52.27, –3.84. HRMS (FAB) *m/z*: 195.0843 ($M+H^+$); calc. for $C_{10}H_{15}SiO_2$: 195.0841.

4-(dimethylsilyl)-*N*,*N*-dimethylbenzamide (1h)

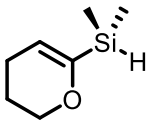


To a solution of dimethylamine hydrochloride (2.45 g, 30.0 mmol) in DCM (50 mL) was added triethylamine (4.2 mL, 30.0 mmol). The mixture was stirred for 30 min before the addition of 4-iodobenzoic acid (6.20 g, 25.0 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide (EDC, 4.66 g, 30.0 mmol). The reaction was stirred for 8 hours at room temperature. Then the reaction mixture was washed with water (50 mL), HCl (aq., 1 M, 50 mL), $NaHCO_3$ (sat. aq., 50 mL) and brine (50 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (50 torr). The crude product was dissolved in Et_2O (5 mL) and treated with hexane (50 mL). The target product 4-iodo-*N*,*N*-dimethylbenzamide (6.88 g, 25.0 mmol, quantitative) crashed out and was collected by filtration.

In a 100 mL round-bottom flask, 4-iodo-*N*,*N*-dimethylbenzamide (1.65 g, 6.0 mmol) in THF (15 mL) was cooled to –78 °C. *i*-PrMgCl (6 mL, 2.0 M in Et_2O) was added dropwise slowly over 5 min. The resulting mixture was allowed to warm to –40 °C within 2 hours and maintained at –40 °C for another 2 hours before the dropwise addition of chlorodimethylsilane (1.3 mL, 12.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with DCM (15 mL × 3). The organic layer

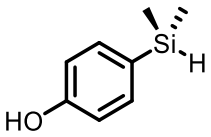
was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (50 torr). The mixture was dissolved in Et_2O (5 mL) and treated with hexane (25 mL). Most of the starting material crashed out and was removed by filtration. The filtrate was collected, concentrated under reduced pressure, and then purified by silica column chromatography with EtOAc / hexane (1:2) to afford **1h** (0.12 g, 0.579 mmol, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 4.43 (hept, *J* = 3.8 Hz, 1H), 3.05 (s, 6H), 0.35 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.74, 139.53, 137.04, 134.11, 126.42, –3.74. HRMS (FAB) *m/z*: 208.1153 ($M+H^+$); calc. for $C_{11}H_{18}ONSi$: 208.1158.

(3,4-Dihydro-2*H*-pyran-6-yl)dimethylsilane (1i)



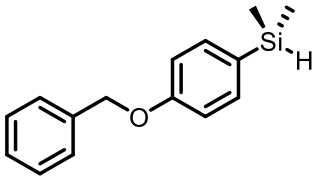
In a 100 mL round-bottom flask, 3,4-dihydro-2*H*-pyran (2.00 g, 24.0 mmol) in THF (1.0 mL) and pentane (40 mL) was cooled to –78 °C. *t*-BuLi (15.5 mL, 1.7 M in pentane) was added dropwise slowly over 20 min. The resulting mixture was allowed to warm to 0 °C within 2 hours and maintained at 0 °C for another 2 hours before the dropwise addition of chlorodimethylsilane (2.6 mL, 24.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (200 torr). The crude product was purified by silica column chromatography with Et_2O / pentane (1: 30) to afford **1i** (2.80 g, 19.7 mmol, 82%). This compound is known (*60*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (t, *J* = 3.8 Hz, 1H), 4.05-3.91 (m, 3H), 2.04 (td, *J* = 6.4, 3.8 Hz, 2H), 1.92-1.83 (m, 2H), 0.19 (d, *J* = 3.8 Hz, 6H).

4-(Dimethylsilyl)phenol (1k)



To a solution of 4-bromophenol (1.73 g, 10.0 mmol) in THF (15 mL) was added NaH (60% in mineral oil, 0.48 g, 12.0 mmol). After the mixture was stirred for 30 min, it was cooled down to –78 °C. *t*-BuLi (6 mL, 1.7 M in pentane) was added dropwise slowly over 15 min. The resulting mixture was stirred at –78 °C for 2 hours before the dropwise addition of chlorodimethylsilane (2.3 mL, 21.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with DCM (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (50 torr). The crude product was purified by silica column chromatography with EtOAc / hexane (1:7) to afford **1k** (0.60 g, 3.94 mmol, 39%). This compound is known (*61*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.78 (s, 1H), 4.40 (hept, *J* = 3.7 Hz, 1H), 0.32 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.61, 135.82, 128.66, 115.16, –3.38.

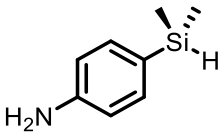
(4-(Benzyloxy)phenyl)dimethylsilane (1ks)



To a solution of 4-bromophenol (5.19 g, 30.0 mmol) in MeCN (50 mL) was added K_2CO_3 (5.53 g, 40.0 mmol). After the mixture was stirred at 40 °C for 30 min, BnBr (3.6 mL, 30.0 mmol) was added over 2 min. The resulting mixture was stirred at 40 °C for 3 hours. The reaction mixture was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (50 torr) to afford the crude product 1-(benzyloxy)-4-bromobenzene (7.85 g, 30.0 mmol, quantitative).

In a 100 mL round-bottom flask, 1-(benzyloxy)-4-bromobenzene (6.57 g, 25.0 mmol) in THF (15 mL) was cooled to –78 °C. *t*-BuLi (19.0 mL, 1.7 M in pentane) was added dropwise slowly over 15 min. The resulting mixture was stirred at –78 °C for 2 hours before the dropwise addition of chlorodimethylsilane (3.6 mL, 32.5 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (50 torr). The crude product was purified by silica column chromatography with pentane to afford **1ks** (4.02 g, 16.6 mmol, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.27 (m, 7H), 7.00 (d, J = 8.6 Hz, 2H), 5.08 (s, 2H), 4.41 (hept, J = 3.7 Hz, 1H), 0.32 (d, J = 3.7 Hz, 6H). HRMS (FAB) *m/z*: 241.1053 ((M+H)–H_2^+); calc. for $C_{15}H_{17}OSi$: 241.1049.

4-(Dimethylsilyl)aniline (23)

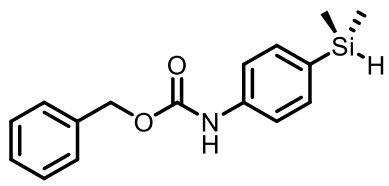


To a solution of 4-bromoaniline (3.44 g, 20.0 mmol) in DCM (30 mL) was added triethylamine (5.6 mL, 20.0 mmol) and *N*,*N*-dimethylpyridin-4-amine (DMAP, 244.3 mg, 2.0 mmol). After the mixture was stirred for 30 min, 1,2-bis(chlorodimethylsilyl)ethane (4.78 g, 20.0 mmol) was added in one portion. The reaction was stirred at 40 °C for 3 hours. The reaction mixture was filtrated through a pad of dry Celite quickly to remove the triethylamine hydrochloride. The resulting solution was concentrated under reduced pressure (50 torr) to afford the crude product 1-(4-bromophenyl)-2,2,5,5-tetramethyl-1,2,5-azadisilolidine. (Note: this compound is moisture sensitive and decomposed on silica.)

The crude 1-(4-bromophenyl)-2,2,5,5-tetramethyl-1,2,5-azadisilolidine in THF (30 mL) in a 100 mL round-bottom flask was cooled to –78 °C. *t*-BuLi (17.6 mL, 1.7 M in pentane) was added dropwise slowly over 15 min. The resulting mixture was stirred at –78 °C for 2 hours before the dropwise addition of chlorodimethylsilane (3.3 mL, 30.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was treated with Et_2O (50 mL) to allow the inorganic salts to crash out. The suspension was filtrated through a pad of Celite and basic alumina (1:1 mixture). The resulting solution was concentrated under reduced pressure (50 torr). The crude product was loaded on silica and allowed to sit for 15 min (for removal of the nitrogen

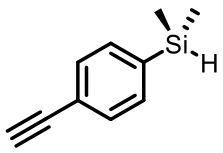
protecting group), before purification by silica column chromatography with EtOAc / hexane (1:7) to afford **23** (1.21 g, 8.00 mmol, 40%). This compound is known (*62*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.84 (s, 2H), 4.38 (hept, *J* = 3.9 Hz, 1H), 0.30 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.82, 135.48, 127.64, 116.07, –3.38.

Benzyl (4-(dimethylsilyl)phenyl)carbamate (23s)



To a solution of 4-(dimethylsilyl)aniline (151.2 mg, 1.0 mmol) in DCM (3 mL) was added pyridine (162 μL, 2.0 mmol). After the mixture was stirred for 10 min, benzyl carbonochloridate (CbzCl, 170 μL, 1.2 mmol) was added in one portion. After stirring at room temperature overnight, the reaction mixture was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (50 torr). The crude product was purified by silica column chromatography with EtOAc / hexane (1:7) to afford **23s** (130.4 mg, 0.457 mmol, 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.46-7.33 (m, 5H), 6.68 (s, 1H), 5.23 (s, 2H), 4.42 (hept, *J* = 3.7 Hz, 1H), 0.34 (d, *J* = 3.7 Hz, 6H). HRMS (FAB) *m/z*: 286.1274 ($M+H^+$); calc. for $C_{16}H_{20}O_2NSi$: 286.1263.

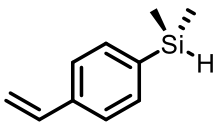
(4-Ethynylphenyl)dimethylsilane (1m)



A solution of ((4-bromophenyl)ethynyl)trimethylsilane (5.06 g, 20.0 mmol) and K_2CO_3 (5.53 g, 40.0 mmol) in MeOH (40 mL) was stirred at room temperature for 4 hours. MeOH was removed under reduced pressure, and the crude product was washed with water (30 mL) and extracted with Et_2O (40 mL). The organic layer was dried over $MgSO_4$, filtrated through a pad of silica, and concentrated under reduced pressure to afford the product 1-bromo-4-ethynylbenzene (3.21 g, 17.7 mmol, 89%).

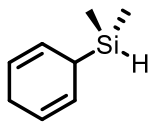
In a 100 mL round-bottom flask, 1-bromo-4-ethynylbenzene (1.81 g, 10.0 mmol) in THF (15 mL) was cooled to –78 °C. *n*-BuLi (8.0 mL, 2.5 M in hexane) was added dropwise very slowly over 30 min. The resulting mixture was stirred at –78 °C for 2 hours before the dropwise addition of a solution of chlorodimethylsilane (1.1 mL, 10.0 mmol) in THF (20 mL). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (200 torr). The crude product was purified by distillation under reduced pressure (1.4 torr) at 45 °C (1.12 g, 6.99 mmol, 70%). This compound is known (*63*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 3.9 Hz, 4H), 4.42 (hept, *J* = 3.8 Hz, 1H), 3.10 (s, 1H), 0.34 (d, *J* = 3.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.83, 134.01, 131.43, 122.91, 83.81, 77.85, –3.77.

Dimethyl(4-vinylphenyl)silane (1n)



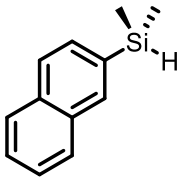
In a 100 mL round-bottom flask, 1-bromo-4-vinylbenzene (1.83 g, 10.0 mmol) in THF (15 mL) was cooled to –78 °C. *n*-BuLi (7.5 mL, 1.6 M in hexane) was added dropwise very slowly over 30 min. The resulting mixture was stirred at –78 °C for 2 hours before the dropwise addition of a solution of chlorodimethylsilane (1.1 mL, 10.0 mmol) in THF (20 mL). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (200 torr). The crude product was purified by silica column chromatography with pentane to afford **1n** (1.29 g, 7.95 mmol, 80%). This compound is known (*64*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.79 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.27 (dd, *J* = 10.9, 0.9 Hz, 1H), 4.43 (hept, *J* = 3.7 Hz, 1H), 0.35 (d, *J* = 3.8 Hz, 6H).

Cyclohexa-2,5-dien-1-yldimethylsilane (1o)



In a 100 mL round-bottom flask, cyclohexa-1,4-diene (2.3 mL, 24.0 mmol) in THF (20 mL) was cooled to –78 °C. *t*-BuLi (15.5 mL, 1.7 M in pentane) and *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (TMEDA, 3.6 mL, 24 mmol) were added simultaneously as separate solutions, dropwise over 20 min. The resulting mixture was allowed to warm to –45 °C in 30 min and maintained at –45 °C for another 1 hour before the dropwise addition of chlorodimethylsilane (2.6 mL, 24.0 mmol). The reaction was allowed to warm to room temperature and stirred for 1.5 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (300 torr). The crude product was purified by silica column chromatography with pentane to afford **1o** (1.24 g, 8.97 mmol, 38%). (Note: this compound is oxygen sensitive and very volatile; storage under argon at –20°C is recommended.) This compound is known (*65*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72-5.64 (m, 2H), 5.61-5.54 (m, 2H), 3.85 (heptd, *J* = 3.5, 1.6 Hz, 1H), 2.80-2.60 (m, 2H), 2.42-2.30 (m, 1H), 0.10 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.91, 122.09, 29.38, 26.50, –6.31.

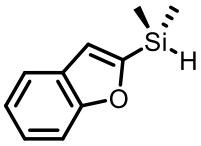
Dimethyl(naphthalen-2-yl)silane (1p)



In a 100 mL round-bottom flask, 2-bromonaphthalene (2.07 g, 10.0 mmol) in THF (15 mL) was cooled to –78 °C. *n*-BuLi (7.5 mL, 1.6 M in hexane) was added dropwise very slowly over 30 min. The resulting mixture was stirred at –78 °C for 2 hours before the dropwise addition of a solution of chlorodimethylsilane (1.1 mL, 10.0 mmol) in THF (20 mL).

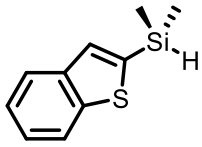
The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (100 torr). The crude product was purified by silica column chromatography with pentane to afford **1p** (1.69 g, 9.07 mmol, 91%). This compound is known (*66*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.87-7.82 (m, 3H), 7.61 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.51-7.48 (m, 2H), 4.56 (hept, *J* = 3.8 Hz, 1H), 0.43 (d, *J* = 3.8 Hz, 6H).

Benzofuran-2-yldimethylsilane (1q)



In a 100 mL round-bottom flask, benzofuran (1.18 g, 10.0 mmol) in THF (15 mL) was cooled to –78 °C. *n*-BuLi (7.5 mL, 1.6 M in hexane) was added dropwise slowly over 20 min. The resulting mixture was allowed to warm to –40 °C within 1 hour and maintained at –40 °C for another 2 hours before the dropwise addition of chlorodimethylsilane (1.1 mL, 10.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (100 torr). The crude product was purified by silica column chromatography with Et_2O / pentane (1:30) to afford **1q** (1.08 g, 6.13 mmol, 61%). This compound is known (*67*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (ddd, *J* = 7.1, 1.3, 0.7 Hz, 1H,), 7.52 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.30 (ddd, *J* = 8.5, 7.5, 1.0 Hz, 1H), 7.22 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 7.04 (d, *J* = 0.7 Hz, 1H), 4.52 (hept, *J* = 3.8 Hz, 1H), 0.44 (d, *J* = 3.8 Hz, 6H).

Benzothiophen-2-yldimethylsilane (1r)



In a 100 mL round-bottom flask, benzothiophene (1.34 g, 10.0 mmol) in THF (15 mL) was cooled to –78 °C. *n*-BuLi (7.5 mL, 1.6 M in hexane) was added dropwise slowly over 20 min. The resulting mixture was allowed to warm to –40 °C within 1 hour and maintained at –40 °C for another 2 hours before the dropwise addition of chlorodimethylsilane (1.1 mL, 10.0 mmol). The reaction was allowed to warm to room temperature and stirred for 8 hours. The reaction mixture was quenched with NH_4Cl (5 mL, sat. aq.) and the product was extracted with Et_2O (15 mL × 3). The organic layer was washed with water (20 mL), brine (20 mL), dried over $MgSO_4$, and then concentrated under reduced pressure (100 torr). The crude product was purified by silica column chromatography with pentane to afford **1r** (1.76 g, 9.14 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.86 (m, 1H), 7.86-7.79 (m, 1H), 7.53 (s, 1H), 7.38-7.30 (m, 2H), 4.63 (hept, *J* = 3.7 Hz, 1H), 0.46 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.87, 141.08, 138.57, 132.18, 124.47, 124.20, 123.63, 122.32, –2.93. HRMS (FAB) *m/z*: 191.0354 ($M–H^-$); calc. for $C_{10}H_{12}SSi$: 191.0351.

V. Synthesis and Characterization of Authentic Organosilicon Products

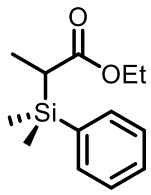
Racemic standard references of organosilicon products were prepared using rhodium-catalyzed Si–H insertion reactions, following the general procedure described below:

General procedure for rhodium-catalyzed Si–H insertion

To a 20 mL vial or 25 mL flask was added silane (1.0 mmol, 1.0 equiv.), $Rh_2(OAc)_4$ (4.4 mg, 1 mol%) and DCM (5 mL). The mixture was cooled to –78 °C, after which diazo compound (1.0 mmol, 1.0 equiv.) was added dropwise to the solution. The reaction was allowed to slowly warm up to room temperature in 8 hours and stirred at room temperature for another 4 hours. Evaporation of the organic solvent and purification by silica column chromatography using EtOAc and hexane as eluents afforded organosilicon products **3**-**20** in 20-70% yields.

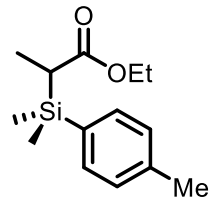
Organosilicon compounds **21** and **22** were prepared by rhodium-catalyzed Si–H insertion between Me-EDA and the corresponding *O*- or *N*-protected silane (**1ks** or **23s**) to give **21a** or **22a**, followed by deprotection under standard palladium-catalyzed hydrogenation condition (10% Pd/C in ethanol under H_2 atmosphere at room temperature for 16 hours). The hydrogenation reaction afforded **21** and **22** in 96% and 88% yield, respectively.

Ethyl 2-(dimethyl(phenyl)silyl)propanoate (3)



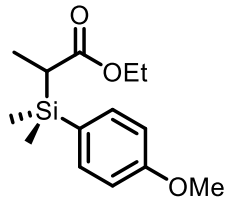
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.46 (m, 2H), 7.43-7.32 (m, 3H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.25 (q, *J* = 7.1 Hz, 1H), 1.17-1.11 (m, 6H), 0.37 (d, *J* = 0.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.13, 136.42, 133.99, 129.57, 127.92, 59.96, 30.14, 14.43, 11.42, –3.92, –4.77. HRMS (FAB) *m/z*: 236.1234 (M^+); calc. for $C_{13}H_{20}O_2Si$: 236.1233.

Ethyl 2-(dimethyl(*p*-tolyl)silyl)propanoate (4)



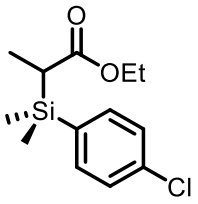
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 2.24 (q, *J* = 7.1 Hz, 1H), 1.19-1.11 (m, 6H), 0.35 (d, *J* = 0.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.21, 139.51, 134.04, 132.72, 128.77, 59.94, 30.22, 21.63, 14.47, 11.44, –3.75, –4.75. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 0.19. HRMS (FAB) *m/z*: 250.1391 (M^+); calc. for $C_{14}H_{22}O_2Si$: 250.1389.

Ethyl 2-(dimethyl(4-methoxyphenyl)silyl)propanoate (5)



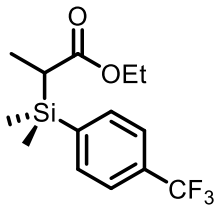
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.22 (q, *J* = 7.1 Hz, 1H), 1.20-1.10 (m, 6H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.24, 160.84, 135.49, 127.18, 113.70, 59.93, 55.18, 30.37, 14.49, 11.45, –3.72, –4.58. ^{29}Si NMR (79 MHz, $CDCl_3$) δ –0.10. HRMS (FAB) *m/z*: 266.1332 (M^+); calc. for $C_{14}H_{22}O_3Si$: 266.1338.

Ethyl 2-(dimethyl(4-chlorophenyl)silyl)propanoate (6)



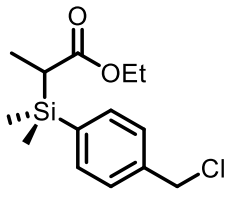
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.3, 1.9 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.23 (q, *J* = 7.1 Hz, 1H), 1.17-1.11 (m, 6H), 0.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.87, 135.98, 135.36, 134.75, 128.19, 60.06, 30.03, 14.45, 11.38, –4.02, –4.61. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 0.59. HRMS (FAB) *m/z*: 270.0847 (M^+); calc. for $C_{13}H_{19}O_2SiCl$: 270.0843.

Ethyl 2-(dimethyl(4-trifloromethylphenyl)silyl)propanoate (7)



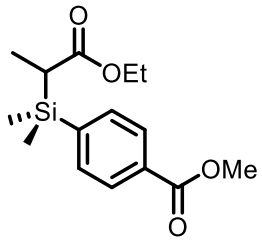
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 4H), 4.01 (qd, *J* = 7.2, 0.7 Hz, 2H), 2.27 (q, *J* = 7.2 Hz, 1H), 1.16 (d, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.40 (d, *J* = 1.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.49, 134.32, 131.52 (q, $J_{C–F}$ = 32.3 Hz), 124.26 (q, $J_{C–F}$ = 272.2 Hz), 124.43 (q, $J_{C–F}$ = 3.8 Hz), 60.16, 29.96, 14.39, 11.39, –4.18, –4.65. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 1.01. HRMS (FAB) *m/z*: 304.1119 (M^+); calc. for $C_{14}H_{19}O_2SiF_3$: 304.1106.

Ethyl 2-(dimethyl(4-chloromethylphenyl)silyl)propanoate (8)



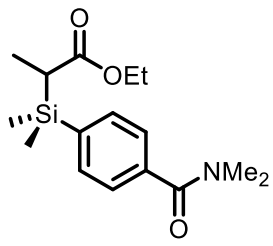
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 4.58 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.25 (q, *J* = 7.1 Hz, 1H), 1.18-1.08 (m, 6H), 0.37 (d, *J* = 1.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.98, 138.72, 136.92, 134.44, 128.02, 60.02, 46.23, 30.05, 14.44, 11.41, –3.97, –4.70. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 0.59. HRMS (FAB) *m/z*: 283.0927 ((M+H)–H_2 $^+$); calc. for $C_{14}H_{20}O_2SiCl$: 283.0921.

Methyl 4-((1-ethoxy-1-oxopropan-2-yl)dimethylsilyl)benzoate (9)



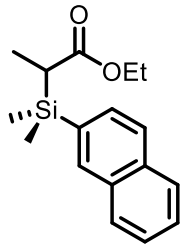
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 4.01 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.92 (s, 3H), 2.27 (q, *J* = 7.2 Hz, 1H), 1.19-1.05 (m, 6H), 0.39 (d, *J* = 1.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.77, 167.27, 142.78, 134.01, 131.00, 128.64, 60.07, 52.31, 29.88, 14.44, 11.37, –4.13, –4.71. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 0.98. HRMS (FAB) *m/z*: 294.1276 (M^+); calc. for $C_{15}H_{22}O_4Si$: 294.1287.

Ethyl 2-((4-(dimethylcarbamoyl)phenyl)dimethylsilyl)propanoate (10)



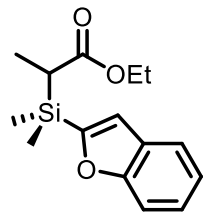
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.11 (s, 3H), 2.97 (s, 3H), 2.26 (q, *J* = 7.2 Hz, 1H), 1.20-1.10 (m, 6H), 0.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.94, 171.59, 138.39, 137.38, 134.01, 126.37, 60.05, 39.67, 35.45, 29.95, 14.49, 11.41, –3.92, –4.75. HRMS (FAB) *m/z*: 308.1689 ($M+H^+$); calc. for $C_{16}H_{26}NO_3Si$: 308.1682.

Ethyl 2-((naphthalen-2-yl)dimethylsilyl)propanoate (11)



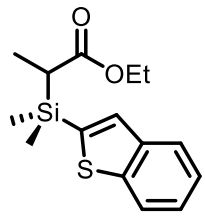
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.87-7.80 (m, 3H), 7.57 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.53-7.46 (m, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.34 (q, *J* = 7.1 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.46 (d, *J* = 2.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.14, 134.88, 133.99, 133.92, 132.92, 130.03, 128.23, 127.84, 127.16, 126.70, 126.15, 60.01, 30.18, 14.44, 11.50, –3.76, –4.71. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 0.76. HRMS (FAB) *m/z*: 286.1395 (M^+); calc. for $C_{17}H_{22}O_2Si$: 286.1389.

Ethyl 2-((benzofuran-2-yl)dimethylsilyl)propanoate (12)



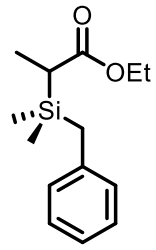
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.50 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.29 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.21 (ddd, *J* = 8.2, 7.8, 1.0 Hz, 1H), 7.05 (d, *J* = 1.0 Hz, 1H), 4.07 (qd, *J* = 7.2, 1.2 Hz, 2H), 2.38 (q, *J* = 7.2 Hz, 1H), 1.24 (d, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.44 (d, *J* = 1.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.57, 159.85, 158.31, 127.82, 124.84, 122.58, 121.29, 117.93, 111.48, 60.22, 29.42, 14.42, 11.24, –4.32, –5.05. ^{29}Si NMR (79 MHz, $CDCl_3$) δ –5.09. HRMS (FAB) *m/z*: 276.1182 (M^+); calc. for $C_{15}H_{20}O_3Si$: 276.1169.

Ethyl 2-(benzothiophen-2-yldimethylsilyl)propanoate (13)



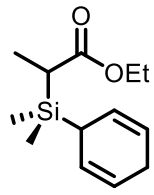
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.85 (m, 1H), 7.85-7.79 (m, 1H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.39-7.30 (m, 2H), 4.08 (qd, *J* = 7.1, 1.1 Hz, 2H), 2.33 (q, *J* = 7.2 Hz, 1H), 1.24 (d, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.47 (d, *J* = 0.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.61, 143.84, 140.93, 137.78, 132.56, 124.64, 124.25, 123.75, 122.30, 60.24, 30.46, 14.47, 11.43, –2.77, –3.64. ^{29}Si NMR (79 MHz, $CDCl_3$) δ –1.51. HRMS (FAB) *m/z*: 292.0963 (M^+); calc. for $C_{15}H_{20}O_2SiS$: 292.0953.

Ethyl 2-(benzyldimethylsilyl)propanoate (14)



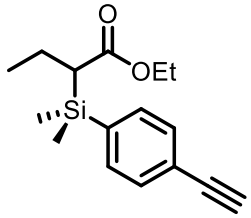
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.17 (m, 2H), 7.11-7.06 (m, 1H), 7.06-6.96 (m, 2H), 4.24-4.02 (m, 2H), 2.24-2.14 (m, 2H), 2.10 (q, *J* = 7.1 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 7.1 Hz, 3H), 0.06- –0.12 (m, *J* = 0.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.19, 139.25, 128.44, 128.42, 124.44, 60.04, 28.95, 24.03, 14.66, 11.17, –4.76, –4.82. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 5.96. HRMS (FAB) *m/z*: 251.1459 ($M+H^+$); calc. for $C_{14}H_{23}O_2Si$: 251.1467.

Ethyl 2-(cyclohexa-2,5-dien-1-yldimethylsilyl)propanoate (15)



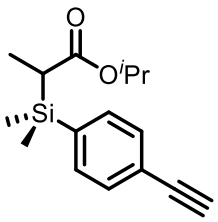
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81-5.52 (m, 4H), 4.17-4.05 (m, 2H), 2.81-2.56 (m, 2H), 2.48-2.36 (m, 1H), 2.19 (q, *J* = 7.1 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 7.2 Hz, 3H), 0.08 (d, *J* = 4.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.24, 125.63, 125.53, 122.65, 122.52, 60.05, 29.47, 28.28, 26.52, 14.59, 11.33, –6.35, –6.70. HRMS (FAB) *m/z*: 237.1313 ((M+H)–H_2^+); calc. for $C_{13}H_{21}O_2Si$: 237.1311.

Ethyl 2-((4-ethynylphenyl)dimethylsilyl)butanoate (16)



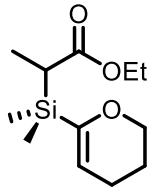
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.42 (m, 4H), 4.13-3.93 (m, 2H), 3.11 (s, 1H), 2.08 (dd, *J* = 11.7, 3.1 Hz, 1H), 1.78 (ddq, *J* = 14.2, 11.7, 7.1 Hz, 1H), 1.40 (dqd, *J* = 13.8, 7.3, 3.1 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.35 (d, *J* = 4.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.05, 137.86, 133.87, 131.36, 123.17, 83.71, 78.06, 59.95, 39.53, 20.60, 15.13, 14.47, –3.96, –4.56. HRMS (FAB) *m/z*: 273.1316 ((M+H)–H_2^+); calc. for $C_{16}H_{21}O_2Si$: 273.1311.

Isopropyl 2-((4-ethynylphenyl)dimethylsilyl)propanoate (17)



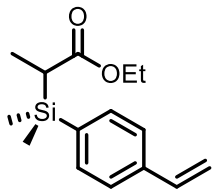
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (app s, 4H), 4.91 (hept, *J* = 6.3 Hz, 1H), 3.11 (s, 1H), 2.21 (q, *J* = 7.1 Hz, 1H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.13 (d, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 6.3 Hz, 3H), 0.36 (d, *J* = 3.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.39, 137.82, 133.93, 131.36, 123.15, 83.73, 78.03, 67.33, 30.02, 22.16, 22.01, 11.45, –3.95, –4.69. HRMS (FAB) *m/z*: 275.1479 ($M+H^+$); calc. for $C_{16}H_{23}O_2Si$: 275.1467.

Ethyl 2-((3,4-dihydro-2*H*-pyran-6-yl)dimethylsilyl)propanoate (18)



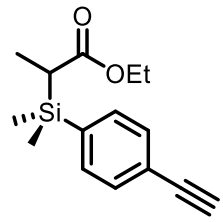
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 (t, *J* = 3.8, 1H), 4.16-4.02 (m, 2H), 3.90 (dd, *J*=5.8, 4.9 Hz, 2H), 2.17 (q, *J* = 7.1 Hz, 1H), 2.05-1.98 (m, 2H), 1.87-1.78 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 7.1 Hz, 3H), 0.14 (d, *J* = 8.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.26, 157.26, 112.83, 65.77, 59.91, 28.78, 22.79, 20.90, 14.61, 11.24, –4.96, –5.98. ^{29}Si NMR (79 MHz, $CDCl_3$) δ –4.02. HRMS (FAB) *m/z*: 243.1410 ($M+H^+$); calc. for $C_{12}H_{23}O_3Si$: 243.1417.

Ethyl 2-((4-vinylphenyl)dimethylsilyl)propanoate (19)



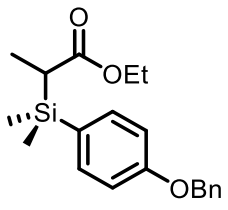
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.79 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.27 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.25 (q, *J* = 7.1 Hz, 1H), 1.16-1.13 (m, 6H), 0.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.09, 138.68, 136.85, 136.00, 134.26, 125.69, 114.65, 59.99, 30.14, 14.46, 11.42, –3.87, –4.75. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 0.26. HRMS (FAB) *m/z*: 262.1384 (M^+); calc. for $C_{15}H_{22}O_2Si$: 262.1389.

Ethyl 2-((4-ethynylphenyl)dimethylsilyl)propanoate (20)



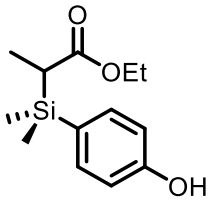
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (m, 4H), 4.01 (qd, *J* = 7.2, 0.6 Hz, 2H), 3.11 (s, 1H), 2.24 (q, *J* = 7.1 Hz, 1H), 1.17-1.10 (m, 6H), 0.37 (d, *J* = 0.7 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.89, 137.69, 133.87, 131.36, 123.20, 83.70, 78.08, 60.04, 29.98, 14.44, 11.38, –4.10, –4.75. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 0.79. HRMS (FAB) *m/z*: 259.1153 ((M+H)–H_2^+); calc. for $C_{15}H_{19}O_2Si$: 259.1154.

Ethyl 2-((4-(benzyloxy)phenyl)dimethylsilyl)propanoate (21a)



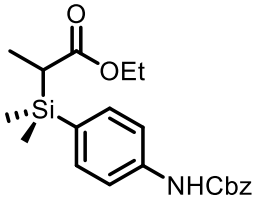
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.30 (m, 7H), 7.05-6.93 (m, 2H), 5.08 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.22 (q, *J* = 7.1 Hz, 1H), 1.20-1.10 (m, 6H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.22, 160.07, 137.01, 135.51, 128.74, 128.13, 127.61, 127.52, 114.56, 69.87, 59.93, 30.35, 14.48, 11.45, –3.75, –4.57. HRMS (FAB) *m/z*: 342.1665 (M^+); calc. for $C_{20}H_{26}O_3Si$: 342.1651.

Ethyl 2-((4-hydroxyphenyl)dimethylsilyl)propanoate (21)



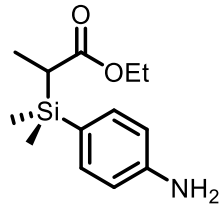
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.49 (s, 1H), 4.03 (qd, *J* = 7.1, 0.6 Hz, 2H), 2.23 (q, *J* = 7.1 Hz, 1H), 1.19-1.12 (m, 6H), 0.35 (d, *J* = 1.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.67, 157.18, 135.68, 126.90, 115.16, 60.12, 30.51, 14.46, 11.43, –3.83, –4.33. HRMS (FAB) *m/z*: 252.1175 (M^+); calc. for $C_{13}H_{20}O_3Si$: 252.1182.

Ethyl 2-((4-(((benzyloxy)carbonyl)amino)phenyl)dimethylsilyl)propanoate (22a)



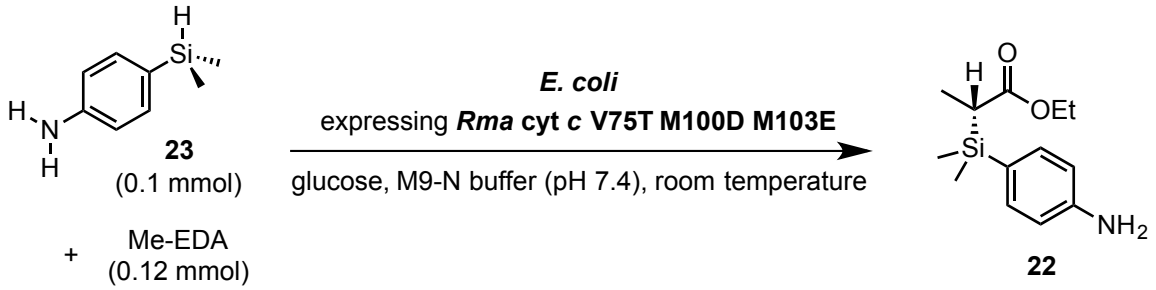
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.30 (m, 9H), 6.70 (s, 1H), 5.20 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.22 (q, *J* = 7.1 Hz, 1H), 1.18-1.10 (m, 6H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.13, 153.24, 139.07, 136.06, 134.98, 130.78, 128.78, 128.56, 128.48, 117.96, 67.24, 59.98, 30.21, 14.49, 11.41, –3.83, –4.68. HRMS (FAB) *m/z*: 385.1710 (M^+); calc. for $C_{21}H_{27}NO_4Si$: 385.1709.

Ethyl 2-((4-aminophenyl)dimethylsilyl)propanoate (22)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.64 (br s, 2H), 2.20 (q, *J* = 7.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 7.1 Hz, 3H), 0.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.40, 147.40, 135.32, 124.37, 114.82, 59.87, 30.47, 14.48, 11.44, –3.68, –4.68. HRMS (FAB) *m/z*: 251.1339 (M^+); calc. for $C_{13}H_{21}NO_2Si$: 251.1342. $[\alpha_D]^{25}$ = +46.1 (*c* 0.505 in cyclohexane, 98% *ee*).

VI. Preparative-Scale Whole-Cell Biocatalytic Reaction



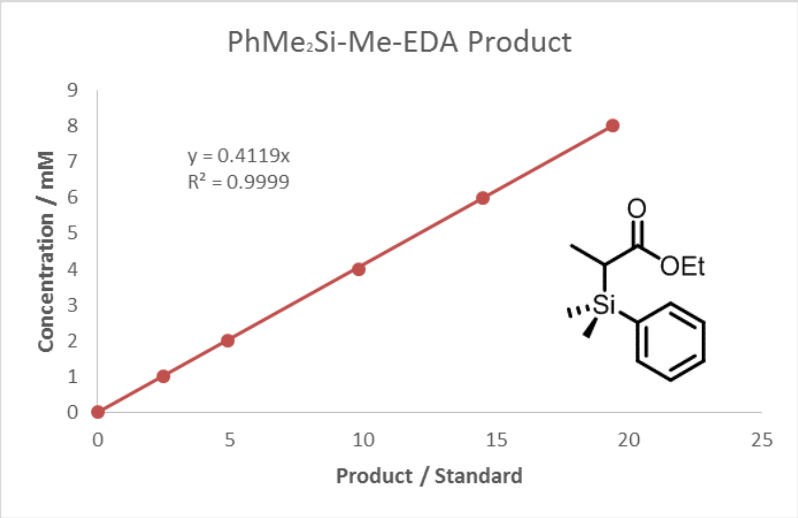
$HB_{amp/chlor}$ (50 mL) in a 250 mL flask was inoculated with an overnight culture (1 mL, $LB_{amp/chlor}$) of recombinant *E. cloni®* EXPRESS BL21(DE3) cells containing a pET22(b)+ plasmid encoding *Rma* cyt *c* V75T M100D M103D, and the pEC86 plasmid. The culture was shaken at 37 °C and 250 rpm (no humidity control) until the OD_{600} was 0.6 (approximately 2 hours). The culture was placed on ice for 30 minutes, and IPTG and 5-ALA were added to final concentrations of 20 μM and 200 μM respectively. The incubator temperature was reduced to 20 °C, and the culture was allowed to shake for 20 hours at 140 rpm. Cells were pelleted by centrifugation (4 °C, 5 min, 4,000xg), resuspended in M9-N buffer and adjusted to OD_{600} = 15. Under anaerobic conditions, to a 5 mL reaction vial was added 960 μL whole-cell solution, 40 μL glucose solution (250 mM in M9-N buffer), 15.8 μL 4-(dimethylsilyl)aniline (**23**, 0.1 mmol) and 4.9 μL Me-EDA (0.04 mmol) at room temperature. The reaction was shaken at 480 rpm. At 4 h intervals, two additional batches of whole cell (960 μL), glucose (40 μL) and Me-EDA (4.9 μL, 0.04 mmol) were added to the reaction. After the reaction was shaken for a total of 20 hours, the reaction mixture was divided between four 2 mL microcentrifuge tubes, and 0.6 mL EtOAc was added to each tube. The reaction mixtures were subjected to vortex (30 seconds) and centrifugation (14,000 rpm, 7 min) to completely separate the organic and aqueous layers. After removal of the organic layers, two addition rounds of extraction were carried out. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated, and purified by silica column chromatography with EtOAc / hexane (1:4 to 1:2) to afford pure organosilicon product **22** (17.6 mg, 0.0700 mmol, 70% yield), together with recovered silane **23** (4.0 mg, 0.0265 mmol, 26.5%). The stereoselectivity of the product was determined as 98% *ee* by chiral SFC. The protein concentration of OD_{600} = 15 whole-cell solution was determined to be 7.43 μM by the ferrous assay after cell lysis by sonication. The total turnover number for this reaction was 3410.

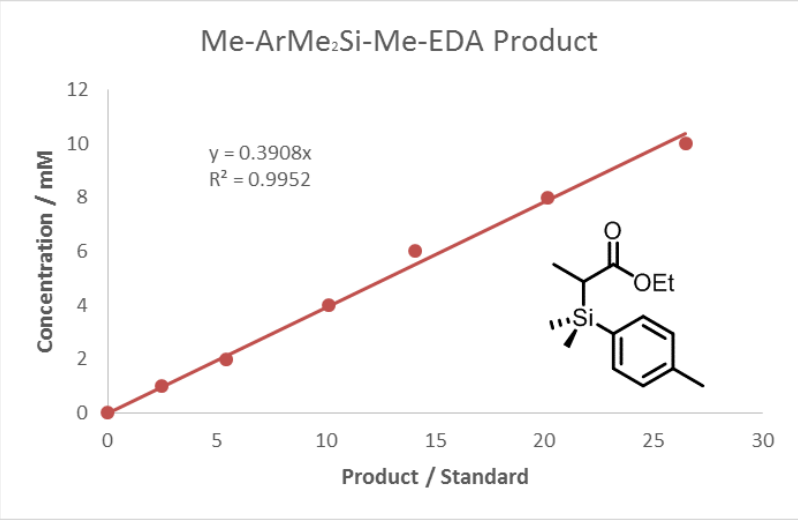
VII. GC Standard Curves for Organosilicon Products

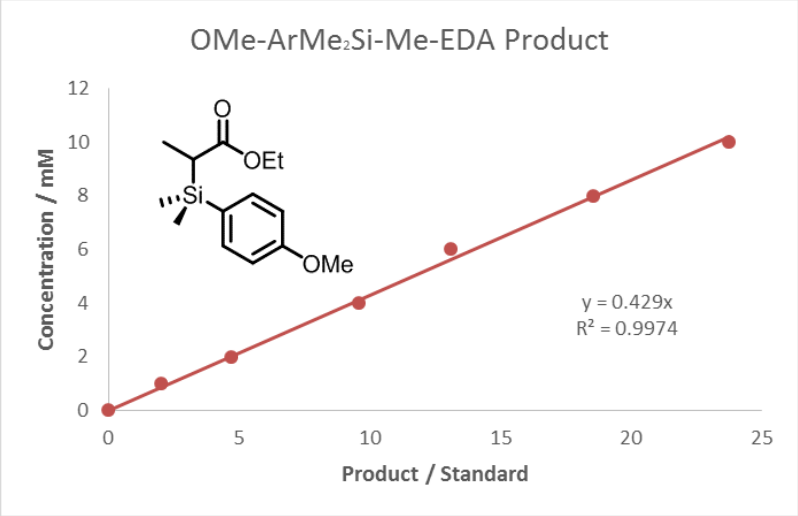
The analysis of product formation in enzymatic reactions was performed based on GC standard curves. The general procedure for preparing analytical samples for GC standard curves is described below:

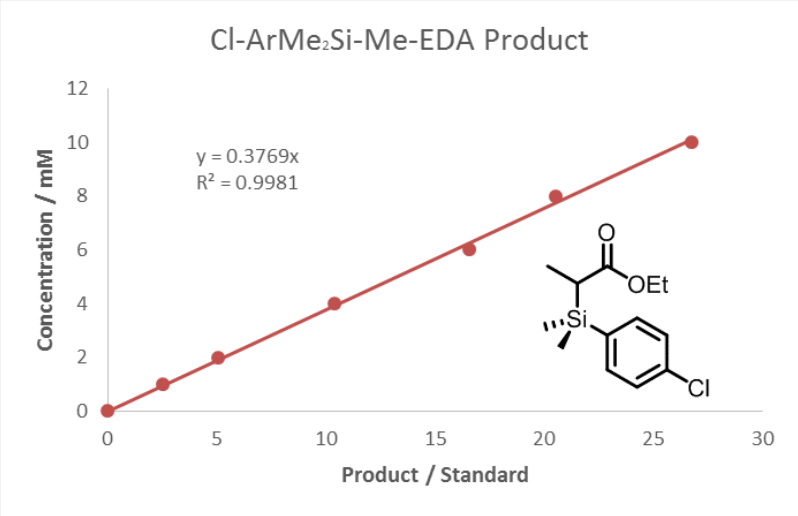
Sample preparation for GC standard curves

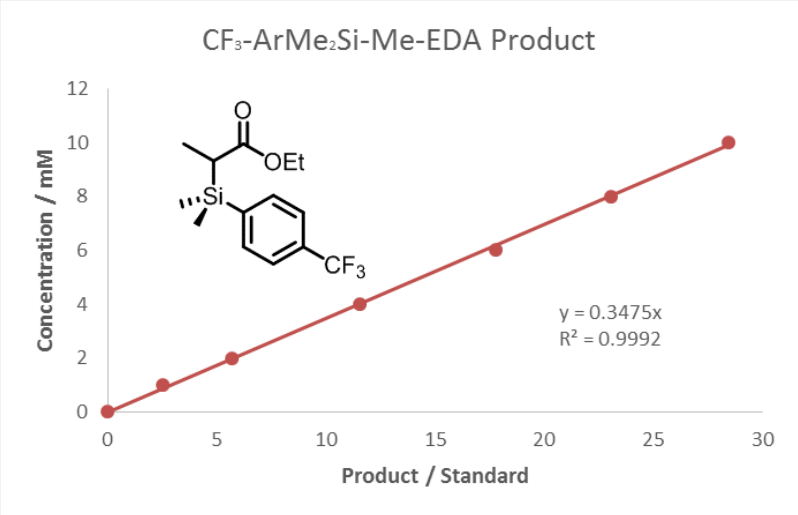
Stock solutions of chemically synthesized organosilicon products at various concentrations (20 to 200 mM in MeCN) were prepared. To a microcentrifuge tube were added 340 µL M9-N buffer, 40 µL $Na_2S_2O_4$ (100 mM in dH_2O), 20 µL organosilicon product, 20 µL internal standard (20 mM 2-phenylethanol in cyclohexane) and 1 mL cyclohexane. The mixture was vortexed (10 seconds, 3 times) then centrifuged (14,000xg, 5 min) to completely separate the organic and aqueous layers. The organic layer (750 µL) was removed for GC analysis. All data points represent the average of duplicate runs. The standard curves plot product concentration in mM (y-axis) against the ratio of product area to internal standard area on the GC (x-axis).

