

*Supporting Information for*

# **Cobalt-Catalyzed Regioselective Stereoconvergent Markovnikov 1,2-Hydrosilylation of Conjugated Dienes**

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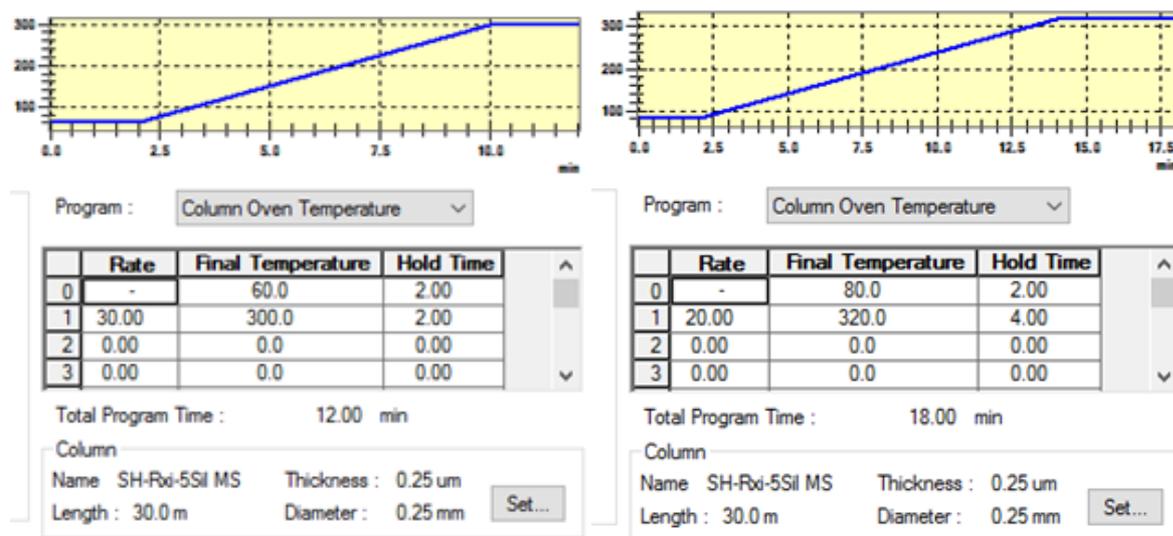
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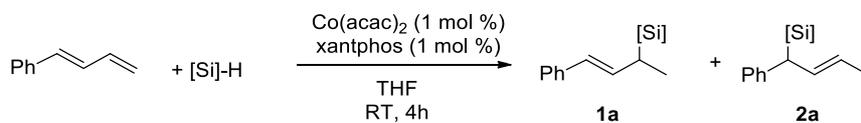
## General Remarks

All the manipulations were performed in an argon-filled glovebox, unless mentioned otherwise. THF, toluene, and hexane were purified by passing the degassed solvents (N<sub>2</sub>) through a column of activated alumina (solvent purification system purchased from Innovative Technologies, Newburyport, MA). The following chemicals were purchased and used as received: Co(acac)<sub>2</sub> (99%, Sigma-Aldrich), CoCl<sub>2</sub> (99.7%, Sigma-Aldrich), CoBr<sub>2</sub> (99%, Sigma-Aldrich), Co(OAc)<sub>2</sub> (99.99%, Sigma-Aldrich), PhSiH<sub>3</sub> (97%, Sigma-Aldrich), Ph<sub>2</sub>SiH<sub>2</sub> (97%, Sigma-Aldrich), MePhSiH<sub>2</sub> (98%, Sigma-Aldrich), Me<sub>2</sub>PhSiH (>98%, Sigma-Aldrich), Et<sub>2</sub>SiH<sub>2</sub> (99%, Sigma-Aldrich), (EtO)<sub>3</sub>SiH (95%, Sigma-Aldrich). PhPDI, <sup>TF</sup>ADPI, PyBox were prepared according to previously reported procedures.<sup>1</sup> (*E*)-1,3-dienes were prepared by Wittig olefination<sup>2</sup> of the corresponding enals<sup>3</sup>. *E/Z*-1,3-dienes were prepared by Wittig olefination of the corresponding aldehydes with allyltriphenylphosphonium bromide according to previously reported procedures.<sup>4</sup> All other reagents and solvents were purchased from commercial sources and used without purification.

<sup>1</sup>H and <sup>13</sup>C spectra were recorded using Bruker 300 MHz, 400 MHz, or 500 MHz NMR spectrometers. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were referenced to resonances of the residual signals of the deuterated solvents. As such, the <sup>1</sup>H and <sup>13</sup>C signals of CDCl<sub>3</sub> were calibrated to 7.26 ppm (singlet) and 77.16 ppm (triplet) respectively. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets and m = multiplet. GC analysis was acquired on Agilent 6850 gas chromatograph equipped with a flame-ionization detector. HR-MS analyses were performed using Thermo Scientific Exactive (APCI). GC-MS analysis was performed on Shimadzu GC-2010 gas chromatograph coupled to a Shimadzu QP2010 mass selective detector. The details of the methods were illustrated as below.



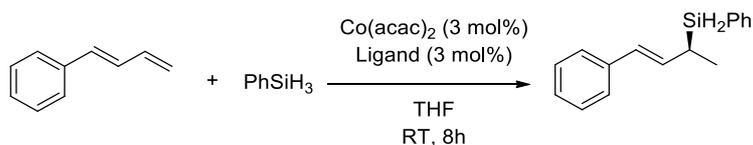
**Reaction Screening of Silane for Hydrosilylation of (*E*)-1-phenyl-1,3-butadiene<sup>a</sup>**



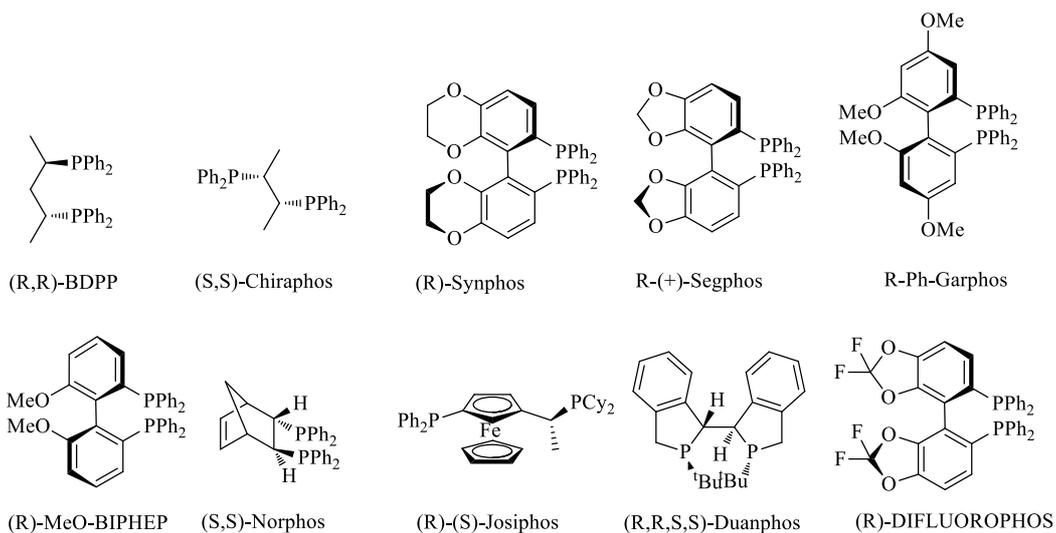
entry	[Si]-H	Yield of <b>1a</b> (%)	<b>1a/4a</b>
1	PhSiH <sub>3</sub>	80	>99:-
2	Ph <sub>2</sub> SiH <sub>2</sub>	84	>99:-
3	Et <sub>2</sub> SiH <sub>2</sub>	-	-
4 <sup>b</sup>	Et <sub>2</sub> SiH <sub>2</sub>	-	-
5	MePhSiH <sub>2</sub>	Trace	-
6 <sup>c</sup>	MePhSiH <sub>2</sub>	80	>99:1
7	(EtO) <sub>3</sub> SiH	-	-
8 <sup>b</sup>	(EtO) <sub>3</sub> SiH	-	-
9	Me <sub>2</sub> PhSiH	-	-
10 <sup>b</sup>	Me <sub>2</sub> PhSiH	-	-

<sup>a</sup>Conditions: (*E*)- 1-phenylbutadiene (0.200 mmol), [Si]-H (0.250 mmol), Co(acac)<sub>2</sub> (2.0 μmol), xantphos (2.0 μmol), THF (0.500 mL), 4 h; yield of isolated product. <sup>b</sup>Reactions were conducted at 50 °C instead. <sup>c</sup>3 mol % catalyst loading was used.

## Reaction Screening of Ligands for Asymmetric Hydrosilylation of 1-phenylbutadiene<sup>a</sup>



Entry	Ligand	Conversion (%) <sup>b</sup>	Enantiomeric Ratio <sup>b</sup>
1	(R,R)-BDPP	>98	59.5:40.5
2	(S,S)-Chiraphos	0	-
3	(R)-Synphos	>98	85:15
4	(R)-(+)-Segphos	>98	86:14
5	R-Ph-Garphos	>98	86:14
6	(R)-MeO-BIPHEP	>98	82.5:17.5
7	(S,S)-Norphos	0	-
8	(R)-(S)-Josiphos	>98	69:31
9	(R,R,S,S)-Duanphos	>98	65:35
10	(R)-difluorophos	77	89.5:10.5
11 <sup>c</sup>	(R)-difluorophos	>98	89:11

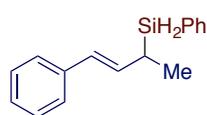


<sup>a</sup>Conditions: (*E*)-diene (0.200 mmol), PhSiH<sub>3</sub> (0.250 mmol), Co(acac)<sub>2</sub> (6.0 μmol), ligand (6.0 μmol), THF (0.5 mL), 8 h; <sup>b</sup>Conversion of diene were determined by GC analysis with tridecane as the internal standard; Enantiomeric ratio was determined by chiral HPLC. <sup>c</sup>Catalyst (5 mol %), 6 hours at room temperature.

## General procedure for Co-catalyzed Markovnikov 1,2-hydrosilylation of *trans*-1,3-dienes

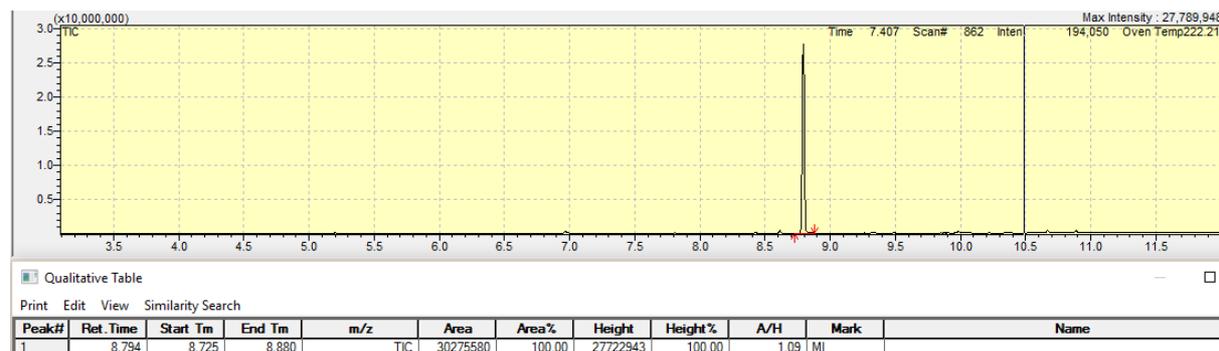
In an Ar-filled glovebox, a mixture of Co(acac)<sub>2</sub> (1.0 mg, 4.0 μmol) and xantphos (2.3 mg, 4.0 μmol) in THF (1 mL) was added into a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding phenylsilane (54.1 mg, 0.500 mmol) and *trans*-1,3-dienes (0.400 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at room temperature for 4 hours. After that, GC-MS analysis was conducted to determine the selectivity of the crude reaction mixture prior concentrating it under vacuum. Subsequently, the residue was purified by flash column chromatography using a mixture of ethyl acetate and hexane as eluent. The details and characterization data of the products are stated below.

### (*E*)-phenyl(4-phenylbut-3-en-2-yl)silane (**1a**)

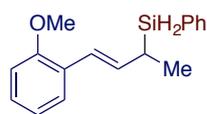


The title compound was isolated (76.3 mg, 80%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63–7.58 (m, 2H), 7.47–7.36 (m, 3H), 7.34–7.28 (m, 4H), 7.23–7.17 (m, 1H), 6.35 (dd, *J* = 15.9, 6.8 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 4.35–4.28 (m, 2H), 2.35–2.23 (m, 1H), 1.32 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.2, 135.9, 133.2, 131.30, 123.0, 128.6, 128.1, 127.4, 126.7, 125.9, 23.0, 15.3. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>Si, [M+H<sup>+</sup>]: 239.1256, Found: 239.1258.

The GC trace for the crude mixture of the reaction to make **1a**.

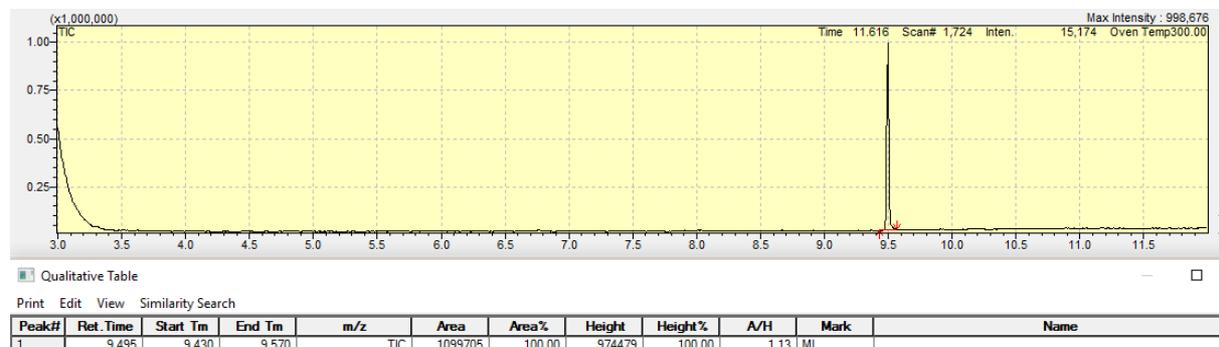


### (*E*)-(4-(2-methoxyphenyl)but-3-en-2-yl)(phenyl)silane (**1b**)

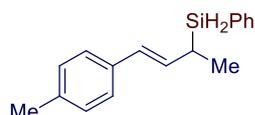


The title compound was isolated (90.2 mg, 84%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (20:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63–7.58 (m, 2H), 7.44–7.35 (m, 4H), 7.20–7.14 (m, 1H), 6.94–6.84 (m, 2H), 6.64 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.33 (dd, *J* = 16.0, 7.8 Hz, 1H), 4.35–4.29 (m, 2H), 3.84 (s, 3H), 2.36–2.24 (m, 1H), 1.32 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.4, 135.9, 133.8, 131.5, 123.0, 128.1, 127.7, 127.3, 126.3, 122.1, 120.8, 111.0, 55.6, 23.5, 15.4. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>20</sub>OSi, [M+H<sup>+</sup>]: 269.1362, Found: 269.1355.

The GC trace for the crude mixture of the reaction to make **1b**.



### (E)-phenyl(4-(p-tolyl)but-3-en-2-yl)silane (**1c**)



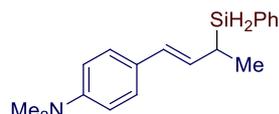
The title compound was isolated (91.9 mg, 91%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68–7.53 (m, 2H), 7.46–7.35 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.37–6.18 (m, 2H), 4.40–4.21 (m, 2H), 2.35 (s, 3H), 2.31–2.22 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.4, 135.9, 135.4, 132.1, 131.4, 129.9, 129.3, 128.1, 127.3, 125.8, 22.9, 21.3, 15.3. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>20</sub>Si, [M+H<sup>+</sup>]: 253.4341, Found: 253.1408.

The GC trace for the crude mixture of the reaction to make **1c**.



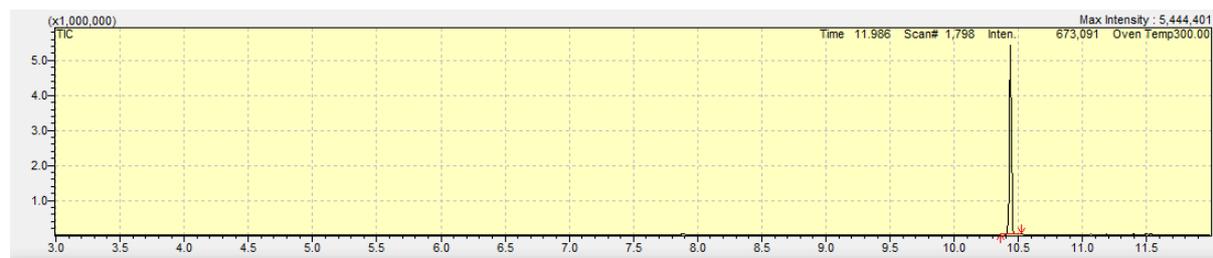
Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.617	10.505	10.705	TIC	2027429	100.00	1656446	100.00	1.22	MI	

### (E)-N,N-dimethyl-4-(3-(phenylsilyl)but-1-en-1-yl)aniline (**1d**)



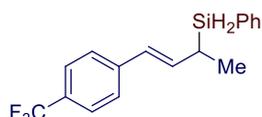
The title compound was isolated (96.7 mg, 86%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (20:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.29–7.17 (m, 3H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 6.08 (d, *J* = 15.9 Hz, 1H), 5.98 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.23–4.09 (m, 2H), 2.79 (s, 6H), 2.15–2.03 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.7, 135.9, 131.7, 129.8, 128.9, 128.0, 127.3, 127.1, 126.7, 112.8, 40.8, 22.7, 15.5. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>18</sub>H<sub>24</sub>NSi, [M+H<sup>+</sup>]: 282.1678, Found: 282.1681.

The GC trace for the crude mixture of the reaction to make **1d**.



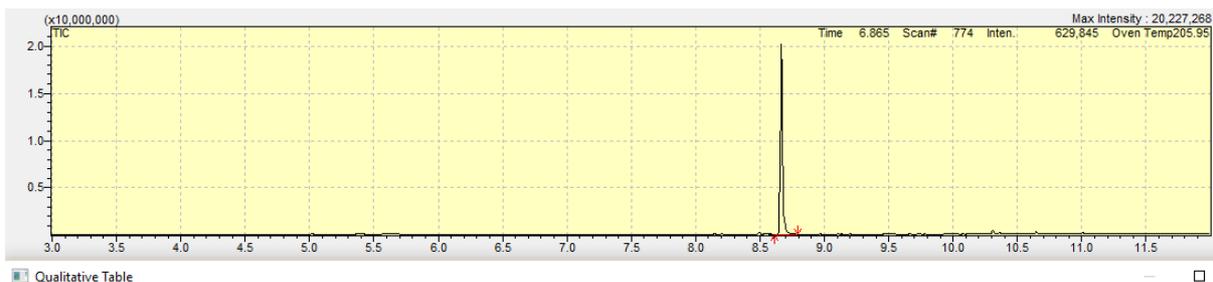
Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.437	10.360	10.525	TIC	5886890	100.00	5413328	100.00	1.09	MI	

### (E)-phenyl(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)silane (**1e**)



The title compound was isolated (108 mg, 88%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (50:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.58 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.48–7.43 (m, 1H), 7.43–7.37 (m, 4H), 6.47 (dd, *J* = 15.9, 7.7 Hz, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 4.35 (d, *J* = 2.9 Hz, 2H), 2.39–2.29 (m, 1H), 1.35 (d, *J* = 7.1 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.7 (d, *J*<sub>C-F</sub> = 1.2 Hz), 136.2, 135.8, 130.9, 130.1, 128.5 (q, *J*<sub>C-F</sub> = 32.4 Hz), 128.2, 126.2, 126.0, 125.6 (q, *J*<sub>C-F</sub> = 3.8 Hz), 124.5 (q, *J*<sub>C-F</sub> = 271.7 Hz), 23.4, 15.1. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -62.30. GC-MS (EI) *m/z* calcd for C<sub>17</sub>H<sub>18</sub>F<sub>3</sub>Si [M]<sup>+</sup>: 306.40, Found: 306.15

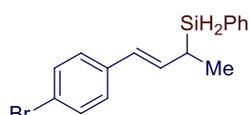
The GC trace for the crude mixture of the reaction to make **1e**.



Qualitative Table

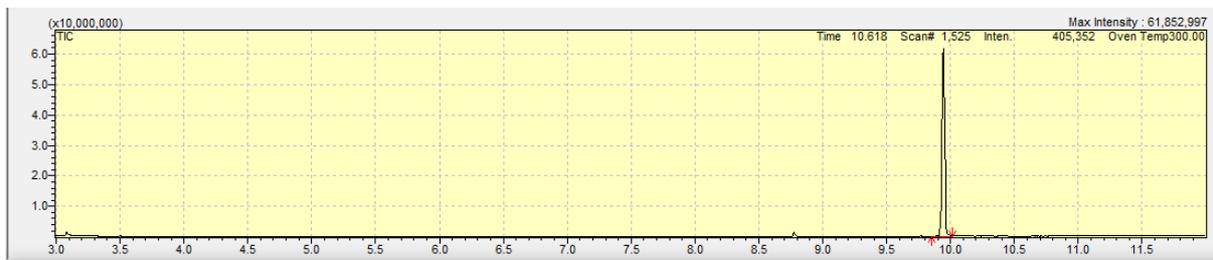
Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	8.665	8.610	8.795	TIC	24923902	100.00	20140224	100.00	1.24	MI	

**(E)-(4-(4-bromophenyl)but-3-en-2-yl)(phenyl)silane (1f)**



The title compound was isolated (101 mg, 80%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.54 (m, 2H), 7.47–7.31 (m, 5H), 7.21–7.10 (m, 2H), 6.33 (dd, *J* = 15.9, 7.6 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 4.39–4.22 (m, 2H), 2.41–2.17 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.1, 135.8, 134.1, 131.7, 131.1, 130.0, 128.1, 127.4, 126.2, 120.3, 23.2, 15.1. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>BrSi, [M+H<sup>+</sup>]: 317.0361, Found: 317.0357.

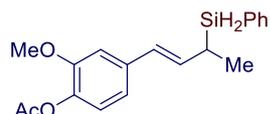
The GC trace for the crude mixture of the reaction to make **1f**.



Qualitative Table

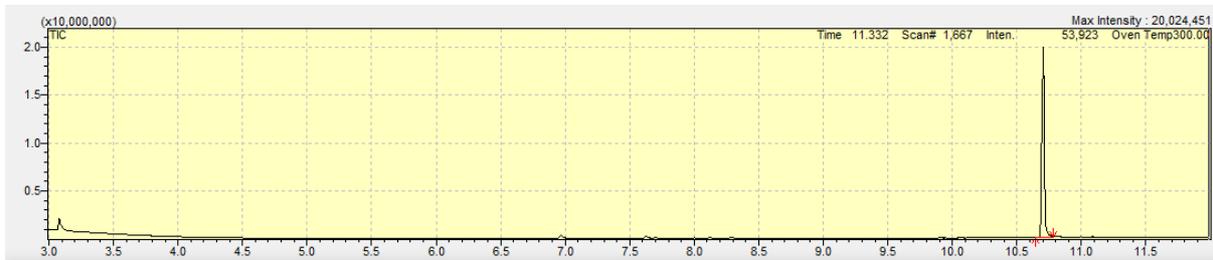
Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.944	9.850	10.015	TIC	98848339	100.00	61674826	100.00	1.60	MI	

**(E)-2-methoxy-4-(3-(phenylsilyl)but-1-en-1-yl)phenyl acetate (1g)**



The title compound was isolated (104 mg, 80%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (10:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60–7.54 (m, 2H), 7.45–7.33 (m, 3H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.89–6.84 (m, 2H), 6.29–6.19 (m, 2H), 4.30 (d, *J* = 2.9 Hz, 2H), 3.83 (s, 3H), 2.31 (s, 3H), 2.28–2.22 (m, 1H), 1.29 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.3, 151.2, 138.7, 137.3, 135.9, 133.6, 131.2, 130.0, 128.1, 126.8, 122.8, 118.4, 109.8, 56.0, 23.0, 20.8, 15.2. GC-MS (EI) *m/z* calcd for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub>Si [M]<sup>+</sup>: 326.13, Found: 326.20

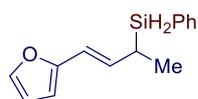
The GC trace for the crude mixture of the reaction to make **1g**.



Qualitative Table

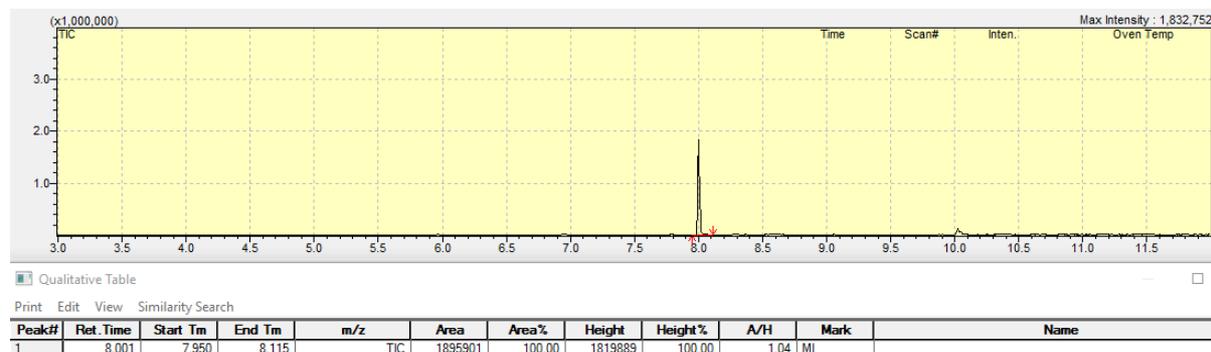
Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	10.702	10.645	10.780	TIC	27168811	100.00	19850716	100.00	1.37	MI	

### (E)-(4-(furan-2-yl)but-3-en-2-yl)(phenyl)silane (**1h**)

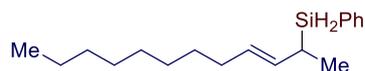


The title compound was isolated (78.6 mg, 86%, *E/Z* = >99:1) as pale yellow oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.54 (m, 2H), 7.44–7.33 (m, 3H), 7.30 (d, *J* = 1.5 Hz, 1H), 6.38–6.25 (m, 2H), 6.14–6.03 (m, 2H), 4.29 (qd, *J* = 6.7, 3.0 Hz, 2H), 2.28–2.17 (m, 1H), 1.27 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.7, 141.2, 135.8, 132.2, 131.2, 123.0, 128.1, 116.2, 111.2, 105.7, 22.9, 15.0. GC-MS (EI) *m/z*: calcd for C<sub>14</sub>H<sub>16</sub>OSi [M]<sup>+</sup>: 228.36, Found: 228.10.

The GC trace for the crude mixture of the reaction to make **1h**.

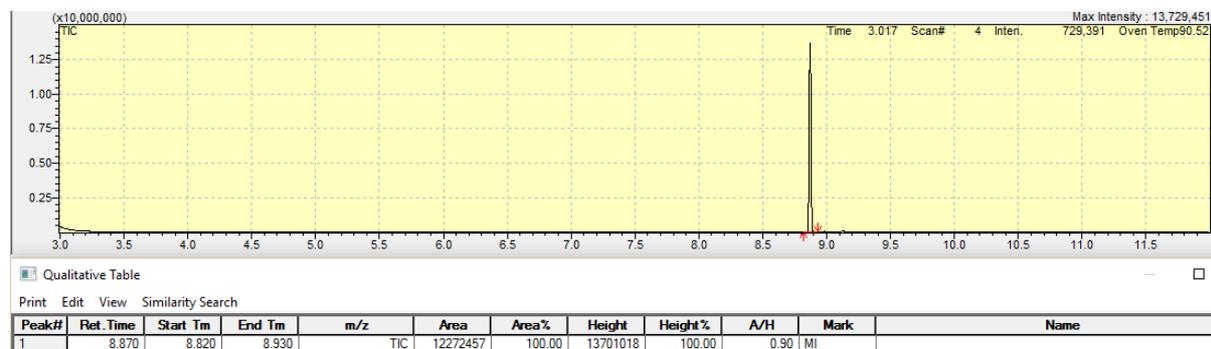


### (E)-dodec-3-en-2-yl(phenyl)silane (**1i**)

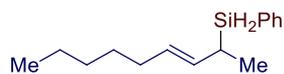


The title compound was isolated (48 mg, 87%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:0 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60–7.55 (m, 2H), 7.44–7.33 (m, 3H), 5.54–5.45 (m, 1H), 5.36–5.27 (m, 1H), 4.29–4.17 (m, 2H), 2.00 (m, 3H), 1.34–1.25 (m, 12H), 1.18 (d, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 6.9 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.8, 132.0, 131.9, 129.7, 128.5, 128.0, 32.9, 32.1, 30.0, 29.7, 29.5, 29.3, 22.9, 21.8, 15.6, 14.3. GC-MS (EI) *m/z*: calcd for C<sub>18</sub>H<sub>30</sub>Si [M]<sup>+</sup>: 274.21; Found: 274.30.

