Supporting Information

Rhodium Catalysts Supported on Phosphorus-Rich Covalent Organic Polymers for Sustainable Hydrosilylation of Alkynes

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1. General Information

Reagents and Materials.

Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. The solvents were purchased from Aladdin in glass bottle and used directly. Alkynes **1a-1t,** and hydrosilanes **2a-2d** are commercially available and no further purification was needed.

Characterisation Methods.

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 400 MHz (100 MHz, 376 MHz and for ^{13}C and ^{19}F, respectively) spectrometer. All ^{1}H NMR spectra were reported in parts per million (ppm) relative to the signals for $CDCl_3$ (7.26 ppm) and DMSO-d_6 (2.50 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CDCl_3$ (77.16 ppm) and DMSO-d_6 (39.52 ppm). For the isolated compounds, ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0 ppm. ^{13}C solid NMR spectrum for **COP-PPh$_3$-RhCl** were recorded on an Agilent DD2-500 MHz NMR spectrometer. Field-Emission Scanning Electron Microscopy (FE-SEM) images were conducted on a Zeiss Sigma300 field-emission scanning electron microscopy. Fourier transform infrared (FTIR) spectroscopy was performed using a VERTEX70 spectrophotometer in the range of 4000 to 400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a ThermoFisher Scientific ESCALAB Xi+ spectrometer. The Rh loading of **COP-PPh$_3$-RhCl** before and after the reaction were detected by Inductively Coupled Plasma Mass Spectrometer (ICP-MS, NexION 350D). The thermogravimetric analysis (TGA) spectra were recorded on METTLER TOLEDO TGA/DSC3+ thermogravimeter from 30 °C to 800 °C at a rate of 10 ℃/min under an air atmosphere.

Abbreviations Used: DBE: 1,2-dibromoethane, MeCN: acetonitrile, DCE: dichloroethane, DCM: dichloromethane, MeOH: methanol, THF: tetrahydrofuran, DMF: *N*,*N*-dimethylformamide, DMSO: dimethyl sulfoxide, EA: ethylacetate, PPh_3: triphenylphosphine.

2. Synthesis and Characterisation of Polymers and Metallized Polymeric Catalysts

2.1 Synthesis of COP-PPh_3.

COP-PPh_3 was synthesized by a facile modified solvent knitting strategy based on the Friedel-Crafts alkylation reaction using DBE as both the solvent and the external crosslinker. Under N_2 atmosphere, triphenylphosphine (5 mmol, 1.31 g) was dispersed in 20 mL DBE and mixed for 30 min. Then anhydrous $AlCl_3$ (15 mmol, 2.0 g) was added to the reaction medium and the mixture was allowed to stir vigorously at 60 °C for 24 h, and 80 °C for 24 h. The resulting precipitate was quenched by the slow addition of 40 mL H_2O, filtered and washed several times with ethanol and deionized water respectively. Finally, the crude product was extracted with ethanol in a Soxhlet extractor for 48 h, the obtained brown solid powder was vacuum dried at 70 °C for another 48 h.

2.2 Synthesis of COP-PPh_3-RhCl.

A 100 mL round bottom flask equipped with a teflon-coated magnetic stirring bar was charged with **COP-PPh_3** (1 g) and rhodium chloride ($RhCl_3 \bullet 3H_2O$, 100 mg), then EtOH (20 mL) was injected into the bottom flask by a syringe under nitrogen atmosphere, the reaction mixture was stirred at 70 °C for 6 h. After the completion of the reaction, the resulting precipitate was filtered and washed several times with deionized water, ethanol and DCM respectively. Finally, the obtained brown solid powder was vacuum dried at 70 ^oC for another 24 h.

2.3 Characterisation of COP-PPh_3-RhCl.

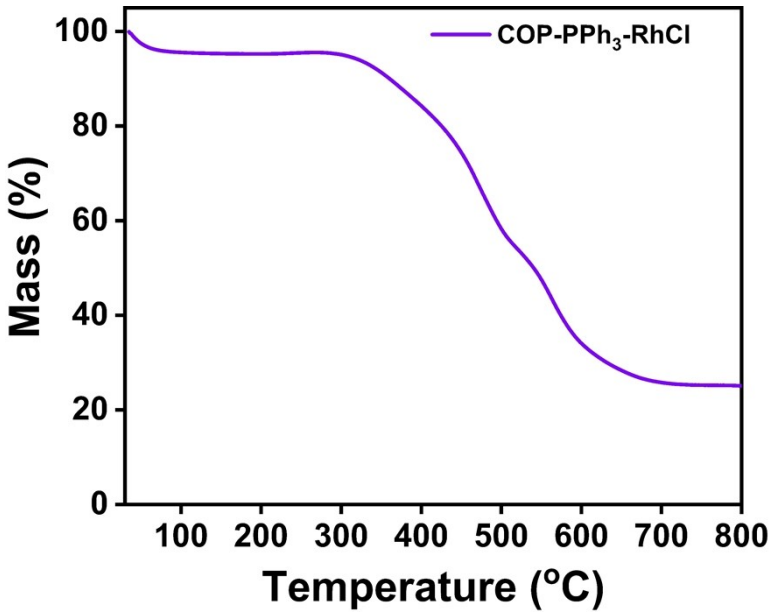


Figure S1. The TGA curve of COP-PPh3-RhCl.

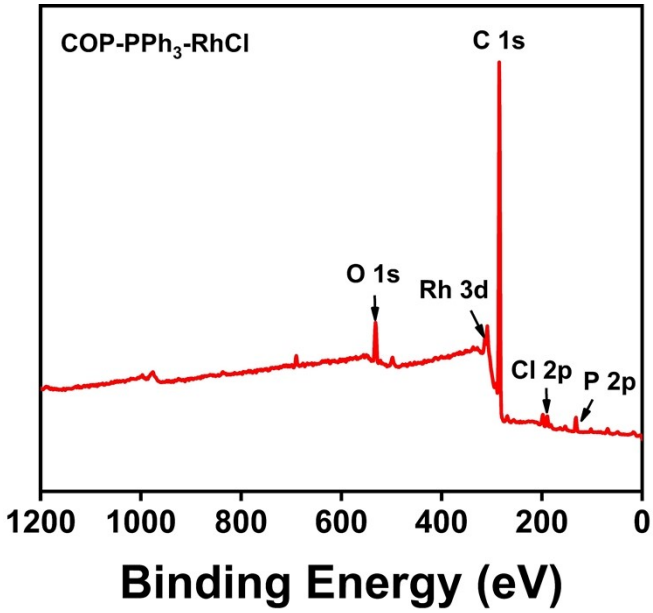


Figure S2. The full-scan XPS spectra of COP-PPh3-RhCl.

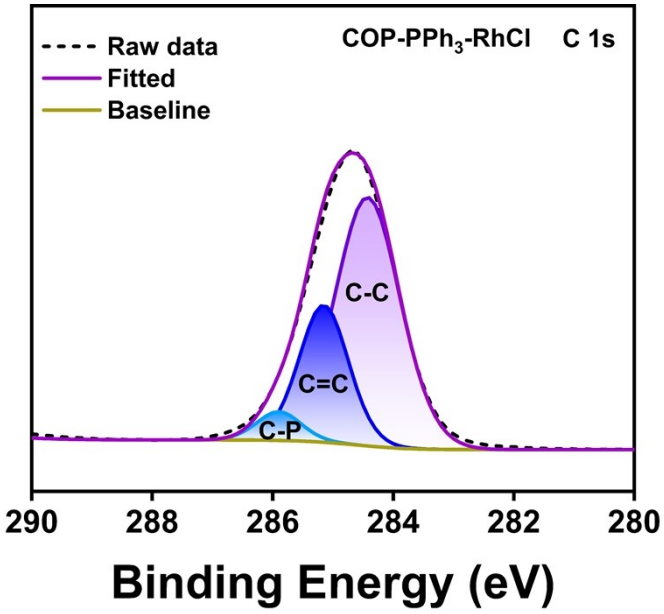


Figure S3. High-resolution C 1s XPS spectra of COP-PPh_3-RhCl.

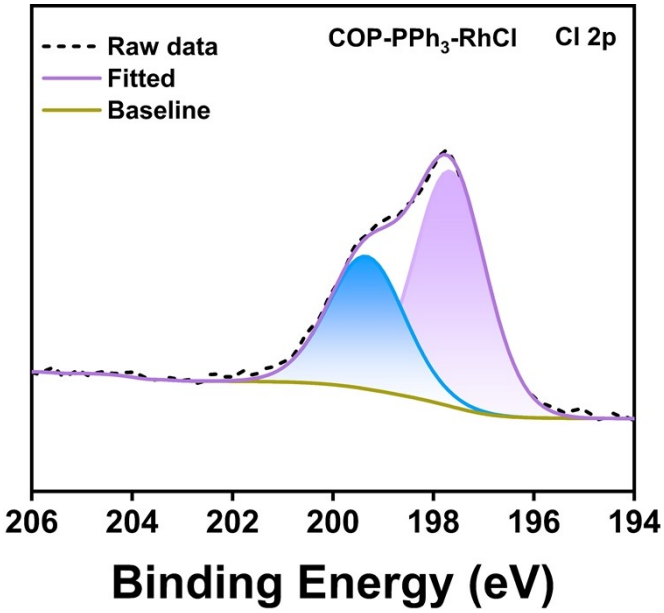


Figure S4. High-resolution Cl 2p XPS spectra of COP-PPh_3-RhCl.

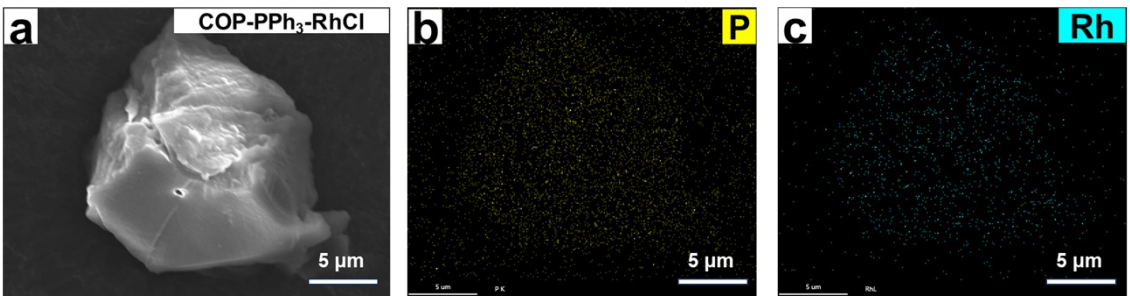
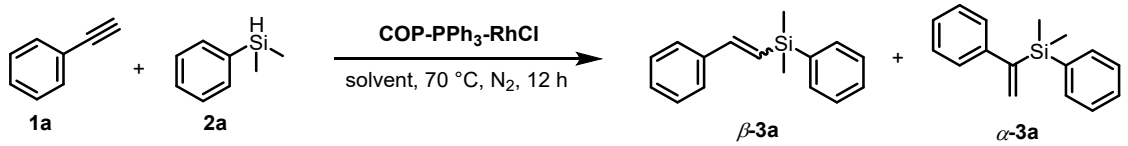


Figure S5. SEM image of COP-PPh_3-RhCl and the corresponding EDS elemental mapping of P and Rh elements.

3. Detailed Optimization of Reaction Conditions

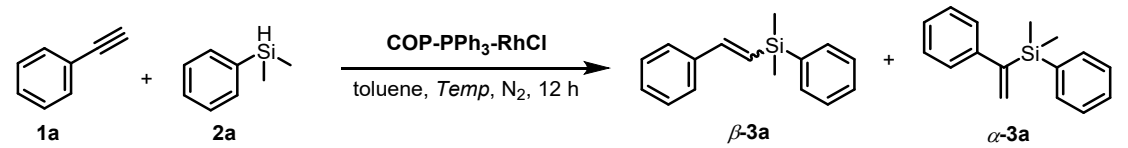
Table S1. Screen of solvents for reaction



Entry	*Solvent*	Yield (**3a**, %)	*E*/*α*
1	THF	39	90:10
2	1,4-dioxane	46	89:11
3	MeCN	38	92:8
4	**Toluene**	**60**	92:8
5	DMF	35	90:10
6	DMSO	20	91:11

Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), COP-PPh_3-RhCl (20 mg, 1.77 mol%), solvent (3 mL), 70 °C, N_2, 12 h. Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard.

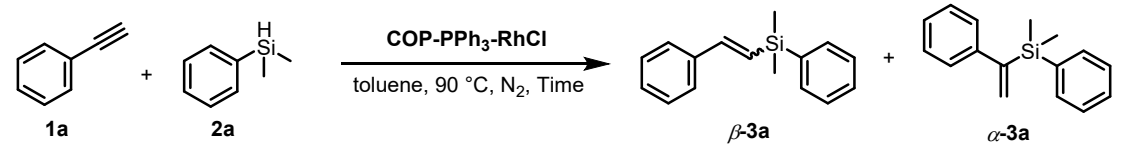
Table S2. Screen of reaction temperature for reaction



Entry	*Temp* (°C)	Yield (**3a**, %)	*E*/*α*
1	50	56	91:9
2	70	60	92:8
3	**90**	**77**	**92:8**
4	110	75	90:10
5	130	73	88:12

Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), COP-PPh_3-RhCl (20 mg, 1.77 mol%), toluene (3 mL), N_2, 12 h. Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard.

Table S3. Screen of reaction time for reaction



Entry	*Time* (h)	Yield (**3a**, %)	*E*/*α*
1	4	47	92:8
2	8	75	91:9
3	**12**	**77**	**92:8**
4	16	73	93:7
5	20	76	91:9

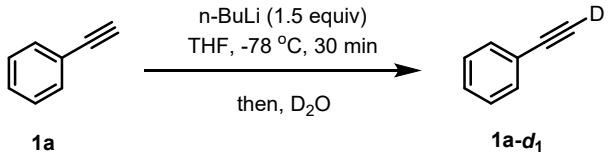
Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), COP-PPh_3-RhCl (20 mg, 1.77 mol%), toluene (3 mL), 90 °C, N_2. Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard.

4. General Procedures for the Syntheses of Vinylsilane Compounds

A sealed tube was charged with alkynes **1** (0.5 mmol), silanes (0.6 mmol), COP-PPh_3-RhCl (20 mg, 1.77 mol%) and toluene (3 mL) under N_2 atmosphere. The mixture was stirred at 90 °C for 12 h. When the reaction was completed, the mixture was filtered, then the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica gel using a mixture of hexanes and ethyl acetate as eluent to give the title compounds **3**.

5. Kinetic Isotope Effect Experiments

5.1 The Procedures for the Syntheses of Phenylacetylene-d_1 (1a-d_1)



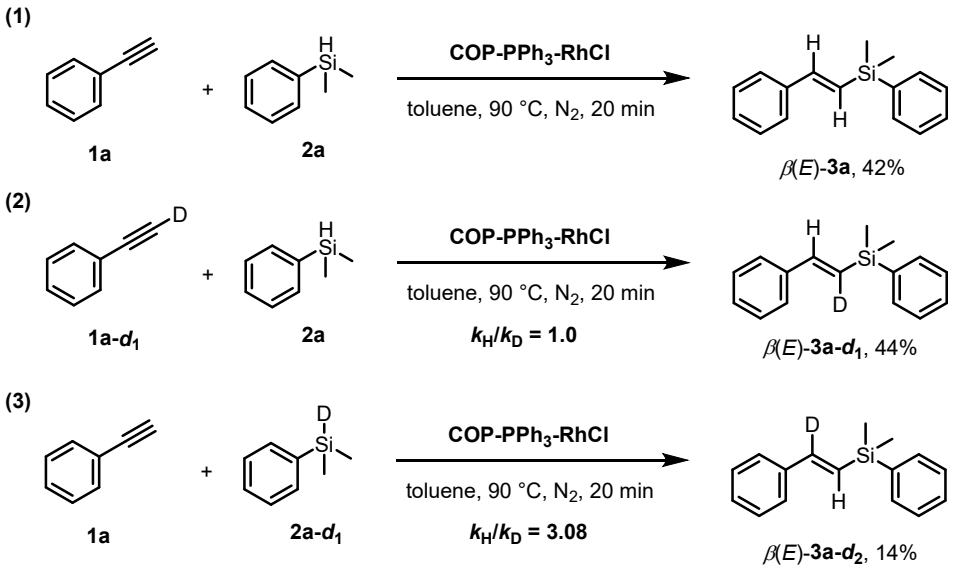
The compound **1a-d_1** was prepared following a modified literature procedure.[1] To a stirred solution of phenylacetylene (1.02 g, 10 mmol, 1.0 equiv) in THF (20 mL) at -78 °C was added n-BuLi (6 mL, 2.5 M in hexanes, 15 mmol, 1.5 equiv) dropwise. The reaction mixture was quenched with D_2O (2.0 mL) after 30 minutes and further stirred at room temperature for 5 minutes. The resulting solution was dried (Na_2SO_4), filtered and concentrated under reduced pressure to yield phenylacetylene-d_1 (788 mg, 77% yield) as a colorless oil, which was used directly without further purification. The deuterium

incorporation was determined to be 99% by ^{1}H NMR. The NMR spectrum was identical with the starting material with the acetylene proton being absent. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 – 7.31 (m, 2H), 7.24 – 7.14 (m, 3H).

5.2 The Procedures for the Syntheses of Dimethyl(phenyl)silane-d_1 (2a-d_1)

The compound **2a-d_1** was prepared following a modified literature procedure.[2] To a stirring suspension of $LiAlD_4$ (210 mg, 5 mmol) in dry Et_2O (12 mL) was added $PhMe_2SiCl$ (2.55 g, 15 mmol) dropwise at ambient temperature under N_2. The reaction mixture was refluxed at 40 °C for 12 h. The reaction was cooled to room temperature. Then, the reaction was quenched by adding aqueous solution of sodium hydroxide (15 mL, 10 wt%) into the crude reaction mixture, which was subsequently extracted by diethyl ether for three times. The resulting solution was dried (Na_2SO_4), filtered and concentrated under reduced pressure to yield $PhMe_2SiD$ as a colorless oil in 74% yield (1.5 g, 99% D), which was used directly without further purification. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 – 7.40 (m, 2H), 7.32 – 7.23 (m, 3H), 0.25 (s, 6H).

5.3 Deuterium Labelling Experiments



(1) A sealed tube was charged with **1a** (1.5 mmol, 153 mg), **2a** (1.8 mmol, 245 mg), **COP-PPh$_3$-RhCl** (30 mg, 0.87 mol%), 1,3,5-trimethoxybenzene (0.825 mmol, 138.8 mg) and toluene (9 mL)

under N_2 atmosphere. The reaction mixture was stirred at 90 °C under precise time control, with samples taken every 5 minutes to monitor the yield of product ***β*(*E*)-3a** by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

(2) A sealed tube was charged with **1a-*d*$_1$** (1.5 mmol, 155 mg), silane **2a** (1.8 mmol, 245 mg), **COP-PPh$_3$-RhCl** (30 mg, 0.87 mol%), 1,3,5-trimethoxybenzene (0.51 mmol, 85.7 mg) and toluene (9 mL) under N_2 atmosphere. The reaction mixture was stirred at 90 °C under precise time control, with samples taken every 5 minutes to monitor the yield of product ***β*(*E*)-3a-*d*$_1$** by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

(3) A sealed tube was charged with **1a** (1.5 mmol, 153 mg), silane **2a-*d*$_1$** (1.8 mmol, 247 mg), **COP-PPh$_3$-RhCl** (30 mg, 0.87 mol%), 1,3,5-trimethoxybenzene (0.329 mmol, 55.4 mg) and toluene (9 mL) under N_2 atmosphere. The reaction mixture was stirred at 90 °C under precise time control, with samples taken every 5 minutes to monitor the yield of product ***β*(*E*)-3a-*d*$_2$** by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

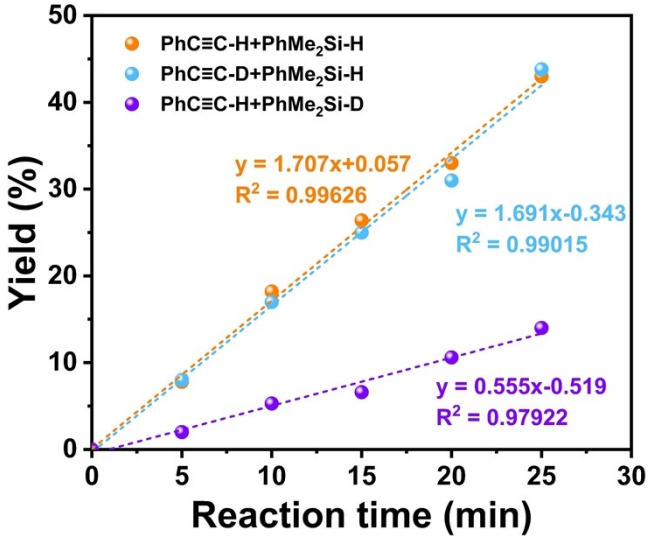


Figure S6. The kinetic curve of yield versus reaction time.

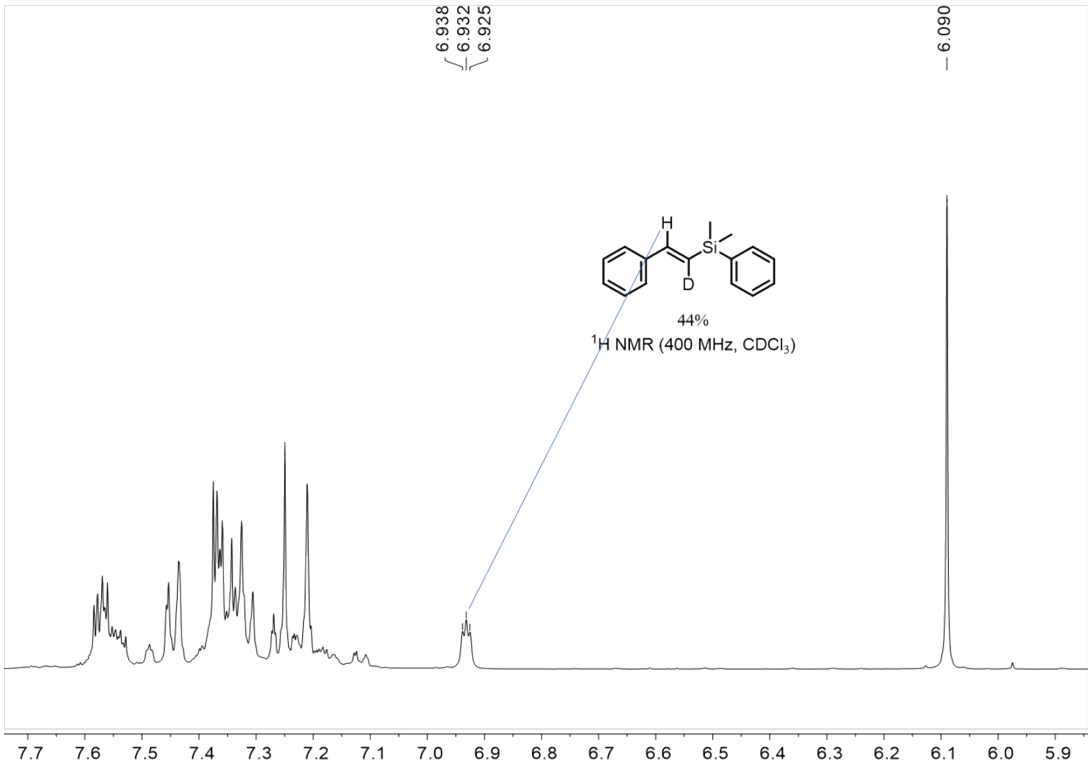


Figure S7. The crude ^{1}H NMR spectrum of compound ***β*(*E*)-3a-d_1**.

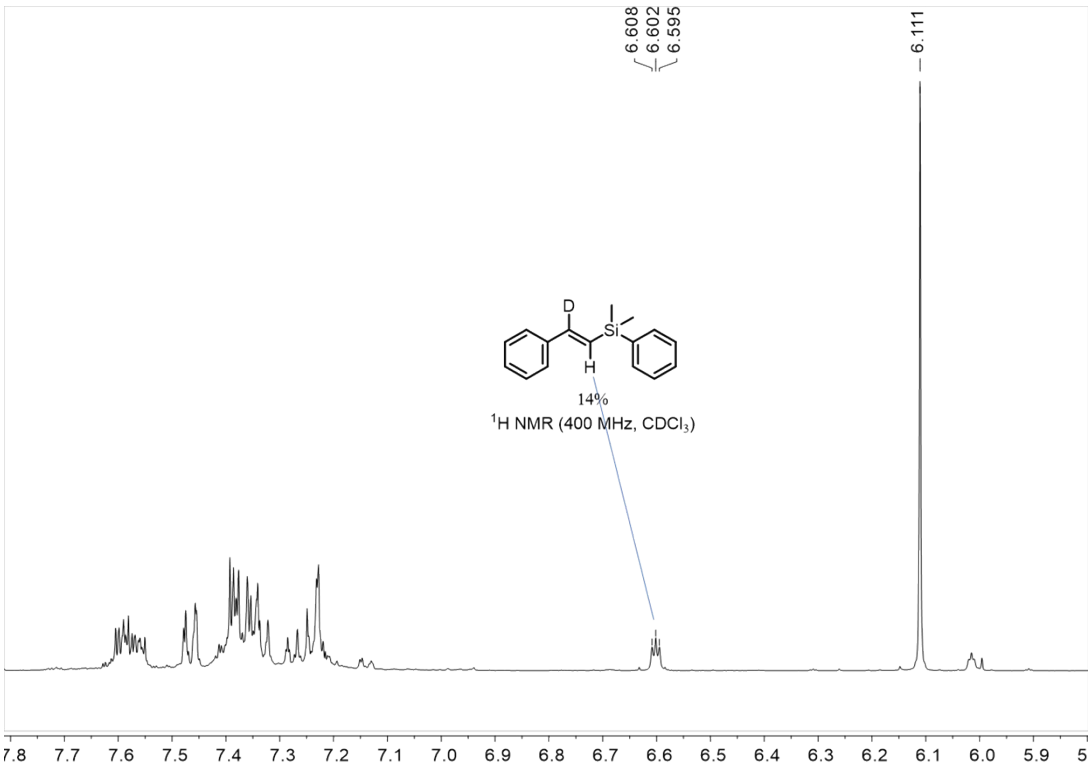
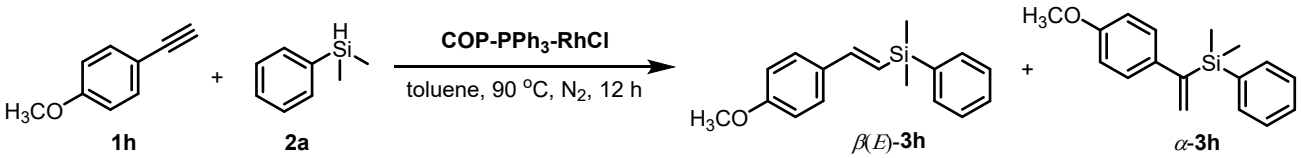


Figure S8. The crude ^{1}H NMR spectrum of compound ***β*(*E*)-3a-d_2**.

6. Reuse Experiment of COP-PPh$_3$-RhCl



To a 10 mL Pyrex reactor equipped with a magnetic stir bar, added 1-ethynyl-4-methoxybenzene (1.0 mmol, 1.0 equiv), dimethylphenylsilane (1.2 mmol, 1.2 equiv) and **COP-PPh$_3$-RhCl** (40 mg, 1.77 mol%), with 6 mL of toluene as solvent. The mixture was stirred at 90 °C for 12 h. When the reaction was completed, the catalyst is recovered through suction filtration, followed by washing and drying before initiating the next catalytic cycle. The resulting filtrate is concentrated under vacuum to yield the crude product. The Yield of **3h** was determined by ^{1}H NMR with CH_2Br_2 as an internal standard. The catalytic cycle was repeated five times, and the recovered catalyst was subjected to Characterisation analysis.

7. XPS Characterisation of COP-PPh$_3$-RhCl after 5 Cycles.

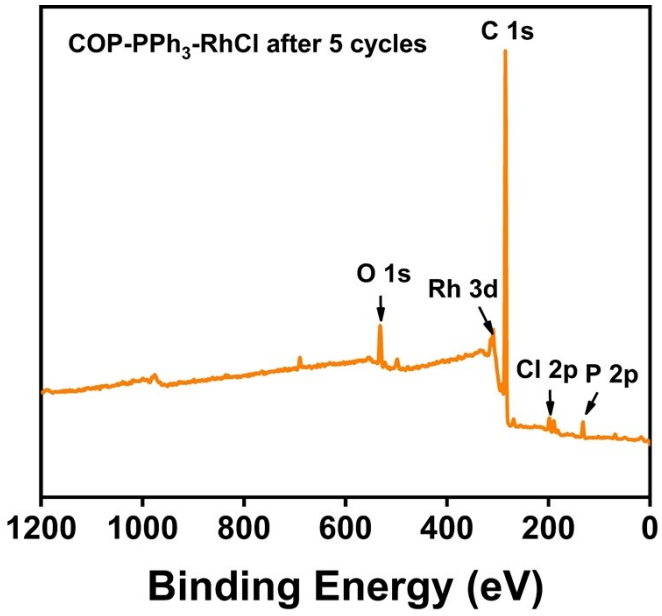


Figure S9. The full-scan XPS spectra of COP-PPh$_3$-RhCl after 5 cycles.