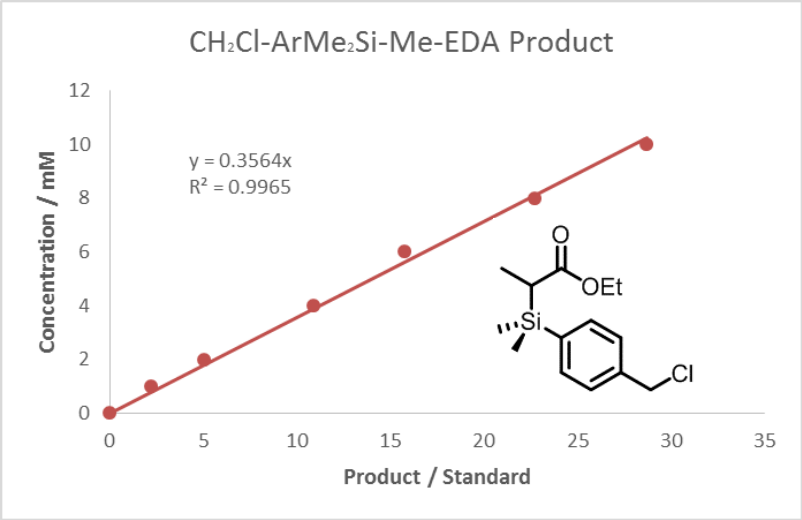


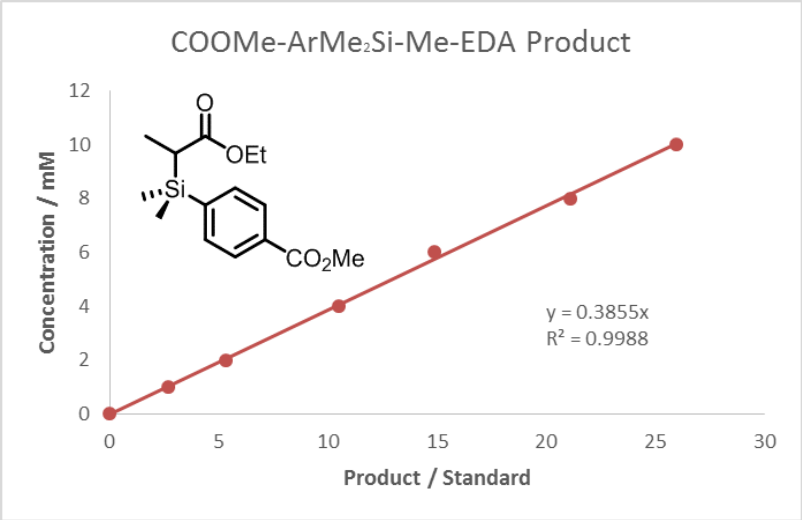


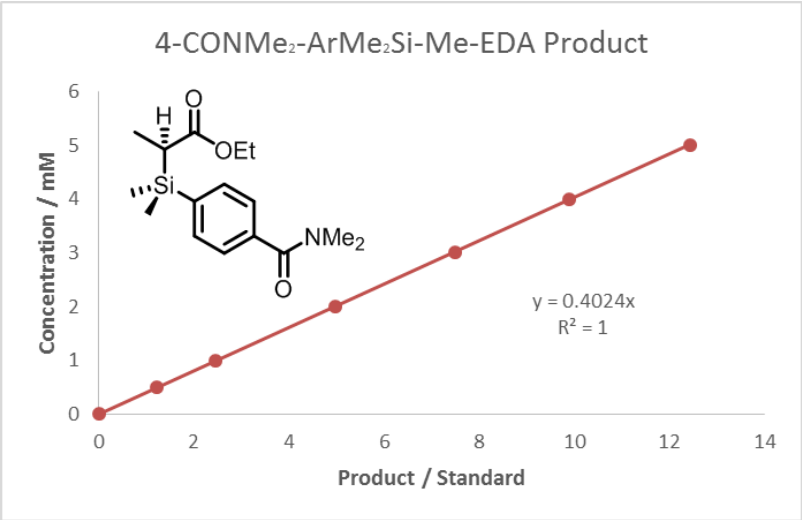

OMe-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.429x
R² = 0.9974
OEt
OMe
Si
O

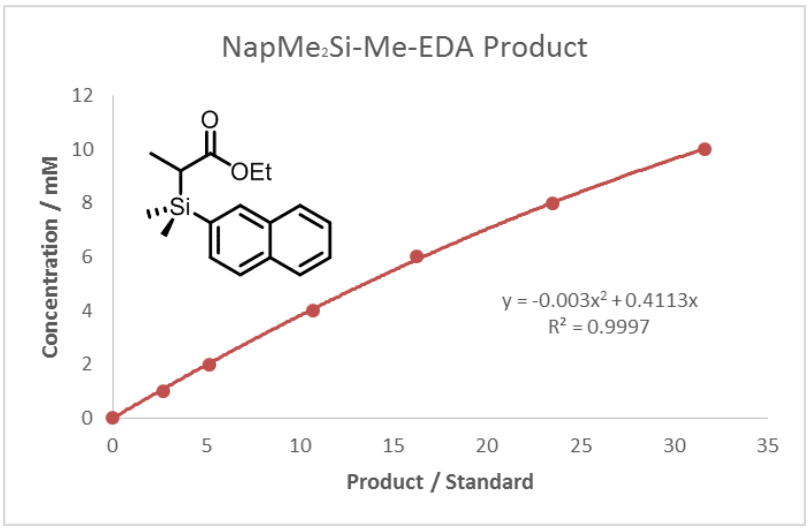

Cl-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3769x
R² = 0.9981
OEt
Cl
Si
O

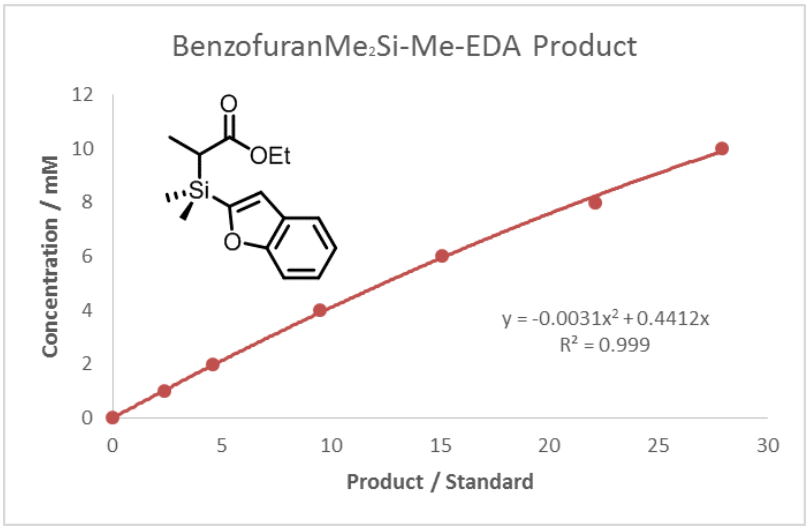

CF3-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3475x
R² = 0.9992
OEt
CF3
Si
O

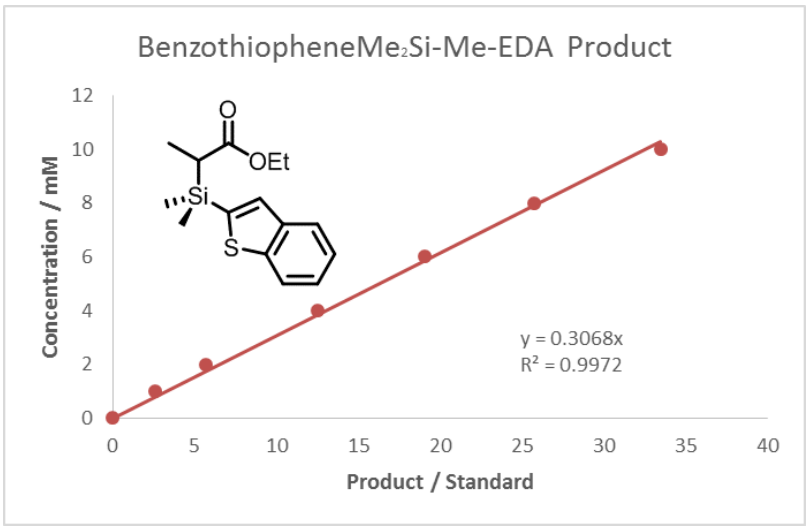

CH2Cl-ArMe2Si-Me-EDA Product
y = 0.3564x
R² = 0.9965
Concentration / mM
Product / Standard
0
2
4
6
8
10
12
0
5
10
15
20
25
30
35
O
OEt
Si
Cl

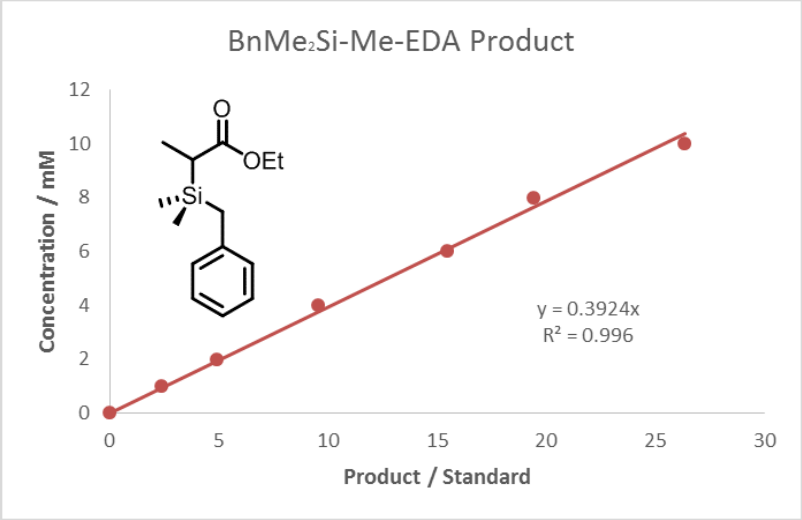

COOMe-ArMe2Si-Me-EDA Product
y = 0.3855x
R² = 0.9988
Concentration / mM
Product / Standard
0
2
4
6
8
10
12
0
5
10
15
20
25
30
O
OEt
Si
CO2Me

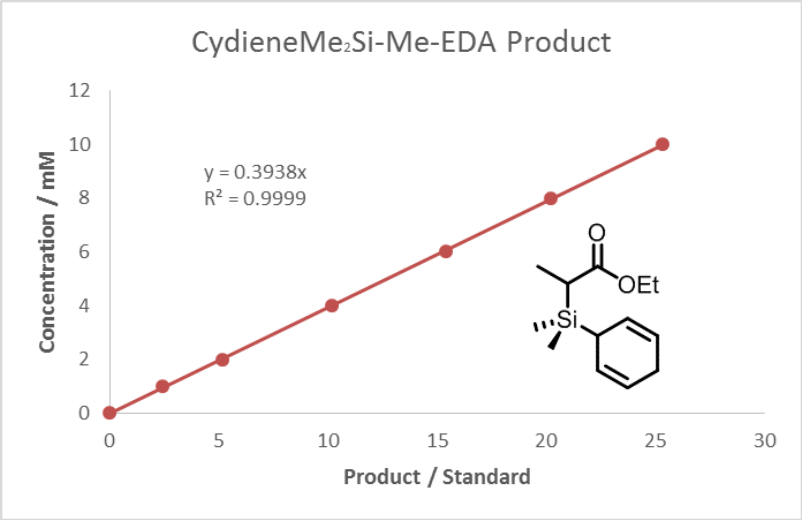

4-CONMe2-ArMe2Si-Me-EDA Product
y = 0.4024x
R² = 1
Concentration / mM
Product / Standard
0
1
2
3
4
5
6
0
2
4
6
8
10
12
14
H
O
OEt
Si
NMe2
O

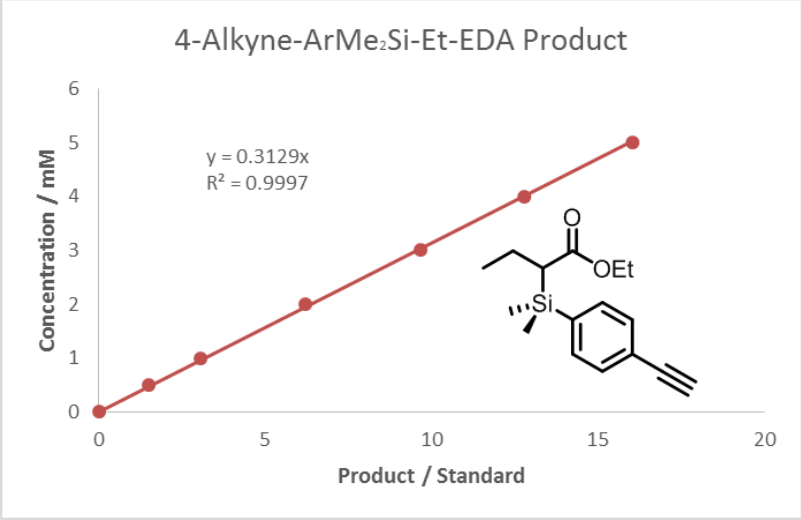

NapMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = -0.003x² + 0.4113x
R² = 0.9997
O
OEt
Si

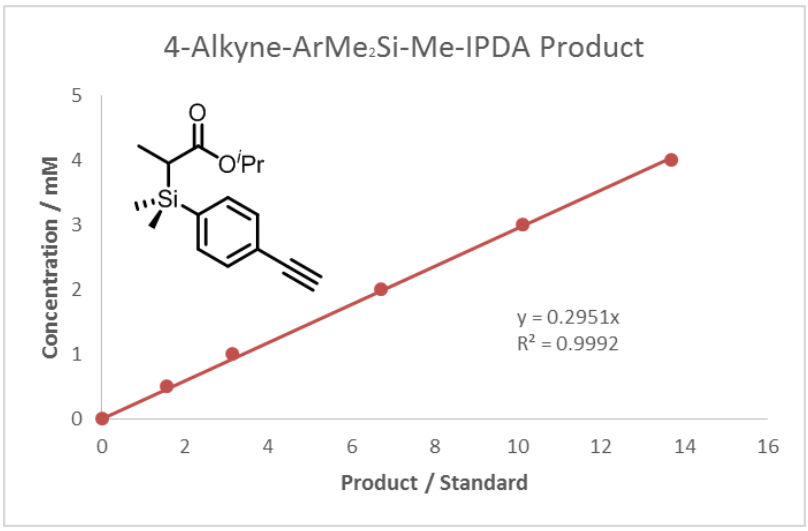

BenzofuranMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = -0.0031x² + 0.4412x
R² = 0.999
O
OEt
Si
O

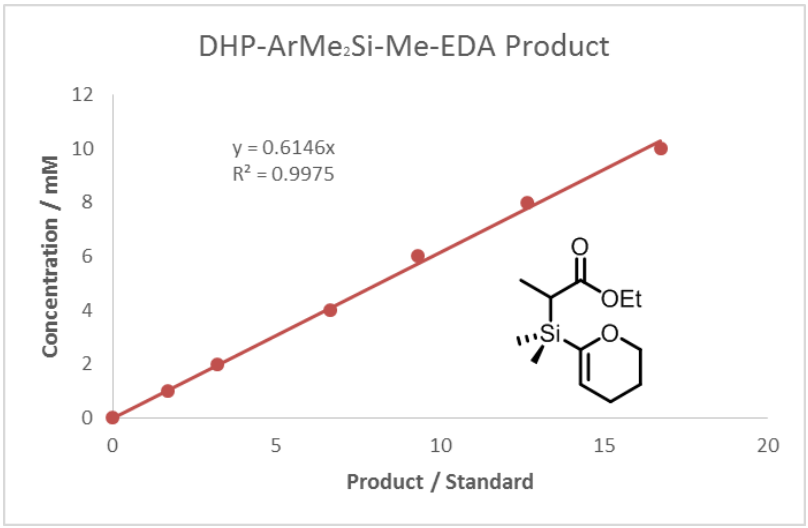

BenzothiopheneMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3068x
R² = 0.9972
O
OEt
Si
S

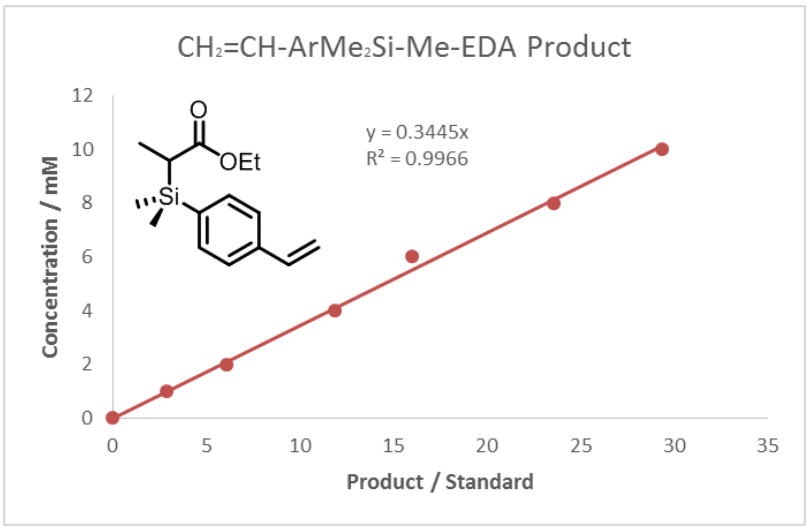

BnMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3924x
R² = 0.996
O
OEt
Si

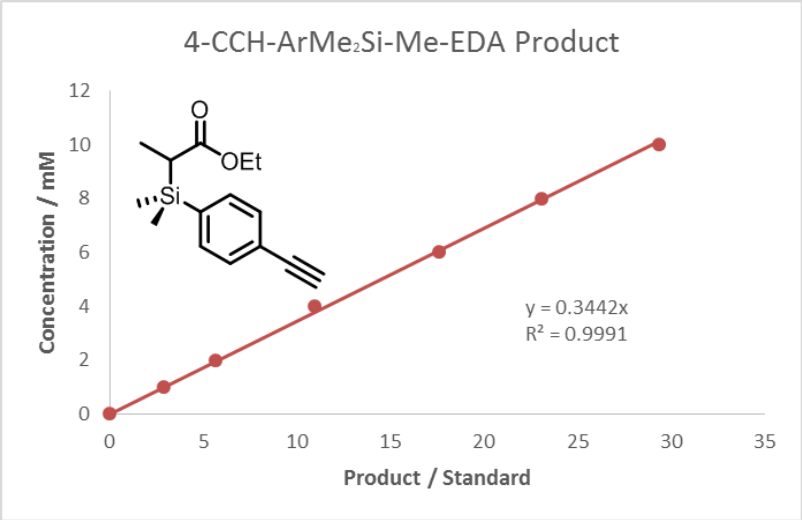

CydieneMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3938x
R² = 0.9999
O
OEt
Si

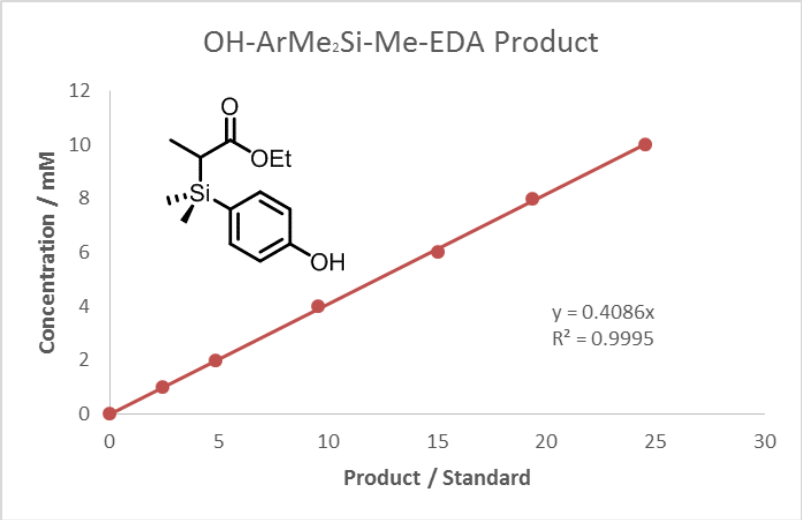

4-Alkyne-ArMe2Si-Et-EDA Product
Concentration / mM
Product / Standard
y = 0.3129x
R² = 0.9997
O
OEt
Si

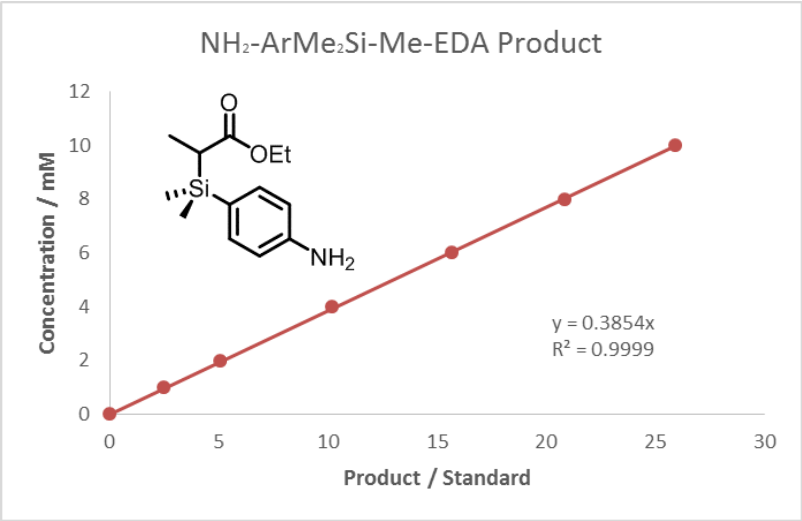

4-Alkyne-ArMe2Si-Me-IPDA Product
Concentration / mM
Product / Standard
y = 0.2951x
R² = 0.9992
O
O^iPr
Si


DHP-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.6146x
R² = 0.9975
O
OEt
Si
O


CH2=CH-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3445x
R² = 0.9966
O
OEt
Si


4-CCH-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3442x
R² = 0.9991
O
OEt
Si

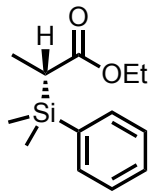

OH-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.4086x
R² = 0.9995
O
OEt
Si
OH


NH2-ArMe2Si-Me-EDA Product
Concentration / mM
Product / Standard
y = 0.3854x
R² = 0.9999
O
OEt
Si
NH2

VIII. Chiral SFC Traces for Racemic and Enzymatically Synthesized Organosilicon Products

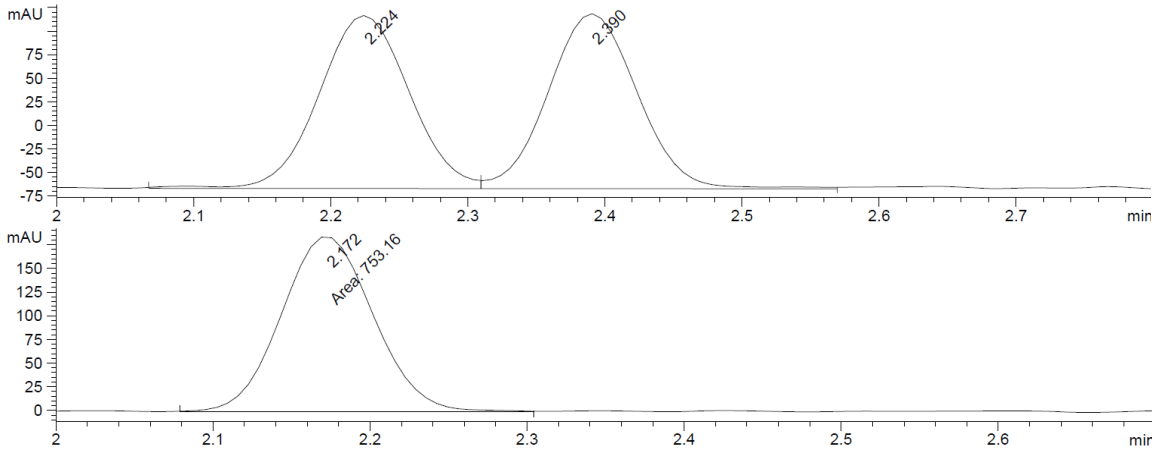
All the *ee* values of enzymatically synthesized organosilicon products were determined using chiral SFC. The chiral SFC traces for racemic and enzymatic products are shown below.

The absolute configuration of enzymatically synthesized organosilicon product **3** was determined to be (*R*) by comparing the HPLC retention times of ***rac*-3** and **3** with that reported in the literature (*12*). The absolute configurations of other organosilicon products were inferred by analogy, assuming the facial selectivity of the diazo reagents remains the same in the biosyntheses of compound **3**-**22**.



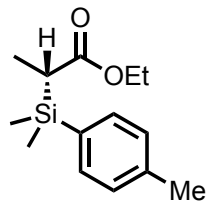
rac or *R*-**3**

Chiralpak IC, 3% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



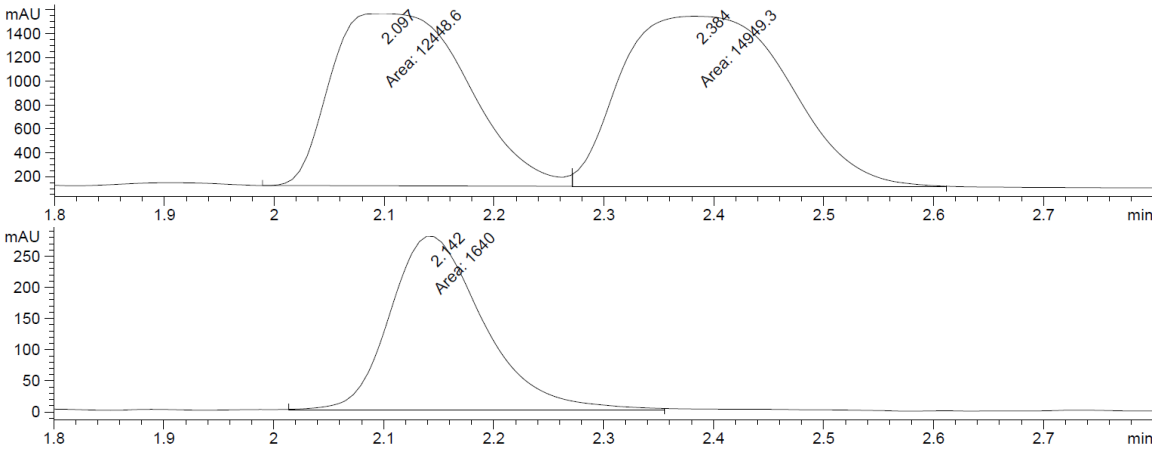
Area% report for ***rac*** and ***R*-3**:

***rac*-3**			***R*-3**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.224	842.723	50.03	2.172	753.160	100.00
2.390	841.657	49.97	-	-	
Total	1684.380	100.00	Total	753.160	100.00



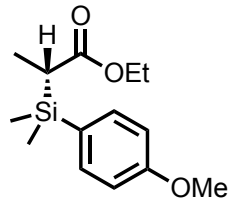
rac or *R*-**4**

Chiralpak AD-H, 3% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



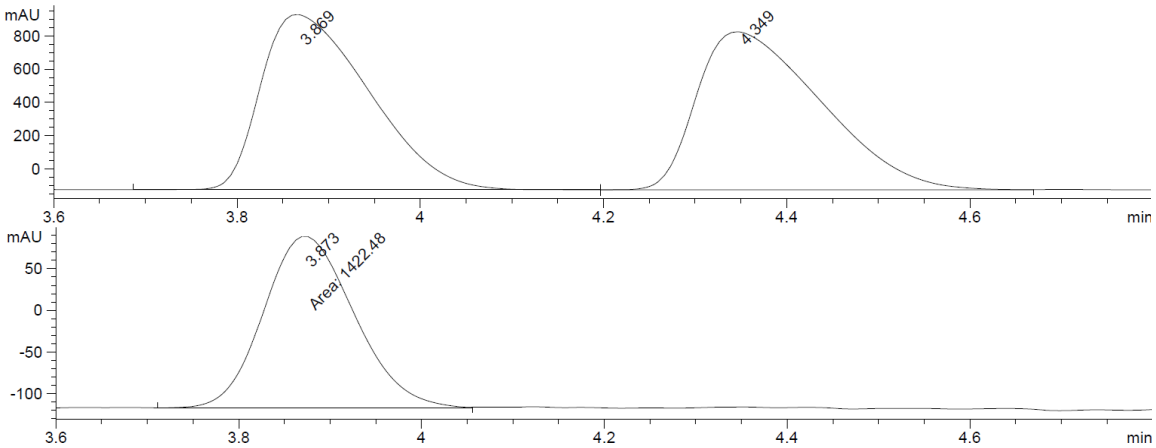
Area% report for ***rac*** and ***R*-4**:

***rac*-4**			***R*-4**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.097	124486	45.44	2.142	16934.0	100.00
2.390	149493	54.56	-	-	
Total	273979	100.00	Total	16934.0	100.00



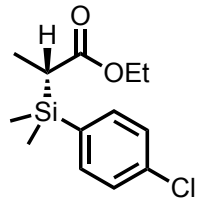
rac or *R*-**5**

Chiralpak IC, 3% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



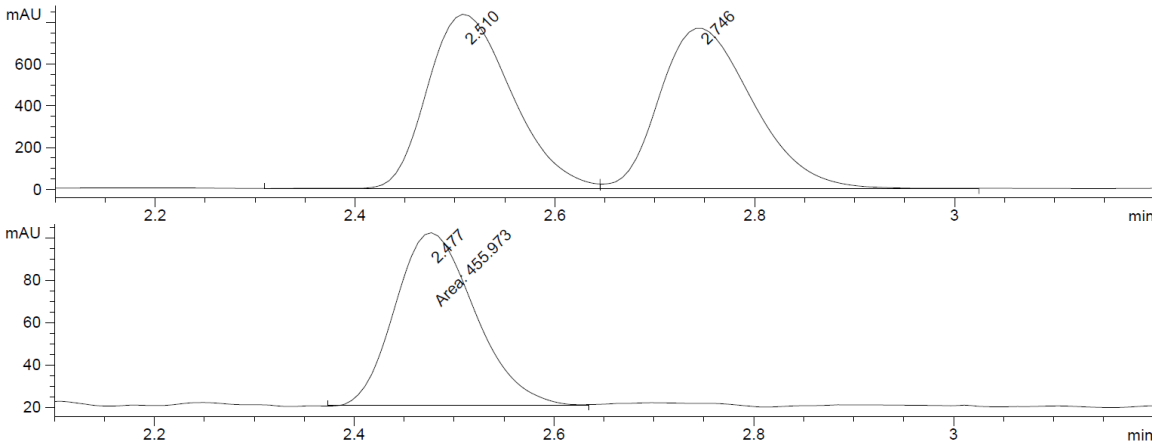
Area% report for ***rac*** and ***R*-5**:

***rac*-5**			***R*-5**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
3.869	8651.07	49.14	3.873	1422.48	100.00
4.349	8955.03	50.86	-	-	
Total	17606.10	100.00	Total	1422.48	100.00



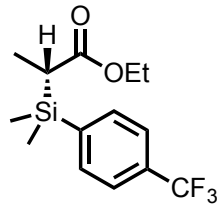
rac or *R*-**6**

Chiralpak AD-H, 3% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



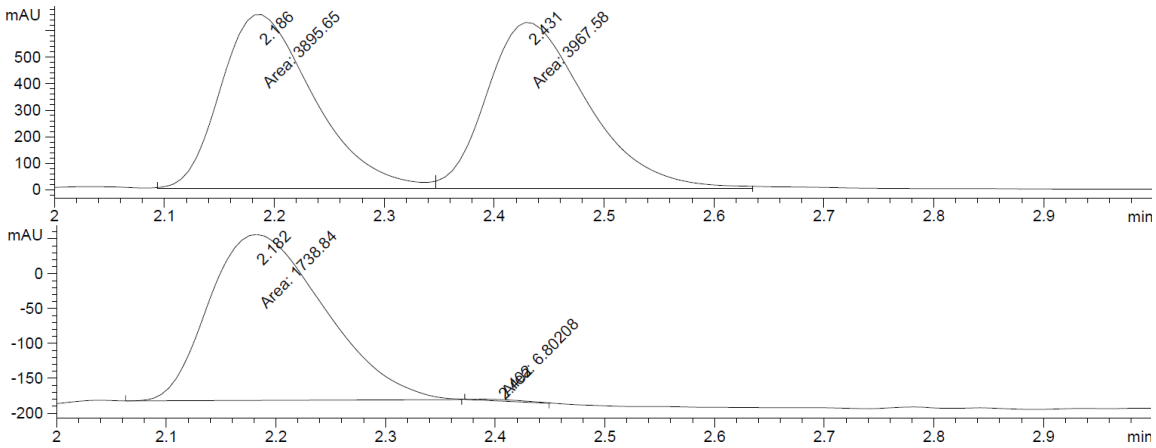
Area% report for ***rac*** and ***R*-6**:

***rac*-6**			***R*-6**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.510	4898.62	49.48	2.477	455.973	100.00
2.746	5001.36	50.52	-	-	
Total	9899.98	100.00	Total	455.973	100.00



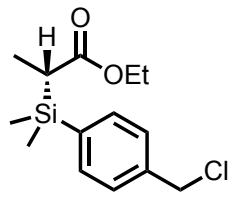
rac or *R*-**7**

Chiralcel OD-H, 2% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



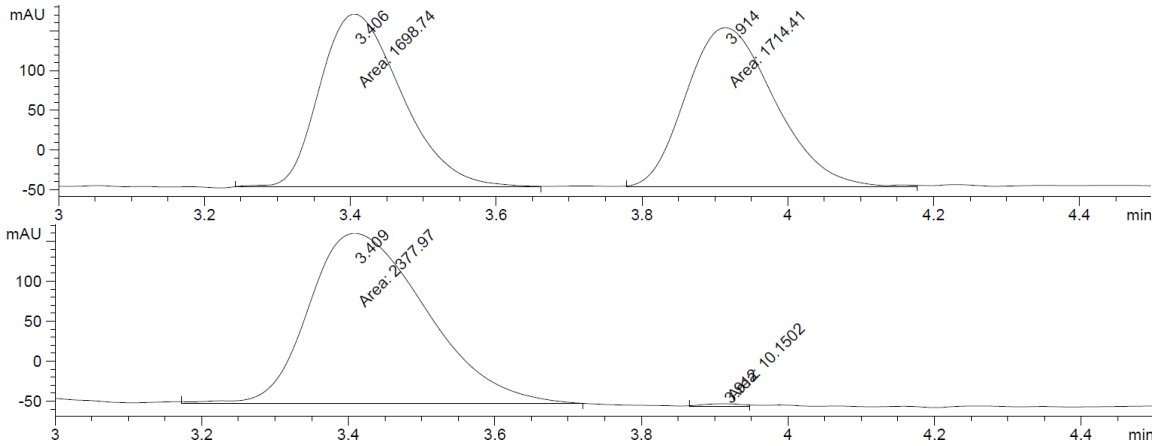
Area% report for ***rac*** and ***R*-7**:

***rac*-7**			***R*-7**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.186	3895.65	49.54	2.182	1738.84	99.61
2.431	3967.58	50.46	2.402	6.80	0.39
Total	7863.23	100.00	Total	1745.65	100.00



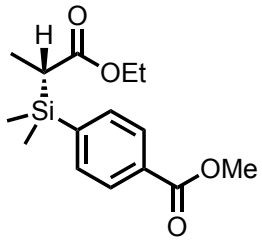
rac or *R*-**8**

Chiralpak AD-H, 3% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



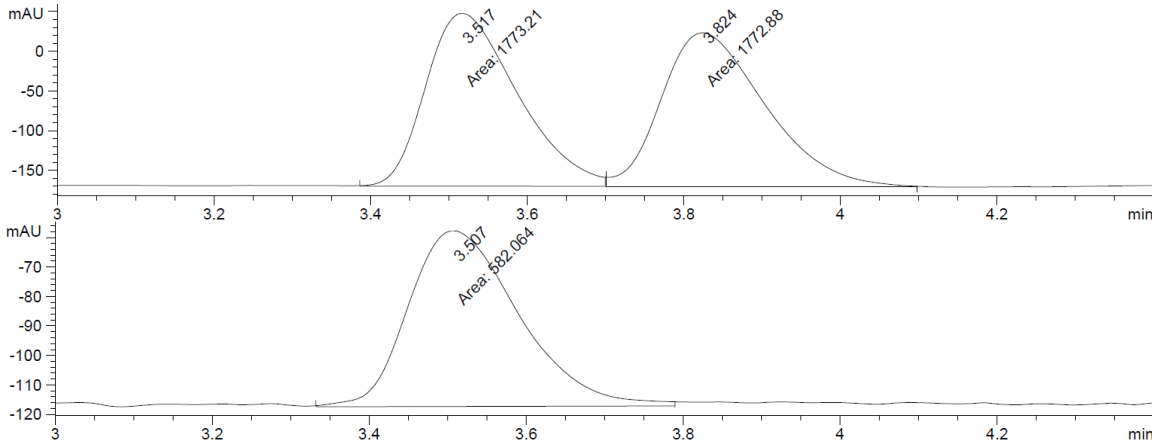
Area% report for ***rac*** and ***R*-8**:

***rac*-8**			***R*-8**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
3.406	1698.74	49.77	3.409	2377.97	99.58
3.914	1714.41	50.23	3.912	10.15	0.42
Total	3413.15	100.00	Total	2388.12	100.00



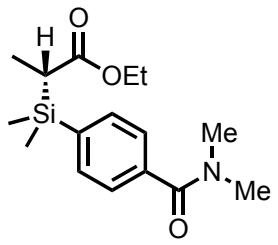
rac or *R*-**9**

Chiralcel OD-H, 5% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



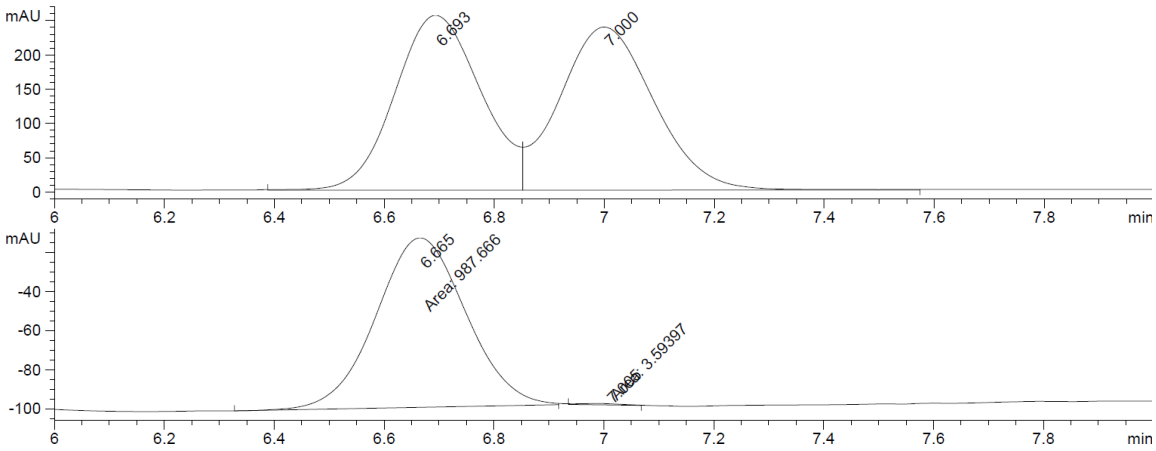
Area% report for ***rac*** and ***R*-9**:

***rac*-9**			***R*-9**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
3.517	1773.21	50.00	3.507	582.064	100.00
3.824	1772.88	50.00	-	-	
Total	3546.09	100.00	Total	582.064	100.00



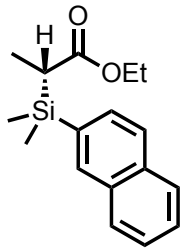
rac or *R*-**10**

Chiralpak IC, 30% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



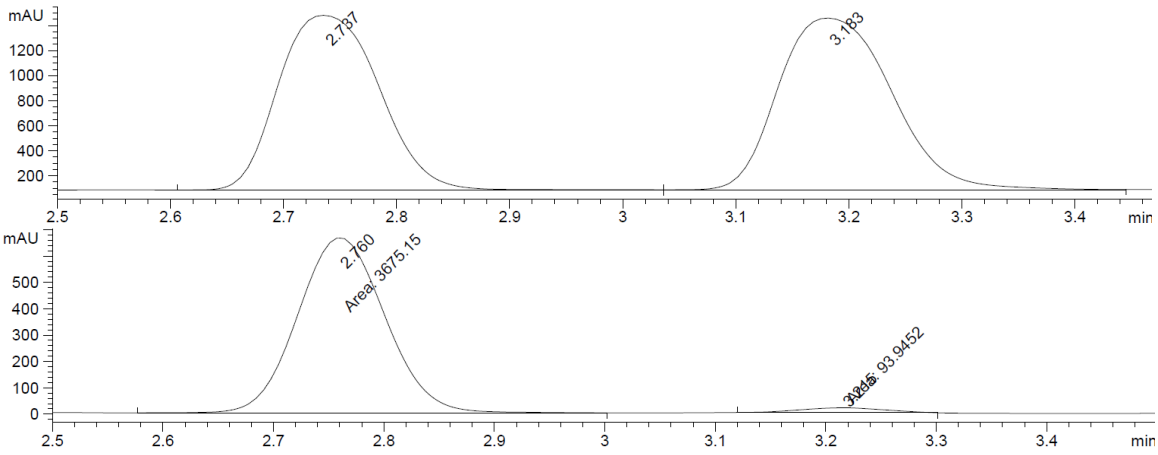
Area% report for ***rac*** and ***R*-10**:

***rac*-10**			***R*-10**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
6.693	2779.93	49.38	6.665	987.666	99.63
7.000	2849.58	50.62	7.005	3.594	0.36
Total	5629.50	100.00	Total	991.260	100.00



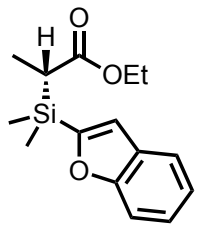
rac or *R*-**11**

Chiralpak IC, 7% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



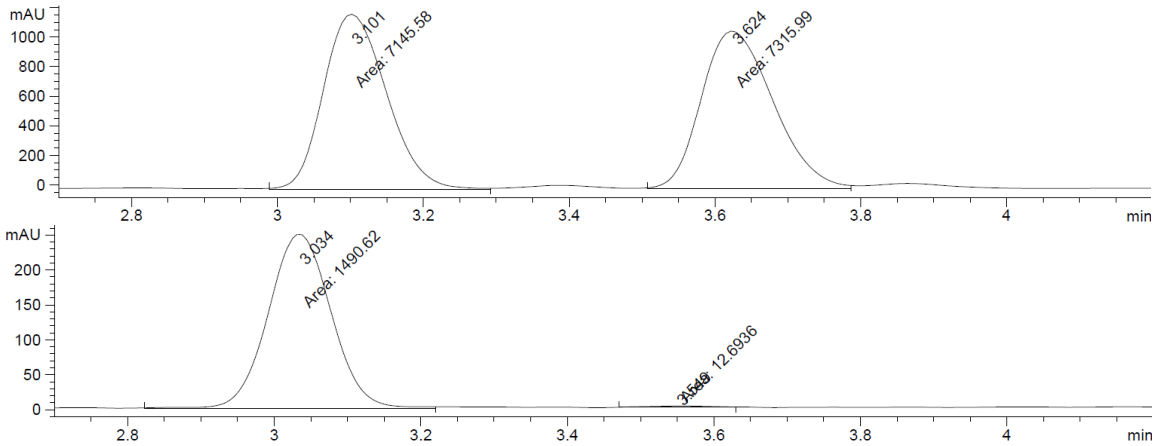
Area% report for ***rac*** and ***R*-11**:

***rac*-11**			***R*-11**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.735	8677.04	47.45	2.760	3675.15	97.51
3.183	9609.04	52.55	3.215	93.95	2.49
Total	18286.1	100.00	Total	3769.10	100.00



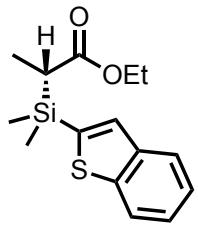
rac or *R*-**12**

Chiralpak IC, 3% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



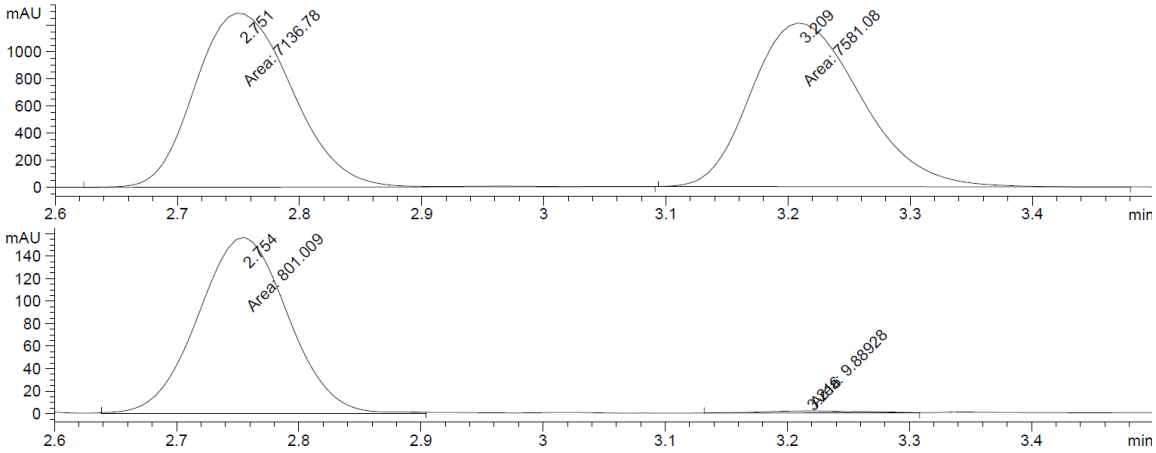
Area% report for ***rac*** and ***R*-12**:

***rac*-12**			***R*-12**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
3.101	7145.58	49.41	3.034	1490.62	99.16
3.624	7315.99	50.59	3.549	12.69	0.84
Total	14461.6	100.00	Total	1503.31	100.00



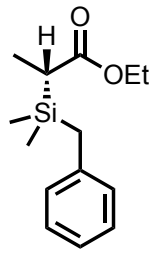
rac or *R*-**13**

Chiralpak IC, 7% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



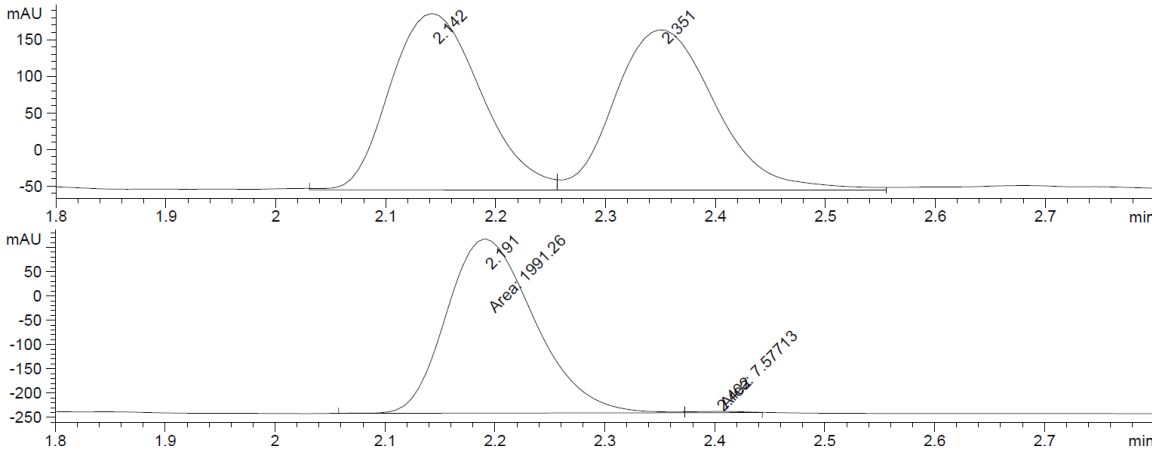
Area% report for ***rac*** and ***R*-13**:

***rac*-13**			***R*-13**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.751	7136.78	48.49	2.764	801.009	98.78
3.209	7581.08	51.51	3.219	9.889	1.22
Total	14717.9	100.00	Total	810.898	100.00



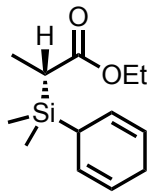
rac or *R*-**14**

Chiralpak AD-H, 3% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



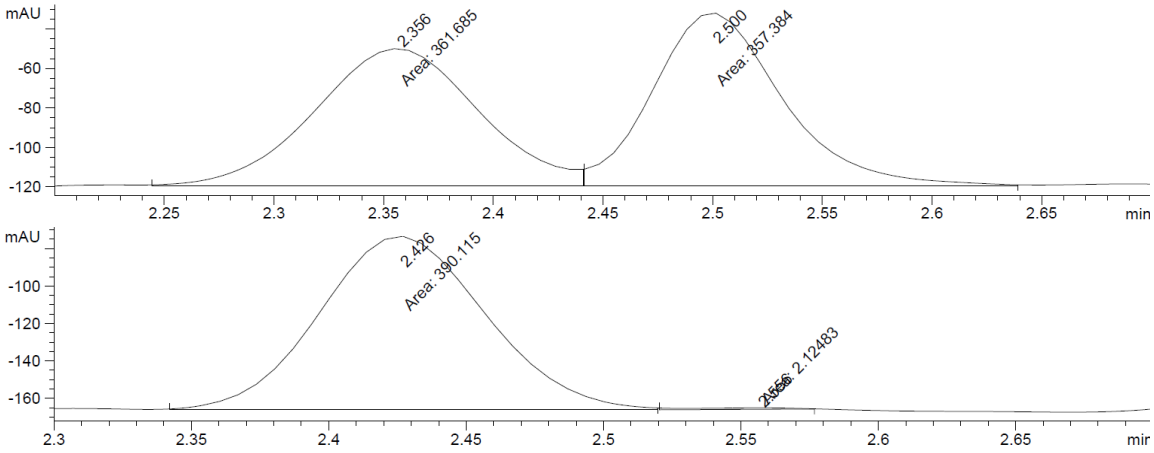
Area% report for ***rac*** and ***R*-14**:

***rac*-14**			***R*-14**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.142	1384.73	49.85	2.191	1991.26	99.62
2.351	1393.07	50.15	2.402	7.58	0.38
Total	2777.80	100.00	Total	1998.84	100.00



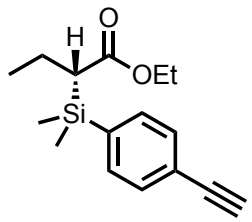
rac or *R*-**15**

Chiralpak IC, 3% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



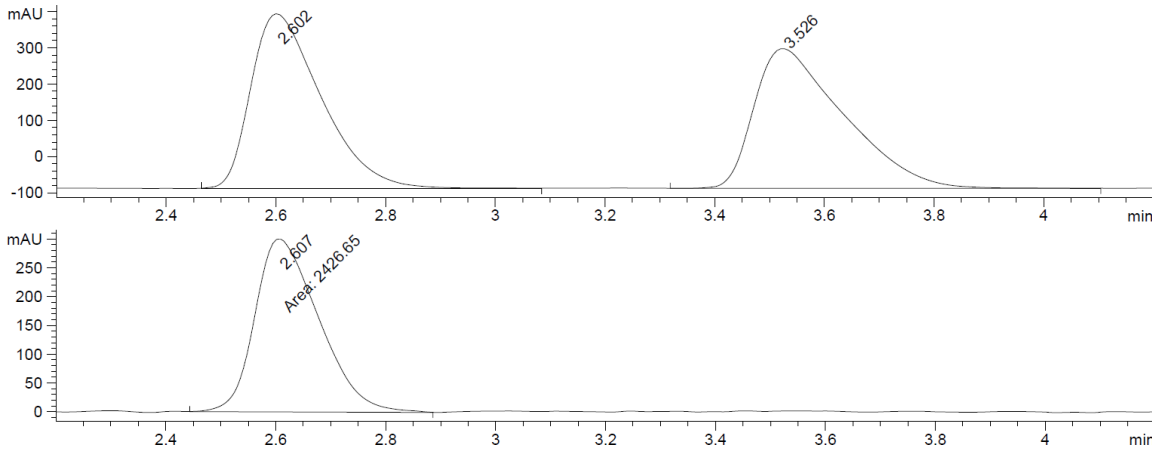
Area% report for ***rac*** and ***R*-15**:

***rac*-15**			***R*-15**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.356	361.685	50.30	2.426	390.115	99.45
2.500	357.384	49.70	2.556	2.125	0.54
Total	719.070	100.00	Total	392.240	100.00



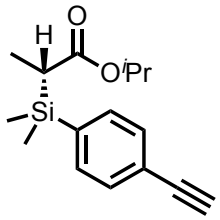
rac or *R*-**16**

Chiralpak AD-H, 3% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



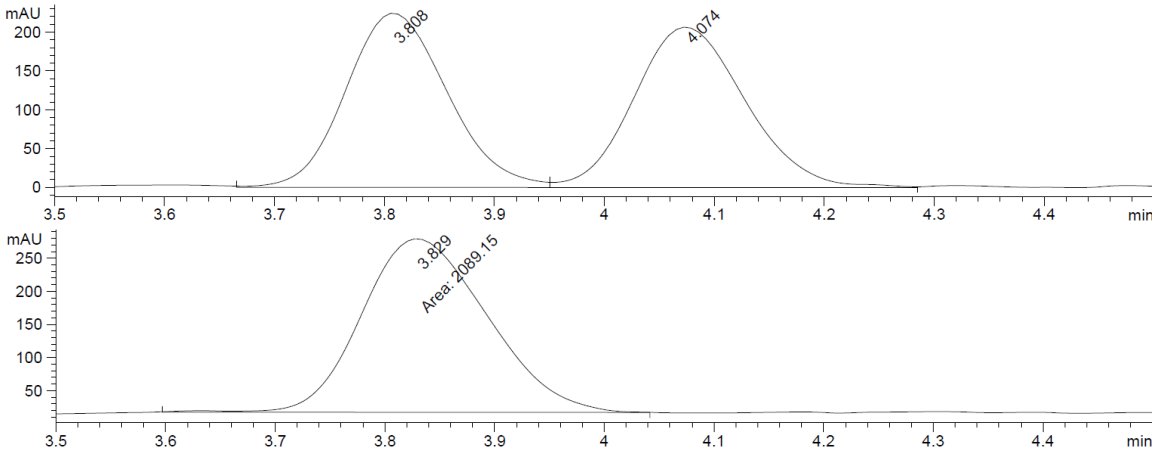
Area% report for ***rac*** and ***R*-16**:

***rac*-16**			***R*-16**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.602	4276.04	49.44	2.607	2426.65	100.00
3.526	4373.23	50.56			
Total	8649.28	100.00	Total	2426.65	100.00



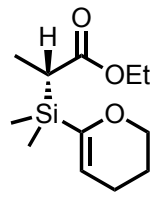
rac or *R*-**17**

Chiralpak IC, 3% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



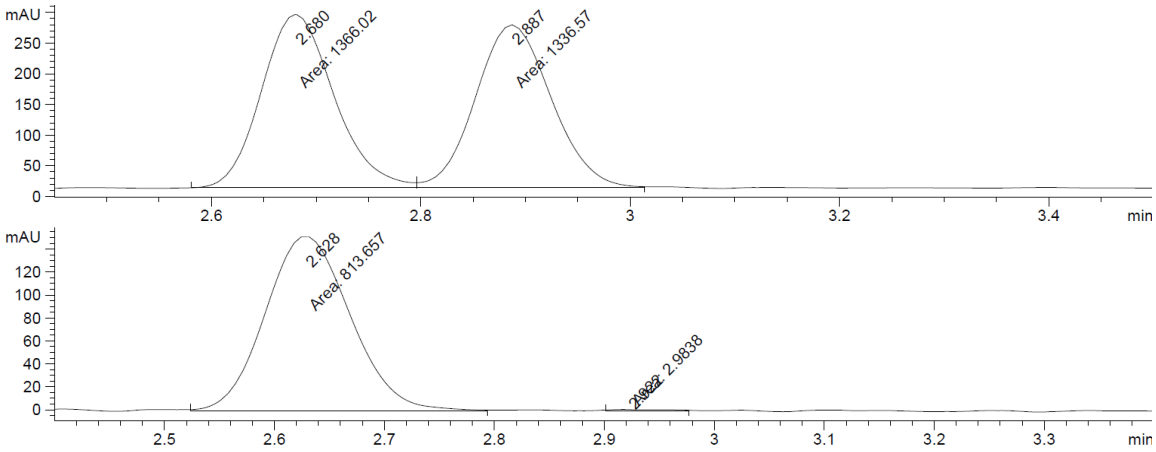
Area% report for ***rac*** and ***R*-17**:

***rac*-17**			***R*-17**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
3.808	1442.74	49.78	3.829	2089.15	100.00
4.074	1455.49	50.22			
Total	2898.23	100.00	Total	2089.15	100.00