The GC trace for the crude mixture of the reaction to make **1i**.

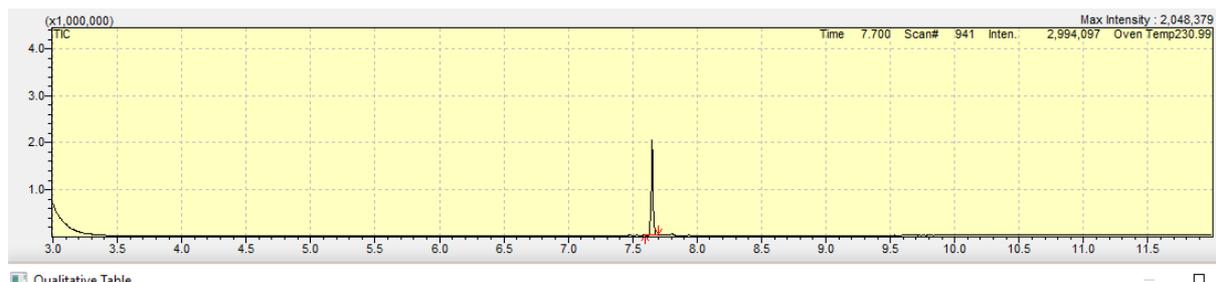


### (E)-non-3-en-2-yl(phenyl)silane (**1j**)



The title compound was isolated (71.0 mg, 76%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:0 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.42–7.33 (m, 3H), 5.52–5.45 (m, 1H), 5.34–5.27 (m, 1H), 4.24–4.19 (m, 2H), 2.05–1.97 (m, 3H), 1.35–1.23 (m, 6H), 1.17 (d, *J* = 7.3 Hz, 3H), 0.88 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.8, 132.0, 131.9, 129.7, 128.5, 128.0, 32.9, 31.5, 29.6, 22.7, 21.8, 15.6, 14.2. GC-MS (EI) *m/z*: calcd for C<sub>15</sub>H<sub>24</sub>Si [M]<sup>+</sup>: 232.16; Found: 232.20.

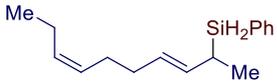
The GC trace for the crude mixture of the reaction to make **1j**.



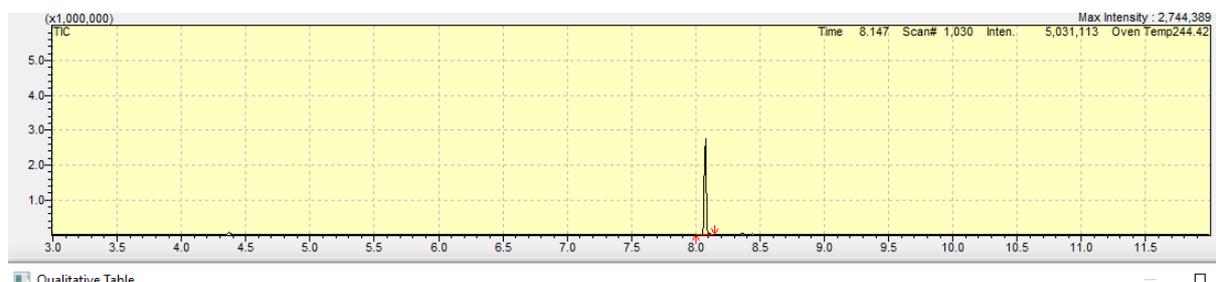
Qualitative Table

Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	7.651	7.595	7.700	TIC	2017779	100.00	2015292	100.00	1.00	MI	

### (3E,7Z)-deca-3,7-dien-2-yl(phenyl)silane (1k)

 The title compound was isolated (62 mg, 64%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:0 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.44–7.33 (m, 3H), 5.53 (dd, *J* = 15.3, 7.4 Hz, 1H), 5.45–5.26 (m, 3H), 4.26–4.18 (m, 2H), 2.11–1.97 (m, 7H), 1.18 (d, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.8, 132.5, 132.0, 131.9, 129.8, 128.7, 128.0, 127.7, 33.1, 27.6, 21.8, 20.7, 15.5, 14.5. GC-MS (EI) *m/z*: calcd for C<sub>16</sub>H<sub>24</sub>Si [M]<sup>+</sup>: 244.16; Found: 244.20.

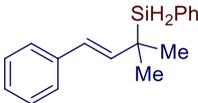
The GC trace for the crude mixture of the reaction to make **1k**.



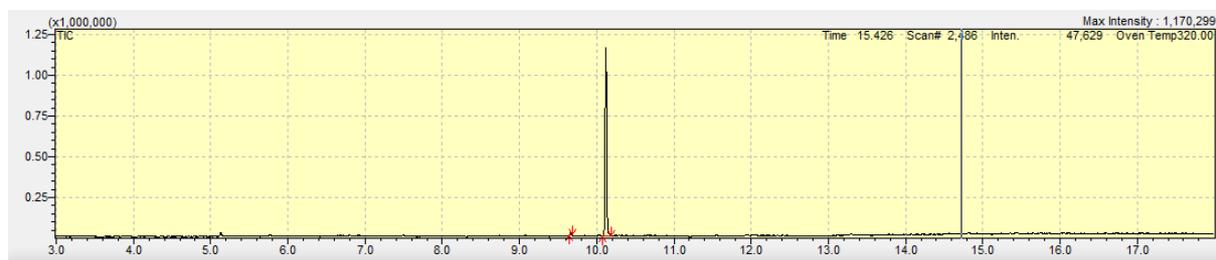
Qualitative Table

Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	8.074	8.000	8.145	TIC	2750405	100.00	2728196	100.00	1.01	MI	

### (E)-(2-methyl-4-phenylbut-3-en-2-yl)(phenyl)silane (1l)

 The title compound was isolated (71.0 mg, 70%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.47–7.24 (m, 7H), 7.22–7.16 (m, 1H), 6.34 (d, *J* = 16.1 Hz, 1H), 6.18 (d, *J* = 16.1 Hz, 1H), 4.25 (s, 2H), 1.27 (m, 6H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.3, 138.3, 136.2, 131.4, 130.0, 128.6, 128.0, 126.8, 126.1, 126.0, 25.7, 24.1. HR-MS(APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>20</sub>Si, [M+H]<sup>+</sup>: 253.1413, Found: 253.1416.

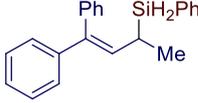
The GC trace for the crude mixture of the reaction to make **1l**.



Qualitative Table

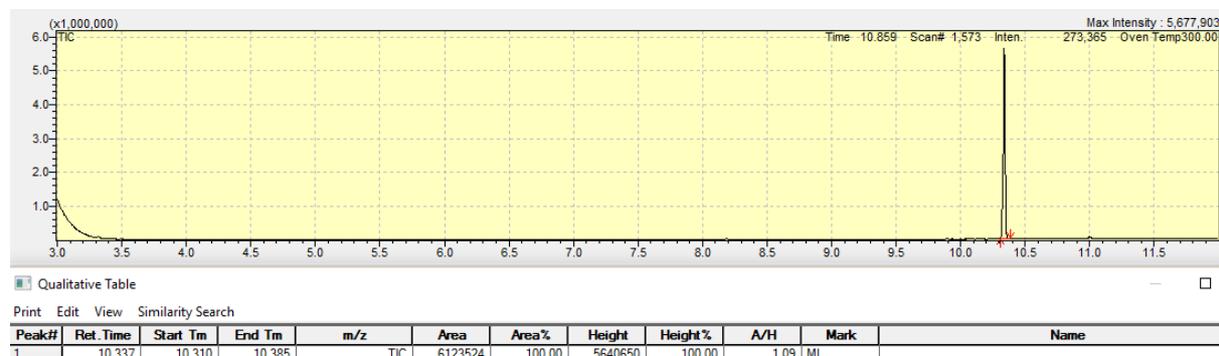
Peak#	Ret. Time	Start Tm	End Tm	m/z	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.668	9.650	9.680	TIC	17402	1.22	16896	1.44	1.03	MI	
2	10.119	10.070	10.190	TIC	1409699	98.78	1157047	98.56	1.22	MI	

### (4,4-diphenylbut-3-en-2-yl)(phenyl)silane (1m)

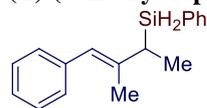
 The title compound was isolated (106 mg, 84%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54–

7.49 (m, 2H), 7.45–7.27 (m, 6H), 7.27–7.16 (m, 5H), 7.08–7.02 (m, 2H), 6.02 (d,  $J = 11.5$  Hz, 1H), 4.33–4.22 (m, 2H), 2.37–2.24 (m, 1H), 1.25 (d,  $J = 7.1$  Hz, 3H).  $\{^1\text{H}\}^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 140.4, 134.0, 135.9, 132.1, 131.4, 123.0, 129.9, 128.4, 128.2, 128.1, 127.1, 126.9, 126.8, 20.8, 16.9. HR-MS (APCI<sup>+</sup>)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{Si}$ ,  $[\text{M}+\text{H}^+]$ : 315.1569, Found: 315.1566.

The GC trace for the crude mixture of the reaction to make **1m**.

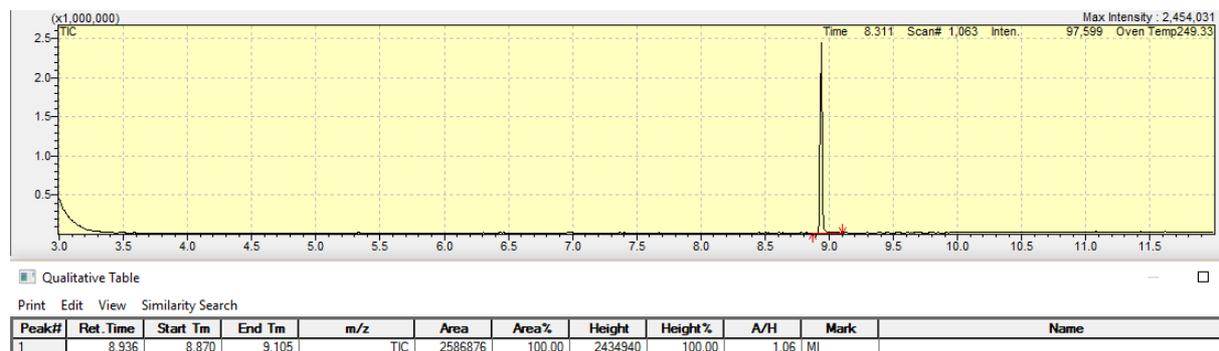


### (E)-(3-methyl-4-phenylbut-3-en-2-yl)(phenyl)silane (**1n**)

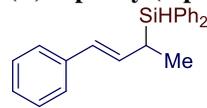


The title compound was isolated (93.0 mg, 92%,  $E/Z = >99:1$ ) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 (d,  $J = 6.5$  Hz, 2H), 7.46–7.27 (m, 5H), 7.19 (d,  $J = 6.9$  Hz, 3H), 6.15 (s, 1H), 4.37 (m, 2H), 2.21–2.12 (m, 1H), 1.90 (s, 3H), 1.34 (d,  $J = 7.3$  Hz, 3H).  $\{^1\text{H}\}^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.3, 139.0, 135.8, 132.0, 129.9, 129.0, 128.1, 128.1, 125.8, 123.5, 29.4, 18.8, 15.6. HR-MS (APCI<sup>+</sup>)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{20}\text{Si}$ ,  $[\text{M}+\text{H}^+]$ : 253.1413, Found: 253.1413.

The GC trace for the crude mixture of the reaction to make **1n**.

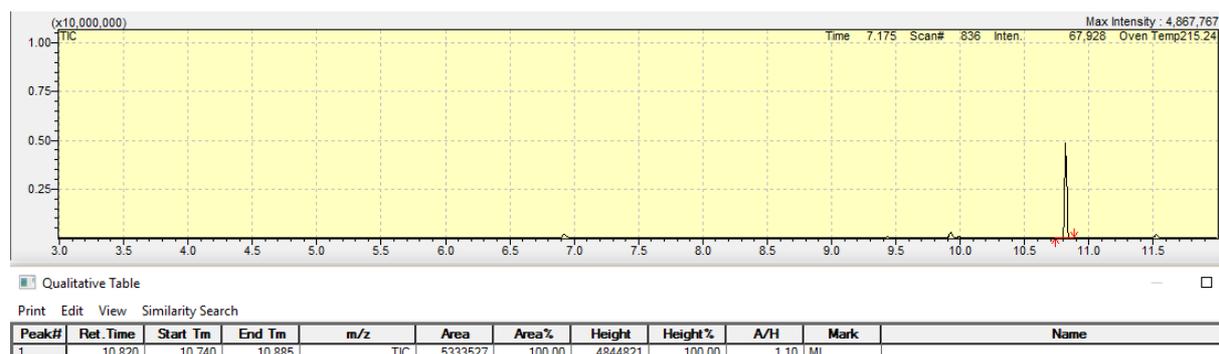


### (E)-diphenyl(4-phenylbut-3-en-2-yl)silane (**1a'**)

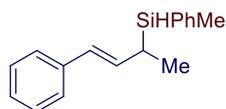


The title compound was isolated (106 mg, 84%,  $E/Z = >99:1$ ) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67–7.58 (m, 4H), 7.46–7.32 (m, 6H), 7.27 (m, 3H), 7.24–7.11 (m, 2H), 6.36 (dd,  $J = 15.9, 7.4$  Hz, 1H), 6.25 (dd,  $J = 16.0, 0.9$  Hz, 1H), 4.83 (d,  $J = 2.8$  Hz, 1H), 2.57–2.44 (m, 1H), 1.33 (d,  $J = 7.2$  Hz, 3H).  $\{^1\text{H}\}^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 135.8, 135.7, 134.5, 133.2, 133.1, 133.0, 130.0, 128.6, 128.1, 128.1, 127.6, 126.6, 125.9, 24.37, 14.9. HR-MS (APCI<sup>+</sup>)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{23}\text{Si}$ ,  $[\text{M}+\text{H}^+]$ : 315.1569, Found: 315.1555.

The GC trace for the crude mixture of the reaction to make **1a'**.

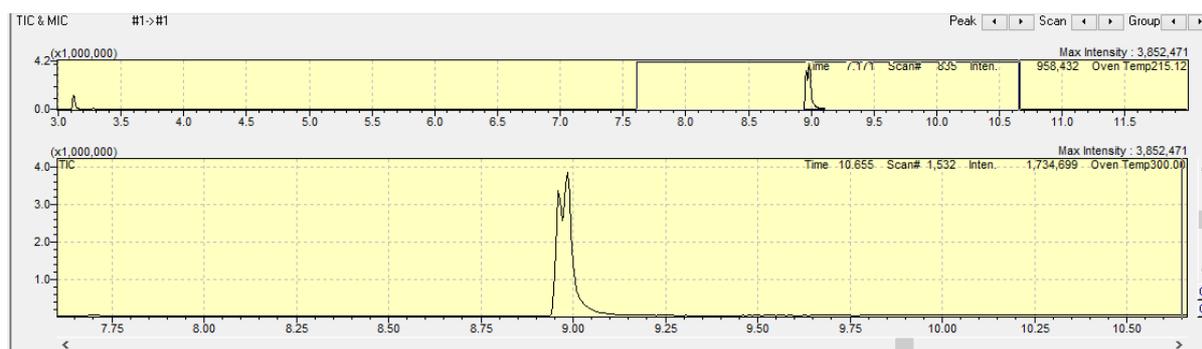


### (E)-Methyl(phenyl)(4-phenylbut-3-en-2-yl)silane (**1a''**)

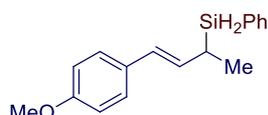


The reaction was conducted with 3 mol % catalyst loading at 0.2 mmol scale. The title compound was isolated (40.3 mg, 80%, *E/Z* = >99:1 dr = 1:1 determined by <sup>1</sup>H NMR analysis) as colourless oil after chromatography on silica gel (100:0 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58–7.54 (m, 2H), 7.44–7.35 (m, 3H), 7.34–7.27 (m, 4H), 7.21–7.16 (m, 1H), 6.35–6.27 (m, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 4.38–4.30 (m, 1H), 2.20–2.10 (m, 1H), 1.27–1.22 (m, 3H), 0.40 (t, *J* = 3.6 Hz, 3H). {<sup>1</sup>H} <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.4, 135.0, 135.0, 134.9, 134.8, 133.6, 133.5, 129.6, 128.6, 128.0, 128.0, 127.0, 126.9, 126.6, 125.8, 25.3, 25.2, 14.6, 14.2, -7.5, -7.7. GC-MS (EI) *m/z*: calcd for C<sub>17</sub>H<sub>20</sub>Si [M]<sup>+</sup>: 252.43; Found: 252.15.

The GC trace for the crude mixture of the reaction to make **1a''**.

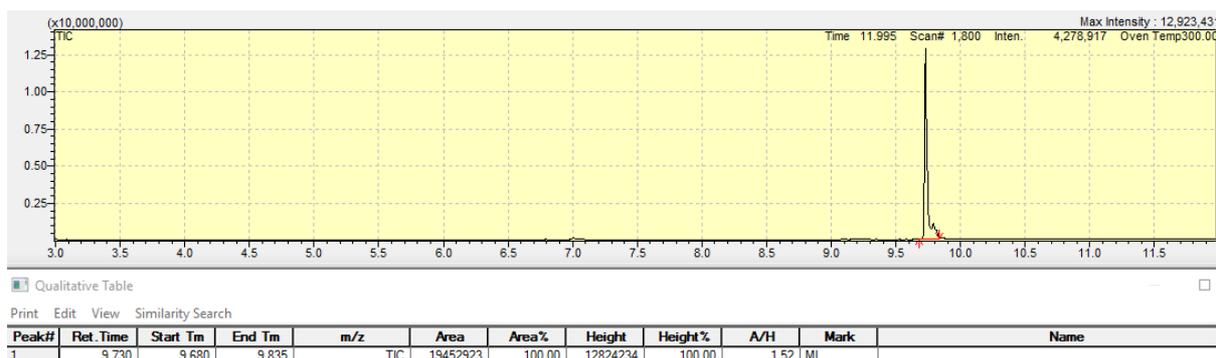


### (E)-(4-(4-methoxyphenyl)but-3-en-2-yl)(phenyl)silane



The title compound was isolated (96.0 mg, 90%, *E/Z* = >99:1.) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.51 (m, 2H), 7.45–7.31 (m, 3H), 7.26–7.22 (m, 2H), 6.85–6.79 (m, 2H), 6.23 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.35–4.19 (m, 2H), 3.80 (s, 3H), 2.28–2.19 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H} <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.7, 135.9, 131.5, 131.1, 131.0, 129.9, 128.1, 127.0, 126.8, 114.1, 55.5, 22.8, 15.4. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>21</sub>O<sub>2</sub>Si, [M+H]<sup>+</sup>: 269.1362, Found: 269.1354.

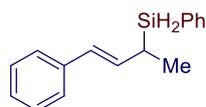
The GC trace for the crude mixture of the reaction to make this compound.



## General procedure for Co-catalyzed Markovnikov 1,2-hydrosilylation of *trans/cis*-1,3-dienes mixture

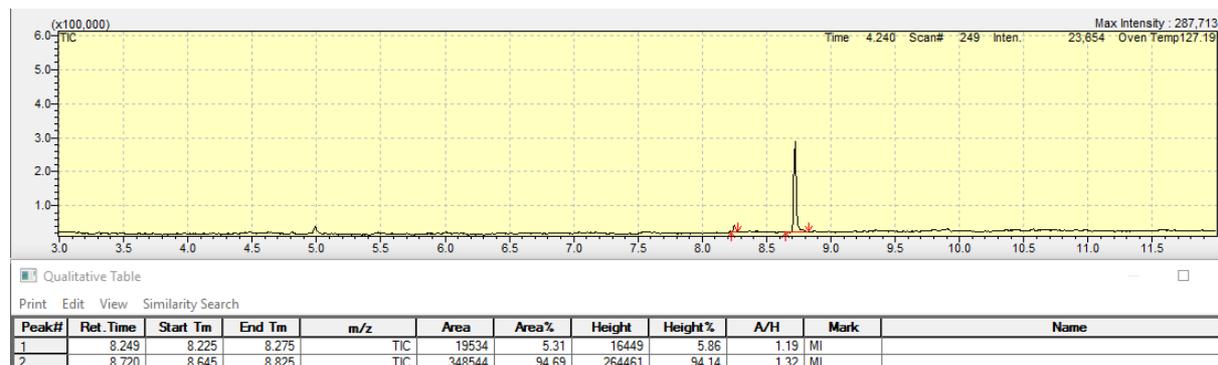
In an Ar-filled glovebox, a mixture of Co(acac)<sub>2</sub> (1.0 mg, 4.0 μmol) and xantphos (2.3 mg, 4.0 μmol) in THF (1 mL) was added into a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding phenylsilane (54.1 mg, 0.500 mmol) and *trans/cis*-1,3-dienes (0.400 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at room temperature for 6 hours or 5 °C for 24 hours. After that, GC-MS analysis was conducted to determine the selectivity of the crude reaction mixture prior concentrating it under vacuum. The residue was then purified by flash column chromatography using a mixture of ethyl acetate and hexane as eluent. The details and characterization data of the products are stated below.

### (*E*)-phenyl(4-phenylbut-3-en-2-yl)silane (1a)

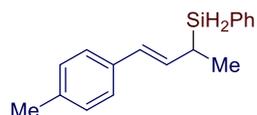


The reaction was stirred for 6 h at 24 °C. The title compound was isolated (76.3 mg, 80%, *E/Z* = >99:1, 1,2/1,4 = 95:5) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63–7.58 (m, 2H), 7.47–7.36 (m, 3H), 7.34–7.28 (m, 4H), 7.23–7.17 (m, 1H), 6.35 (dd, *J* = 15.9, 6.8 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 4.35–4.28 (m, 2H), 2.35–2.23 (m, 1H), 1.32 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.2, 135.9, 133.2, 131.3, 123.0, 128.6, 128.1, 127.4, 126.7, 125.9, 23.0, 15.3. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>Si, [M+H<sup>+</sup>]: 239.1256, Found: 239.1258.

The GC trace for the crude mixture of the reaction to make **1a**.

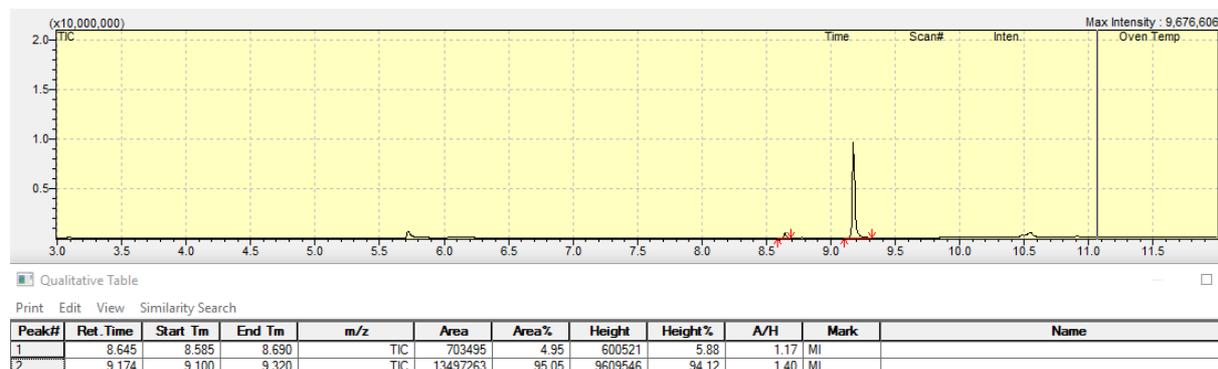


### (*E*)-phenyl(4-(*p*-tolyl)but-3-en-2-yl)silane (1c)

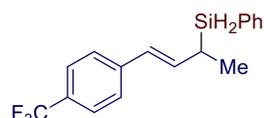


The reaction was stirred for 24 h at 5 °C. The title compound was isolated (77.7 mg, 77%, *E/Z* = >99:1, 1,2/1,4 = 95:5) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68–7.53 (m, 2H), 7.46–7.35 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.28 (m, 2H), 4.40–4.21 (m, 2H), 2.35 (s, 3H), 2.31–2.22 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.4, 135.9, 135.4, 132.1, 131.4, 129.9, 129.3, 128.1, 127.3, 125.8, 22.9, 21.3, 15.3. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>20</sub>Si, [M+H<sup>+</sup>]: 253.4341, Found: 253.1408.

The GC trace for the crude mixture of the reaction to make **1c**.

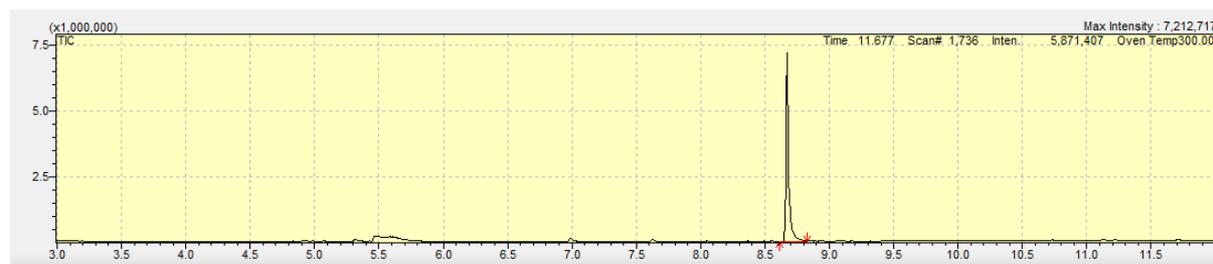


### (E)-phenyl(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)silane (**1e**)

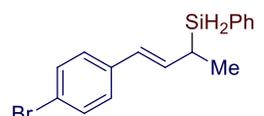


The reaction was stirred for 6 h at 24 °C. The title compound was isolated (79.0 mg, 65%, *E/Z* = >99:1, 1.2/1,4 = 99:1) as colourless oil after chromatography on silica gel (50:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.58 (m, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.48–7.43 (m, 1H), 7.43–7.37 (m, 4H), 6.47 (dd, *J* = 15.9, 7.7 Hz, 1H), 6.31 (d, *J* = 16.3 Hz, 1H), 4.35 (d, *J* = 2.9 Hz, 2H), 2.39–2.29 (m, 1H), 1.35 (d, *J* = 7.1 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 141.7 (d, *J*<sub>C-F</sub> = 1.2 Hz), 136.2, 135.8, 130.9, 130.1, 128.5 (q, *J*<sub>C-F</sub> = 32.4 Hz), 128.2, 126.2, 126.0, 125.6 (q, *J*<sub>C-F</sub> = 3.8 Hz), 124.5 (q, *J*<sub>C-F</sub> = 271.7 Hz), 23.4, 15.1. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -62.30. GC-MS (EI) *m/z* calcd for C<sub>17</sub>H<sub>18</sub>F<sub>3</sub>Si [M]<sup>+</sup>: 306.40, Found: 306.15

The GC trace for the crude mixture of the reaction to make **1e**.