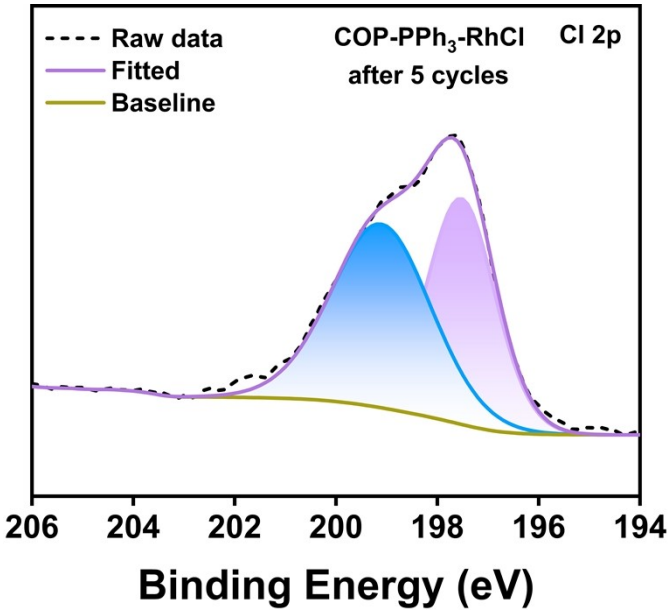
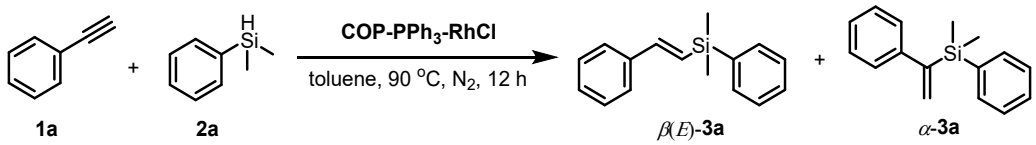


Figure S10. High-resolution Cl 2p XPS spectra of COP-PPh_3-RhCl after 5 cycles.

8. Characterisation Data for Products

We determined the configuration of the vinylsilane products based on the differences in the chemical shifts and coupling constants of the alkene protons. The proton coupling constant is largest in *β*(*E*)-configured aryl alkenes, followed by *β*(*Z*) isomers, while the *α*-configured aryl alkenes exhibit the smallest values. For vinyl silicon compounds, the coupling constant of hydrogen protons in *β*(*E*)-configured aryl alkenes is approximately 19 Hz, while that in *β*(*Z*)-configured aryl alkenes is about 15 Hz, and in *α*-configured aryl alkenes, it is around 2.8 Hz.

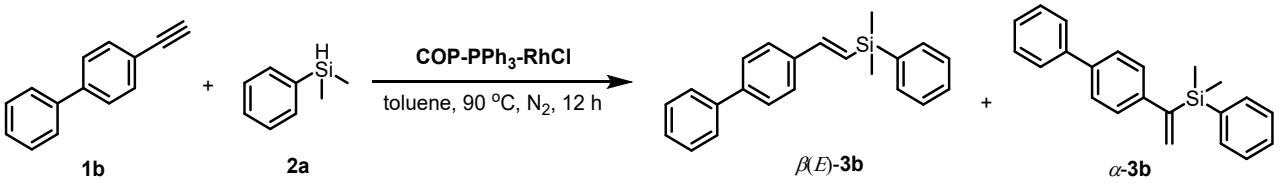
(*E*)-Dimethyl(phenyl)(styryl)silane (*β*(*E*)-3a) and dimethyl(phenyl)(1-phenylvinyl)silane (*α*-3a)



91.8 mg, 77%, *β*(*E*)/*α* = 92/8

The mixture of compound *β*(*E*)-**3a** and compound *α*-**3a** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds *α*-**3a** could not be separated as pure forms from major isomer *β*(*E*)-**3a**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 6.01 (d, *J* = 2.8 Hz, 0.08H) and δ 5.69 (d, *J* = 2.8 Hz, 0.08H) in $CDCl_3$ with that at δ 6.01 (d, *J* = 2.9 Hz, 1H) and δ 5.69 (d, *J* = 2.8 Hz, 1H) in $CDCl_3$ reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the *β*(*E*) isomer 7.63 – 7.52 (overlapped, 2.76H), 7.50 – 7.43 (overlapped, 1.84H), 7.42 – 7.36 (overlapped, 2.76H), 7.36 – 7.30 (overlapped, 1.84H), 6.97 (d, *J* = 19.2 Hz, 0.92H), 6.61 (d, *J* = 19.2 Hz, 0.92H), 0.46 (overlapped, 5.52H). δ the *α* isomer 7.63 – 7.52 (overlapped, 0.24H), 7.50 – 7.43 (overlapped, 0.16H), 7.42 – 7.36 (overlapped, 0.24H), 7.36 – 7.30 (overlapped, 0.16H), 6.01 (d, *J* = 2.8 Hz, 0.08H), 5.69 (d, *J* = 2.8 Hz, 0.08H), 0.46 (overlapped, 0.48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the *β*(*E*) isomer 145.4, 138.7, 138.3, 134.1, 129.2, 128.7, 128.3, 128.0, 127.2, 126.6, -2.4. The data of the *β*(*E*) isomer are consistent with those previously reported.[4]

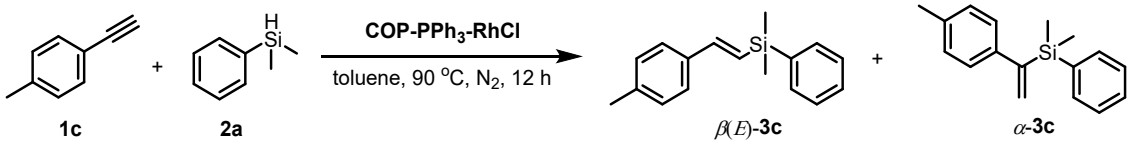
(*E*)-(2-([1,1'-Biphenyl]-4-yl)vinyl)dimethyl(phenyl)silane (*β*(*E*)-3b) and (1-([1,1'-biphenyl]-4-yl)vinyl)dimethyl(phenyl)silane (*α*-3b)



105.4 mg, 67%, $\beta(E)/\alpha$ = 87/13

The mixture of compound $\beta(E)$-**3b** and compound α-**3b** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds α-**3b** could not be separated as pure forms from major isomer $\beta(E)$-**3b**. Because compound α-**3b** has not been reported in the literature, the comparison with the alkenyl proton signal in the ^{1}H NMR spectrum ($CDCl_3$) of previously reported α-**3a** bearing the closely related structure was made as an additional effort to identify the structure of the isomer. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 6.02 (d, J = 2.8, 0.13H) and δ 5.66 (d, J = 2.8 Hz, 0.13H) in $CDCl_3$ with that at δ 6.01 (d, J = 2.8 Hz, 0.08H) and δ 5.69 (d, J = 2.8 Hz, 0.08H) in $CDCl_3$ reported previously. ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.58 – 7.52 (overlapped, 3.48H), 7.53 – 7.51 (overlapped, 1.74H), 7.48 – 7.45 (overlapped, 1.74H), 7.39 – 7.35 (overlapped, 1.74H), 7.34 – 7.31 (overlapped, 2.61H), 7.30 – 7.26 (overlapped, 0.87H), 6.94 (d, J = 19.2 Hz, 0.87H), 6.59 (d, J = 18.8 Hz, 0.87H), 0.41 (s, 5.22H). δ the α isomer 7.58 – 7.52 (overlapped, 0.52H), 7.53 – 7.51 (overlapped, 0.26H), 7.48 – 7.45 (overlapped, 0.26H), 7.39 – 7.35 (overlapped, 0.26H), 7.34 – 7.31 (overlapped, 0.39H), 7.30 – 7.26 (overlapped, 0.13H), 6.02 (d, J = 2.8 Hz, 0.13H), 5.66 (d, J = 2.8 Hz, 0.13H), 0.41 (s, 0.78H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 144.9, 141.0, 140.8, 138.7, 137.3, 134.1, 129.2, 128.9, 128.0, 127.5, 127.4, 127.4, 127.1, 127.0, -2.4. The data of the $\beta(E)$ isomer are consistent with those previously reported.[5] HRMS (ESI) *m/z*: calcd for $C_{22}H_{23}Si$ $[M+H]^+$: 315.1564, found 315.1570.

(*E*)-Dimethyl(4-methylstyryl)(phenyl)silane ($\beta(E)$-3c) and dimethyl(phenyl)(1-(*p*-tolyl)vinyl)silane (α-3c)

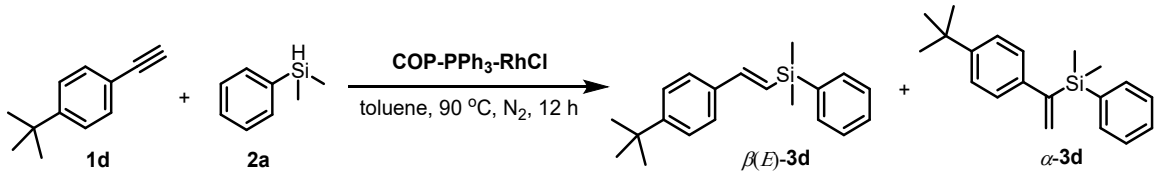


96.0 mg, 76%, $\beta(E)/\alpha$ = 92/8

The mixture of compound $\beta(E)$-**3c** and compound α-**3c** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds α-**3c** could not be separated as pure forms from major isomer $\beta(E)$-**3c**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 6.00 (d, J = 2.8 Hz, 0.08H) and δ 5.65 (d, J = 2.8 Hz, 0.08H) in $CDCl_3$ with that at δ 6.04 (d, J = 2.9 Hz, 1H) and δ 5.69 (d, J = 2.9 Hz, 1H) in $CDCl_3$ reported in the

literature.[6] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the *β*(*E*) isomer 7.60 – 7.56 (overlapped, 1.84H), 7.38 – 7.34 (overlapped, 4.60H), 7.14 (overlapped, 1.84H), 6.93 (d, *J* = 19.2 Hz, 0.92H), 6.53 (d, *J* = 19.2 Hz, 0.92H), 2.34 (s, 2.76H), 0.44 (s, 5.52H). δ the *α* isomer 7.60 – 7.56 (overlapped, 0.16H), 7.38 – 7.34 (overlapped, 0.40H), 7.14 (overlapped, 0.16H), 6.00 (d, *J* = 2.8 Hz, 0.08H), 5.65 (d, *J* = 2.8 Hz, 0.08H), 2.34 (s, 0.24H), 0.44 (s, 0.48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the *β*(*E*) isomer 145.3, 134.1, 133.1, 129.4, 129.1, 127.9, 127.8, 126.6, 126.2, 125.8, 21.4, -2.3. The data of the *β*(*E*) isomer are consistent with those previously reported.[5]

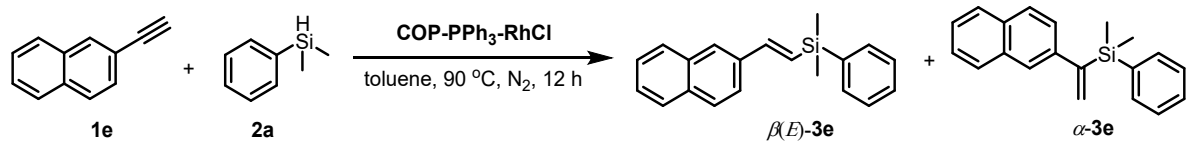
(*E*)-4-(*tert*-Butylstyryl)dimethyl(phenylsilane (*β*(*E*)-3d) and (1-(4-(*tert*-butyl)phenyl)vinyl)dimethyl(phenyl)silane (*α*-3d)



119.0 mg, 82%, *β*(*E*)/*α* = 89/11

The mixture of compound *β*(*E*)-**3d** and compound *α*-**3d** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds *α*-**3d** could not be separated as pure forms from major isomer *β*(*E*)-**3d**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 6.04 (d, *J* = 2.9 Hz, 0.11H) and δ 5.66 (d, *J* = 2.9 Hz, 0.11H) in $CDCl_3$ with that at δ 6.11 – 6.00 (d, *J* = 2.8 Hz, 1H) and δ 5.72 – 5.62 (d, *J* = 2.9 Hz, 1H) in $CDCl_3$ reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the *β*(*E*) isomer 7.60 – 7.53 (overlapped, 1.78H), 7.42 – 7.39 (overlapped, 1.78H), 7.38 – 7.32 (overlapped, 4.45H), 6.95 (d, *J* = 19.1 Hz, 0.89H), 6.55 (d, *J* = 19.1 Hz, 0.89H), 1.32 (s, 8.01H), 0.44 (s, 5.34H). δ the *α* isomer 7.60 – 7.53 (overlapped, 0.22H), 7.42 – 7.39 (overlapped, 0.22H), 7.38 – 7.32 (overlapped, 0.55H), 6.04 (d, *J* = 2.9 Hz, 0.11H), 5.66 (d, *J* = 2.9 Hz, 0.11H), 1.32 (s, 0.99H), 0.44 (s, 0.66H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the *β*(*E*) isomer 151.5, 145.3, 138.9, 134.1, 133.1, 129.1, 127.9, 126.4, 126.1, 125.6, 34.7, 31.4, -2.3. The data of the *β*(*E*) isomer are consistent with those previously reported.[8]

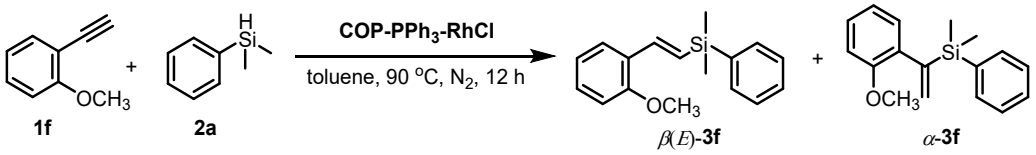
(*E*)-Dimethyl(2-(naphthalen-2-yl)vinyl)(phenyl)silane (*β*(*E*)-3e) and dimethyl(1-(naphthalen-2-yl)vinyl)(phenyl)silane (*α*-3e)



89.4 mg, 62%, $\beta(E)/\alpha$ = 88/12

The mixture of compound $\beta(E)$-**3e** and compound α-**3e** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds α-**3e** could not be separated as pure forms from major isomer $\beta(E)$-**3e**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 6.13 (d, J = 2.8 Hz, 0.12H) and δ 5.80 (d, J = 2.8 Hz, 0.12H) in $CDCl_3$ with the alkenyl proton signals in the ^{1}H NMR spectrum ($CDCl_3$) of α-**3a** at δ 6.01 (d, J = 2.8 Hz, 0.08H) and δ 5.69 (d, J = 2.8 Hz, 0.08H) in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.84 – 7.80 (overlapped, 2.64H), 7.73 – 7.70 (overlapped, 0.88H), 7.66 – 7.57 (overlapped, 2.64H), 7.48 – 7.46 (overlapped, 1.76H), 7.43 – 7.40 (overlapped, 2.64H), 7.15 (d, J = 18.8 Hz, 0.88H), 6.75 (d, J = 19.2 Hz, 0.88H), 0.51 (s, 5.28H). δ the α isomer 7.84 – 7.80 (overlapped, 0.36H), 7.73 – 7.70 (overlapped, 0.12H), 7.66 – 7.57 (overlapped, 0.36H), 7.48 – 7.46 (overlapped, 0.24H), 7.43 – 7.40 (overlapped, 0.36H), 6.13 (d, J = 2.8 Hz, 0.12H), 5.80 (d, J = 2.8 Hz, 0.12H), 0.49 (s, 0.72H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 145.4, 138.7, 135.7, 134.1, 133.5, 133.1, 129.2, 128.3, 128.3, 128.0, 127.8, 127.7, 127.0, 126.4, 126.2, 123.5, -2.3. HRMS (ESI) *m/z*: calcd for $C_{20}H_{21}Si$ $[M+H]^+$: 289.1407, found 289.1410.

(*E*)-(2-Methoxystyryl)dimethyl(phenyl)silane ($\beta(E)$-3f) and (1-(2-methoxyphenyl)vinyl)dimethyl(phenyl)silane (α-3f)

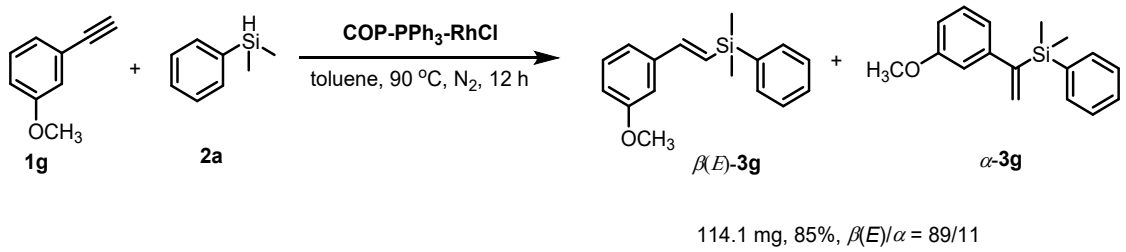


85.9 mg, 64%, $\beta(E)/\alpha$ = 89/11

The mixture of compound $\beta(E)$-**3f** and compound α-**3f** was isolated by silica gel column chromatography (Hexane/EA = 20:1) as a colorless oil. Compounds α-**3f** could not be separated as pure forms from major isomer $\beta(E)$-**3f**. Because compound α-**3f** has not been reported in the literature, the comparison with the alkenyl proton signal in the ^{1}H NMR spectrum ($CDCl_3$) of α-**3h** bearing the closely related structure was made as an additional effort to identify the structure of the isomer. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.91 (d, J = 2.8 Hz, 0.11H) and 5.67 (d, J = 2.8 Hz, 0.11H) in $CDCl_3$ with the alkenyl proton signals in the ^{1}H NMR spectrum ($CDCl_3$) of α-**3h** at δ 5.89 (d, J = 2.8 Hz, 0.15H) and δ 5.53 (d, J = 2.8 Hz,

0.15H) in $CDCl_3$. ^1H NMR (400 MHz, $CDCl_3$, two isomers) δ the *β*(*E*) isomer 7.60 – 7.55 (overlapped, 2.67H), 7.42 – 7.35 (overlapped, 2.67H), 7.42 – 7.35 (overlapped, 0.89H), 7.26 – 7.22 (overlapped, 0.89H), 6.95 – 6.91 (overlapped, 0.89H), 6.87 (d, *J* = 8.0 Hz, 0.89H), 6.55 (d, *J* = 19.2 Hz, 0.89H), 3.84 (s, 2.67H), 0.44 (s, 5.34H). δ the *α* isomer 7.60 – 7.55 (overlapped, 0.33H), 7.42 – 7.35 (overlapped, 0.33H), 7.26 – 7.22 (overlapped, 0.11H), 6.95 – 6.91 (overlapped, 0.11H), 5.91 (d, *J* = 2.8 Hz, 0.11H), 5.67 (d, *J* = 2.8 Hz, 0.11H), 3.54 (s, 0.33H), 0.35 (s, 0.66H). ^{13}C NMR (101 MHz, $CDCl_3$) δ the *β*(*E*) isomer 156.8, 139.7, 139.2, 134.1, 129.3, 129.1, 127.9, 127.5, 127.4, 126.5, 120.7, 111.1, 55.6, -2.3. The data of the *β*(*E*) isomer are consistent with those previously reported.[9] HRMS (ESI) *m/z*: calcd for $C_{17}H_{21}OSi$ $[M+H]^+$: 269.1356, found 269.1353.

(*E*)-(3-Methoxystyryl)dimethyl(phenyl)silane (*β*(*E*)-3g) and (1-(3-methoxyphenyl)vinyl)dimethyl(phenyl)silane (*α*-3g)

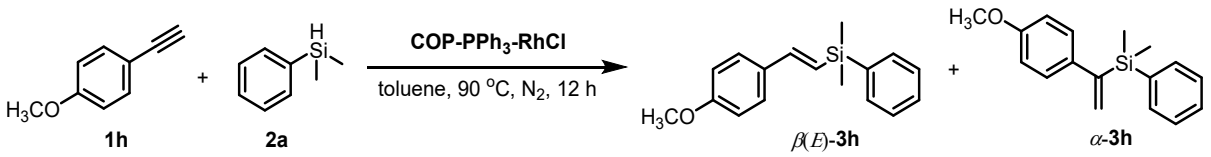


114.1 mg, 85%, *β*(*E*)/*α* = 89/11

The mixture of compound *β*(*E*)-**3g** and compound *α*-**3g** was isolated by silica gel column chromatography (Hexane/EA = 20:1) as a colorless oil. Compounds *α*-**3g** could not be separated as pure forms from major isomer *β*(*E*)-**3g**. Because compound *α*-**3g** has not been reported in the literature, the comparison with the alkenyl proton signal in the ^1H NMR spectrum ($CDCl_3$) of *α*-**3f** bearing the closely related structure was made as an additional effort to identify the structure of the isomer. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.97 (d, *J* = 2.8 Hz, 0.11H) and δ 5.65 (d, *J* = 2.8 Hz, 0.11H) in $CDCl_3$ with the alkenyl proton signal in the ^1H NMR spectrum ($CDCl_3$) of *α*-**3f** at δ 5.91 (d, *J* = 2.8 Hz, 0.11H) and δ 5.67 (d, *J* = 2.8 Hz, 0.11H) in $CDCl_3$. ^1H NMR (400 MHz, $CDCl_3$, two isomers) δ the *β*(*E*) isomer 7.56 – 7.54 (overlapped, 1.78H), 7.35 – 7.33 (overlapped, 2.67H), 7.21 (t, *J* = 8.0 Hz, 0.89H), 7.02 – 7.00 (overlapped, 0.89H), 6.97 – 6.96 (m, 0.89H), 6.89 (d, *J* = 18.8 Hz, 0.89H), 6.79 (dd, *J* = 8.0, 2.4 Hz, 0.89H), 6.56 (d, *J* = 19.2 Hz, 0.89H), 3.78 (s, 2.67H), 0.42 (s, 5.34H). δ the *α* isomer 7.56 – 7.54 (overlapped, 0.22H), 7.35 – 7.33 (overlapped, 0.33H), 7.14 – 7.08 (m, 0.22H), 7.02 – 7.00 (overlapped, 0.11H), 6.71 – 6.68 (m, 0.11H), 5.97 (d, *J* = 2.8 Hz, 0.11H), 5.65 (d, *J* = 2.8 Hz, 0.11H), 3.64 (s, 0.33H), 0.40 (s, 0.66H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the *β*(*E*) isomer 160.0, 145.3, 139.8, 138.7, 134.1, 129.6, 129.2, 128.0, 127.6, 119.4, 114.3, 111.5, 55.4, -2.4. The data of the *β*(*E*) isomer are consistent with those previously

reported.[9] HRMS (ESI) *m/z*: calcd for $C_{17}H_{21}OSi$ $[M+H]^+$: 269.1356, found 269.1361.

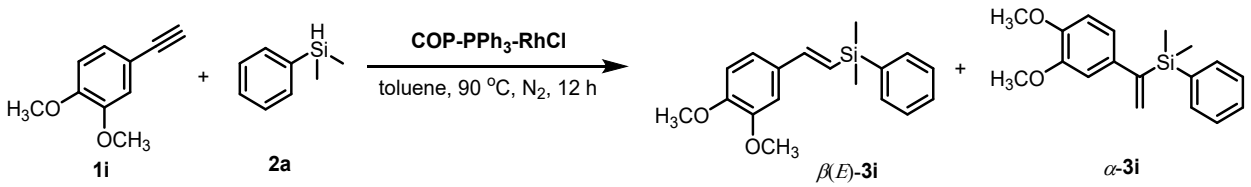
(*E*)-(4-Methoxystyryl)dimethyl(phenyl)silane (*β*(*E*)-3h) and (1-(4-methoxyphenyl)vinyl)dimethyl(phenyl)silane (*α*-3h)



128.8 mg, 96%, *β*(*E*)/*α* = 85/15

The mixture of compound *β*(*E*)-**3h** and compound *α*-**3h** was isolated by silica gel column chromatography (Hexane/EA = 20:1) as a colorless oil. Compounds *α*-**3h** could not be separated as pure forms from major isomer *β*(*E*)-**3h**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.89 (d, *J* = 2.8 Hz, 0.15H) and δ 5.53 (d, *J* = 2.8 Hz, 0.15H) in $CDCl_3$ with that at δ 5.99 (d, *J* = 2.4 Hz, 1H) and δ 5.63 (d, *J* = 2.4 Hz, 1H) in $CDCl_3$ reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the *β*(*E*) isomer 7.50 – 7.46 (overlapped, 1.70H), 7.31 – 7.29 (overlapped, 1.70H), 7.28 – 7.26 (m, 2.55H), 6.80 (d, *J* = 19.2 Hz, 0.85H), 6.80– 6.77 (overlapped, 1.70H), 6.33 (d, *J* = 19.2 Hz, 0.85H), 3.71 (s, 2.55H), 0.34 (s, 5.10H). δ the *α* isomer 7.50 – 7.46 (overlapped, 0.30H), 7.31 – 7.29 (overlapped, 0.30H), 7.01 – 6.98 (m, 0.45H), 6.80– 6.77 (overlapped, 0.30H), 5.89 (d, *J* = 2.8 Hz, 0.15H), 5.53 (d, *J* = 2.8 Hz, 0.15H), 3.67 (s, 0.45H), 0.33 (s, 0.90H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the *β*(*E*) isomer 159.5, 144.9, 139.9, 136.3, 134.1, 133.1, 129.4, 127.8, 127.5, 114.0, 55.4, -1.0. The data of the *β*(*E*) isomer are consistent with those previously reported.[9]

(*E*)-(3,4-Dimethoxystyryl)dimethyl(phenyl)silane (*β*(*E*)-3i) and (1-(3,4-di methoxyphenyl)vinyl)dimethyl(phenyl)silane (*α*-3i)

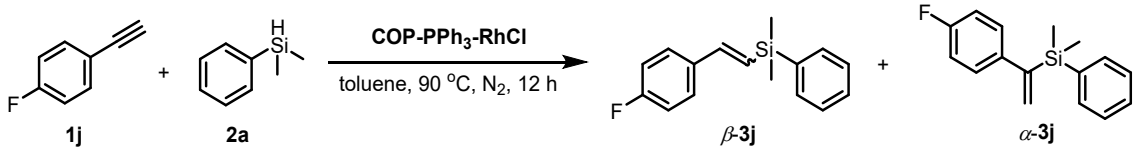


92.5 mg, 62%, *β*(*E*)/*α* = 86/14

The mixture of compound *β*(*E*)-**3i** and compound *α*-**3i** was isolated by silica gel column chromatography (Hexane/EA = 20:1) as a colorless oil. Compounds *α*-**3i** could not be separated as pure forms from major isomer *β*(*E*)-**3i**. Because compound *α*-**3i** has not been reported in the literature, the comparison with the alkenyl proton signal in the ^{1}H NMR spectrum ($CDCl_3$) of *α*-**3h** bearing the

closely related structure was made as an additional effort to identify the structure of the isomer. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 6.05 (d, J = 2.8 Hz, 0.14H) and δ 5.70 (d, J = 2.8 Hz, 0.14H) in $CDCl_3$ with the alkenyl proton signal in the ^1H NMR spectrum ($CDCl_3$) of α-**3h** at 5.89 (d, J = 2.8 Hz, 0.15H) and δ 5.53 (d, J = 2.8 Hz, 0.15H) in $CDCl_3$ reported previously. ^1H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.65 – 7.60 (overlapped, 1.72H), 7.42 – 7.39 (overlapped, 2.58H), 7.07 (overlapped, 0.86H), 7.02 (overlapped, 0.86H), 6.93 (d, J = 18.8 Hz, 0.86H), 6.86 – 6.83 (overlapped, 0.86H), 6.47 (d, J = 19.2 Hz, 0.86H), 3.93 (s, 2.58H), 3.90 (s, 2.58H), 0.49 (s, 5.16H). δ the α isomer 7.65 – 7.60 (overlapped, 0.28H), 7.42 – 7.39 (overlapped, 0.42H), 7.07 (overlapped, 0.14H), 7.02 (overlapped, 0.14H), 6.86 – 6.83 (overlapped, 0.14H), 6.05 (d, J = 2.8 Hz, 0.14H), 5.70 (d, J = 2.8 Hz, 0.14H), 3.86 (s, 0.42H), 3.69 (s, 0.42H), 0.47 (s, 0.84H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 149.3, 149.0, 144.9, 138.7, 134.0, 131.3, 129.1, 127.8, 124.4, 120.0, 110.8, 108.4, 55.9, 55.8, -2.4. The data of the $\beta(E)$ isomer are consistent with those previously reported.[10] HRMS (ESI) *m/z*: calcd for $C_{18}H_{23}O_2Si$ $[M+H]^+$: 299.1462, found 299.1460.

(4-Fluorostyryl)dimethyl(phenyl)silane (β-3j) and (1-(4-fluorophenyl)vinyl)(dimethyl)phenylsilane (α-3j)



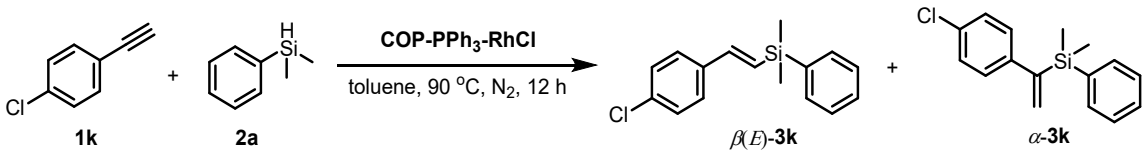
1j **2a** β-**3j** α-**3j**

125.0 mg, 97%, $\beta(E)/\beta(Z)/\alpha$ = 84/10/6

The mixture of compound β-**3j** and compound α-**3j** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds $\beta(Z)$-**3j** and α-**3j** could not be separated as pure forms from major isomer $\beta(E)$-**3j**. As for $\beta(Z)$-**3j**, the generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 5.80 (d, J = 15.2 Hz, 0.10H) in $CDCl_3$ with that at δ 5.99 (d, J = 15.0 Hz, 1H) in $CDCl_3$ reported in the literature.[11] As for α-**3j**, the generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.76 (d, J = 2.8 Hz, 0.06H) and δ 5.48 (d, J = 2.8 Hz, 0.06H) in $CDCl_3$ with that at δ 5.98 – 5.93 (d, J = 2.73 Hz, 1H), 5.70 - 5.65 (d, J = 2.76 Hz, 1H) in $CDCl_3$ reported in the literature.[12] ^1H NMR (400 MHz, $CDCl_3$, three isomers) δ the $\beta(E)$ isomer 7.39 – 7.31 (overlapped, 1.68H), 7.23 – 7.13 (overlapped, 4.20H), 6.88 – 6.79 (overlapped, 1.68H), 6.70 (d, J = 19.2 Hz, 0.84H), 6.56 (d, J = 18.8 Hz, 0.84H), 0.24 (s, 5.04H). δ the $\beta(Z)$ isomer 7.39 – 7.31 (overlapped, 0.20H), 7.23 – 7.13 (overlapped, 0.60H), 6.88 – 6.79 (overlapped, 0.20H), 5.80 (d, J = 15.2 Hz, 0.10H), 0.14 (s, 0.60H). δ the α isomer 7.39 – 7.31 (overlapped, 0.12H), 7.23 –

7.13 (overlapped, 0.30H), 6.88 – 6.79 (overlapped, 0.12H), 5.76 (d, J = 2.8 Hz, 0.06H), 5.48 (d, J = 2.8 Hz, 0.06H), 0.21 (s, 0.36H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 162.8 (d, J = 246 Hz), 144.1, 138.6, 134.0, 133.1, 129.2, 128.2 (d, J = 8.1 Hz), 128.0, 127.0 (d, J = 2.2 Hz), 115.6 (d, J = 21.5 Hz), -2.4. ^{19}F NMR (376 MHz, $CDCl_3$, three isomers) δ the $\beta(E)$ isomer -113.7 (s, 0.84F); δ the $\beta(Z)$ isomer -114.3 (s, 0.10F); δ the α isomer -116.8 (s, 0.06F). The data of the $\beta(E)$ isomer are consistent with those previously reported.[9] HRMS (ESI) *m/z*: calcd for $C_{16}H_{18}FSi$ $[M+H]^+$: 257.1156, found 257.1161.