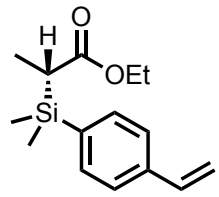
rac or *R*-**18**

Chiralpak IC, 3% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



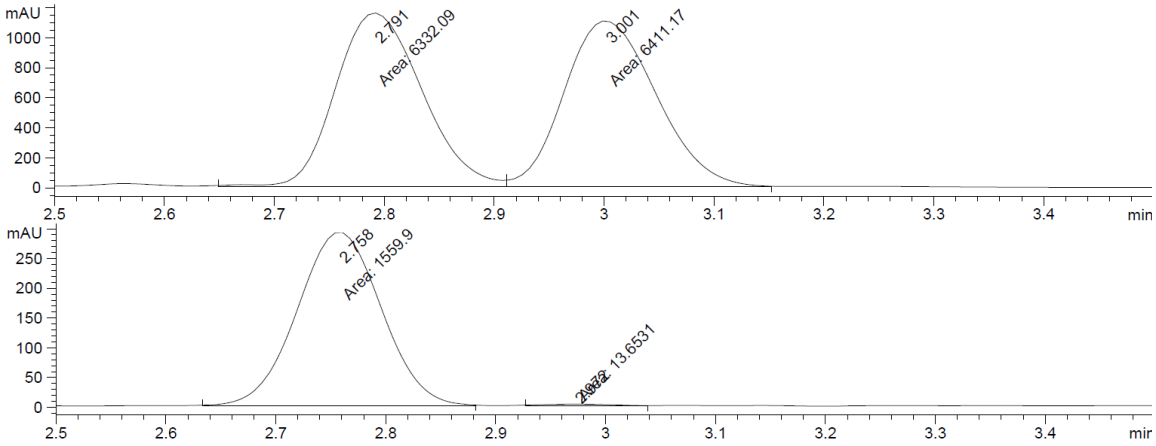
Area% report for ***rac*** and ***R*-18**:

***rac*-18**			***R*-18**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.680	1366.02	50.54	2.628	813.657	99.63
2.887	1336.57	49.46	2.922	2.984	0.37
Total	2702.59	100.00	Total	816.641	100.00



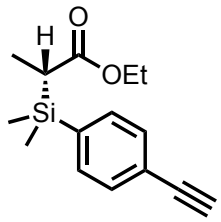
rac or *R*-**19**

Chiralpak IC, 3% *i*-PrOH in CO_2, 3.5 mL/min, 210 nm



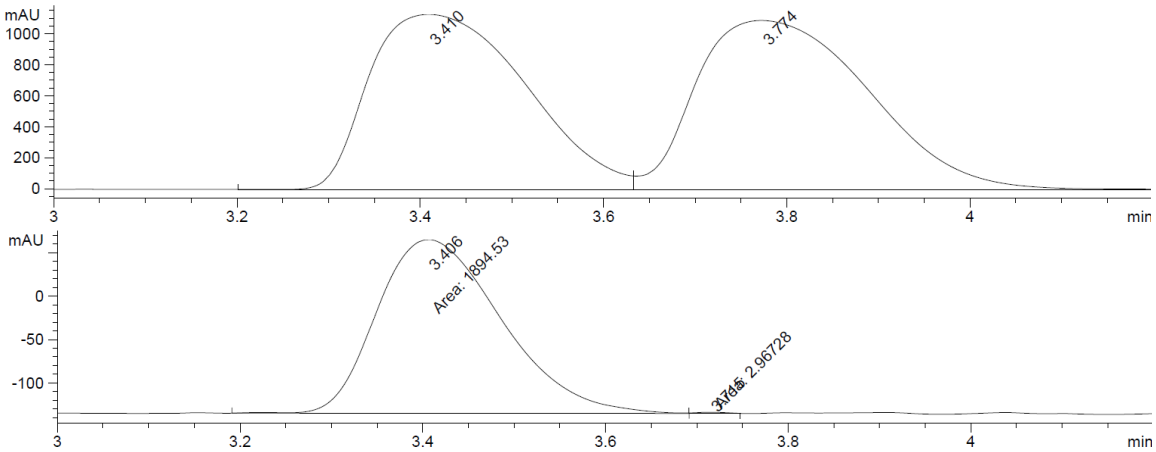
Area% report for ***rac*** and ***R*-19**:

***rac*-19**			***R*-19**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
2.791	6332.09	49.69	2.758	1559.90	99.13
3.001	6411.17	50.31	2.972	13.65	0.87
Total	12743.3	100.00	Total	1573.56	100.00



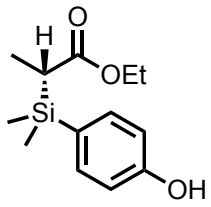
rac or *R*-**20**

Chiralcel OD-H, 3% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



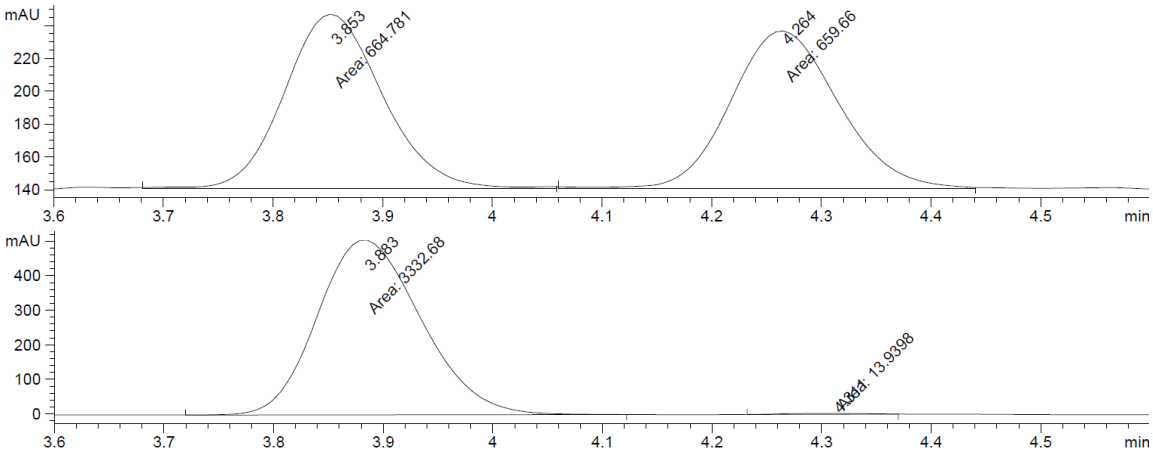
Area% report for ***rac*** and ***R*-20**:

***rac*-20**			***R*-20**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
3.410	13436.2	48.40	3.406	1894.53	99.84
3.774	14326.4	51.60	3.715	2.97	0.16
Total	27762.6	100.00	Total	1897.50	100.00



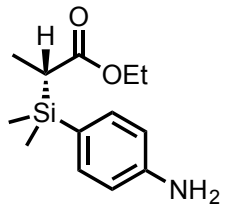
rac or *R*-**21**

Chiralpak IC, 10% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



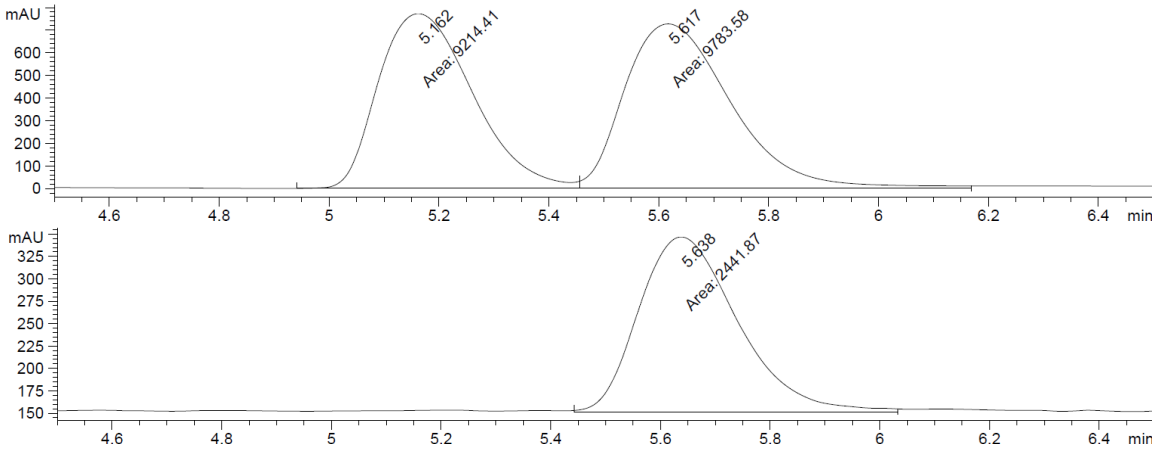
Area% report for ***R*-21**:

***rac*-21**			***R*-21**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
3.853	664.781	50.19	3.883	3332.68	99.58
4.264	659.660	49.81	4.331	13.94	0.42
Total	1324.441	100.00	Total	3346.62	100.00



rac or *R*-**22**

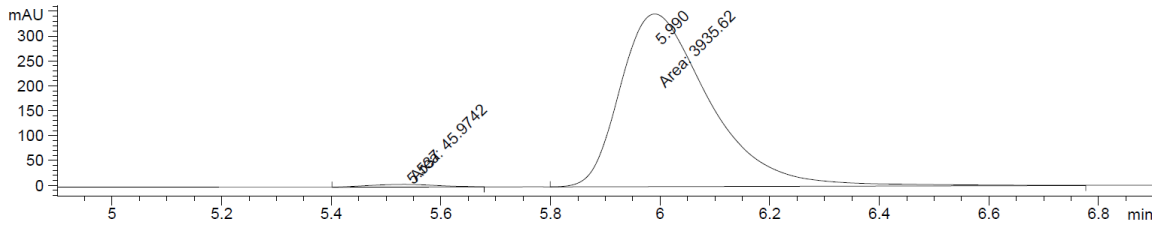
Chiralpak AD-H, 10% *i*-PrOH in CO_2, 2.5 mL/min, 210 nm



Area% report for ***rac*** and ***R*-22**:

***rac*-22**			***R*-22**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
5.162	9214.41	48.50	-	-	
5.617	9783.58	51.50	5.638	195.47	100.00
Total	18998.0	100.00	Total	195.47	100.00

Preparative-scale reaction (0.1 mmol):



Area% report for ***R*-22**:

***R*-22** (OD 15-whole cell)		
Retention Time (min)	Area (mAU*s)	Area %
5.537	45.97	1.15
5.990	3935.62	98.85
Total	3981.59	100.00

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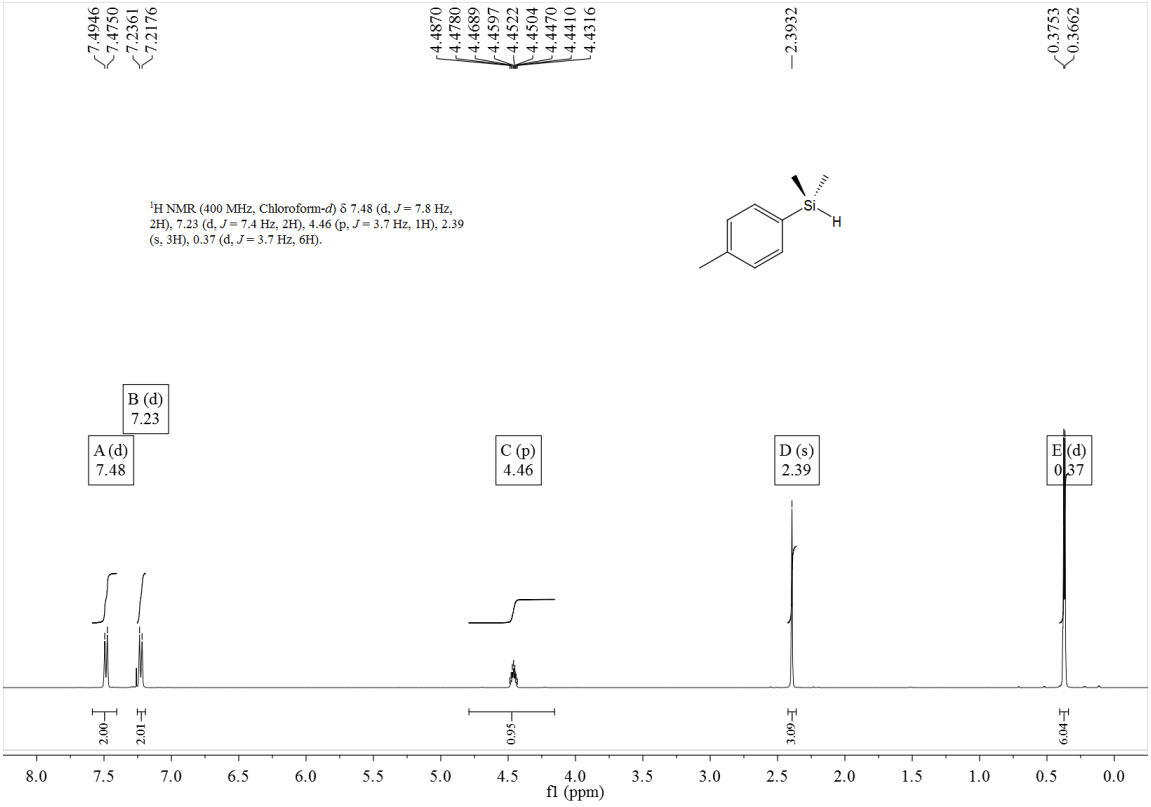
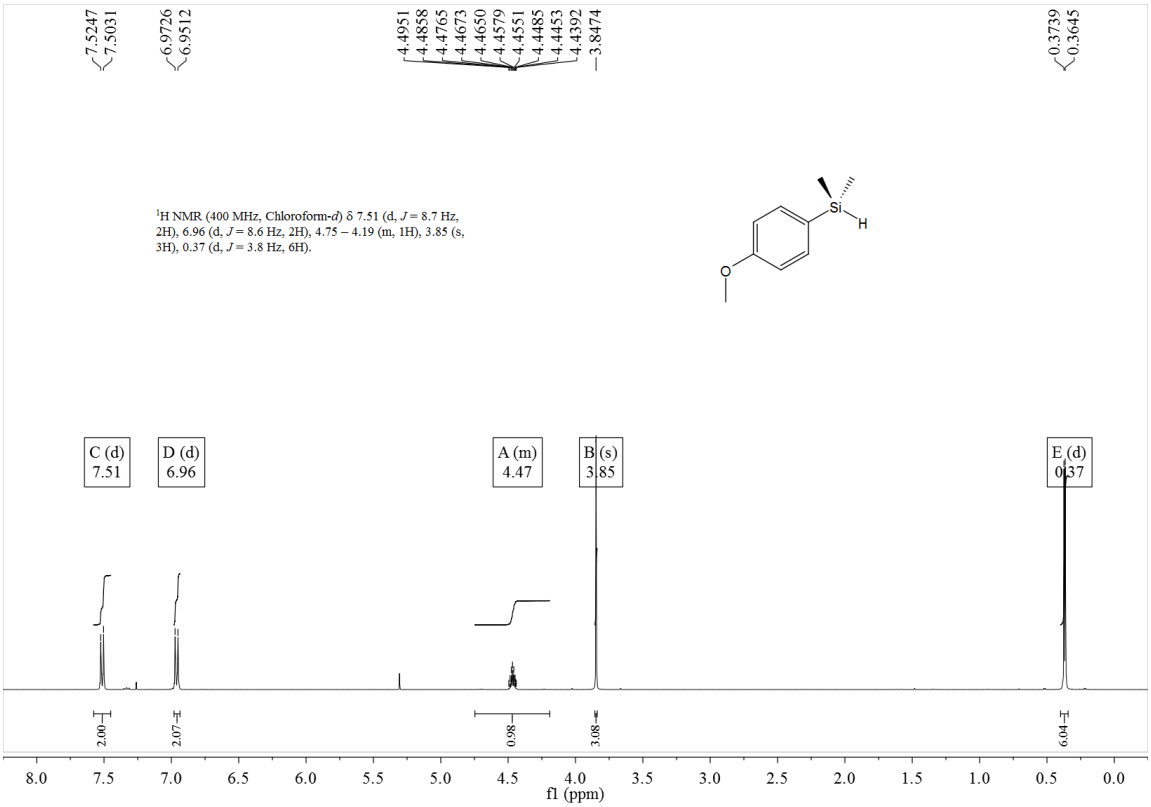
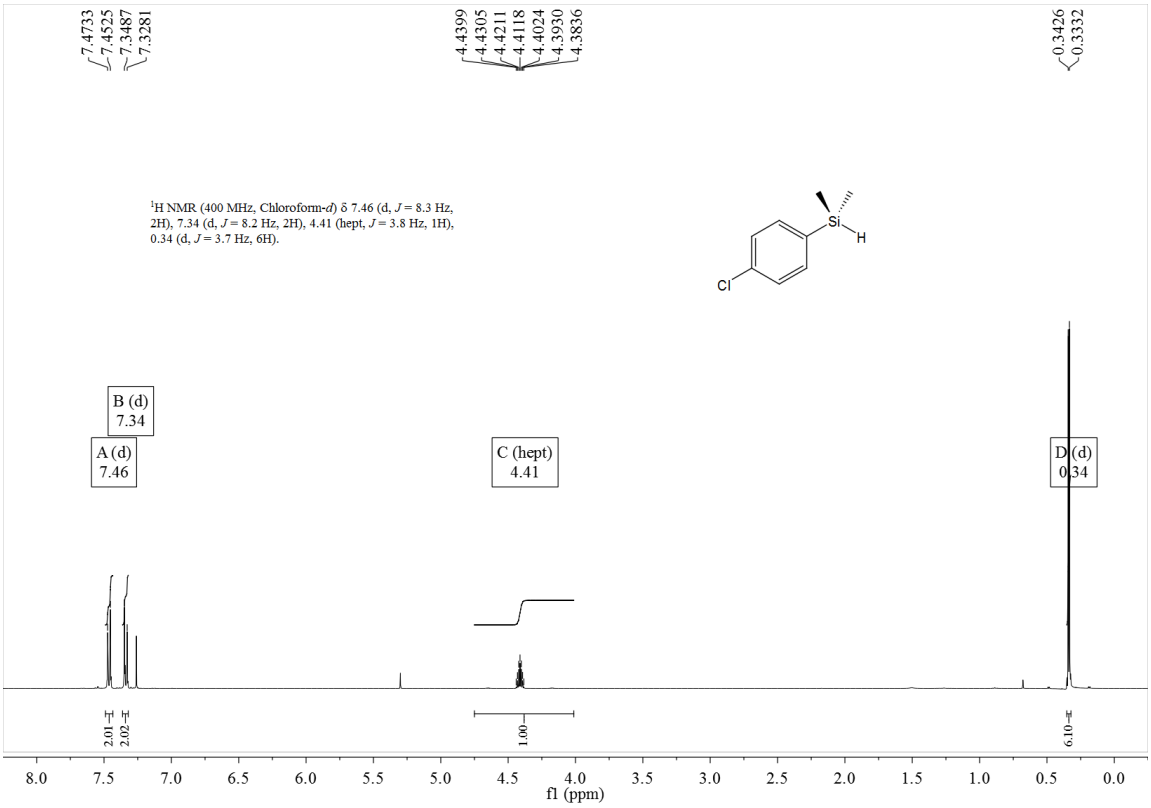
X. NMR Spectra



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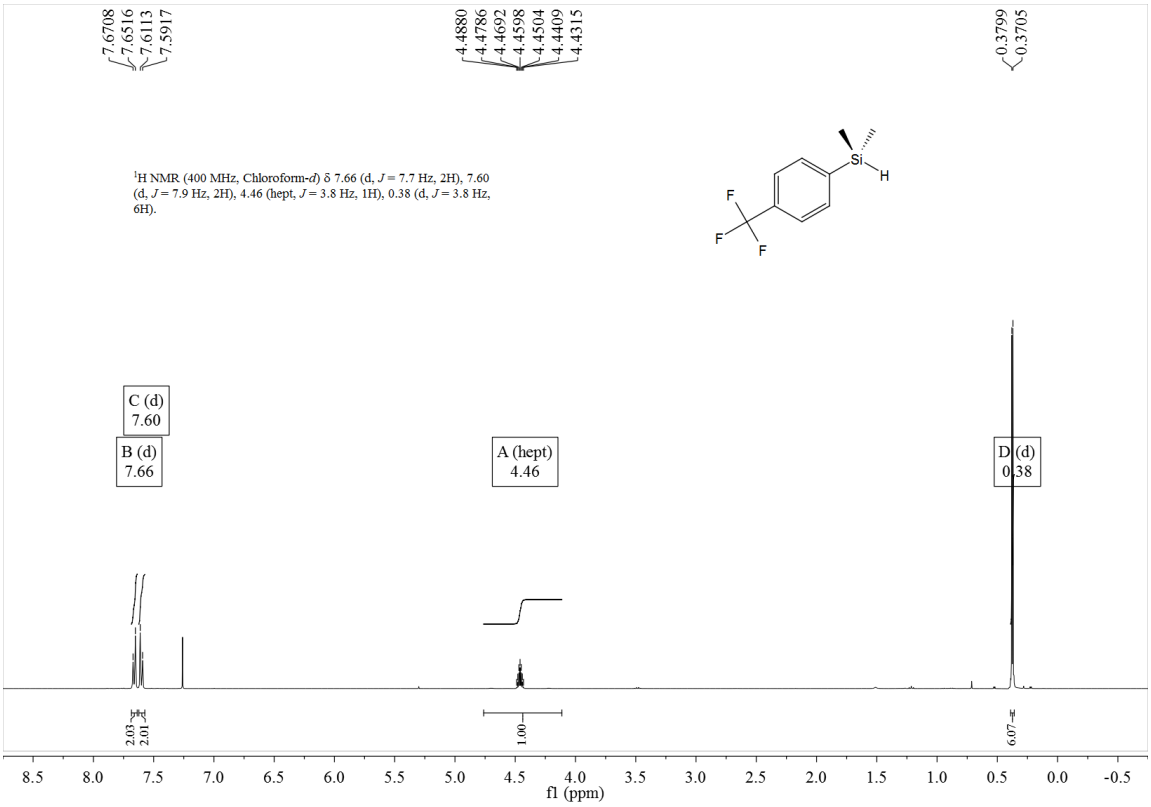
4.4305
4.4211
4.4118
4.4024
4.3930
4.3836
0.3426
0.3332
1H NMR (400 MHz, Chloroform-d) δ 7.46 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 4.41 (hept, J = 3.8 Hz, 1H), 0.34 (d, J = 3.7 Hz, 6H).
Si
H
Cl
B (d) 7.34
A (d) 7.46
C (hept) 4.41
D (d) 0.34
2.01
2.02
1.00
6.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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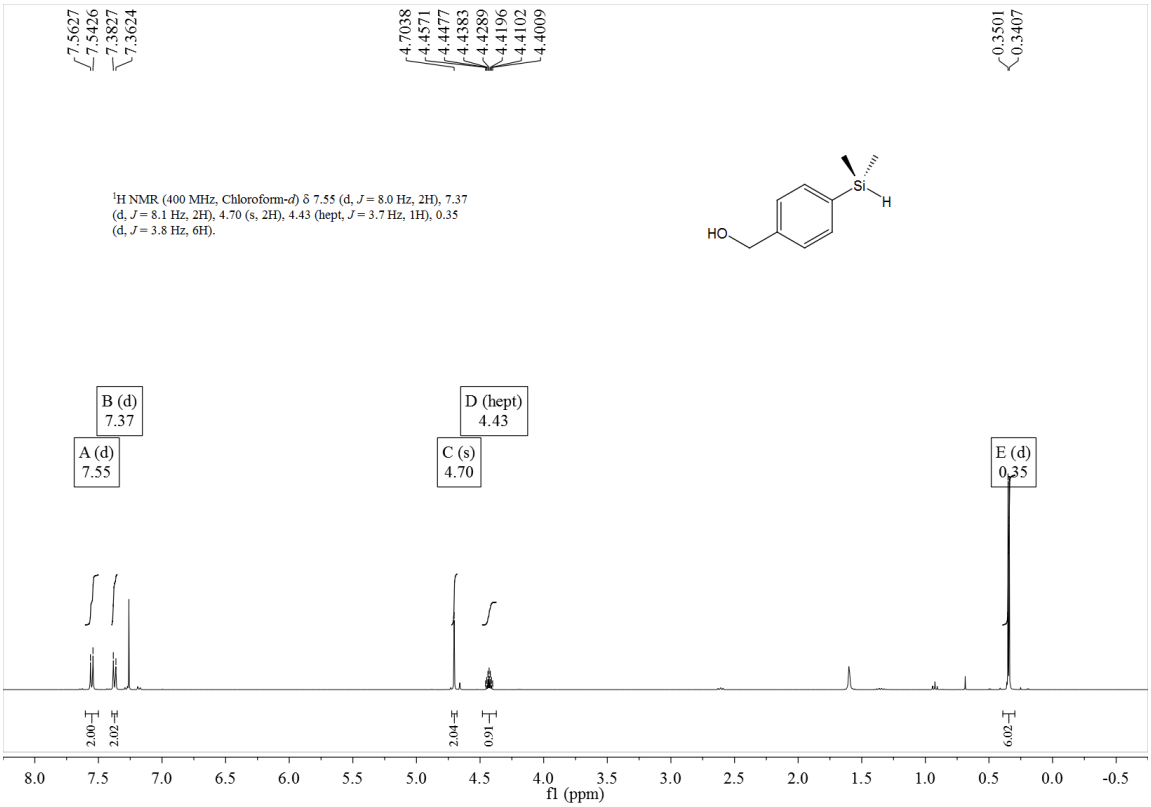
4.4880
4.4786
4.4692
4.4598
4.4504
4.4409
4.4315
0.3799
0.3705
1H NMR (400 MHz, Chloroform-d) δ 7.66 (d, J = 7.7 Hz, 2H), 7.60 (d, J = 7.9 Hz, 2H), 4.46 (hept, J = 3.8 Hz, 1H), 0.38 (d, J = 3.8 Hz, 6H).
Si
H
F
F
F
C (d) 7.60
B (d) 7.66
A (hept) 4.46
D (d) 0.38
2.03
2.01
1.00
6.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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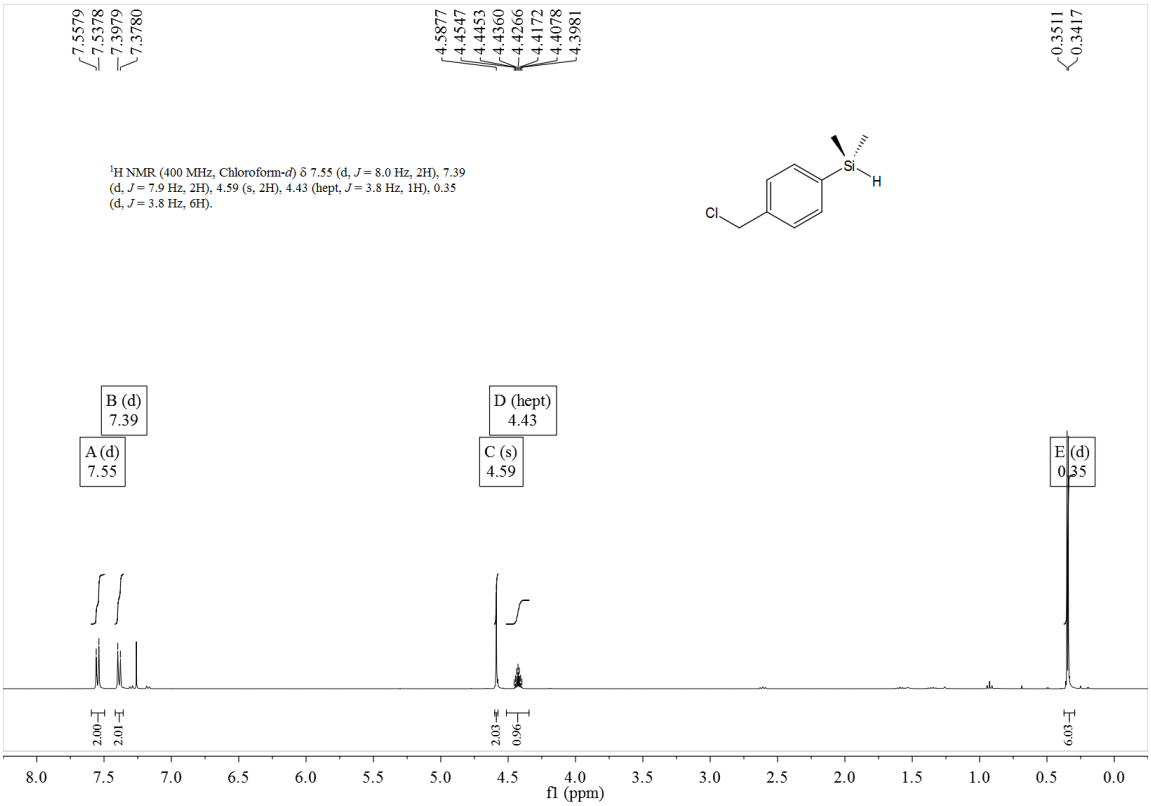
4.4477
4.4383
4.4289
4.4196
4.4102
4.4009
0.3501
0.3407
1H NMR (400 MHz, Chloroform-d) δ 7.55 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 4.70 (s, 2H), 4.43 (hept, J = 3.7 Hz, 1H), 0.35 (d, J = 3.8 Hz, 6H).
HO
Si
H
B (d) 7.37
A (d) 7.55
D (hept) 4.43
C (s) 4.70
E (d) 0.35
2.00
2.02
2.04
0.91
6.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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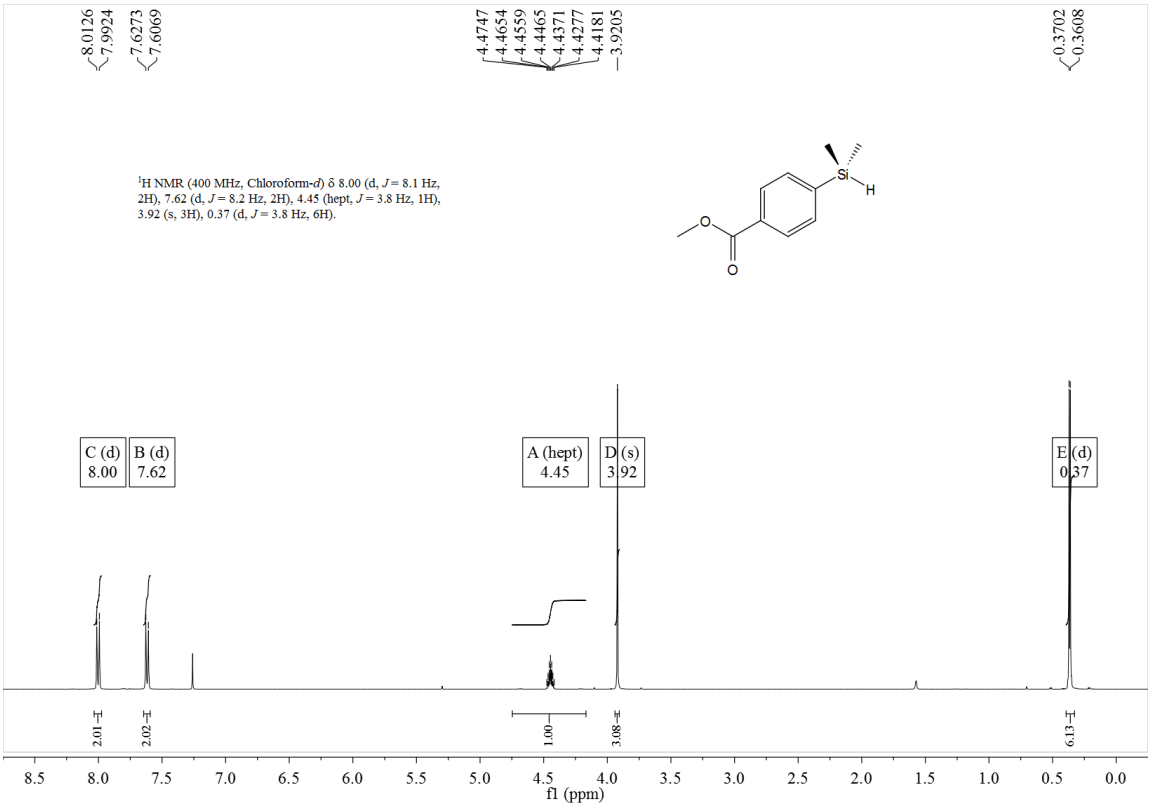
4.4453
4.4360
4.4266
4.4172
4.4078
4.3981
0.3511
0.3417
1H NMR (400 MHz, Chloroform-d) δ 7.55 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.9 Hz, 2H), 4.59 (s, 2H), 4.43 (hept, J = 3.8 Hz, 1H), 0.35 (d, J = 3.8 Hz, 6H).
Cl
Si
H
B (d) 7.39
A (d) 7.55
D (hept) 4.43
C (s) 4.59
E (d) 0.35
2.00
2.01
2.03
0.96
6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.6069
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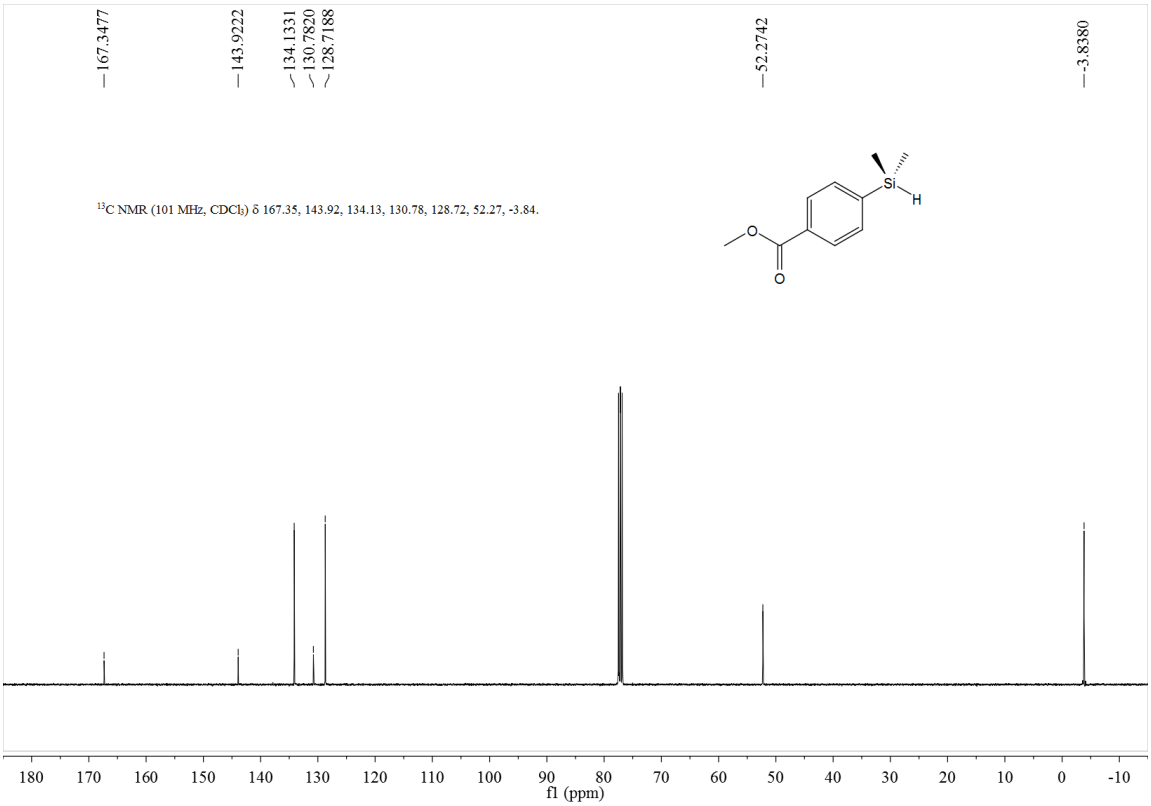
4.4654
4.4559
4.4465
4.4371
4.4277
4.4181
3.9205
0.3702
0.3608
[1]H NMR (400 MHz, Chloroform-d) δ 8.00 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 4.45 (hept, J = 3.8 Hz, 1H), 3.92 (s, 3H), 0.37 (d, J = 3.8 Hz, 6H).
Si
H
O
O
C (d) 8.00
B (d) 7.62
A (hept) 4.45
D (s) 3.92
E (d) 0.37
2.01
2.02
1.00
3.08
6.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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134.1331
130.7820
128.7188
52.2742
-3.8380
[13]C NMR (101 MHz, CDCl3) δ 167.35, 143.92, 134.13, 130.78, 128.72, 52.27, -3.84.
Si
H
O
O
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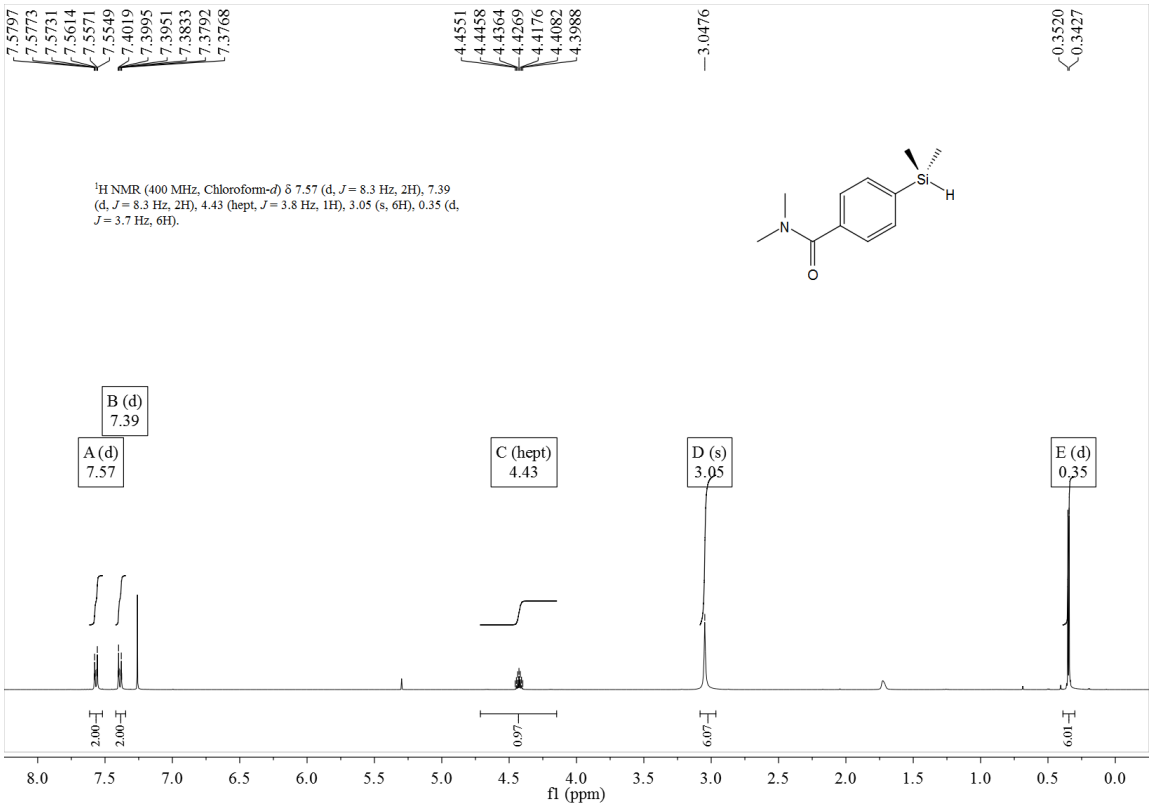
f1 (ppm)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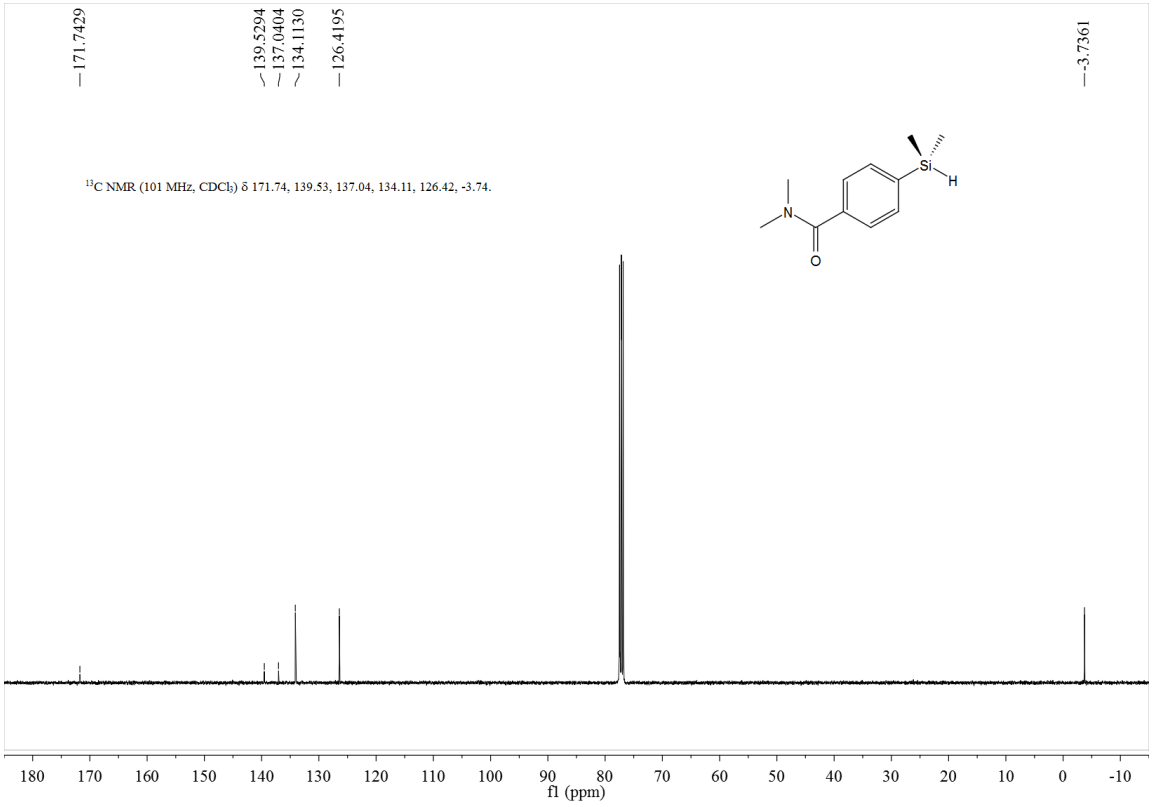
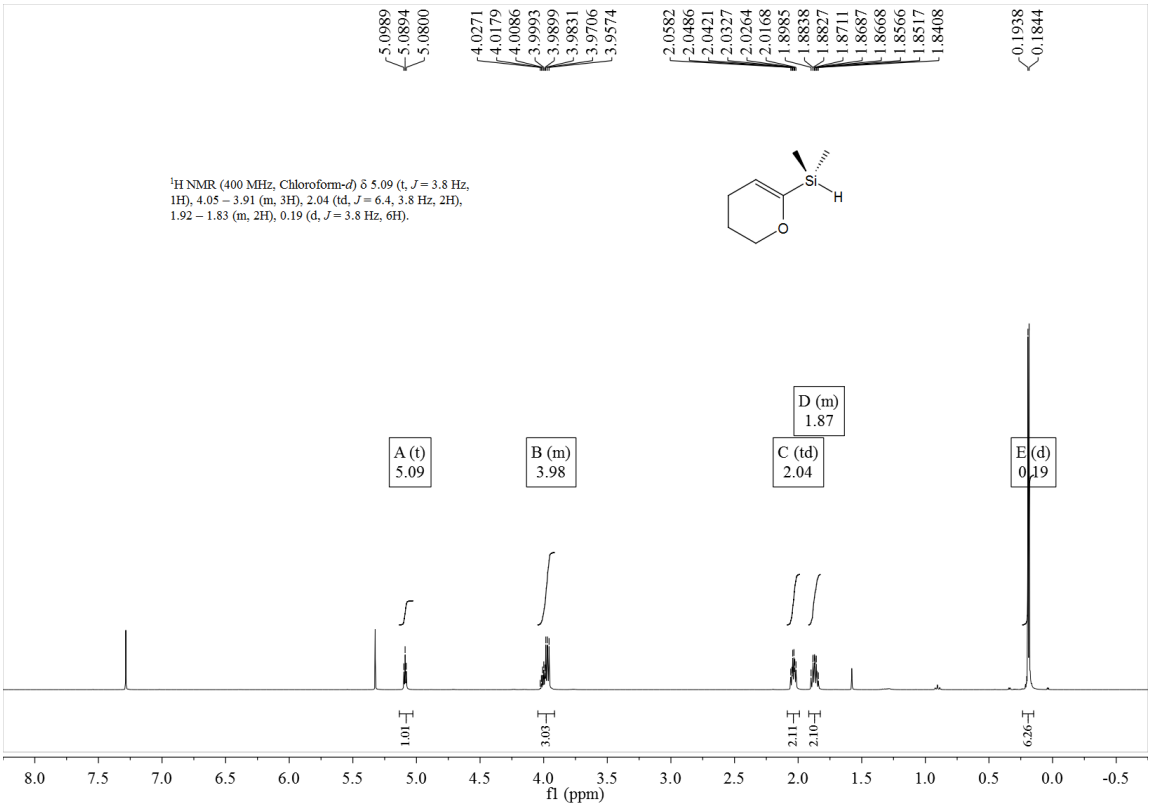
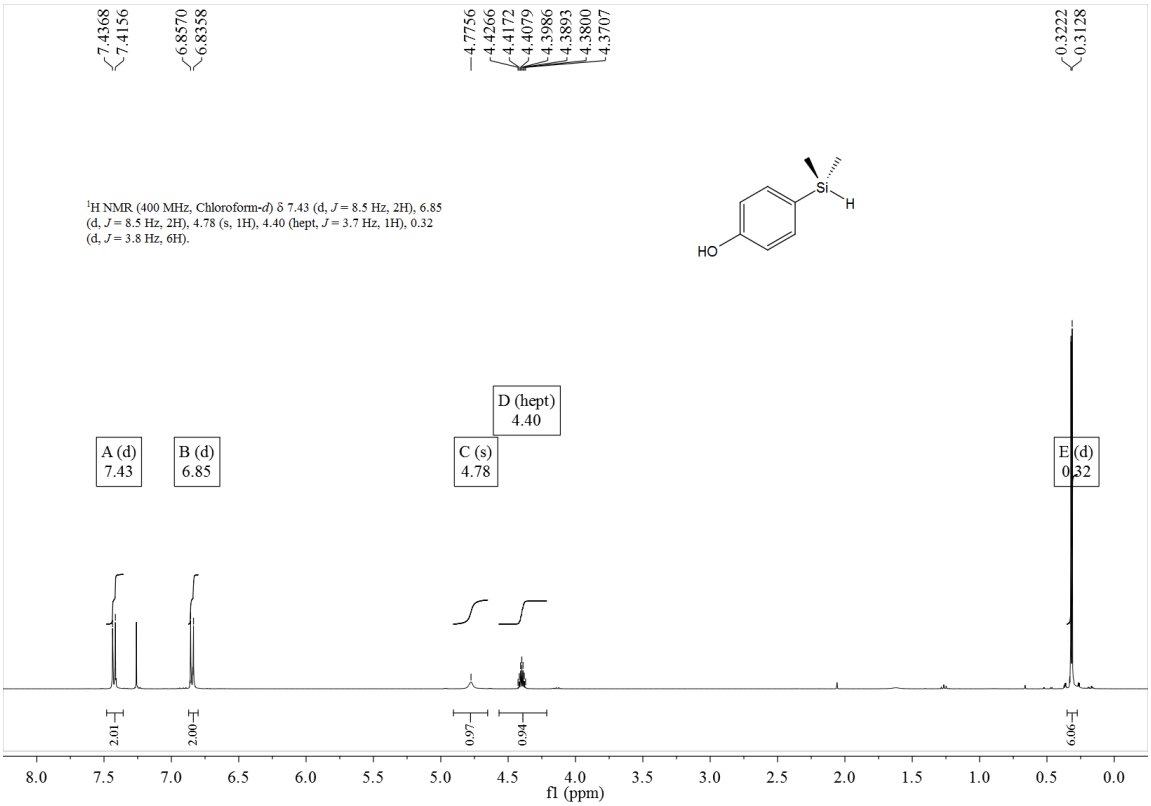
7.3768
4.4551
4.4458
4.4364
4.4269
4.4176
4.4082
4.3988
3.0476
0.3520
0.3427
[1]H NMR (400 MHz, Chloroform-d) δ 7.57 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 4.43 (hept, J = 3.8 Hz, 1H), 3.05 (s, 6H), 0.35 (d, J = 3.7 Hz, 6H).
Si
H
N
O
B (d) 7.39
A (d) 7.57
C (hept) 4.43
D (s) 3.05
E (d) 0.35
2.00
2.00
0.97
6.07
6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

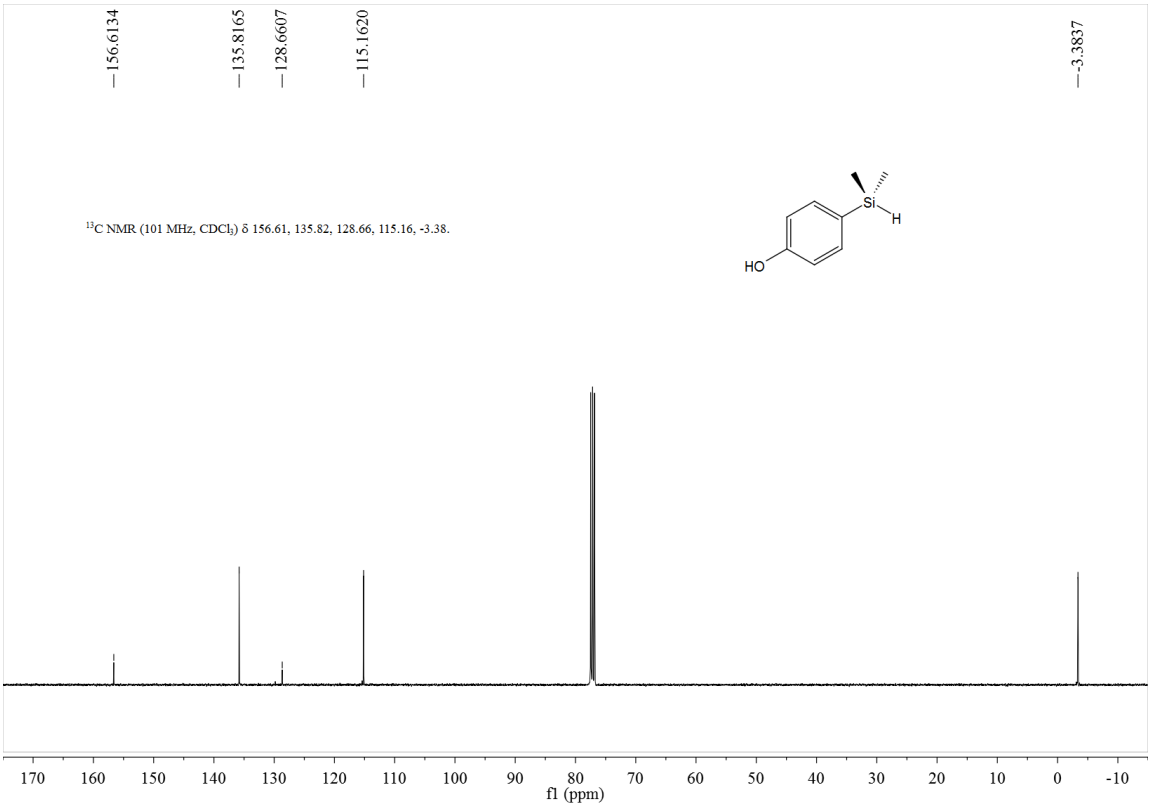

171.7429
139.5294
137.0404
134.1130
126.4195
-3.7361
[13]C NMR (101 MHz, CDCl3) δ 171.74, 139.53, 137.04, 134.11, 126.42, -3.74.
Si
H
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

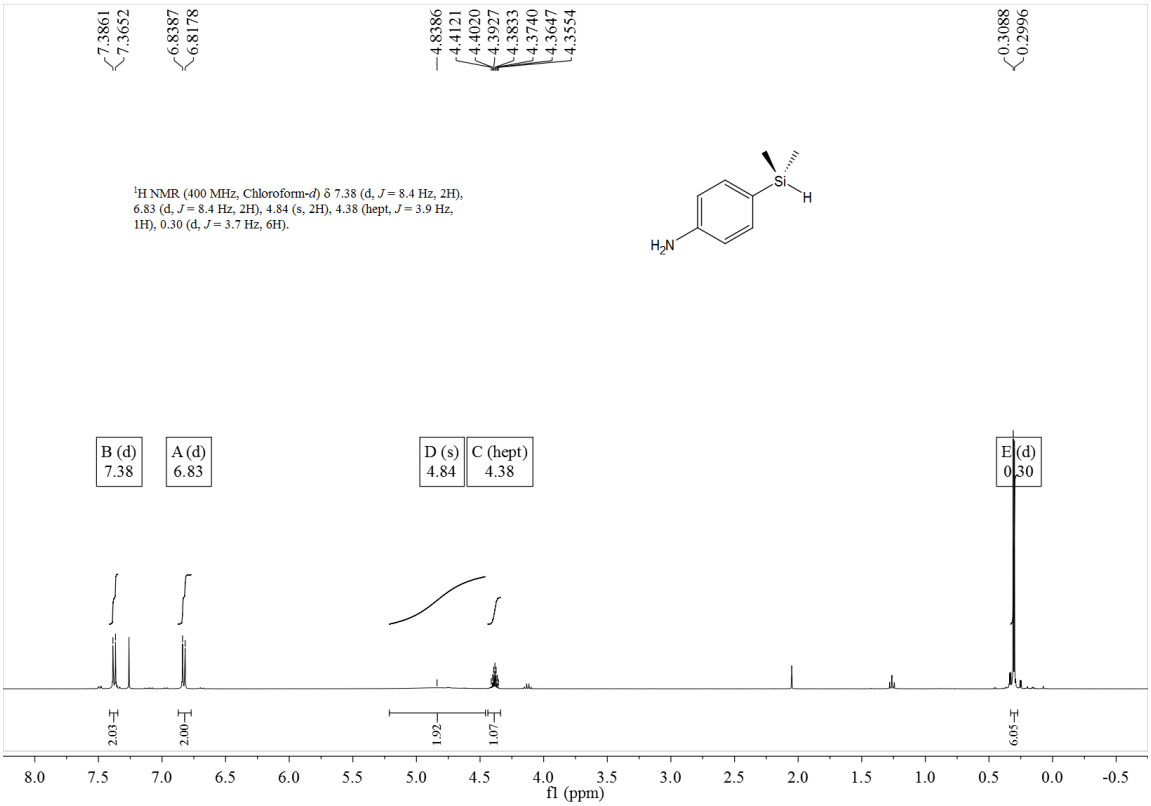


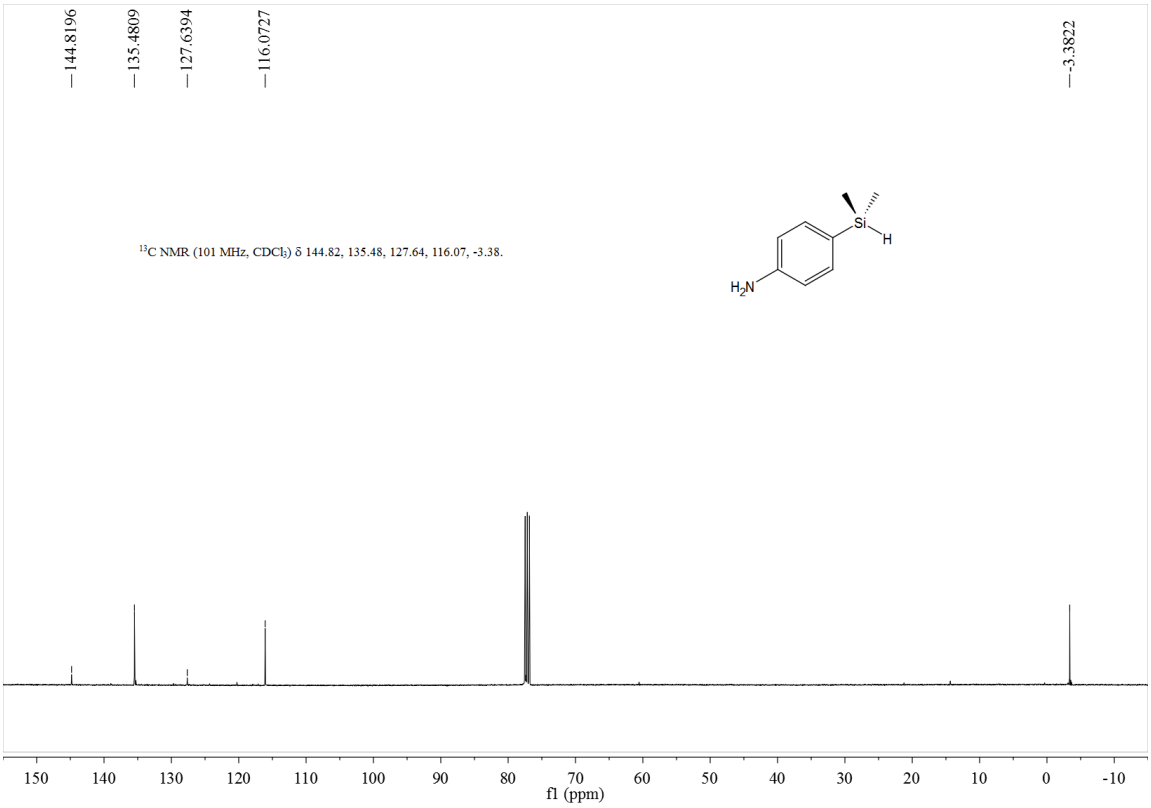
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.09 (t, *J* = 3.8 Hz, 1H), 4.05 – 3.91 (m, 3H), 2.04 (td, *J* = 6.4, 3.8 Hz, 2H), 1.92 – 1.83 (m, 2H), 0.19 (d, *J* = 3.8 Hz, 6H).