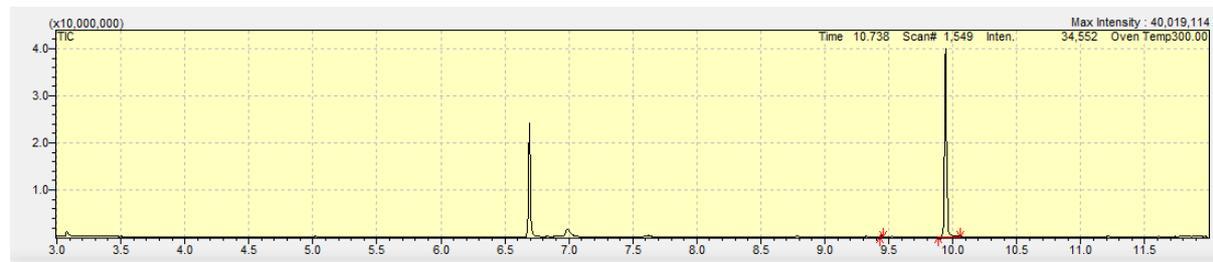


Peak#	Ret. Time	Start Tm	End Tm	<i>m/z</i>	Area	Area%	Height	Height%	A/H	Mark	Name
1	8.671	8.610	8.825	TIC	10871644	100.00	7168690	100.00	1.52	MI	

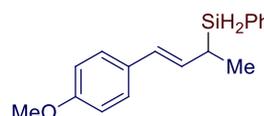


**(E)-(4-(4-bromophenyl)but-3-en-2-yl)(phenyl)silane (**1f**)**  
The reaction was stirred for 6 h at 24 °C. The title compound was isolated (66.0 mg, 52%, *E/Z* = >99:1, 1.2/1,4 = 99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.54 (m, 2H), 7.47–7.31 (m, 5H), 7.21–7.10 (m, 2H), 6.33 (dd, *J* = 15.9, 7.6 Hz, 1H), 6.20 (d, *J* = 16.0 Hz, 1H), 4.39–4.22 (m, 2H), 2.41–2.17 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.1, 135.8, 134.1, 131.7, 131.1, 130.0, 128.1, 127.4, 126.2, 120.3, 23.2, 15.1. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>BrSi, [M+H]<sup>+</sup>: 317.0361, Found: 317.0357.

The GC trace for the crude mixture of the reaction to make **1f**.

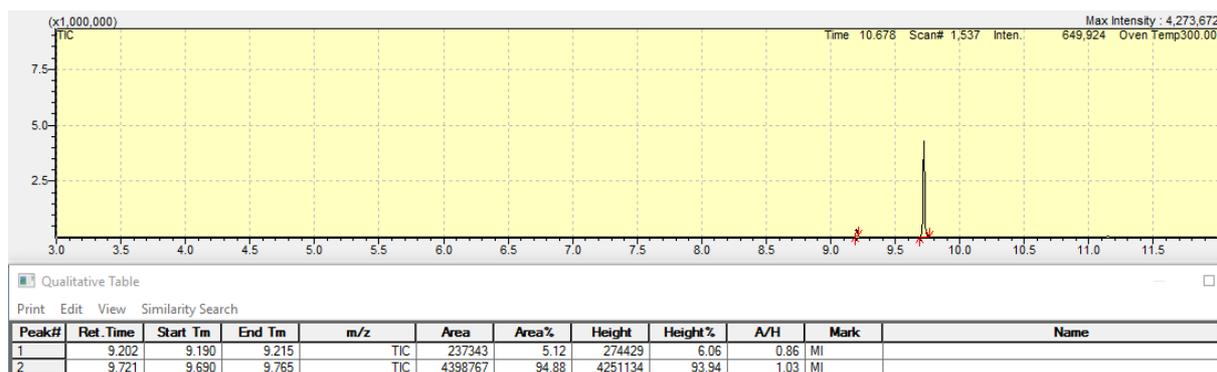


Peak#	Ret. Time	Start Tm	End Tm	<i>m/z</i>	Area	Area%	Height	Height%	A/H	Mark	Name
1	9.442	9.430	9.460	TIC	340806	0.69	339798	0.84	1.00	MI	
2	9.943	9.885	10.060	TIC	49099775	99.31	39890559	99.16	1.23	MI	

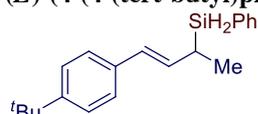


**(E)-(4-(4-methoxyphenyl)but-3-en-2-yl)(phenyl)silane (**1o**)**  
The reaction was stirred for 6 h at 24 °C. The title compound was isolated (97.6 mg, 91%, *E/Z* = >99:1, 1.2/1,4 = 95:5) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.51 (m, 2H), 7.45–7.31 (m, 3H), 7.26–7.22 (m, 2H), 6.85–6.79 (m, 2H), 6.23 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.35–4.19 (m, 2H), 3.80 (s, 3H), 2.28–2.19 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.7, 135.9, 131.5, 131.1, 131.0, 129.9, 128.1, 127.0, 126.8, 114.1, 55.5, 22.8, 15.4. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>21</sub>OSi, [M+H]<sup>+</sup>: 269.1362, Found: 269.1354.

The GC trace for the crude mixture of the reaction to make **1o**.

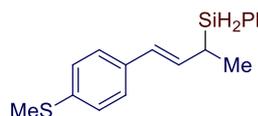
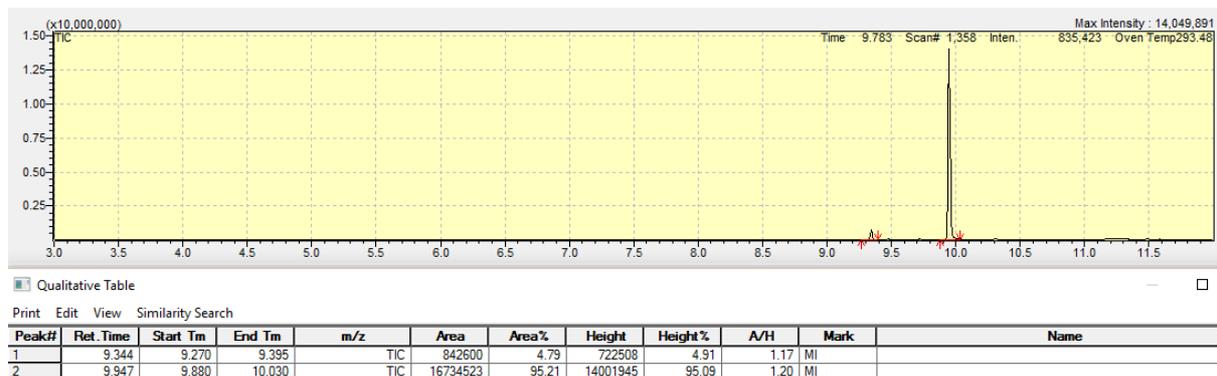


**(E)-(4-(4-(tert-butyl)phenyl)but-3-en-2-yl)(phenyl)silane (1p)**



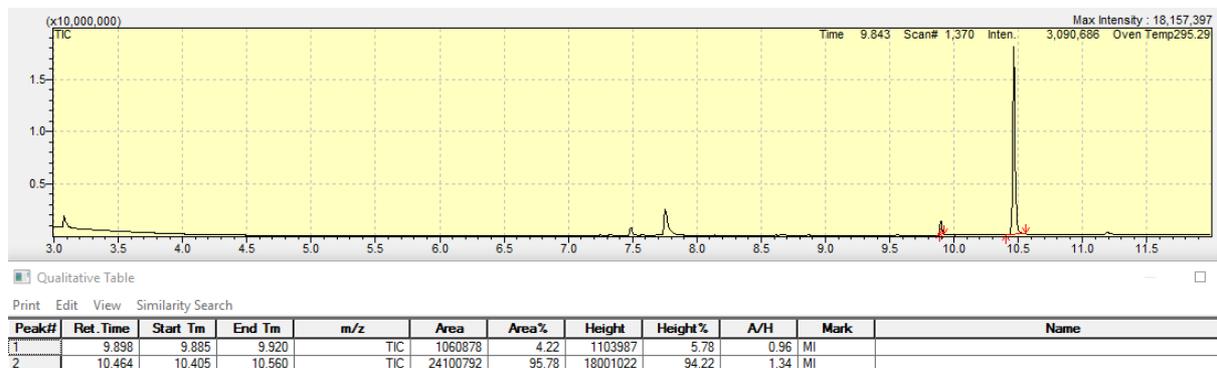
The reaction was stirred for 24 h at 5 °C. The title compound was isolated (98.1 mg, 83%, *E/Z* = >99:1, 1,2/1.4 = 95:5) as colourless oil after chromatography on silica gel (200:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51–7.45 (m, 2H), 7.34–7.27 (m, 2H), 7.25–7.13 (m, 5H), 6.21–6.17 (m, 2H), 4.26–4.15 (m, 2H), 2.22–2.10 (m, 1H), 1.25–1.18 (m, 12H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.8, 135.9, 135.4, 132.4, 131.4, 129.9, 128.1, 127.2, 125.6, 125.5, 34.1, 31.5, 22.9, 15.3. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>20</sub>H<sub>26</sub>Si, [M+H]<sup>+</sup>: 295.5139, Found: 295.1875.

The GC trace for the crude mixture of the reaction to make **1p**.

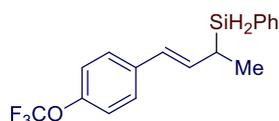


**(E)-(4-(4-(methylthio)phenyl)but-3-en-2-yl)(phenyl)silane (1q)**  
 The reaction was stirred for 24 h at 5 °C. The title compound was isolated (76.7 mg, 67%, *E/Z* = >99:1, 1,2/1.4 = 94:6) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.55 (m, 2H), 7.47–7.34 (m, 3H), 7.28–7.17 (m, 4H), 6.31 (dd, *J* = 15.9, 7.1 Hz, 1H), 6.23 (d, *J* = 16.0 Hz, 1H), 4.35–4.27 (m, 2H), 2.49 (s, 3H), 2.32–2.22 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.5, 135.8, 135.4, 132.8, 131.3, 130.0, 128.1, 127.2, 126.8, 126.3, 23.0, 16.3, 15.2. GC-MS (EI) *m/z*: calcd for C<sub>17</sub>H<sub>20</sub>OSSi [M]<sup>+</sup>: 284.11; Found: 284.15.

The GC trace for the crude mixture of the reaction to make **1q**.

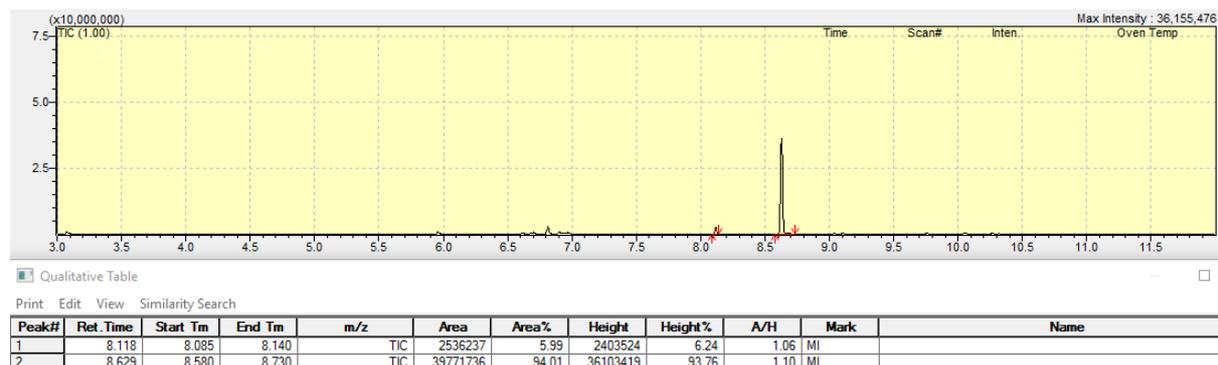


### (E)-phenyl(4-(4-(trifluoromethoxy)phenyl)but-3-en-2-yl)silane (**1r**)

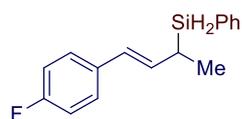


The reaction was stirred for 24 h at 5 °C. The title compound was isolated (87.7 mg, 68%, *E/Z* = >99:1, 1,2/1.4 = 94:6) as colourless oil after chromatography on silica gel (100:0 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.44–7.27 (m, 5H), 7.16–7.07 (m, 2H), 6.31 (dd, *J* = 15.9, 7.1 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 2.9 Hz, 2H), 2.33–2.18 (m, 1H), 1.30 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.0, 137.0, 135.8, 134.4, 131.1, 130.1, 128.2, 127.0, 126.0, 121.2, 120.7 (q, *J*<sub>C-F</sub> = 256.7 Hz), 23.2, 15.2. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -57.88. GC-MS (EI) *m/z*: calcd for C<sub>17</sub>H<sub>17</sub>F<sub>3</sub>OSi [M]<sup>+</sup>: 322.10; Found: 322.10.

The GC trace for the crude mixture of the reaction to make **1r**.

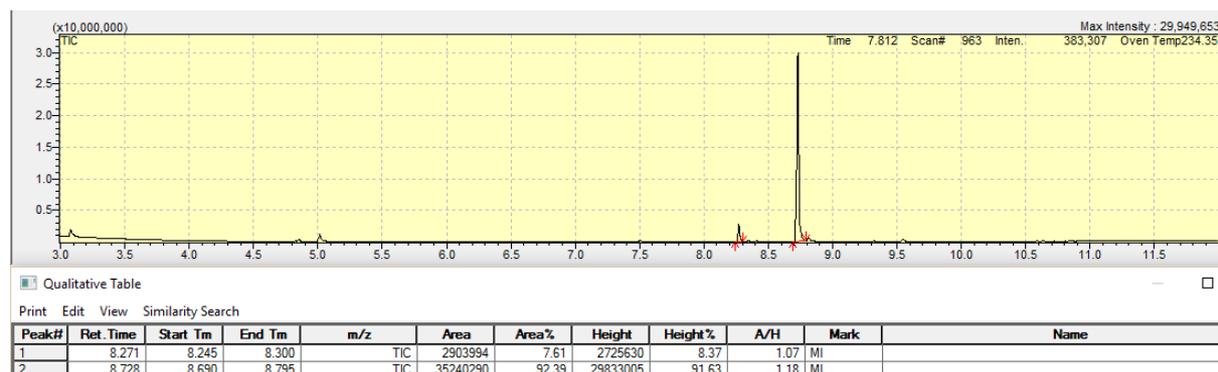


### (E)-(4-(4-fluorophenyl)but-3-en-2-yl)(phenyl)silane (**1s**)

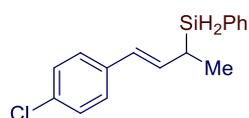


The reaction was stirred for 24 h at 5 °C. The title compound was isolated (76.7 mg, 75%, *E/Z* = >99:1, 1,2/1.4 = 92:8) as colourless oil after chromatography on silica gel (50:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64–7.56 (m, 2H), 7.44–7.34 (m, 3H), 7.29–7.23 (m, 2H), 7.03–6.95 (m, 2H), 6.25 (m, 2H), 4.41–4.27 (m, 2H), 2.34–2.20 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.9 (d, *J*<sub>C-F</sub> = 245.4 Hz), 135.8, 134.4 (d, *J*<sub>C-F</sub> = 3.3 Hz), 132.9 (d, *J*<sub>C-F</sub> = 2.2 Hz), 131.2, 130.0, 128.1, 127.3 (d, *J*<sub>C-F</sub> = 7.8 Hz), 126.3, 115.4 (d, *J*<sub>C-F</sub> = 21.5 Hz), 23.0, 15.3. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -116.01. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>FSi, [M+H]<sup>+</sup>: 257.3980, Found: 257.1162.

The GC trace for the crude mixture of the reaction to make **1s**.

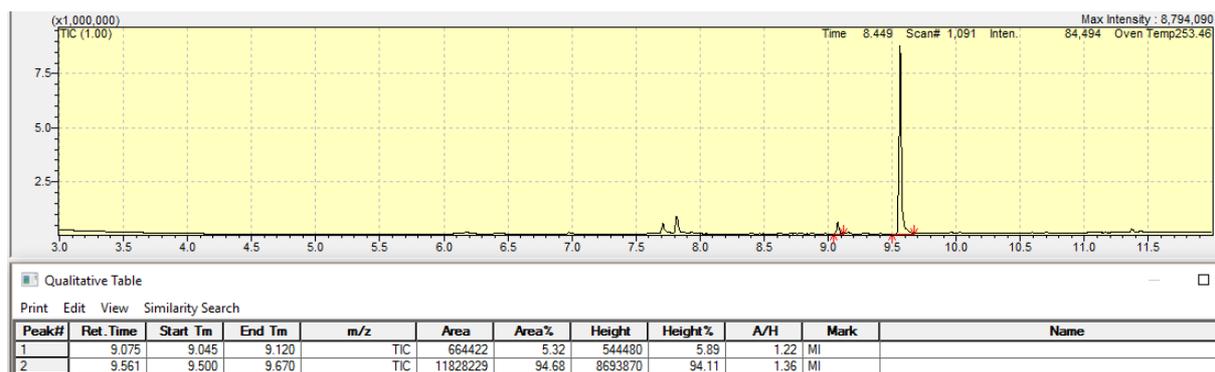


### (E)-(4-(4-chlorophenyl)but-3-en-2-yl)(phenyl)silane (**1t**)

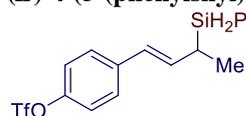


The reaction was stirred for 24 h at 5 °C. The title compound was isolated (71.5 mg, 66%, *E/Z* = >99:1, 1,2/1.4 = 95:5) as colourless oil after chromatography on silica gel (100:0 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.49–7.39 (m, 3H), 7.31–7.22 (m, 4H), 6.35 (dd, *J* = 15.9, 7.4 Hz, 1H), 6.25 (d, *J* = 16.1 Hz, 1H), 4.35 (d, *J* = 2.7 Hz, 2H), 2.36–2.24 (m, 1H), 1.34 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.7, 135.8, 134.0, 132.2, 131.1, 130.0, 128.7, 128.1, 127.1, 126.2, 23.1, 15.2. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>ClSi, [M+H]<sup>+</sup>: 273.8526, Found: 273.0860.

The GC trace for the crude mixture of the reaction to make **1t**.

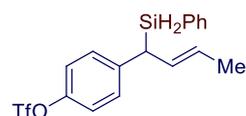


**(E)-4-(3-(phenylsilyl)but-1-en-1-yl)phenyl trifluoromethanesulfonate (1u)**



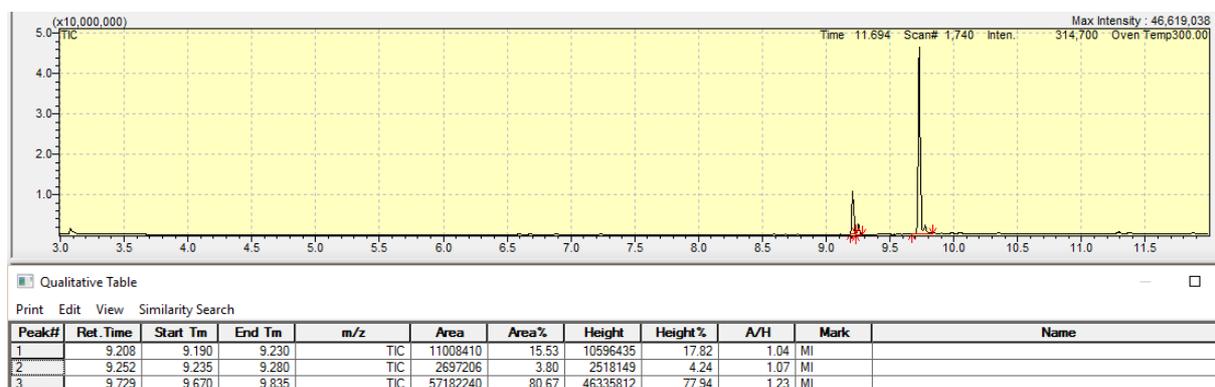
The reaction was stirred for 6 h at 24 °C. The title compound was isolated (140.8 mg, 91%, *E/Z* = >99:1, 1,2/1,4 (and minor isomer) = 80:20) as colourless oil after chromatography on silica gel (10:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.43–7.33 (m, 4H), 7.20–7.12 (m, 3H), 6.35 (dd, *J* = 15.9, 7.5 Hz, 1H), 6.24 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 2.9 Hz, 2H), 2.35–2.22 (m, 1H), 1.30 (d, *J* = 7.1 Hz, 3H). {<sup>1</sup>H} <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.2, 138.6, 135.8, 130.9, 130.1, 129.2, 128.2, 127.3, 125.5, 122.1 (q, *J*<sub>C-F</sub> = 311.7 Hz), 121.5, 23.3, 15.1. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -72.83. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>18</sub>F<sub>3</sub>O<sub>3</sub>SSi, [M+H<sup>+</sup>]: 387.0698, Found: 387.0698.

**(E)-4-(1-(phenylsilyl)but-2-en-1-yl)phenyl trifluoromethanesulfonate (2u)**

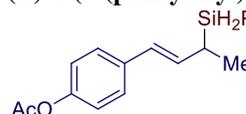


The title minor compound was isolated via chromatography on silica gel (10:1 hexane/EtOAc) together with the major 1,2-hydrosilylation product. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.77 (ddq, *J* = 15.0, 8.6, 1.5 Hz, 1H), 5.58–5.48 (m, 1H).

The GC trace for the crude mixture of the reaction to make **1u**.

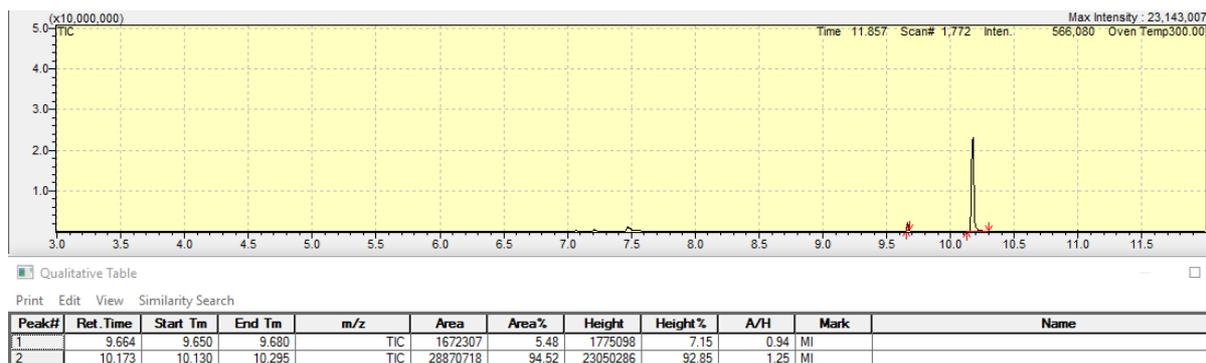


**(E)-4-(3-(phenylsilyl)but-1-en-1-yl)phenyl acetate (1v)**

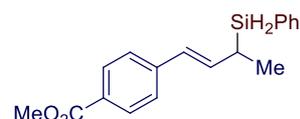


The reaction was stirred for 24 h at 5 °C. The title compound was isolated (106 mg, 89%, *E/Z* = >99:1, 1,2/1,4 = 95:5) as colourless oil after chromatography on silica gel (25:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.45–7.33 (m, 3H), 7.31–7.27 (m, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.31–6.21 (m, 2H), 4.29 (d, *J* = 2.9 Hz, 2H), 2.32–2.25 (m, 4H), 1.29 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H} <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.7, 149.5, 136.1, 135.8, 133.5, 131.2, 130.0, 128.1, 126.8, 126.5, 121.7, 23.0, 21.3, 15.2. GC-MS (EI) *m/z*: calcd for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>Si [M]<sup>+</sup>: 296.12; Found: 296.15.

The GC trace for the crude mixture of the reaction to make **1v**.

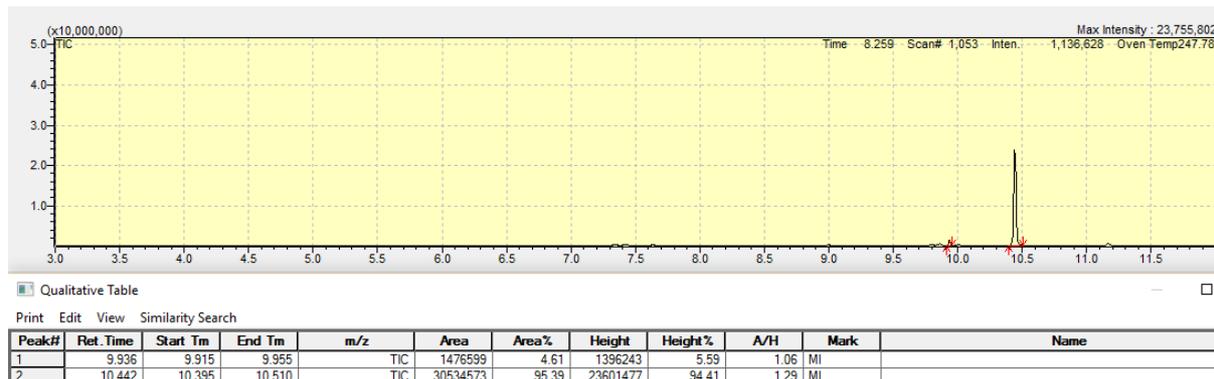


**(E)-methyl 4-(3-(phenylsilyl)but-1-en-1-yl)benzoate (1w)**

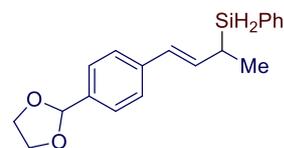


The reaction was stirred for 24 h at 5 °C with 0.2 mmol scale. The title compound was isolated (43.0 mg, 73%, *E/Z* = >99:1, 1,2/1.4 = 95:5) as colourless oil after chromatography on silica gel (25:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00–7.93 (m, 3H), 7.59–7.55 (m, 2H), 7.41–7.34 (m, 3H), 7.28–7.23 (m, 1H), 6.47 (dd, *J* = 15.9, 7.7 Hz, 1H), 6.29 (d, *J* = 16.6 Hz, 1H), 4.31 (dd, *J* = 2.9, 0.8 Hz, 2H), 3.91 (s, 3H), 2.36–2.26 (m, 1H), 1.31 (d, *J* = 7.1 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 142.7, 136.4, 135.8, 130.9, 130.0, 129.8, 128.5, 128.2, 126.6, 125.7, 52.1, 23.5, 15.1. GC-MS (EI) *m/z*: calcd for C<sub>18</sub>H<sub>20</sub>O<sub>2</sub>Si [M]<sup>+</sup>: 296.12; Found: 296.15.

The GC trace for the crude mixture of the reaction to make **1w**.

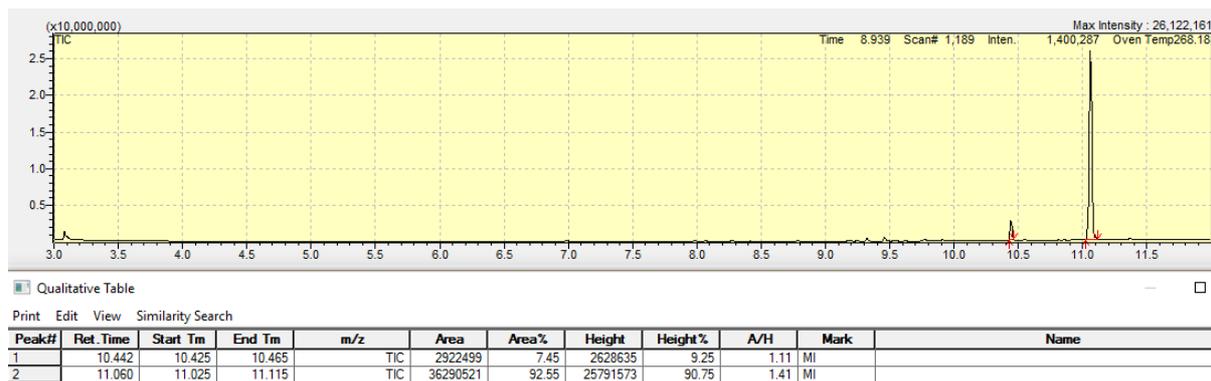


**(E)-(4-(4-(1,3-dioxolan-2-yl)phenyl)but-3-en-2-yl)(phenyl)silane (1x)**

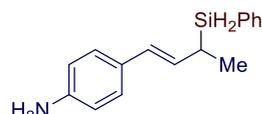


The reaction was stirred for 6 h at 24 °C. The title compound was isolated (94.8 mg, 76%, *E/Z* = >99:1, 1,2/1.4 = 93:7) as colourless oil after chromatography on silica gel (10:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61–7.55 (m, 2H), 7.42–7.32 (m, 7H), 6.37 (dd, *J* = 15.9, 7.3 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 5.81 (s, 1H), 4.32 (d, *J* = 2.9 Hz, 2H), 4.16–4.11 (m, 2H), 4.06–4.01 (m, 2H), 2.34–2.24 (m, 1H), 1.31 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.1, 136.2, 135.8, 133.9, 131.2, 130.0, 128.1, 127.0, 126.8, 125.8, 103.8, 65.4, 23.1, 15.2. GC-MS (EI) *m/z*: calcd for C<sub>19</sub>H<sub>22</sub>O<sub>2</sub>Si [M]<sup>+</sup>: 310.14; Found: 309.15.

The GC trace for the crude mixture of the reaction to make **1x**.