(*E*)-(4-Chlorostyryl)dimethyl(phenyl)silane (*β*(*E*)-3k) and (1-(4-chlorophenyl)vinyl)dimethyl(phenyl)silane (*α*-3k)

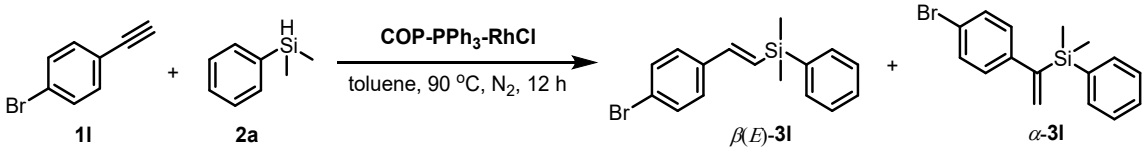


1k **2a** ***β*(*E*)-3k** ***α*-3k**

122.8 mg, 90%, *β*(*E*)/*α* = 89/11

The mixture of compound *β*(*E*)-**3k** and compound *α*-**3k** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds *α*-**3k** could not be separated as pure forms from major isomer *β*(*E*)-**3k**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.93 (d, J = 2.8 Hz, 0.11H) and δ 5.66 (d, J = 2.8 Hz, 0.11H) in $CDCl_3$ with that at δ 5.99 (d, J = 2.7 Hz, 1H) and δ 5.71 (d, J = 2.7 Hz, 1H) in $CDCl_3$ reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.56 – 7.47 (overlapped, 1.78H), 7.36 – 7.30 (overlapped, 4.45H), 7.28 – 7.24 (overlapped, 1.78H), 6.85 (d, J = 19.2 Hz, 0.89H), 6.53 (d, J = 19.2 Hz, 0.89H), 0.41 (s, 5.34H). δ the α isomer 7.56 – 7.47 (overlapped, 0.22H), 7.36 – 7.30 (overlapped, 0.55H), 7.28 – 7.24 (overlapped, 0.22H), 5.93 (d, J = 2.8 Hz, 0.11H), 5.66 (d, J = 2.8 Hz, 0.11H), 0.41 (s, 0.66H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 144.0, 138.4, 136.8, 134.0, 133.1, 129.3, 128.8, 128.2, 128.0, 127.8, -2.5. The data of the $\beta(E)$ isomer are consistent with those previously reported.[9]

(*E*)-(4-Bromostyryl)dimethyl(phenyl)silane (*β*(*E*)-3l) and (1-(4-bromophenyl)vinyl)dimethyl(phenyl)silane (*α*-3l)

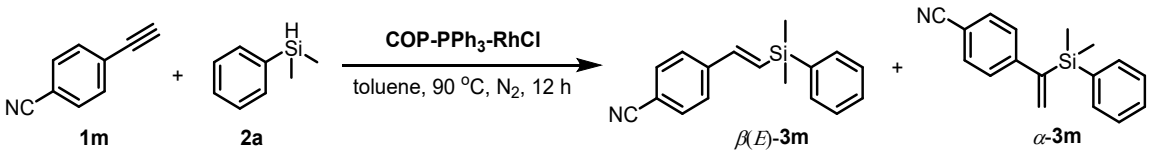


1l **2a** ***β*(*E*)-3l** ***α*-3l**

101.5 mg, 64%, *β*(*E*)/*α* = 87/13

The mixture of compound *β*(*E*)-**3l** and compound *α*-**3l** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds *α*-**3l** could not be separated as pure forms from major isomer *β*(*E*)-**3l**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 5.87 (d, *J* = 2.8 Hz, 0.13H) and δ 5.59 (d, *J* = 2.8 Hz, 0.13H) in $CDCl_3$ with that at δ 5.99 (d, *J* = 2.7 Hz, 1H) and δ 5.71 (d, *J* = 2.7 Hz, 1H) in $CDCl_3$ reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the *E* isomer 7.48 – 7.43 (overlapped, 1.74H), 7.33 (d, *J* = 8.4 Hz, 1.74H), 7.29 – 7.24 (overlapped, 2.61H), 7.18 (d, *J* = 8.4 Hz, 1.74H), 6.76 (d, *J* = 19.2 Hz, 0.87H), 6.48 (d, *J* = 19.2 Hz, 0.87H), 0.34 (s, 5.22H). δ the *Z* isomer 7.48 – 7.43 (overlapped, 0.26H), 7.29 – 7.24 (overlapped, 0.65H), 6.86 (d, *J* = 8.4 Hz, 0.26H), 5.87 (d, *J* = 2.8 Hz, 0.13H), 5.59 (d, *J* = 2.8 Hz, 0.13H), 0.31 (s, 0.78H).^{13}C NMR (100 MHz, $CDCl_3$) δ the *E* isomer 144.0, 138.3, 137.2, 134.0, 131.7, 129.3, 128.4, 128.1, 128.0, 122.1, -2.5. The data of the *β*(*E*) isomer are consistent with those previously reported.[4]

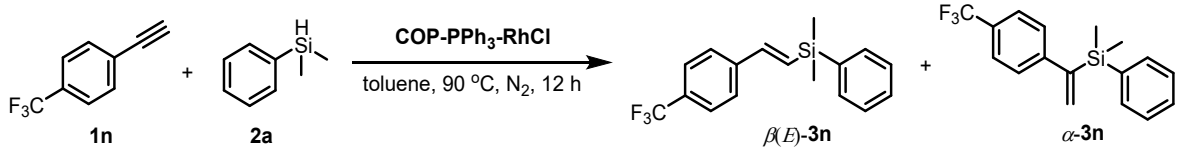
(*E*)-4-(2-(Dimethyl(phenyl)silyl)vinyl)benzonitrile (*β*(*E*)-3m)



52.7 mg, 40%, *β*(*E*)/*α* > 99/1

The product was purified by silica gel column chromatography (Hexane/EA = 100:1) to afford *β*(*E*)-**3m** (52.7 mg, 40%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.59 (m, 2H), 7.59-7.54 (m, 2H), 7.53-7.48 (m, 2H), 7.41-7.38 (m, 3H), 6.92 (d, *J* = 19.2 Hz, 1H), 6.76 (d, *J* = 18.8 Hz, 1H), 0.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 142.3, 137.7, 134.0, 132. 7, 132.5, 129.4, 128.1, 127.1, 119.1, 111.3, -2.7. The data are consistent with those previously reported.[4]

(*E*)-Dimethyl(phenyl)(4-(trifluoromethyl)styryl)silane (*β*(*E*)-3n) and dimethyl(phenyl)(1-(4-(trifluoromethyl)phenyl)vinyl)silane (*α*-3n)

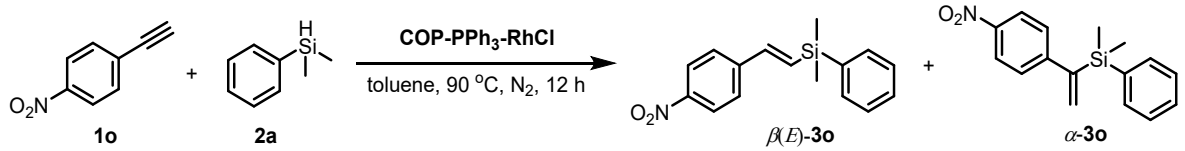


113.4 mg, 74%, *β*(*E*)/*α* = 88/12

The mixture of compound *β*(*E*)-**3n** and compound *α*-**3n** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds *α*-**3n** could not be separated as pure forms from major isomer *β*(*E*)-**3n**. The generation thereof was additionally confirmed by comparison of its

distinct alkenyl proton signals at δ 5.94 (d, J = 2.4 Hz, 0.12H) and δ 5.71 (d, J = 2.8 Hz, 0.12H) in $CDCl_3$ with that at δ 6.02 (d, J = 2.7 Hz, 1H) and δ 5.78 (d, J = 2.7 Hz, 1H) in $CDCl_3$ reported in the literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.55 – 7.44 (overlapped, 5.28H), 7.35 – 7.30 (overlapped, 2.64H), 6.91 (d, J = 19.2 Hz, 0.88H), 6.65 (d, J = 18.8 Hz, 0.88H), 0.42 (s, 5.28H); δ the α isomer 7.55 – 7.44 (overlapped, 0.72H), 7.35 – 7.30 (overlapped, 0.36H), 5.94 (d, J = 2.4 Hz, 0.12H), 5.71 (d, J = 2.8 Hz, 0.12H), 0.38 (s, 0.72H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 143.8, 141.6, 138.1, 134.1, 131.0, 130.1, 129.8, 129.4, 128.1, 126.8, 125.7, 125.7, 125.6, 125.6, -2.5. ^{19}F NMR (376 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer -62.3 (s, 2.64F); δ the α isomer -62.2 (s, 0.36F). The data of the $\beta(E)$ isomer are consistent with those previously reported.[13]

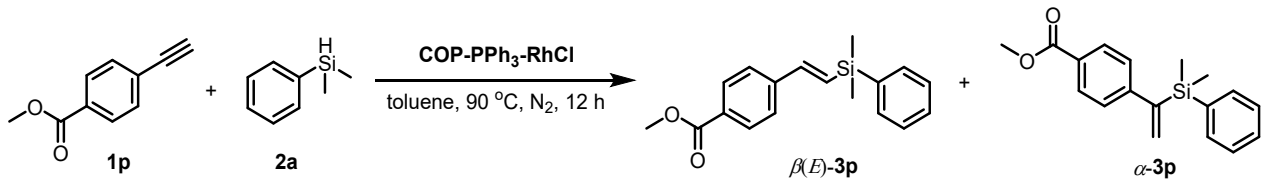
(*E*)-Dimethyl(4-nitrostyryl)(phenyl)silane (*β*(*E*)-3o) and dimethyl(1-(4-nitrophenyl)vinyl)(phenyl)silane (*α*-3o)



53.8 mg, 38%, $\beta(E)/\alpha$ = 87/13

The mixture of compound $\beta(E)$-**3o** and compound α-**3o** was isolated by silica gel column chromatography (Hexane/EA = 10:1) as a colorless oil. Compounds α-**3o** could not be separated as pure forms from major isomer $\beta(E)$-**3o**. Because compound α-**3o** has not been reported in the literature, the comparison with the alkenyl proton signal in the ^{1}H NMR spectrum ($CDCl_3$) of α-**3a** bearing the closely related structure was made as an additional effort to identify the structure of the isomer. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 5.97 (d, J = 2.4 Hz, 0.13H) and δ 5.76 (d, J = 2.4 Hz, 0.13H) in $CDCl_3$ with the alkenyl proton signals in the ^{1}H NMR spectrum ($CDCl_3$) of α-**3a** at δ 6.01 (d, J = 2.8, Hz 0.08H) and δ 5.69 (d, J = 2.8 Hz, 0.08H) in $CDCl_3$ reported previously. ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 8.11 (d, J = 8.8 Hz, 1.74H), 7.52 – 7.45 (overlapped, 3.48H), 7.36 – 7.28 (overlapped, 2.61H), 6.91 (d, J = 19.2 Hz, 0.87H), 6.75 (d, J = 19.2 Hz, 0.87H), 0.41 (s, 5.22H). δ the α isomer 8.01 (d, J = 8.8 Hz, 0.26H), 7.52 – 7.45 (overlapped, 0.52H), 7.36 – 7.28 (overlapped, 0.39H), 5.97 (d, J = 2.4 Hz, 0.13H), 5.76 (d, J = 2.4 Hz, 0.13H), 0.37 (s, 0.78H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 147.3, 144.2, 142.8, 137.6, 134.0, 134.0, 129.5, 128.1, 127.2, 124.1, -2.7. The data of the $\beta(E)$ isomer are consistent with those previously reported.[4] HRMS (ESI) *m/z*: calcd for $C_{16}H_{18}NO_2Si$ $[M+H]^+$: 284.1101, found 284.1105.

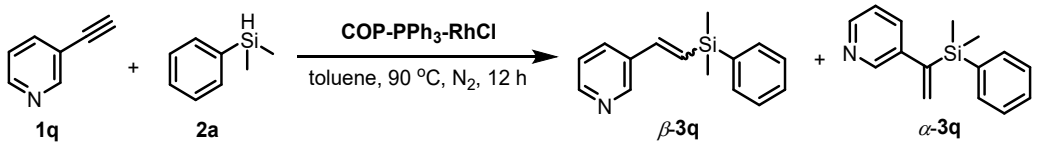
Methyl (*E*)-4-(2-(dimethyl(phenyl)silyl)vinyl)benzoate (*β*(*E*)-3p) and methyl 4-(1-(dimethyl(phenyl)silyl)vinyl)benzoate (*α*-3p)



97.8 mg, 66%, *β*(*E*)/*α* = 89/11

The mixture of compound *β*(*E*)-**3p** and compound *α*-**3p** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds *α*-**3p** could not be separated as pure forms from major isomer *β*(*E*)-**3p**. Because compound *α*-**3p** has not been reported in the literature, the comparison with the alkenyl proton signal in the ^{1}H NMR spectrum ($CDCl_3$) of *α*-**3a** bearing the closely related structure was made as an additional effort to identify the structure of the isomer. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 6.01 (d, *J* = 2.8 Hz, 0.11H) and δ 5.74 (d, *J* = 2.8 Hz, 0.11H) in $CDCl_3$ with the alkenyl proton signals in the ^{1}H NMR spectrum ($CDCl_3$) of *α*-**3a** at δ 6.01 (d, *J* = 2.8 Hz, 0.08H) and δ 5.69 (d, *J* = 2.8 Hz, 0.08H) in $CDCl_3$ reported previously. ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the *β*(*E*) isomer 8.00 (d, *J* = 8.4 Hz, 1.78H), 7.58 – 7.52 (overlapped, 1.78H), 7.49 (d, *J* = 8.4 Hz, 1.78H), 7.39 – 7.35 (overlapped, 2.67H), 6.96 (d, *J* = 19.2 Hz, 0.89H), 6.73 (d, *J* = 19.2 Hz, 0.89H), 3.91 (s, 2.67H), 0.46 (s, 5.34H). δ the *α* isomer 7.96 (d, *J* = 8.4 Hz, 0.22H), 7.58 – 7.52 (overlapped, 0.22H), 7.39 – 7.35 (overlapped, 0.33H), 7.15 (d, *J* = 8.4 Hz, 0.22H), 6.01 (d, *J* = 2.8 Hz, 0.11H), 5.74 (d, *J* = 2.8 Hz, 0.11H), 3.88 (s, 0.33H), 0.42 (s, 0.66H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the *β*(*E*) isomer 170.0, 144.2, 142.5, 138.1, 134.0, 131.0, 130.0, 129.6, 129.3, 128.0, 126.5, 52.2, -2.5. The data of the *β*(*E*) isomer are consistent with those previously reported.[14] HRMS (ESI) *m/z*: calcd for $C_{18}H_{21}O_2Si$ $[M+H]^+$: 297.1305, found 297.1309.

3-(2-(Dimethyl(phenyl)silyl)vinyl)pyridine (*β*-3q) and 3-(1-(dimethylphenylsilyl)ethenyl)pyridine (*α*-3q)

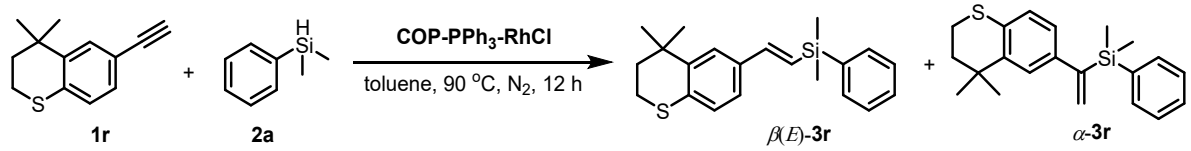


18.0 mg, 15%, *β*(*E*)/*β*(*Z*)/*α* = 86/7/7

The mixture of compound *β*-**3q** and compound *α*-**3q** was isolated by silica gel column chromatography (Hexane/EA = 20:1) as a colorless oil. Compounds *β*(*Z*)-**3q** and *α*-**3q** could not be separated as pure forms from major isomer *β*(*E*)-**3q**. As for *β*(*Z*)-**3q**, the generation thereof was additionally confirmed

by comparison of its distinct alkenyl proton signal at δ 6.10 (d, J = 15.2 Hz, 0.07H) in $CDCl_3$ with that at δ 6.13 (d, J = 15.2 Hz, 1H) in $CDCl_3$ reported in the literature.[15] As for **α-3q**, because compound **α-3q** has not been reported in the literature, the comparison with the alkenyl proton signal in the ^{1}H NMR spectrum ($CDCl_3$) of **α-3a** bearing the closely related structure was made as an additional effort to identify the structure of the isomer. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.93 (d, J = 2.4 Hz, 0.07H) and δ 5.71 (d, J = 2.4 Hz, 0.07H) in $CDCl_3$ with the alkenyl proton signals in the ^{1}H NMR spectrum ($CDCl_3$) of **α-3a** at δ 6.01 (d, J = 2.8 Hz, 0.08H) and δ 5.69 (d, J = 2.8 Hz, 0.08H) in $CDCl_3$ reported previously. ^{1}H NMR (400 MHz, $CDCl_3$, three isomers) δ the **β**(*E*) isomer 8.54 (s, 0.86H), 8.40 – 8.38 (overlapped, 0.86H), 7.70 – 7.67 (overlapped, 0.86H), 7.50 – 7.47 (overlapped, 1.72H), 7.32 – 7.24 (overlapped, 2.58H), 7.20 – 7.16 (overlapped, 0.86H), 6.83 (d, J = 19.2 Hz, 0.86H), 6.61 (d, J = 18.8 Hz, 0.86H), 0.38 (s, 5.58H). δ the **β**(*Z*) isomer 8.40 – 8.38 (overlapped, 0.14H), 7.70 – 7.67 (overlapped, 0.07H), 7.50 – 7.47 (overlapped, 0.14H), 7.32 – 7.24 (overlapped, 0.21H), 7.20 – 7.16 (overlapped, 0.07H), 5.93 (d, J = 2.4 Hz, 0.07H), 5.71 (d, J = 2.4 Hz, 0.07H), 0.33 (s, 0.42H). δ the **α** isomer 8.40 – 8.38 (overlapped, 0.14H), 7.70 – 7.67 (overlapped, 0.07H), 7.50 – 7.47 (overlapped, 0.21H), 7.32 – 7.24 (overlapped, 0.21H), 7.20 – 7.16 (overlapped, 0.07H), 6.10 (d, J = 15.2 Hz, 0.07H), 0.33 (s, 0.42H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the *E* isomer 149.1, 148.7, 141.6, 138.0, 134.0, 133.1, 133.0, 130.8, 129.4, 128.1, 123.6, -2.6. The data the **β**(*E*) isomer are consistent with those previously reported.[16] HRMS (ESI) *m/z*: calcd for $C_{15}H_{18}NSi$ [M+H$^+$]: 240.1203, found 240.1203.

(*E*)-(2-(4,4-Dimethylthiochroman-6-yl)vinyl)dimethyl(phenyl)silane (*β*(*E*)-3r) and (1-(4,4-dimethylthiochroman-6-yl)vinyl)dimethyl(phenyl)silane (*α*-3r)

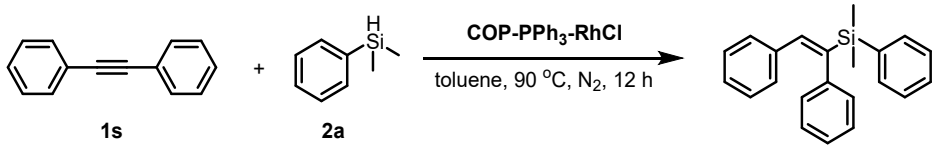


150.6 mg, 89%, *β*(*E*)/*α* = 82/18

The mixture of compound *β*(*E*)-**3r** and compound *α*-**3r** was isolated by silica gel column chromatography (Hexane/EA = 100:1) as a colorless oil. Compounds *α*-**3r** could not be separated as pure forms from major isomer *β*(*E*)-**3r**. Because compound *β*(*E*)-**3r** and *α*-**3r** have not been reported in the literature, the comparison with the alkenyl proton signals in the ^{1}H NMR spectrum ($CDCl_3$) of *β*(*E*)-**3a** and *α*-**3a** bearing the closely related structure was made as an additional effort to identify the structure of the isomers. As for *β*(*E*)-**3r**, the generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 6.78 (d, J = 18.8 Hz, 0.82H), 6.39 (d, J = 19.2 Hz,

0.82H) in $CDCl_3$ with the alkenyl proton signals in the ^1H NMR spectrum ($CDCl_3$) of $\beta(E)$-**3a** at δ 6.97 (d, J = 19.2 Hz, 0.92H) and 6.61 (d, J = 19.2 Hz, 0.92H) in $CDCl_3$ reported previously. As for α-**3r**, the generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 5.92 (d, J = 2.0 Hz, 0.18H) and δ 5.55 (d, J = 2.4 Hz, 0.18H) in $CDCl_3$ with the alkenyl proton signals in the ^1H NMR spectrum ($CDCl_3$) of α-**3a** at δ 6.01 (d, J = 2.8 Hz, 0.08H) and δ 5.69 (d, J = 2.8 Hz, 0.08H) in $CDCl_3$ reported previously. ^1H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.52 – 7.42 (overlapped, 1.64H), 7.36 – 7.19 (overlapped, 3.28H), 7.14 – 7.07 (overlapped, 0.82H), 7.00 – 6.91 (overlapped, 0.82H), 6.78 (d, J = 18.8 Hz, 0.82H), 6.39 (d, J = 19.2 Hz, 0.82H), 2.94 – 2.91 (m, 1.64H), 1.87 – 1.84 (m, 1.64H), 1.24 (s, 4.92H), 0.34 (s, 4.92H). δ the α isomer 7.52 – 7.42 (overlapped, 0.36H), 7.36 – 7.19 (overlapped, 0.72H), 7.14 – 7.07 (overlapped, 0.18H), 7.00 – 6.91 (overlapped, 0.18H), 5.92 (d, J = 2.0 Hz, 0.18H), 5.55 (d, J = 2.4 Hz, 0.18H), 2.89 – 2.85 (m, 0.36H), 1.81 – 1.78 (m, 0.36H), 1.24 (s, 1.08H), 0.33 (s, 1.08H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 145.3, 142.0, 138.9, 134.3, 134.1, 132.2, 129.1, 127.9, 126.8, 125.2, 125.1, 123.9, 37.7, 33.1, 30.2, 23.3, -2.3. HRMS (ESI) *m/z*: calcd for $C_{21}H_{27}SSi$ $[M+H]^+$: 339.1597, found 339.1601.

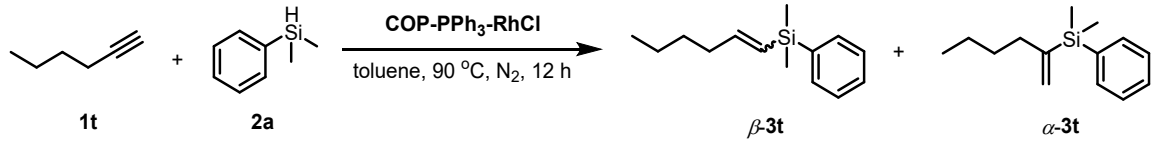
(*E*)-(1,2-Diphenylvinyl)dimethyl(phenyl)silane (3s)



(*E*)-**3s**, 108.5 mg, 69%

The product was purified by silica gel column chromatography (Hexane/EA = 100:1) to afford *E*-**3s** (108.5 mg, 69%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.28 – 7.23 (m, 3H), 7.15 – 7.06 (m, 3H), 7.00 – 6.94 (m, 3H), 6.87 – 6.78 (m, 4H), 6.74 (s, 1H), 0.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 142.4, 139.3, 137.8, 137.4, 134.4, 129.7, 129.2, 128.7, 128.0, 127.9, 127.8, 127.3, 125.8, -2.9. The data are consistent with those previously reported.[14]

Hex-1-en-1-yldimethyl(phenyl)silane (β-3t) and Hex-1-en-2-yldimethyl(phenyl)silane (α-3t)

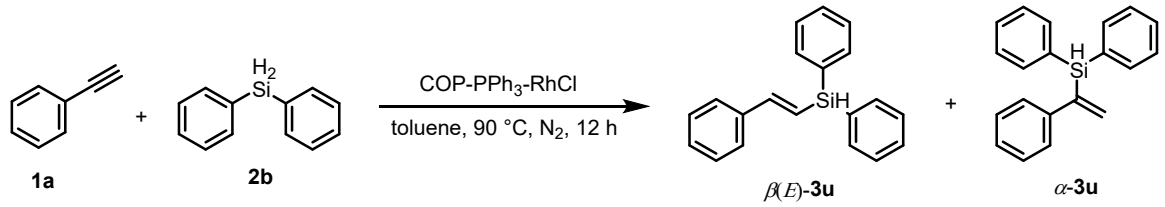


55.7 mg, 51%, $\beta(E)/\beta(Z)/\alpha$ = 87/4/9

The mixture of compound β-**3t** and compound α-**3t** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds $\beta(Z)$-**3t** and α-**3t** could not be separated as pure forms from

major isomer $\beta(E)$-**3t**. As for $\beta(Z)$-**3t**, the generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signal at δ 6.47 (dt, J = 14.4, 7.6 Hz, 0.04H) in $CDCl_3$ with that at 6.43 (dt, J = 14.5, 7.4 Hz, 1H) in $CDCl_3$ reported in the literature.[11] As for α-**3t**, the generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.74 – 5.69 (m, 0.09H) in $CDCl_3$ with that at δ 5.75 – 5.72 (m, 1H) in $CDCl_3$ reported in the literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$, three isomers) δ the $\beta(E)$ isomer 7.57 – 7.52 (overlapped, 1.74H), 7.40 – 7.37 (overlapped, 2.61H), 6.16 (dt, J = 18.8, 6.0 Hz, 0.87H), 5.79 (d, J = 18.4 Hz, 0.87H), 2.23 – 2.14 (overlapped, 1.74H), 1.45 – 1.31 (overlapped, 3.48H), 0.98 – 0.82 (overlapped, 2.61H), 0.35 (s, 5.22H). δ the α isomer 7.57 – 7.52 (overlapped, 0.18H), 7.40 – 7.37 (overlapped, 0.27H), 5.74 – 5.69 (m, 0.09H), 5.46 – 5.44 (overlapped, 0.09H), 2.01 – 2.91 (overlapped, 0.18H), 1.45 – 1.31 (overlapped, 0.36H), 0.98 – 0.82 (overlapped, 0.27H), 0.41 (s, 0.54H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 149.6, 139.5, 134.0, 128.9, 127.8, 127.3, 36.7, 30.9, 22.4, 14.2, -2.3. The data of the $\beta(E)$ isomer are consistent with those previously reported.[9]

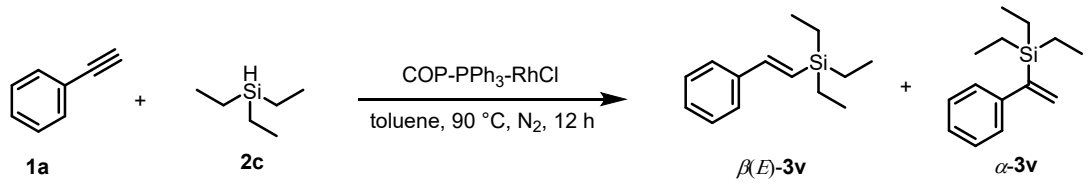
(E)-Diphenyl(styryl)silane ($\beta(E)$3u) and diphenyl(1-phenylvinyl)silane (α-3u)



54.4 mg, 38%, $\beta(E)/\alpha$ = 92/8

The mixture of compound $\beta(E)$-**3u** and compound α-**3u** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds α-**3u** could not be separated as pure forms from major isomer $\beta(E)$-**3u**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 6.20 (dd, J = 2.5, 1.0 Hz, 1H) and δ 5.60 (d, J = 2.5 Hz, 1H) in $CDCl_3$ with that at δ 6.28 (dd, J = 2.5, 1.0 Hz, 1H) and δ 5.68 (d, J = 2.5 Hz, 1H) in $CDCl_3$ reported in the literature.[7] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.56 – 7.51 (m, 4H), 7.40 – 7.34 (m, 2H), 7.33 – 7.22 (m, 9H), 7.00 (d, J = 19.2 Hz, 1H), 6.63 (dd, J = 19.2 Hz, J = 3.2 Hz, 1H), 5.17 (d, J = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 149.3, 138.0, 135.7, 133.7, 130.0, 128.7, 128.7, 128.2, 126.9, 121.7. The data of the $\beta(E)$ isomer are consistent with those previously reported.[17]