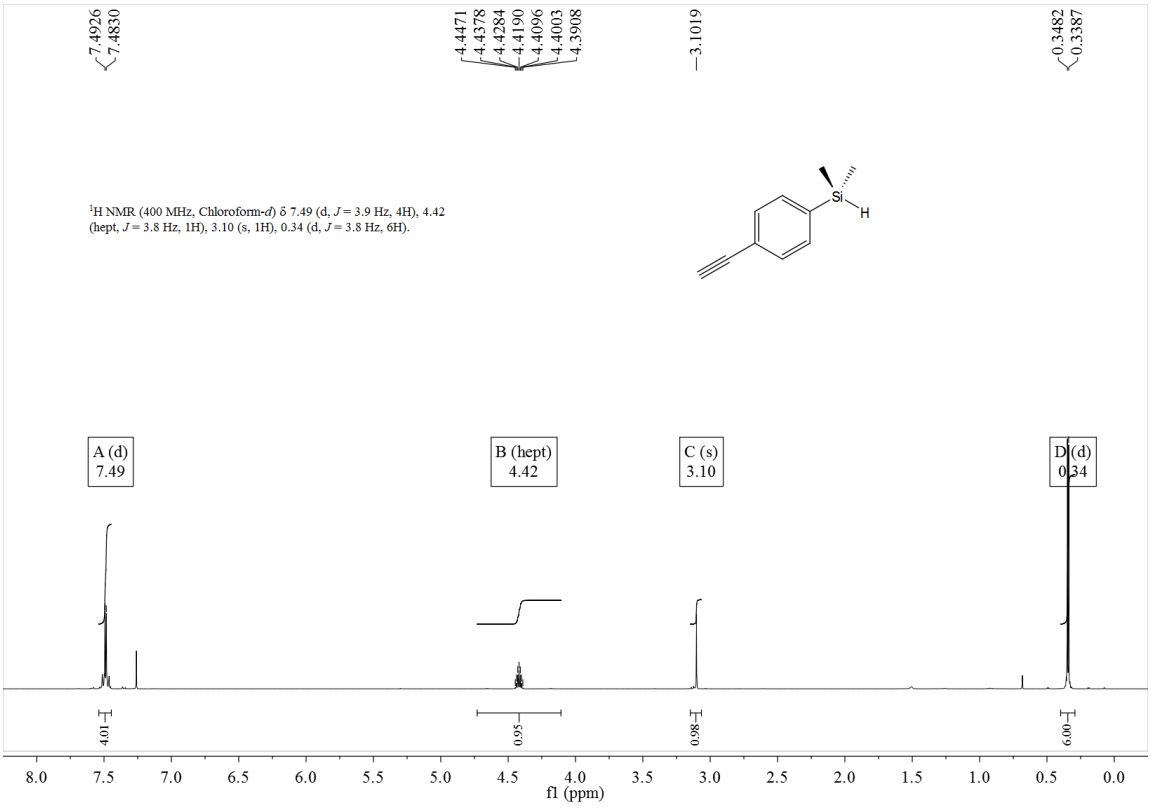
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 4.78 (s, 1H), 4.40 (hept, *J* = 3.7 Hz, 1H), 0.32 (d, *J* = 3.8 Hz, 6H).


156.6134
135.8165
128.6607
115.1620
-3.3837
13C NMR (101 MHz, CDCl3) δ 156.61, 135.82, 128.66, 115.16, -3.38.
Si
H
HO
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

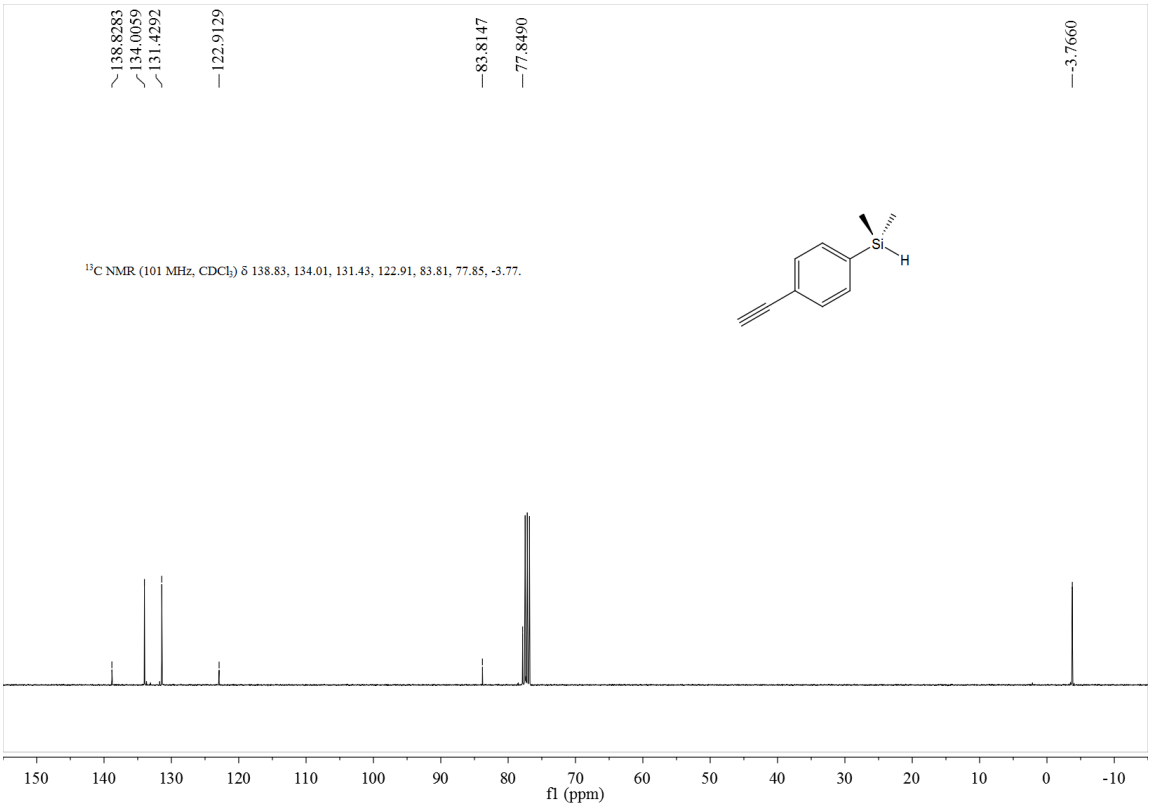

7.3861
7.3652
6.8387
6.8178
4.8386
4.4121
4.4020
4.3927
4.3833
4.3740
4.3647
4.3554
0.3088
0.2996
1H NMR (400 MHz, Chloroform-d) δ 7.38 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 4.84 (s, 2H), 4.38 (hept, J = 3.9 Hz, 1H), 0.30 (d, J = 3.7 Hz, 6H).
Si
H
H2N
B (d) 7.38
A (d) 6.83
D (s) 4.84
C (hept) 4.38
E (d) 0.30
2.03
2.00
1.92
1.07
6.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



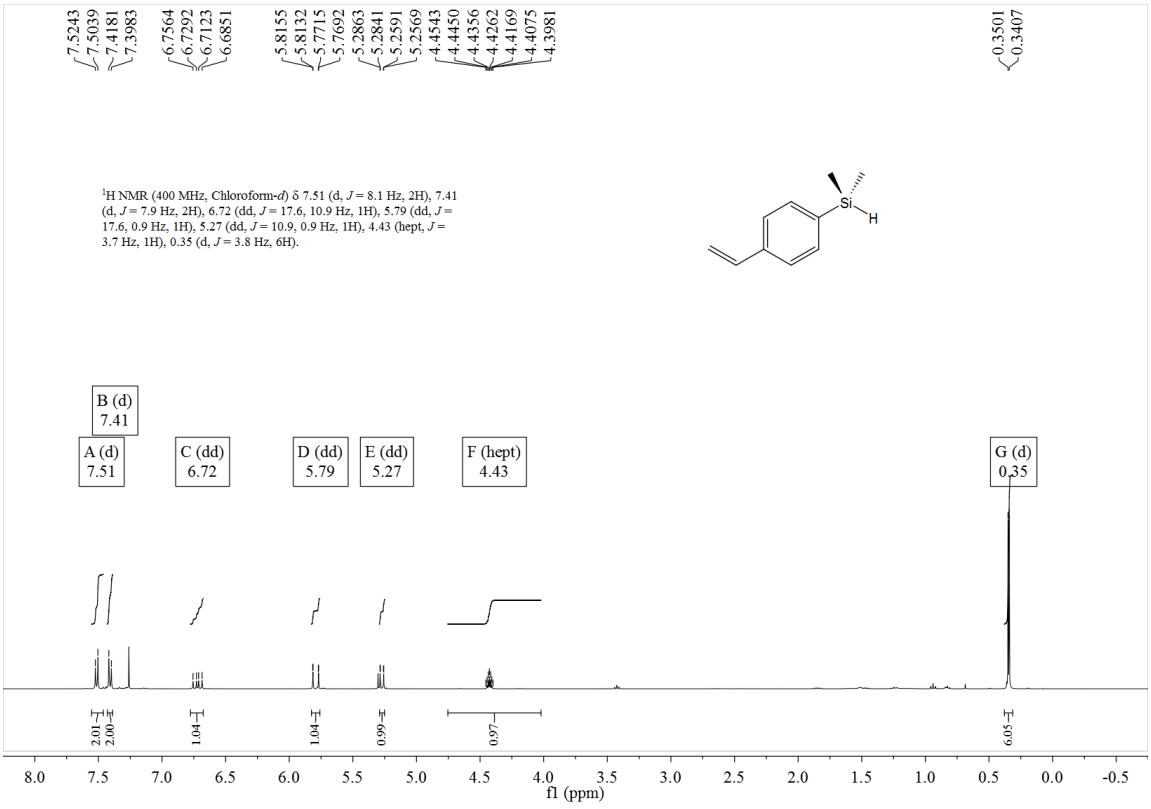
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.82, 135.48, 127.64, 116.07, -3.38.



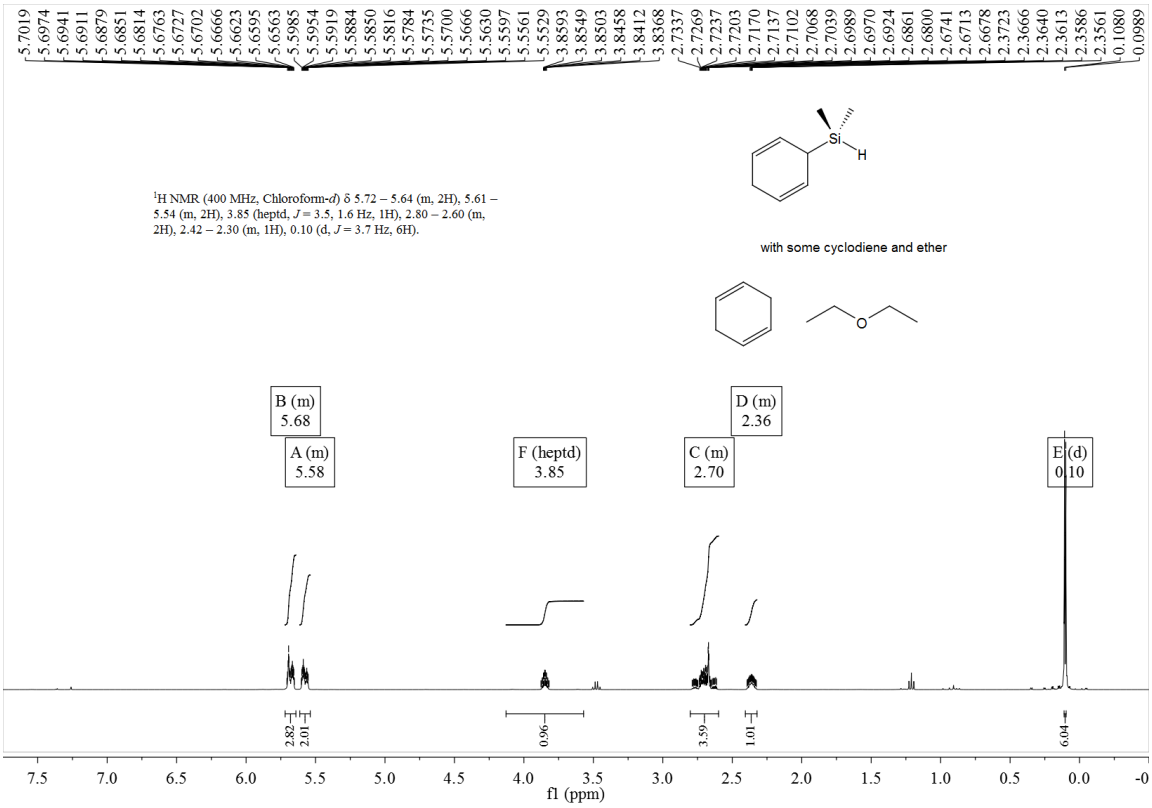
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 3.9 Hz, 4H), 4.42 (hept, *J* = 3.8 Hz, 1H), 3.10 (s, 1H), 0.34 (d, *J* = 3.8 Hz, 6H).

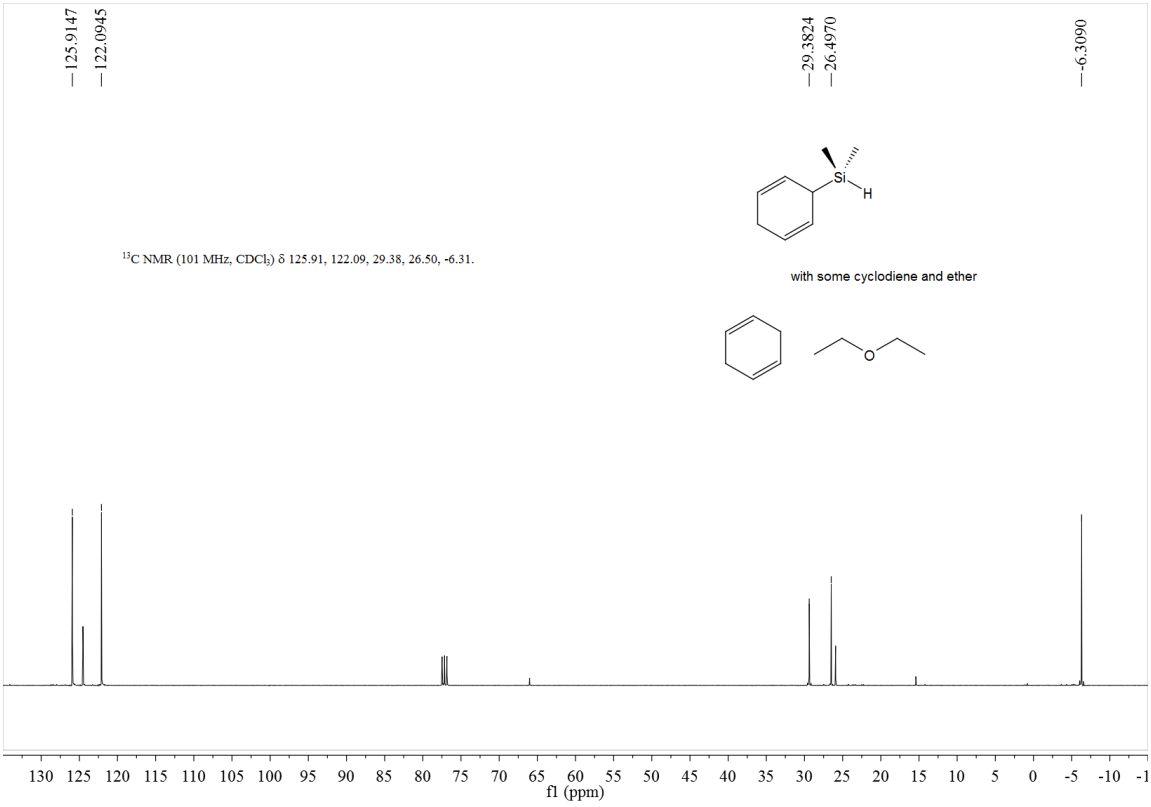


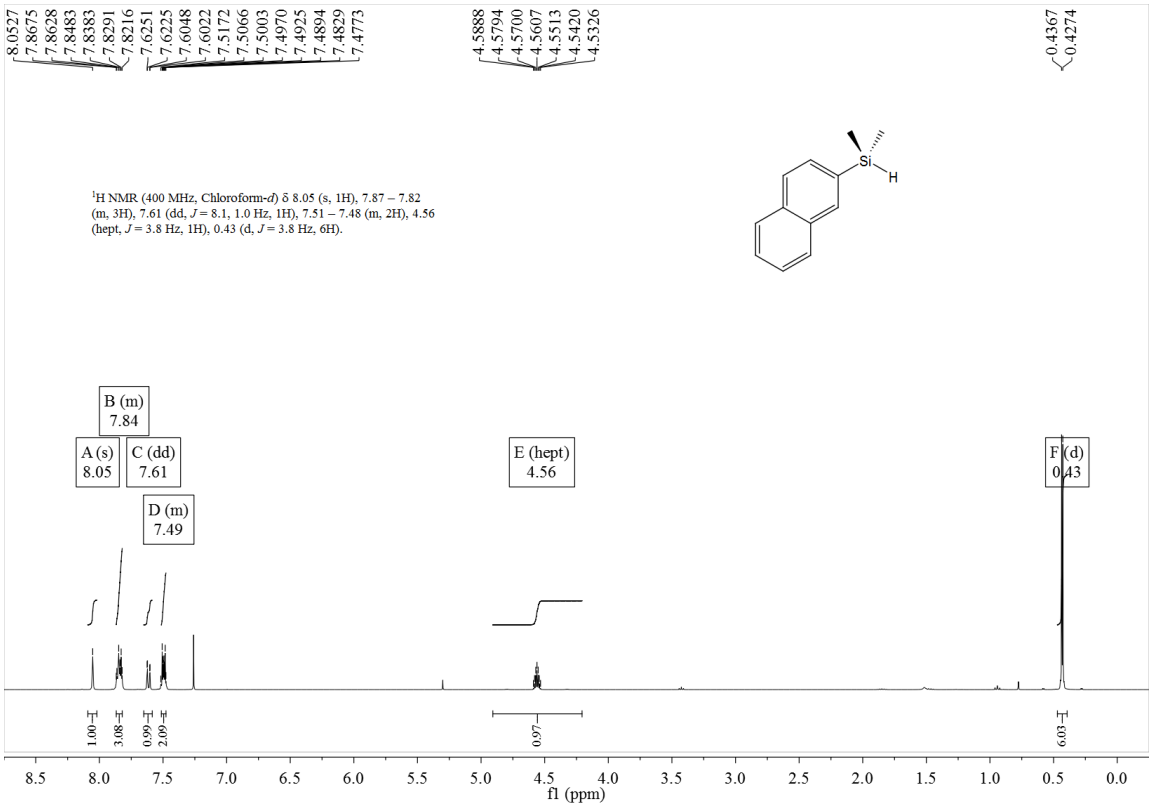
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.83, 134.01, 131.43, 122.91, 83.81, 77.85, -3.77.

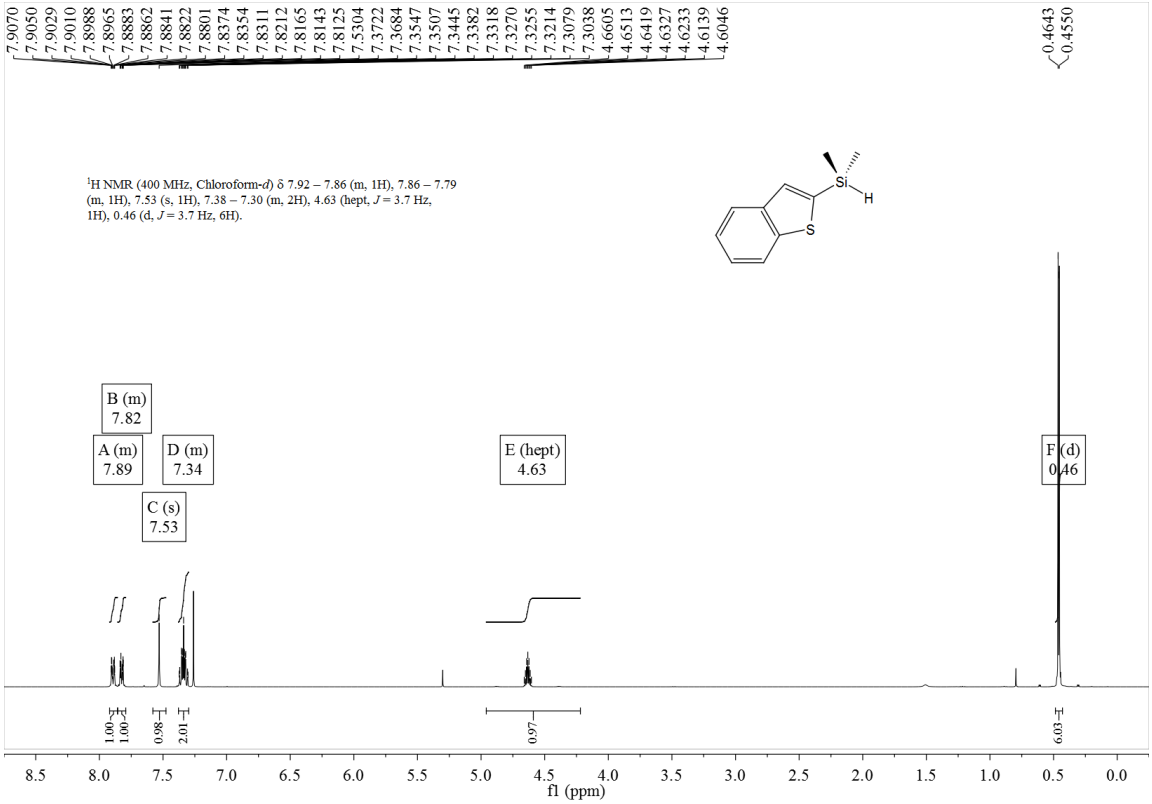


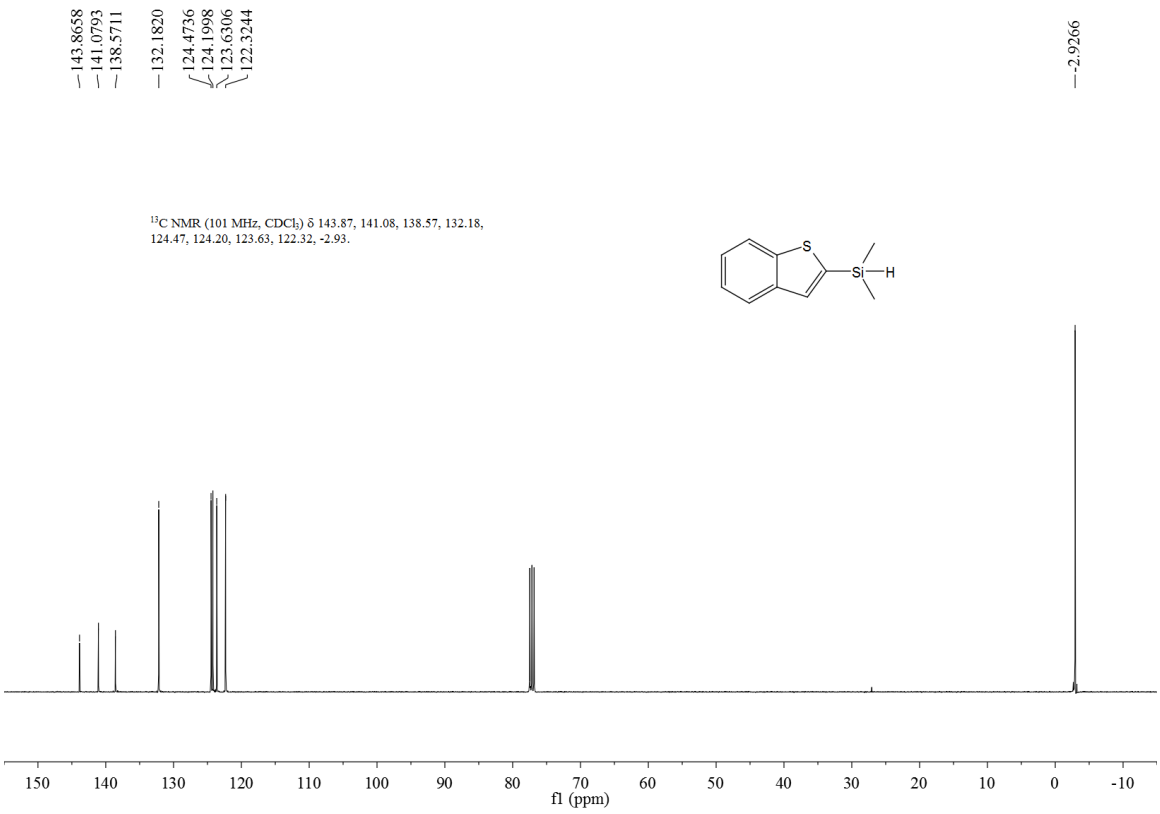
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.79 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.27 (dd, *J* = 10.9, 0.9 Hz, 1H), 4.43 (hept, *J* = 3.7 Hz, 1H), 0.35 (d, *J* = 3.8 Hz, 6H).

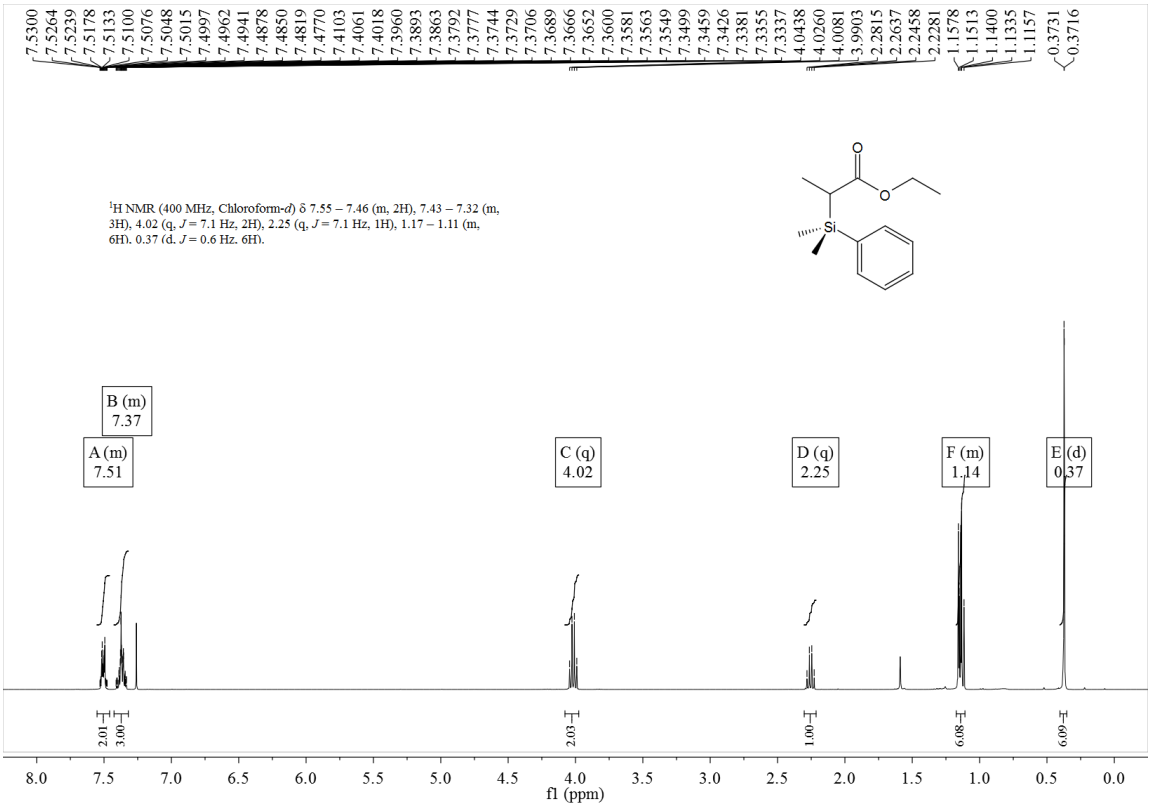

5.7019
5.6974
5.6941
5.6911
5.6879
5.6851
5.6814
5.6763
5.6727
5.6702
5.6666
5.6623
5.6595
5.6563
5.5985
5.5954
5.5919
5.5884
5.5850
5.5816
5.5784
5.5735
5.5700
5.5666
5.5630
5.5597
5.5561
5.5529
3.8593
3.8549
3.8503
3.8458
3.8412
3.8368
2.7337
2.7269
2.7237
2.7203
2.7170
2.7137
2.7102
2.7068
2.7039
2.6989
2.6970
2.6924
2.6861
2.6800
2.6741
2.6713
2.6678
2.3723
2.3666
2.3640
2.3613
2.3586
2.3561
0.1080
0.0989
Si
H
1H NMR (400 MHz, Chloroform-d) δ 5.72 – 5.64 (m, 2H), 5.61 – 5.54 (m, 2H), 3.85 (heptd, J = 3.5, 1.6 Hz, 1H), 2.80 – 2.60 (m, 2H), 2.42 – 2.30 (m, 1H), 0.10 (d, J = 3.7 Hz, 6H).
with some cyclodiene and ether
O
B (m) 5.68
A (m) 5.58
F (heptd) 3.85
D (m) 2.36
C (m) 2.70
E (d) 0.10
2.82
2.01
0.96
3.59
1.01
6.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

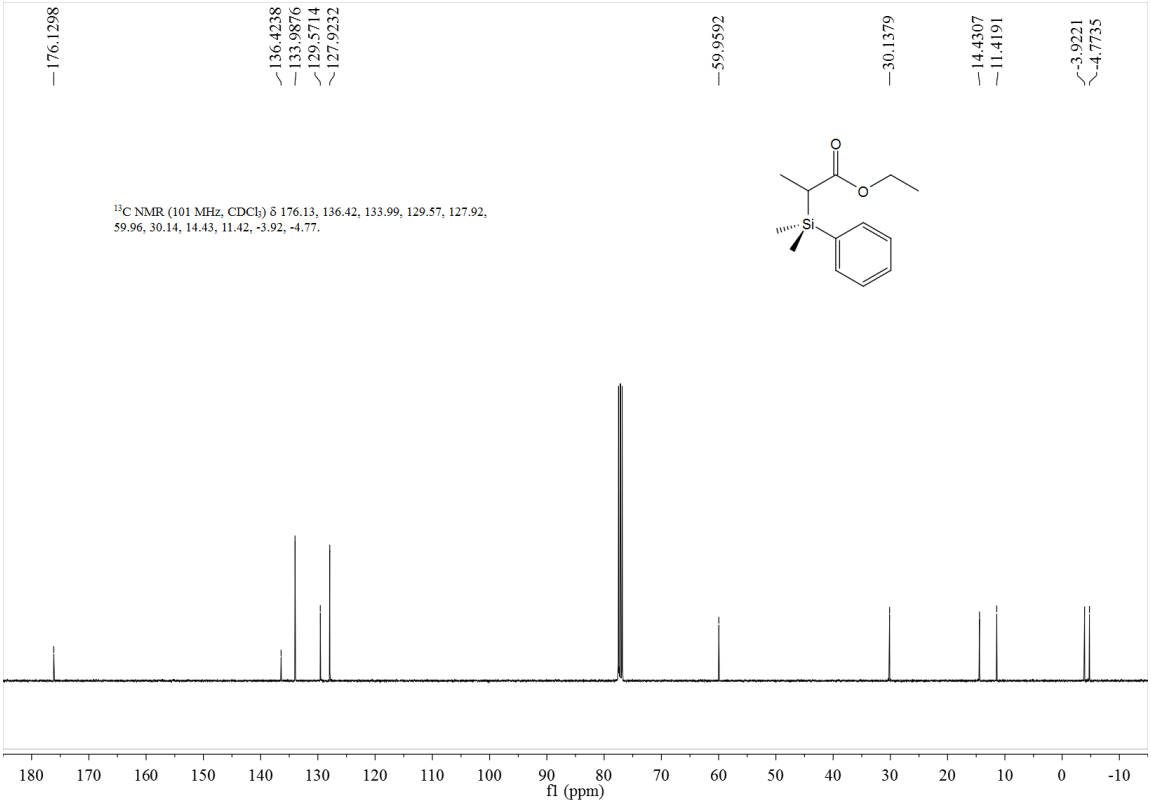

125.9147
122.0945
29.3824
26.4970
-6.3090
Si
H
13C NMR (101 MHz, CDCl3) δ 125.91, 122.09, 29.38, 26.50, -6.31.
with some cyclodiene and ether
O
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -1
f1 (ppm)

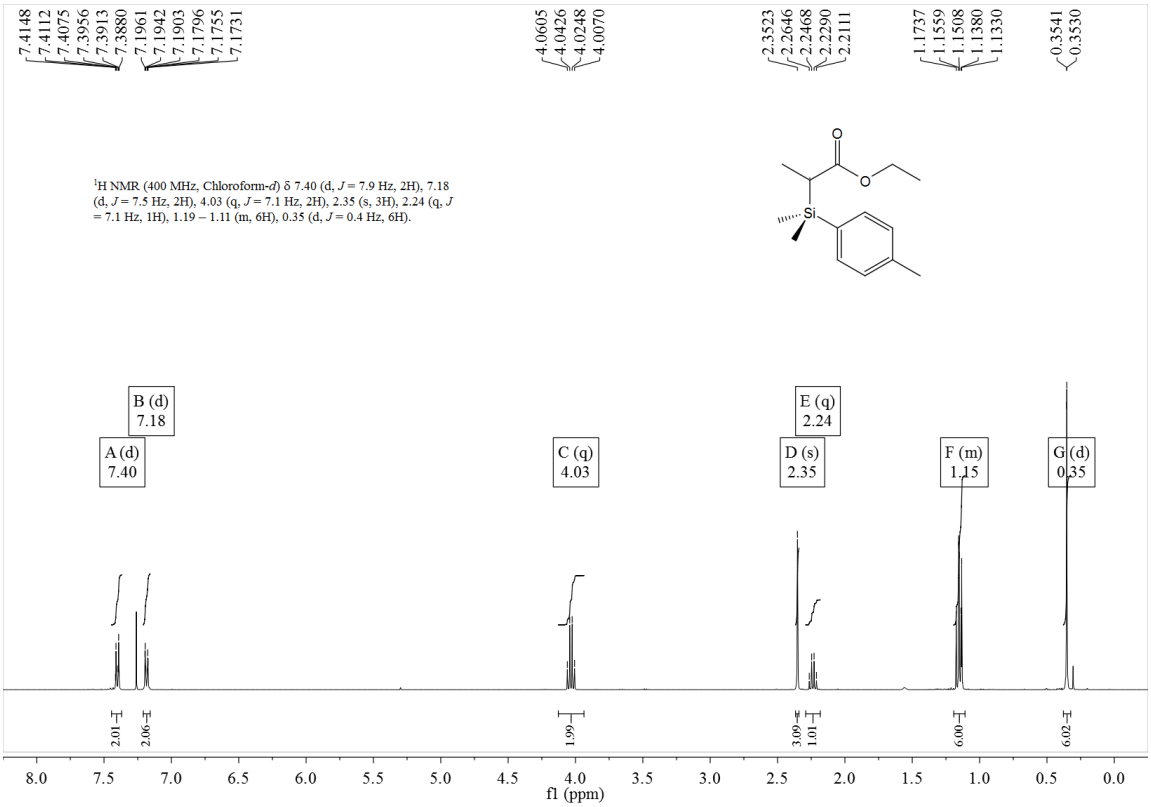

8.0527
7.8675
7.8628
7.8483
7.8383
7.8291
7.8216
7.6251
7.6225
7.6048
7.6022
7.5172
7.5066
7.5003
7.4970
7.4925
7.4894
7.4829
7.4773
4.5888
4.5794
4.5700
4.5607
4.5513
4.5420
4.5326
0.4367
0.4274
Si
H
1H NMR (400 MHz, Chloroform-d) δ 8.05 (s, 1H), 7.87 – 7.82 (m, 3H), 7.61 (dd, J = 8.1, 1.0 Hz, 1H), 7.51 – 7.48 (m, 2H), 4.56 (hept, J = 3.8 Hz, 1H), 0.43 (d, J = 3.8 Hz, 6H).
B (m) 7.84
A (s) 8.05
C (dd) 7.61
D (m) 7.49
E (hept) 4.56
F (d) 0.43
1.00
3.08
0.99
2.09
0.97
6.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

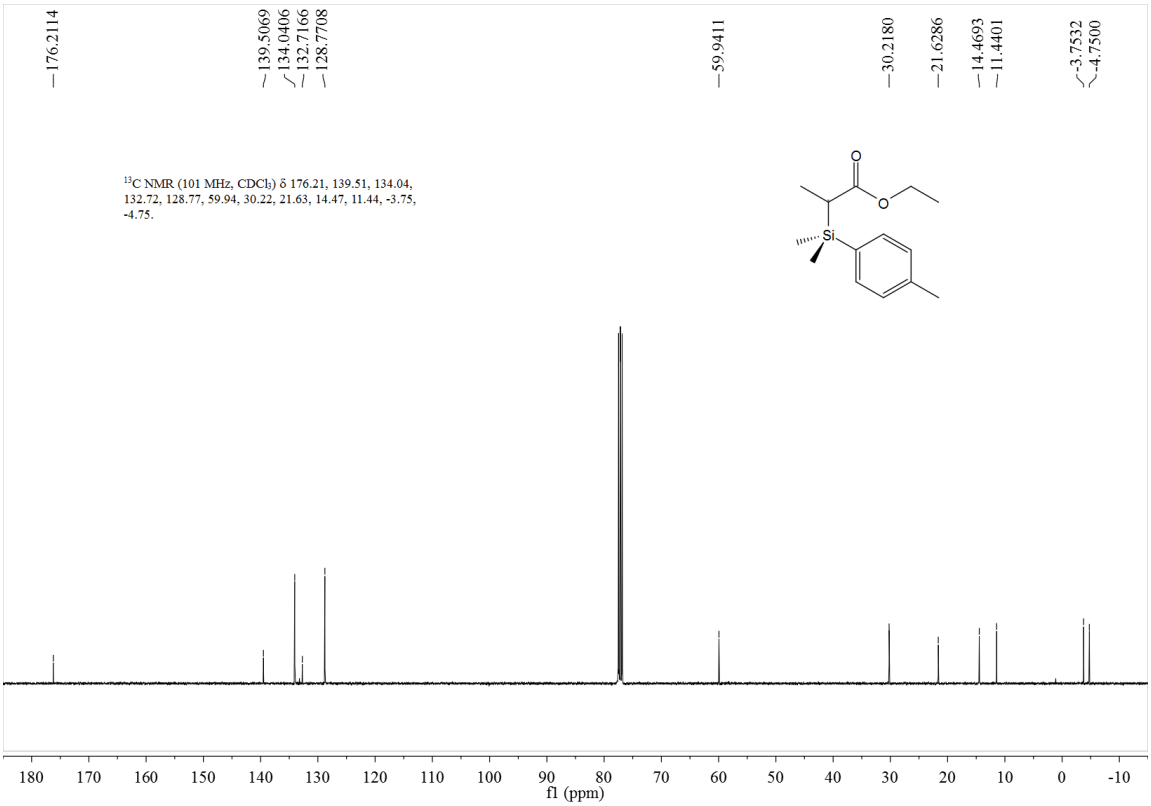

7.9070
7.9050
7.9029
7.9010
7.8988
7.8965
7.8883
7.8862
7.8841
7.8822
7.8801
7.8374
7.8354
7.8311
7.8212
7.8165
7.8143
7.8125
7.5304
7.3722
7.3684
7.3547
7.3507
7.3445
7.3382
7.3318
7.3270
7.3255
7.3214
7.3079
7.3038
4.6605
4.6513
4.6419
4.6327
4.6233
4.6139
4.6046
0.4643
0.4550
Si
H
S
1H NMR (400 MHz, Chloroform-d) δ 7.92 – 7.86 (m, 1H), 7.86 – 7.79 (m, 1H), 7.53 (s, 1H), 7.38 – 7.30 (m, 2H), 4.63 (hept, J = 3.7 Hz, 1H), 0.46 (d, J = 3.7 Hz, 6H).
B (m) 7.82
A (m) 7.89
D (m) 7.34
C (s) 7.53
E (hept) 4.63
F (d) 0.46
1.00
1.00
0.98
2.01
0.97
6.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

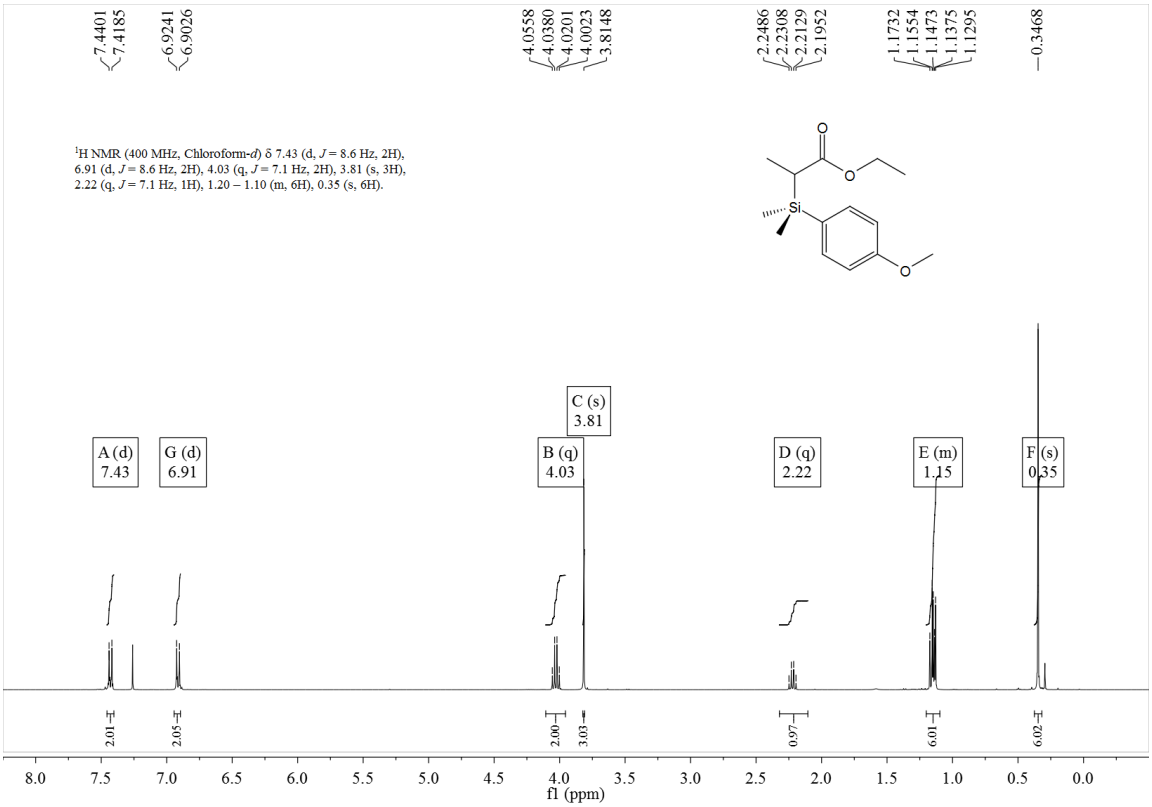

143.8658
141.0793
138.5711
132.1820
124.4736
124.1998
123.6306
122.3244
-2.9266
13C NMR (101 MHz, CDCl3) δ 143.87, 141.08, 138.57, 132.18, 124.47, 124.20, 123.63, 122.32, -2.93.
S
Si
H
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

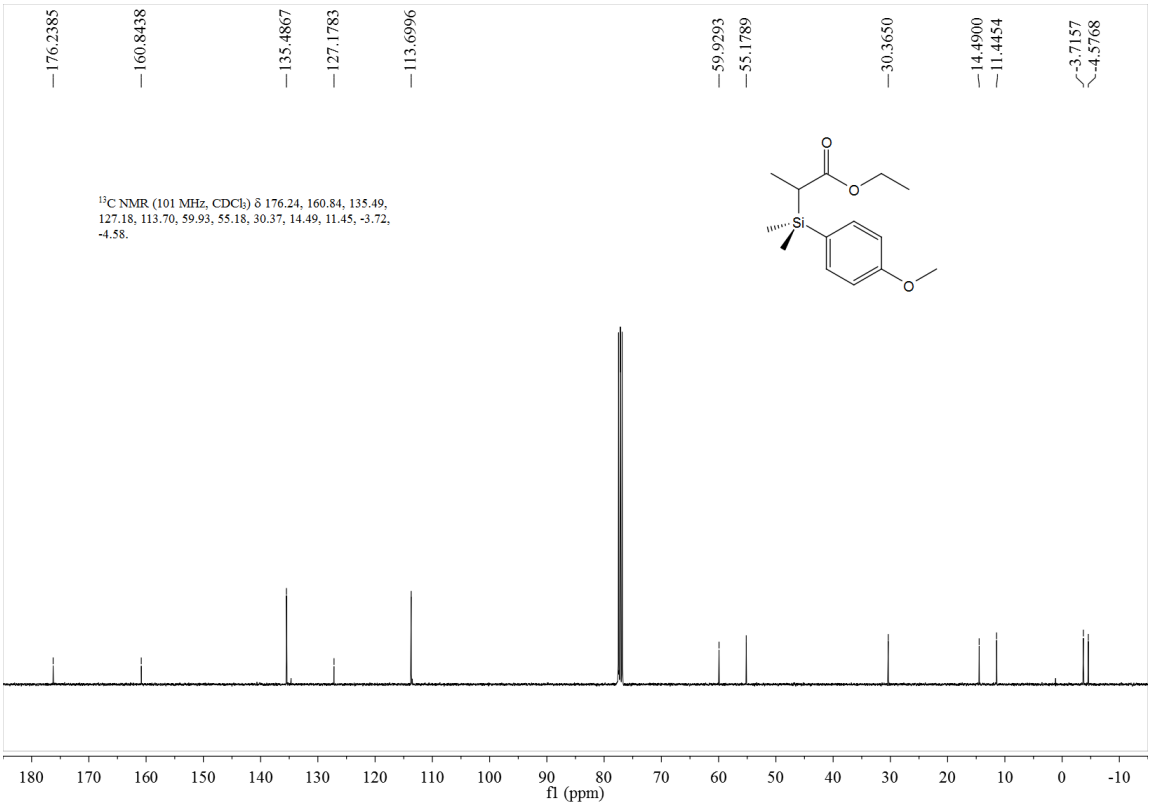

7.5300
7.5264
7.5239
7.5178
7.5133
7.5100
7.5076
7.5048
7.5015
7.4997
7.4962
7.4941
7.4878
7.4850
7.4819
7.4770
7.4103
7.4061
7.4018
7.3960
7.3893
7.3863
7.3792
7.3777
7.3744
7.3729
7.3706
7.3689
7.3666
7.3652
7.3600
7.3581
7.3563
7.3549
7.3499
7.3459
7.3426
7.3381
7.3355
7.3337
4.0438
4.0260
4.0081
3.9903
2.2815
2.2637
2.2458
2.2281
1.1578
1.1513
1.1400
1.1335
1.1157
0.3731
0.3716
^{1}H NMR (400 MHz, Chloroform-d) δ 7.55 – 7.46 (m, 2H), 7.43 – 7.32 (m, 3H), 4.02 (q, J = 7.1 Hz, 2H), 2.25 (q, J = 7.1 Hz, 1H), 1.17 – 1.11 (m, 6H), 0.37 (d, J = 0.6 Hz, 6H).
O
O
Si
B (m) 7.37
A (m) 7.51
C (q) 4.02
D (q) 2.25
F (m) 1.14
E (d) 0.37
2.01
3.00
2.03
1.00
6.08
6.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