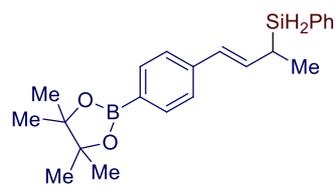
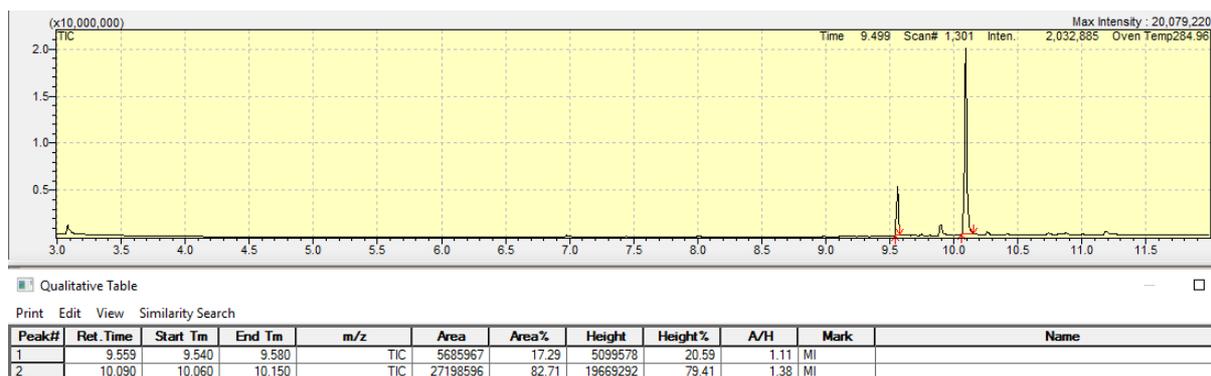


### (E)-4-(3-(phenylsilyl)but-1-en-1-yl)aniline (**1y**)



The reaction was stirred for 6 h at 24 °C. The title compound was isolated (83.0 mg, 82%, *E/Z* = >99:1, 1,2/1.4 = 83:17) as colourless oil after chromatography on silica gel (5:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61–7.56 (m, 2H), 7.42–7.34 (m, 3H), 7.15–7.07 (m, 2H), 6.63–6.60 (m, 2H), 6.19 (d, *J* = 16.0 Hz, 1H), 6.11 (dd, *J* = 15.9, 7.3 Hz, 1H), 4.32–4.22 (m, 2H), 3.61 (s, 2H), 2.26–2.17 (m, 1H), 1.27 (d, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.3, 135.9, 131.6, 129.9, 129.5, 128.7, 128.1, 127.2, 127.0, 115.3, 22.7, 15.4. GC-MS (EI) *m/z*: calcd for C<sub>16</sub>H<sub>19</sub>NSi [M]<sup>+</sup>: 253.41; Found: 253.15.

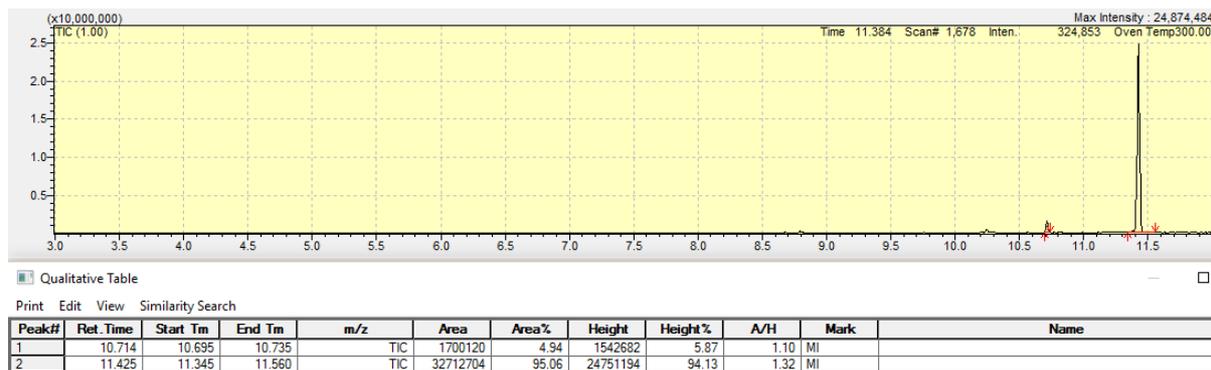
The GC trace for the crude mixture of the reaction to make **1y**.



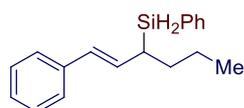
### (E)-phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)but-3-en-2-yl)silane (**1z**)

The reaction was stirred for 6 h at 24 °C. The title compound was isolated (127 mg, 87%, *E/Z* = >99:1, 1,2/1.4 = 95:5) as colourless oil after chromatography on silica gel (30:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.58 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.45–7.29 (m, 5H), 6.42 (dd, *J* = 15.9, 7.6 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 4.32 (d, *J* = 2.8 Hz, 2H), 2.34–2.23 (m, 1H), 1.36 (s, 12H), 1.31 (d, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 140.9, 135.8, 135.2, 134.4, 131.1, 130.0, 128.1, 127.5, 125.2, 83.8, 25.0, 23.2, 15.1. The carbon connected with boron could not be observed due to quadrupole of boron. GC-MS (EI) *m/z*: calcd for C<sub>22</sub>H<sub>29</sub>BO<sub>2</sub>Si ([M]<sup>+</sup>): 364.20; Found: 364.25.

The GC trace for the crude mixture of the reaction to make **1z**.

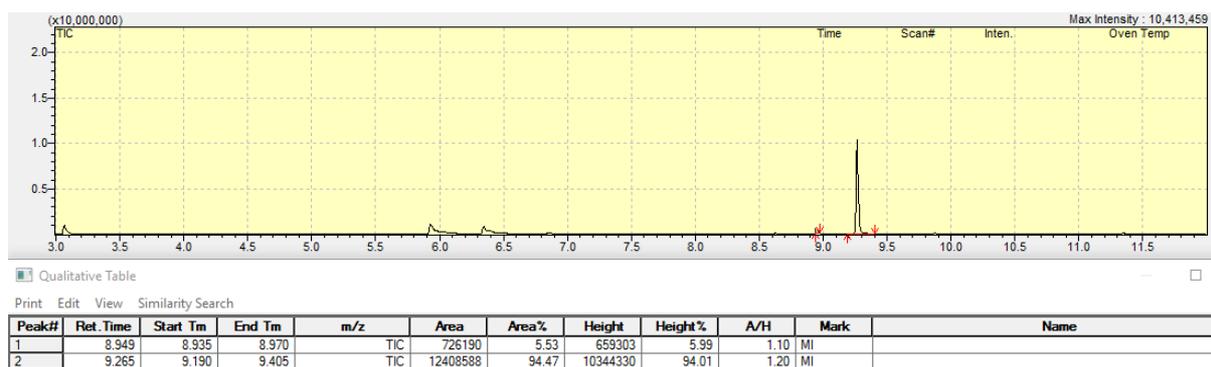


### (E)-phenyl(1-phenylhex-1-en-3-yl)silane (1aa)

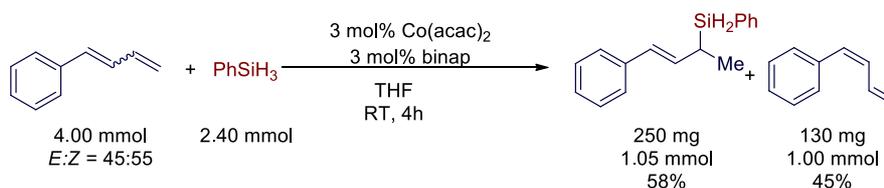


The reaction was stirred for 48 h at 24 °C. The title compound was isolated (61.0 mg, 57%, *E/Z* = >99:1, 1,2/1.4 = 94:6) as colourless oil after chromatography on silica gel (100:0 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.38–7.31 (m, 3H), 7.25 (d, *J* = 3.3 Hz, 4H), 7.17–7.11 (m, 1H), 6.24 (d, *J* = 15.9 Hz, 1H), 6.11 (dd, *J* = 15.8, 9.2 Hz, 1H), 4.31–4.26 (m, 2H), 2.21–2.13 (m, 1H), 1.62–1.54 (m, 2H), 1.49–1.39 (m, 1H), 1.37–1.27 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H). {<sup>1</sup>H} <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.2, 135.9, 132.1, 131.4, 129.9, 128.9, 128.6, 128.1, 126.7, 125.9, 32.9, 29.5, 22.6, 14.0. GC-MS (EI) *m/z*: calcd for C<sub>18</sub>H<sub>22</sub>Si [M]<sup>+</sup>: 266.45; Found: 266.20.

The GC trace for the crude mixture of the reaction to make **1aa**.

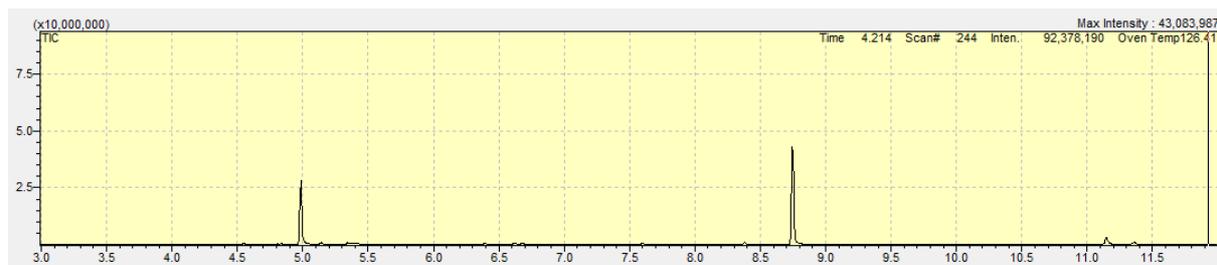


### General procedure for Separation of *cis*-1,3-dienes via hydrosilylation reaction

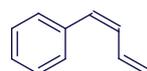


In an Ar-filled glovebox, a mixture of Co(acac)<sub>2</sub> (19.0 mg, 0.120 mmol) and binap (45.0 mg, 0.120 mmol) in THF (5 mL) was added into a 20-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding phenylsilane (0.260 g, 2.40 mmol) and *trans/cis*-1,3-dienes (0.520 g, 4.00 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at room temperature for 6 hours. After that, a GC-MS analysis was done and the crude reaction mixture was concentrated under vacuum using a 30 °C water bath and the residue was purified by flash column chromatography using hexane and ethyl acetate (100:1) as eluents yielding (*E*)-allylsilane **1a** (0.250 g, 1.05 mmol, 58%) as a colorless oil and recovering (*Z*)-1-phenyl-1,3-diene (*Z/E* = 98:2, 0.130 g, 1.0 mmol, 45%).

The GC trace for the crude reaction mixture to form **1a** (*t<sub>r</sub>* = 5.0 min) and (*Z*)-1-phenyl-1,3-diene (*t<sub>r</sub>* = 8.8 min).



### (Z)-1-phenyl-1,3-diene

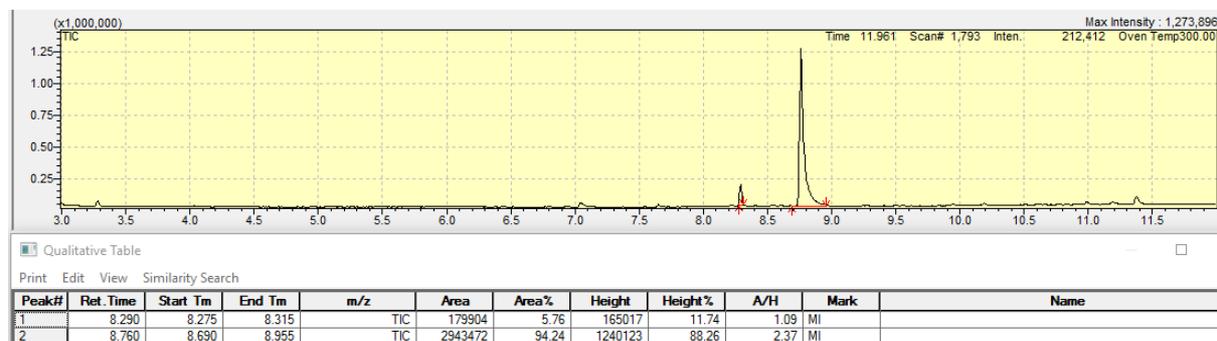


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.31 (m, 4H), 7.28–7.22 (m, 1H), 6.89 (dddd,  $J = 16.9$ , 11.2, 10.1, 1.0 Hz, 1H), 6.47 (d,  $J = 11.5$  Hz, 1H), 6.27 (t,  $J = 11.3$  Hz, 1H), 5.38 (ddd,  $J = 16.9$ , 1.8, 0.9 Hz, 1H), 5.23 (dt,  $J = 10.1$ , 2.1 Hz, 1H).  $\{^1\text{H}\}^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 133.4, 130.9, 130.6, 129.2, 128.4, 127.2, 119.8. GC-MS (EI)  $m/z$ : calcd for  $\text{C}_{10}\text{H}_{10}$   $[\text{M}]^+$ : 130.08; Found: 129.15.

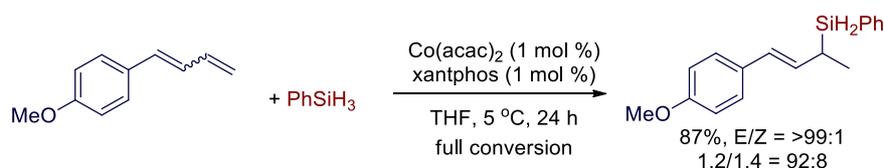
### General procedure for Co-catalyzed Markovnikov 1,2-hydrosilylation of trans/cis 1,3-dienes (Outside glovebox under nitrogen protection)

$\text{Co}(\text{acac})_2$  (1.0 mg, 4.0  $\mu\text{mol}$ ) and xantphos (2.3 mg, 4.0  $\mu\text{mol}$ ) were pre-weighed in air on the open bench and added into a 25 mL Schlenk flask. The Schlenk flask was back-filled with  $\text{N}_2$  thrice and dry THF (1 mL) was then added. The resulting mixture was stirred for 2 mins to give a pale pink solution. Subsequently, phenylsilane (54.1 mg, 0.500 mmol) and 1-phenylbutadiene (51.6 mg, 0.400 mmol) were added with the aid of a microsyringe which gave a pale-yellow solution. Upon stirring the mixture for 6 hours, a GC-MS analysis was conducted to determine the selectivity of the crude reaction mixture prior concentrating it under vacuum. Subsequently, the residue was purified by flash column chromatography using a mixture of ethyl acetate and hexane as eluent yielding (*E*)-phenyl(4-phenylbut-3-en-2-yl)silane **1a** (74.7mg, 78%, *E/Z* = >99:1, 1,2/1,4 = 94:6) as a colorless oil.

The GC trace for the crude mixture of the reaction to form **1a**.



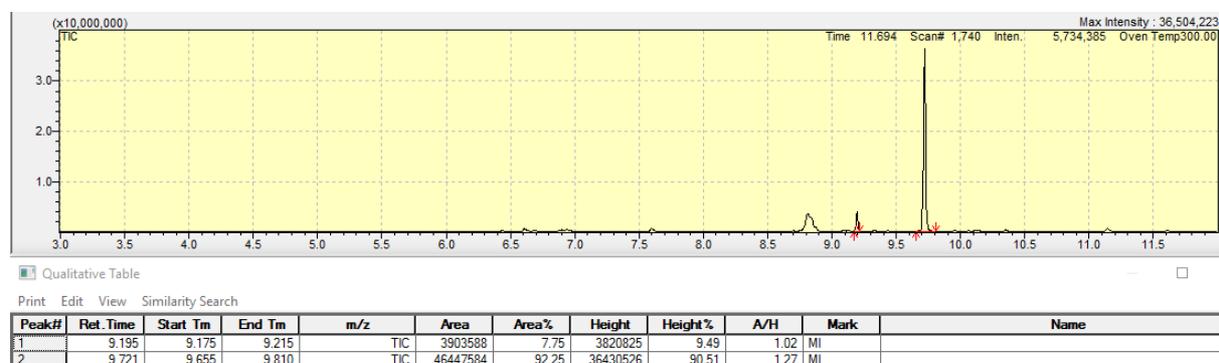
### General procedure for gram scale Co-catalyzed Markovnikov 1,2-hydrosilylation of 1,3-dienes



$\text{Co}(\text{acac})_2$  (25.7 mg, 0.100 mmol) and xantphos (57.9 mg, 0.100 mmol) were weighted in air on the open bench and added into a 100 mL Schlenk flask. The Schlenk flask was back-filled with  $\text{N}_2$  thrice and dry THF (25 mL) was then added. The resulting mixture was stirred for 2 mins to give a pale pink solution prior adding phenylsilane (1.35 g, 12.5 mmol) and 1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1.60 g, 10.0 mmol) successively. The Schlenk flask was removed from the glove box, and the mixture was stirred at room

temperature for 6 hours. Subsequently, a GC-MS analysis was conducted to determine the selectivity of the crude reaction mixture prior concentrating it under vacuum. The residue was then purified by flash column chromatography using a mixture of ethyl acetate and hexane as eluent yielding (*E*)-(4-(4-methoxyphenyl)but-3-en-2-yl)(phenyl)silane **1o** (2.34 g, 87 %, *E/Z* = >99:1, 1,2/1.4 = 92:8) as a colorless oil.

The GC trace for the crude reaction mixture to form **1o**.



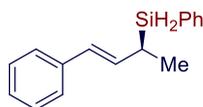
### General procedure for asymmetric Co-catalyzed Markovnikov 1,2-hydrosilylation of *trans*-1,3-dienes

In an Ar-filled glovebox, a mixture of Co(acac)<sub>2</sub> (5.1 mg, 20 μmol) and (*R*)-difluorophos (14.0 mg, 20 μmol) in THF (1 mL) was added into a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding phenylsilane (54.1 mg, 0.500 mmol) and *trans*-1,3-dienes (0.400 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at room temperature for 6 hours. After that, the crude reaction mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of ethyl acetate and hexane as eluent. The details and characterization data of the products are stated below. The enantiopurity of the product was analyzed by chiral HPLC or oxidized to (*E*)-allylic alcohol prior analysing with chiral HPLC.

### Procedure for oxidation of (*E*)-allylsilanes

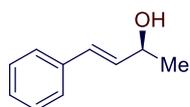
A mixture of (*E*)-allylsilane (0.200 mmol) and KHCO<sub>3</sub> (0.200 mmol) was added into a mixture of THF (0.5 mL) and methanol (0.5 mL) in a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins. Subsequently, 30% aqueous H<sub>2</sub>O<sub>2</sub> (0.500 mmol) was dropwise slowly into the reaction mixture and then stirred at room temperature for 5 hours. Anhydrous sodium thiosulfate was then added to quench the excess oxidant prior it was extracted with ethyl acetate, dried over sodium sulfate, filtered and concentrated under vacuum. The residue was then purified by flash column chromatography using hexane and ethyl acetate as eluents yielding (*E*)-allylic alcohol.

### (*S,E*)-phenyl(4-phenylbut-3-en-2-yl)silane (**1a**)

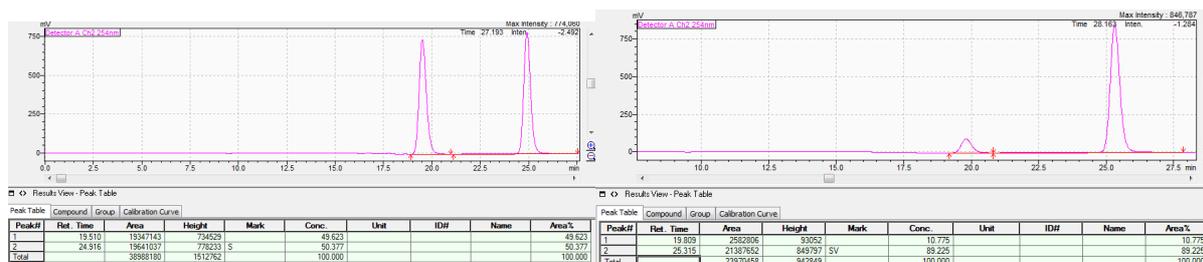


The reaction was stirred for 6 h at 24 °C. The title compound was isolated (68.0 mg, 71%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63–7.58 (m, 2H), 7.47–7.36 (m, 3H), 7.34–7.28 (m, 4H), 7.23–7.17 (m, 1H), 6.35 (dd, *J* = 15.9, 6.8 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 4.35–4.28 (m, 2H), 2.35–2.23 (m, 1H), 1.32 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.2, 135.9, 133.2, 131.30, 123.0, 128.6, 128.1, 127.4, 126.7, 125.9, 23.0, 15.3. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>16</sub>H<sub>18</sub>Si, [M+H]<sup>+</sup>: 239.1256, Found: 239.1258. Optical Rotation: [α]<sub>D</sub><sup>20</sup> = -15.00 (c = 0.20 g/cm<sup>3</sup>, CHCl<sub>3</sub>). The absolute configuration was assigned by oxidizing it to the corresponding allylic alcohol (**1a''**).

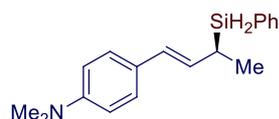
### (*S,E*)-4-phenylbut-3-en-2-ol (**1a''**)



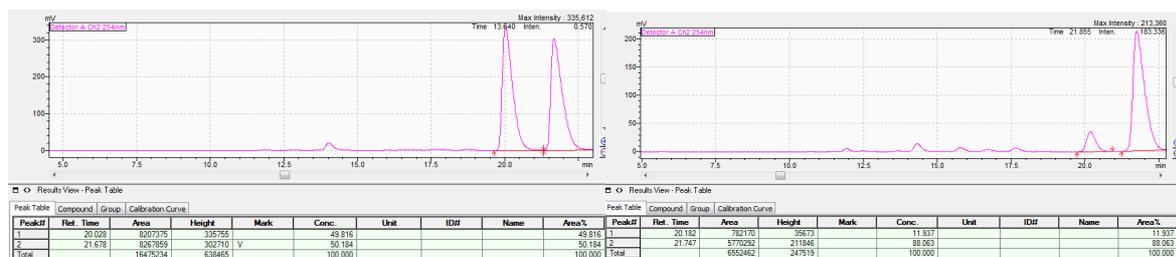
The title compound was isolated (34.5 mg, 82%, 88:11 er) as colourless oil after chromatography on silica gel (10:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.34–7.29 (m, 2H), 7.26–7.21 (m, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.55–4.44 (m, 1H), 1.38 (d, *J* = 6.4 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.9, 133.7, 129.6, 128.7, 127.8, 126.6, 69.1, 23.6. Optical Rotation: [α]<sub>D</sub><sup>20</sup> = -16.10 (c = 0.20 g/cm<sup>3</sup>, CHCl<sub>3</sub>). The absolute configuration was assigned by comparing with the optical rotation reported in the literature.<sup>5</sup> HPLC condition: Chiral column IB, n-hexane/*i*-PrOH = 90:10, flow rate = 0.35 mL/min, wavelength = 254 nm, t<sub>R</sub> = 19.8 min for minor isomer, t<sub>R</sub> = 25.3 min for major isomer.



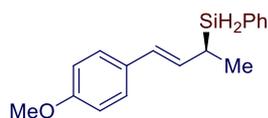
### (*S,E*)-*N,N*-dimethyl-4-(3-(phenylsilyl)but-1-en-1-yl)aniline (**1d**)



The title compound was isolated (91.0 mg, 80%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (20:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.29 – 7.17 (m, 3H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 6.08 (d, *J* = 15.9 Hz, 1H), 5.98 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.23 – 4.09 (m, 2H), 2.79 (s, 6H), 2.15 – 2.03 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.7, 135.9, 131.7, 129.8, 128.9, 128.0, 127.3, 127.1, 126.7, 112.8, 40.8, 22.7, 15.5. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>18</sub>H<sub>24</sub>NSi, [M+H<sup>+</sup>]: 282.1678, Found: 282.1681. The absolute configuration was assigned by analog to that of **1a**. Optical Rotation: [α]<sub>D</sub><sup>20</sup> = -21.00 (c = 0.30 g/cm<sup>3</sup>, CHCl<sub>3</sub>). HPLC condition: Chiral column IB, n-hexane/*i*-PrOH = 99.9:0.1, flow rate = 0.35 mL/min, wavelength = 254 nm, t<sub>R</sub> = 20.2 min for minor isomer, t<sub>R</sub> = 21.7 min for major isomer.

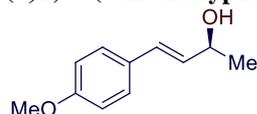


### (*S,E*)-4-(4-methoxyphenyl)but-3-en-2-yl(phenyl)silane (**1o**)

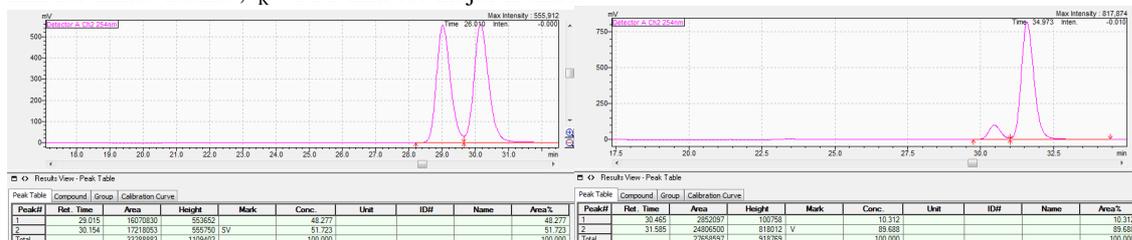


The reaction was stirred for 12 h at 24 °C. The title compound was isolated (42.0 mg, 61%, *E/Z* = >99:1) as colourless oil after chromatography on silica gel (100:1 hexane/EtOAc). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62–7.51 (m, 2H), 7.45–7.31 (m, 3H), 7.26–7.22 (m, 2H), 6.85–6.79 (m, 2H), 6.23 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 15.9, 6.9 Hz, 1H), 4.35–4.19 (m, 2H), 3.80 (s, 3H), 2.28–2.19 (m, 1H), 1.28 (d, *J* = 7.2 Hz, 3H). {<sup>1</sup>H}<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.7, 135.9, 131.5, 131.1, 131.0, 129.9, 128.1, 127.0, 126.8, 114.1, 55.5, 22.8, 15.4. HR-MS (APCI<sup>+</sup>) *m/z* calcd for C<sub>17</sub>H<sub>21</sub>OSi, [M+H<sup>+</sup>]: 269.1362, Found: 269.1354. Optical Rotation: [α]<sub>D</sub><sup>20</sup> = -21.00 (c = 0.30 g/cm<sup>3</sup>, CHCl<sub>3</sub>). The absolute configuration was assigned by oxidizing it to the corresponding allylic alcohol (**1o''**).

### (*S,E*)-4-(4-methoxyphenyl)but-3-en-2-ol (**1o''**)



The title compound was isolated (31.7 mg, 73%, 90:10 er) as colourless oil after chromatography on silica gel (10:1 hexane/EtOAc).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.28 (m, 2H), 6.88–6.83 (m, 2H), 6.51 (d,  $J = 15.9$  Hz, 1H), 6.13 (dd,  $J = 15.9$ , 6.6 Hz, 1H), 4.47 (p,  $J = 6.3$  Hz, 1H), 3.81 (s, 3H), 1.37 (d,  $J = 6.4$  Hz, 3H).  $\{^1\text{H}\}^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 131.6, 129.6, 129.2, 127.8, 114.2, 69.3, 55.5, 23.6. Optical Rotation:  $[\alpha]_{\text{D}}^{20} = -10.70$  ( $c = 0.30$  g/cm $^3$ ,  $\text{CHCl}_3$ ). The absolute configuration was assigned by analog to that of **1a''**. HPLC condition: Chiral column IB, n-hexane/*i*-PrOH = 93:7, flow rate = 0.35 mL/min, wavelength = 254 nm,  $t_{\text{R}} = 30.4$  min for minor isomer,  $t_{\text{R}} = 31.5$  min for major isomer.