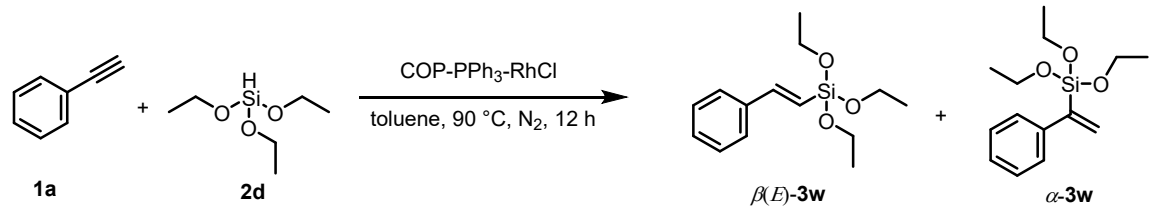
(E)-Triethyl(styryl)silane ($\beta(E)$-3v) and triethyl(1-phenylvinyl)silane (α-3v)



54.6 mg, 50%, $\beta(E)/\alpha$ = 92/8

The mixture of compound $\beta(E)$-**3v** and compound α-**3v** was isolated by silica gel column chromatography (Hexane) as a colorless oil. Compounds α-**3v** could not be separated as pure forms from major isomer $\beta(E)$-**3v**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 5.79 (d, J = 3.2 Hz, 0.08H) and δ 5.49 (d, J = 3.2 Hz, 0.08H) in $CDCl_3$ with that at δ 5.86 (dd, J = 2.5, 1.0 Hz, 1H) and δ 5.56 (d, J = 2.5 Hz, 1H) in $CDCl_3$ reported in the literature.[18] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.37 – 7.34 (overlapped, 1.84H), 7.25 – 7.21 (overlapped, 1.84H), 7.18 – 7.12 (overlapped, 0.92H), 6.82 (d, J = 19.2 Hz, 0.92H), 6.34 (d, J = 19.2 Hz, 0.92H), 0.93 – 0.89 (overlapped, 8.28H), 0.61 – 0.55 (overlapped, 5.52H); δ the α isomer 7.37 – 7.34 (overlapped, 0.16H), 7.25 – 7.21 (overlapped, 0.16H), 7.18 – 7.12 (overlapped, 0.08H), 5.79 (d, J = 3.2 Hz, 0.08H), 5.49 (d, J = 3.2 Hz, 0.08H), 0.93 – 0.89 (overlapped, 0.72H), 0.61 – 0.55 (overlapped, 0.48H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the $\beta(E)$ isomer 145.0, 138.6, 128.6, 128.0, 126.5, 126.0, 7.6, 3.7. The data of the $\beta(E)$ isomer are consistent with those previously reported.[19]

(*E*)-Triethoxy(styryl)silane ($\beta(E)$-3w) and triethoxy(1-phenylvinyl)silane (α-3w)



38.6 mg, 29%, $\beta(E)/\alpha$ = 94/6

The mixture of compound $\beta(E)$-**3w** and compound α-**3w** was isolated by silica gel column chromatography (Hexane/EA = 20:1) as a colorless oil. Compounds α-**3w** could not be separated as pure forms from major isomer $\beta(E)$-**3w**. The generation thereof was additionally confirmed by comparison of its distinct alkenyl proton signals at δ 6.06 (d, J = 3.2 Hz, 0.06H) and δ 5.89 (d, J = 2.8 Hz, 0.06H) in $CDCl_3$ with that at δ 6.15 (d, J = 3.0 Hz, 1H) and δ 5.97 (d, J = 3.0 Hz, 1H) in $CDCl_3$ reported in the literature.[20] ^{1}H NMR (400 MHz, $CDCl_3$, two isomers) δ the $\beta(E)$ isomer 7.41 – 7.38 (overlapped, 1.88H), 7.28 – 7.20 (overlapped, 2.82H), 7.14 (d, J = 19.2 Hz, 0.94H), 6.10 (d, J = 19.2 Hz, 0.94H), 3.81 (q, J = 6.8 Hz, 5.64H), 1.19 (t, J = 7.2 Hz, 8.46H). δ the α isomer 7.41 – 7.38 (overlapped, 0.12H), 7.28 – 7.20 (overlapped, 0.18H), 6.06 (d, J = 3.2 Hz, 0.06H), 5.89 (d, J = 2.8 Hz, 0.06H), 3.76 (q, J = 6.8 Hz, 0.36H), 1.14 (t, J = 6.4 Hz, 0.54H). ^{13}C NMR (100 MHz, $CDCl_3$) δ the

$\beta(E)$ isomer 149.3, 137.7, 128.9, 128.7, 126.9, 117.8, 58.7, 18.4. The data of the $\beta(E)$ isomer are consistent with those previously reported.[21]

9. References

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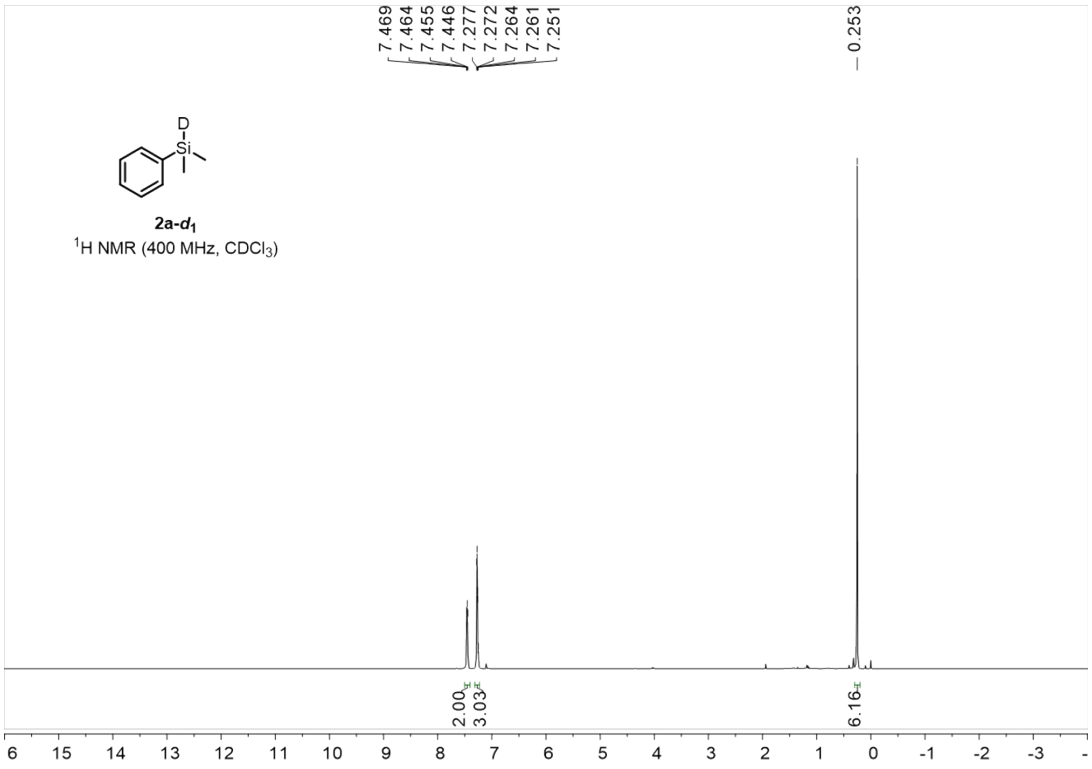
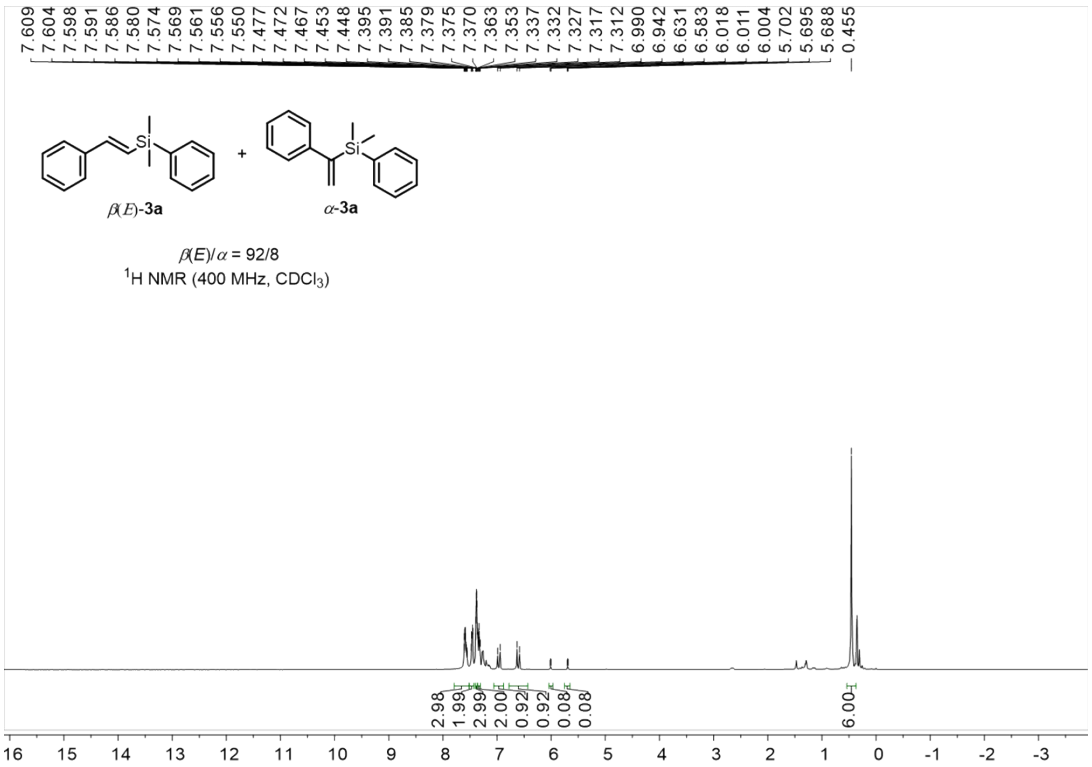
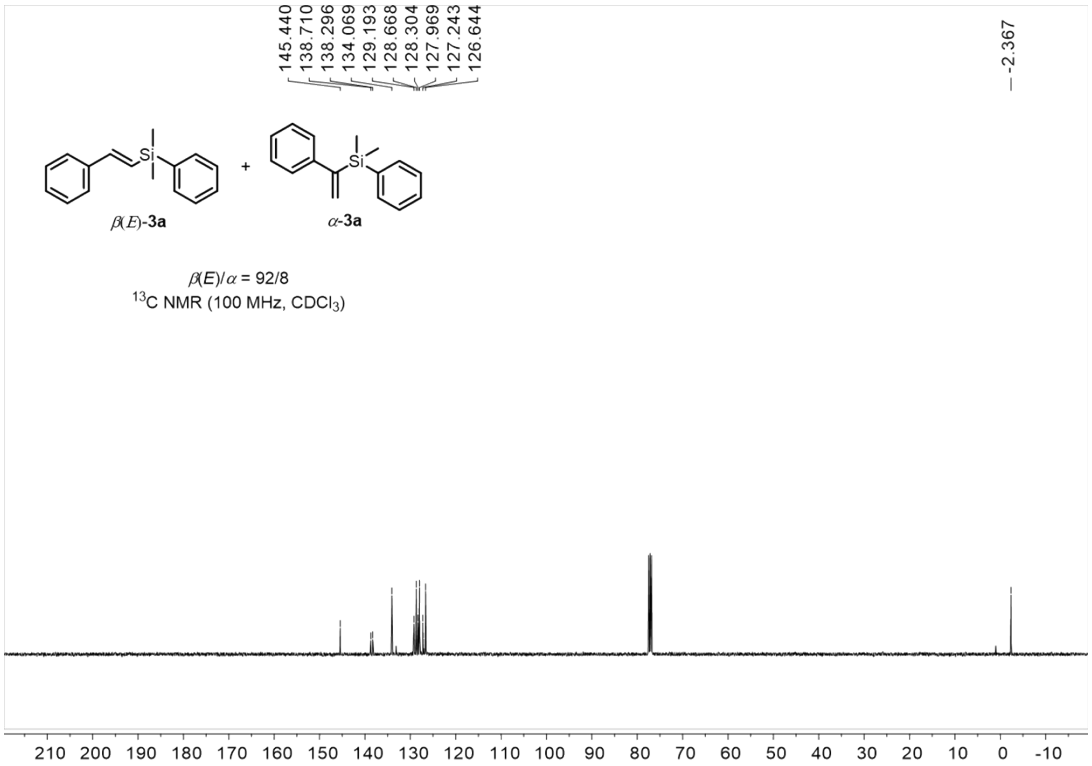
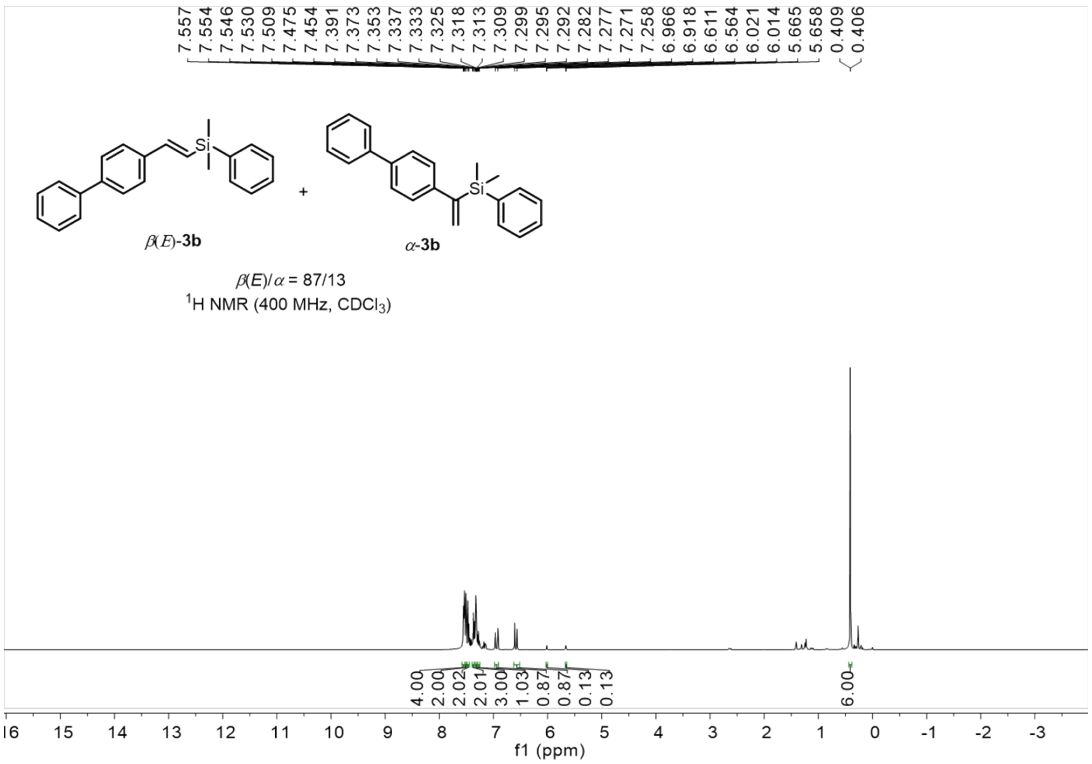
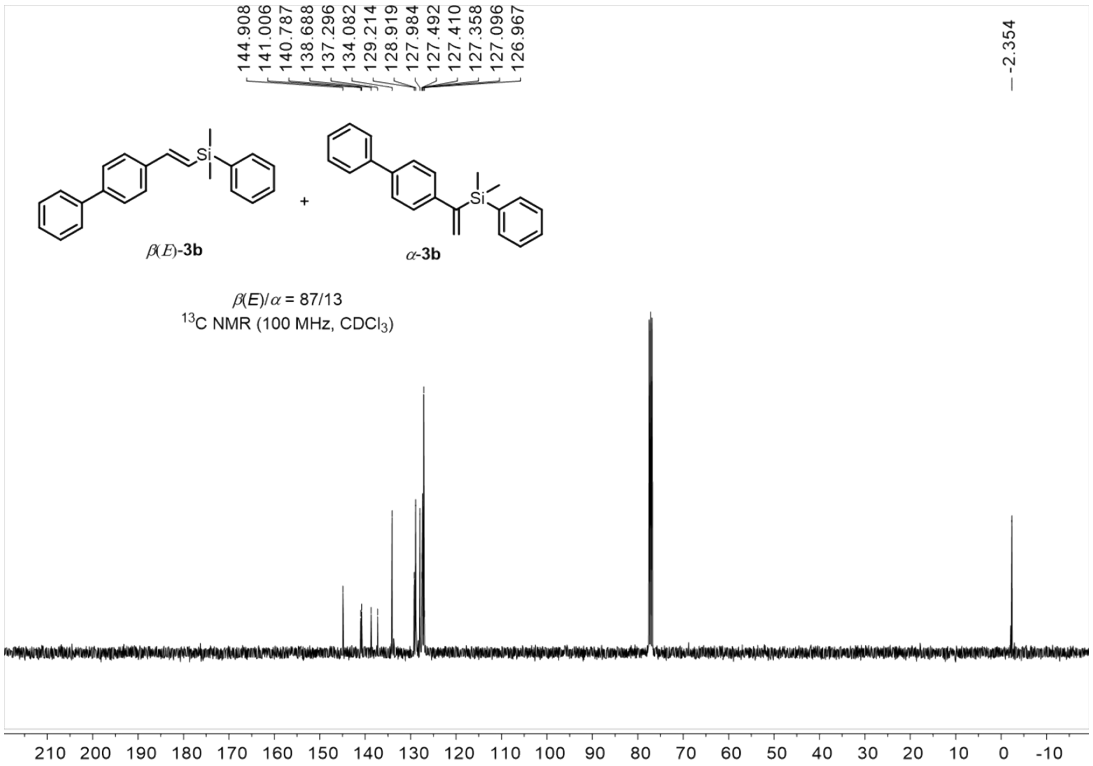
10. NMR Spectra

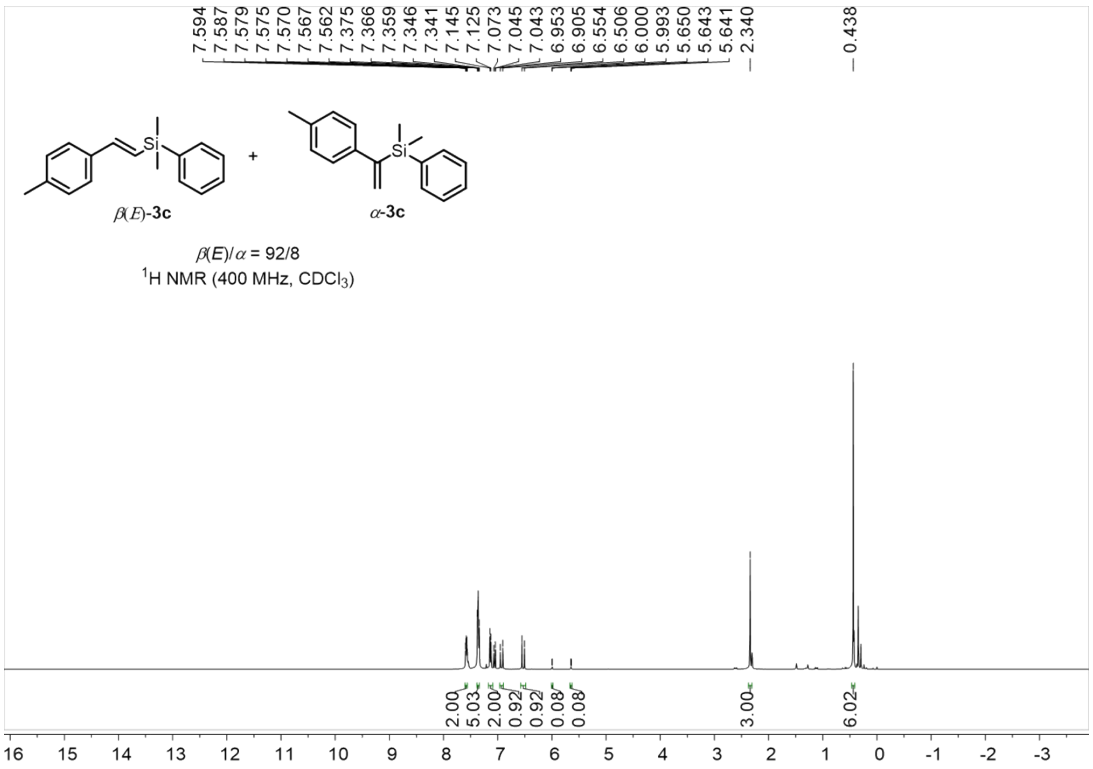


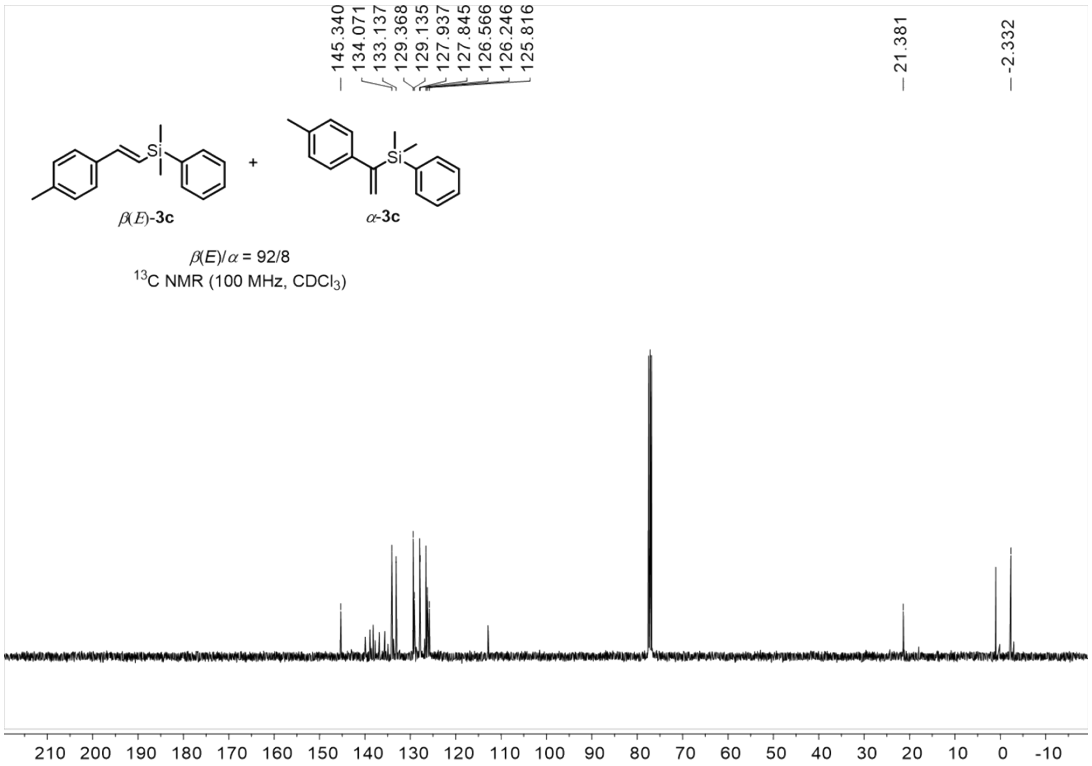


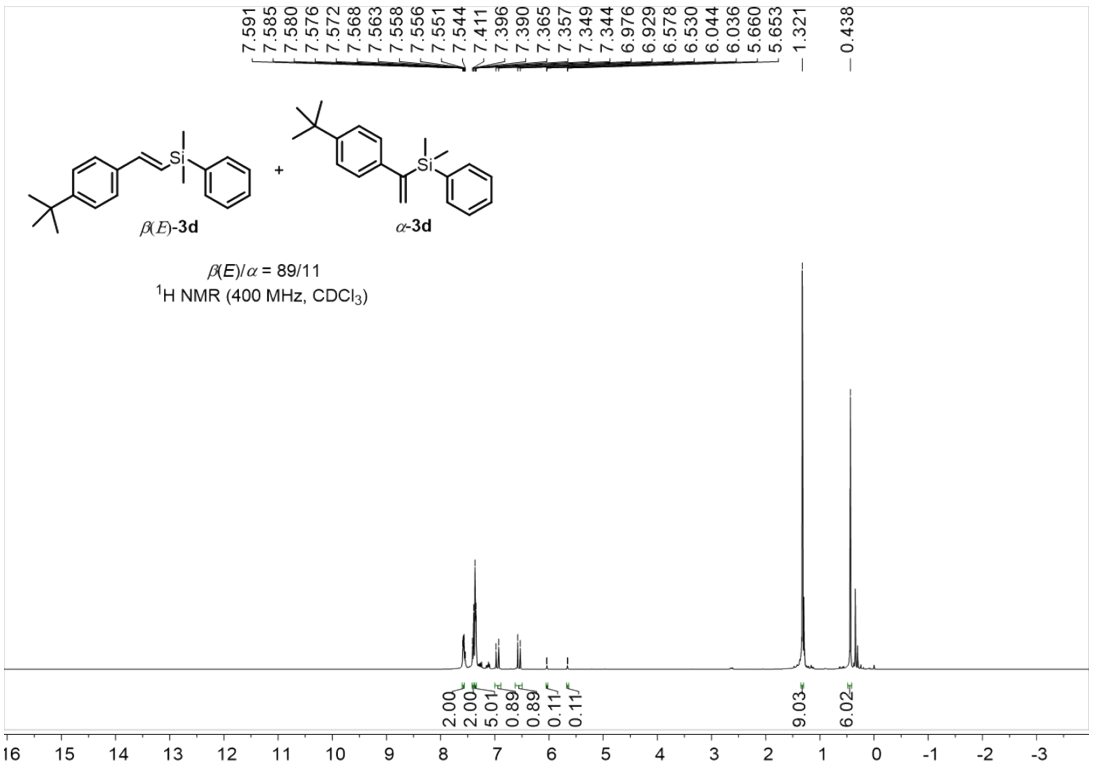

145.440
138.710
138.296
134.069
129.193
128.668
128.304
127.969
127.243
126.644
-2.367
β(E)-3a
α-3a
β(E)/α = 92/8
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

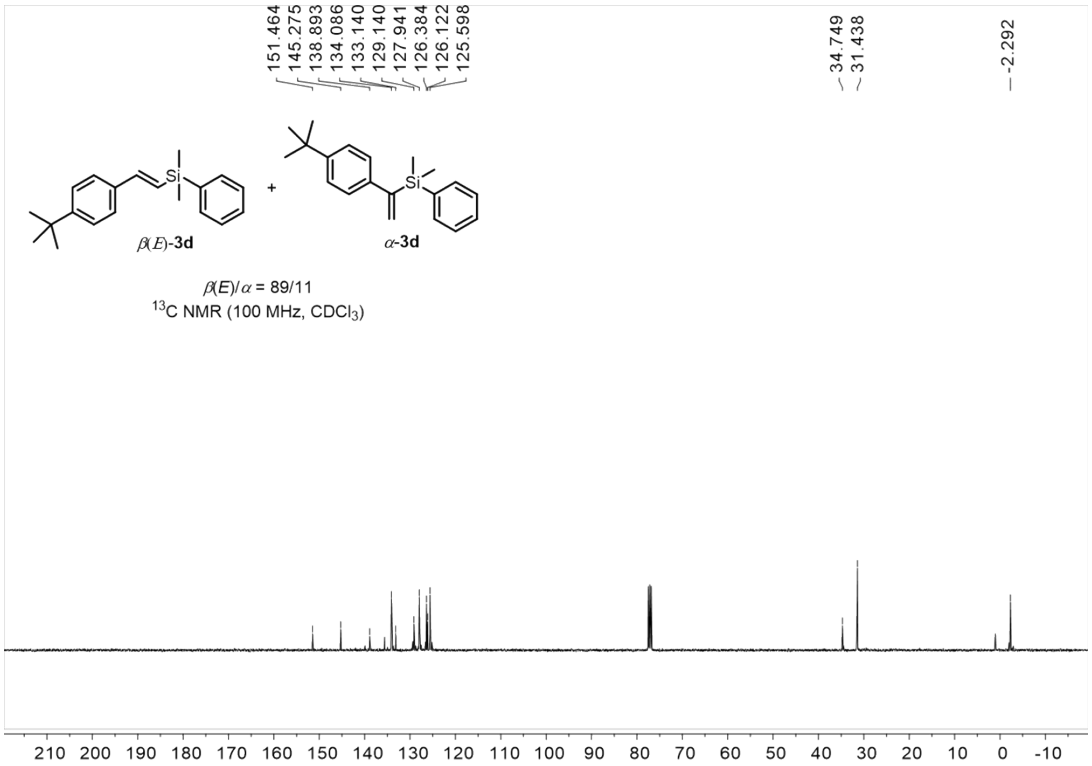

7.557
7.554
7.546
7.530
7.509
7.475
7.454
7.391
7.373
7.353
7.337
7.333
7.325
7.318
7.313
7.309
7.299
7.295
7.292
7.282
7.277
7.271
7.258
6.966
6.918
6.611
6.564
6.021
6.014
5.665
5.658
0.409
0.406
β(E)-3b
α-3b
β(E)/α = 87/13
1H NMR (400 MHz, CDCl3)
4.00
2.00
2.02
2.01
3.00
1.03
0.87
0.87
0.13
0.13
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