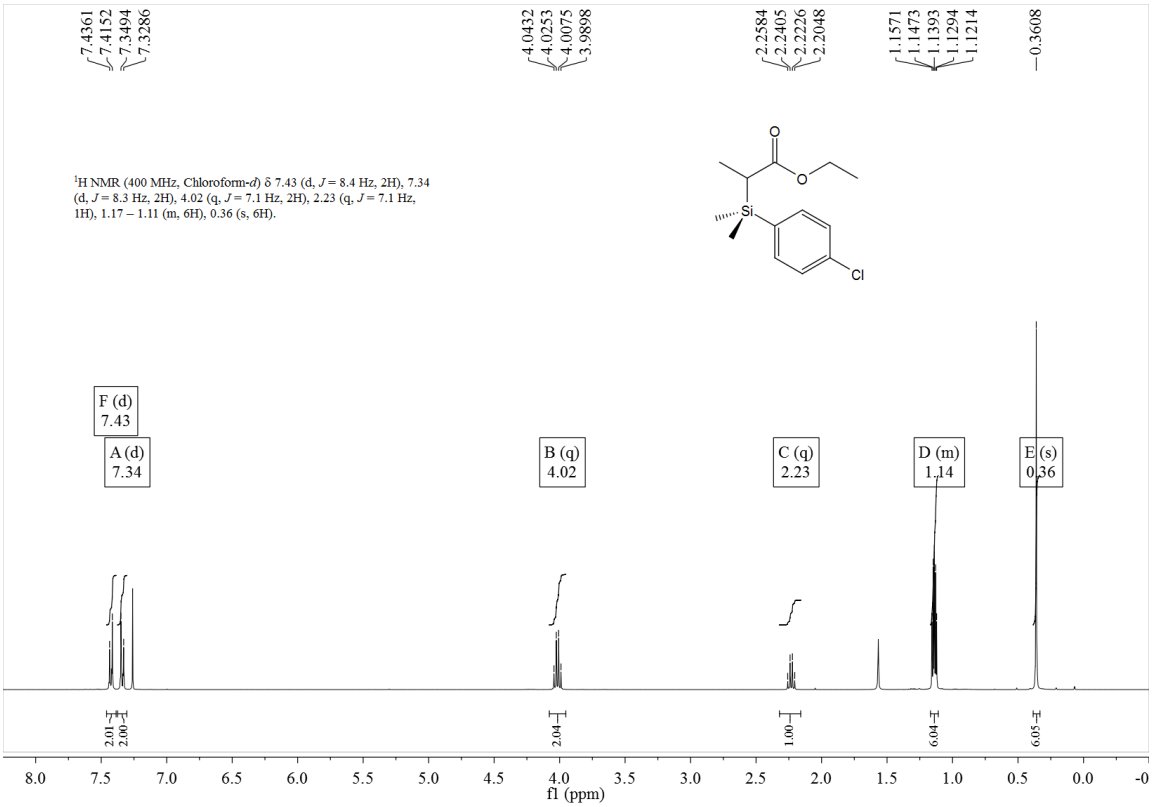

176.1298
136.4238
133.9876
129.5714
127.9232
59.9592
30.1379
14.4307
11.4191
-3.9221
-4.7735
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.13, 136.42, 133.99, 129.57, 127.92, 59.96, 30.14, 14.43, 11.42, -3.92, -4.77.
O
O
Si
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

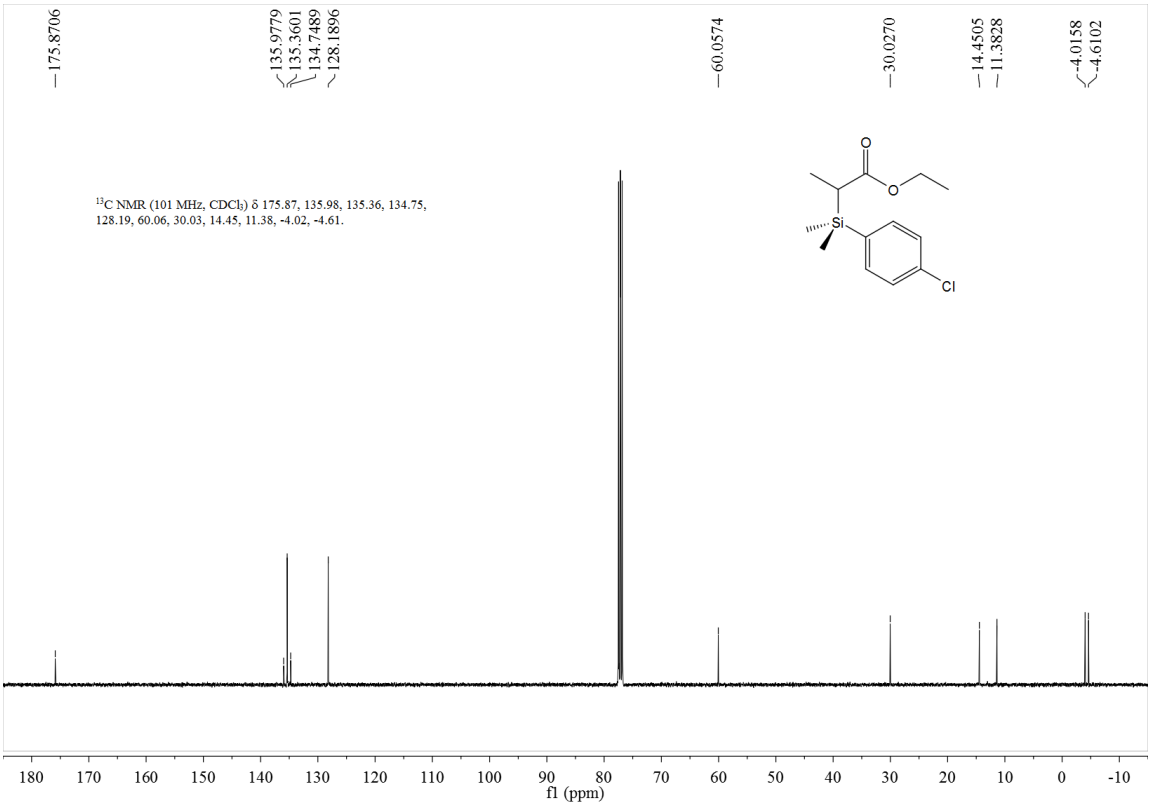

7.4148
7.4112
7.4075
7.3956
7.3913
7.3880
7.1961
7.1942
7.1903
7.1796
7.1755
7.1731
4.0605
4.0426
4.0248
4.0070
2.3523
2.2646
2.2468
2.2290
2.2111
1.1737
1.1559
1.1508
1.1380
1.1330
0.3541
0.3530
[1]H NMR (400 MHz, Chloroform-d) δ 7.40 (d, J = 7.9 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 4.03 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.24 (q, J = 7.1 Hz, 1H), 1.19 – 1.11 (m, 6H), 0.35 (d, J = 0.4 Hz, 6H).
O
O
Si
B (d) 7.18
A (d) 7.40
C (q) 4.03
E (q) 2.24
D (s) 2.35
F (m) 1.15
G (d) 0.35
2.01
2.06
1.99
3.09
1.01
6.00
6.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

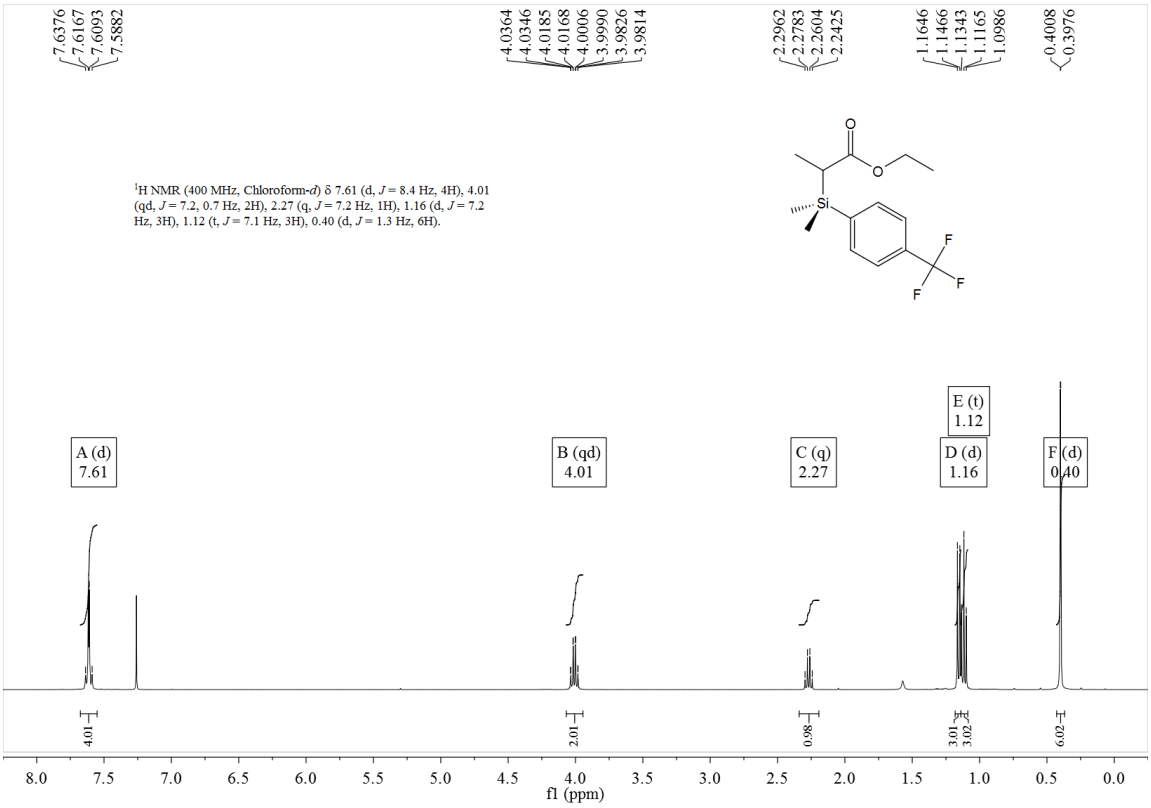

176.2114
139.5069
134.0406
132.7166
128.7708
59.9411
30.2180
21.6286
14.4693
11.4401
-3.7532
-4.7500
[13]C NMR (101 MHz, CDCl3) δ 176.21, 139.51, 134.04, 132.72, 128.77, 59.94, 30.22, 21.63, 14.47, 11.44, -3.75, -4.75.
O
O
Si
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

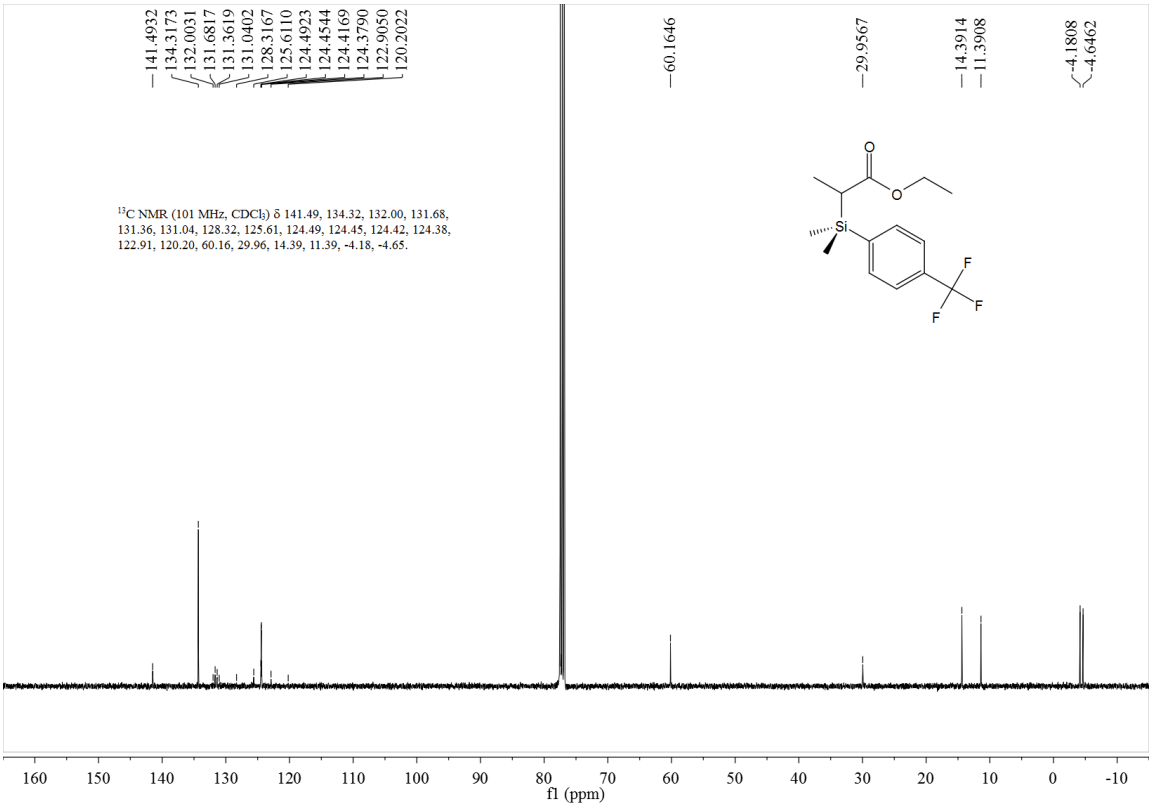

7.4401
7.4185
6.9241
6.9026
4.0558
4.0380
4.0201
4.0023
3.8148
2.2486
2.2308
2.2129
2.1952
1.1732
1.1554
1.1473
1.1375
1.1295
0.3468
[1]H NMR (400 MHz, Chloroform-d) δ 7.43 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 4.03 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 2.22 (q, J = 7.1 Hz, 1H), 1.20 – 1.10 (m, 6H), 0.35 (s, 6H).
A (d) 7.43
G (d) 6.91
B (q) 4.03
C (s) 3.81
D (q) 2.22
E (m) 1.15
F (s) 0.35
2.01
2.05
2.00
3.03
0.97
6.01
6.02
f1 (ppm)

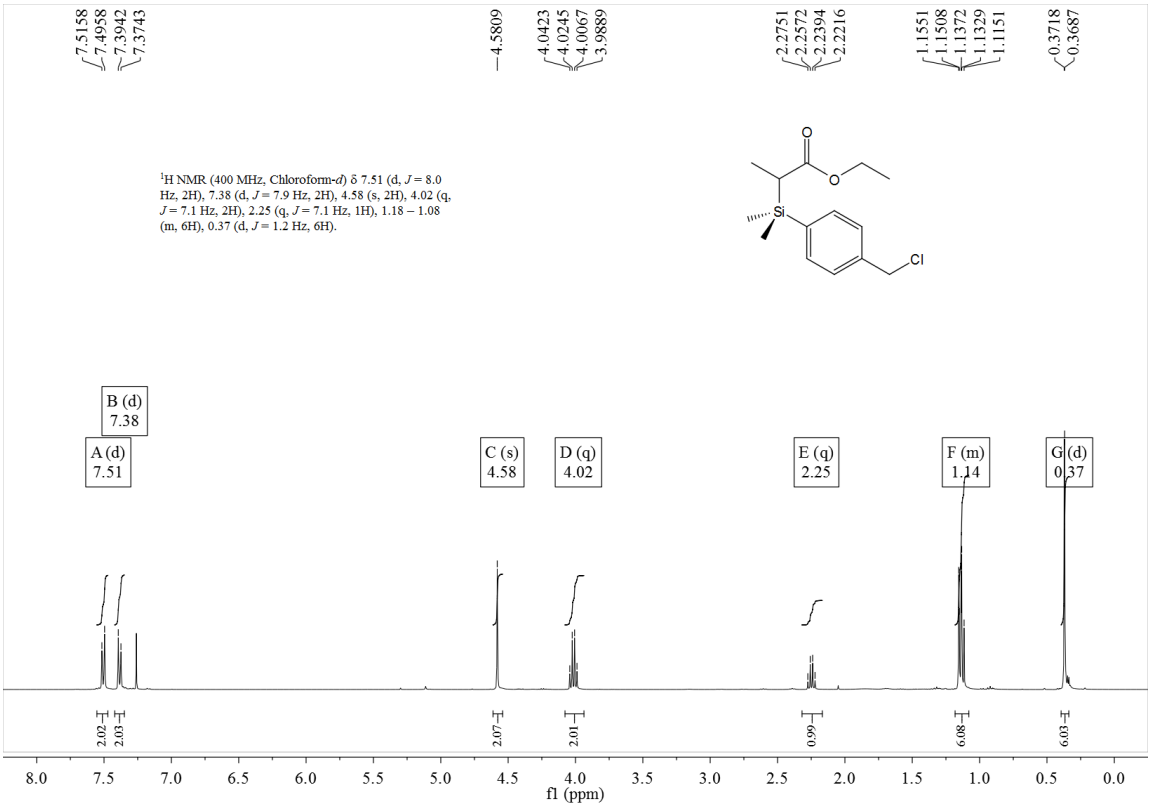

176.2385
160.8438
135.4867
127.1783
113.6996
59.9293
55.1789
30.3650
14.4900
11.4454
-3.7157
-4.5768
[13]C NMR (101 MHz, CDCl3) δ 176.24, 160.84, 135.49, 127.18, 113.70, 59.93, 55.18, 30.37, 14.49, 11.45, -3.72, -4.58.
f1 (ppm)

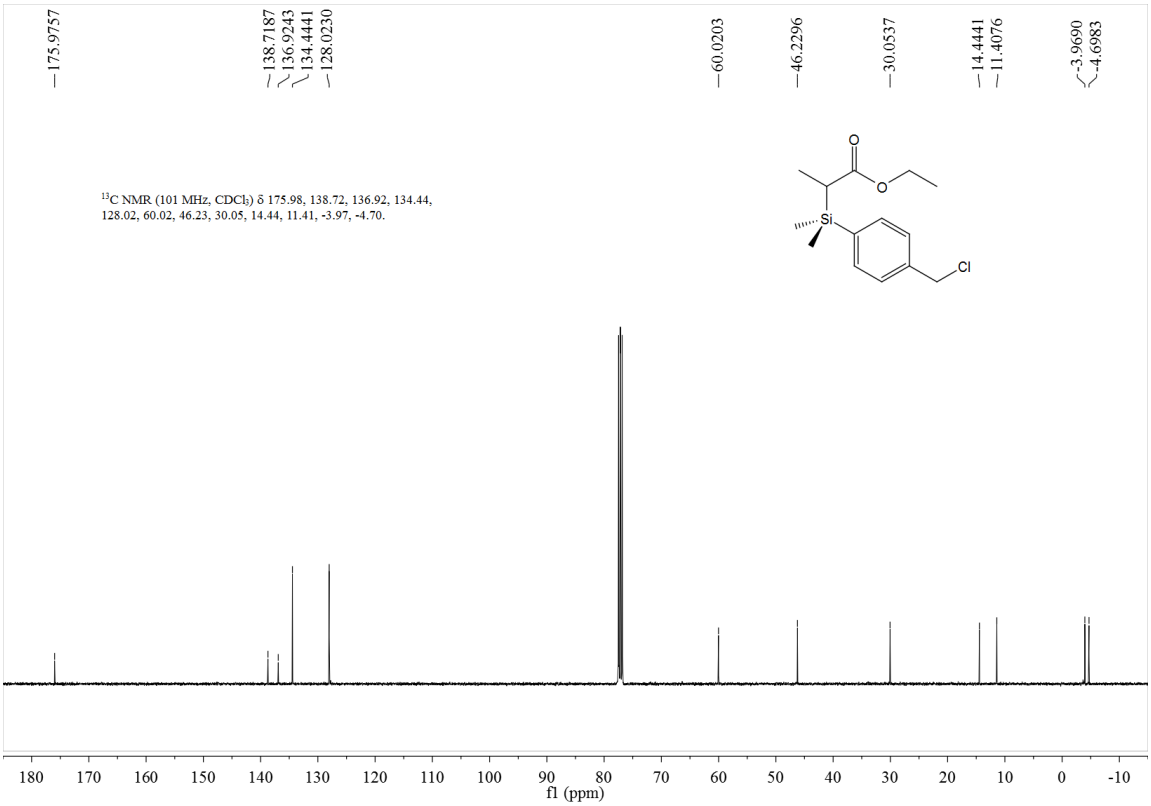

7.4361
7.4152
7.3494
7.3286
4.0432
4.0253
4.0075
3.9898
2.2584
2.2405
2.2226
2.2048
1.1571
1.1473
1.1393
1.1294
1.1214
0.3608
[1]H NMR (400 MHz, Chloroform-d) δ 7.43 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.23 (q, J = 7.1 Hz, 1H), 1.17 – 1.11 (m, 6H), 0.36 (s, 6H).
O
O
Si
Cl
F (d) 7.43
A (d) 7.34
B (q) 4.02
C (q) 2.23
D (m) 1.14
E (s) 0.36
2.01
2.00
2.04
1.00
6.04
6.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

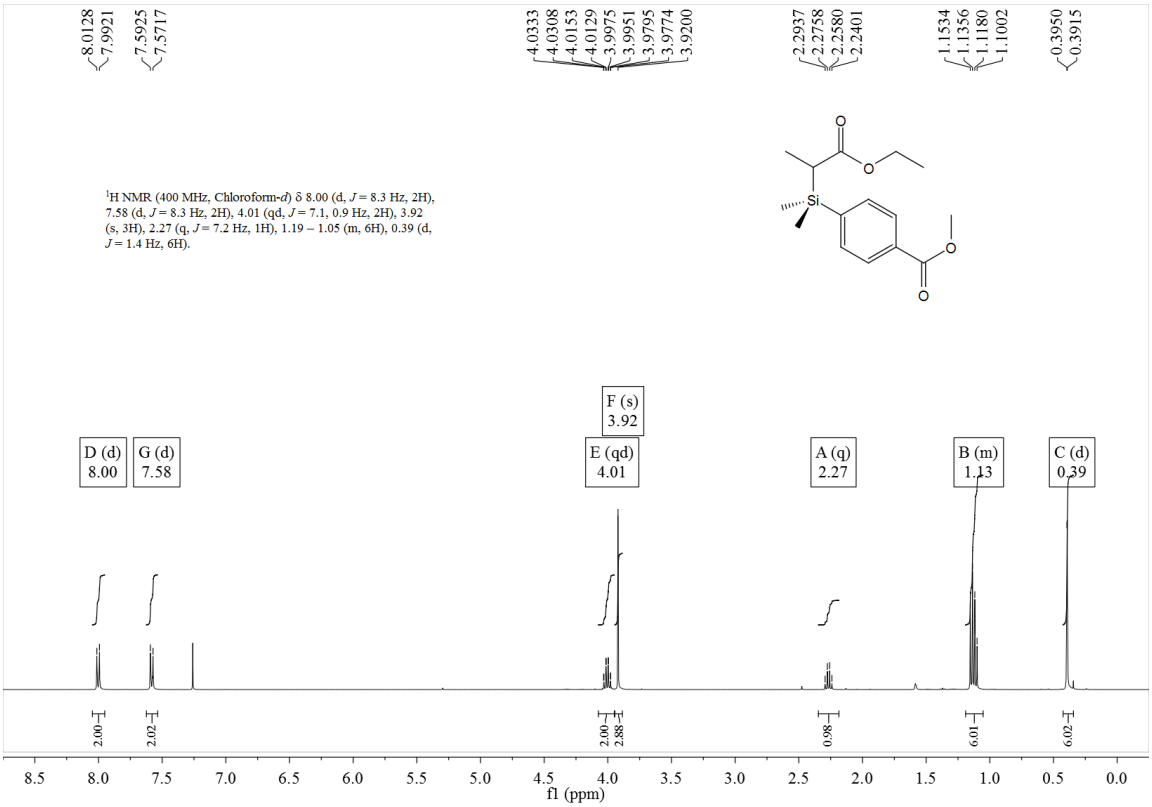

175.8706
135.9779
135.3601
134.7489
128.1896
60.0574
30.0270
14.4505
11.3828
-4.0158
-4.6102
[13]C NMR (101 MHz, CDCl3) δ 175.87, 135.98, 135.36, 134.75, 128.19, 60.06, 30.03, 14.45, 11.38, -4.02, -4.61.
O
O
Si
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

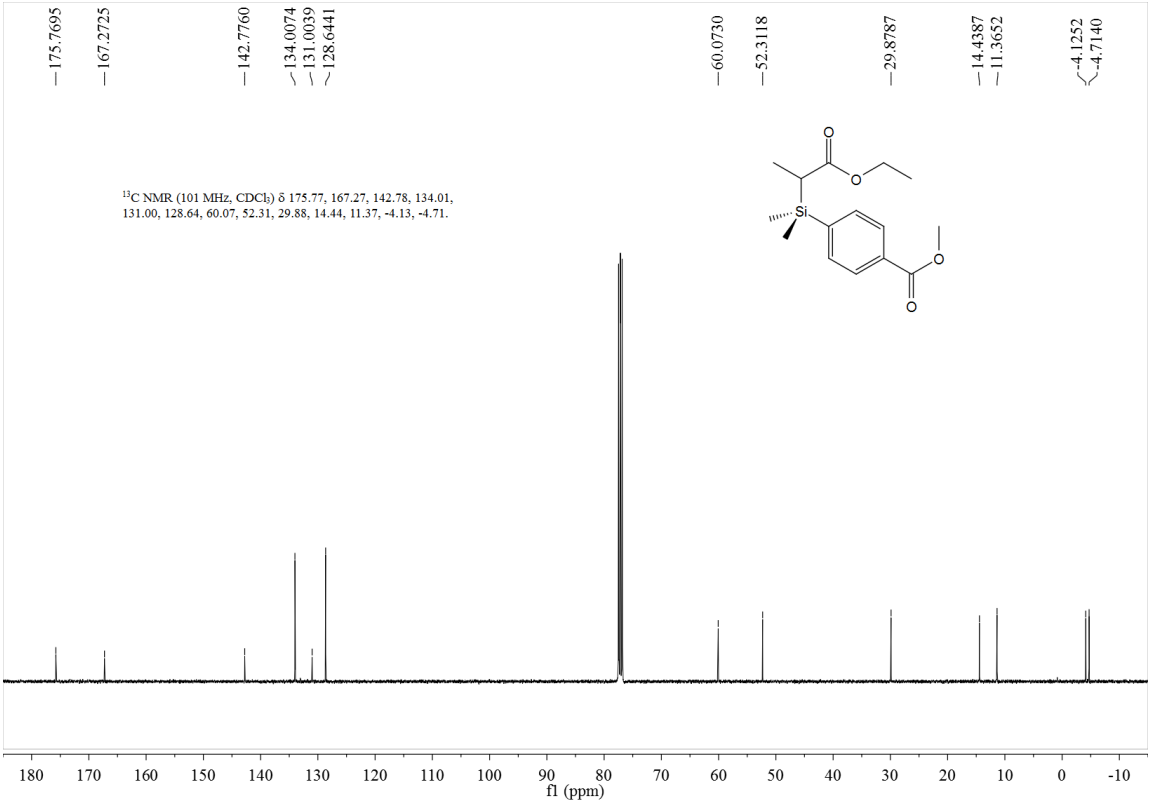

7.6376
7.6167
7.6093
7.5882
4.0364
4.0346
4.0185
4.0168
4.0006
3.9990
3.9826
3.9814
2.2962
2.2783
2.2604
2.2425
1.1646
1.1466
1.1343
1.1165
1.0986
0.4008
0.3976
1H NMR (400 MHz, Chloroform-d) δ 7.61 (d, J = 8.4 Hz, 4H), 4.01 (qd, J = 7.2, 0.7 Hz, 2H), 2.27 (q, J = 7.2 Hz, 1H), 1.16 (d, J = 7.2 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H), 0.40 (d, J = 1.3 Hz, 6H).
A (d) 7.61
B (qd) 4.01
C (q) 2.27
D (d) 1.16
E (t) 1.12
F (d) 0.40
4.01
2.01
0.98
3.01
3.02
6.02
f1 (ppm)

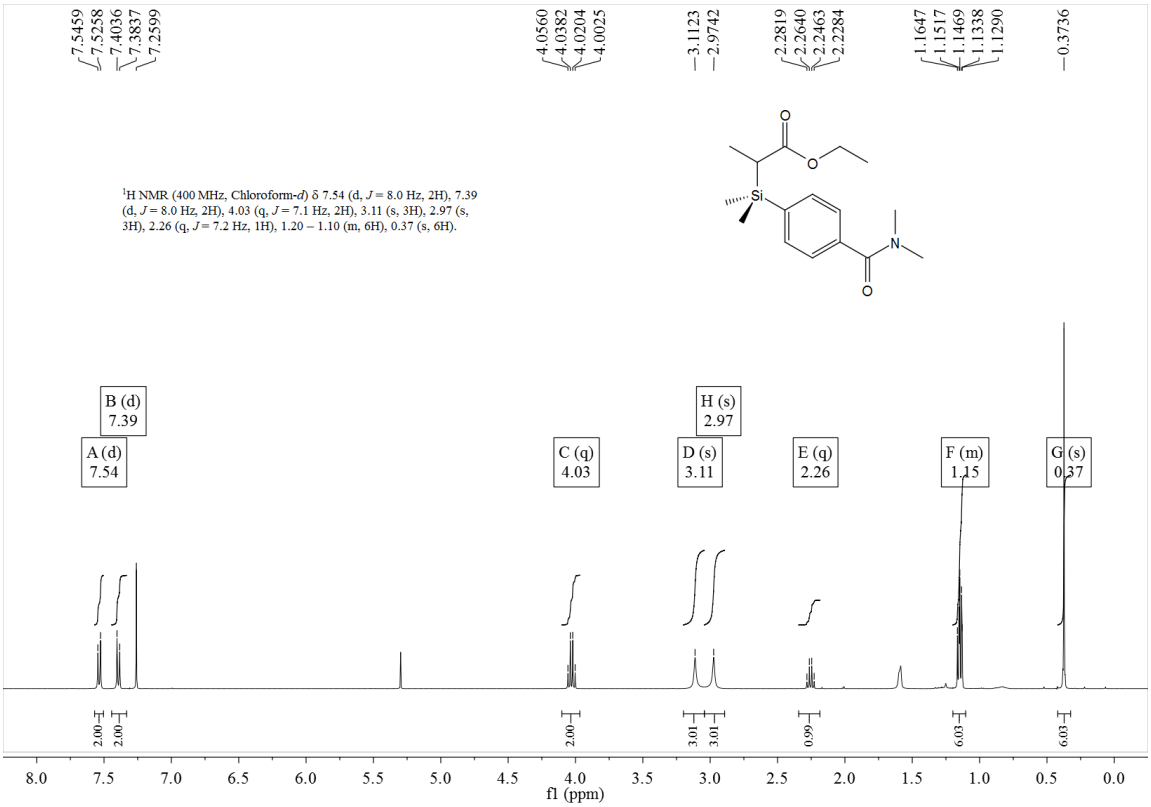

141.4932
134.3173
132.0031
131.6817
131.3619
131.0402
128.3167
125.6110
124.4923
124.4544
124.4169
124.3790
122.9050
120.2022
60.1646
29.9567
14.3914
11.3908
-4.1808
-4.6462
13C NMR (101 MHz, CDCl3) δ 141.49, 134.32, 132.00, 131.68, 131.36, 131.04, 128.32, 125.61, 124.49, 124.45, 124.42, 124.38, 122.91, 120.20, 60.16, 29.96, 14.39, 11.39, -4.18, -4.65.
f1 (ppm)

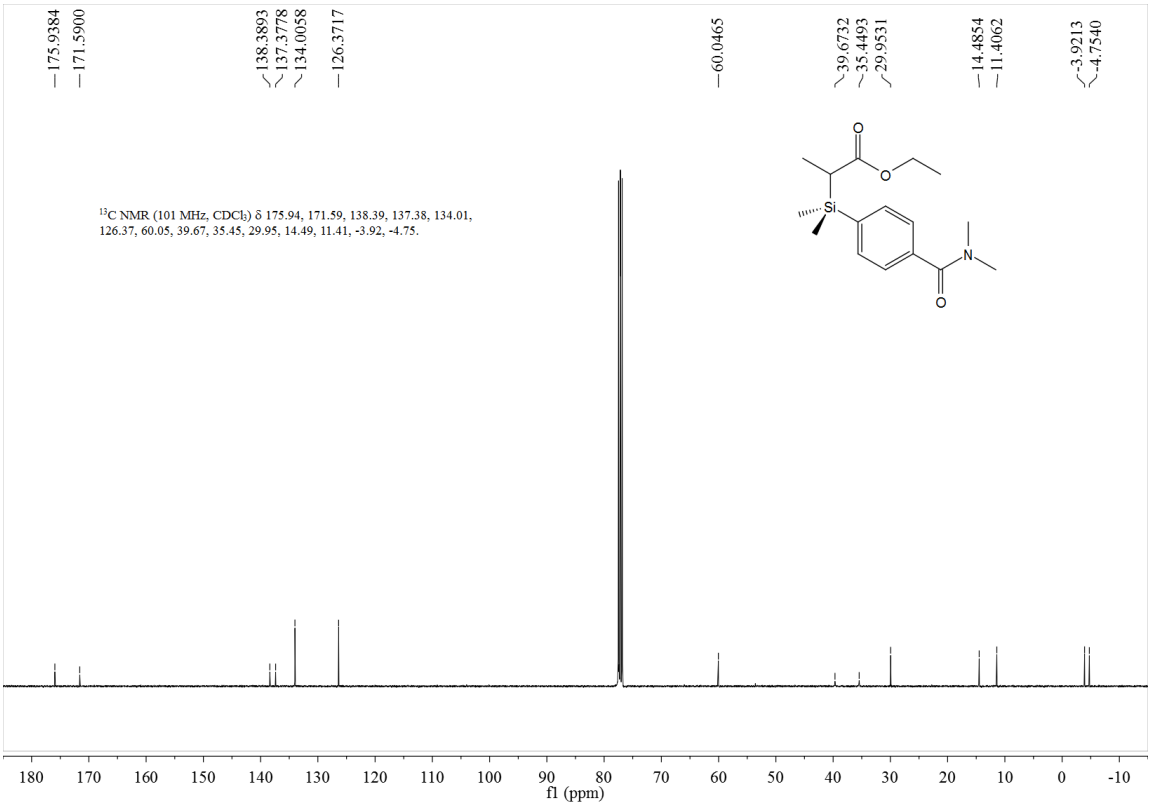

7.5158
7.4958
7.3942
7.3743
4.5809
4.0423
4.0245
4.0067
3.9889
2.2751
2.2572
2.2394
2.2216
1.1551
1.1508
1.1372
1.1329
1.1151
0.3718
0.3687
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 4.58 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.25 (q, *J* = 7.1 Hz, 1H), 1.18 – 1.08 (m, 6H), 0.37 (d, *J* = 1.2 Hz, 6H).
O
O
Si
Cl
B (d) 7.38
A (d) 7.51
C (s) 4.58
D (q) 4.02
E (q) 2.25
F (m) 1.14
G (d) 0.37
2.02
2.03
2.07
2.01
0.99
6.08
6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

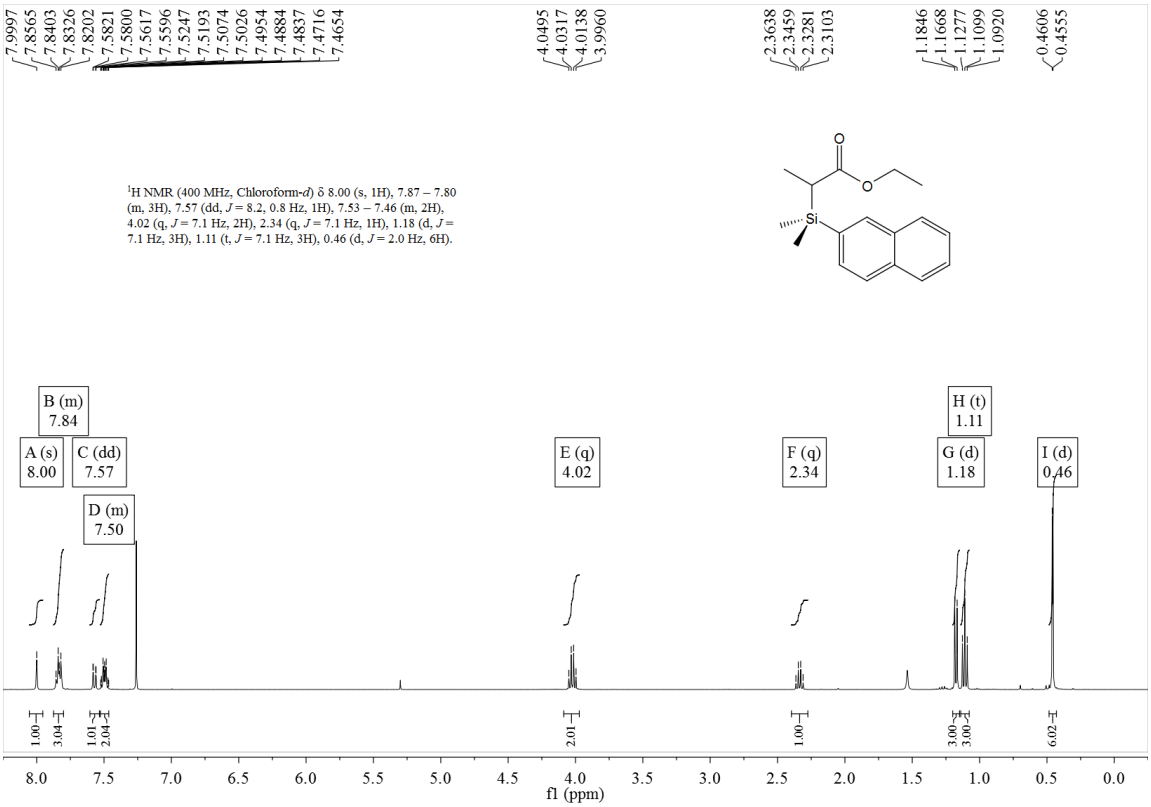

175.9757
138.7187
136.9243
134.4441
128.0230
60.0203
46.2296
30.0537
14.4441
11.4076
-3.9690
-4.6983
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.98, 138.72, 136.92, 134.44, 128.02, 60.02, 46.23, 30.05, 14.44, 11.41, -3.97, -4.70.
O
O
Si
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

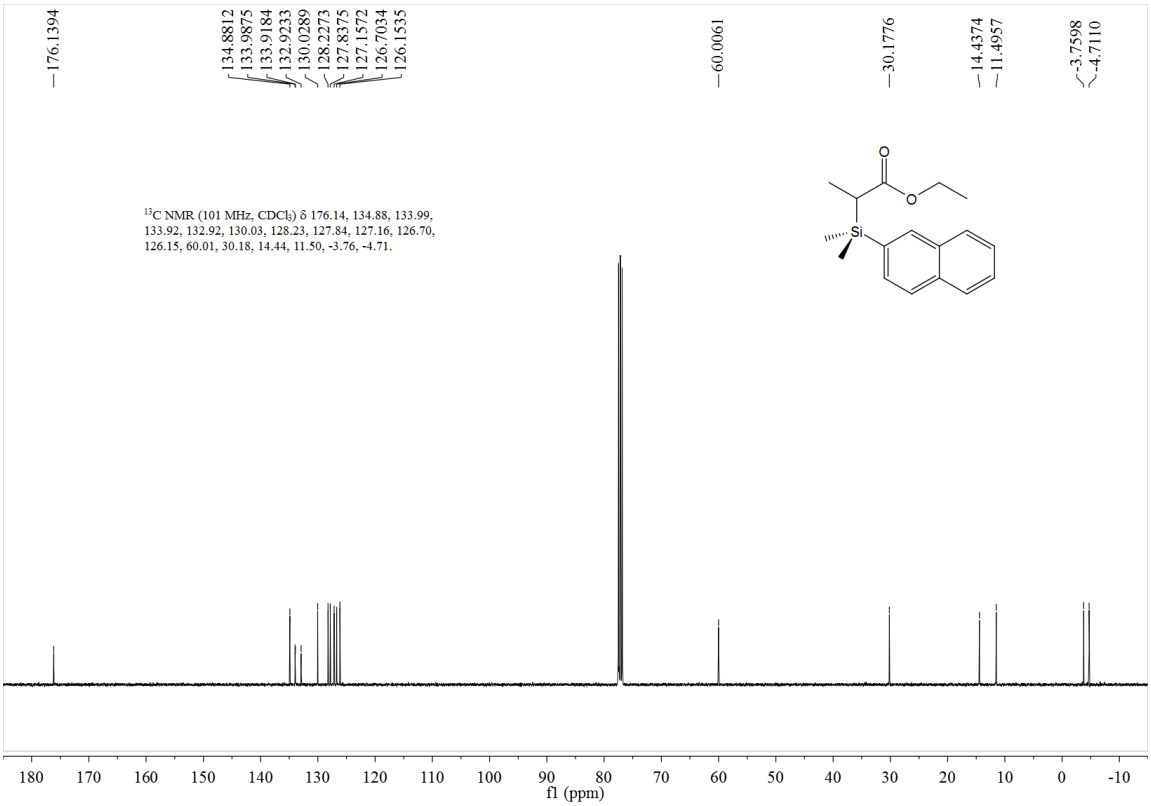

8.0128
7.9921
7.5925
7.5717
4.0333
4.0308
4.0153
4.0129
3.9975
3.9951
3.9795
3.9774
3.9200
2.2937
2.2758
2.2580
2.2401
1.1534
1.1356
1.1180
1.1002
0.3950
0.3915
Si
O
O
O
O
D (d) 8.00
G (d) 7.58
F (s) 3.92
E (qd) 4.01
A (q) 2.27
B (m) 1.13
C (d) 0.39
2.00
2.02
2.00
2.88
0.98
6.01
6.02
fl (ppm)

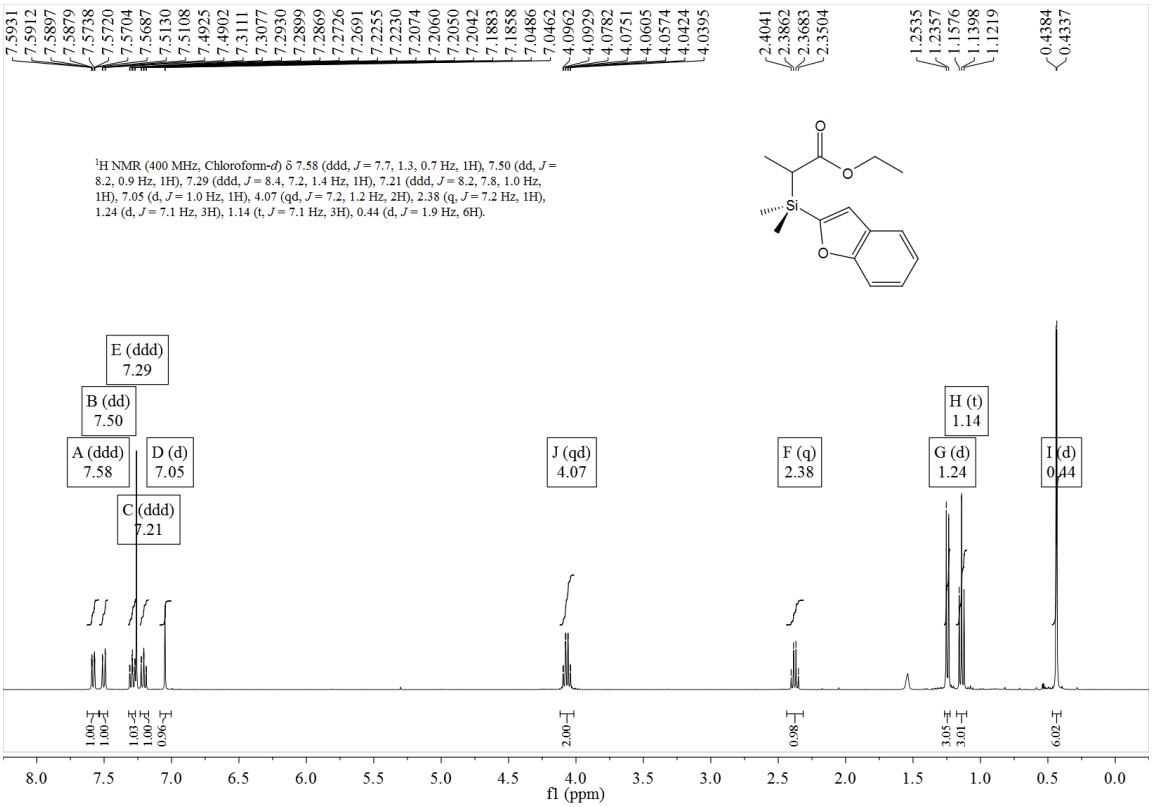

175.7695
167.2725
142.7760
134.0074
131.0039
128.6441
60.0730
52.3118
29.8787
14.4387
11.3652
-4.1252
-4.7140
Si
O
O
O
O
fl (ppm)

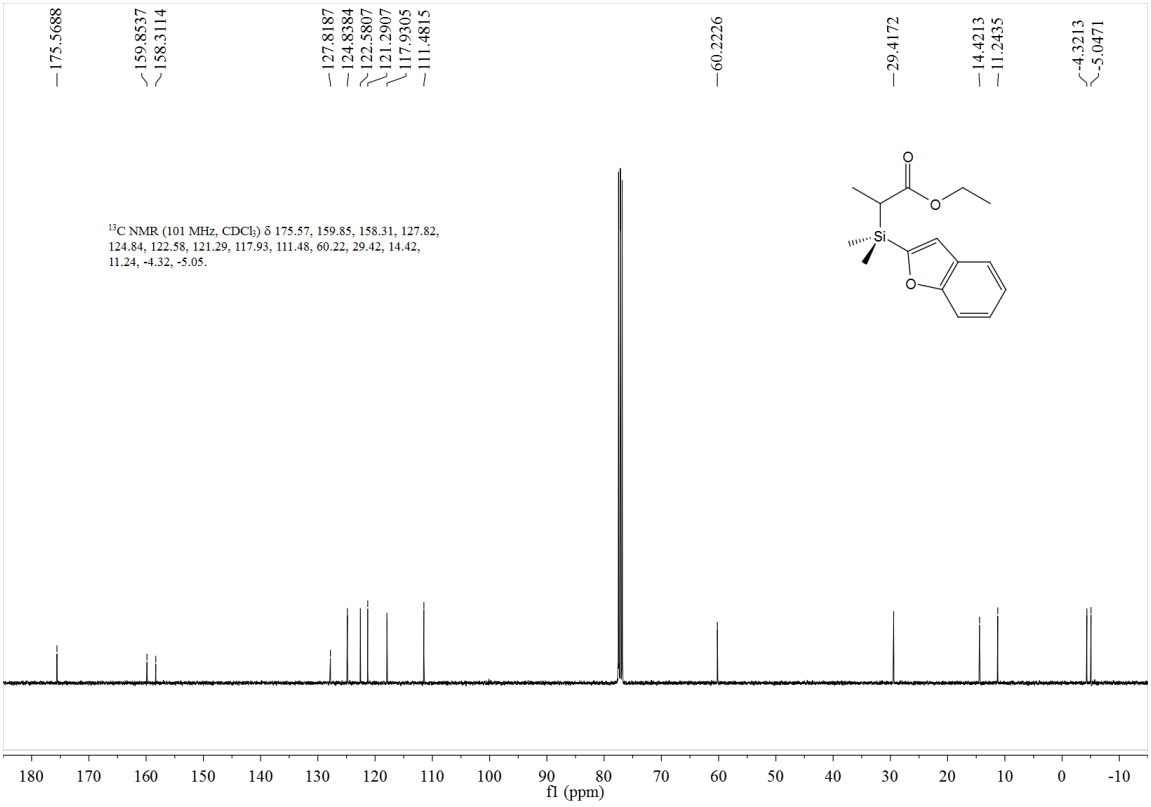

7.5459
7.5258
7.4036
7.3837
7.2599
4.0560
4.0382
4.0204
4.0025
3.1123
2.9742
2.2819
2.2640
2.2463
2.2284
1.1647
1.1517
1.1469
1.1338
1.1290
0.3736
[1]H NMR (400 MHz, Chloroform-d) δ 7.54 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 4.03 (q, J = 7.1 Hz, 2H), 3.11 (s, 3H), 2.97 (s, 3H), 2.26 (q, J = 7.2 Hz, 1H), 1.20 – 1.10 (m, 6H), 0.37 (s, 6H).
B (d) 7.39
A (d) 7.54
C (q) 4.03
H (s) 2.97
D (s) 3.11
E (q) 2.26
F (m) 1.15
G (s) 0.37
2.00
2.00
2.00
3.01
3.01
0.99
6.03
6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

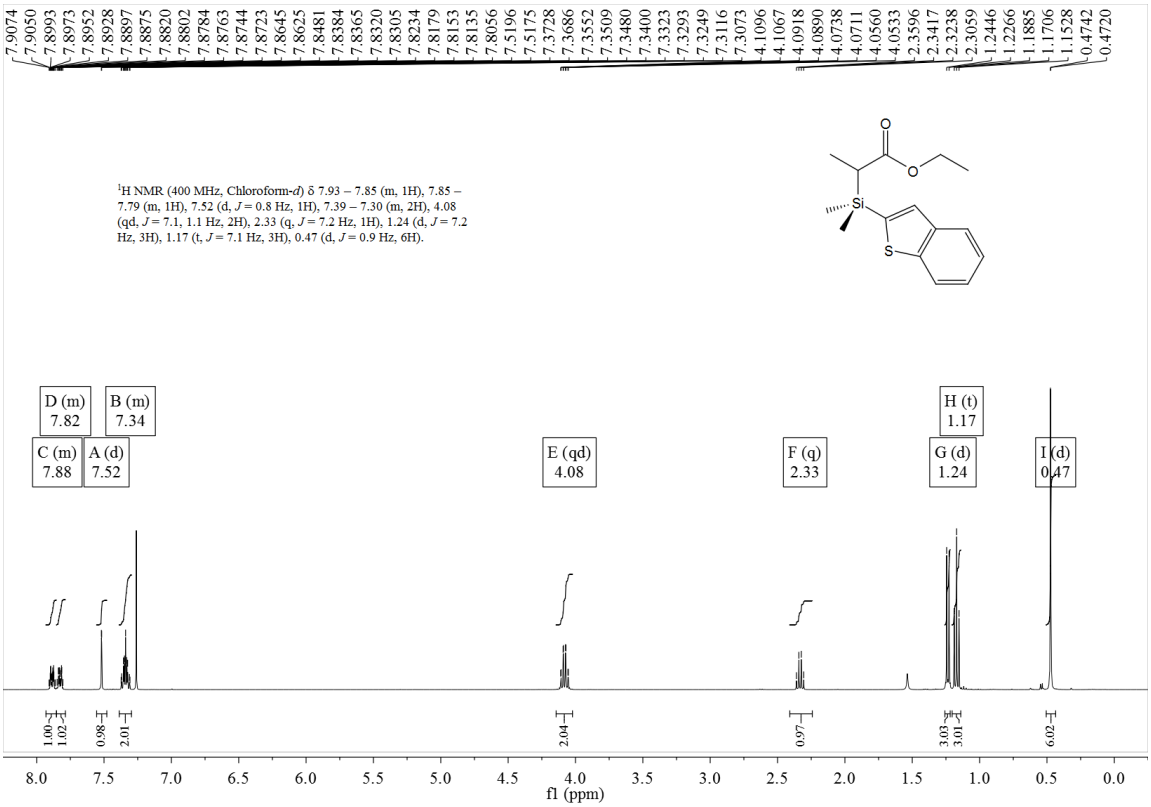

175.9384
171.5900
138.3893
137.3778
134.0058
126.3717
60.0465
39.6732
35.4493
29.9531
14.4854
11.4062
-3.9213
-4.7540
[13]C NMR (101 MHz, CDCl3) δ 175.94, 171.59, 138.39, 137.38, 134.01, 126.37, 60.05, 39.67, 35.45, 29.95, 14.49, 11.41, -3.92, -4.75.
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