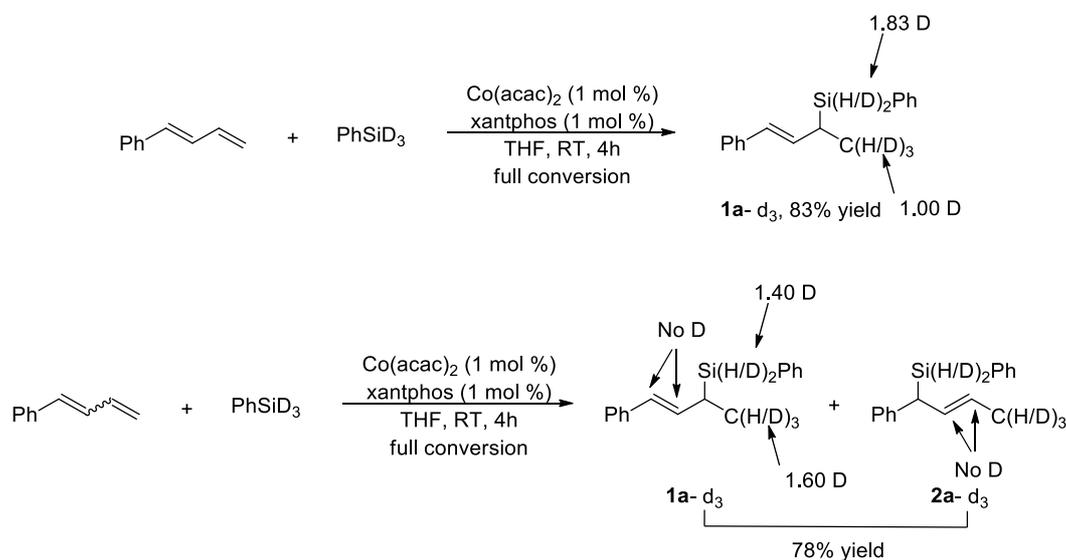


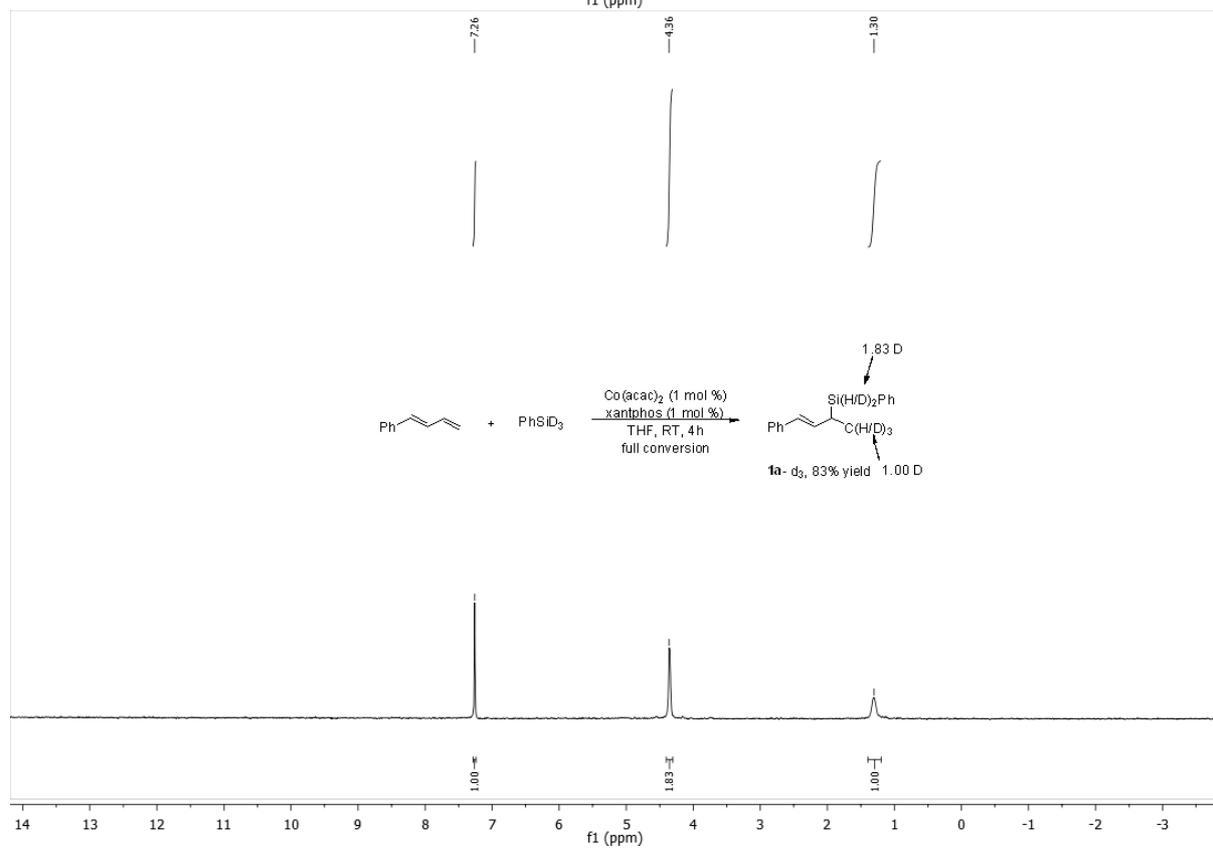
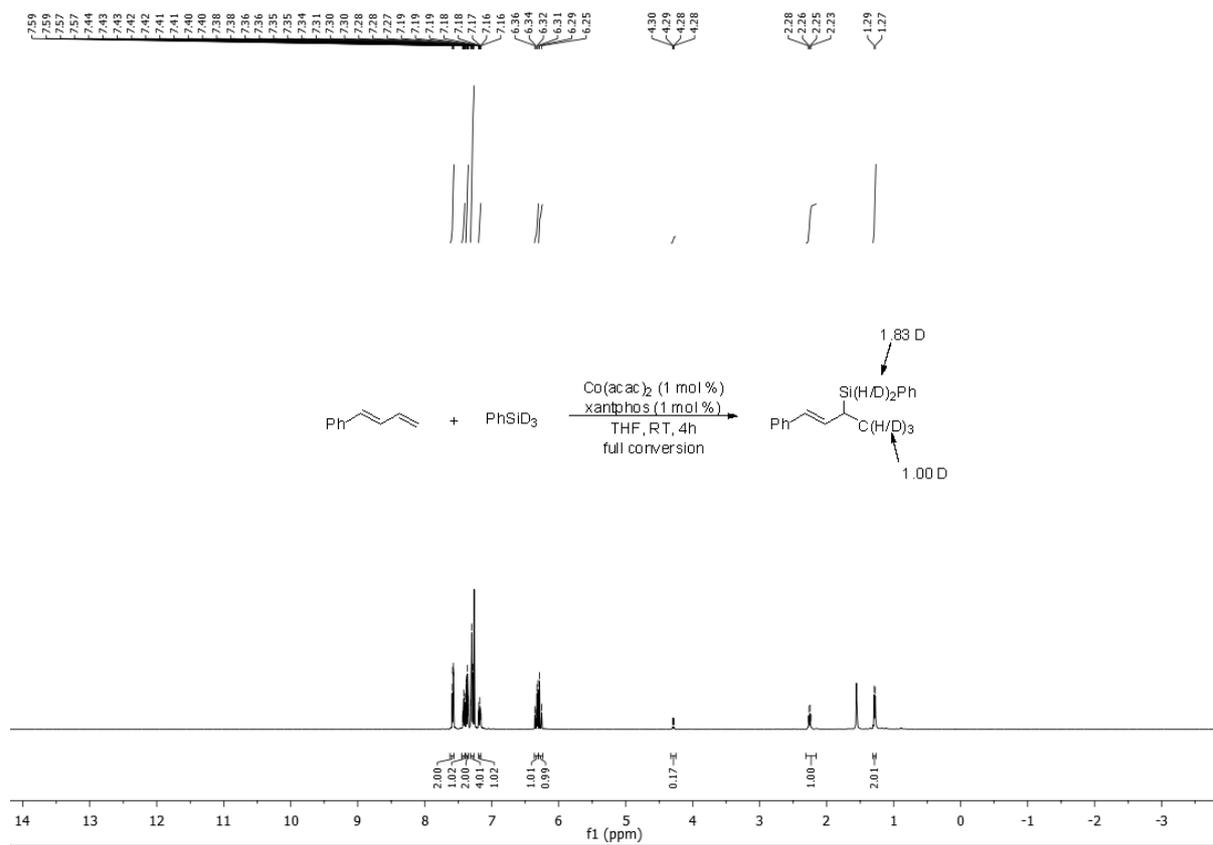
### Mechanistic studies

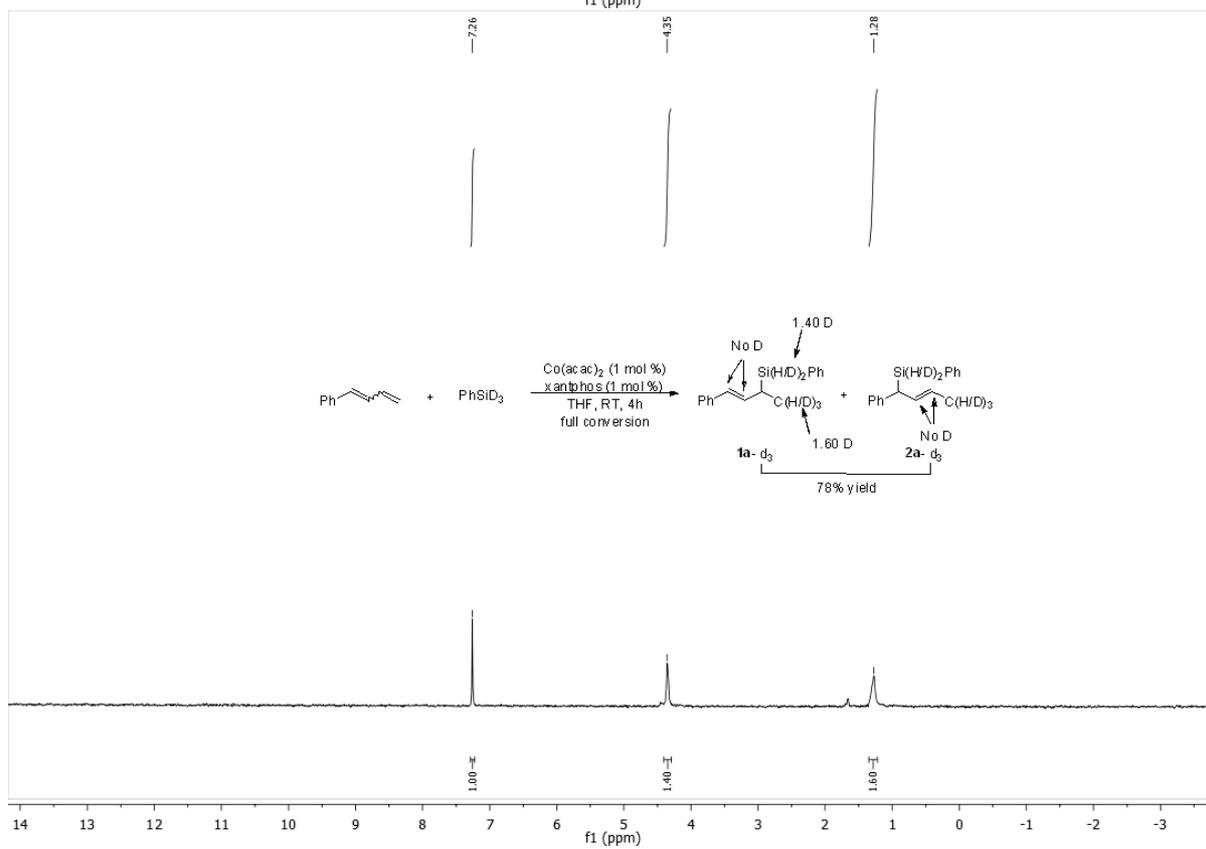
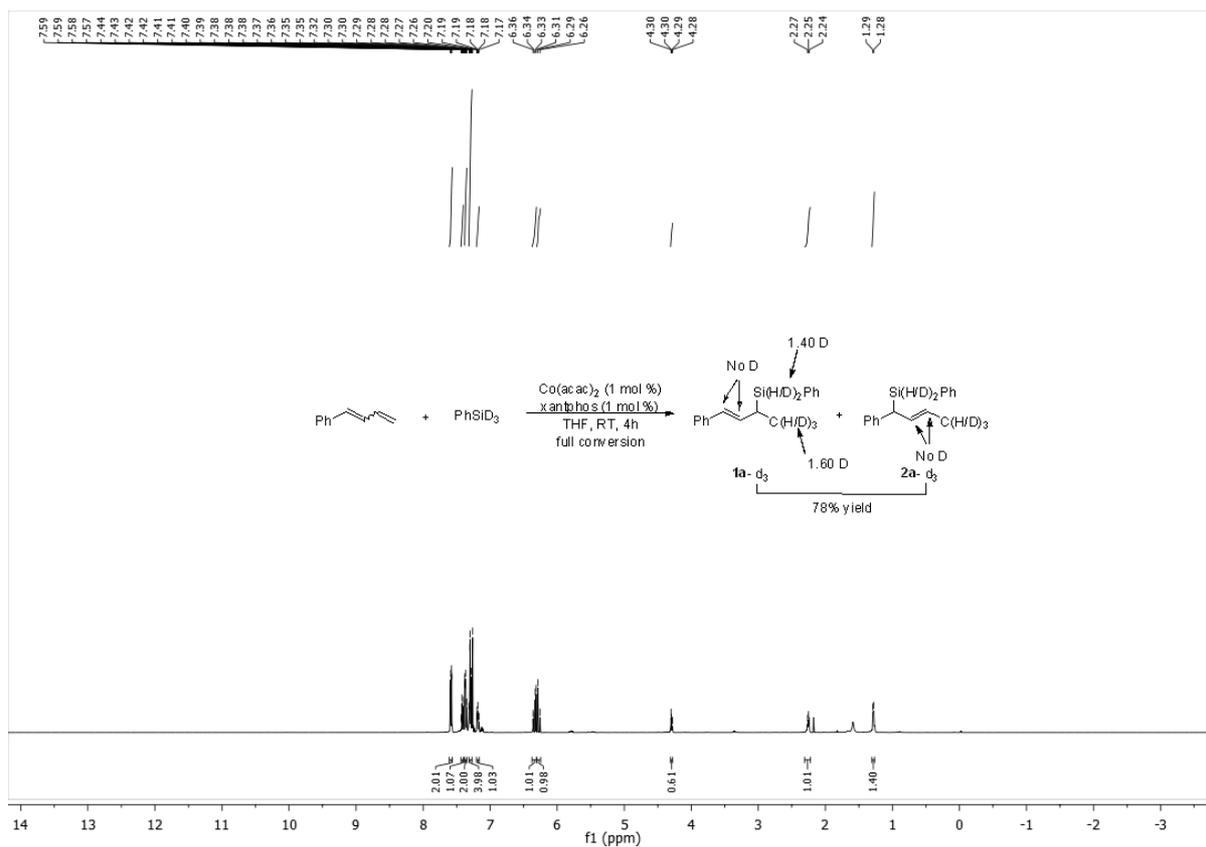
#### Procedure for Deuterium-labeling Experiments

Note:  $\text{PhSiD}_3$ <sup>6</sup> was synthesized based on previously reported procedure.

In an Ar-filled glovebox, a mixture of  $\text{Co}(\text{acac})_2$  (0.5 mg, 2.0  $\mu\text{mol}$ ) and xantphos (1.2 mg, 2.0  $\mu\text{mol}$ ) in THF (0.5 mL) was added into a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding  $\text{PhSiD}_3$  (27.8 mg, 0.25 mmol) and 1,3-dienes (0.2 mmol) successively. The vial was removed from the glove box, and the mixture was stirred at room temperature for 4 hours. After that, the crude reaction mixture was concentrated under vacuum and the residue was purified by flash column chromatography using a mixture of ethyl acetate and hexane (100:1) as eluent. The details and characterization data of the products are stated below. Equimolar of chloroform-*d* was added as the internal standard for  $^2\text{H}$  NMR analysis.

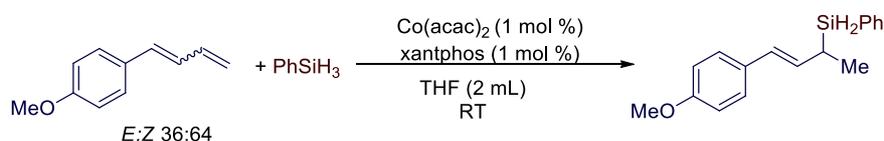




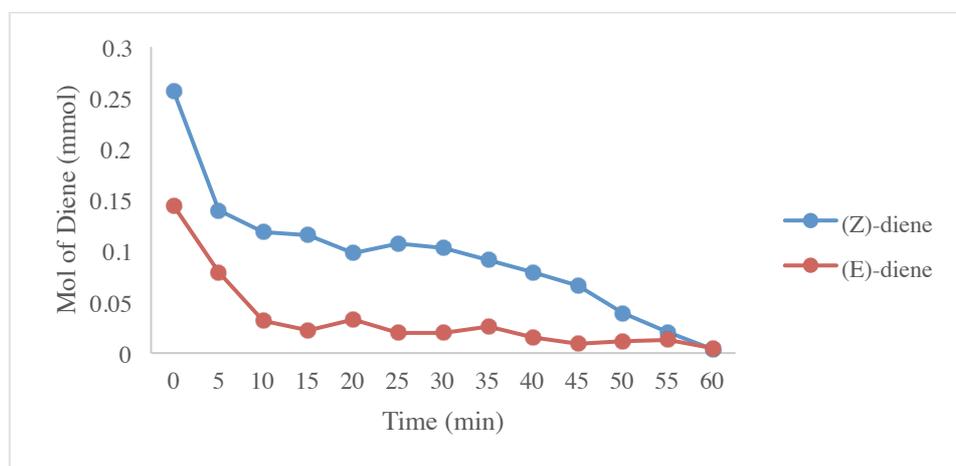


## Reaction monitoring

### General Procedure for Reaction monitoring of (*E/Z*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene with phenylsilane



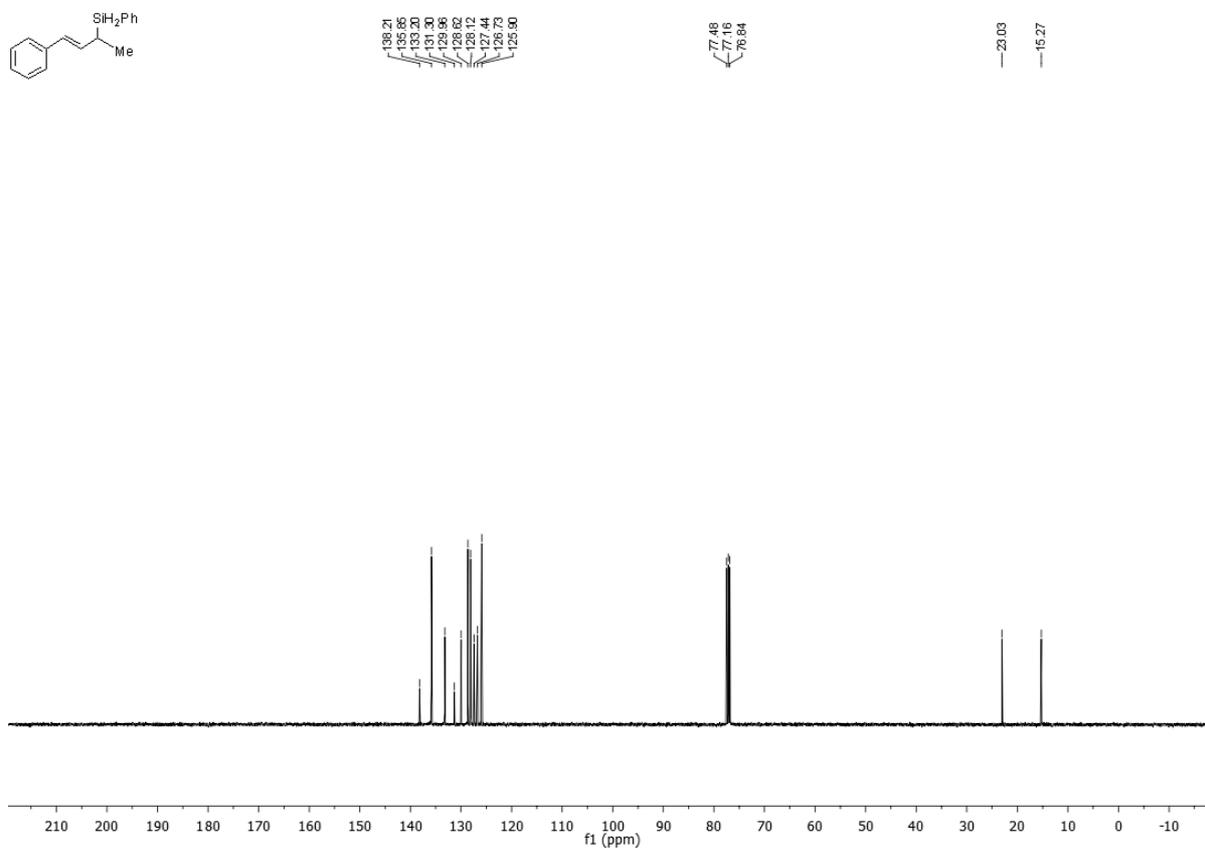
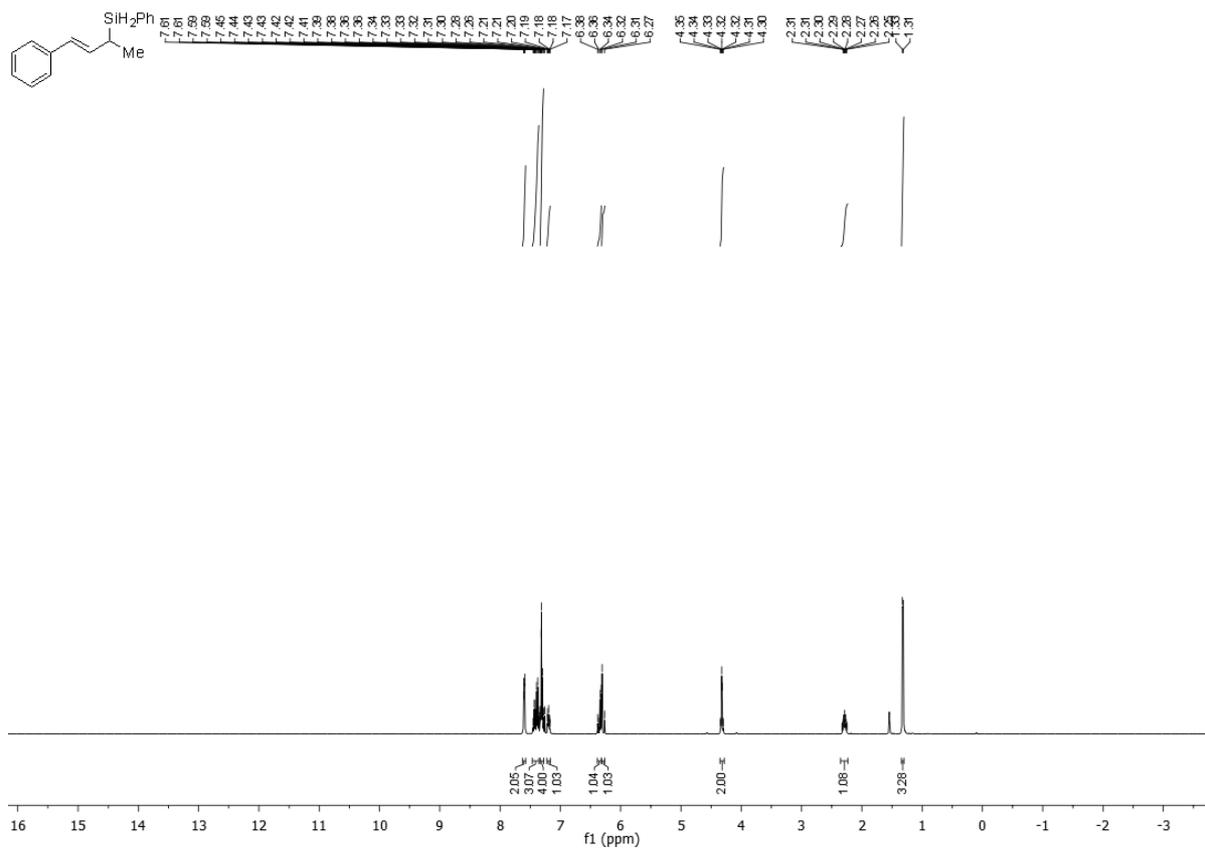
In an Ar-filled glovebox, a mixture of (1.0 mg, 4.0  $\mu\text{mol}$ ) and xantphos (2.3 mg, 4.0  $\mu\text{mol}$ ) in THF (2 mL) was added into a 4-mL screw-capped vial containing a magnetic stirring bar. The resulting mixture was stirred for 2 mins prior adding phenylsilane (54.1 mg, 0.5 mmol) and 1-(buta-1,3-dien-1-yl)-4-methoxybenzene (64.1 mg, 0.4 mmol) successively. Lastly, tridecane (27.7 mg, 0.15 mmol) was added into the reaction mixture as an internal standard. The mixture was stirred at room temperature. A GC analysis was done for the crude mixture for every 5 minutes to monitor the reaction. It was found that the (*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene was consumed at a significantly higher rate than (*Z*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene.