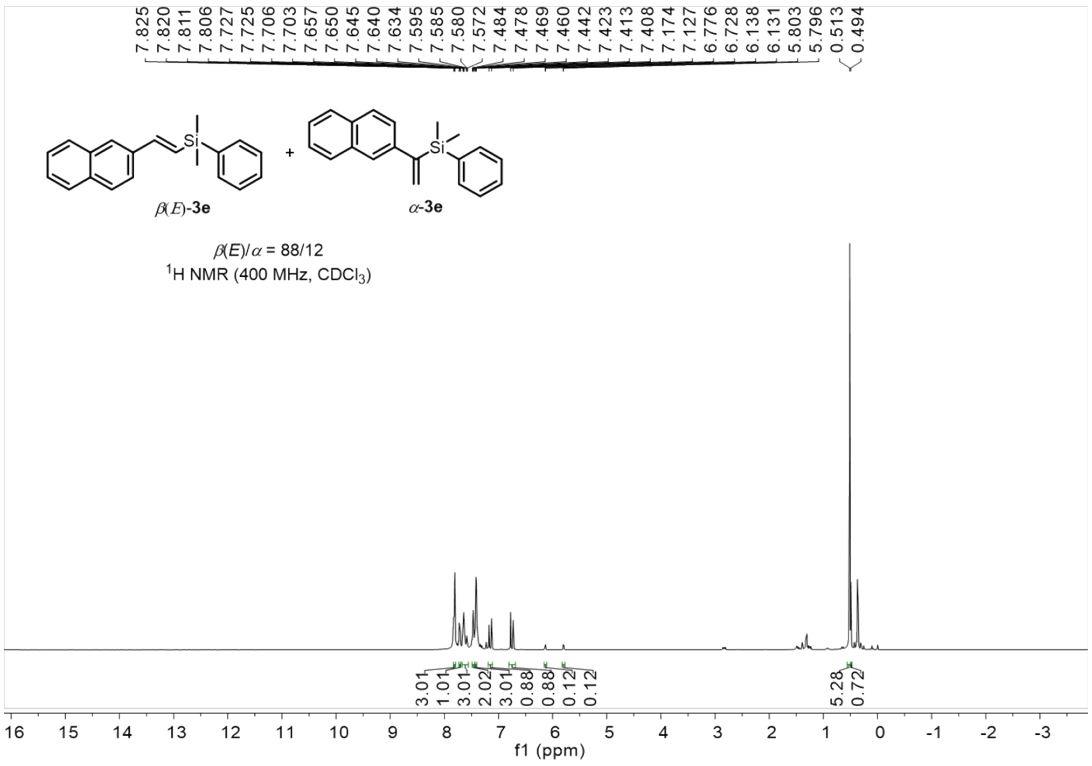

144.908
141.006
140.787
138.688
137.296
134.082
129.214
128.919
127.984
127.492
127.410
127.358
127.096
126.967
-2.354
β(E)-3b
α-3b
β(E)/α = 87/13
13C NMR (100 MHz, CDCl3)

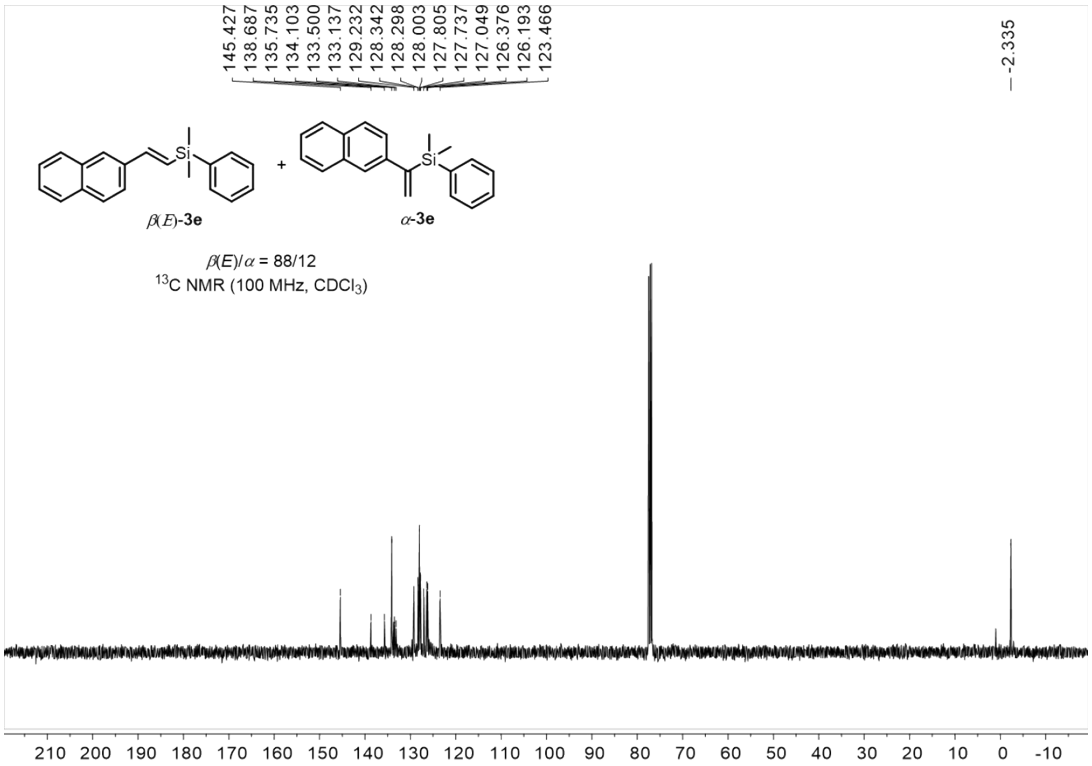

7.594
7.587
7.579
7.575
7.570
7.567
7.562
7.375
7.366
7.359
7.346
7.341
7.145
7.125
7.073
7.045
7.043
6.953
6.905
6.554
6.506
6.000
5.993
5.650
5.643
5.641
2.340
0.438
β(E)-3c
α-3c
β(E)/α = 92/8
1H NMR (400 MHz, CDCl3)
2.00
5.03
2.00
0.92
0.92
0.08
0.08
3.00
6.02


145.340
134.071
133.137
129.368
129.135
127.937
127.845
126.566
126.246
125.816
21.381
-2.332
β(E)-3c
α-3c
β(E)/α = 92/8
13C NMR (100 MHz, CDCl3)


7.591
7.585
7.580
7.576
7.572
7.568
7.563
7.558
7.556
7.551
7.544
7.411
7.396
7.390
7.365
7.357
7.349
7.344
6.976
6.929
6.578
6.530
6.044
6.036
5.660
5.653
1.321
0.438
β(E)-3d
α-3d
β(E)/α = 89/11
1H NMR (400 MHz, CDCl3)
2.00
2.00
5.01
0.89
0.89
0.11
0.11
9.03
6.02


151.464
145.275
138.893
134.086
133.140
129.140
127.941
126.384
126.122
125.598
34.749
31.438
-2.292
β(E)-3d
α-3d
β(E)/α = 89/11
13C NMR (100 MHz, CDCl3)


7.825
7.820
7.811
7.806
7.727
7.725
7.706
7.703
7.657
7.650
7.645
7.640
7.634
7.595
7.585
7.580
7.572
7.484
7.478
7.469
7.460
7.442
7.423
7.413
7.408
7.174
7.127
6.776
6.728
6.138
6.131
5.803
5.796
0.513
0.494
β(E)-3e
α-3e
β(E)/α = 88/12
1H NMR (400 MHz, CDCl3)
3.01
1.01
3.01
2.02
3.01
0.88
0.88
0.12
0.12
5.28
0.72
f1 (ppm)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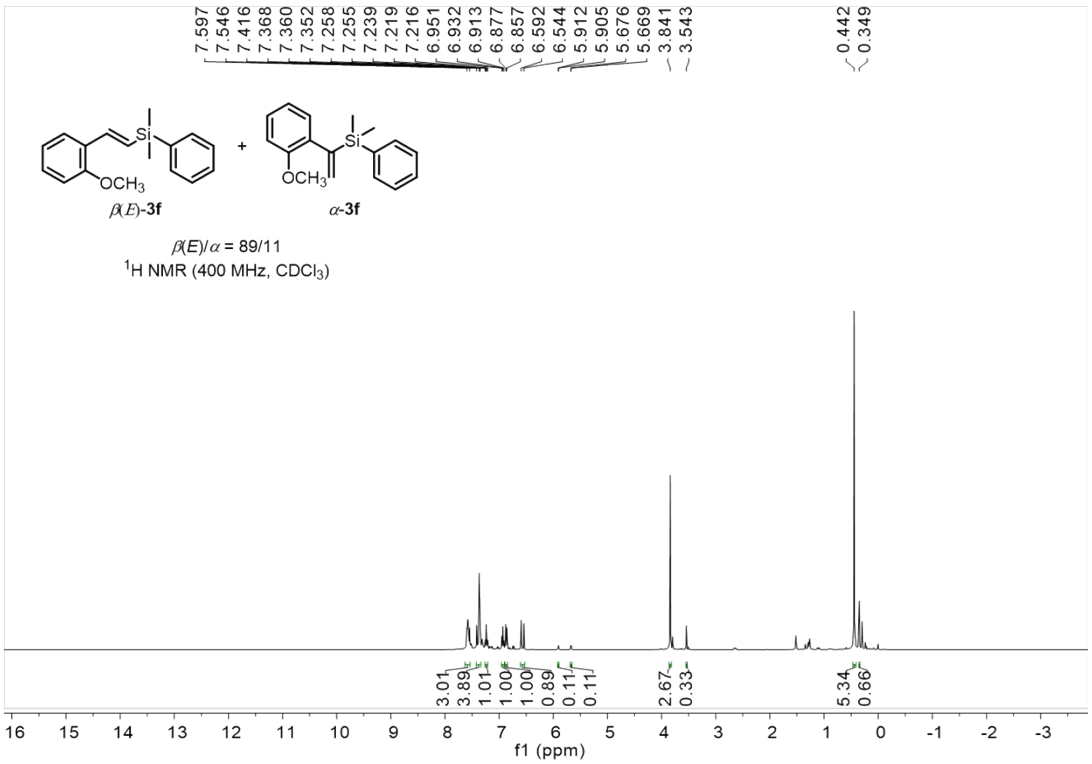
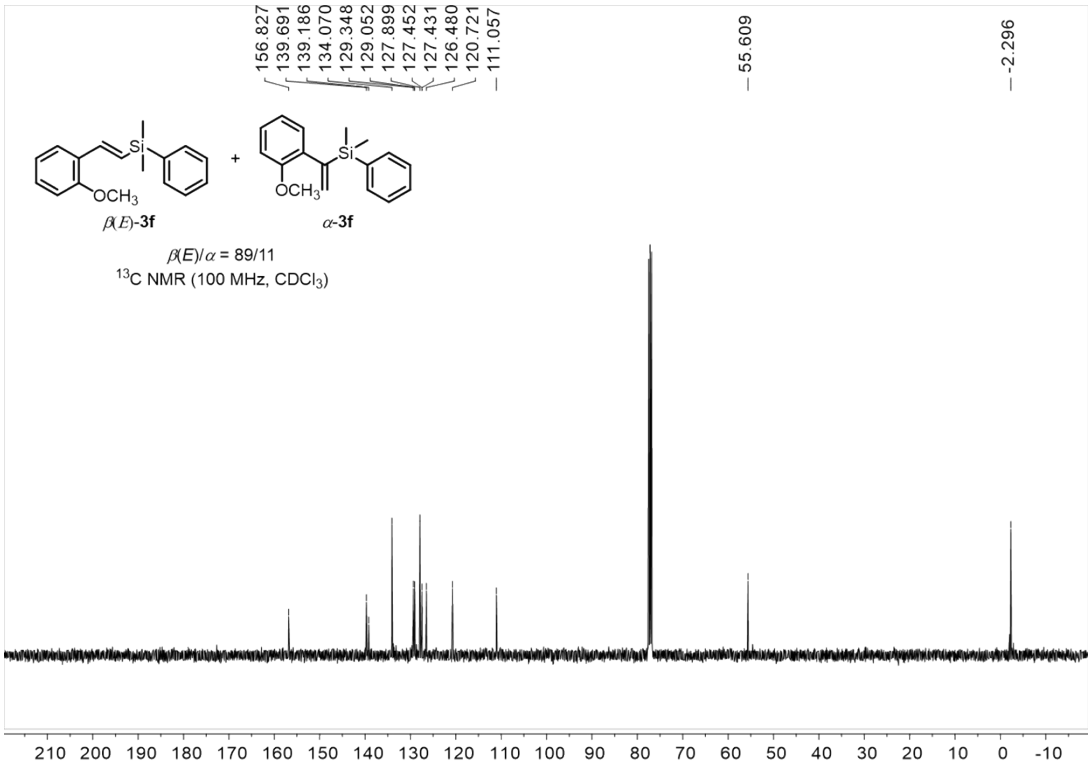
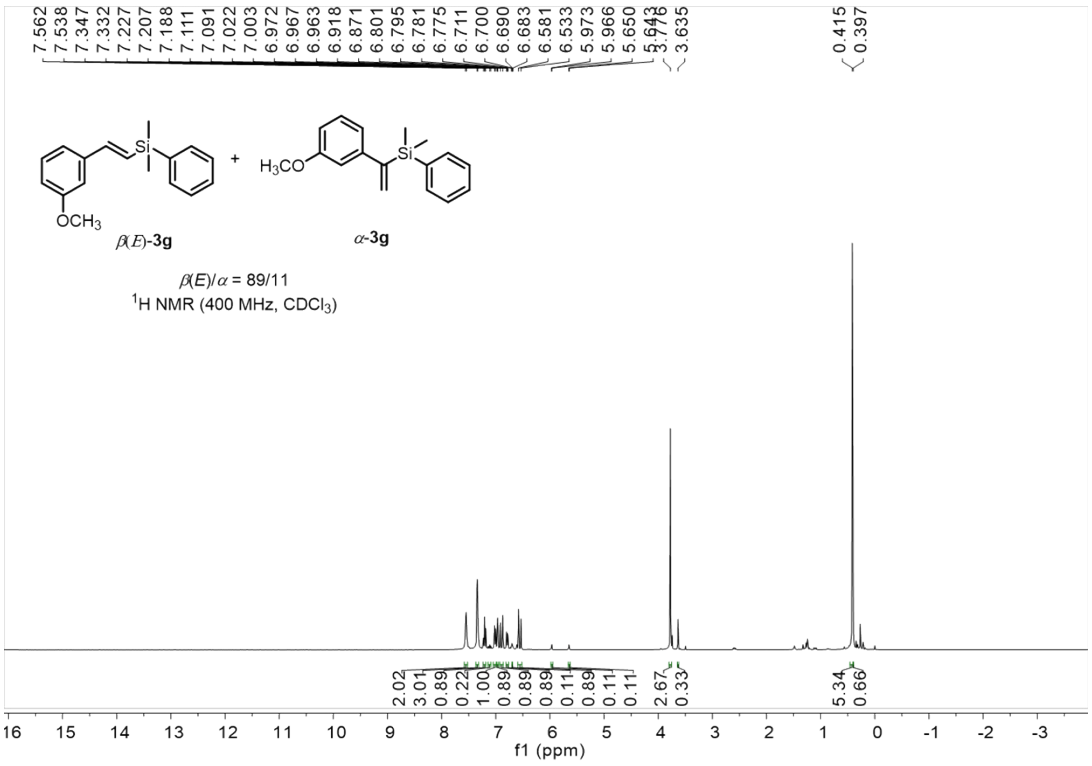
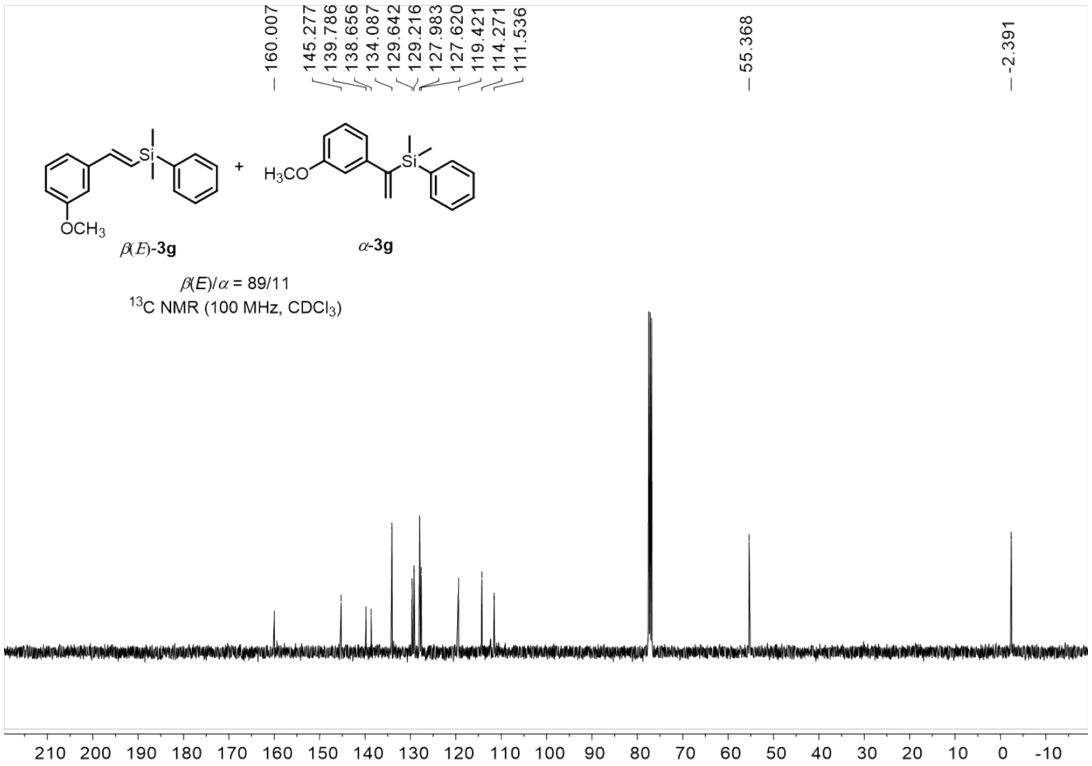
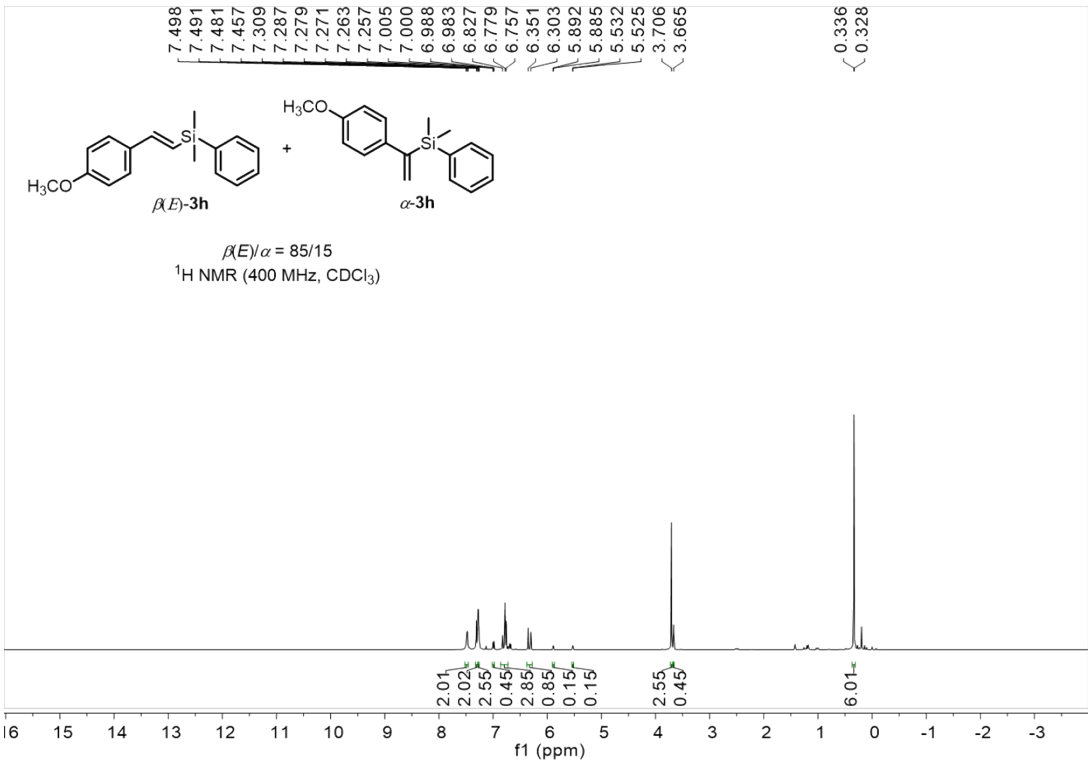
138.687
135.735
134.103
133.500
133.137
129.232
128.342
128.298
128.003
127.805
127.737
127.049
126.376
126.193
123.466
-2.335
β(E)-3e
α-3e
β(E)/α = 88/12
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

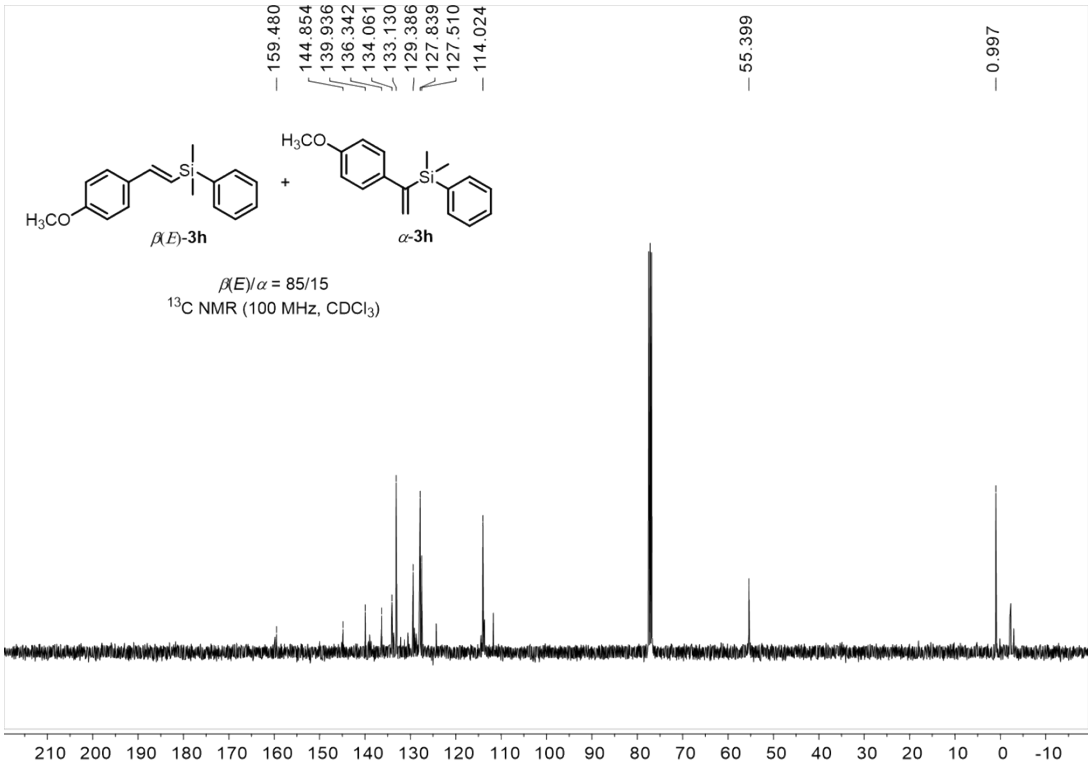

7.597
7.546
7.416
7.368
7.360
7.352
7.258
7.255
7.239
7.219
7.216
6.951
6.932
6.913
6.877
6.857
6.592
6.544
5.912
5.905
5.676
5.669
3.841
3.543
0.442
0.349
OCH3
β(E)-3f
α-3f
β(E)/α = 89/11
1H NMR (400 MHz, CDCl3)
3.01
3.89
1.01
1.00
1.00
0.89
0.11
0.11
2.67
0.33
5.34
0.66
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

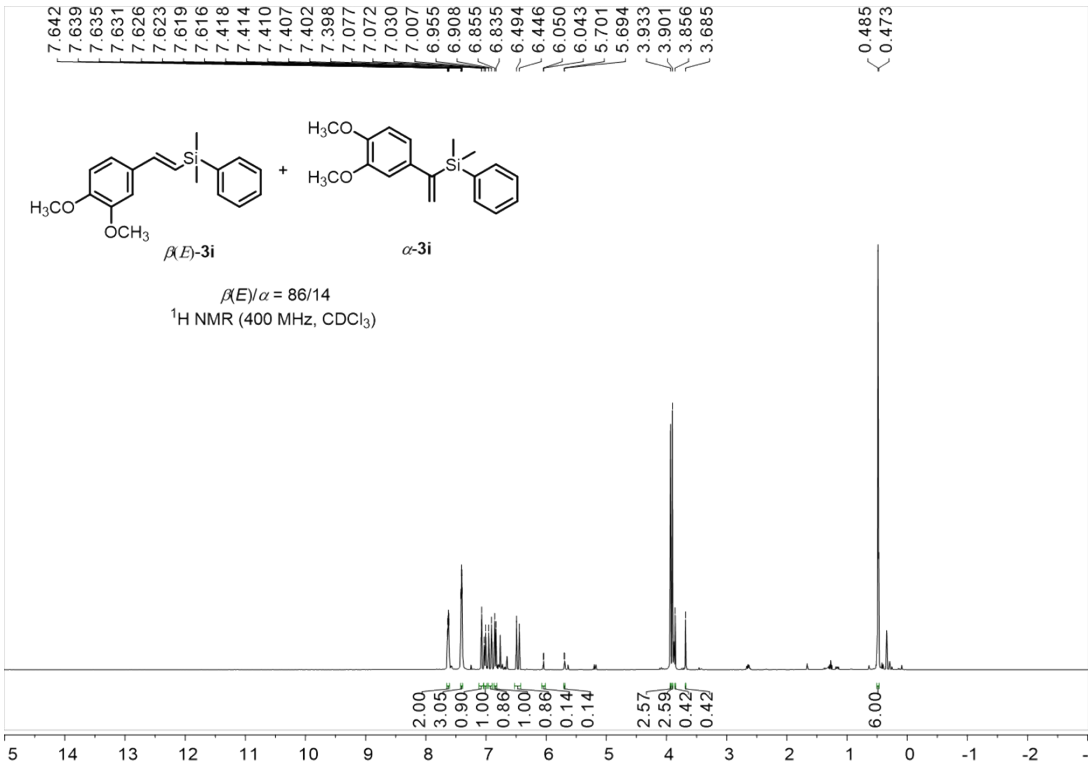

156.827
139.691
139.186
134.070
129.348
129.052
127.899
127.452
127.431
126.480
120.721
111.057
55.609
-2.296
OCH3
β(E)-3f
α-3f
β(E)/α = 89/11
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

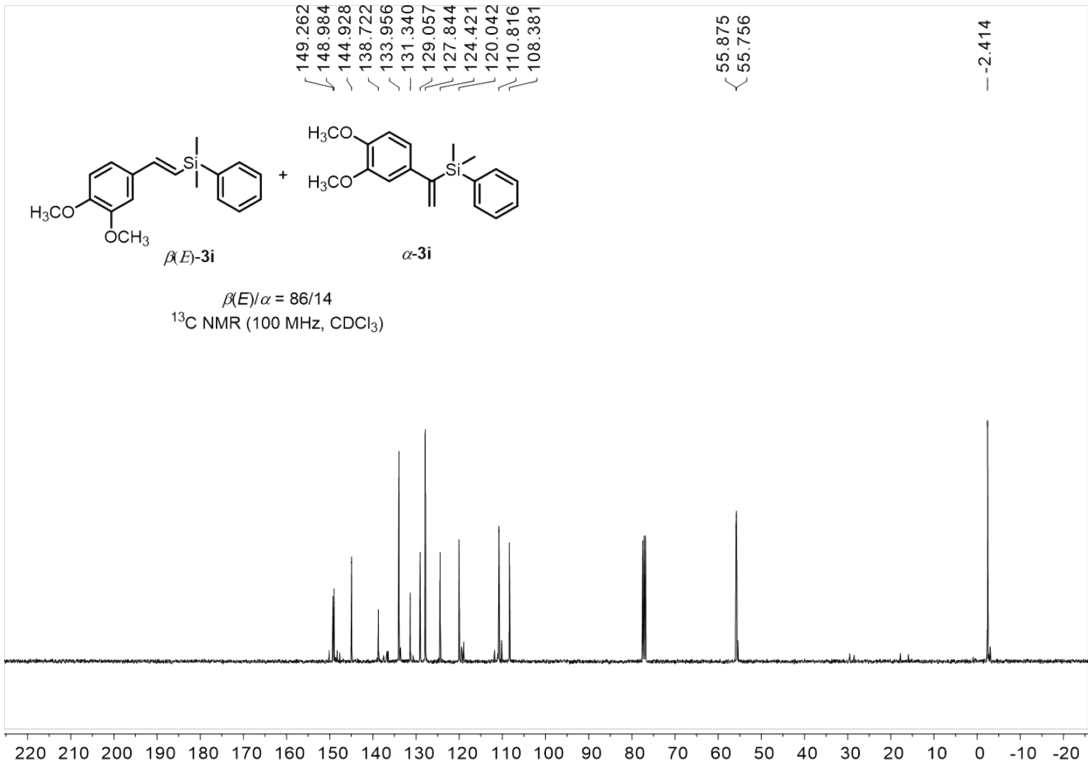

7.562
7.538
7.347
7.332
7.227
7.207
7.188
7.111
7.091
7.022
7.003
6.972
6.967
6.963
6.918
6.871
6.801
6.795
6.781
6.775
6.711
6.700
6.690
6.683
6.581
6.533
5.973
5.966
5.650
3.635
0.415
0.397
H3CO
OCH3
β(E)-3g
α-3g
β(E)/α = 89/11
1H NMR (400 MHz, CDCl3)
2.02
3.01
0.89
0.22
1.00
0.89
0.89
0.89
0.11
0.89
0.11
0.11
2.67
0.33
5.34
0.66
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