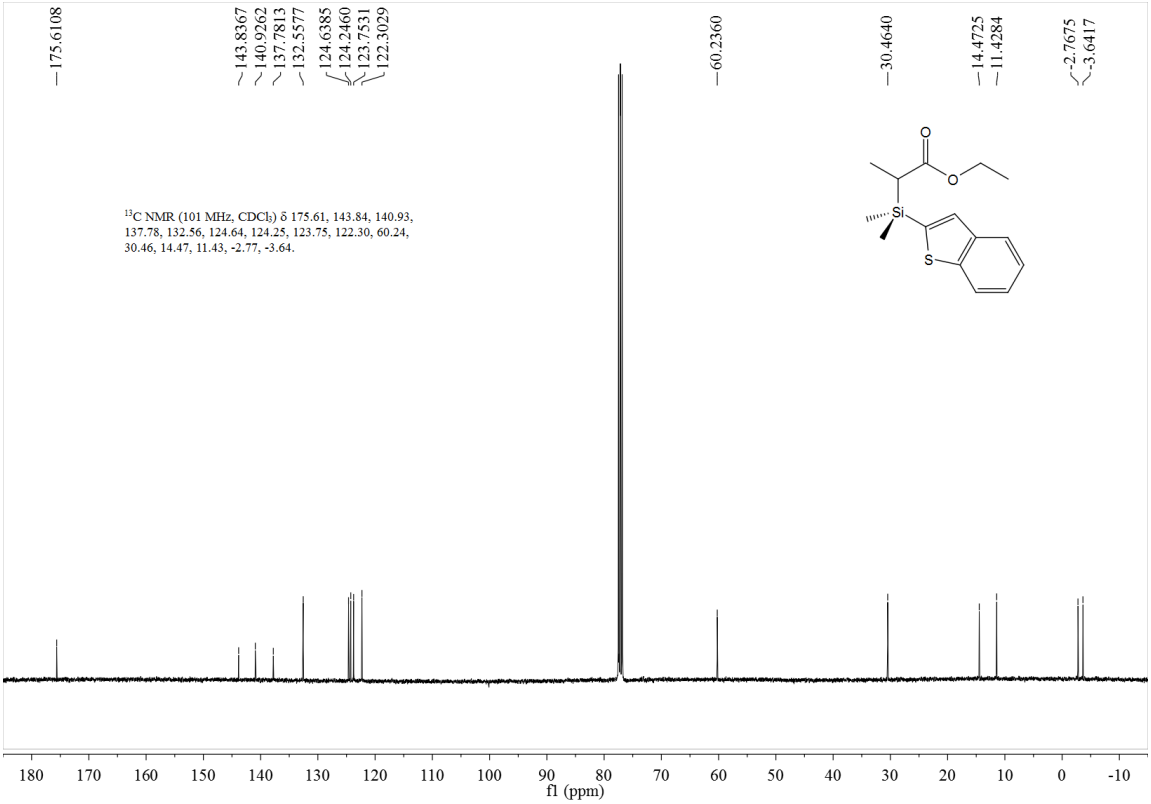

7.9997
7.8565
7.8403
7.8326
7.8202
7.5821
7.5800
7.5617
7.5596
7.5247
7.5193
7.5074
7.5026
7.4954
7.4884
7.4837
7.4716
7.4654
4.0495
4.0317
4.0138
3.9960
2.3638
2.3459
2.3281
2.3103
1.1846
1.1668
1.1277
1.1099
1.0920
0.4606
0.4555
[1]H NMR (400 MHz, Chloroform-d) δ 8.00 (s, 1H), 7.87 – 7.80 (m, 3H), 7.57 (dd, J = 8.2, 0.8 Hz, 1H), 7.53 – 7.46 (m, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.34 (q, J = 7.1 Hz, 1H), 1.18 (d, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H), 0.46 (d, J = 2.0 Hz, 6H).
O
O
Si
B (m) 7.84
A (s) 8.00
C (dd) 7.57
D (m) 7.50
E (q) 4.02
F (q) 2.34
H (t) 1.11
G (d) 1.18
I (d) 0.46
1.00
3.04
1.01
2.04
2.01
1.00
3.00
3.00
6.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

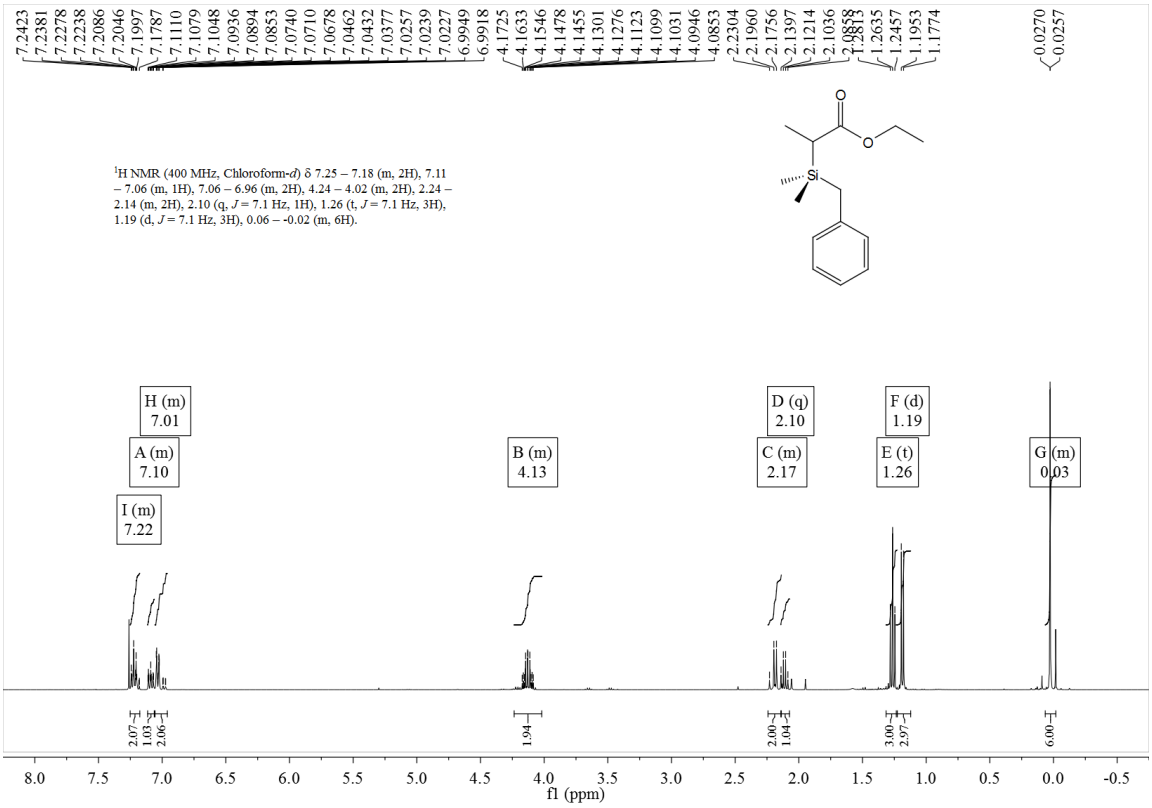

176.1394
134.8812
133.9875
133.9184
132.9233
130.0289
128.2273
127.8375
127.1572
126.7034
126.1535
60.0061
30.1776
14.4374
11.4957
-3.7598
-4.7110
[13]C NMR (101 MHz, CDCl3) δ 176.14, 134.88, 133.99, 133.92, 132.92, 130.03, 128.23, 127.84, 127.16, 126.70, 126.15, 60.01, 30.18, 14.44, 11.50, -3.76, -4.71.
O
O
Si
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

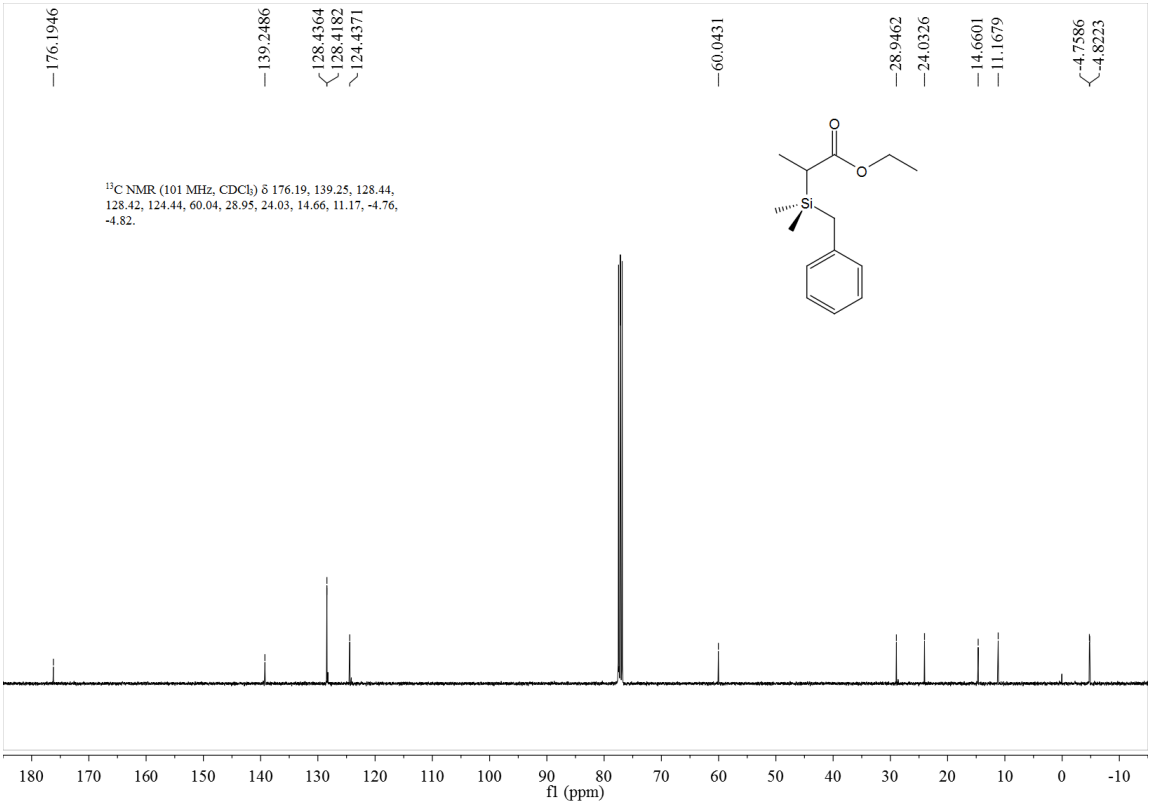

7.5931
7.5912
7.5897
7.5879
7.5738
7.5720
7.5704
7.5687
7.5130
7.5108
7.4925
7.4902
7.3111
7.3077
7.2930
7.2899
7.2869
7.2726
7.2691
7.2255
7.2230
7.2074
7.2060
7.2050
7.2042
7.1883
7.1858
7.0486
7.0462
4.0962
4.0929
4.0782
4.0751
4.0605
4.0574
4.0424
4.0395
2.4041
2.3862
2.3683
2.3504
1.2535
1.2357
1.1576
1.1398
1.1219
0.4384
0.4337
1H NMR (400 MHz, Chloroform-d) δ 7.58 (ddd, J = 7.7, 1.3, 0.7 Hz, 1H), 7.50 (dd, J = 8.2, 0.9 Hz, 1H), 7.29 (ddd, J = 8.4, 7.2, 1.4 Hz, 1H), 7.21 (ddd, J = 8.2, 7.8, 1.0 Hz, 1H), 7.05 (d, J = 1.0 Hz, 1H), 4.07 (qd, J = 7.2, 1.2 Hz, 2H), 2.38 (q, J = 7.2 Hz, 1H), 1.24 (d, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H), 0.44 (d, J = 1.9 Hz, 6H).
E (ddd) 7.29
B (dd) 7.50
A (ddd) 7.58
D (d) 7.05
C (ddd) 7.21
J (qd) 4.07
F (q) 2.38
H (t) 1.14
G (d) 1.24
I (d) 0.44
1.00
1.00
1.03
1.00
0.96
2.00
0.98
3.05
3.01
6.02
f1 (ppm)

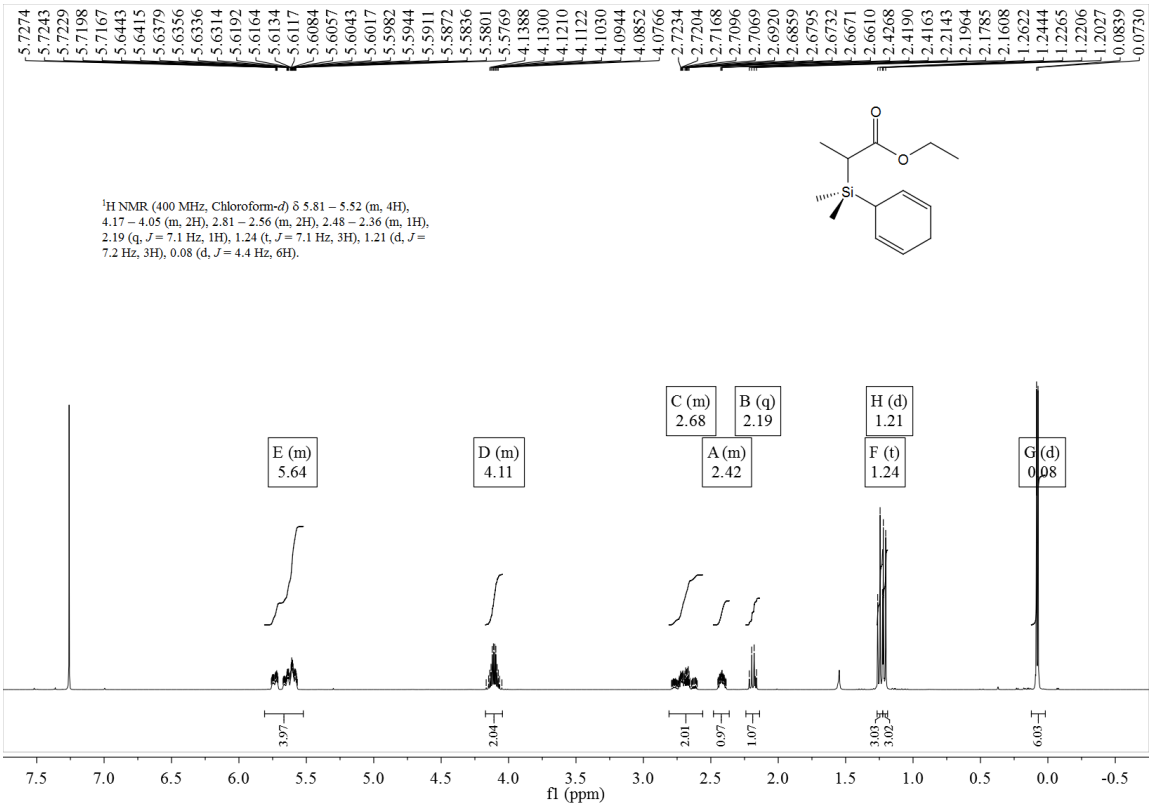

175.5688
159.8537
158.3114
127.8187
124.8384
122.5807
121.2907
117.9305
111.4815
60.2226
29.4172
14.4213
11.2435
-4.3213
-5.0471
13C NMR (101 MHz, CDCl3) δ 175.57, 159.85, 158.31, 127.82, 124.84, 122.58, 121.29, 117.93, 111.48, 60.22, 29.42, 14.42, 11.24, -4.32, -5.05.
f1 (ppm)

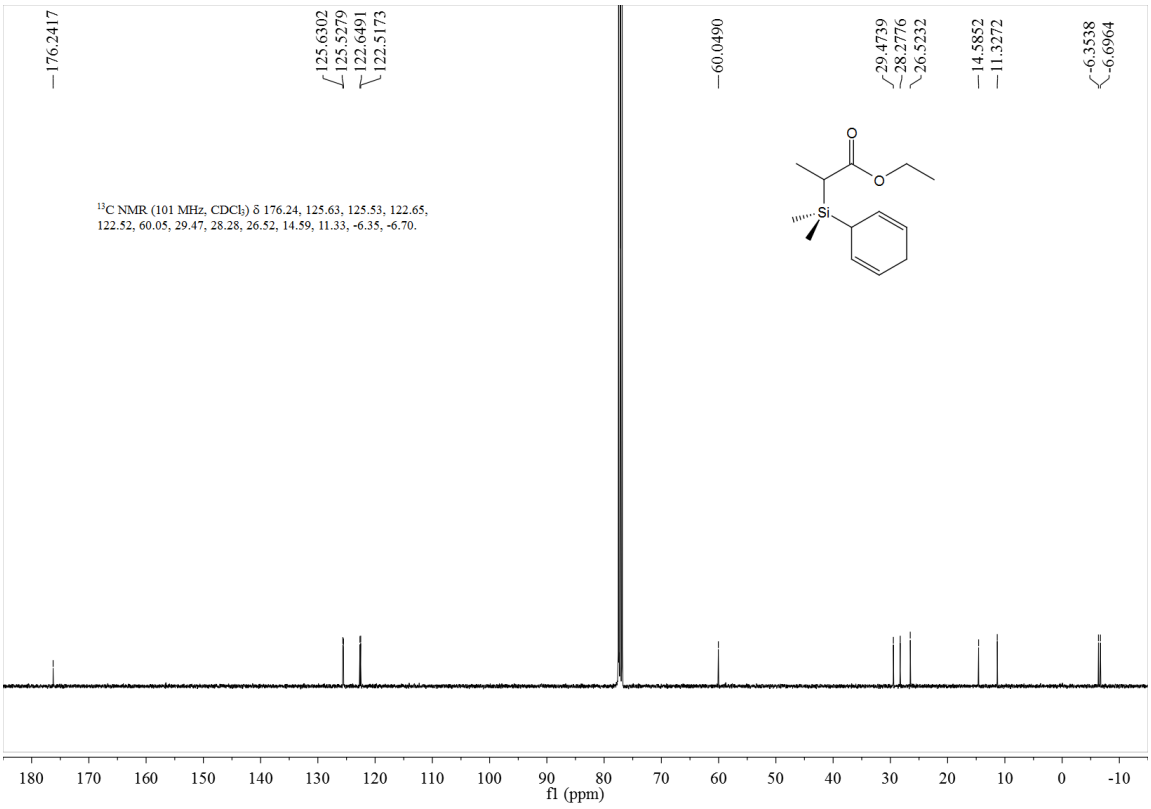

7.9074
7.9050
7.8993
7.8973
7.8952
7.8928
7.8897
7.8875
7.8820
7.8802
7.8784
7.8763
7.8744
7.8723
7.8645
7.8625
7.8481
7.8384
7.8365
7.8320
7.8305
7.8234
7.8179
7.8153
7.8135
7.8056
7.5196
7.5175
7.3728
7.3686
7.3552
7.3509
7.3480
7.3400
7.3323
7.3293
7.3249
7.3116
7.3073
4.1096
4.1067
4.0918
4.0890
4.0738
4.0711
4.0560
4.0533
2.3596
2.3417
2.3238
2.3059
1.2446
1.2266
1.1885
1.1706
1.1528
0.4742
0.4720
1H NMR (400 MHz, Chloroform-d) δ 7.93 – 7.85 (m, 1H), 7.85 – 7.79 (m, 1H), 7.52 (d, J = 0.8 Hz, 1H), 7.39 – 7.30 (m, 2H), 4.08 (qd, J = 7.1, 1.1 Hz, 2H), 2.33 (q, J = 7.2 Hz, 1H), 1.24 (d, J = 7.2 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H), 0.47 (d, J = 0.9 Hz, 6H).
O
O
Si
S
D (m) 7.82
B (m) 7.34
C (m) 7.88
A (d) 7.52
E (qd) 4.08
F (q) 2.33
H (t) 1.17
G (d) 1.24
I (d) 0.47
1.00
1.02
0.98
2.01
2.04
0.97
3.03
3.01
6.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

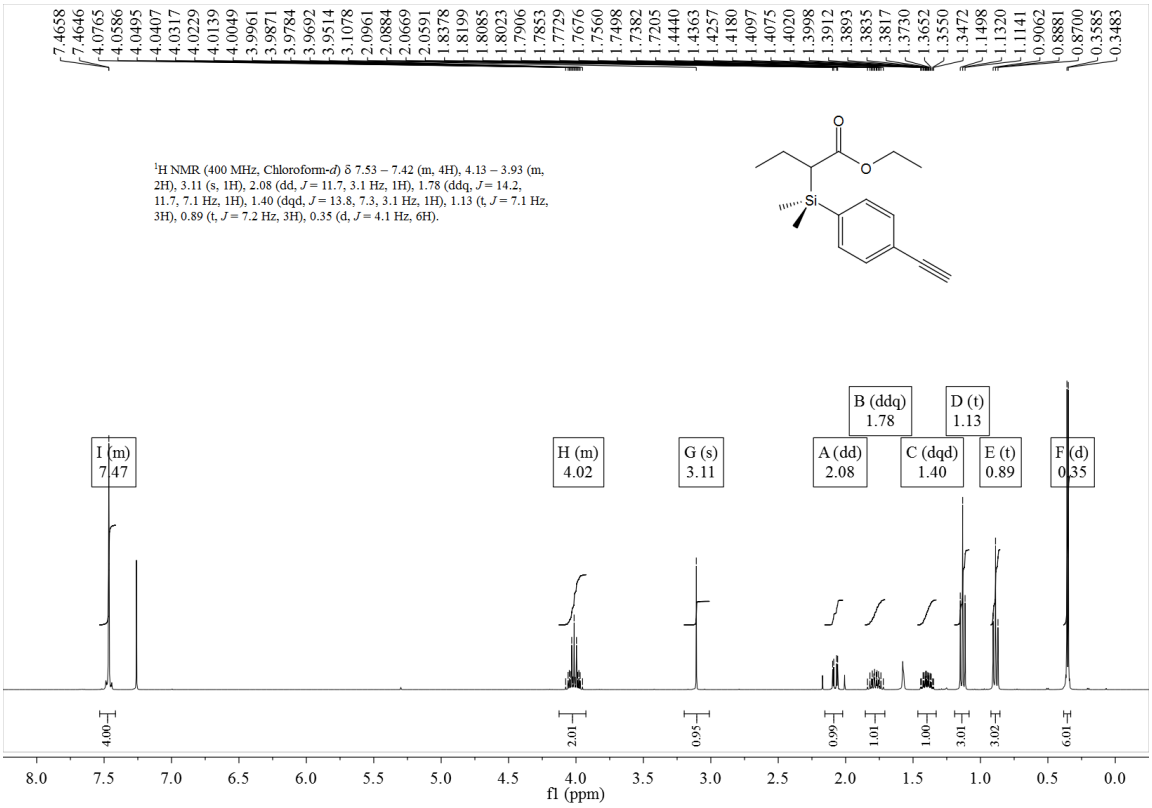

175.6108
143.8367
140.9262
137.7813
132.5577
124.6385
124.2460
123.7531
122.3029
60.2360
30.4640
14.4725
11.4284
-2.7675
-3.6417
13C NMR (101 MHz, CDCl3) δ 175.61, 143.84, 140.93, 137.78, 132.56, 124.64, 124.25, 123.75, 122.30, 60.24, 30.46, 14.47, 11.43, -2.77, -3.64.
O
O
Si
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

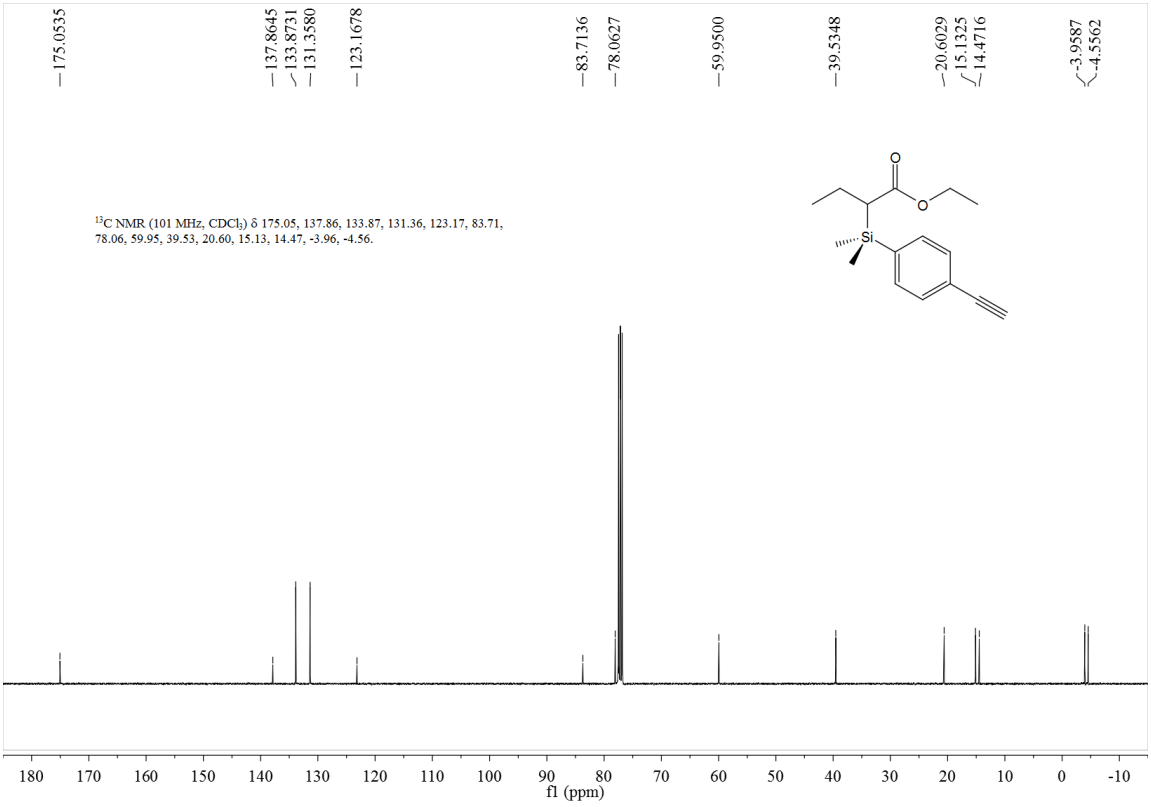

7.2423
7.2381
7.2278
7.2238
7.2086
7.2046
7.1997
7.1787
7.1110
7.1079
7.1048
7.0936
7.0894
7.0853
7.0740
7.0710
7.0678
7.0462
7.0432
7.0377
7.0257
7.0239
7.0227
6.9949
6.9918
4.1725
4.1633
4.1546
4.1478
4.1455
4.1301
4.1276
4.1123
4.1099
4.1031
4.0946
4.0853
2.2304
2.1960
2.1756
2.1397
2.1214
2.1036
2.0858
2.0813
1.2635
1.2457
1.1953
1.1774
0.0270
0.0257
[1]H NMR (400 MHz, Chloroform-d) δ 7.25 – 7.18 (m, 2H), 7.11 – 7.06 (m, 1H), 7.06 – 6.96 (m, 2H), 4.24 – 4.02 (m, 2H), 2.24 – 2.14 (m, 2H), 2.10 (q, J = 7.1 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.19 (d, J = 7.1 Hz, 3H), 0.06 – -0.02 (m, 6H).
H (m) 7.01
A (m) 7.10
I (m) 7.22
B (m) 4.13
D (q) 2.10
C (m) 2.17
F (d) 1.19
E (t) 1.26
G (m) 0.03
2.07
1.03
2.06
1.94
2.00
1.04
3.00
2.97
6.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

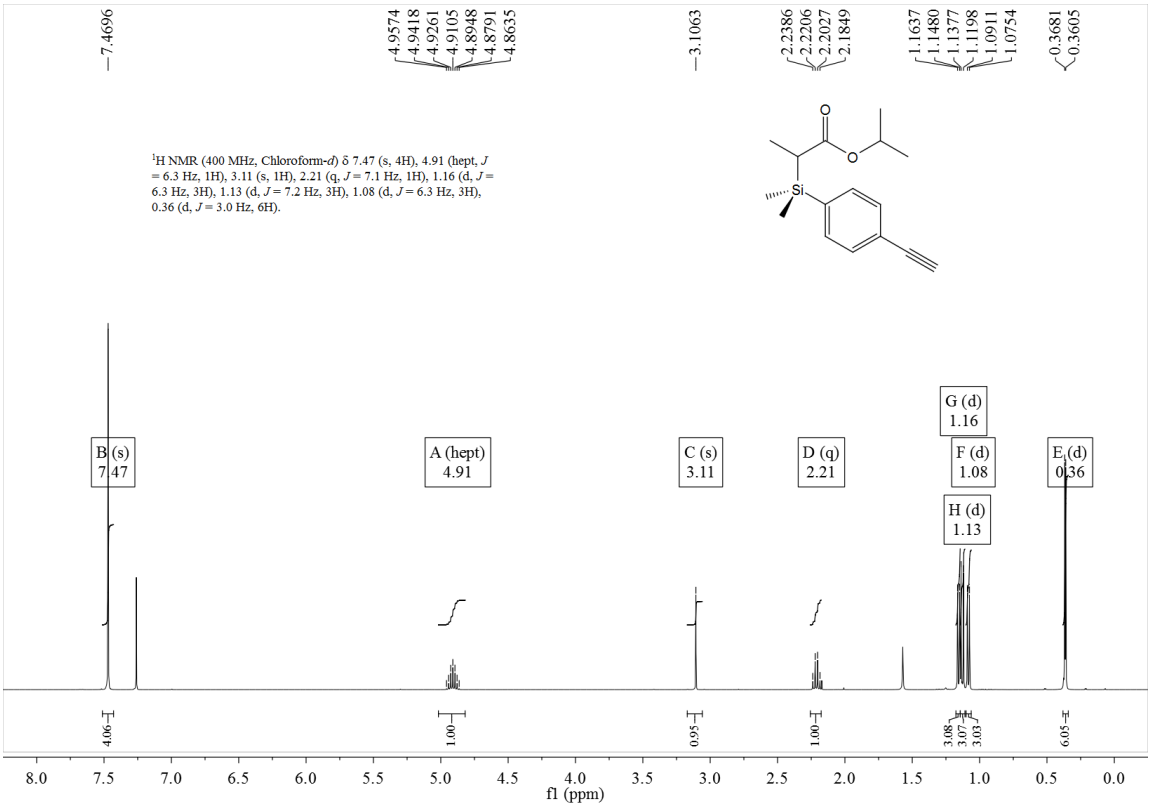

176.1946
139.2486
128.4364
128.4182
124.4371
60.0431
28.9462
24.0326
14.6601
11.1679
-4.7586
-4.8223
[13]C NMR (101 MHz, CDCl3) δ 176.19, 139.25, 128.44, 128.42, 124.44, 60.04, 28.95, 24.03, 14.66, 11.17, -4.76, -4.82.
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

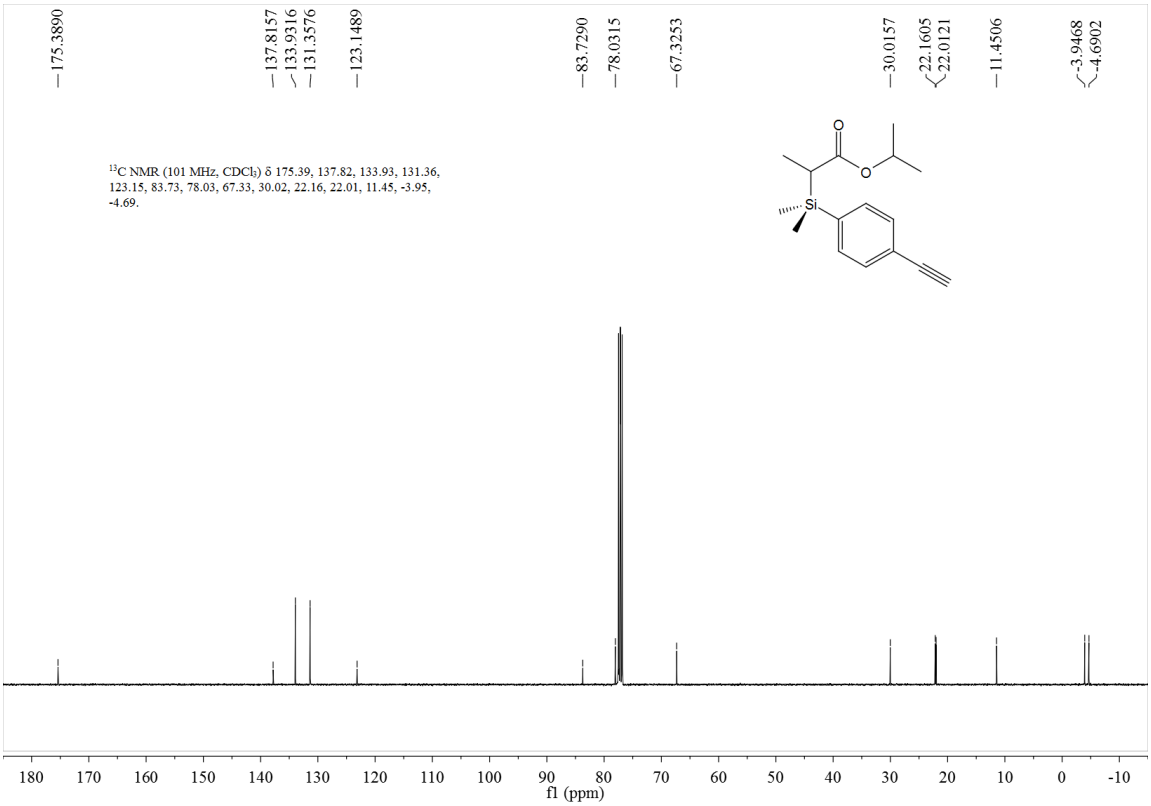

5.7274
5.7243
5.7229
5.7198
5.7167
5.6443
5.6415
5.6379
5.6356
5.6336
5.6314
5.6192
5.6164
5.6134
5.6117
5.6084
5.6057
5.6043
5.6017
5.5982
5.5944
5.5911
5.5872
5.5836
5.5801
5.5769
4.1388
4.1300
4.1210
4.1122
4.1030
4.0944
4.0852
4.0766
2.7234
2.7204
2.7168
2.7096
2.7069
2.6920
2.6859
2.6795
2.6732
2.6671
2.6610
2.4268
2.4190
2.4163
2.2143
2.1964
2.1785
2.1608
1.2622
1.2444
1.2265
1.2206
1.2027
0.0839
0.0730
O
O
Si
[1]H NMR (400 MHz, Chloroform-d) δ 5.81 – 5.52 (m, 4H), 4.17 – 4.05 (m, 2H), 2.81 – 2.56 (m, 2H), 2.48 – 2.36 (m, 1H), 2.19 (q, J = 7.1 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.21 (d, J = 7.2 Hz, 3H), 0.08 (d, J = 4.4 Hz, 6H).
E (m) 5.64
D (m) 4.11
C (m) 2.68
A (m) 2.42
B (q) 2.19
H (d) 1.21
F (t) 1.24
G (d) 0.08
3.97
2.04
2.01
0.97
1.07
3.03
3.02
6.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

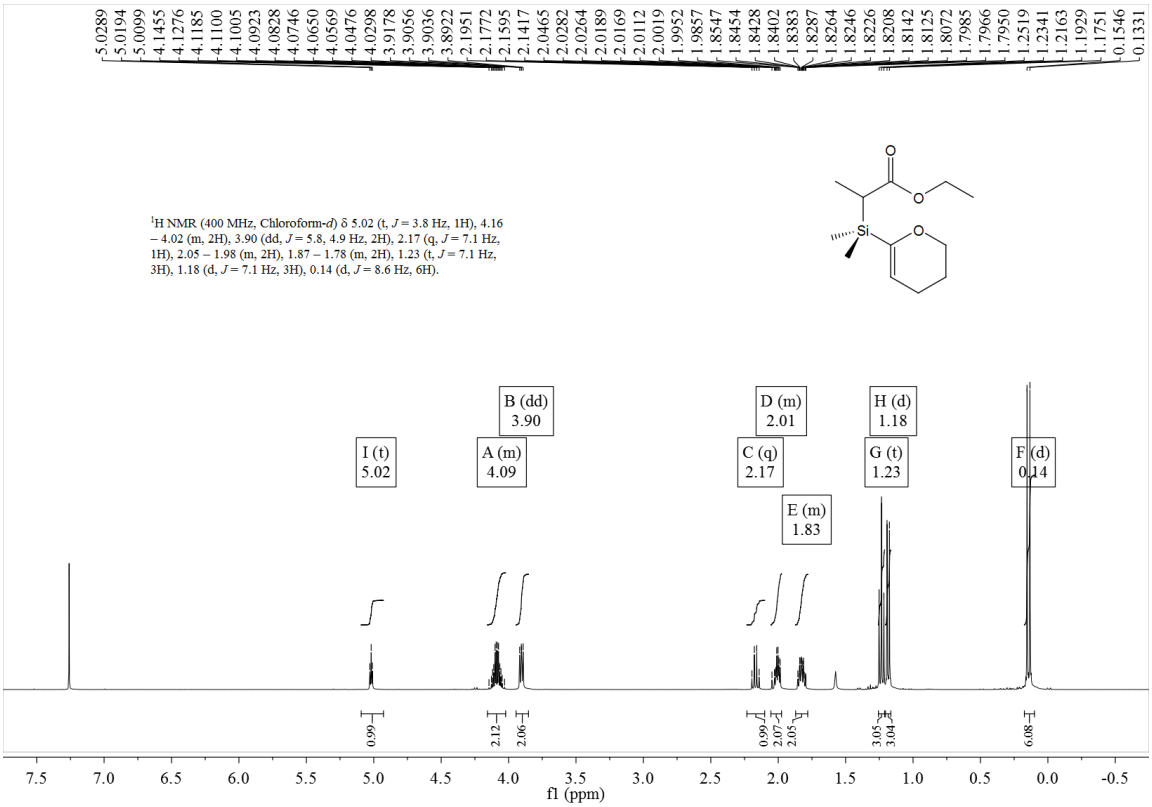

176.2417
125.6302
125.5279
122.6491
122.5173
60.0490
29.4739
28.2776
26.5232
14.5852
11.3272
-6.3538
-6.6964
O
O
Si
[13]C NMR (101 MHz, CDCl3) δ 176.24, 125.63, 125.53, 122.65, 122.52, 60.05, 29.47, 28.28, 26.52, 14.59, 11.33, -6.35, -6.70.
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

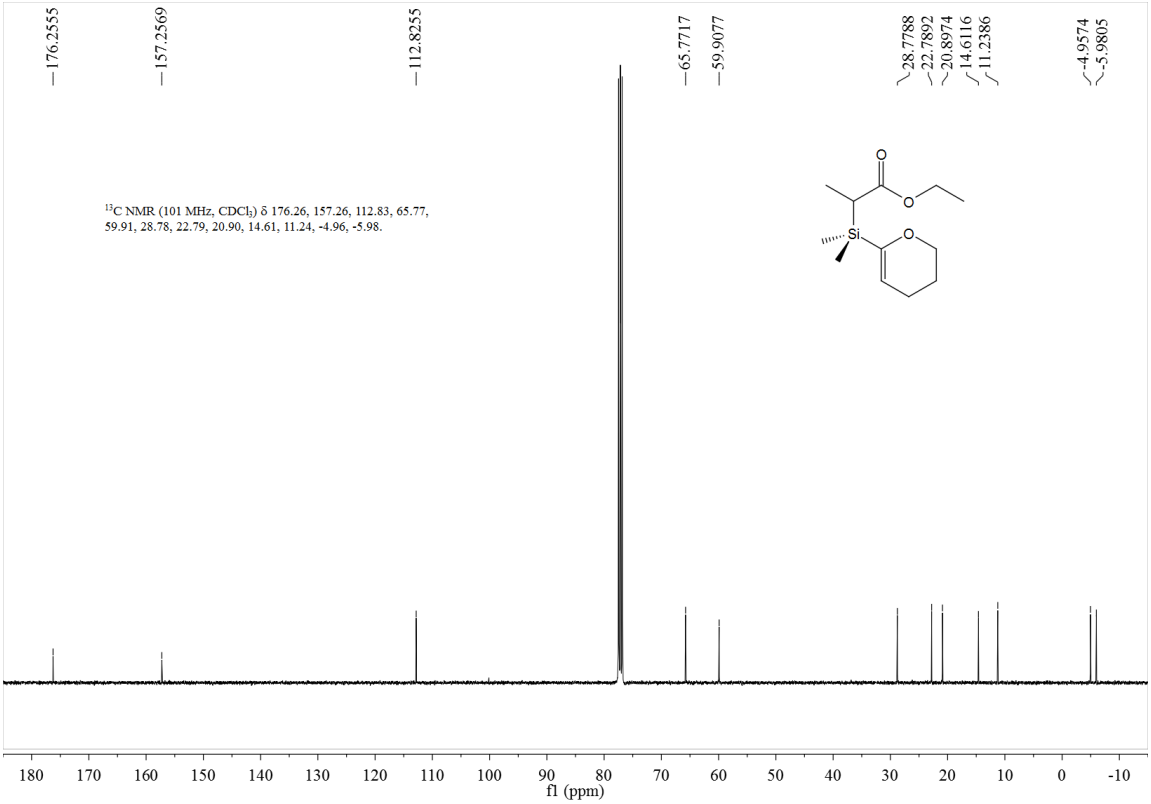

7.4658
7.4646
4.0765
4.0586
4.0495
4.0407
4.0317
4.0229
4.0139
4.0049
3.9961
3.9871
3.9784
3.9692
3.9514
3.1078
2.0961
2.0884
2.0669
2.0591
1.8378
1.8199
1.8085
1.8023
1.7906
1.7853
1.7729
1.7676
1.7560
1.7498
1.7382
1.7205
1.4440
1.4363
1.4257
1.4180
1.4097
1.4075
1.4020
1.3998
1.3912
1.3893
1.3835
1.3817
1.3730
1.3652
1.3550
1.3472
1.1498
1.1320
1.1141
0.9062
0.8881
0.8700
0.3585
0.3483
1H NMR (400 MHz, Chloroform-d) δ 7.53 – 7.42 (m, 4H), 4.13 – 3.93 (m, 2H), 3.11 (s, 1H), 2.08 (dd, J = 11.7, 3.1 Hz, 1H), 1.78 (ddq, J = 14.2, 11.7, 7.1 Hz, 1H), 1.40 (dqd, J = 13.8, 7.3, 3.1 Hz, 1H), 1.13 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H), 0.35 (d, J = 4.1 Hz, 6H).
O
O
Si
I (m) 7.47
H (m) 4.02
G (s) 3.11
A (dd) 2.08
B (ddq) 1.78
C (dqd) 1.40
D (t) 1.13
E (t) 0.89
F (d) 0.35
4.00
2.01
0.95
0.99
1.01
1.00
3.01
3.02
6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

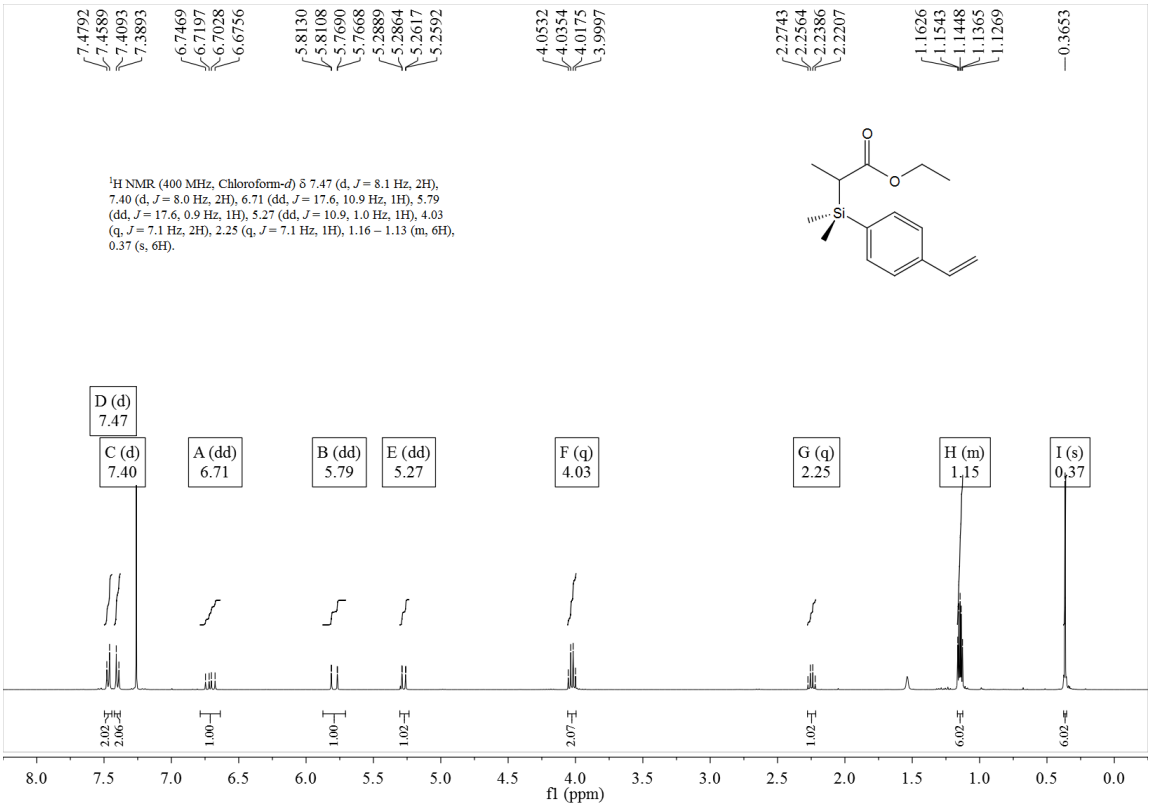

175.0535
137.8645
133.8731
131.3580
123.1678
83.7136
78.0627
59.9500
39.5348
20.6029
15.1325
14.4716
-3.9587
-4.5562
13C NMR (101 MHz, CDCl3) δ 175.05, 137.86, 133.87, 131.36, 123.17, 83.71, 78.06, 59.95, 39.53, 20.60, 15.13, 14.47, -3.96, -4.56.
O
O
Si
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

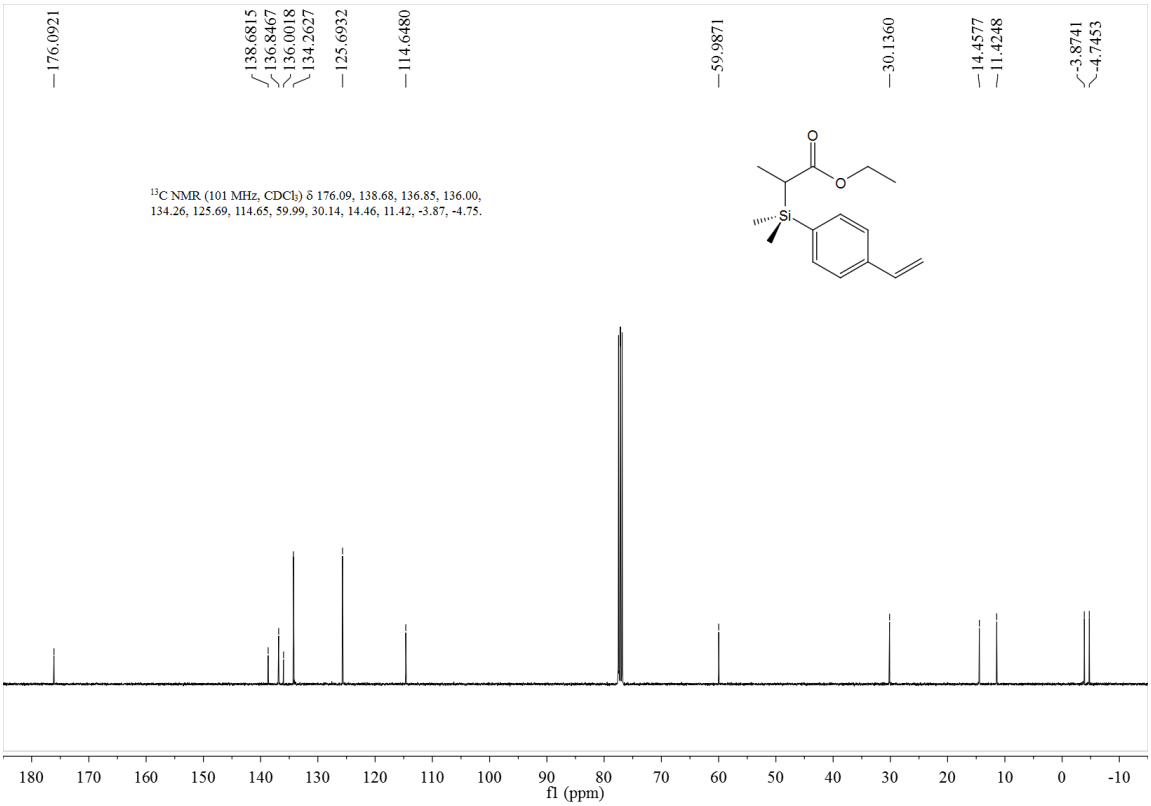

7.4696
4.9574
4.9418
4.9261
4.9105
4.8948
4.8791
4.8635
3.1063
2.2386
2.2206
2.2027
2.1849
1.1637
1.1480
1.1377
1.1198
1.0911
1.0754
0.3681
0.3605
[1]H NMR (400 MHz, Chloroform-d) δ 7.47 (s, 4H), 4.91 (hept, J = 6.3 Hz, 1H), 3.11 (s, 1H), 2.21 (q, J = 7.1 Hz, 1H), 1.16 (d, J = 6.3 Hz, 3H), 1.13 (d, J = 7.2 Hz, 3H), 1.08 (d, J = 6.3 Hz, 3H), 0.36 (d, J = 3.0 Hz, 6H).
O
O
Si
B (s) 7.47
A (hept) 4.91
C (s) 3.11
D (q) 2.21
G (d) 1.16
F (d) 1.08
H (d) 1.13
E (d) 0.36
4.06
1.00
0.95
1.00
3.08
3.07
3.03
6.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