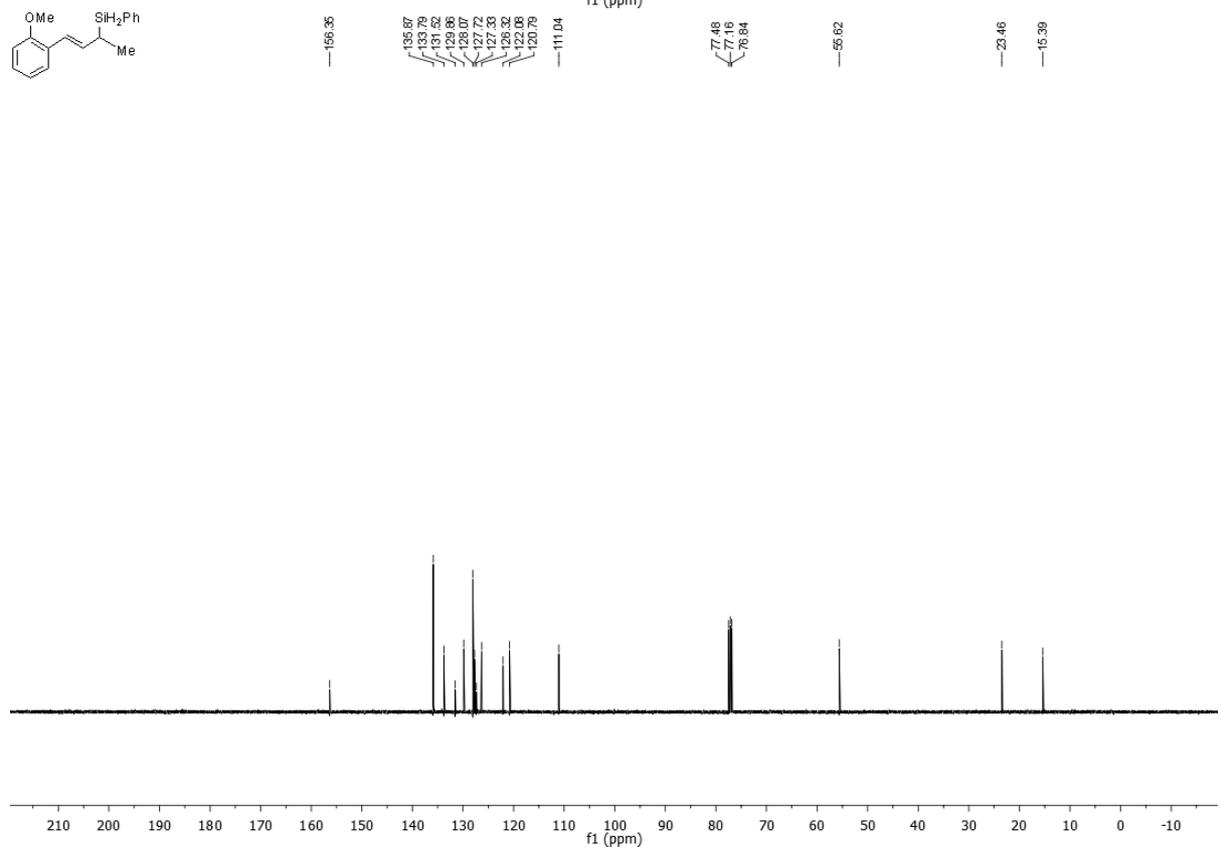
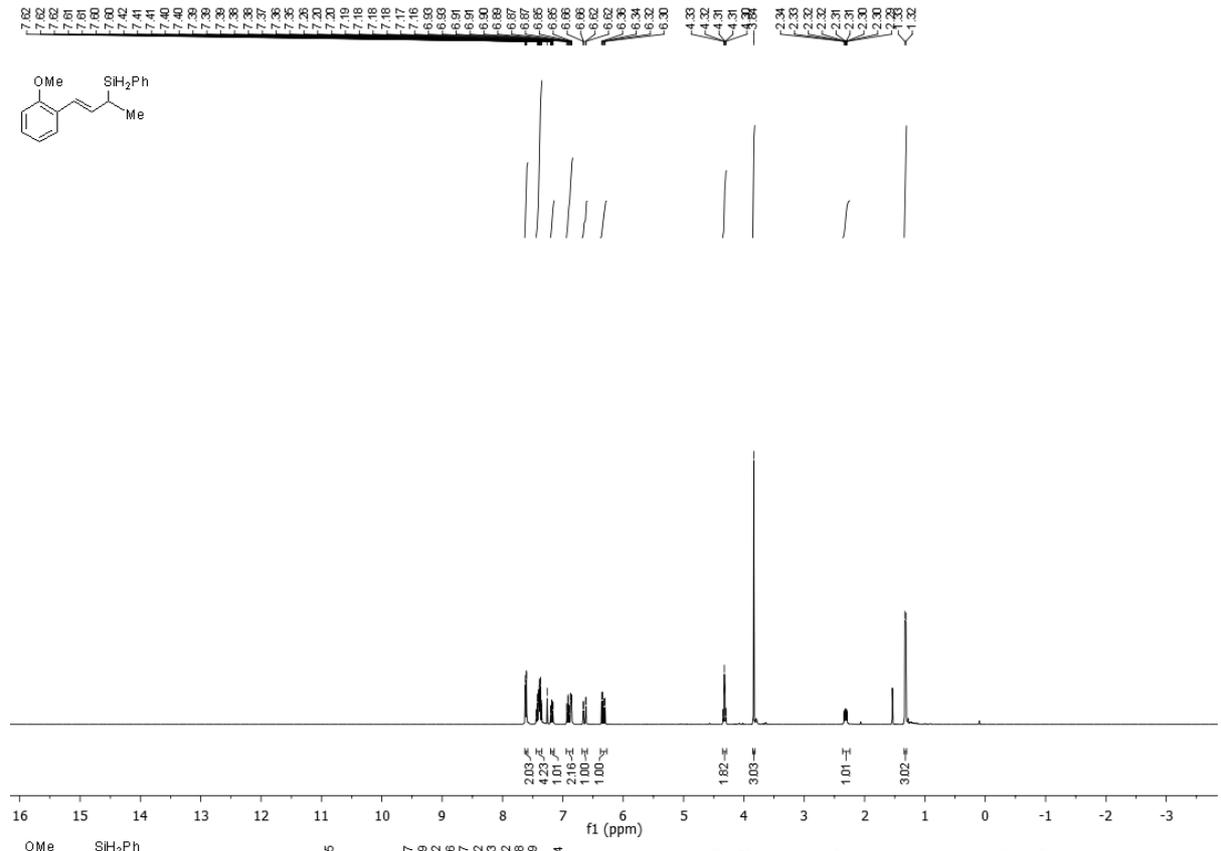


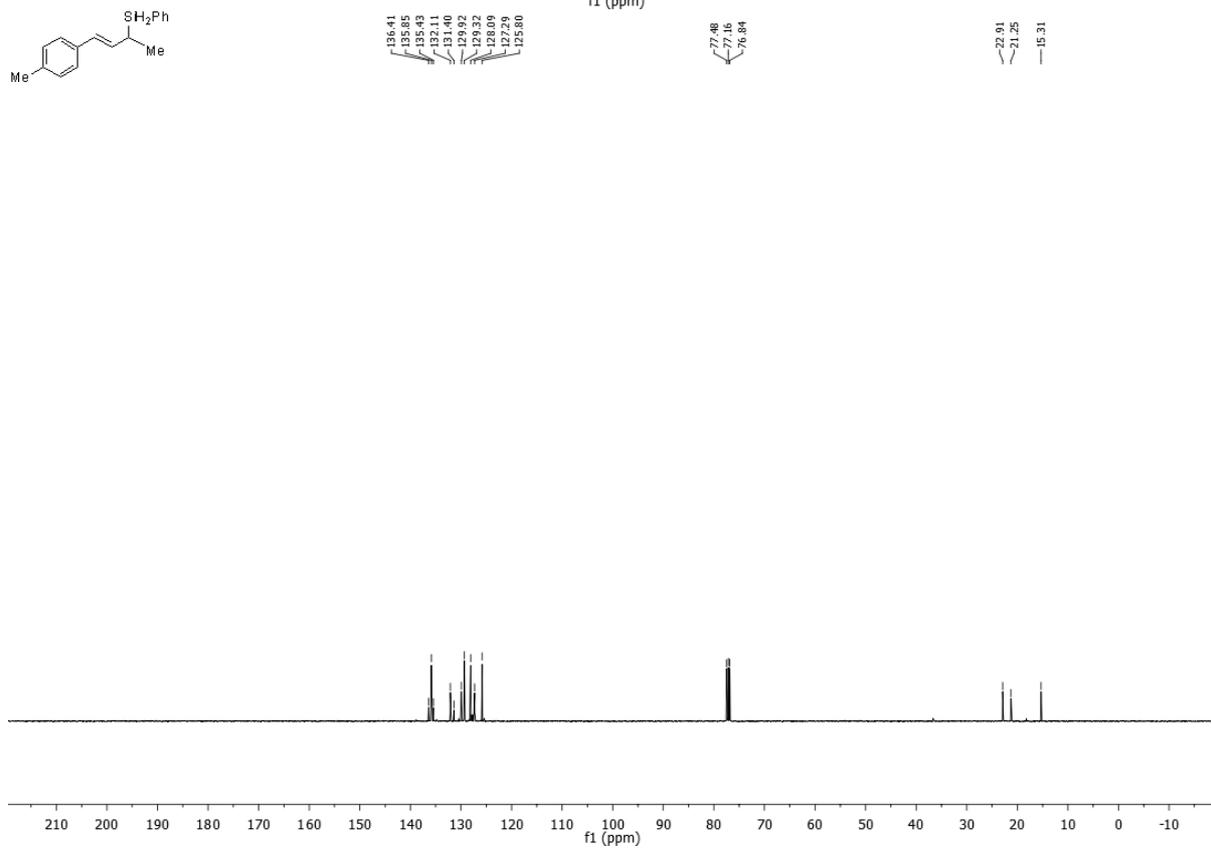
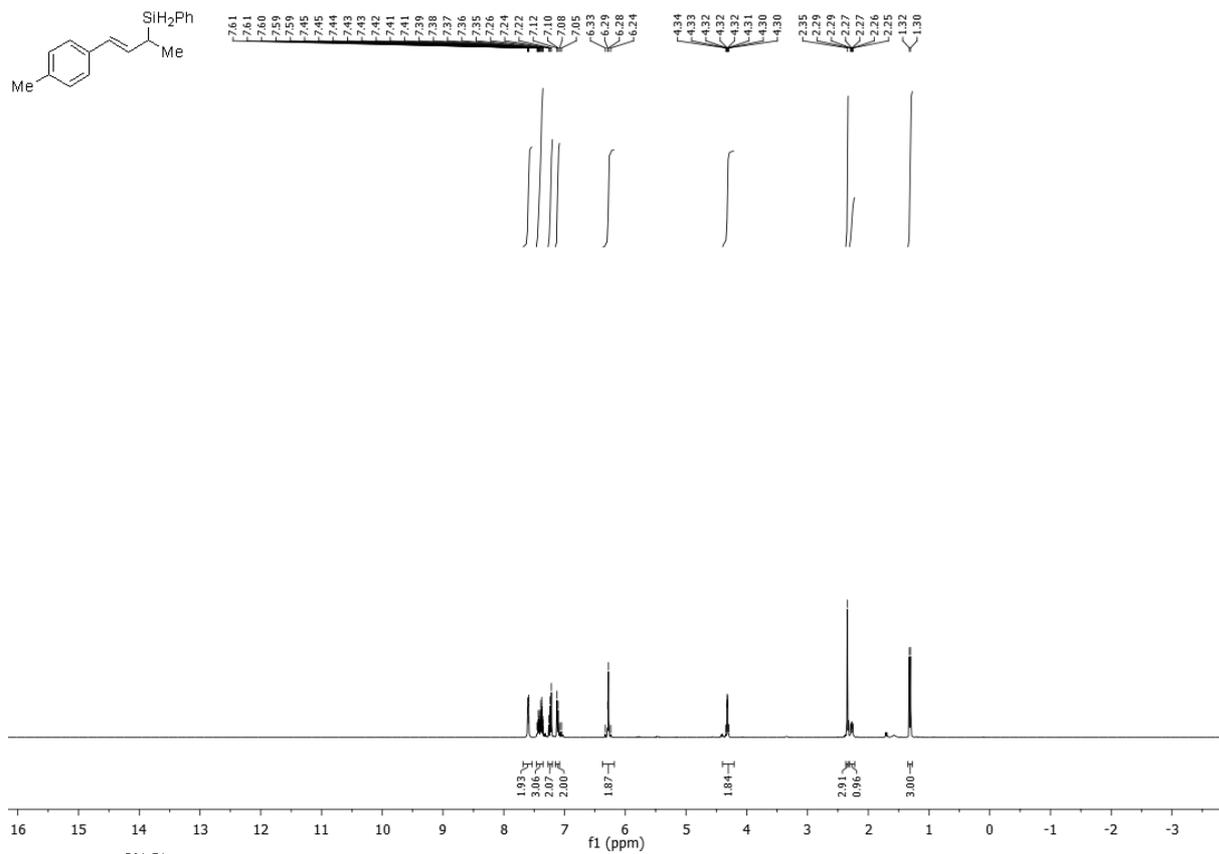
## References

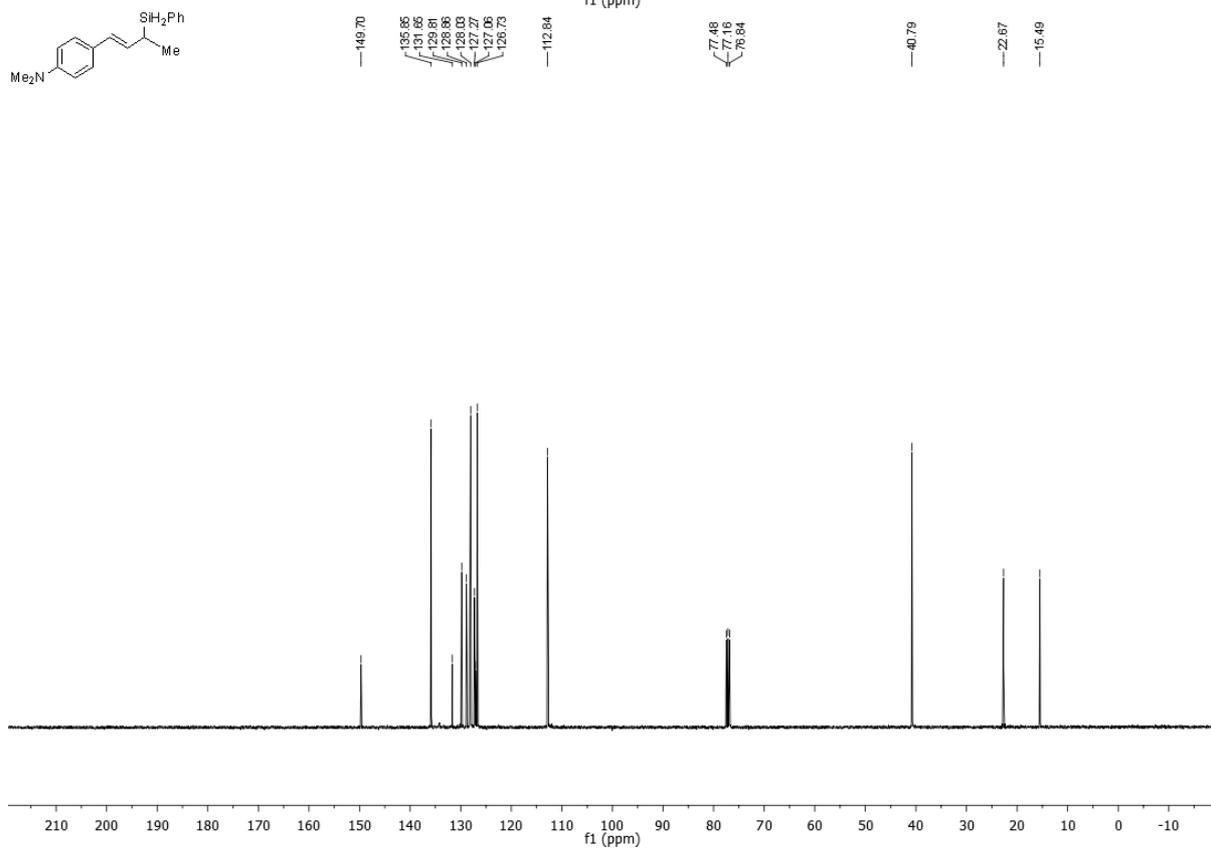
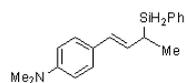
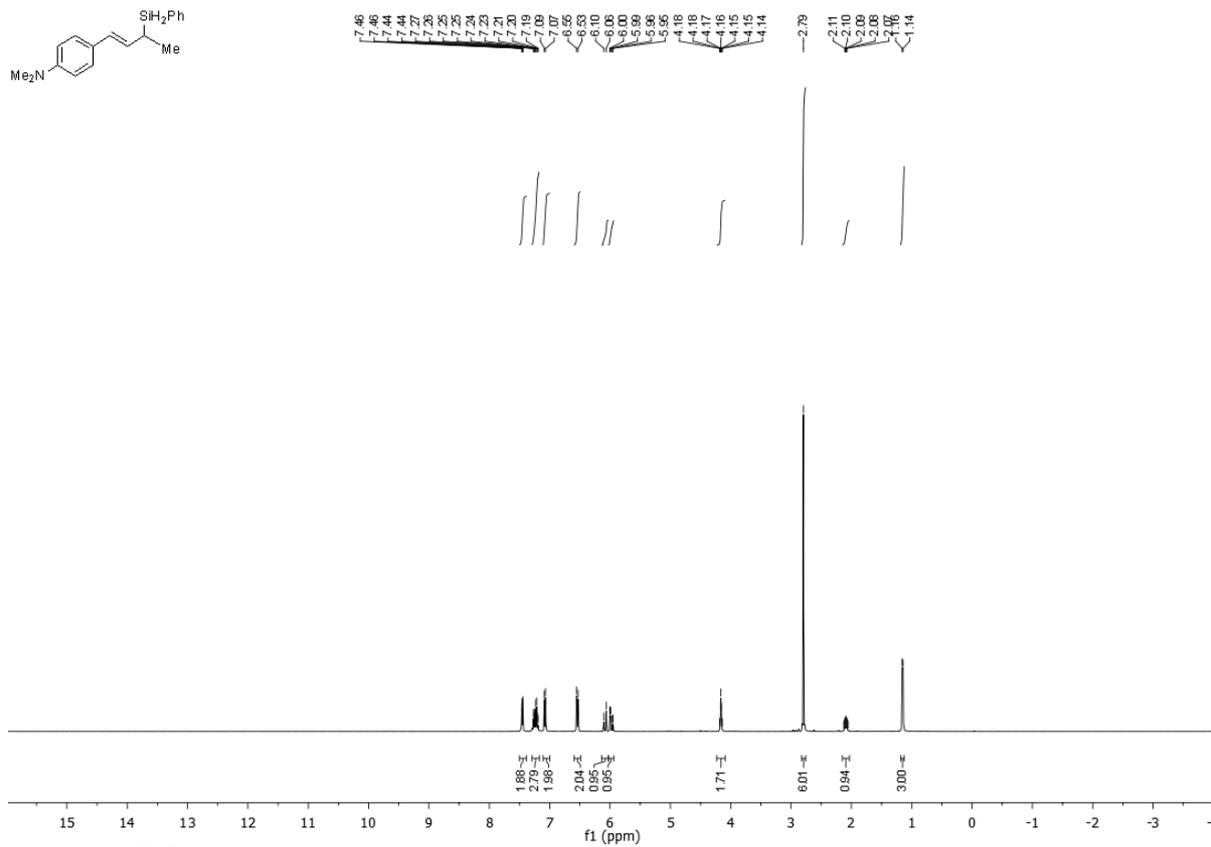
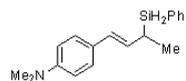
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# NMR Spectra

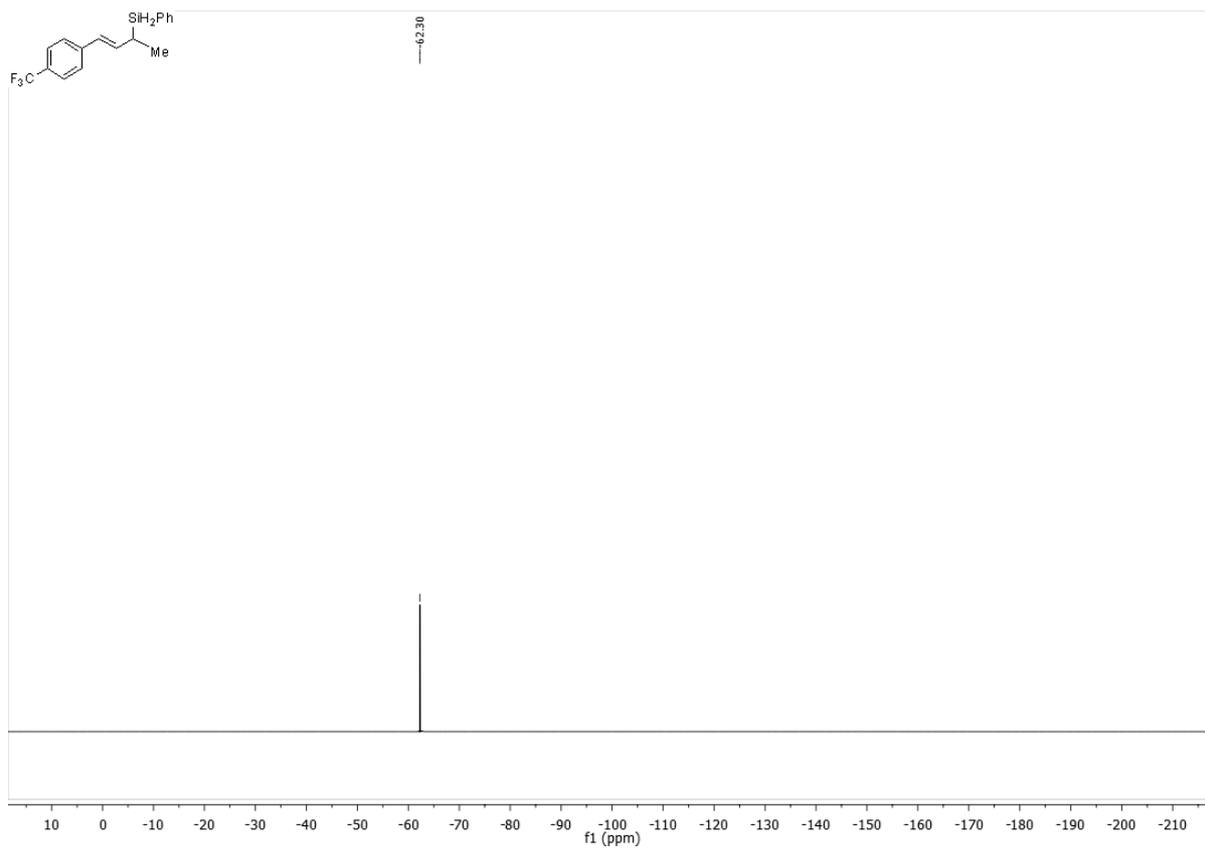


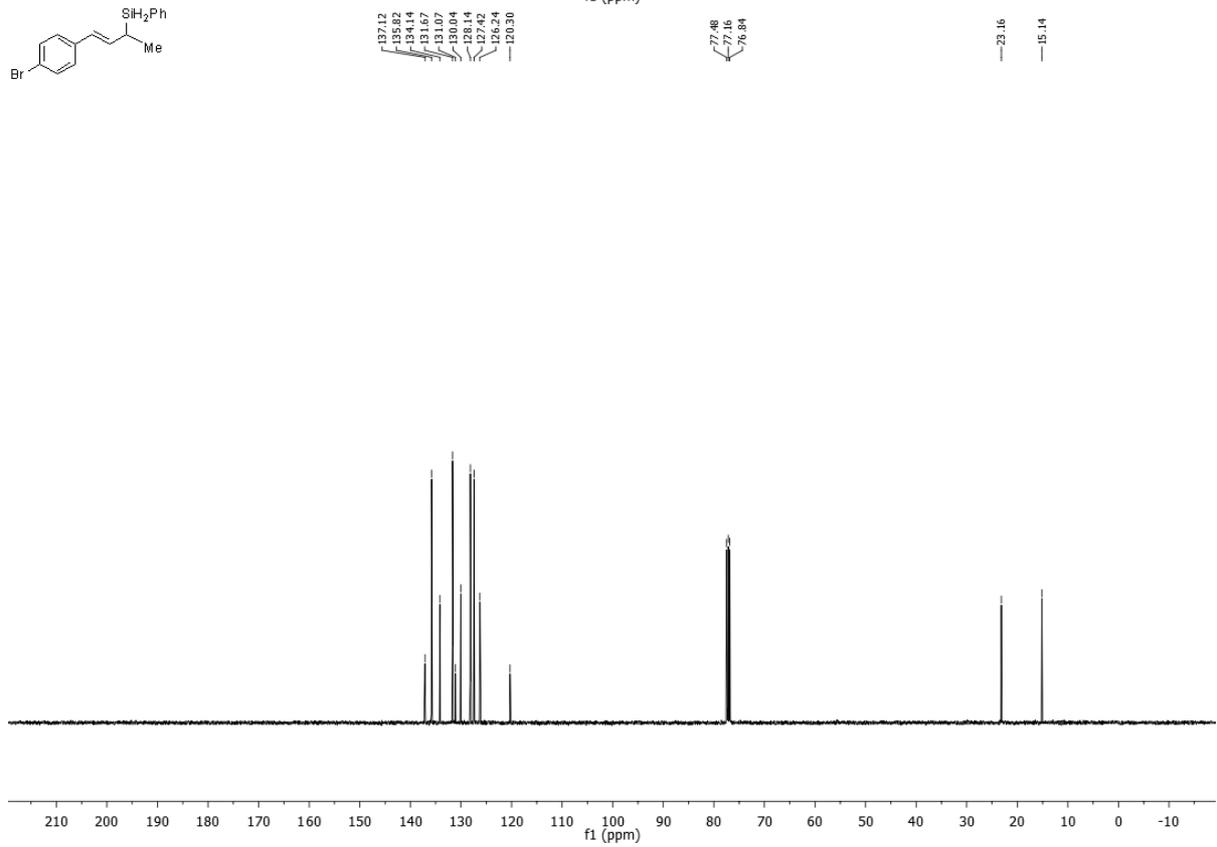
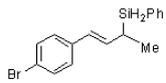
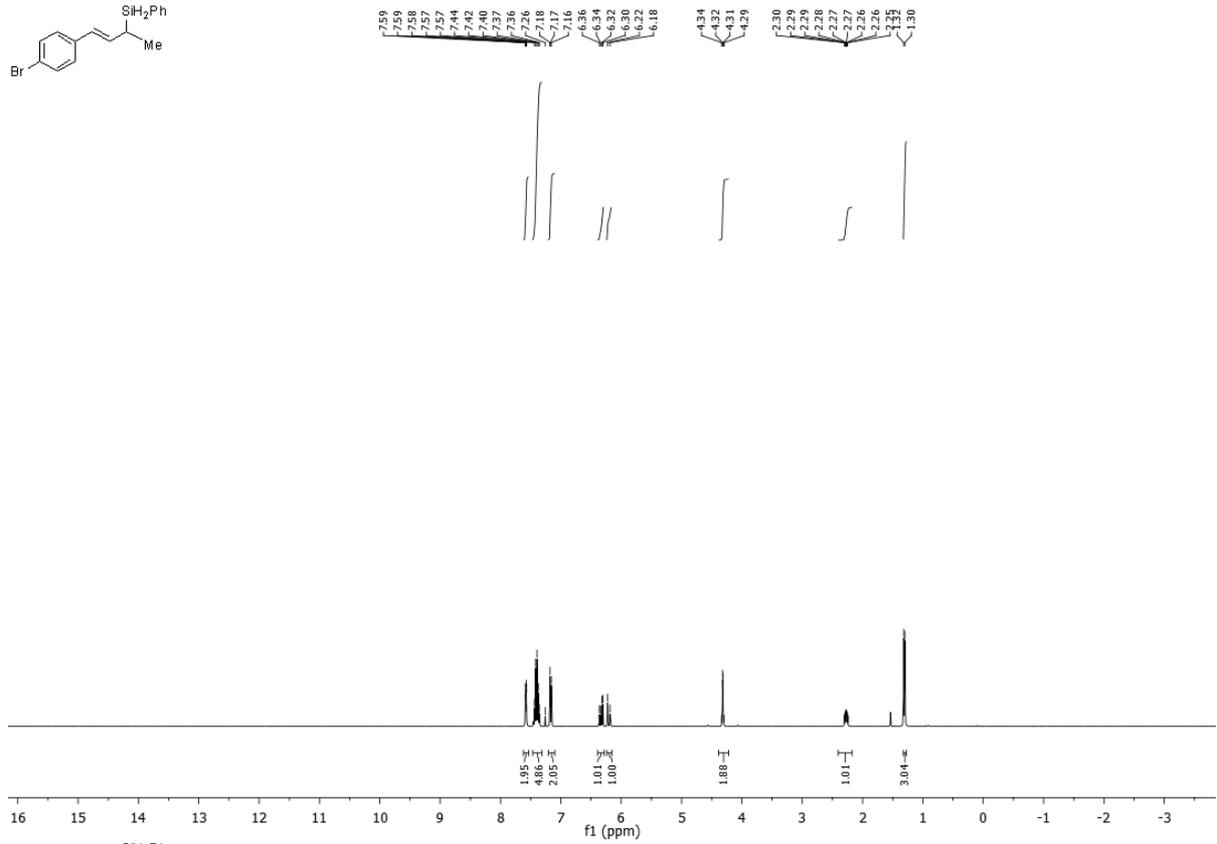
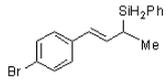