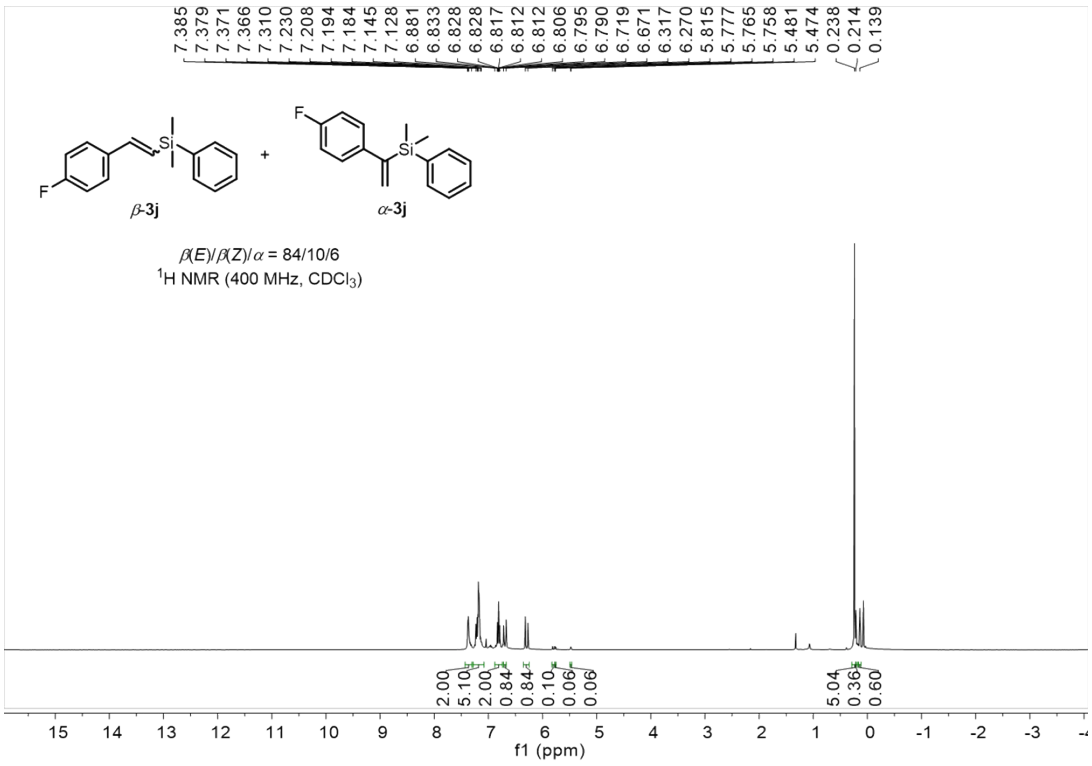

160.007
145.277
139.786
138.656
134.087
129.642
129.216
127.983
127.620
119.421
114.271
111.536
55.368
-2.391
OCH3
H3CO
Si
β(E)-3g
α-3g
β(E)/α = 89/11
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

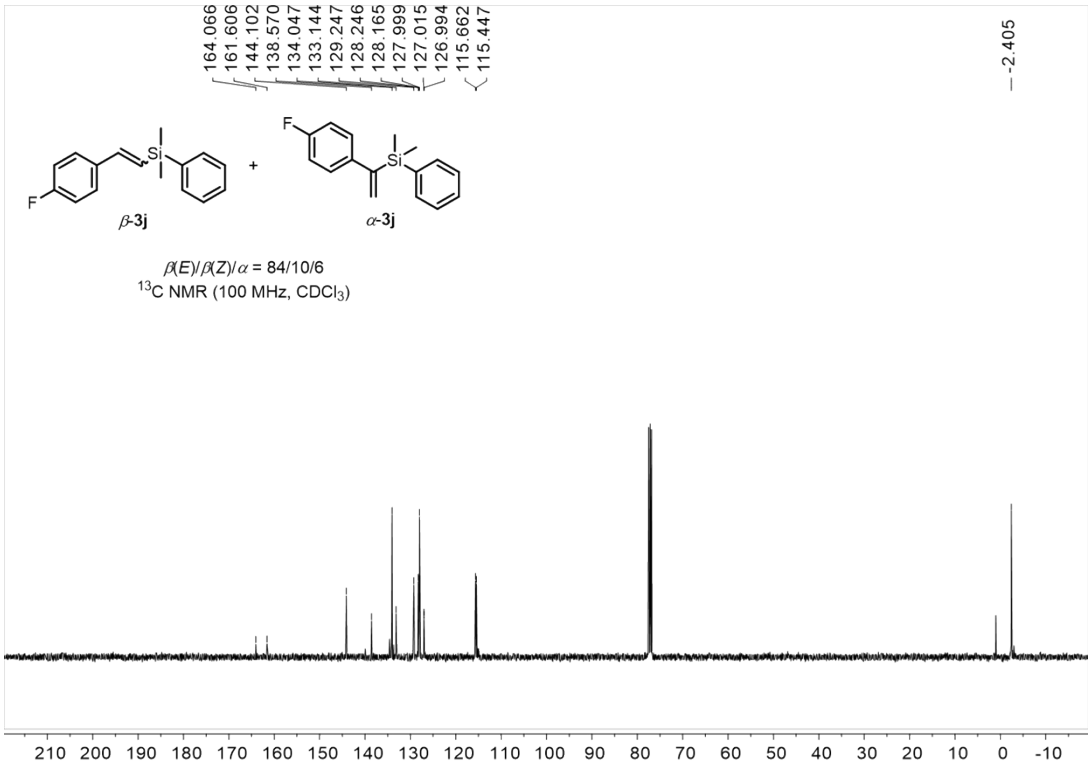

7.498
7.491
7.481
7.457
7.309
7.287
7.279
7.271
7.263
7.257
7.005
7.000
6.988
6.983
6.827
6.779
6.757
6.351
6.303
5.892
5.885
5.532
5.525
3.706
3.665
0.336
0.328
H3CO
Si
β(E)-3h
α-3h
β(E)/α = 85/15
1H NMR (400 MHz, CDCl3)
2.01
2.02
2.55
0.45
2.85
0.85
0.15
0.15
2.55
0.45
6.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

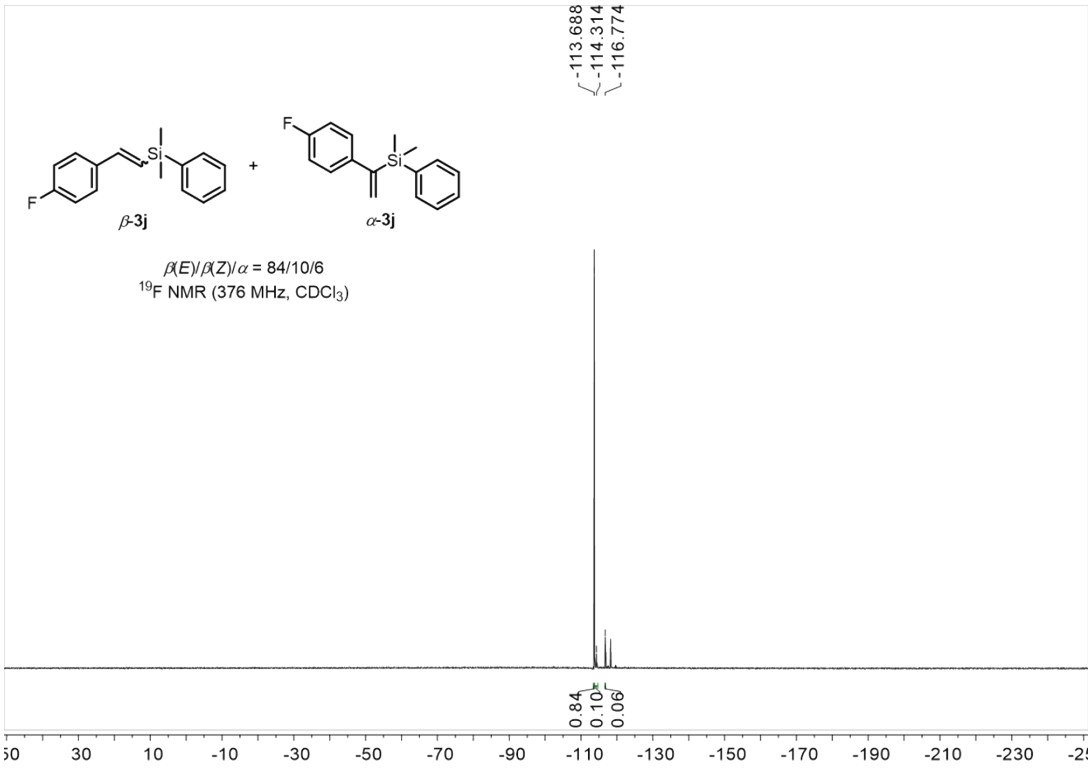

159.480
144.854
139.936
136.342
134.061
133.130
129.386
127.839
127.510
114.024
55.399
0.997
H3CO
Si
+
H3CO
Si
β(E)-3h
α-3h
β(E)/α = 85/15
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

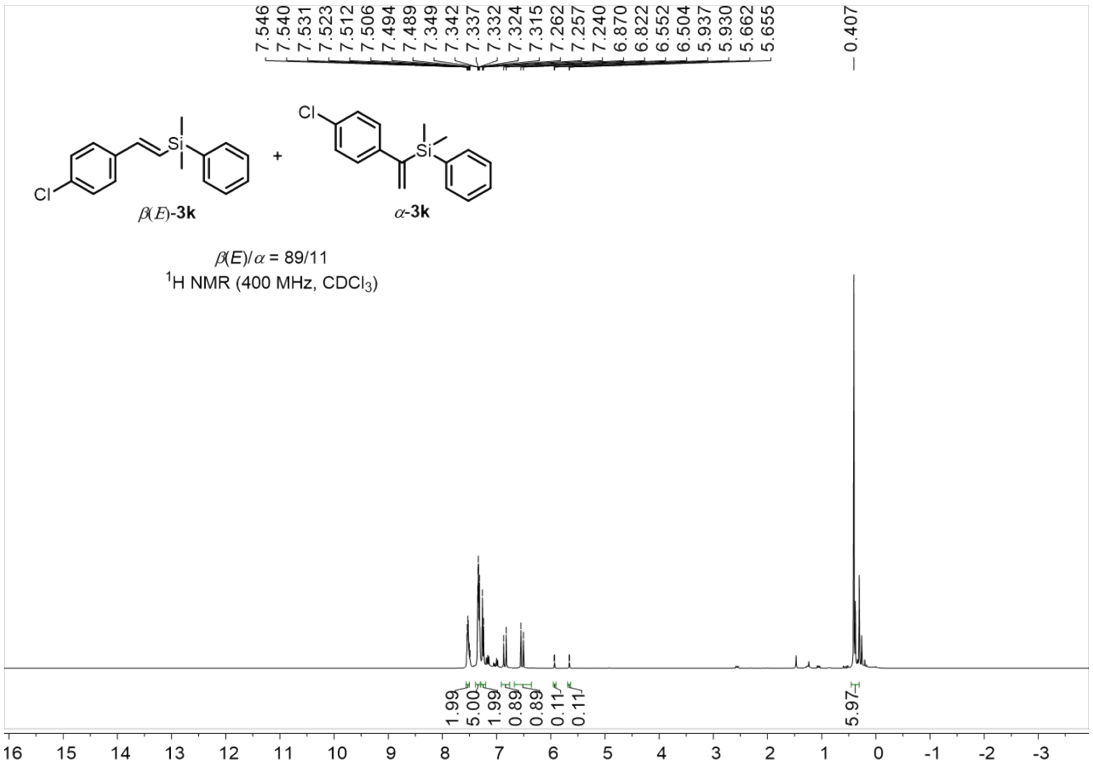

7.642
7.639
7.635
7.631
7.626
7.623
7.619
7.616
7.418
7.414
7.410
7.407
7.402
7.398
7.077
7.072
7.030
7.007
6.955
6.908
6.855
6.835
6.494
6.446
6.050
6.043
5.701
5.694
3.933
3.901
3.856
3.685
0.485
0.473
H3CO
OCH3
Si
+
H3CO
H3CO
Si
β(E)-3i
α-3i
β(E)/α = 86/14
1H NMR (400 MHz, CDCl3)
2.00
3.05
0.90
1.00
0.86
1.00
0.86
0.14
0.14
2.57
2.59
0.42
0.42
6.00
5 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -

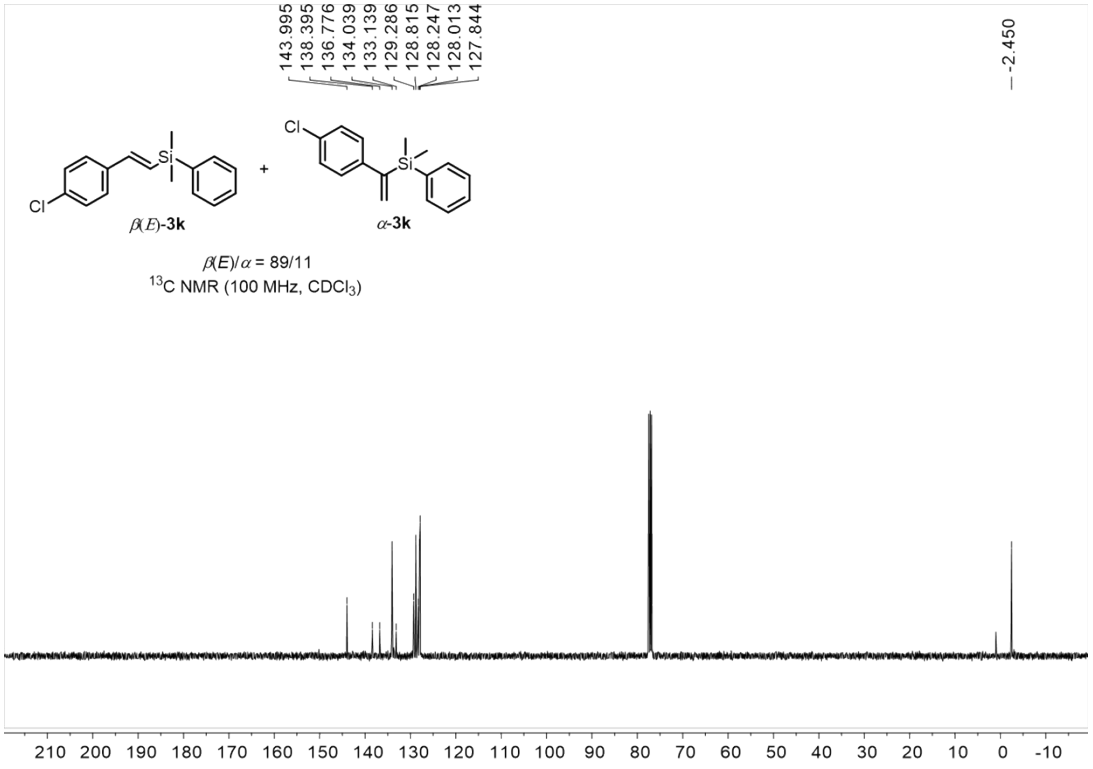

149.262
148.984
144.928
138.722
133.956
131.340
129.057
127.844
124.421
120.042
110.816
108.381
55.875
55.756
-2.414
H3CO
OCH3
Si
+
H3CO
H3CO
Si
β(E)-3i
α-3i
β(E)/α = 86/14
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

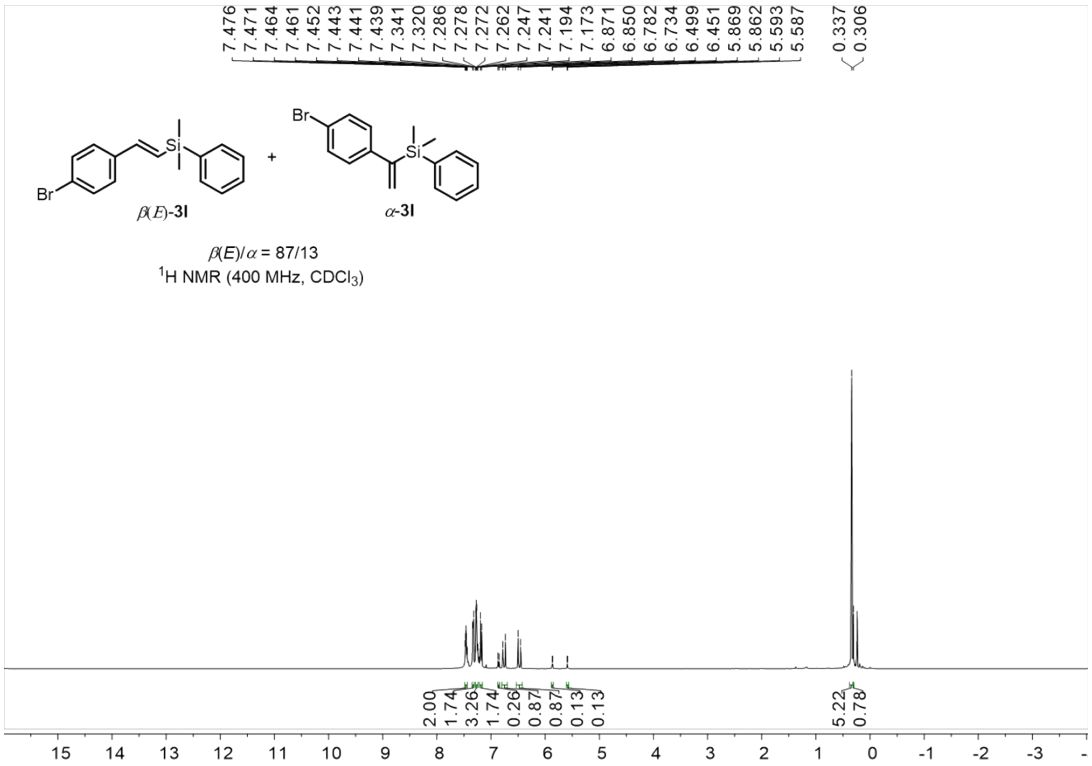

7.385
7.379
7.371
7.366
7.310
7.230
7.208
7.194
7.184
7.145
7.128
6.881
6.833
6.828
6.828
6.817
6.812
6.812
6.806
6.795
6.790
6.719
6.671
6.317
6.270
5.815
5.777
5.765
5.758
5.481
5.474
0.238
0.214
0.139
F
Si
+
F
Si
β-3j
α-3j
β(E)/β(Z)/α = 84/10/6
1H NMR (400 MHz, CDCl3)
2.00
5.10
2.00
0.84
0.84
0.10
0.06
0.06
5.04
0.36
0.60
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

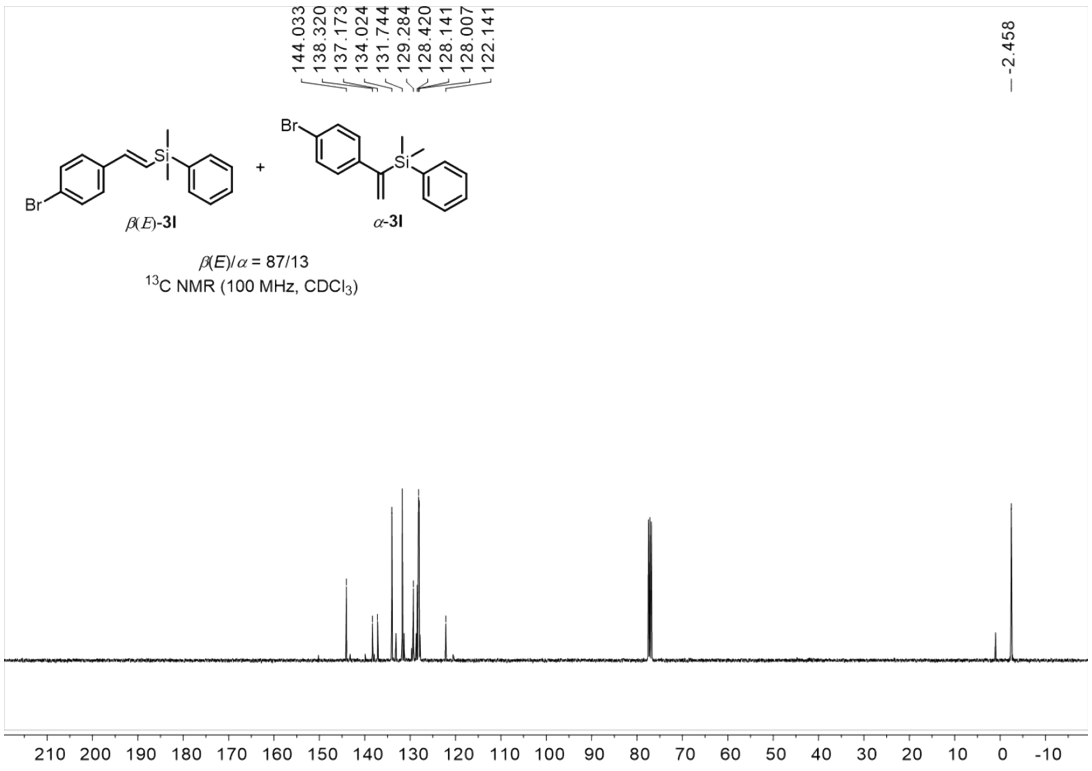

164.066
161.606
144.102
138.570
134.047
133.144
129.247
128.246
128.165
127.999
127.015
126.994
115.662
115.447
-2.405
F
Si
+
F
Si
β-3j
α-3j
β(E)/β(Z)/α = 84/10/6
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

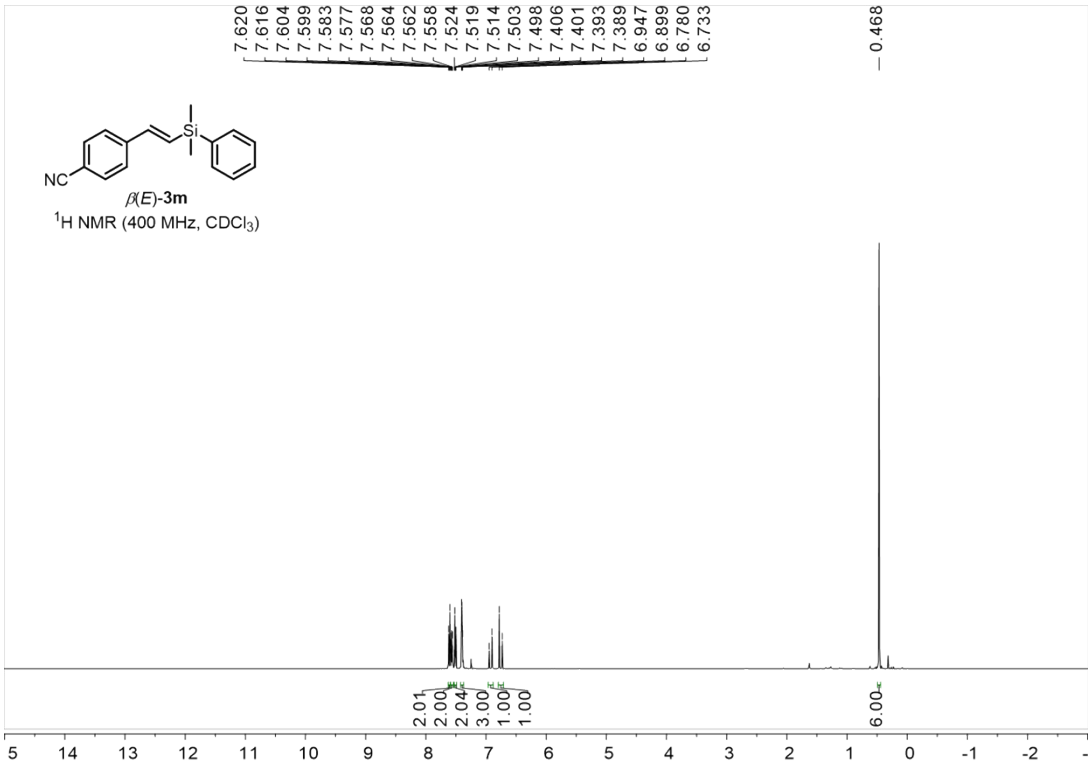

-113.688
-114.314
-116.774
F
Si
+
F
Si
β-3j
α-3j
β(E)/β(Z)/α = 84/10/6
19F NMR (376 MHz, CDCl3)
0.84
0.10
0.06
50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25

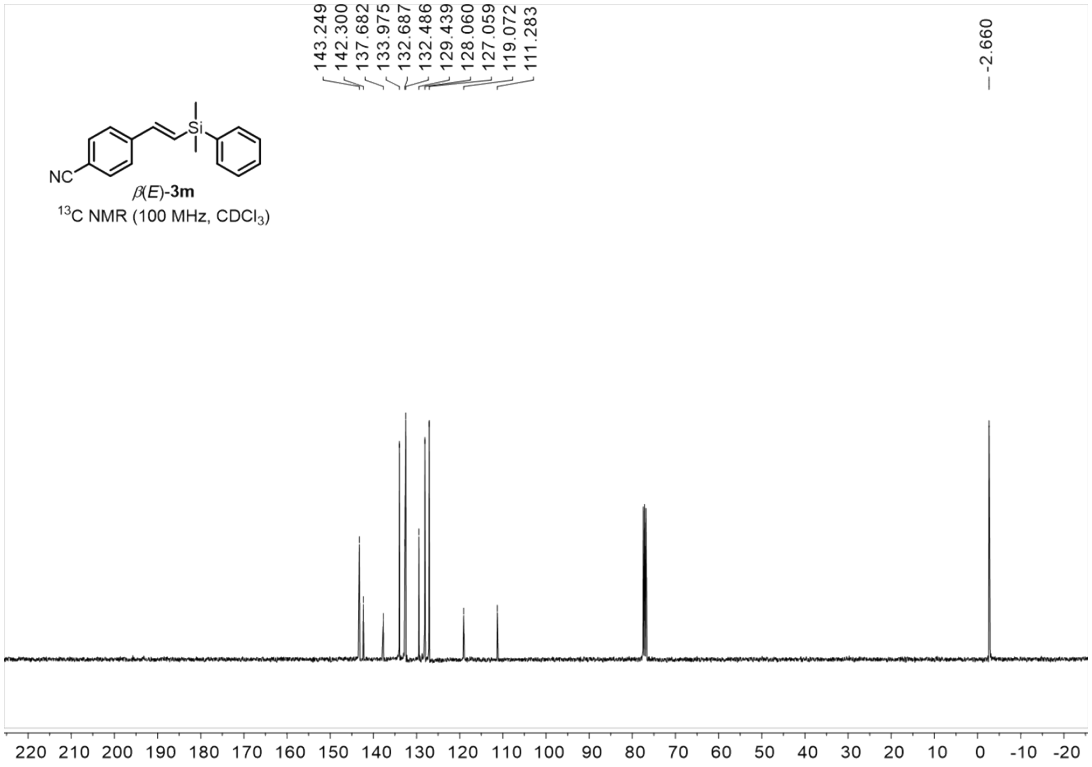

7.546
7.540
7.531
7.523
7.512
7.506
7.494
7.489
7.349
7.342
7.337
7.332
7.324
7.315
7.262
7.257
7.240
6.870
6.822
6.552
6.504
5.937
5.930
5.662
5.655
0.407
Cl
Si
+
Cl
Si
β(E)-3k
α-3k
β(E)/α = 89/11
1H NMR (400 MHz, CDCl3)
1.99
5.00
1.99
0.89
0.89
0.11
0.11
5.97
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

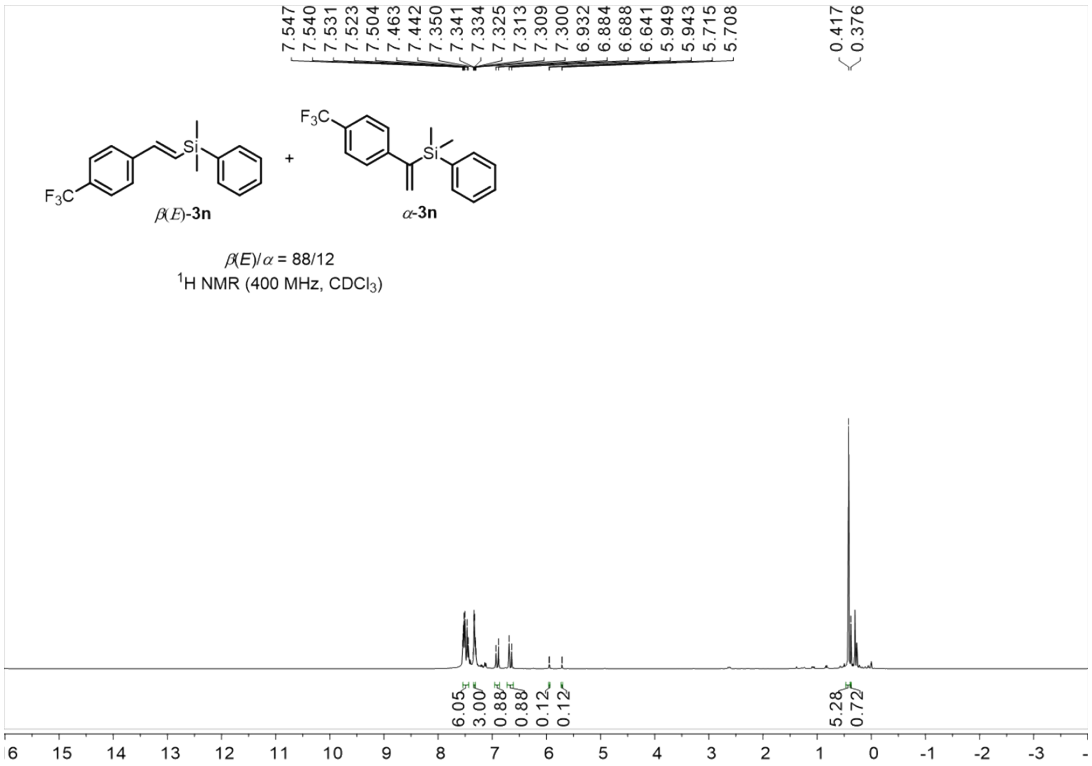

143.995
138.395
136.776
134.039
133.139
129.286
128.815
128.247
128.013
127.844
-2.450
Cl
Si
+
Cl
Si
β(E)-3k
α-3k
β(E)/α = 89/11
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