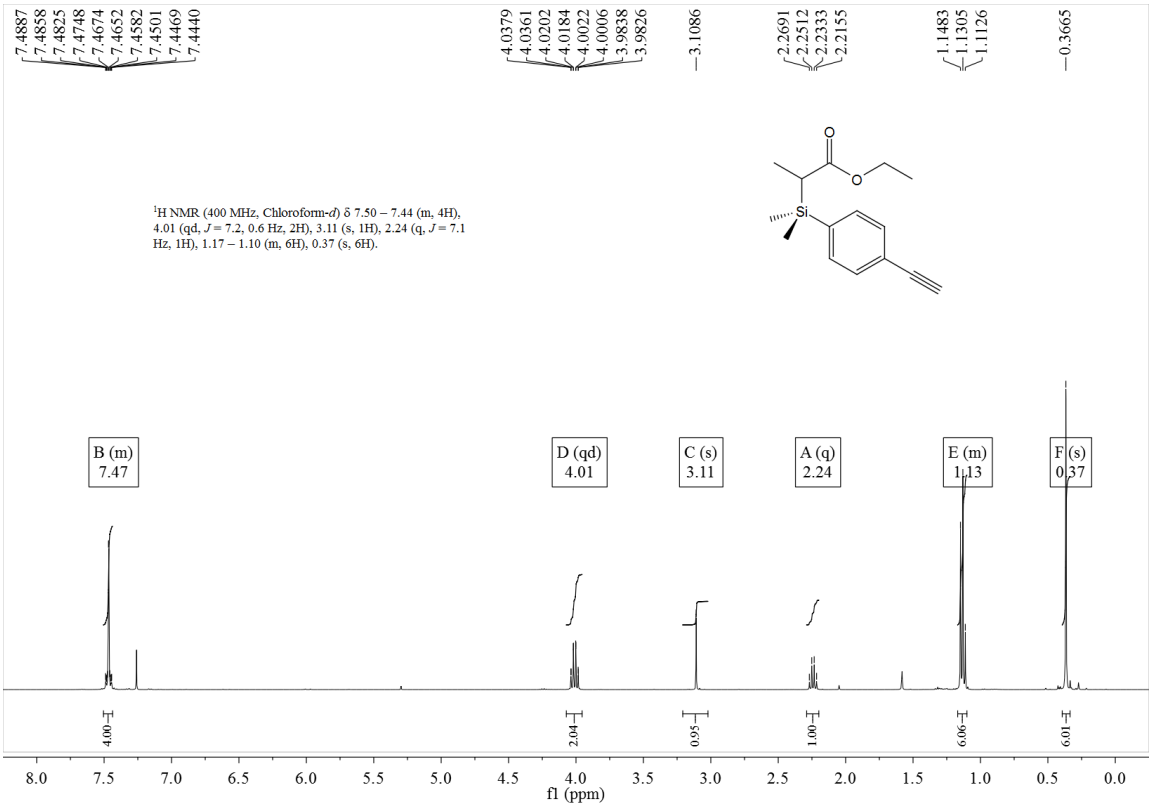

175.3890
137.8157
133.9316
131.3576
123.1489
83.7290
78.0315
67.3253
30.0157
22.1605
22.0121
11.4506
-3.9468
-4.6902
[13]C NMR (101 MHz, CDCl3) δ 175.39, 137.82, 133.93, 131.36, 123.15, 83.73, 78.03, 67.33, 30.02, 22.16, 22.01, 11.45, -3.95, -4.69.
O
O
Si
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

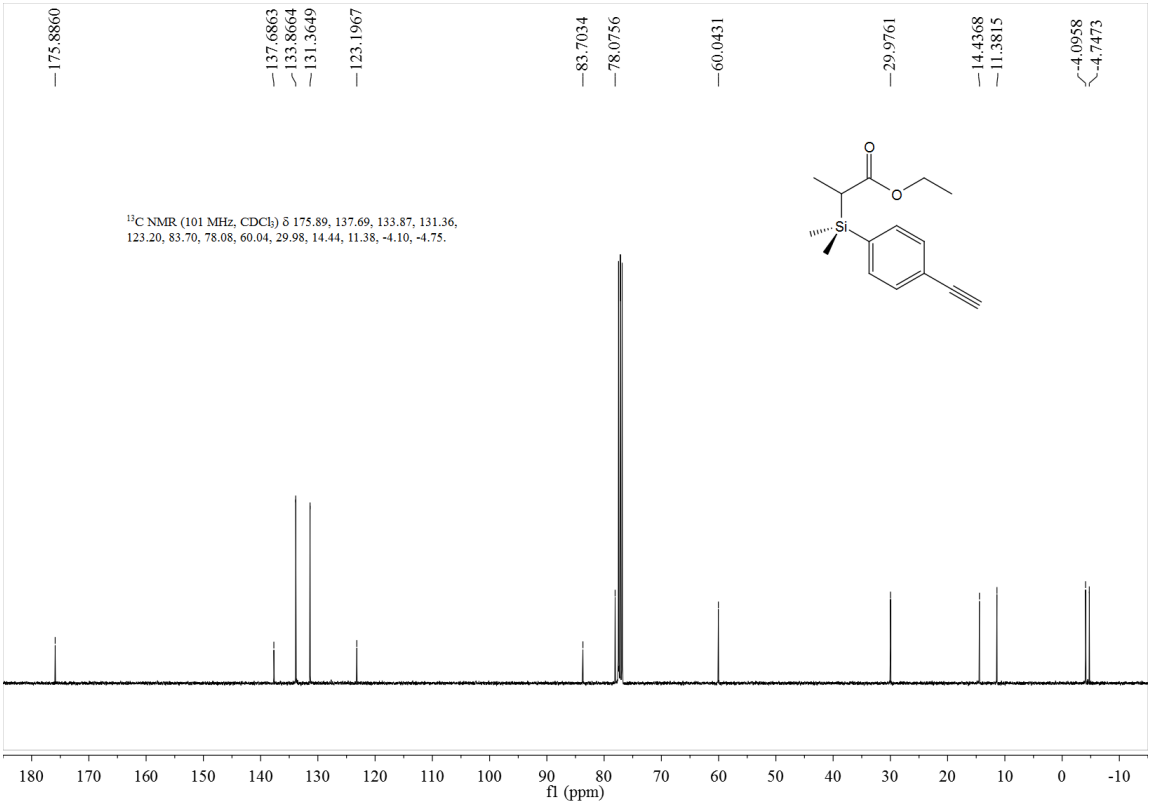

5.0289
5.0194
5.0099
4.1455
4.1276
4.1185
4.1100
4.1005
4.0923
4.0828
4.0746
4.0650
4.0569
4.0476
4.0298
3.9178
3.9056
3.9036
3.8922
2.1951
2.1772
2.1595
2.1417
2.0465
2.0282
2.0264
2.0189
2.0169
2.0112
2.0019
1.9952
1.9857
1.8547
1.8454
1.8428
1.8402
1.8383
1.8287
1.8264
1.8246
1.8226
1.8208
1.8142
1.8125
1.8072
1.7985
1.7966
1.7950
1.2519
1.2341
1.2163
1.1929
1.1751
0.1546
0.1331
[1]H NMR (400 MHz, Chloroform-d) δ 5.02 (t, J = 3.8 Hz, 1H), 4.16 – 4.02 (m, 2H), 3.90 (dd, J = 5.8, 4.9 Hz, 2H), 2.17 (q, J = 7.1 Hz, 1H), 2.05 – 1.98 (m, 2H), 1.87 – 1.78 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.18 (d, J = 7.1 Hz, 3H), 0.14 (d, J = 8.6 Hz, 6H).
O
O
Si
O
I (t) 5.02
A (m) 4.09
B (dd) 3.90
C (q) 2.17
D (m) 2.01
E (m) 1.83
G (t) 1.23
H (d) 1.18
F (d) 0.14
0.99
2.12
2.06
0.99
2.07
2.05
3.05
3.04
6.08
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

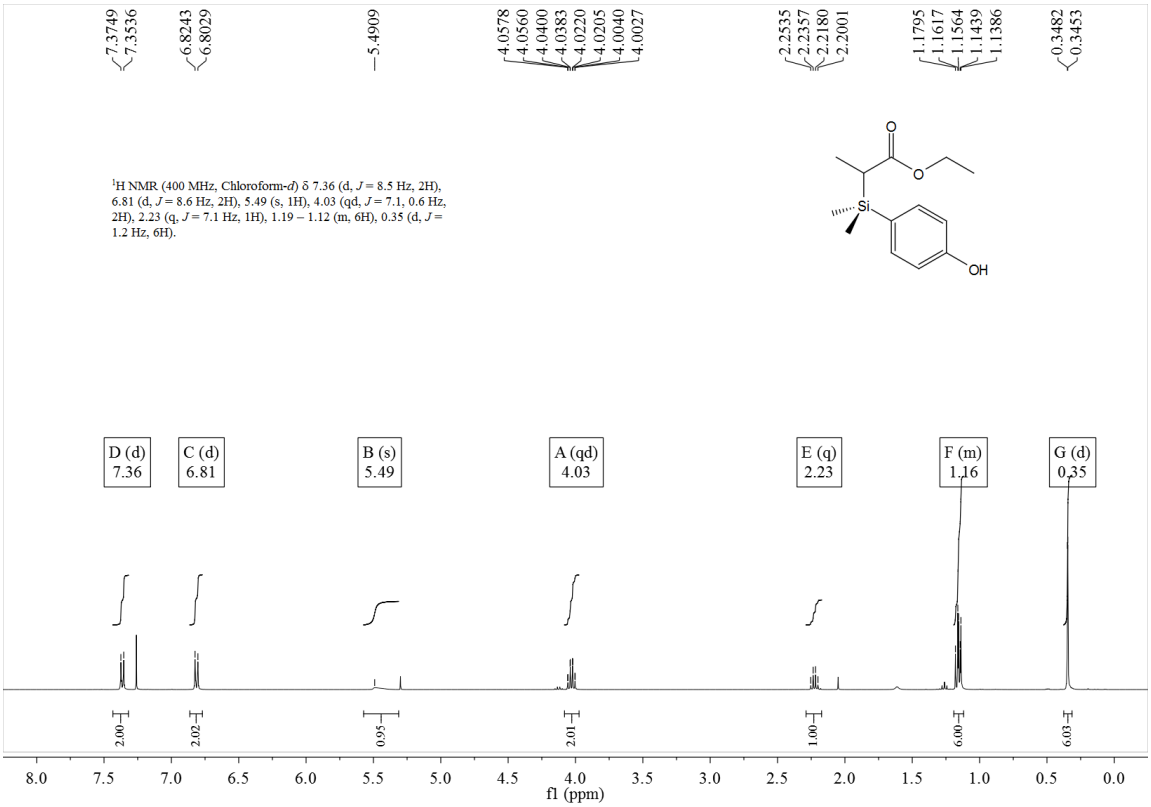

176.2555
157.2569
112.8255
65.7717
59.9077
28.7788
22.7892
20.8974
14.6116
11.2386
-4.9574
-5.9805
[13]C NMR (101 MHz, CDCl3) δ 176.26, 157.26, 112.83, 65.77, 59.91, 28.78, 22.79, 20.90, 14.61, 11.24, -4.96, -5.98.
O
O
Si
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

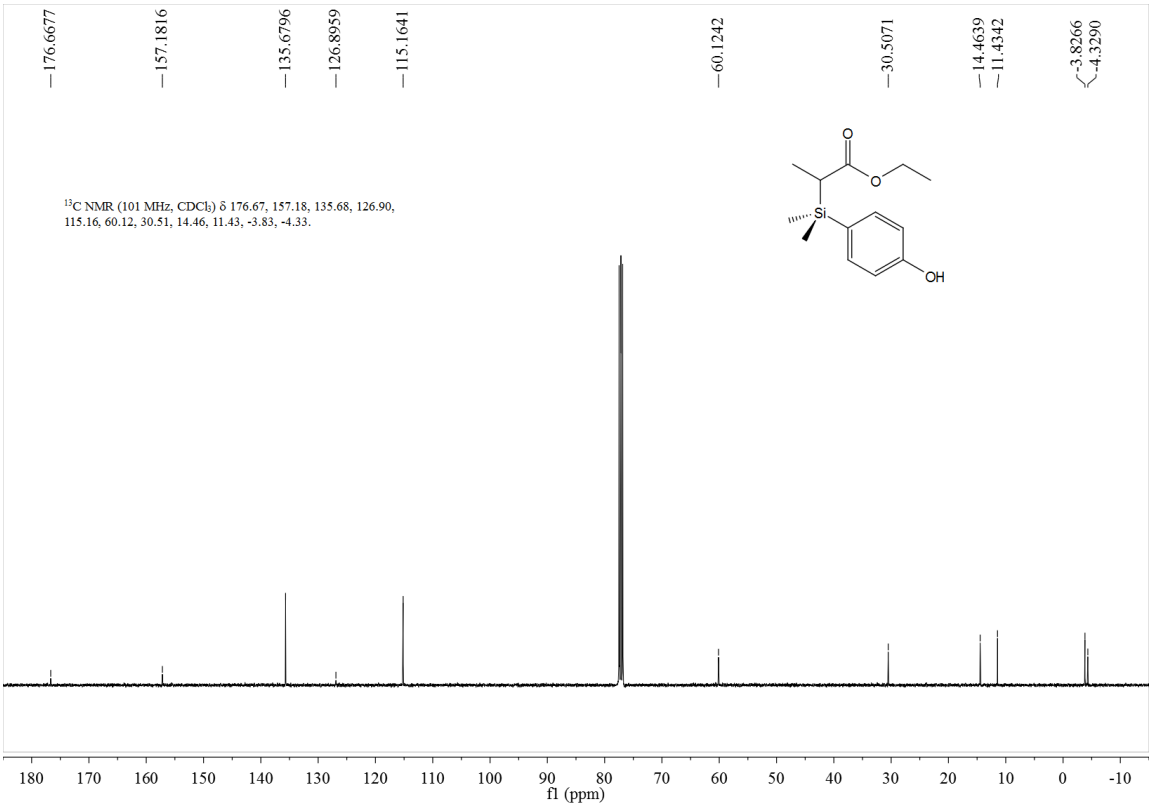

7.4792
7.4589
7.4093
7.3893
6.7469
6.7197
6.7028
6.6756
5.8130
5.8108
5.7690
5.7668
5.2889
5.2864
5.2617
5.2592
4.0532
4.0354
4.0175
3.9997
2.2743
2.2564
2.2386
2.2207
1.1626
1.1543
1.1448
1.1365
1.1269
0.3653
[1]H NMR (400 MHz, Chloroform-d) δ 7.47 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 5.79 (dd, J = 17.6, 0.9 Hz, 1H), 5.27 (dd, J = 10.9, 1.0 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 2.25 (q, J = 7.1 Hz, 1H), 1.16 – 1.13 (m, 6H), 0.37 (s, 6H).
O
O
Si
D (d) 7.47
C (d) 7.40
A (dd) 6.71
B (dd) 5.79
E (dd) 5.27
F (q) 4.03
G (q) 2.25
H (m) 1.15
I (s) 0.37
2.02
2.06
1.00
1.00
1.02
2.07
1.02
6.02
6.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

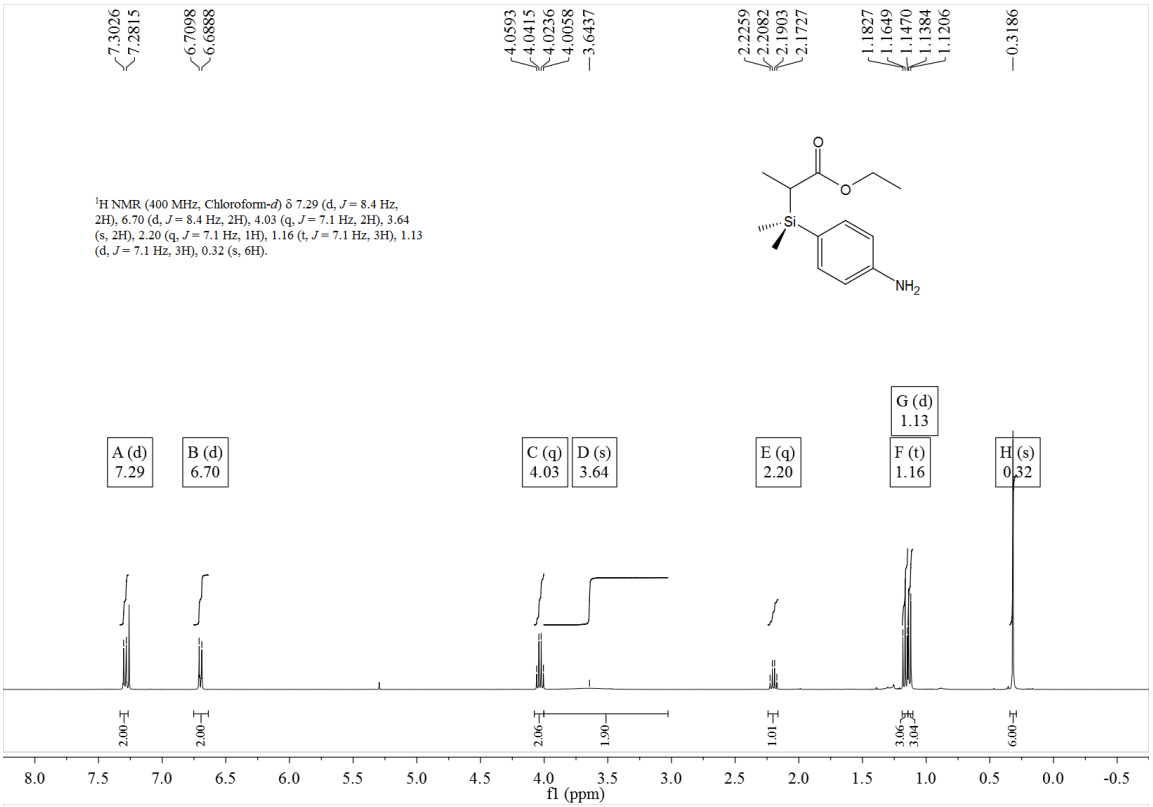

176.0921
138.6815
136.8467
136.0018
134.2627
125.6932
114.6480
59.9871
30.1360
14.4577
11.4248
-3.8741
-4.7453
[13]C NMR (101 MHz, CDCl3) δ 176.09, 138.68, 136.85, 136.00, 134.26, 125.69, 114.65, 59.99, 30.14, 14.46, 11.42, -3.87, -4.75.
O
O
Si
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.4887
7.4858
7.4825
7.4748
7.4674
7.4652
7.4582
7.4501
7.4469
7.4440
4.0379
4.0361
4.0202
4.0184
4.0022
4.0006
3.9838
3.9826
3.1086
2.2691
2.2512
2.2333
2.2155
1.1483
1.1305
1.1126
0.3665
Si
O
O
[1]H NMR (400 MHz, Chloroform-d) δ 7.50 – 7.44 (m, 4H), 4.01 (qd, J = 7.2, 0.6 Hz, 2H), 3.11 (s, 1H), 2.24 (q, J = 7.1 Hz, 1H), 1.17 – 1.10 (m, 6H), 0.37 (s, 6H).
B (m) 7.47
D (qd) 4.01
C (s) 3.11
A (q) 2.24
E (m) 1.13
F (s) 0.37
4.00
2.04
0.95
1.00
6.06
6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

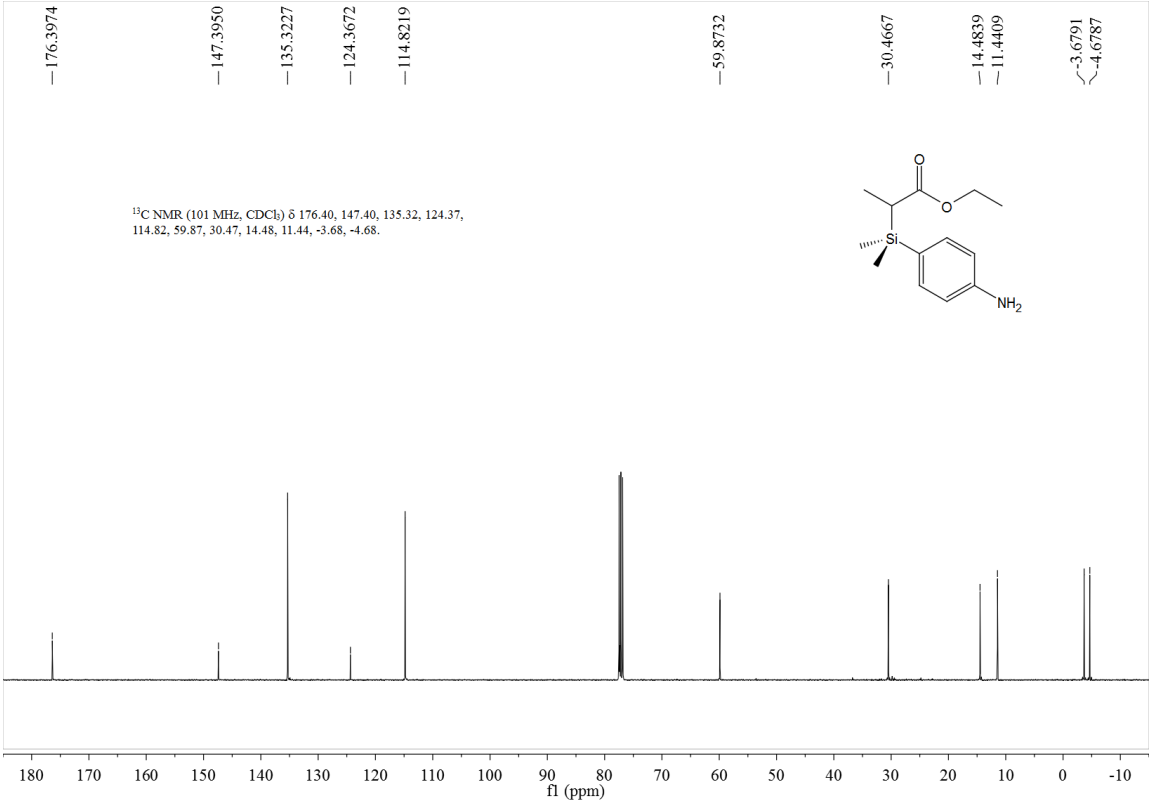

175.8860
137.6863
133.8664
131.3649
123.1967
83.7034
78.0756
60.0431
29.9761
14.4368
11.3815
-4.0958
-4.7473
Si
O
O
[13]C NMR (101 MHz, CDCl3) δ 175.89, 137.69, 133.87, 131.36, 123.20, 83.70, 78.08, 60.04, 29.98, 14.44, 11.38, -4.10, -4.75.
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.3749
7.3536
6.8243
6.8029
5.4909
4.0578
4.0560
4.0400
4.0383
4.0220
4.0205
4.0040
4.0027
2.2535
2.2357
2.2180
2.2001
1.1795
1.1617
1.1564
1.1439
1.1386
0.3482
0.3453
[1]H NMR (400 MHz, Chloroform-d) δ 7.36 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.49 (s, 1H), 4.03 (qd, J = 7.1, 0.6 Hz, 2H), 2.23 (q, J = 7.1 Hz, 1H), 1.19 – 1.12 (m, 6H), 0.35 (d, J = 1.2 Hz, 6H).
O
O
Si
OH
D (d) 7.36
C (d) 6.81
B (s) 5.49
A (qd) 4.03
E (q) 2.23
F (m) 1.16
G (d) 0.35
2.00
2.02
0.95
2.01
1.00
6.00
6.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

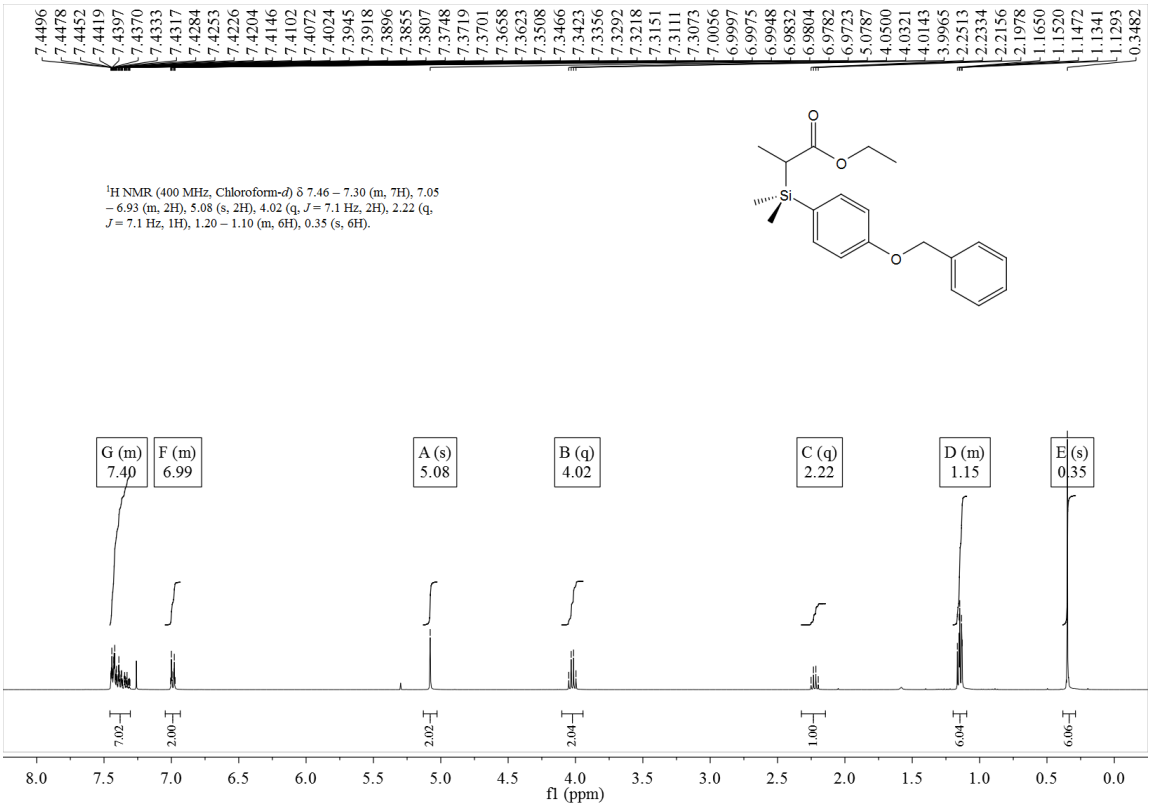

176.6677
157.1816
135.6796
126.8959
115.1641
60.1242
30.5071
14.4639
11.4342
-3.8266
-4.3290
[13]C NMR (101 MHz, CDCl3) δ 176.67, 157.18, 135.68, 126.90, 115.16, 60.12, 30.51, 14.46, 11.43, -3.83, -4.33.
O
O
Si
OH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

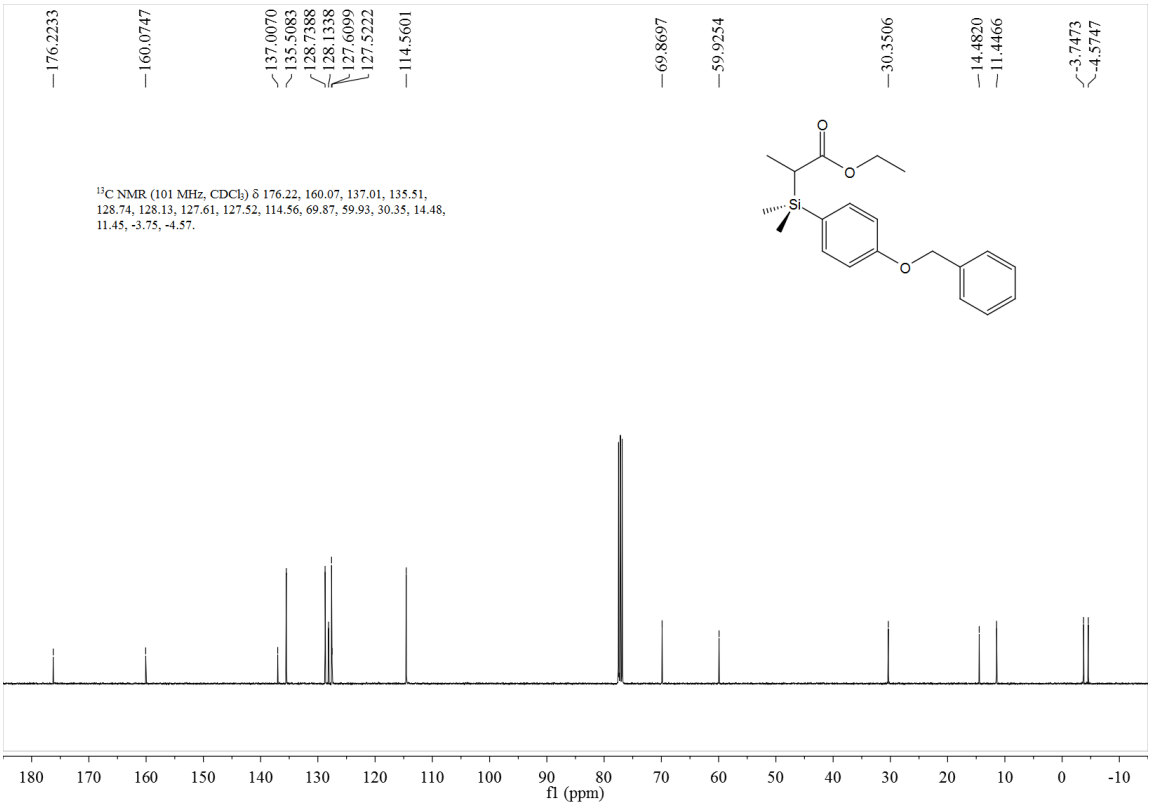


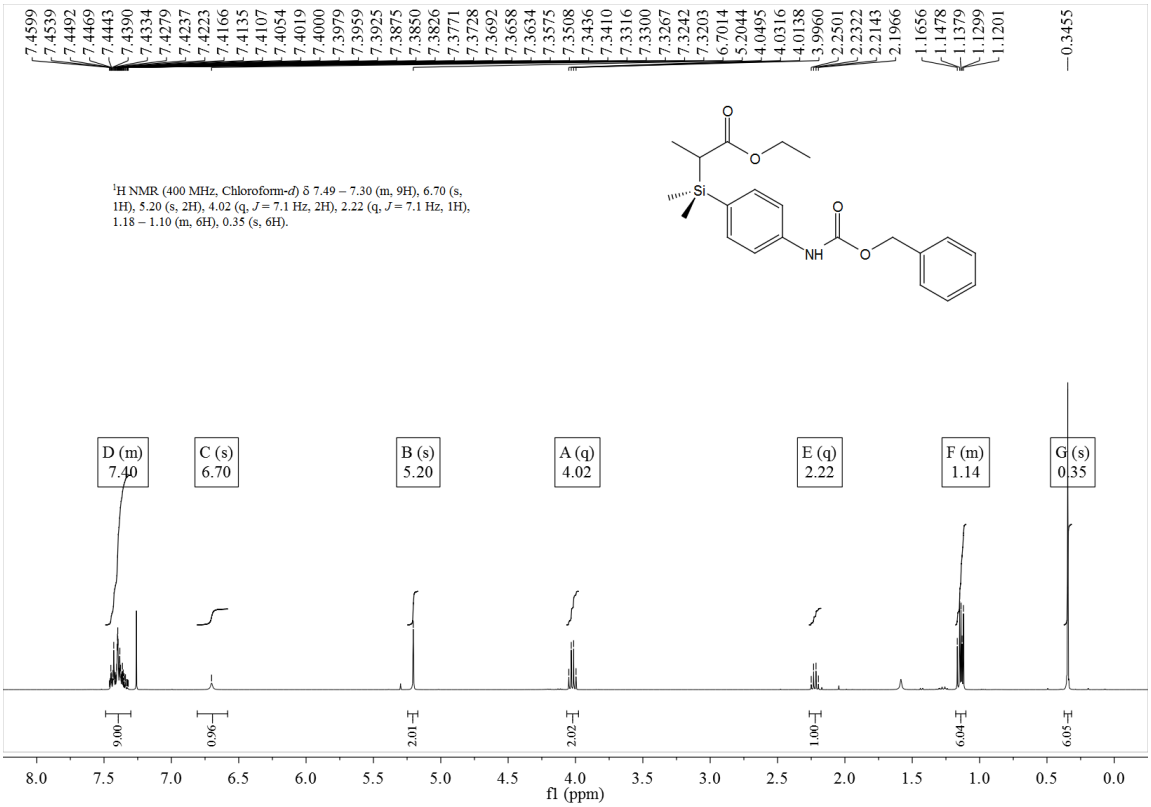
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.64 (s, 2H), 2.20 (q, *J* = 7.1 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.13 (d, *J* = 7.1 Hz, 3H), 0.32 (s, 6H).

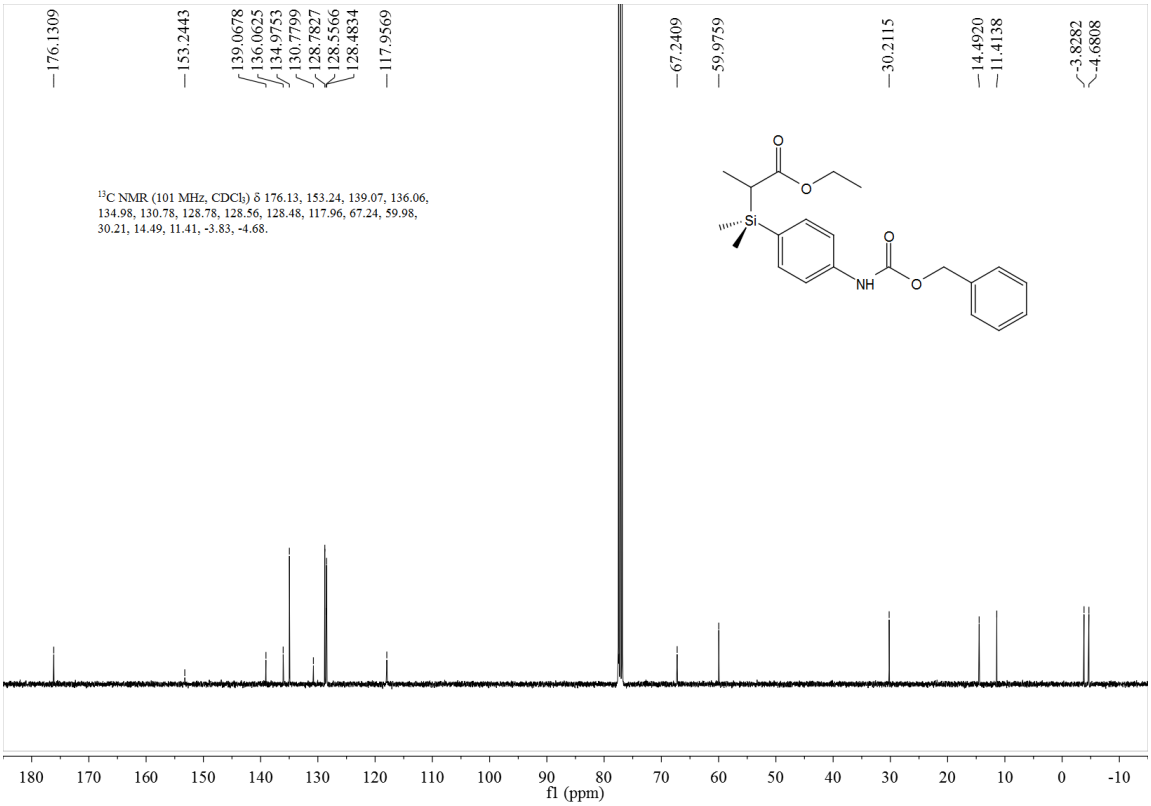


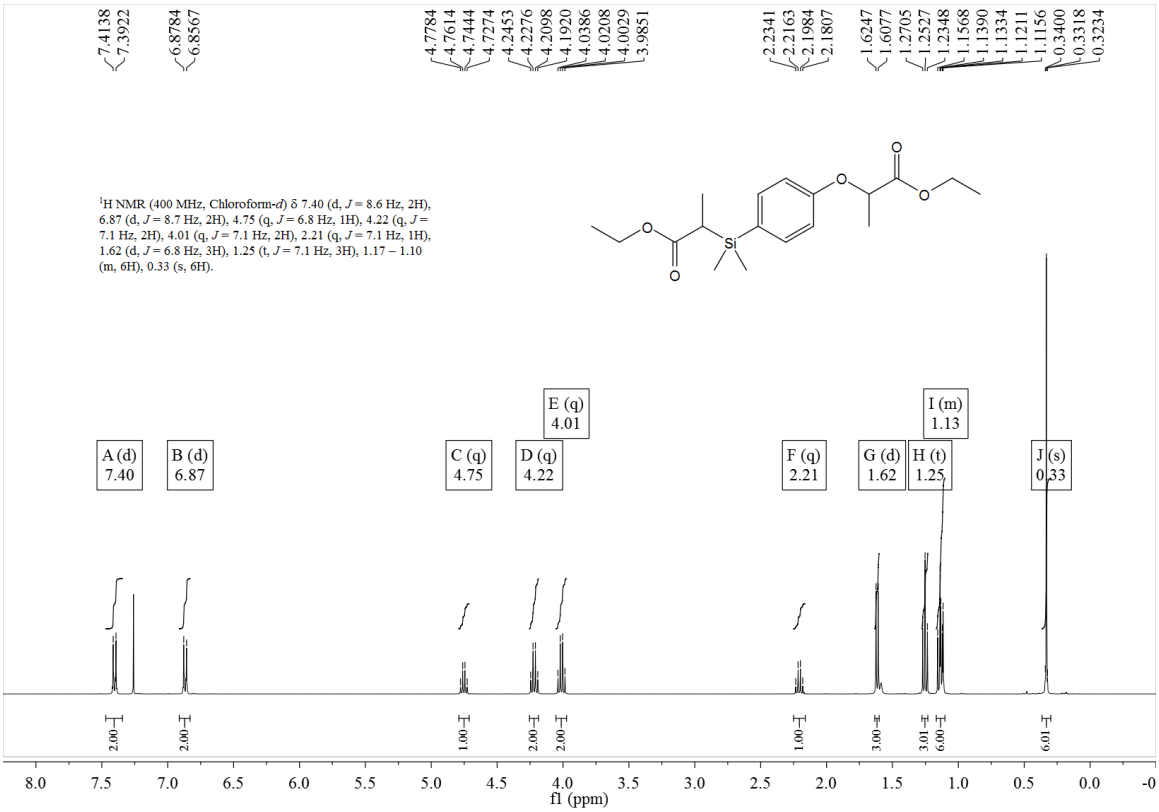
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.40, 147.40, 135.32, 124.37, 114.82, 59.87, 30.47, 14.48, 11.44, -3.68, -4.68.

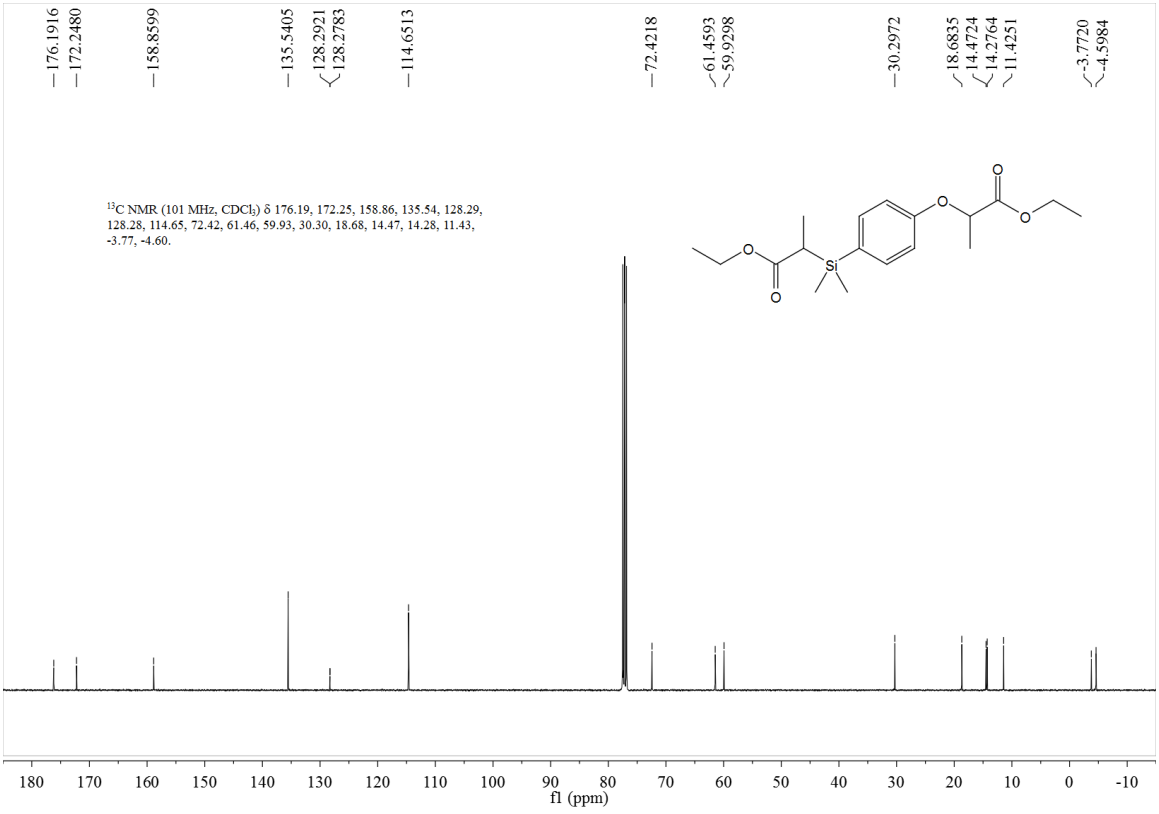

7.4496
7.4478
7.4452
7.4419
7.4397
7.4370
7.4333
7.4317
7.4284
7.4253
7.4226
7.4204
7.4146
7.4102
7.4072
7.4024
7.3945
7.3918
7.3896
7.3855
7.3807
7.3748
7.3719
7.3701
7.3658
7.3623
7.3508
7.3466
7.3423
7.3356
7.3292
7.3218
7.3151
7.3111
7.3073
7.0056
6.9997
6.9975
6.9948
6.9832
6.9804
6.9782
6.9723
5.0787
4.0500
4.0321
4.0143
3.9965
2.2513
2.2334
2.2156
2.1978
1.1650
1.1520
1.1472
1.1341
1.1293
0.3482
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.30 (m, 7H), 7.05 – 6.93 (m, 2H), 5.08 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.22 (q, *J* = 7.1 Hz, 1H), 1.20 – 1.10 (m, 6H), 0.35 (s, 6H).
Si
O
O
G (m) 7.40
F (m) 6.99
A (s) 5.08
B (q) 4.02
C (q) 2.22
D (m) 1.15
E (s) 0.35
7.02
2.00
2.02
2.04
1.00
6.04
6.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

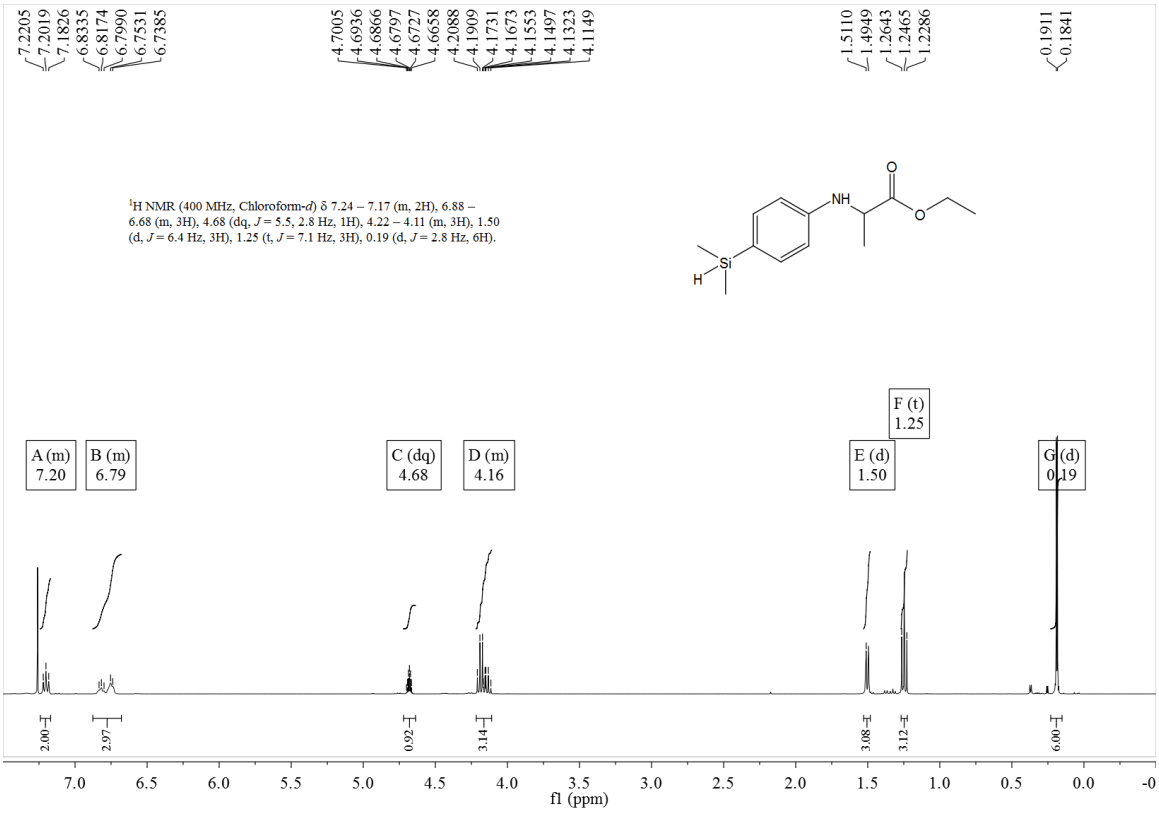

176.2233
160.0747
137.0070
135.5083
128.7388
128.1338
127.6099
127.5222
114.5601
69.8697
59.9254
30.3506
14.4820
11.4466
-3.7473
-4.5747
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.22, 160.07, 137.01, 135.51, 128.74, 128.13, 127.61, 127.52, 114.56, 69.87, 59.93, 30.35, 14.48, 11.45, -3.75, -4.57.
Si
O
O
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

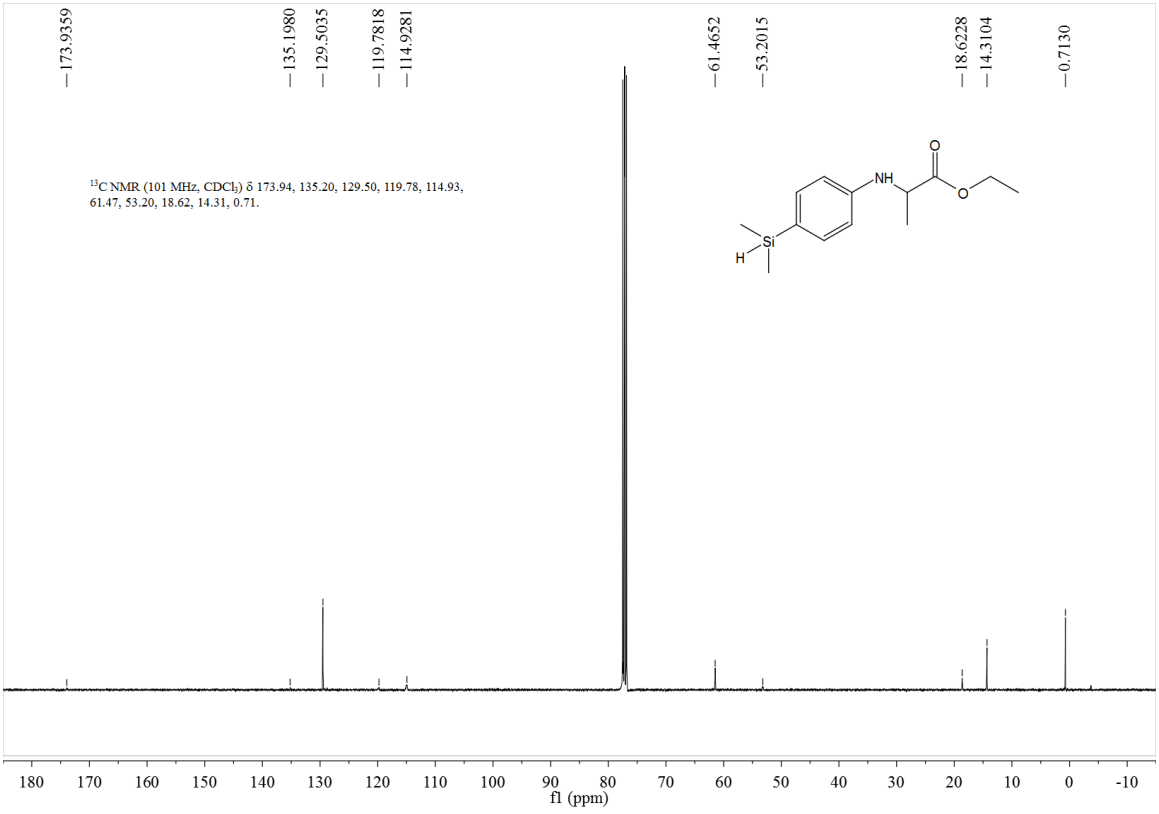

7.4599
7.4539
7.4492
7.4469
7.4443
7.4390
7.4334
7.4279
7.4237
7.4223
7.4166
7.4135
7.4107
7.4054
7.4019
7.4000
7.3979
7.3959
7.3925
7.3875
7.3850
7.3826
7.3771
7.3728
7.3692
7.3658
7.3634
7.3575
7.3508
7.3436
7.3410
7.3316
7.3300
7.3267
7.3242
7.3203
6.7014
5.2044
4.0495
4.0316
4.0138
3.9960
2.2501
2.2322
2.2143
2.1966
1.1656
1.1478
1.1379
1.1299
1.1201
0.3455
1H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.30 (m, 9H), 6.70 (s, 1H), 5.20 (s, 2H), 4.02 (q, J = 7.1 Hz, 2H), 2.22 (q, J = 7.1 Hz, 1H), 1.18 – 1.10 (m, 6H), 0.35 (s, 6H).
O
O
Si
O
NH
O
D (m) 7.40
C (s) 6.70
B (s) 5.20
A (q) 4.02
E (q) 2.22
F (m) 1.14
G (s) 0.35
9.00
0.96
2.01
2.02
1.00
6.04
6.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

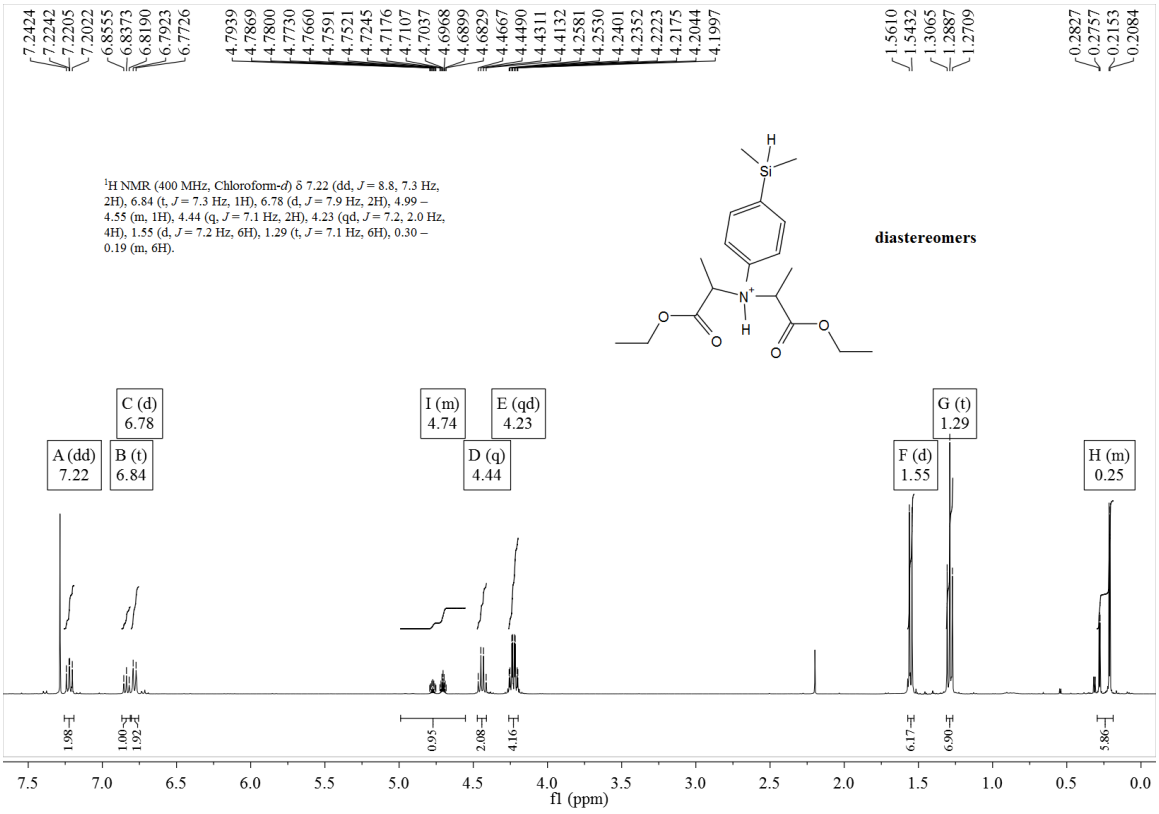

176.1309
153.2443
139.0678
136.0625
134.9753
130.7799
128.7827
128.5566
128.4834
117.9569
67.2409
59.9759
30.2115
14.4920
11.4138
-3.8282
-4.6808
13C NMR (101 MHz, CDCl3) δ 176.13, 153.24, 139.07, 136.06, 134.98, 130.78, 128.78, 128.56, 128.48, 117.96, 67.24, 59.98, 30.21, 14.49, 11.41, -3.83, -4.68.
O
O
Si
O
NH
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