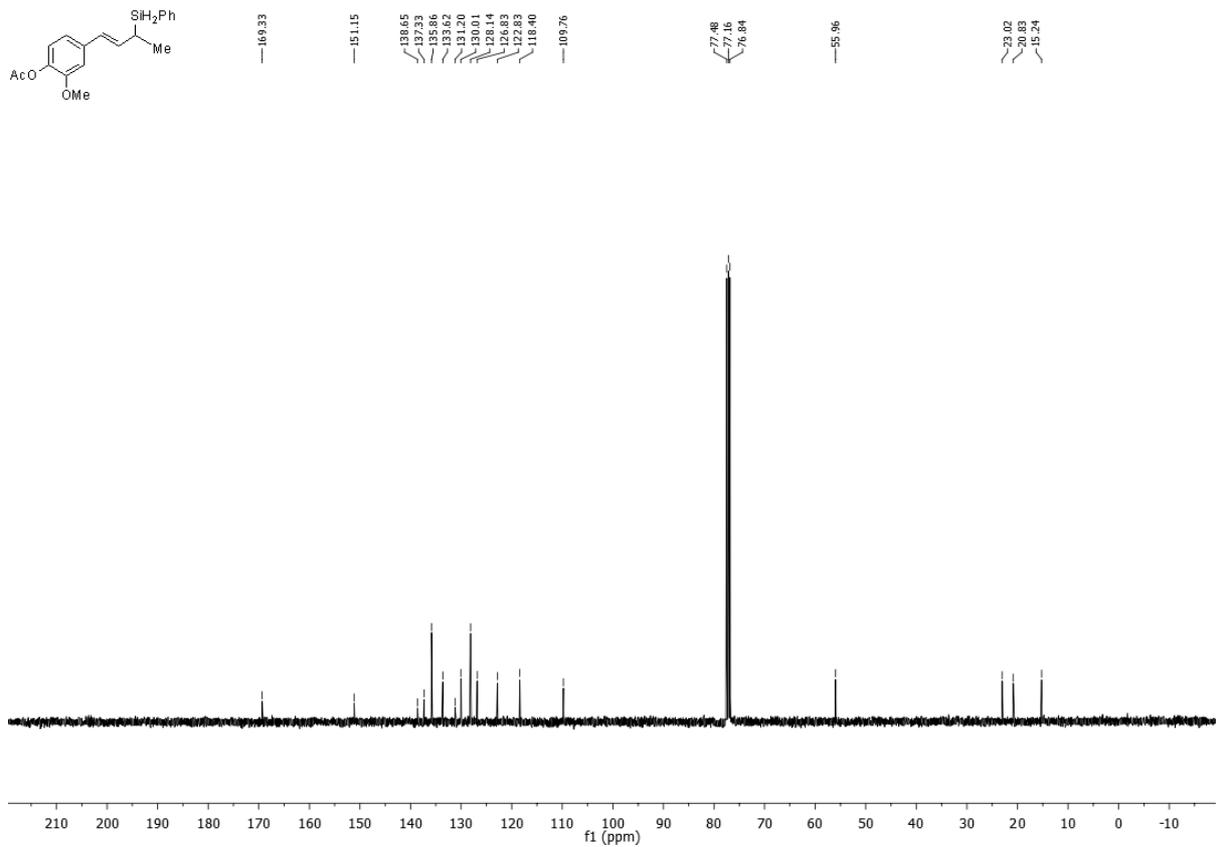
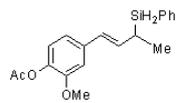
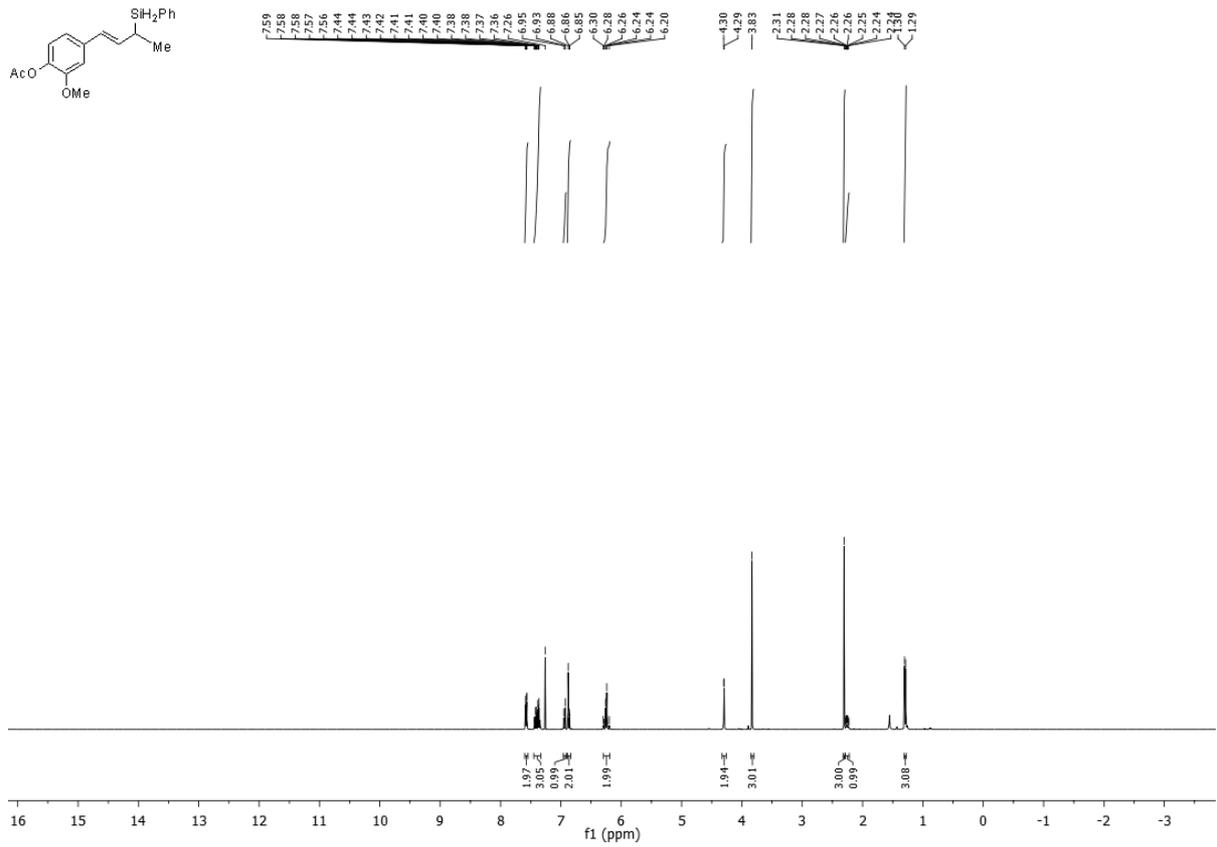
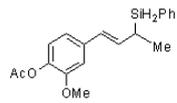


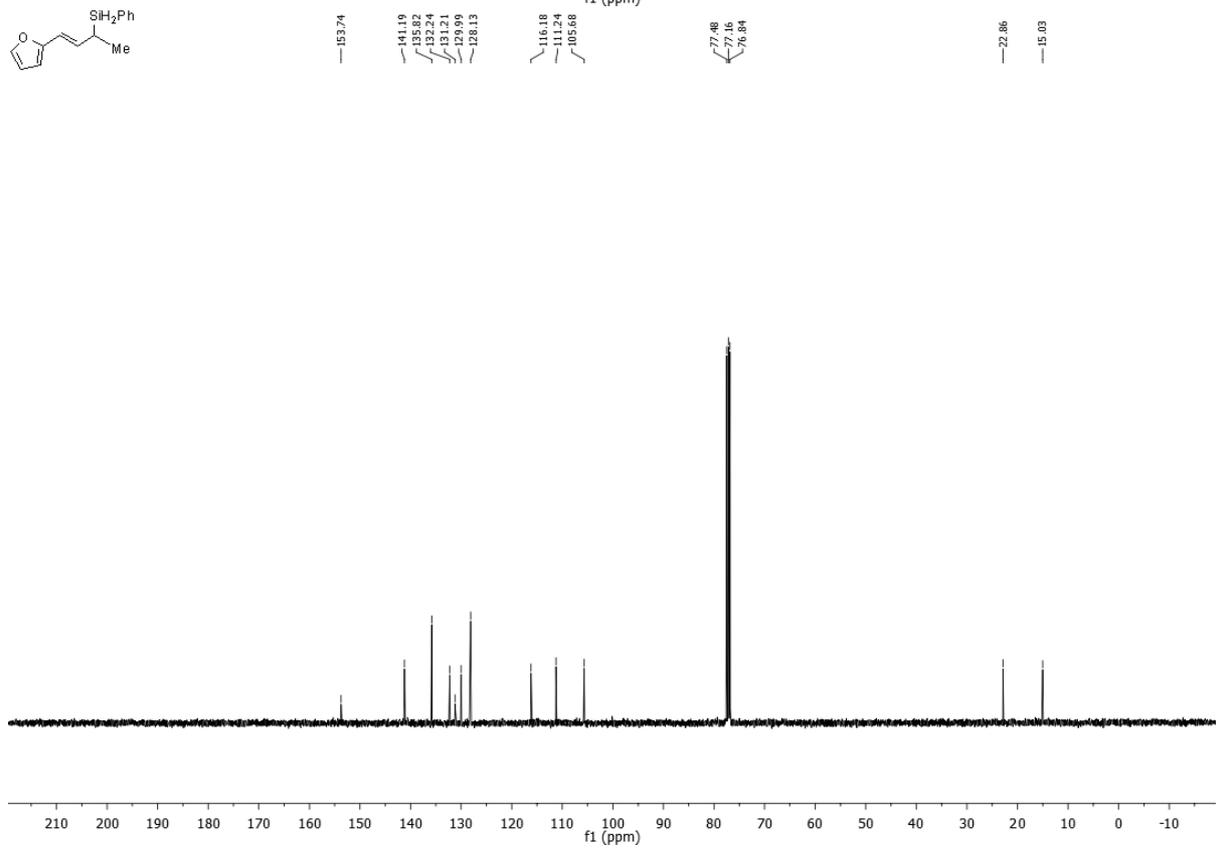
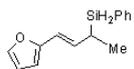
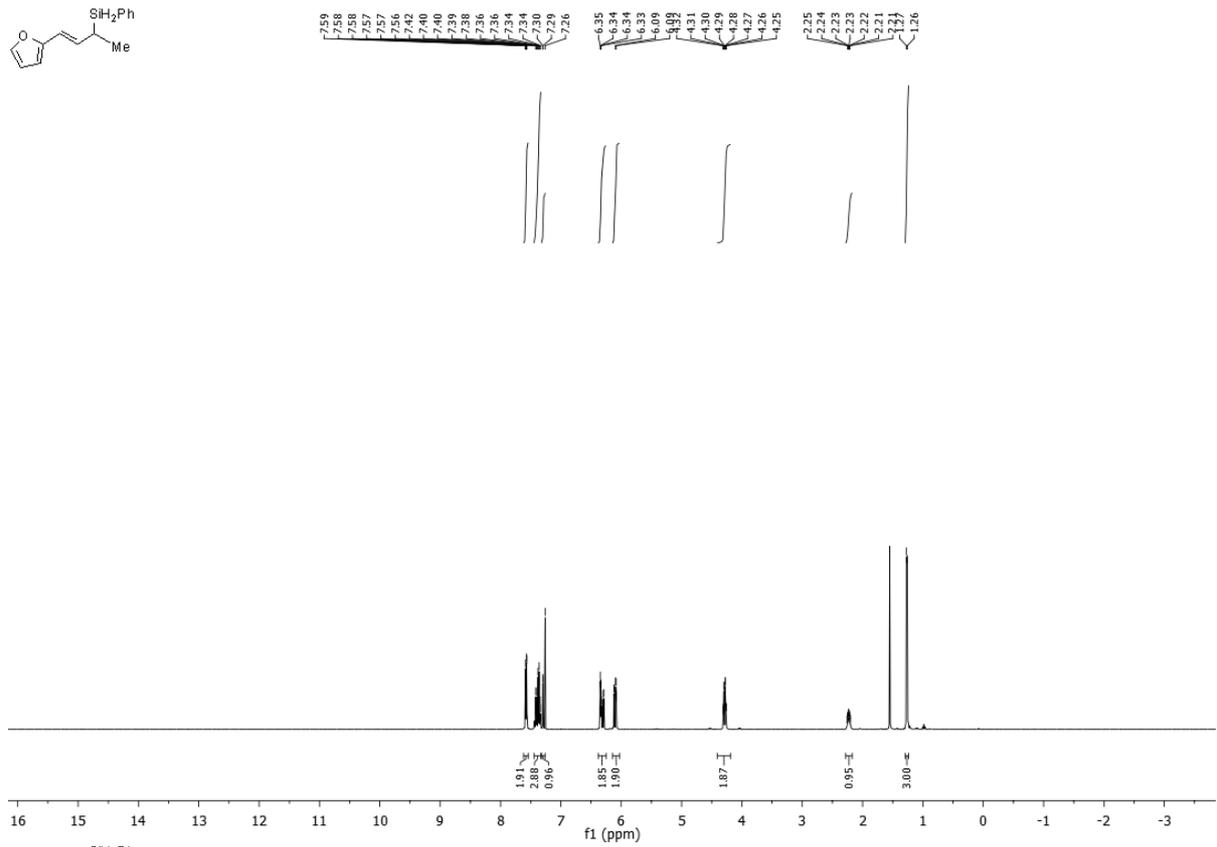
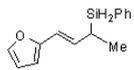




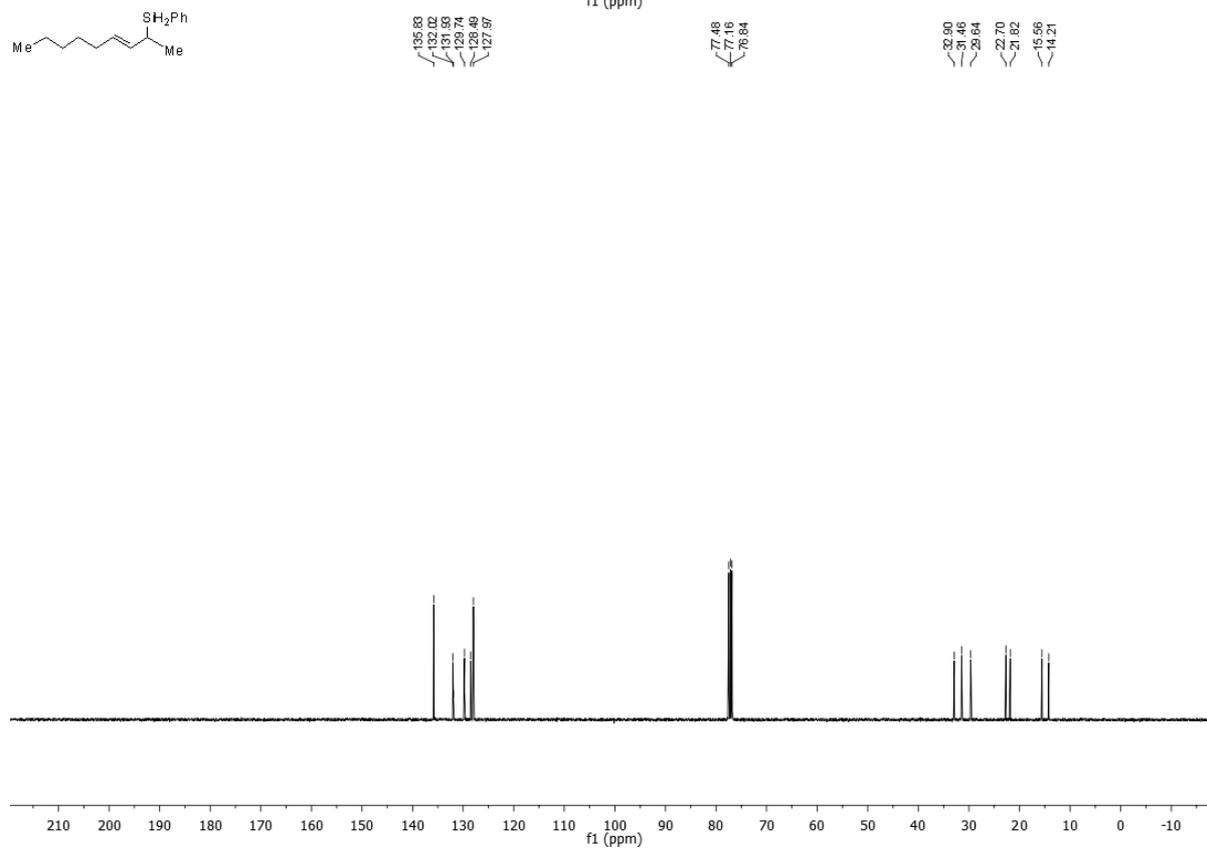
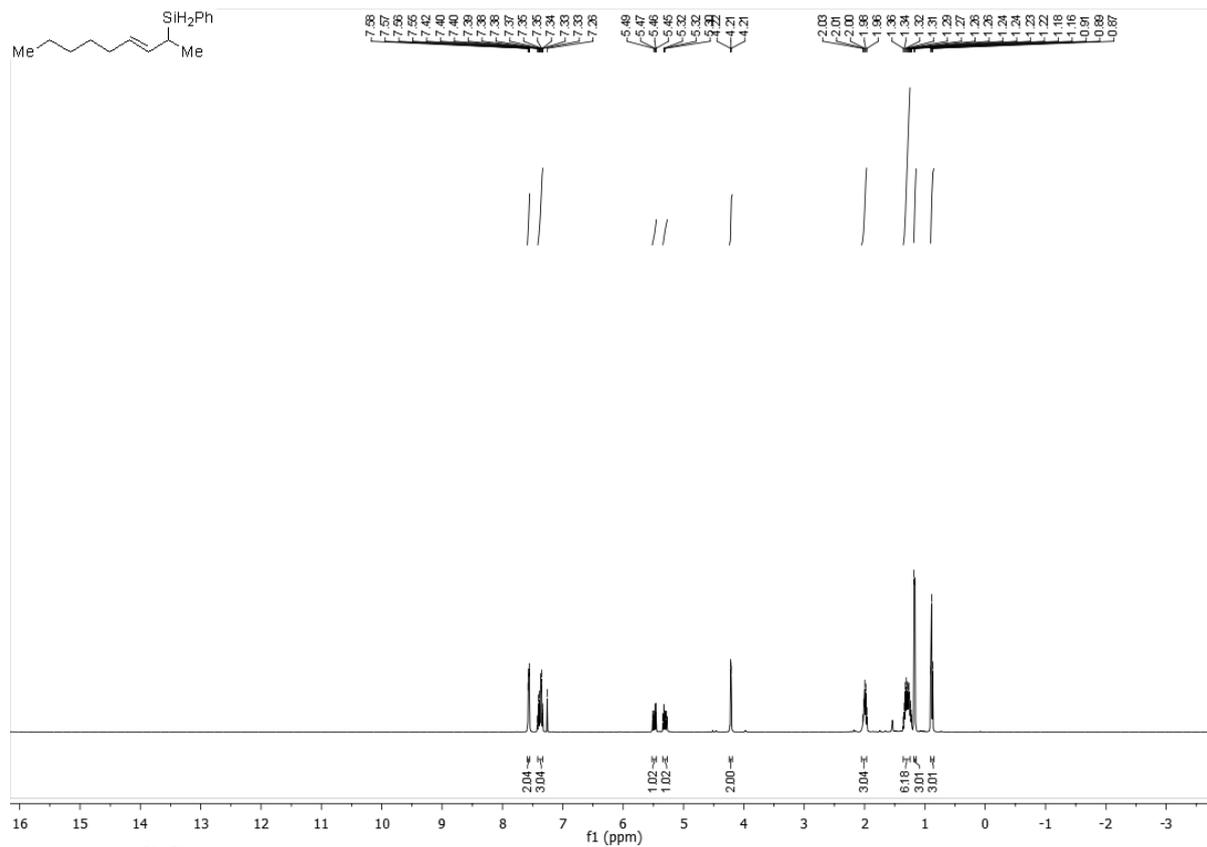


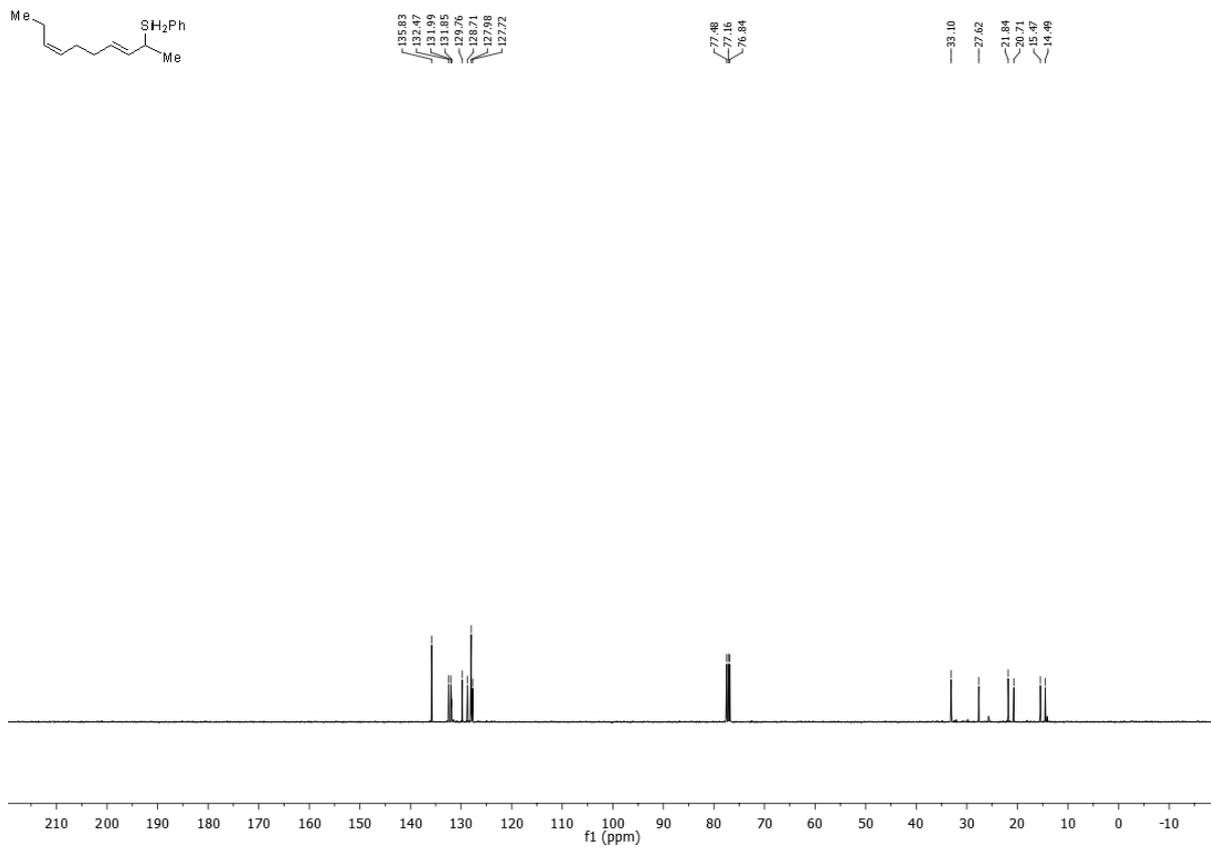
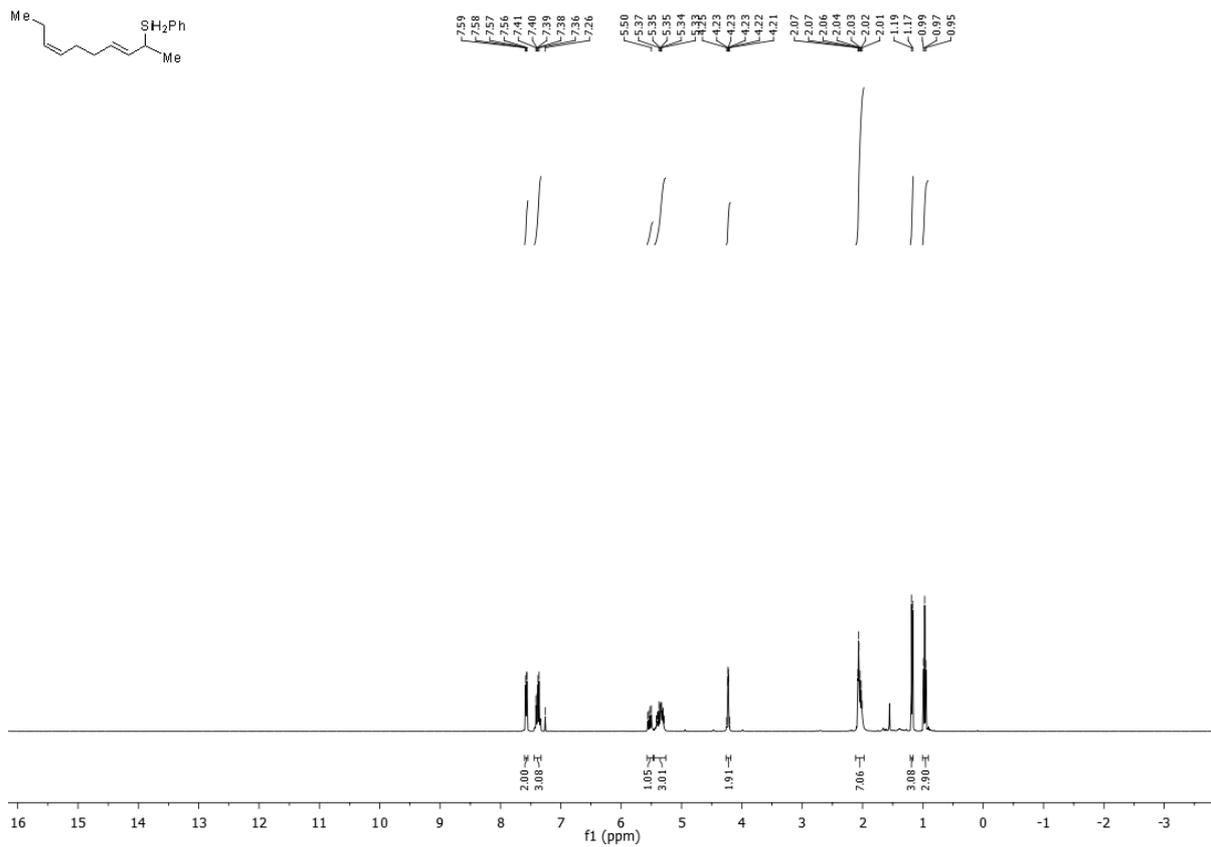


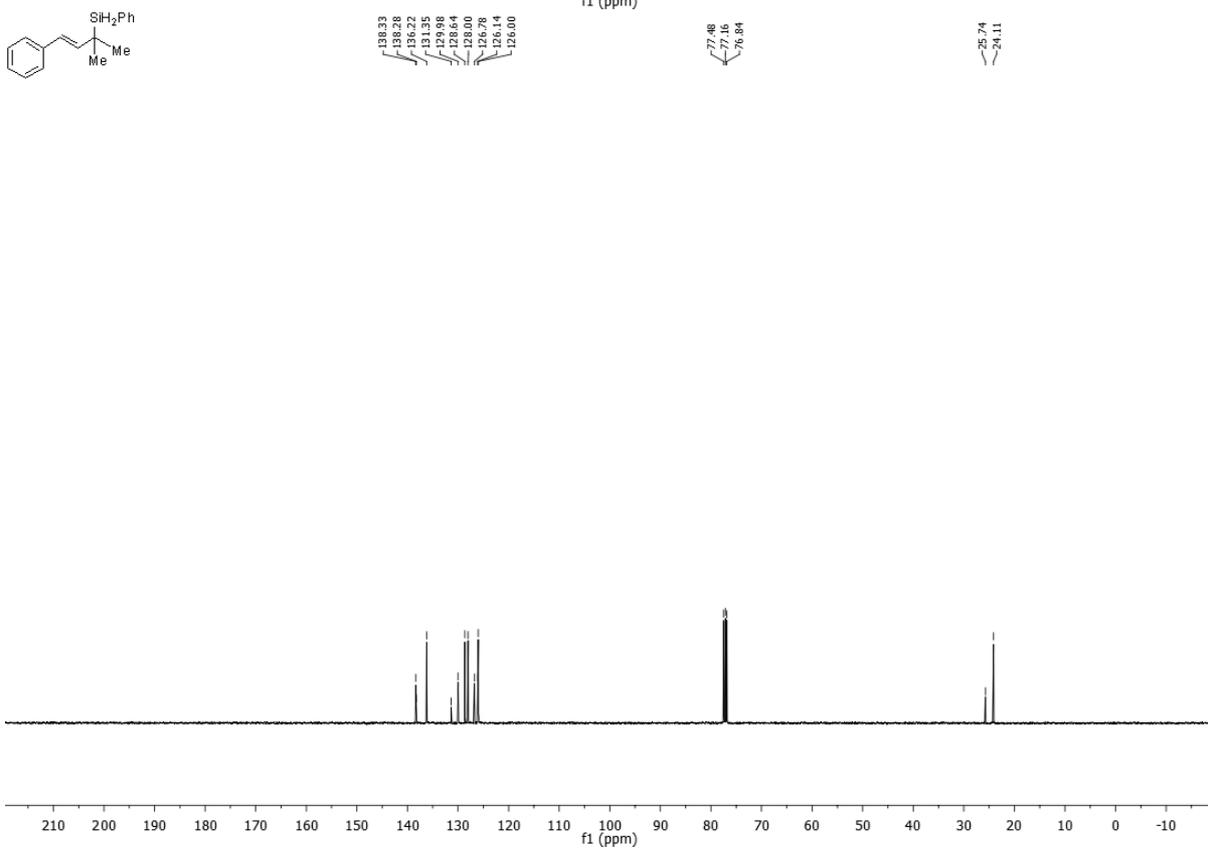
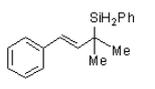
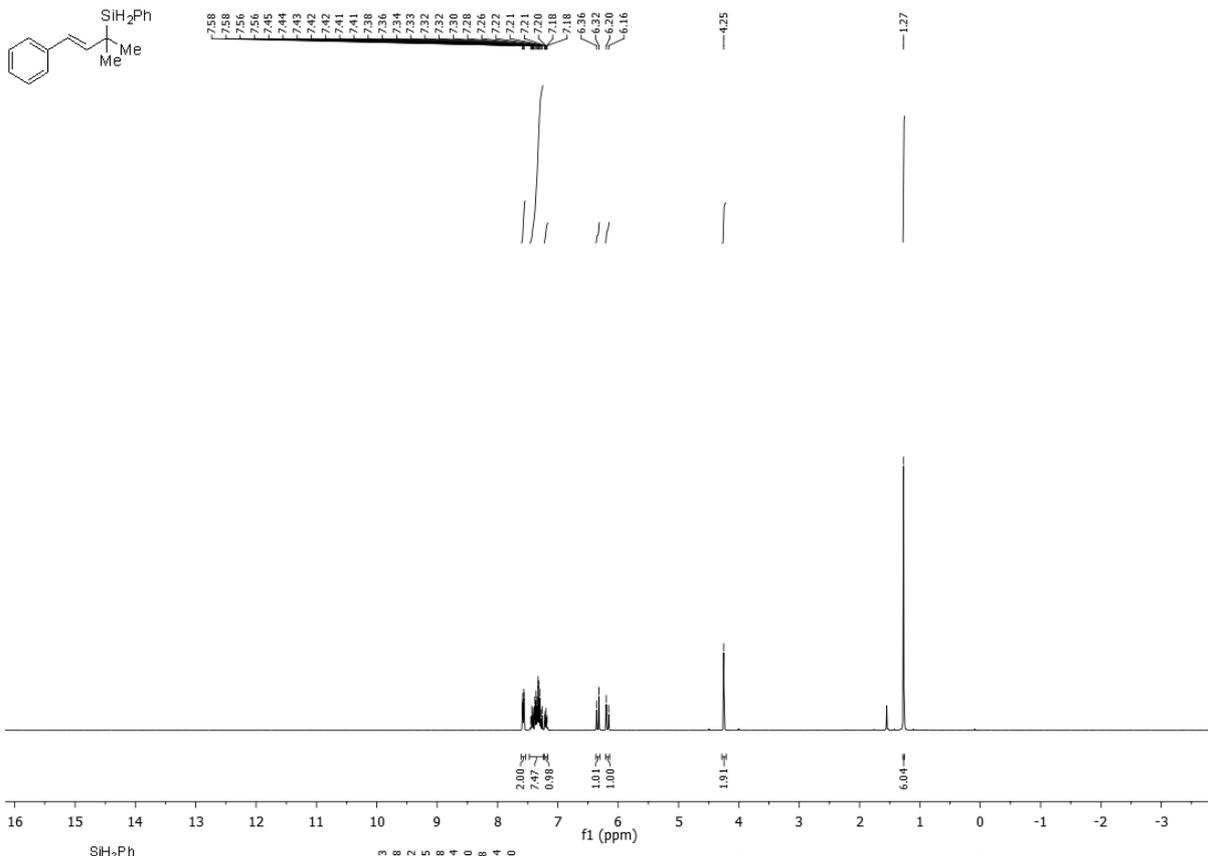
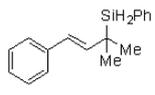