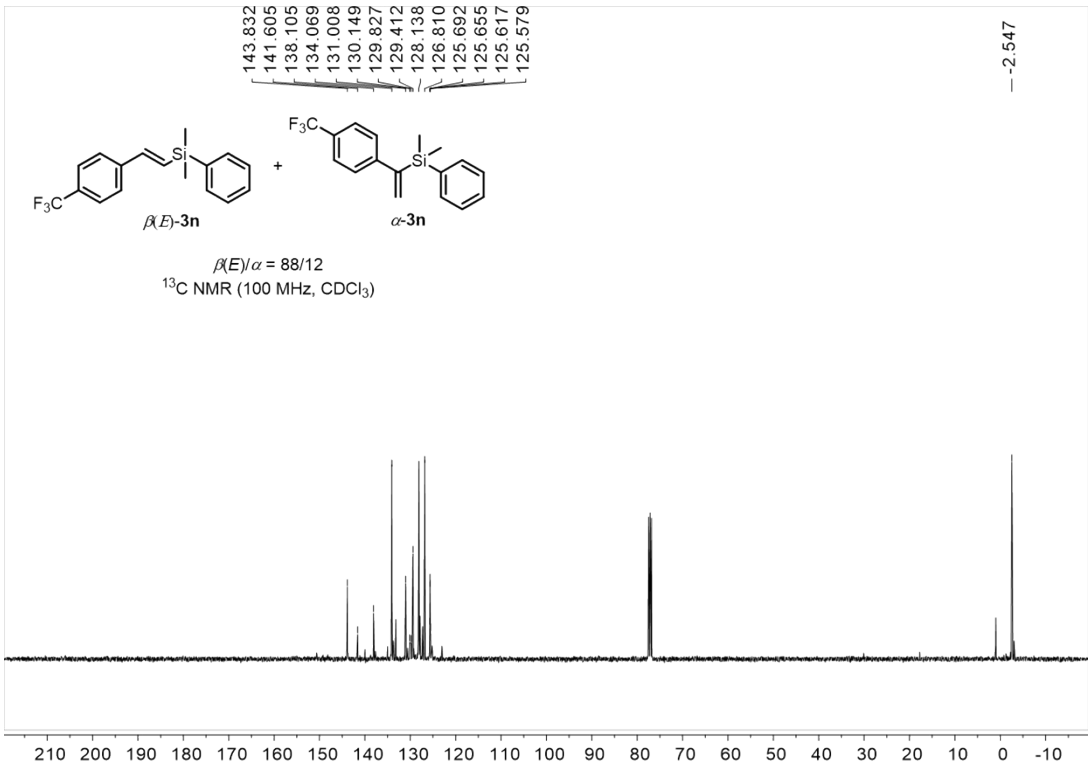

7.476
7.471
7.464
7.461
7.452
7.443
7.441
7.439
7.341
7.320
7.286
7.278
7.272
7.262
7.247
7.241
7.194
7.173
6.871
6.850
6.782
6.734
6.499
6.451
5.869
5.862
5.593
5.587
0.337
0.306
Br
Si
+
Br
Si
β(E)-3l
α-3l
β(E)/α = 87/13
1H NMR (400 MHz, CDCl3)
2.00
1.74
3.26
1.74
0.26
0.87
0.87
0.13
0.13
5.22
0.78
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3

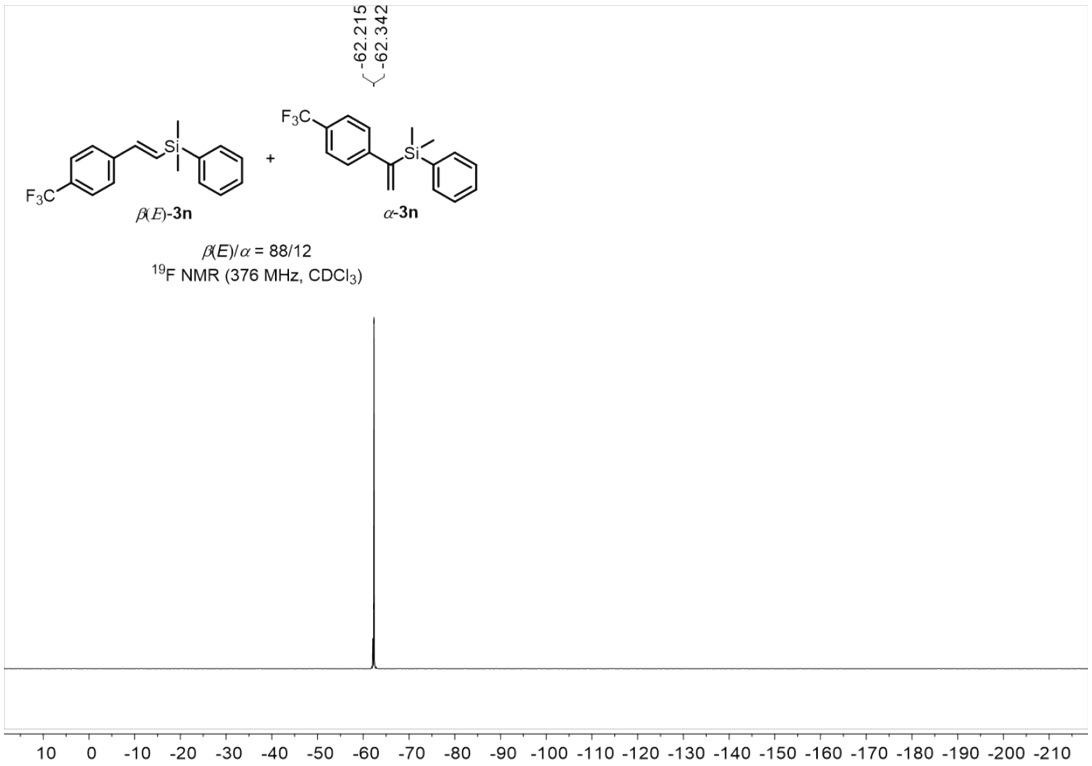

144.033
138.320
137.173
134.024
131.744
129.284
128.420
128.141
128.007
122.141
-2.458
Br
Si
+
Br
Si
β(E)-3l
α-3l
β(E)/α = 87/13
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

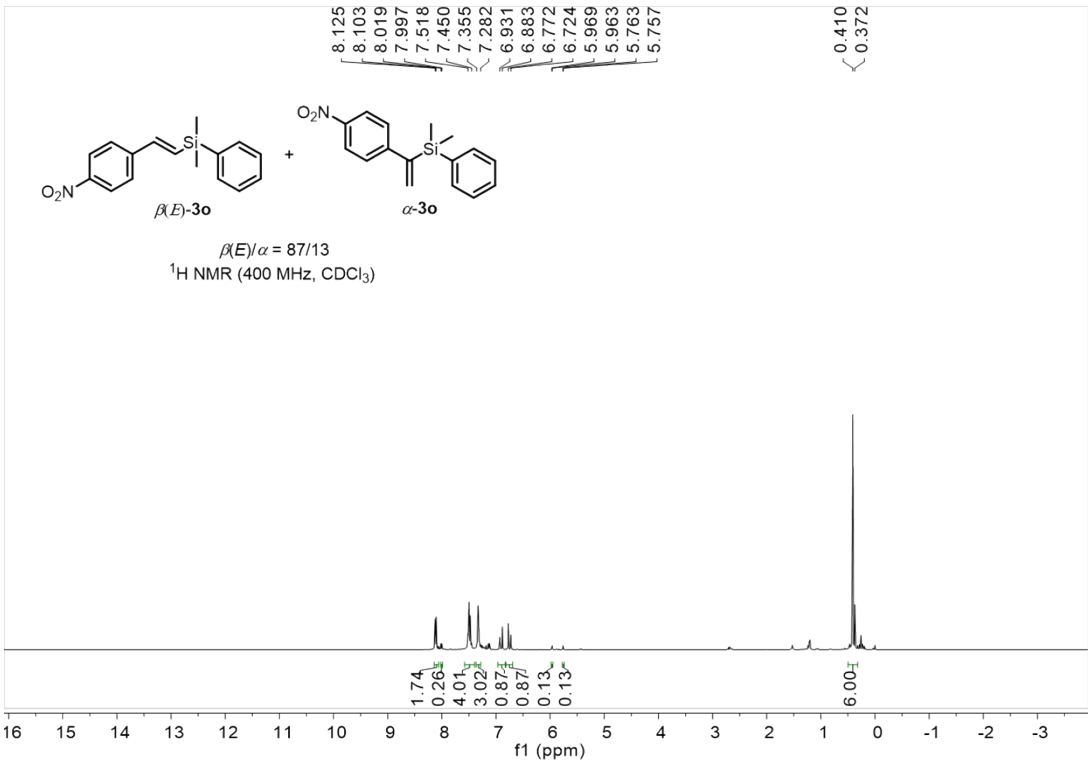

7.620
7.616
7.604
7.599
7.583
7.577
7.568
7.564
7.562
7.558
7.524
7.519
7.514
7.503
7.498
7.406
7.401
7.393
7.389
6.947
6.899
6.780
6.733
0.468
NC
Si
β(E)-3m
1H NMR (400 MHz, CDCl3)
2.01
2.00
2.04
3.00
1.00
1.00
6.00
5 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2

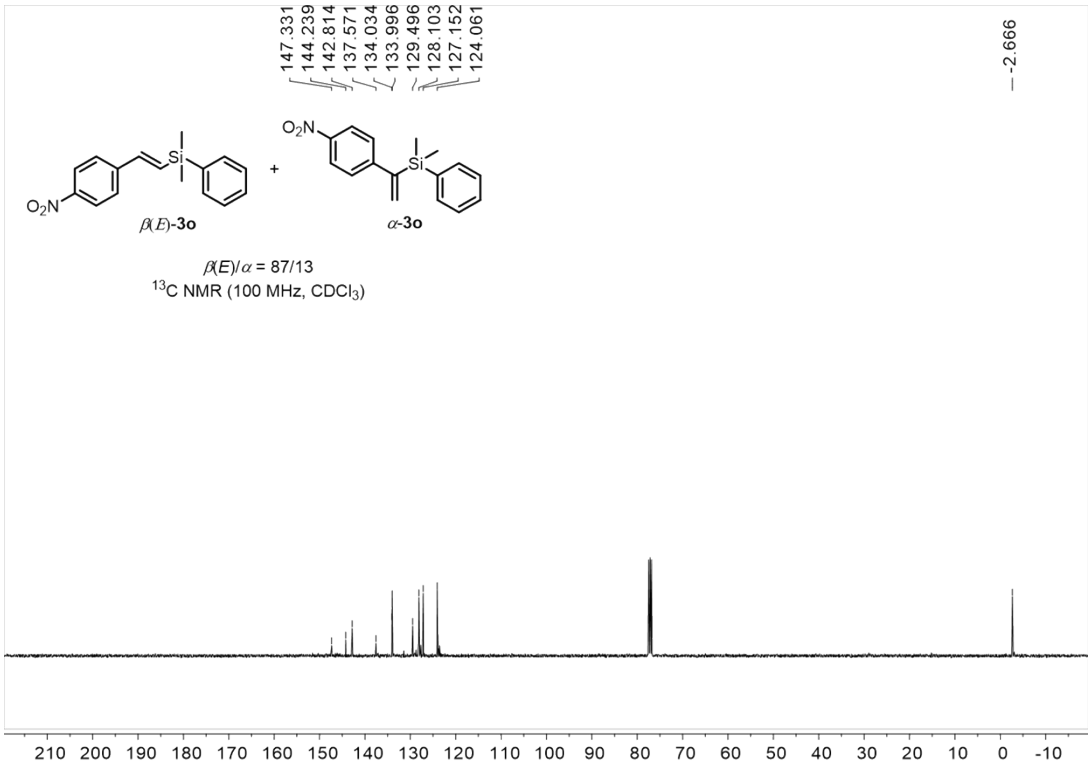

143.249
142.300
137.682
133.975
132.687
132.486
129.439
128.060
127.059
119.072
111.283
-2.660
NC
Si
β(E)-3m
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

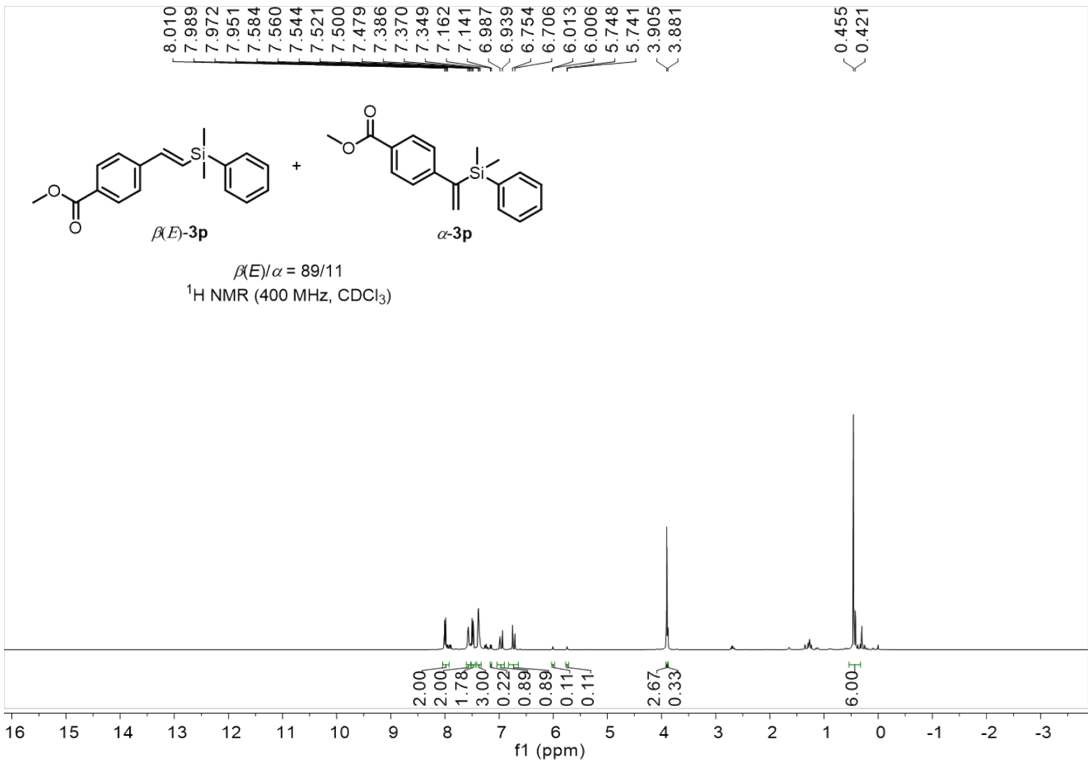

7.547
7.540
7.531
7.523
7.504
7.463
7.442
7.350
7.341
7.334
7.325
7.313
7.309
7.300
6.932
6.884
6.688
6.641
5.949
5.943
5.715
5.708
0.417
0.376
F3C
Si
β(E)-3n
α-3n
β(E)/α = 88/12
1H NMR (400 MHz, CDCl3)
6.05
3.00
0.88
0.88
0.12
0.12
5.28
0.72

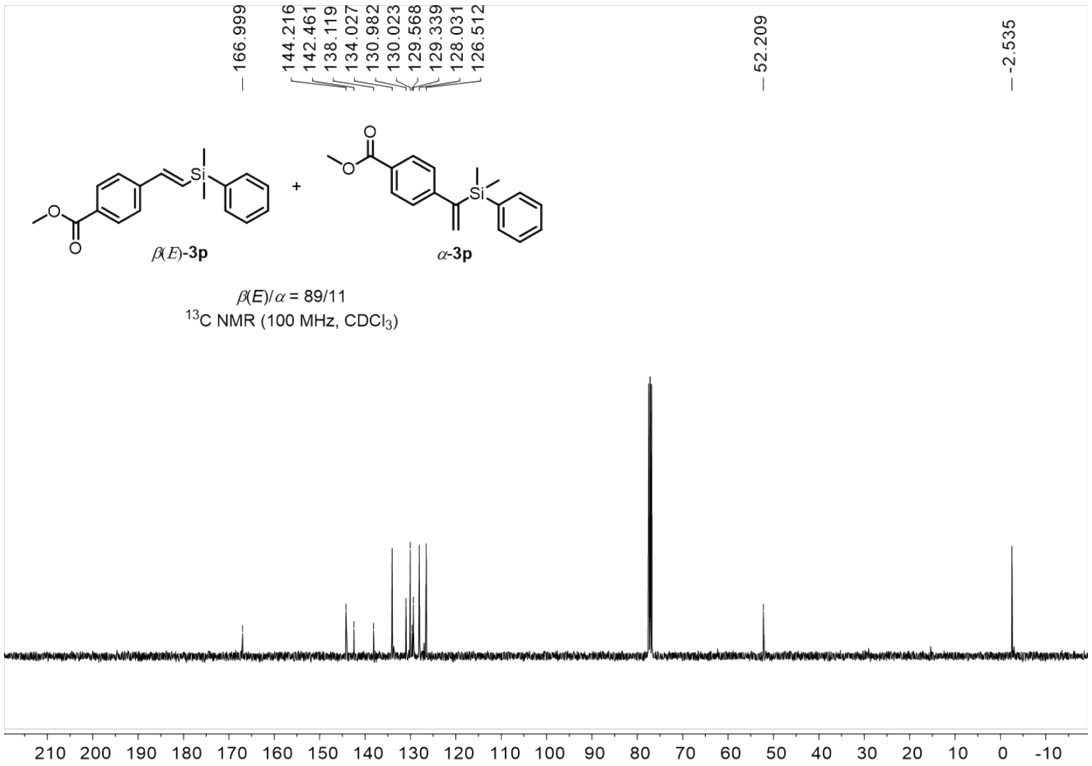

143.832
141.605
138.105
134.069
131.008
130.149
129.827
129.412
128.138
126.810
125.692
125.655
125.617
125.579
-2.547
F3C
Si
β(E)-3n
α-3n
β(E)/α = 88/12
13C NMR (100 MHz, CDCl3)

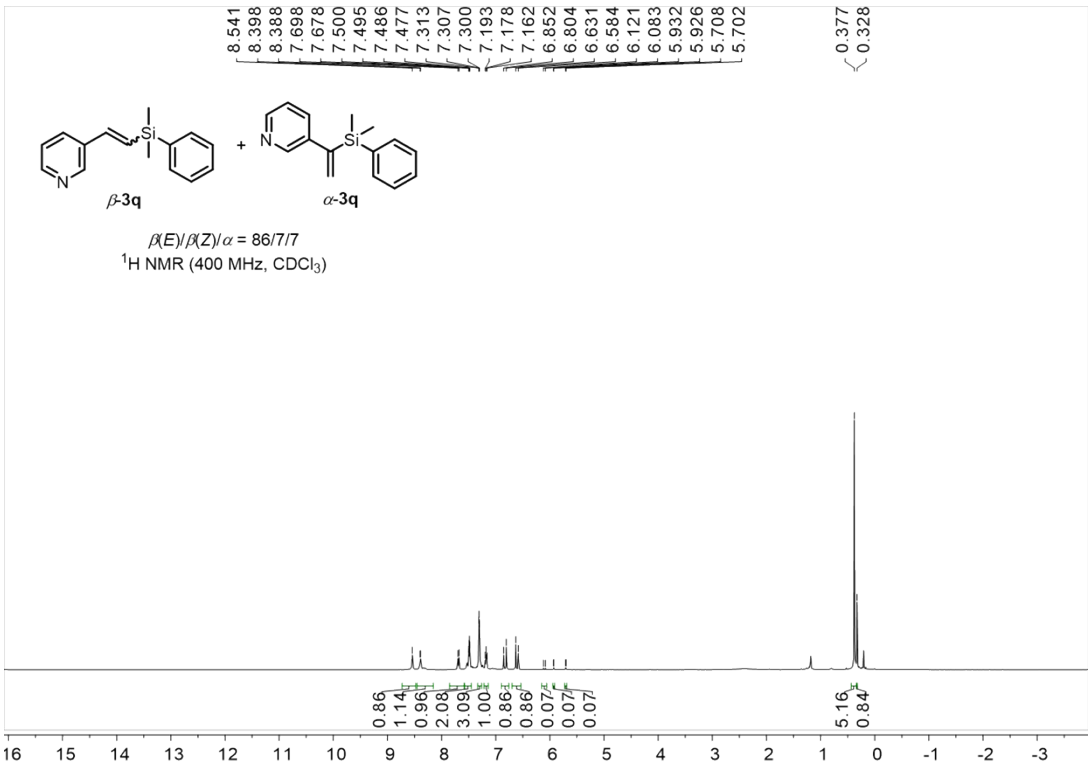

-62.215
-62.342
F3C
Si
+
F3C
Si
β(E)-3n
α-3n
β(E)/α = 88/12
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

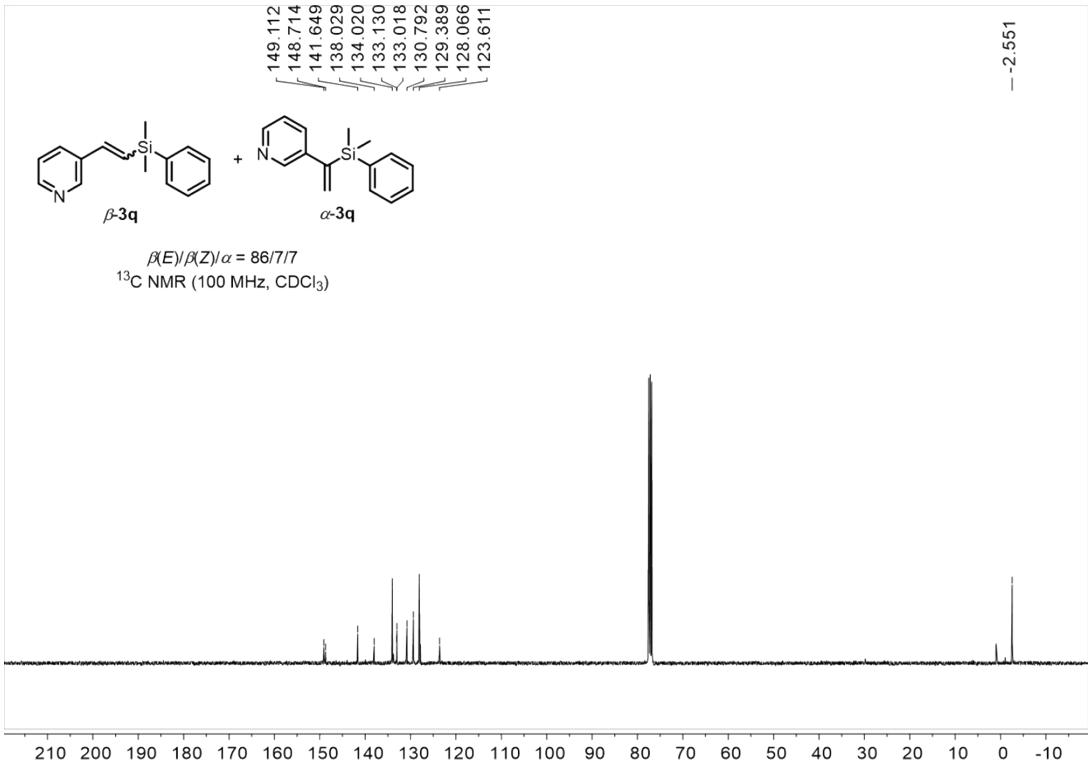

8.125
8.103
8.019
7.997
7.518
7.450
7.355
7.282
6.931
6.883
6.772
6.724
5.969
5.963
5.763
5.757
0.410
0.372
O2N
Si
+
O2N
Si
β(E)-3o
α-3o
β(E)/α = 87/13
1H NMR (400 MHz, CDCl3)
1.74
0.26
4.01
3.02
0.87
0.87
0.13
0.13
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

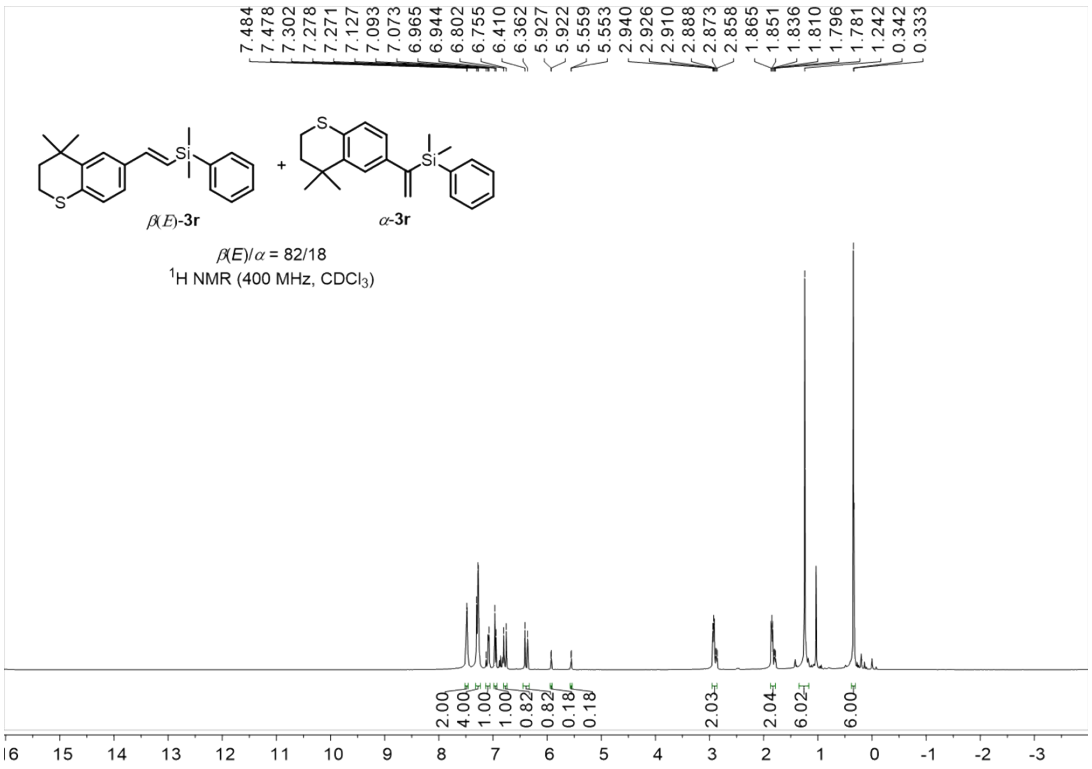

147.331
144.239
142.814
137.571
134.034
133.996
129.496
128.103
127.152
124.061
-2.666
O2N
Si
+
O2N
Si
β(E)-3o
α-3o
β(E)/α = 87/13
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

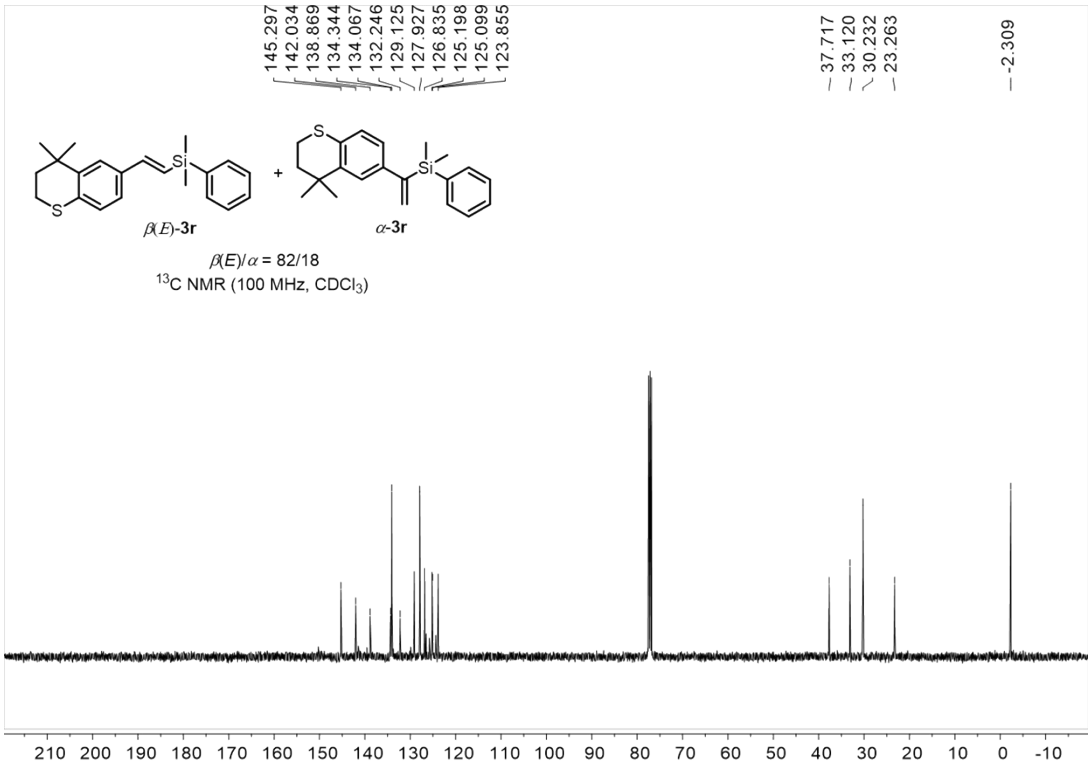

8.010
7.989
7.972
7.951
7.584
7.560
7.544
7.521
7.500
7.479
7.386
7.370
7.349
7.162
7.141
6.987
6.939
6.754
6.706
6.013
6.006
5.748
5.741
3.905
3.881
0.455
0.421
O
O
Si
+
O
O
Si
β(E)-3p
α-3p
β(E)/α = 89/11
1H NMR (400 MHz, CDCl3)
2.00
2.00
1.78
3.00
0.22
0.89
0.89
0.11
0.11
2.67
0.33
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

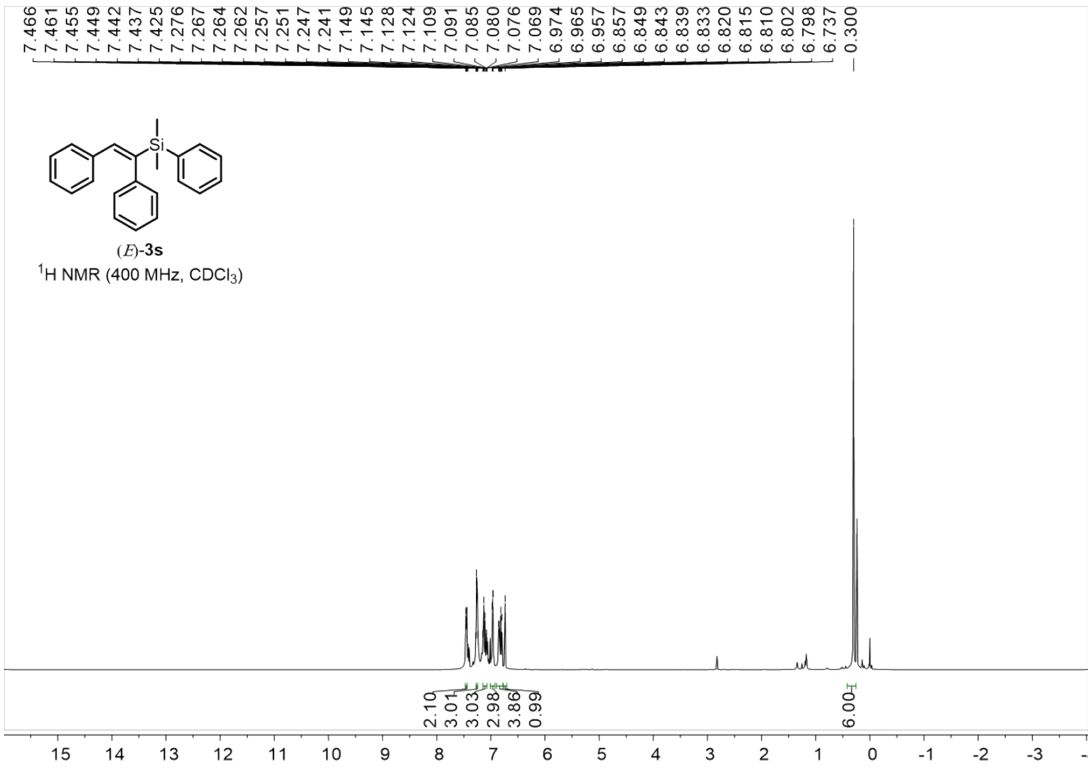

166.999
144.216
142.461
138.119
134.027
130.982
130.023
129.568
129.339
128.031
126.512
52.209
-2.535
β(E)-3p
α-3p
β(E)/α = 89/11
13C NMR (100 MHz, CDCl3)