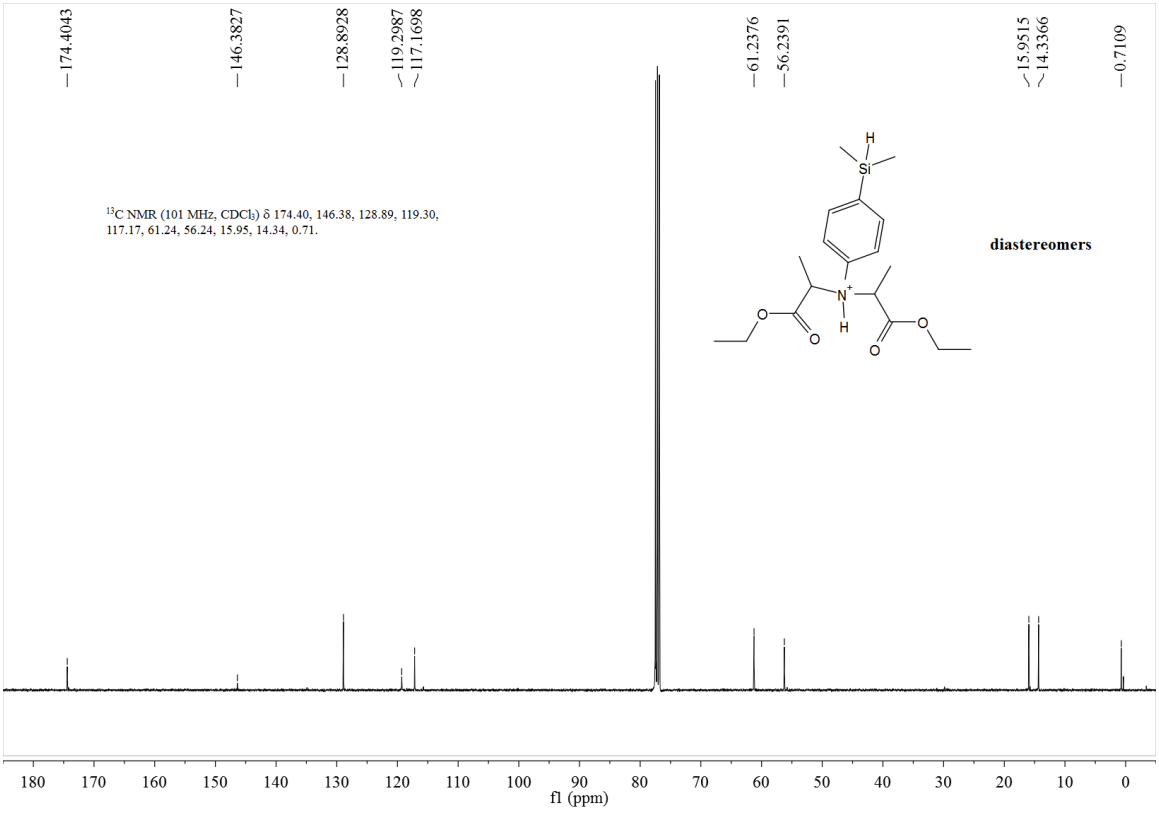

7.4138
7.3922
6.8784
6.8567
4.7784
4.7614
4.7444
4.7274
4.2453
4.2276
4.2098
4.1920
4.0386
4.0208
4.0029
3.9851
2.2341
2.2163
2.1984
2.1807
1.6247
1.6077
1.2705
1.2527
1.2348
1.1568
1.1390
1.1334
1.1211
1.1156
0.3400
0.3318
0.3234
¹H NMR (400 MHz, Chloroform-d) δ 7.40 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.75 (q, J = 6.8 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 4.01 (q, J = 7.1 Hz, 2H), 2.21 (q, J = 7.1 Hz, 1H), 1.62 (d, J = 6.8 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 1.17 – 1.10 (m, 6H), 0.33 (s, 6H).
A (d) 7.40
B (d) 6.87
C (q) 4.75
D (q) 4.22
E (q) 4.01
F (q) 2.21
G (d) 1.62
H (t) 1.25
I (m) 1.13
J (s) 0.33
2.00
2.00
1.00
2.00
2.00
1.00
3.00
3.01
6.00
6.01
f1 (ppm)

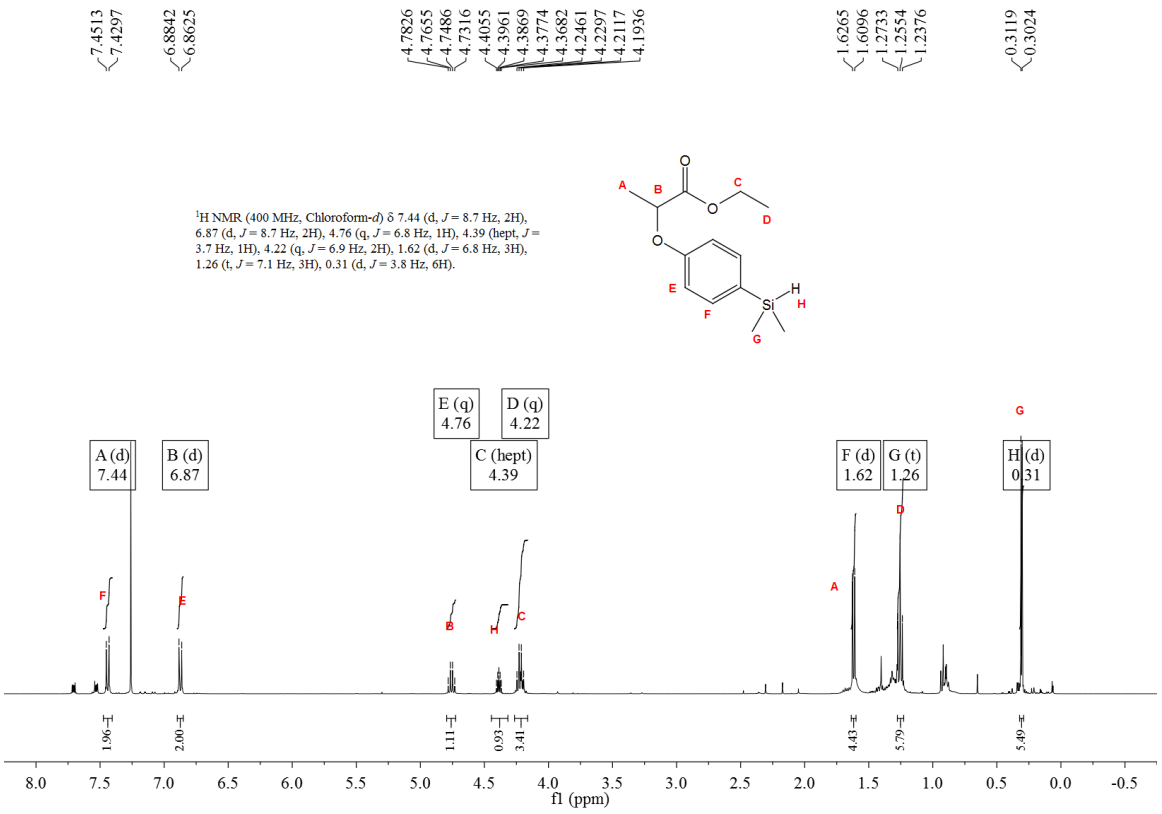

176.1916
172.2480
158.8599
135.5405
128.2921
128.2783
114.6513
72.4218
61.4593
59.9298
30.2972
18.6835
14.4724
14.2764
11.4251
-3.7720
-4.5984
¹³C NMR (101 MHz, CDCl₃) δ 176.19, 172.25, 158.86, 135.54, 128.29, 128.28, 114.65, 72.42, 61.46, 59.93, 30.30, 18.68, 14.47, 14.28, 11.43, -3.77, -4.60.
f1 (ppm)


7.2205
7.2019
7.1826
6.8335
6.8174
6.7990
6.7531
6.7385
4.7005
4.6936
4.6866
4.6797
4.6727
4.6658
4.2088
4.1909
4.1731
4.1673
4.1553
4.1497
4.1323
4.1149
1.5110
1.4949
1.2643
1.2465
1.2286
0.1911
0.1841
1H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.17 (m, 2H), 6.88 – 6.68 (m, 3H), 4.68 (dq, J = 5.5, 2.8 Hz, 1H), 4.22 – 4.11 (m, 3H), 1.50 (d, J = 6.4 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 0.19 (d, J = 2.8 Hz, 6H).
NH
O
O
Si
H
A (m) 7.20
B (m) 6.79
C (dq) 4.68
D (m) 4.16
E (d) 1.50
F (t) 1.25
G (d) 0.19
2.00
2.97
0.92
3.14
3.08
3.12
6.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

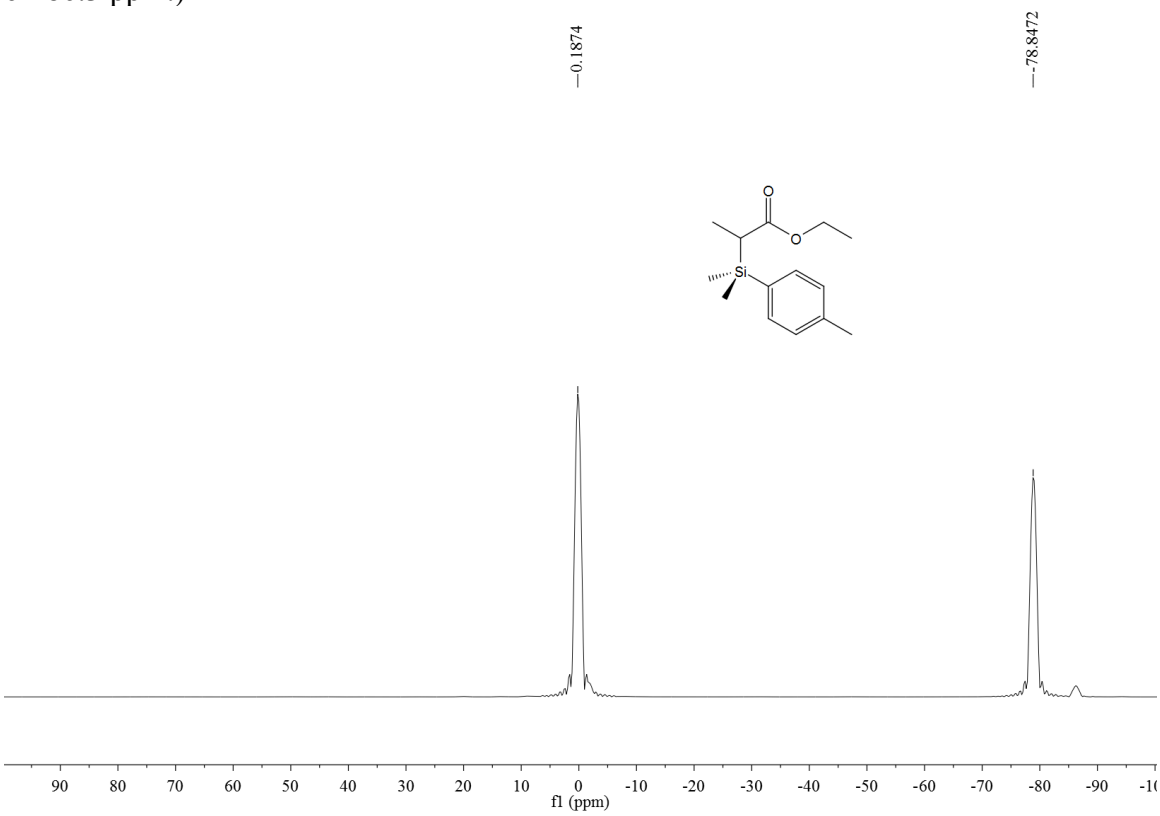

173.9359
135.1980
129.5035
119.7818
114.9281
61.4652
53.2015
18.6228
14.3104
0.7130
13C NMR (101 MHz, CDCl3) δ 173.94, 135.20, 129.50, 119.78, 114.93, 61.47, 53.20, 18.62, 14.31, 0.71.
NH
O
O
Si
H
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

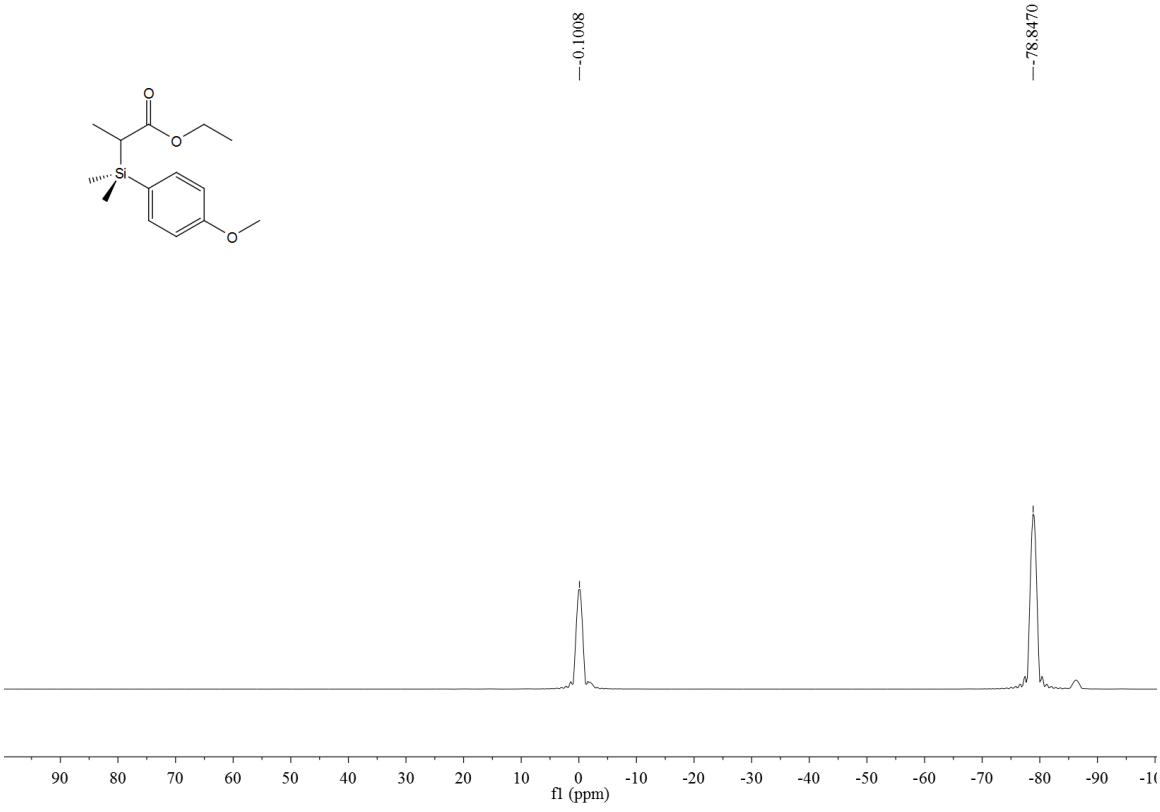

7.2424
7.2242
7.2205
7.2022
6.8555
6.8373
6.8190
6.7923
6.7726
4.7939
4.7869
4.7800
4.7730
4.7660
4.7591
4.7521
4.7245
4.7176
4.7107
4.7037
4.6968
4.6899
4.6829
4.4667
4.4490
4.4311
4.4132
4.2581
4.2530
4.2401
4.2352
4.2223
4.2175
4.2044
4.1997
1.5610
1.5432
1.3065
1.2887
1.2709
0.2827
0.2757
0.2153
0.2084
1H NMR (400 MHz, Chloroform-d) δ 7.22 (dd, J = 8.8, 7.3 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 7.9 Hz, 2H), 4.99 – 4.55 (m, 1H), 4.44 (q, J = 7.1 Hz, 2H), 4.23 (qd, J = 7.2, 2.0 Hz, 4H), 1.55 (d, J = 7.2 Hz, 6H), 1.29 (t, J = 7.1 Hz, 6H), 0.30 – 0.19 (m, 6H).
diastereomers
A (dd) 7.22
B (t) 6.84
C (d) 6.78
D (q) 4.44
E (qd) 4.23
F (d) 1.55
G (t) 1.29
H (m) 0.25
I (m) 4.74
1.98
1.00
1.92
0.95
2.08
4.16
6.17
6.90
5.86
f1 (ppm)

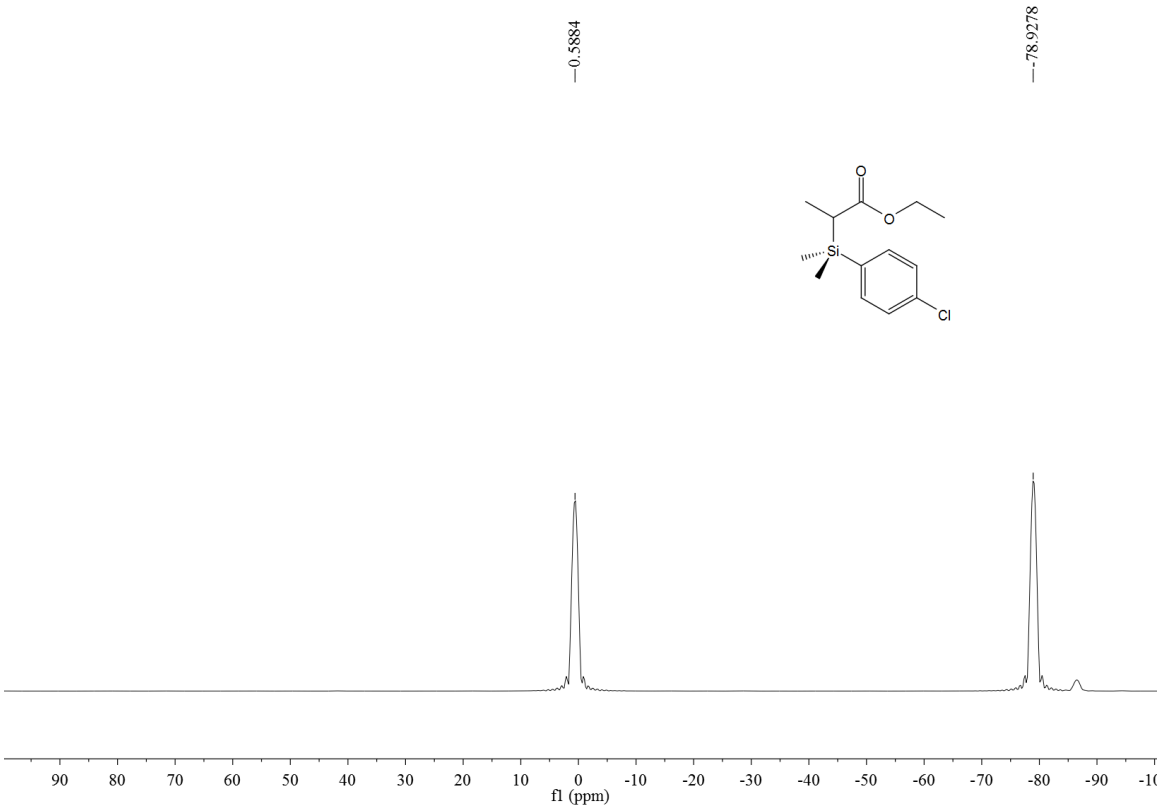

174.4043
146.3827
128.8928
119.2987
117.1698
61.2376
56.2391
15.9515
14.3366
0.7109
13C NMR (101 MHz, CDCl3) δ 174.40, 146.38, 128.89, 119.30, 117.17, 61.24, 56.24, 15.95, 14.34, 0.71.
diastereomers
f1 (ppm)

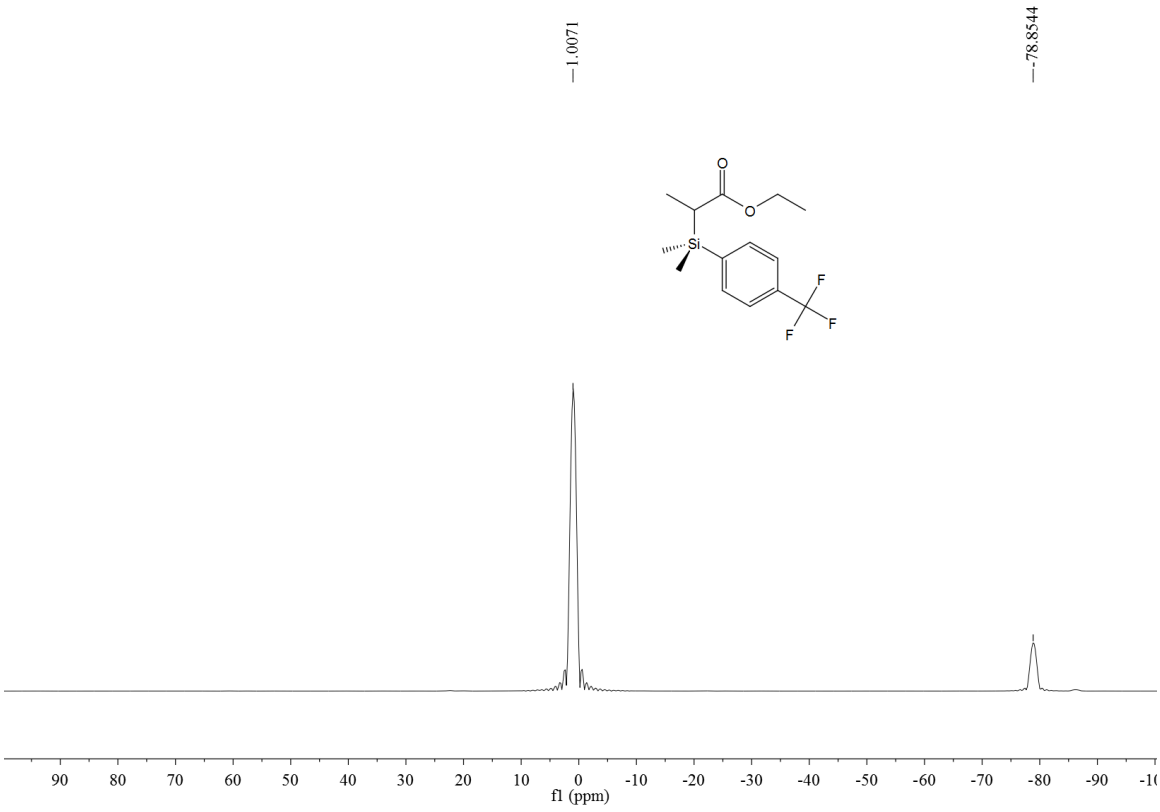

7.4513
7.4297
6.8842
6.8625
4.7826
4.7655
4.7486
4.7316
4.4055
4.3961
4.3869
4.3774
4.3682
4.2461
4.2297
4.2117
4.1936
1.6265
1.6096
1.2733
1.2554
1.2376
0.3119
0.3024
A
B
C
D
E
F
G
H
Si
O
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.76 (q, *J* = 6.8 Hz, 1H), 4.39 (hept, *J* = 3.7 Hz, 1H), 4.22 (q, *J* = 6.9 Hz, 2H), 1.62 (d, *J* = 6.8 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 0.31 (d, *J* = 3.8 Hz, 6H).
A (d) 7.44
B (d) 6.87
E (q) 4.76
D (q) 4.22
C (hept) 4.39
F (d) 1.62
G (t) 1.26
H (d) 0.31
1.96
2.00
1.11
0.93
3.41
4.43
5.79
5.49
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

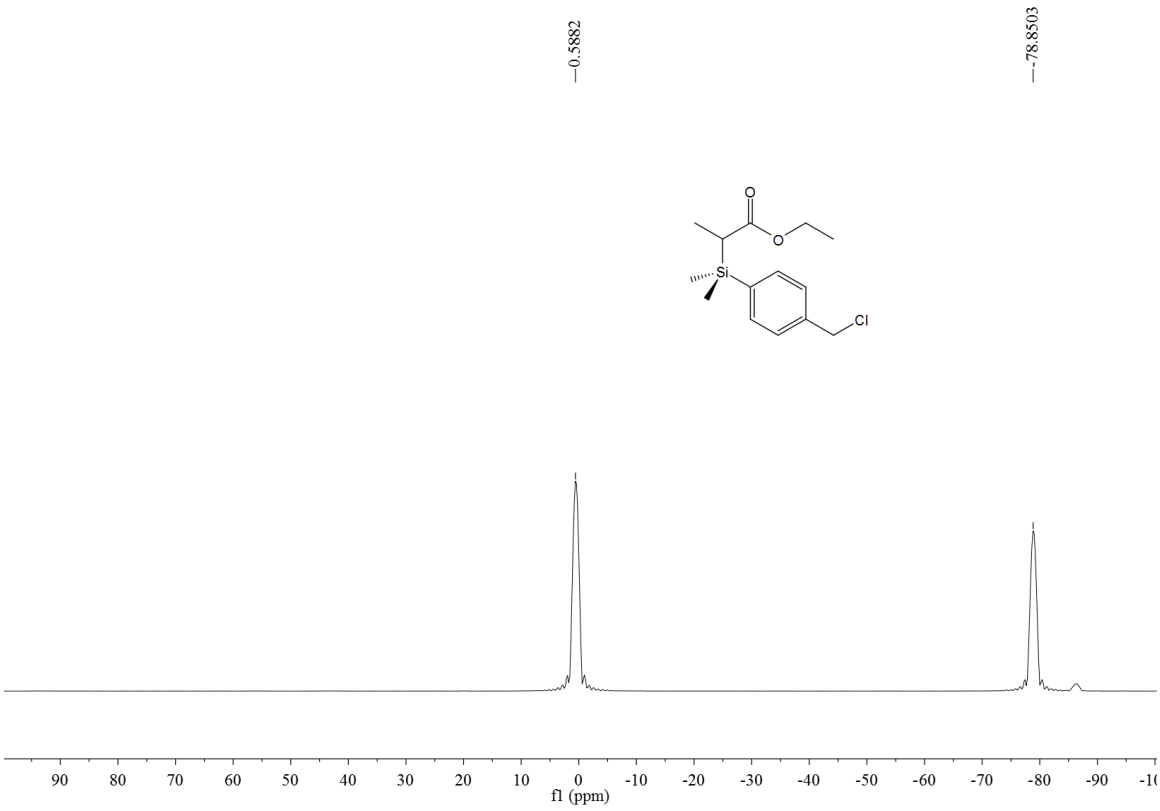
^{29}Si NMR (79 Hz, $CDCl_3$; referenced at δ −78.9 ppm using tetramethoxysilane as internal standard. This internal standard contained a small amount of impurity, which appeared at δ −86.3 ppm.)

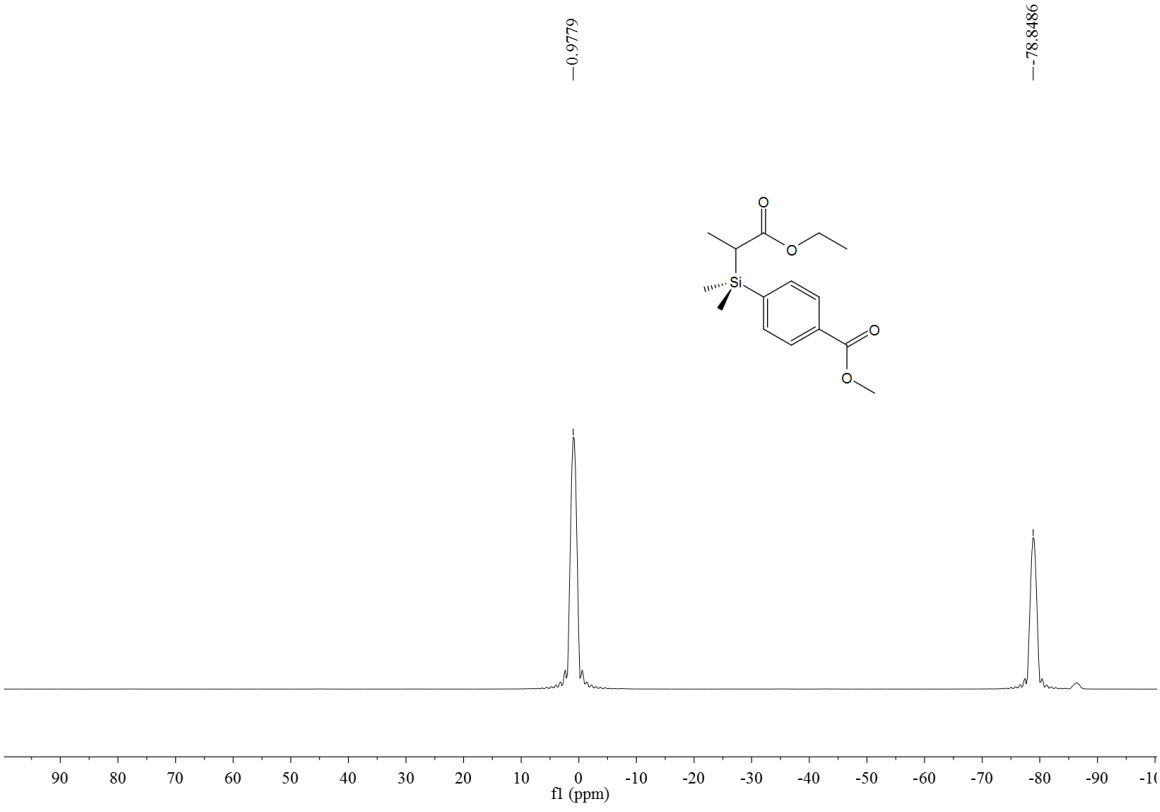


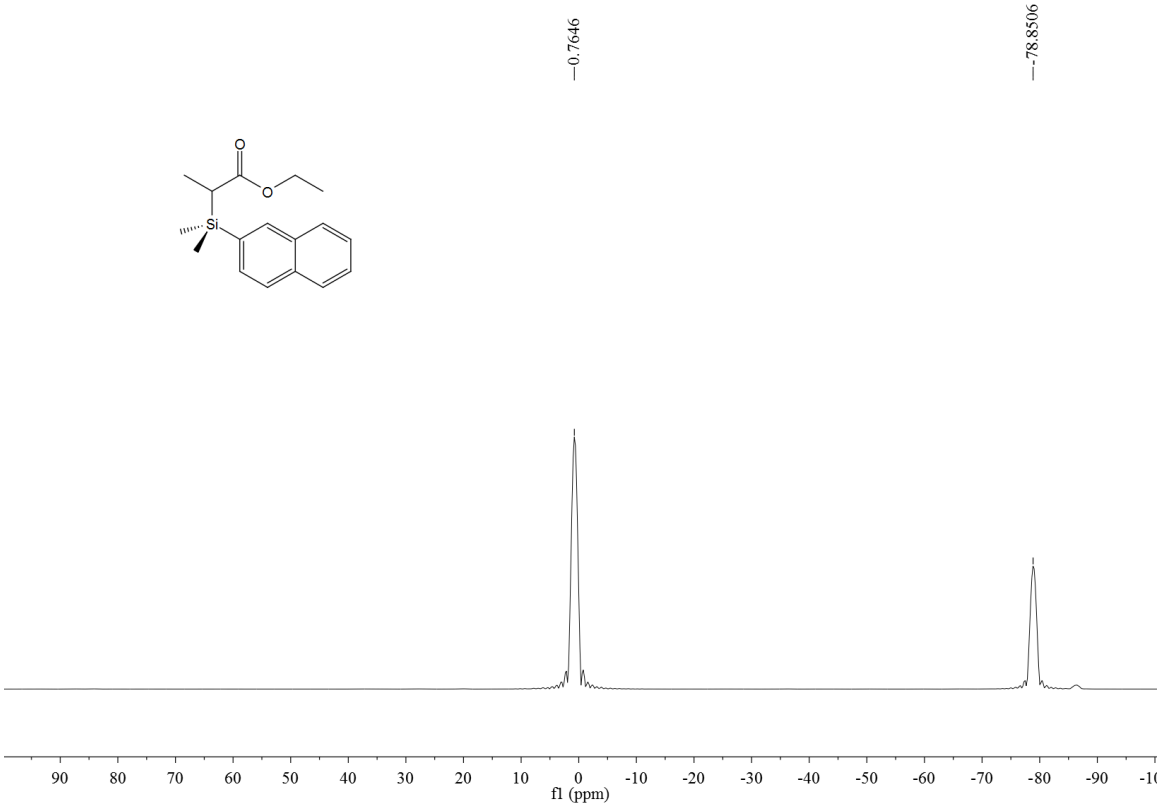


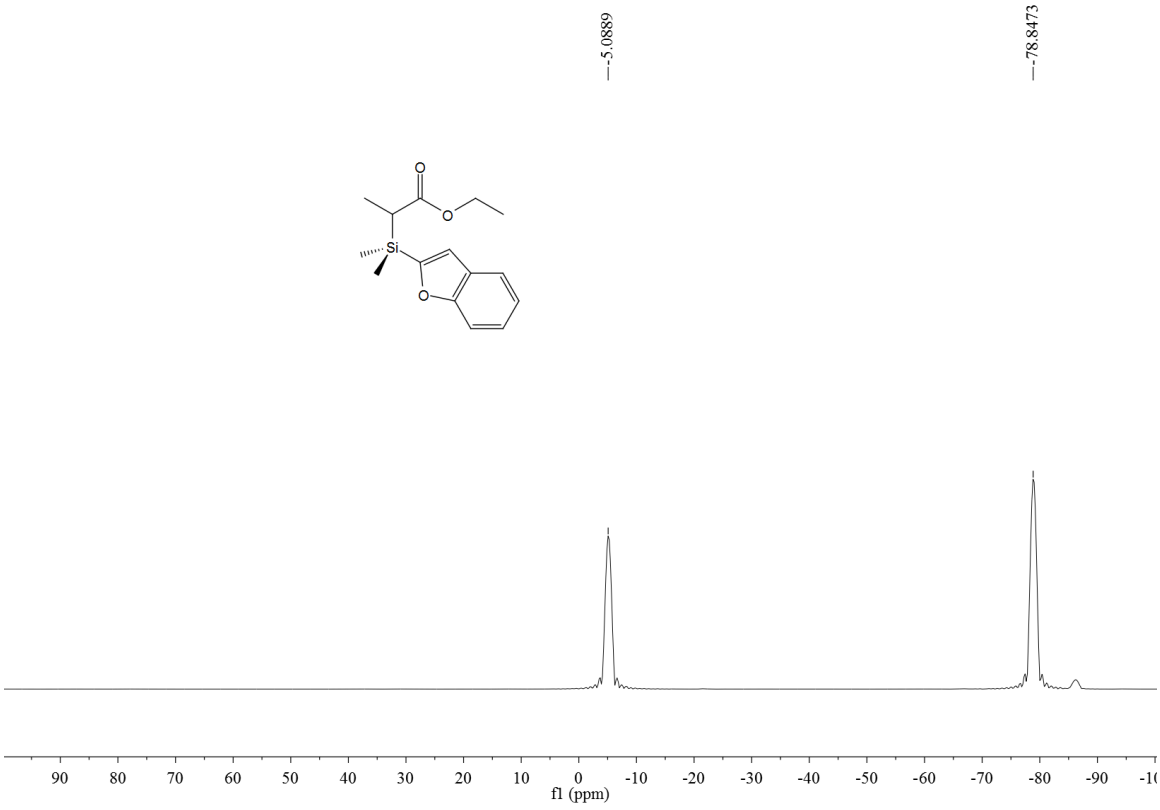

0.5884
-78.9278
O
O
Si
Cl
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)

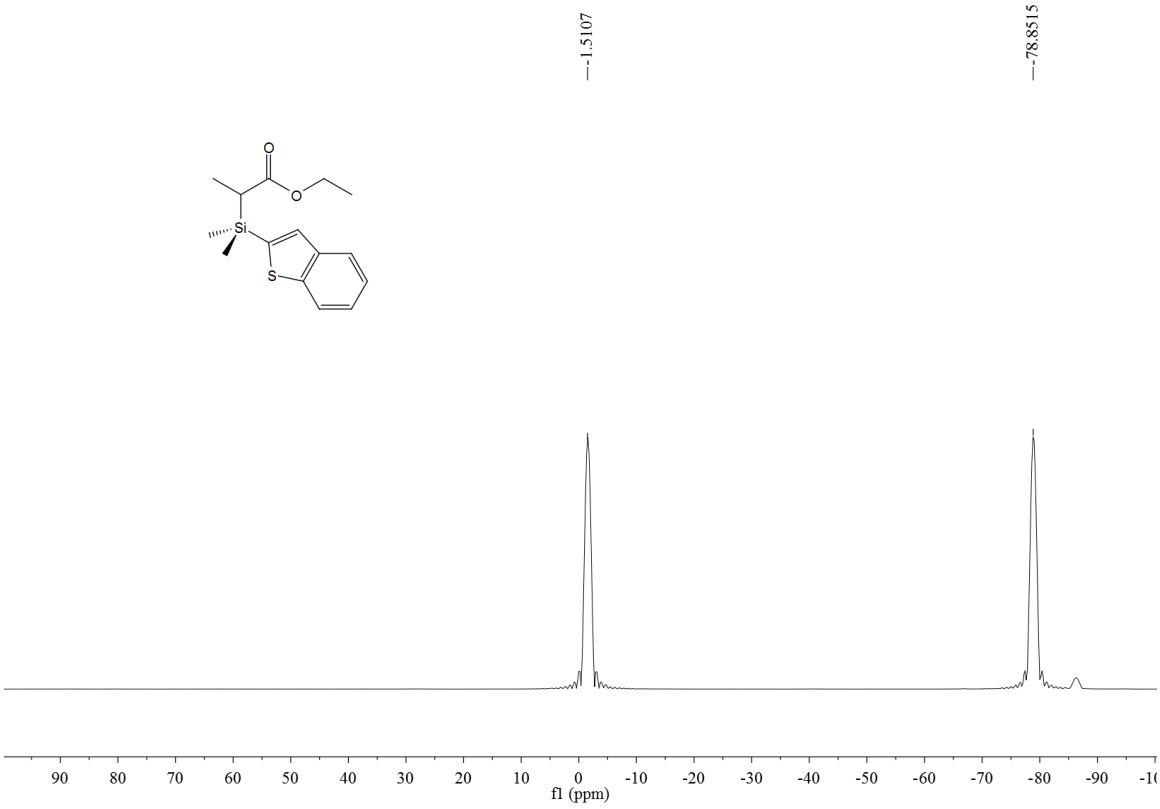

1.0071
-78.8544
O
O
Si
F
F
F
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)

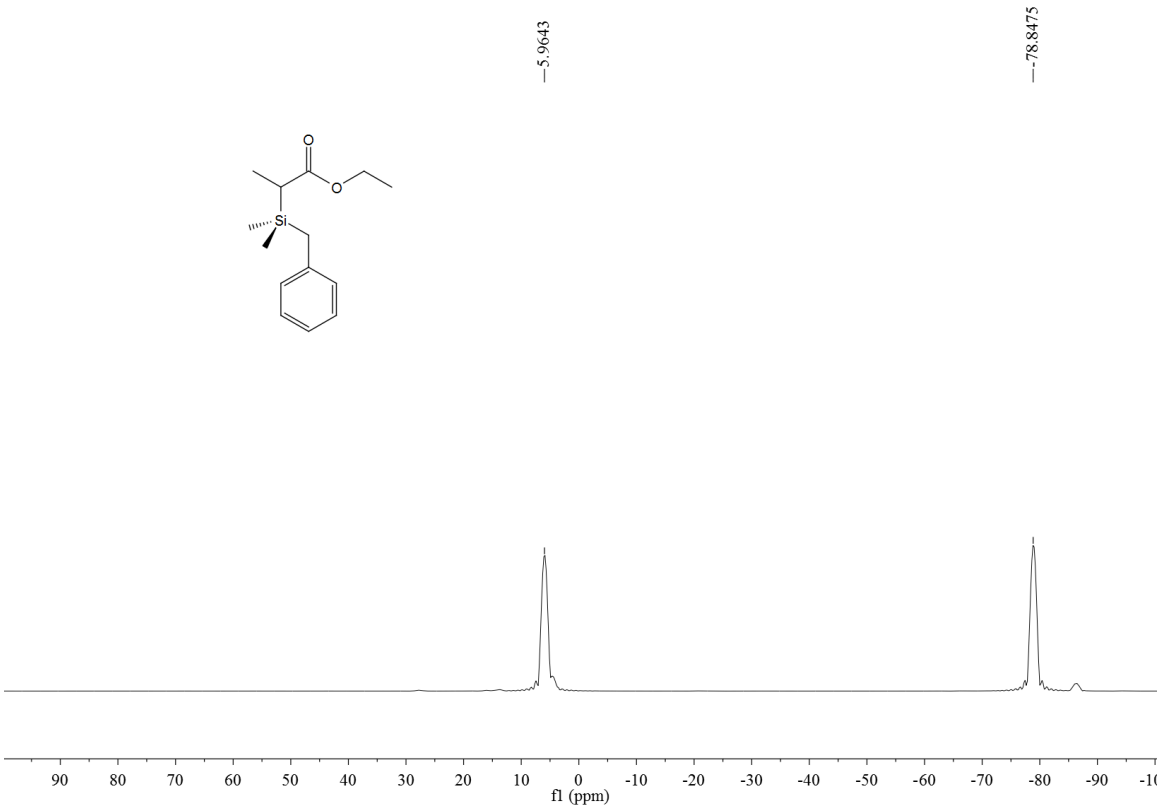

0.5882
-78.8503
O
O
Si
Cl
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)

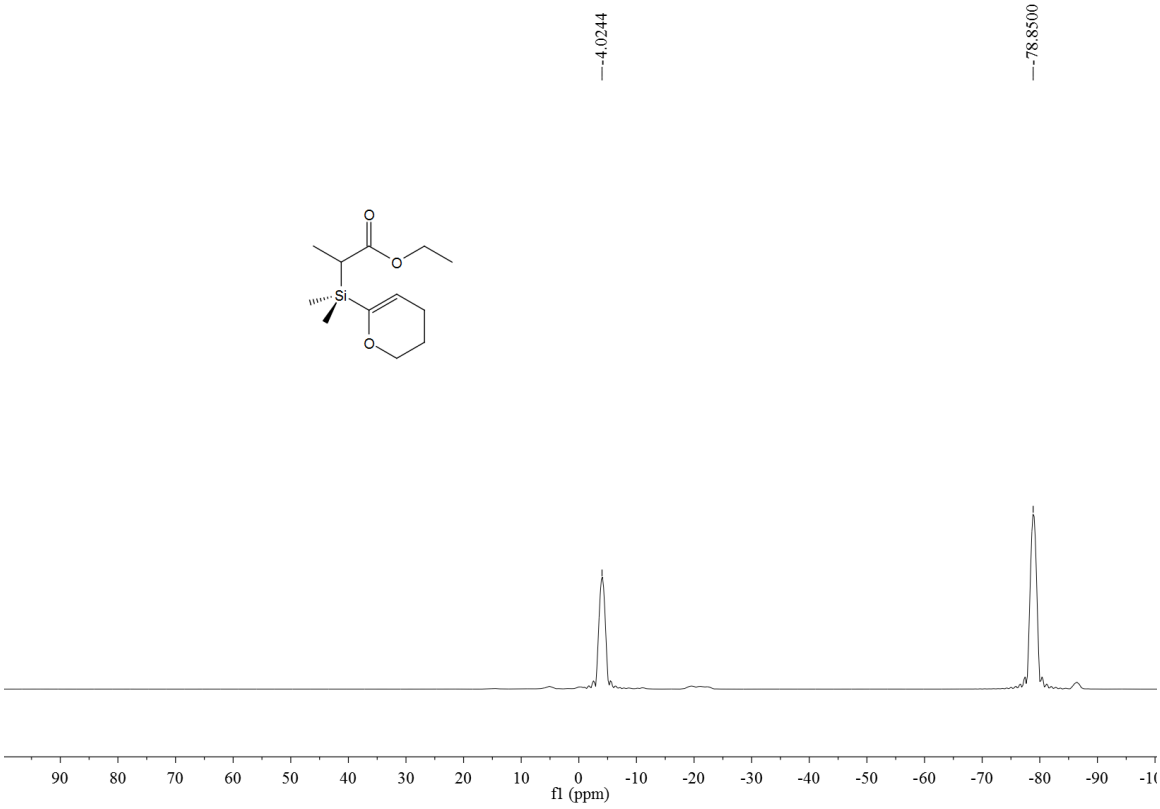

0.9779
-78.8486
O
O
Si
O
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)

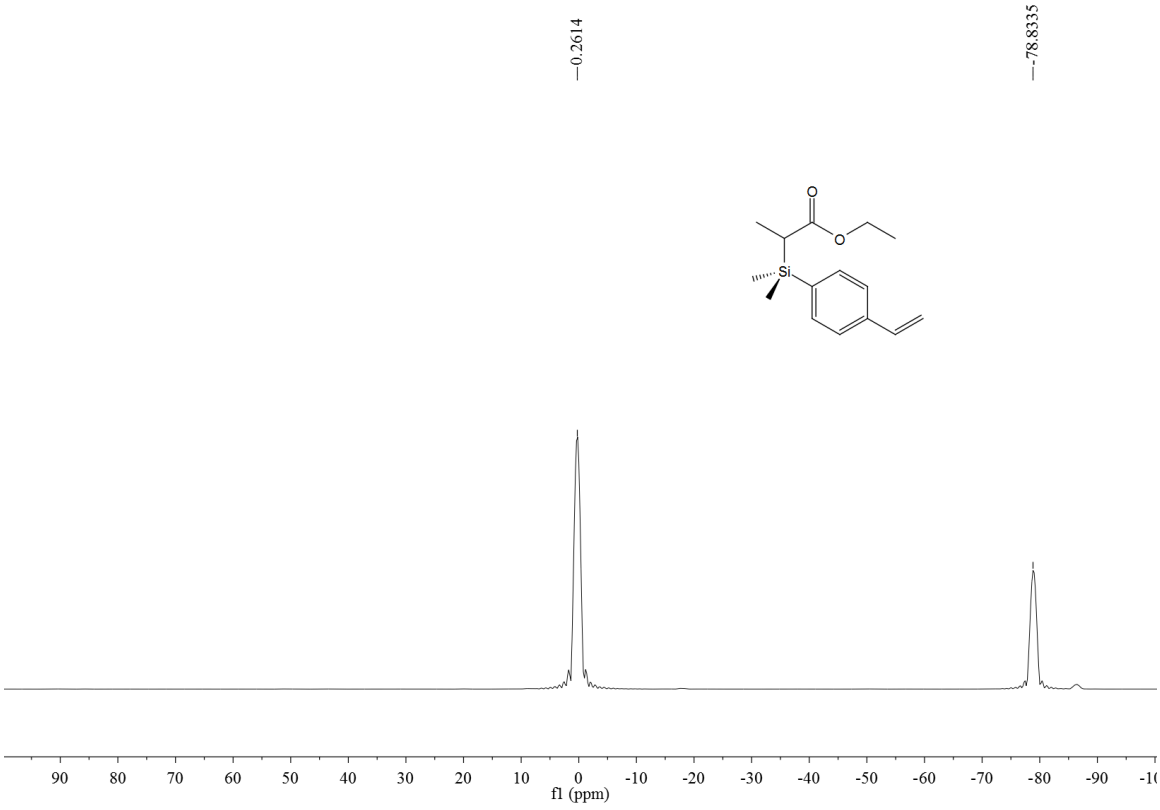

0.7646
-78.8506
O
O
Si
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

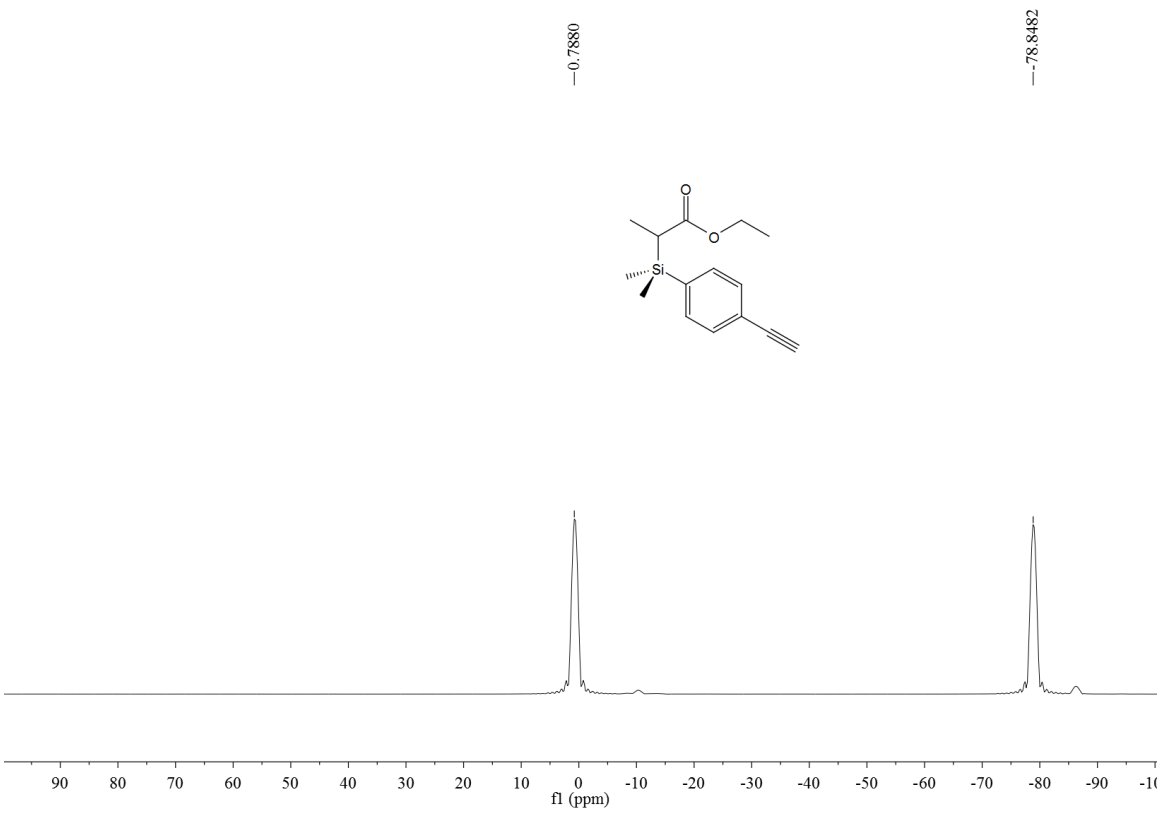

-5.0889
-78.8473
O
O
Si
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


-1.5107
-78.8515
O
O
Si
S
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)


-5.9643
-78.8475
O
O
Si
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)


-4.0244
-78.8500
O
O
Si
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)


-0.2614
-78.8335
O
O
Si
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)


0.7880
-78.8482
O
O
Si
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)