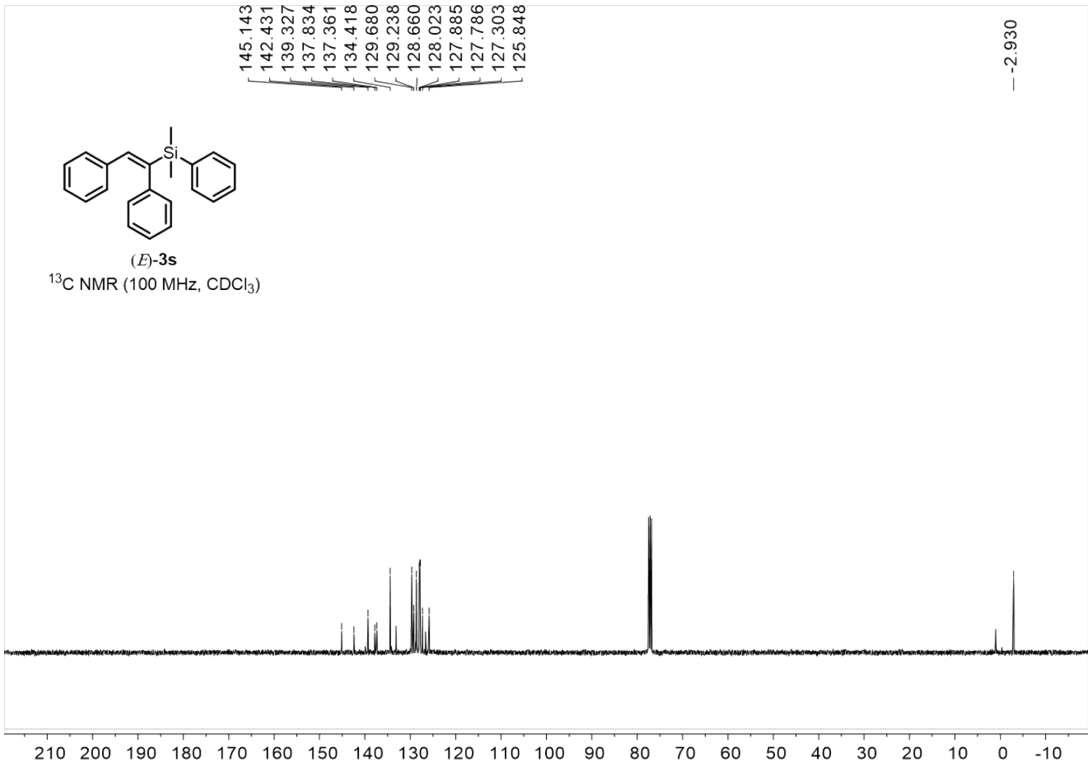

8.541
8.398
8.388
7.698
7.678
7.500
7.495
7.486
7.477
7.313
7.307
7.300
7.193
7.178
7.162
6.852
6.804
6.631
6.584
6.121
6.083
5.932
5.926
5.708
5.702
0.377
0.328
β-3q
α-3q
β(E)/β(Z)/α = 86/7/7
1H NMR (400 MHz, CDCl3)
0.86
1.14
0.96
2.08
3.09
1.00
0.86
0.86
0.07
0.07
0.07
5.16
0.84


149.112
148.714
141.649
138.029
134.020
133.130
133.018
130.792
129.389
128.066
123.611
-2.551
β-3q
α-3q
β(E)/β(Z)/α = 86/7/7
13C NMR (100 MHz, CDCl3)


7.484
7.478
7.302
7.278
7.271
7.127
7.093
7.073
6.965
6.944
6.802
6.755
6.410
6.362
5.927
5.922
5.559
5.553
2.940
2.926
2.910
2.888
2.873
2.858
1.865
1.851
1.836
1.810
1.796
1.781
1.242
0.342
0.333
β(E)-3r
α-3r
β(E)/α = 82/18
1H NMR (400 MHz, CDCl3)
2.00
4.00
1.00
1.00
0.82
0.82
0.18
0.18
2.03
2.04
6.02
6.00

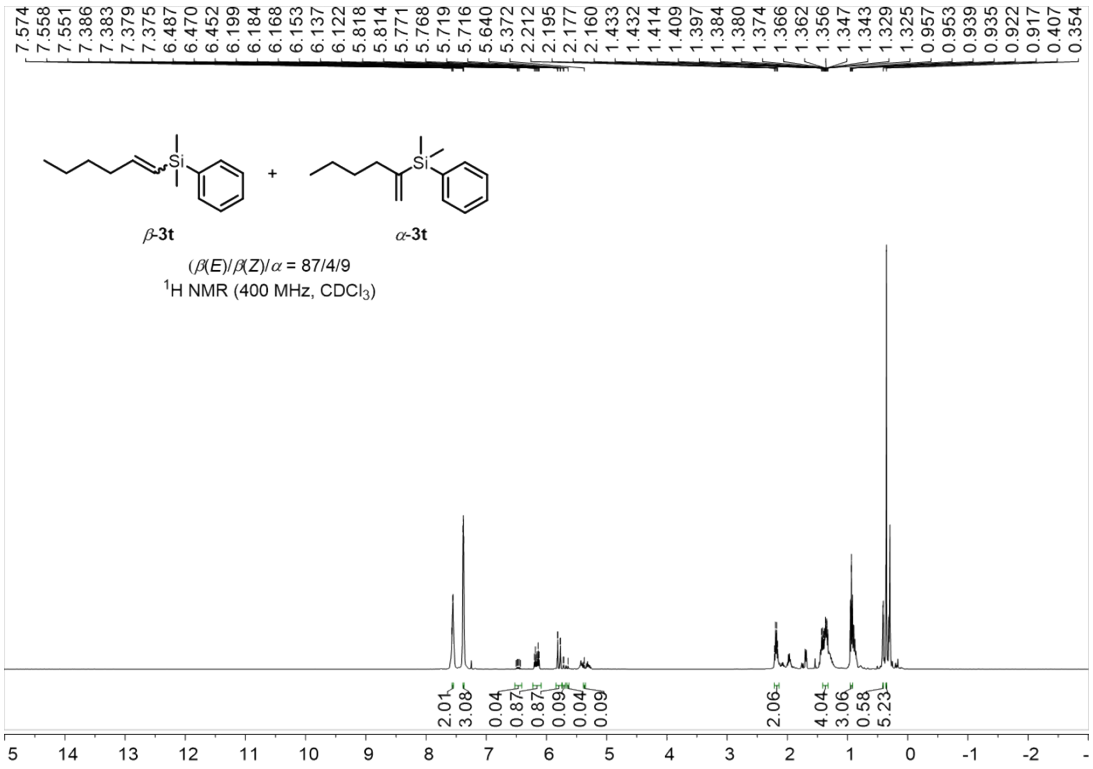

145.297
142.034
138.869
134.344
134.067
132.246
129.125
127.927
126.835
125.198
125.099
123.855
37.717
33.120
30.232
23.263
-2.309
β(E)-3r
α-3r
β(E)/α = 82/18
13C NMR (100 MHz, CDCl3)


7.466
7.461
7.455
7.449
7.442
7.437
7.425
7.276
7.267
7.264
7.262
7.257
7.251
7.247
7.241
7.149
7.145
7.128
7.124
7.109
7.091
7.085
7.080
7.076
7.069
6.974
6.965
6.957
6.857
6.849
6.843
6.839
6.833
6.820
6.815
6.810
6.802
6.798
6.737
0.300
(E)-3s
1H NMR (400 MHz, CDCl3)
2.10
3.01
3.03
2.98
3.86
0.99
6.00



(*E*)-**3s**

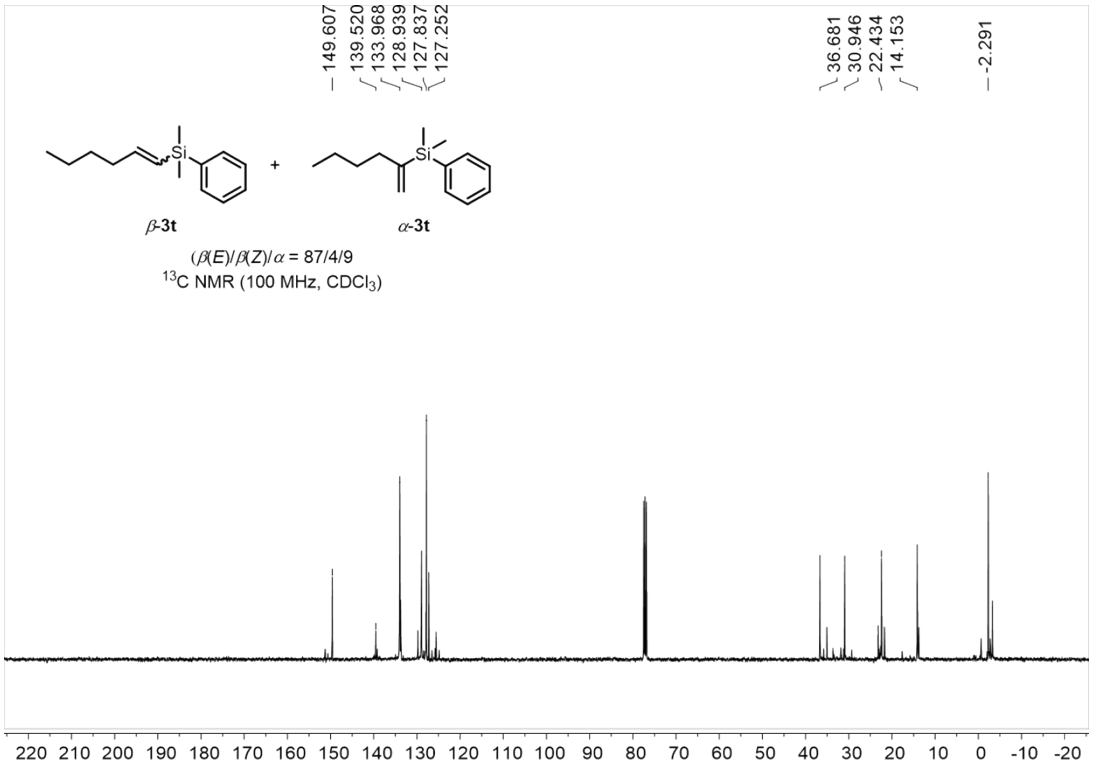
^{13}C NMR (100 MHz, $CDCl_3$)

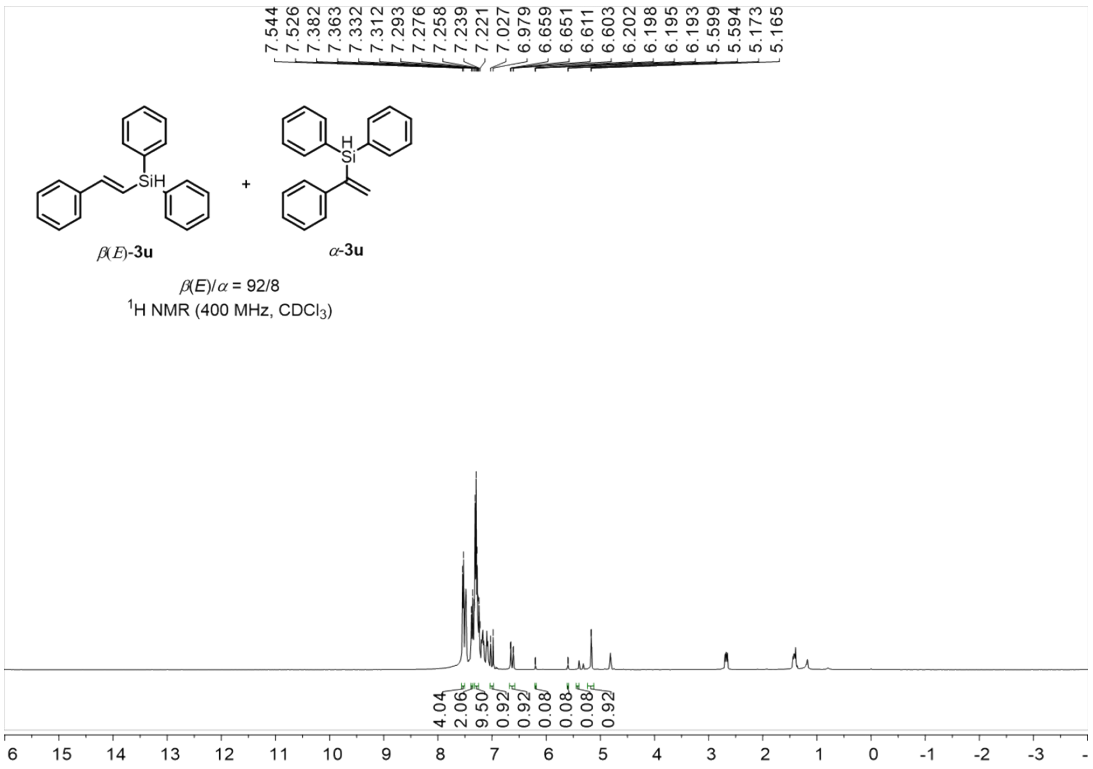


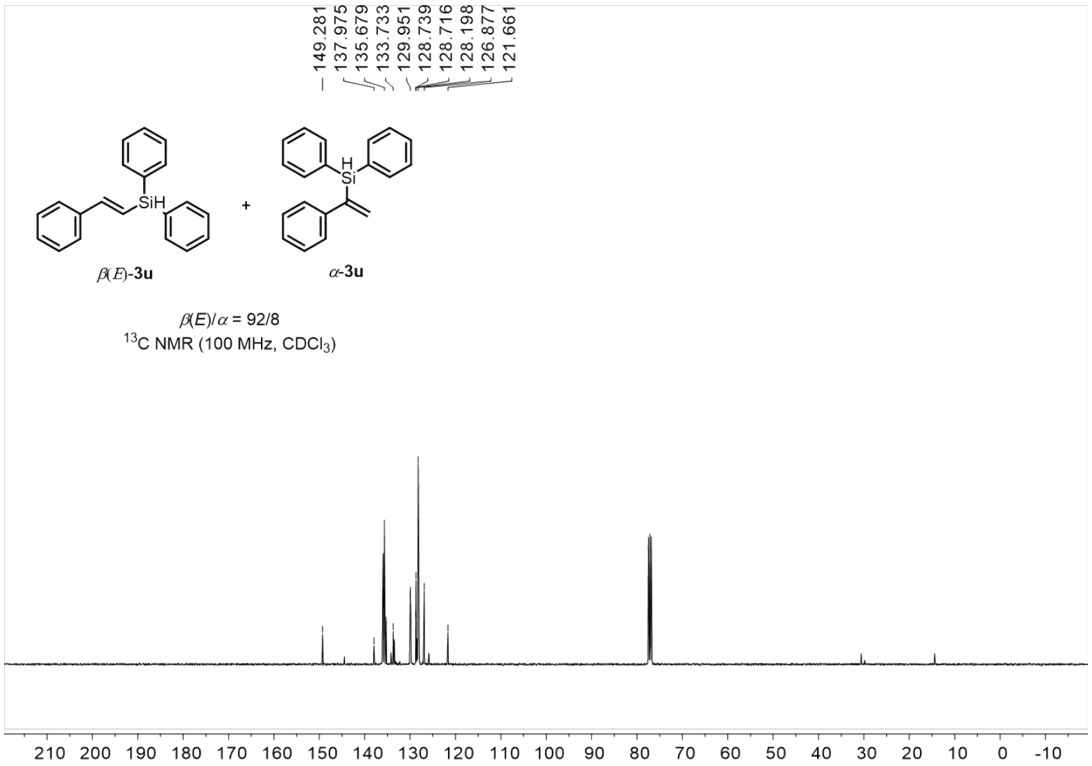
β-**3t** + *α*-**3t**

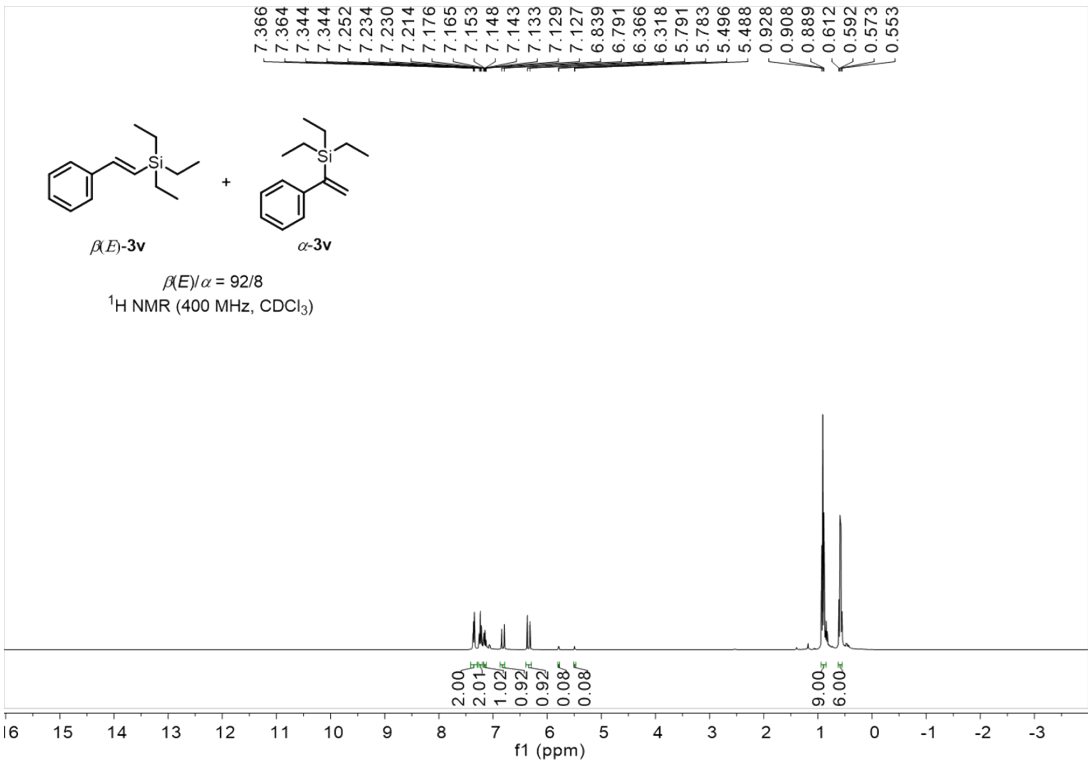
(*β*(*E*)/*β*(*Z*)/*α* = 87/4/9

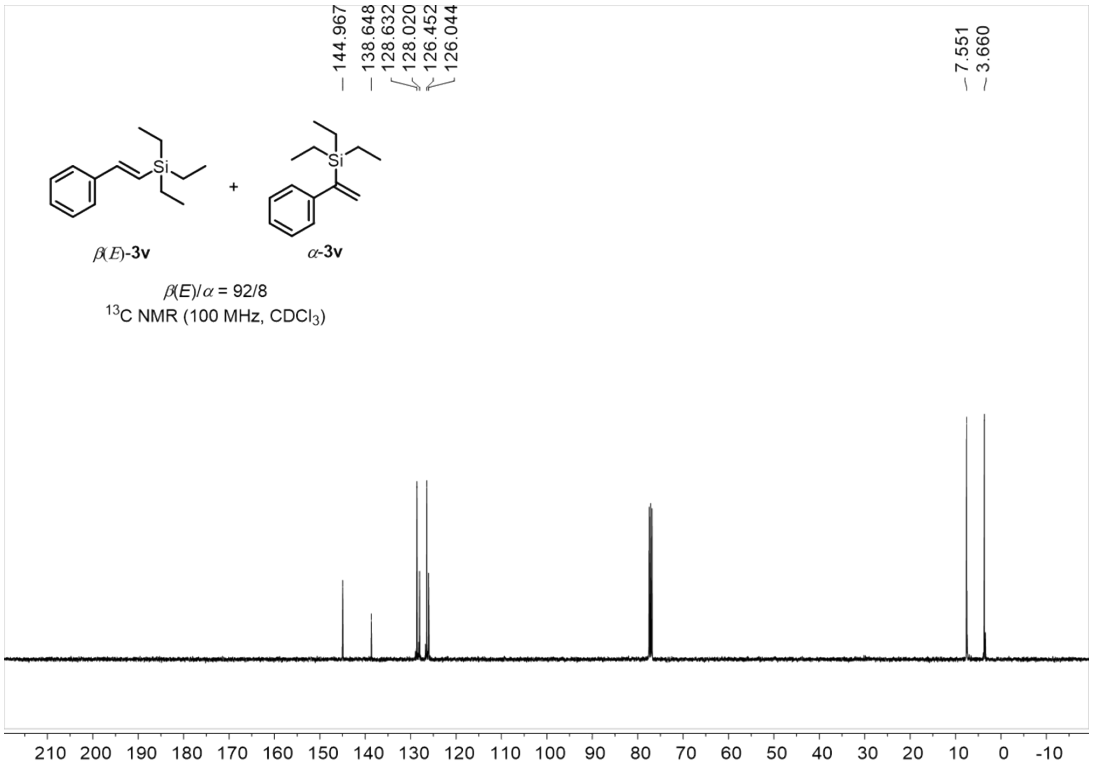
^{1}H NMR (400 MHz, $CDCl_3$)

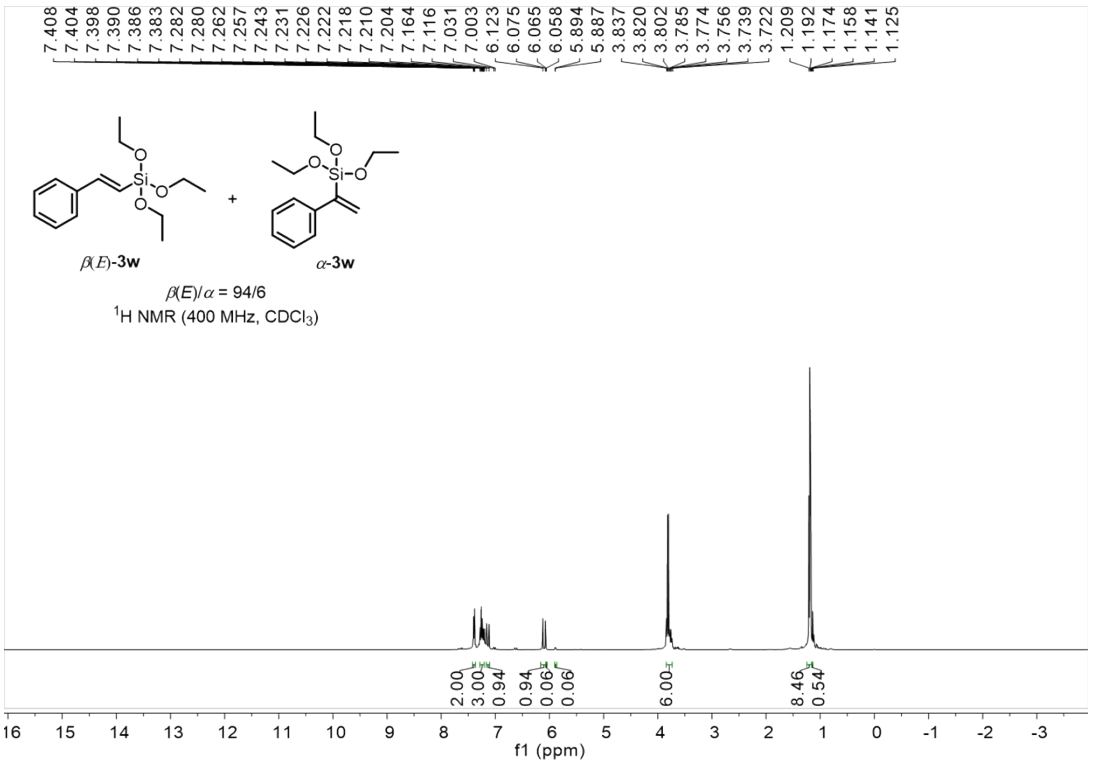

149.607
139.520
133.968
128.939
127.837
127.252
36.681
30.946
22.434
14.153
-2.291
β-3t
α-3t
(β(E)/β(Z)/α = 87/4/9
13C NMR (100 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20

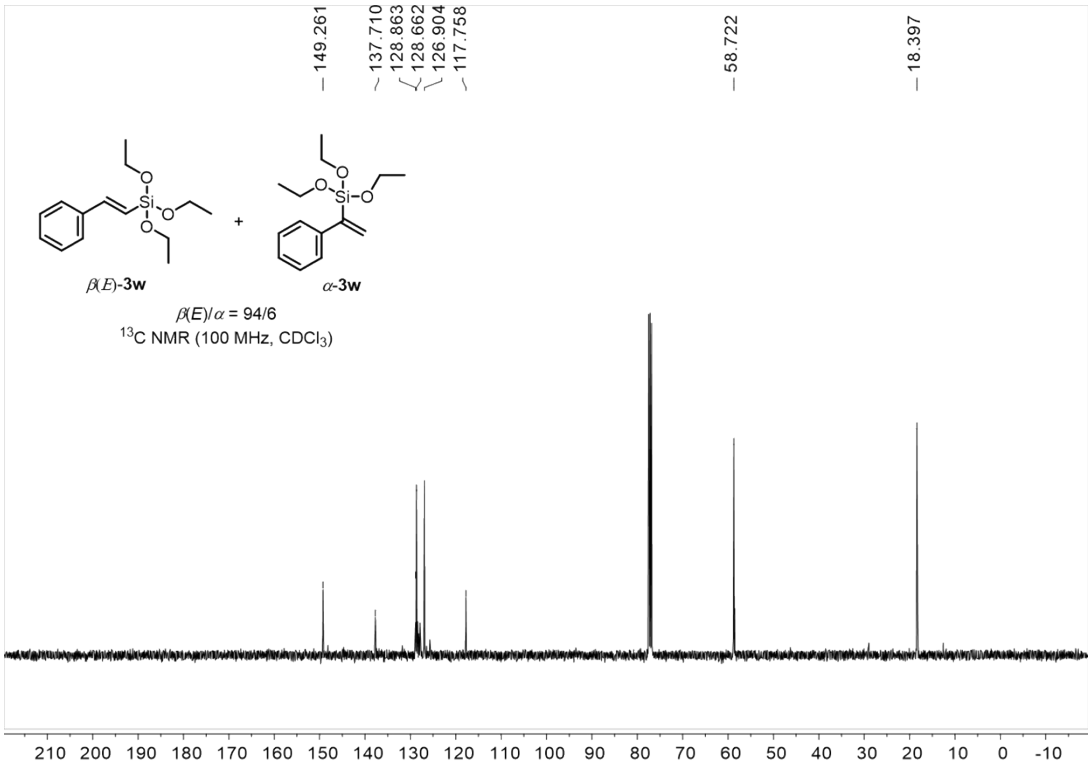

7.544
7.526
7.382
7.363
7.332
7.312
7.293
7.276
7.258
7.239
7.221
7.027
6.979
6.659
6.651
6.611
6.603
6.202
6.198
6.195
6.193
5.599
5.594
5.173
5.165
β(E)-3u
α-3u
β(E)/α = 92/8
1H NMR (400 MHz, CDCl3)
4.04
2.06
9.50
0.92
0.92
0.08
0.08
0.08
0.92
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -


149.281
137.975
135.679
133.733
129.951
128.739
128.716
128.198
126.877
121.661
SiH
+
Si
H
β(E)-3u
α-3u
β(E)/α = 92/8
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.366
7.364
7.344
7.344
7.252
7.234
7.230
7.214
7.176
7.165
7.153
7.148
7.143
7.133
7.129
7.127
6.839
6.791
6.366
6.318
5.791
5.783
5.496
5.488
0.928
0.908
0.889
0.612
0.592
0.573
0.553
Si
+
β(E)-3v
α-3v
β(E)/α = 92/8
1H NMR (400 MHz, CDCl3)
2.00
2.01
1.02
0.92
0.92
0.08
0.08
9.00
6.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


144.967
138.648
128.632
128.020
126.452
126.044
7.551
3.660
β(E)-3v
α-3v
β(E)/α = 92/8
13C NMR (100 MHz, CDCl3)


7.408
7.404
7.398
7.390
7.386
7.383
7.282
7.280
7.262
7.257
7.243
7.231
7.226
7.222
7.218
7.210
7.204
7.164
7.116
7.031
7.003
6.123
6.075
6.065
6.058
5.894
5.887
3.837
3.820
3.802
3.785
3.774
3.756
3.739
3.722
1.209
1.192
1.174
1.158
1.141
1.125
β(E)-3w
α-3w
β(E)/α = 94/6
1H NMR (400 MHz, CDCl3)
2.00
3.00
0.94
0.94
0.06
0.06
6.00
8.46
0.54
f1 (ppm)


149.261
137.710
128.863
128.662
126.904
117.758
58.722
18.397
β(E)-3w
α-3w
β(E)/α = 94/6
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10