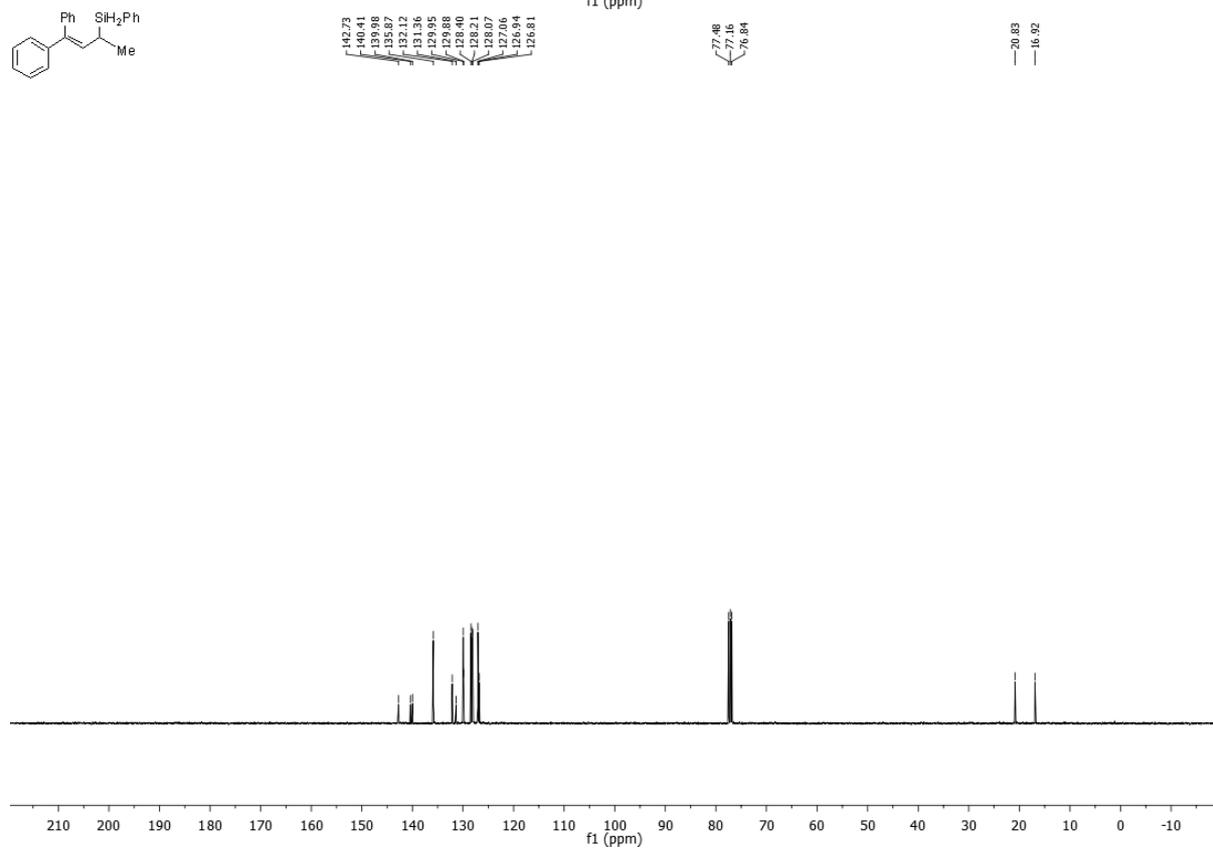
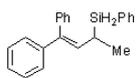
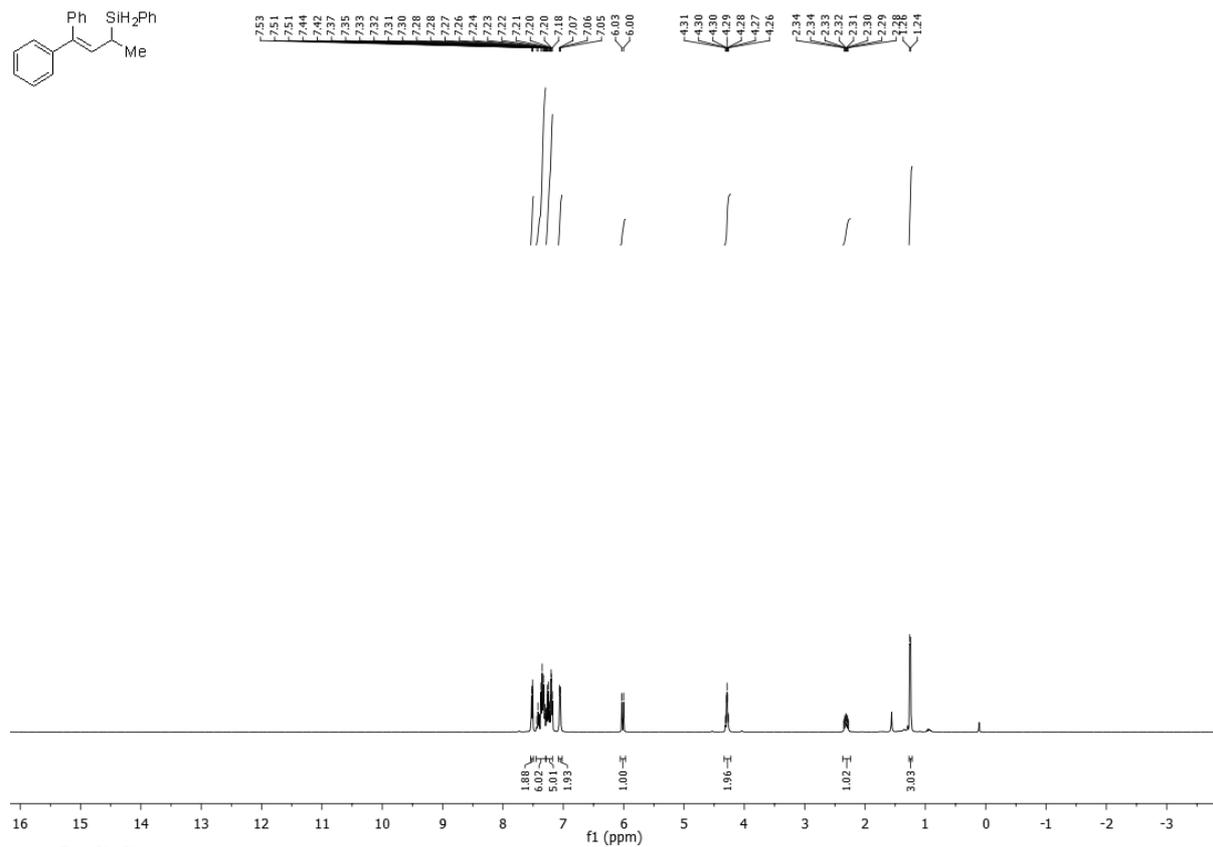
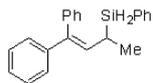


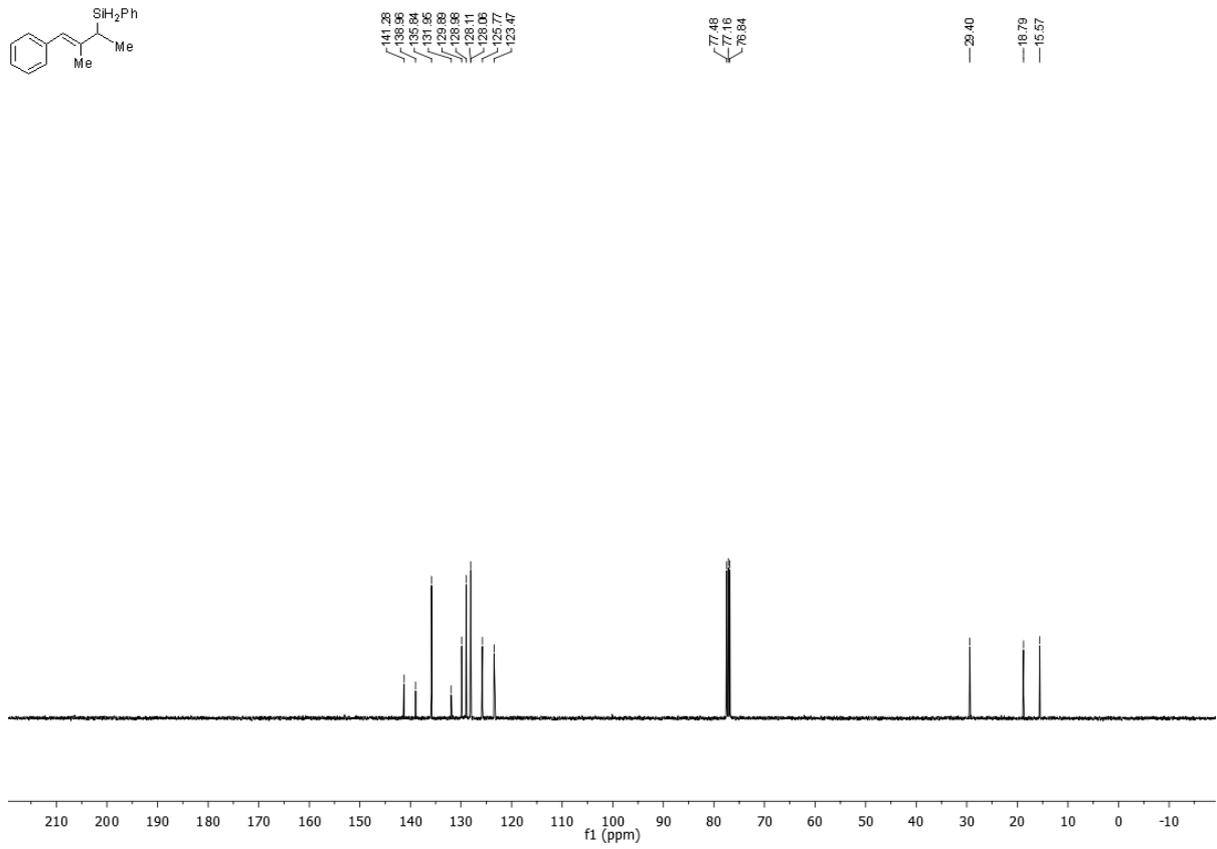
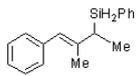
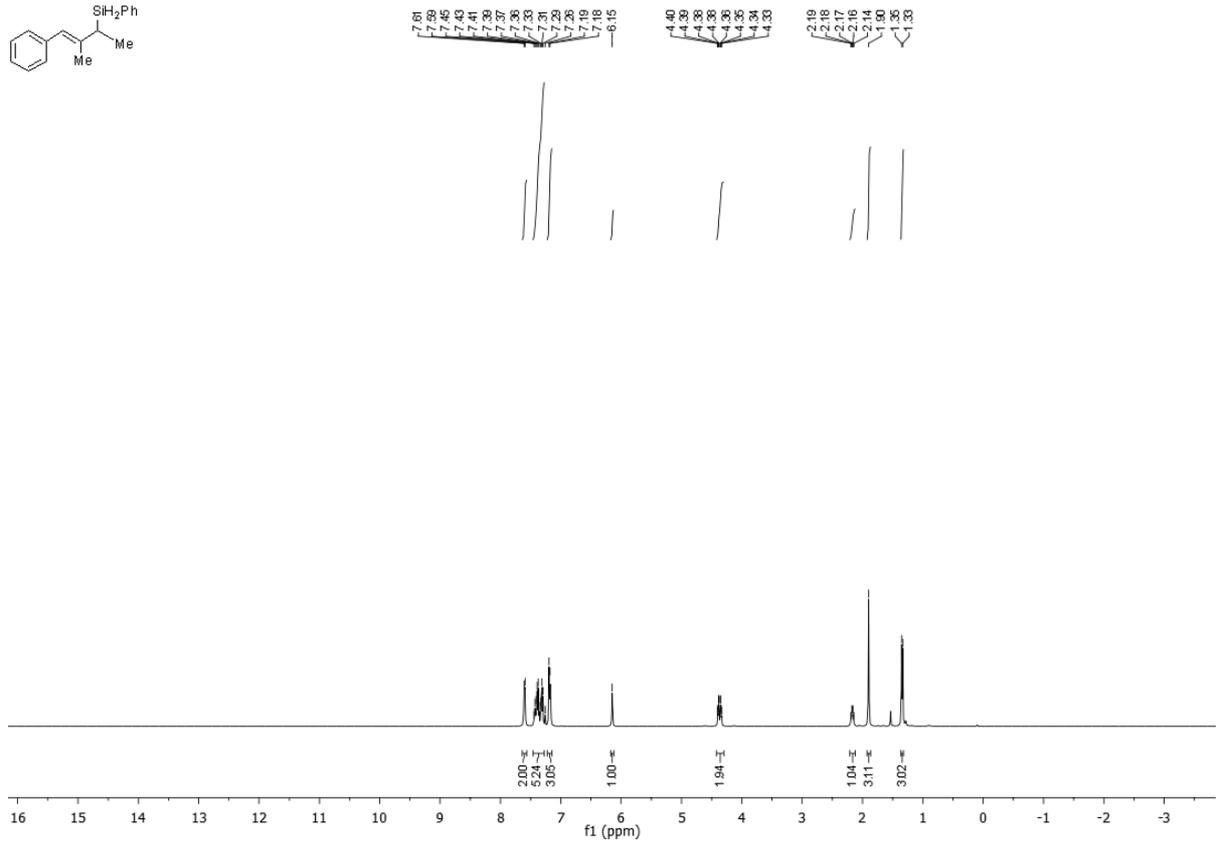
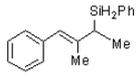


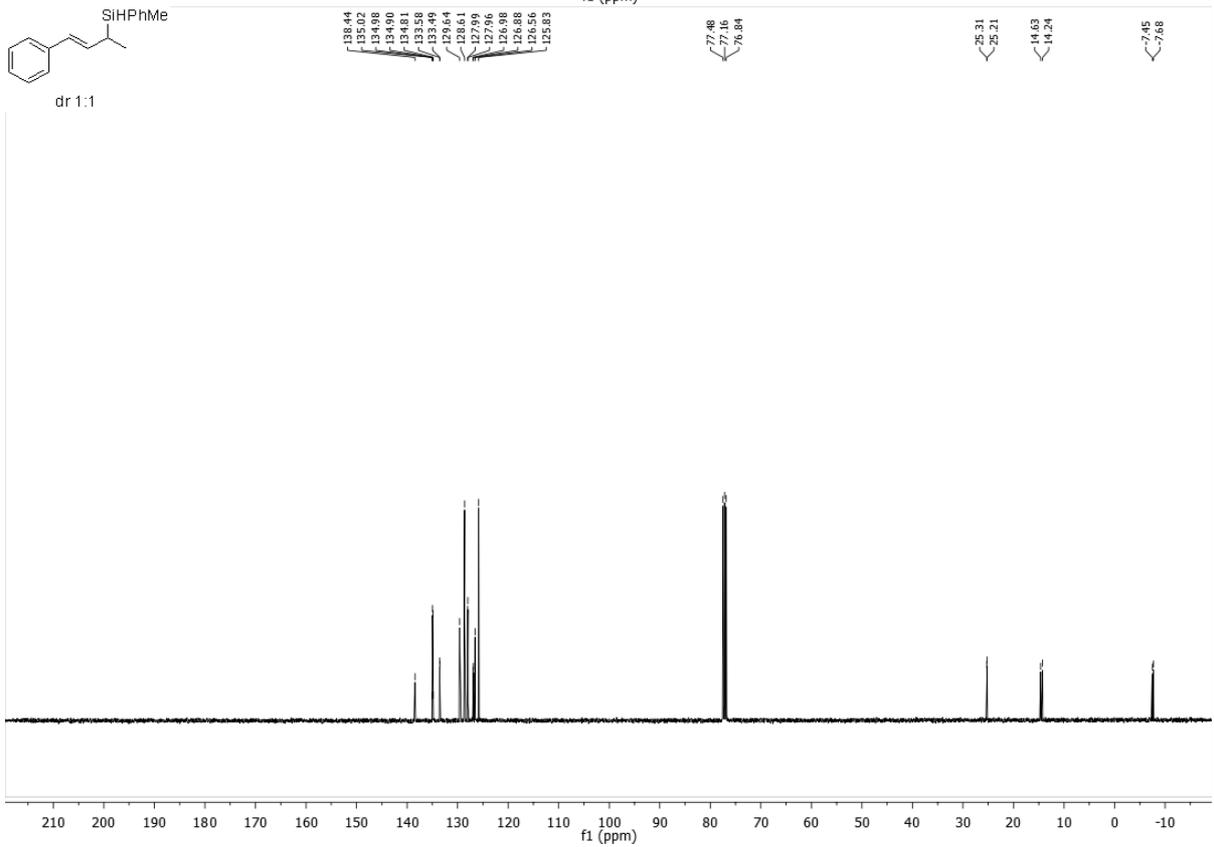
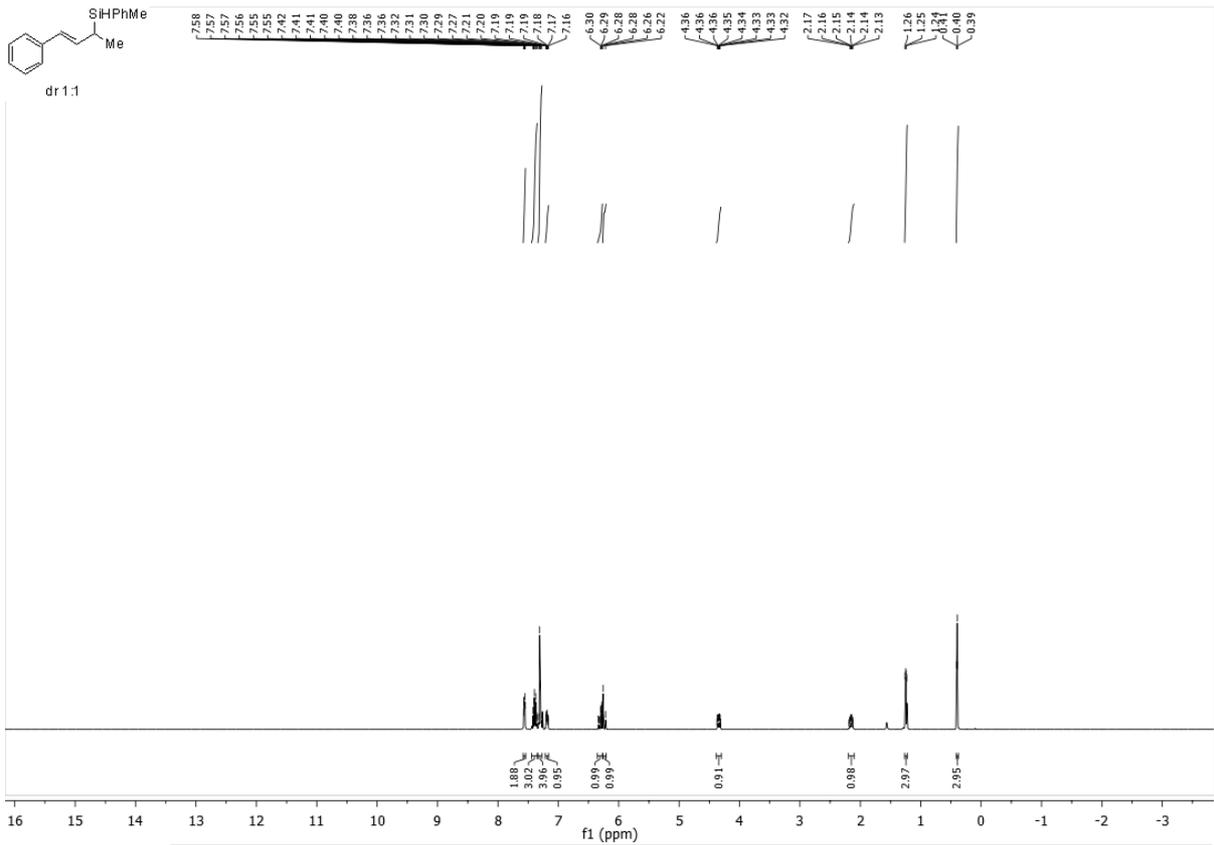


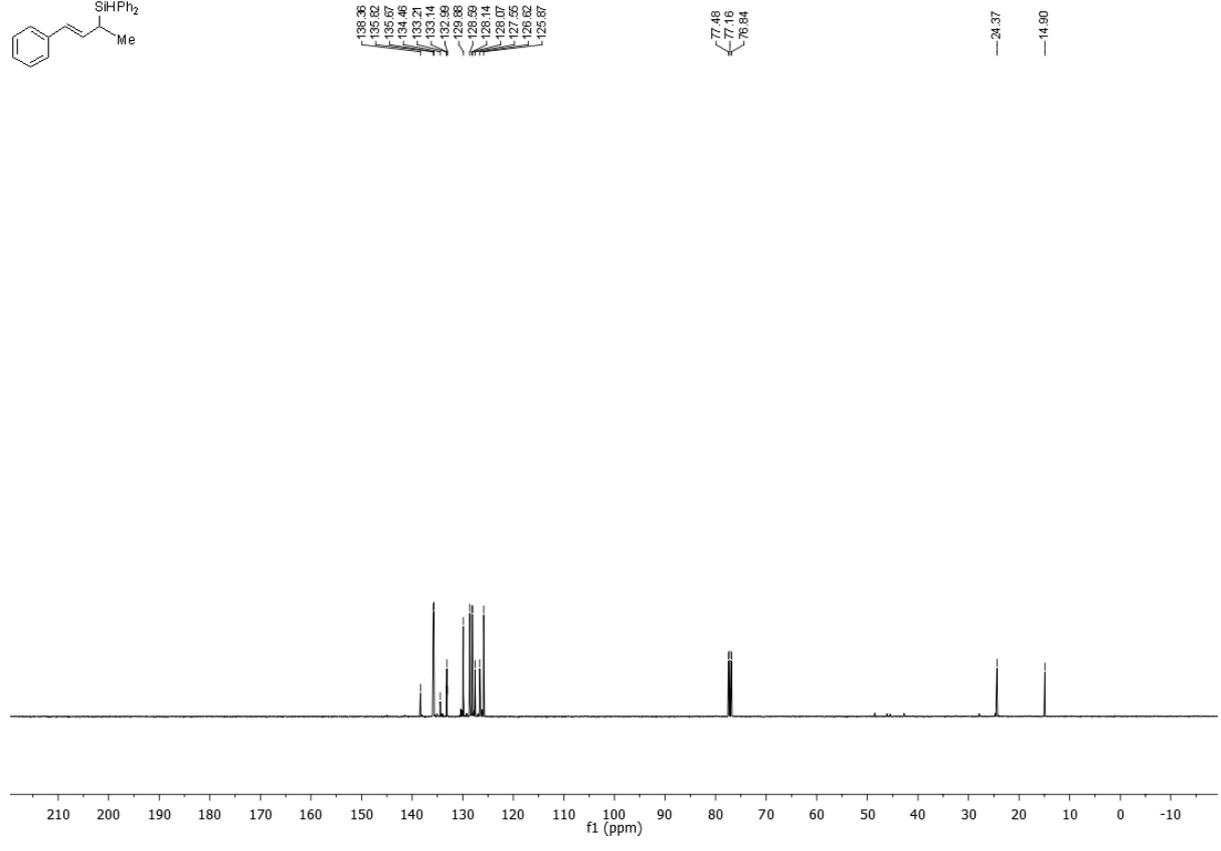
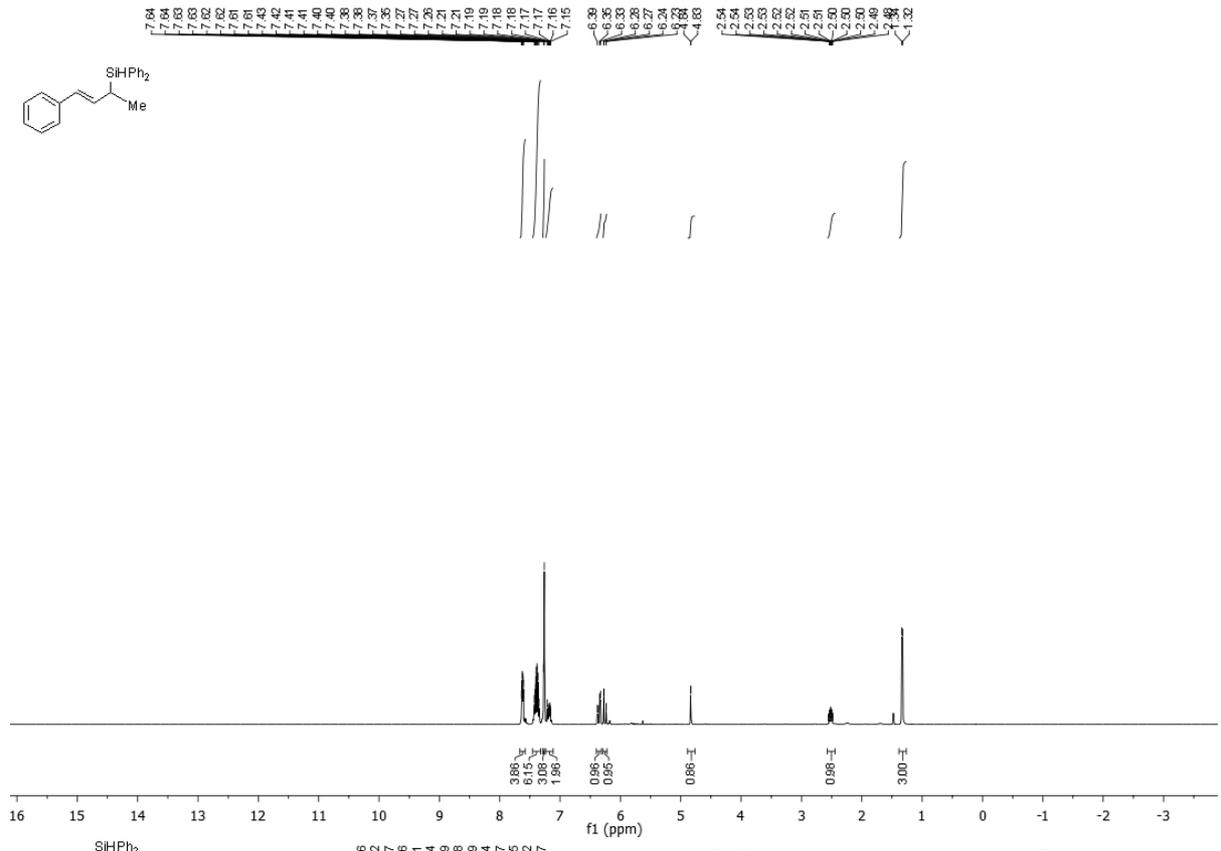


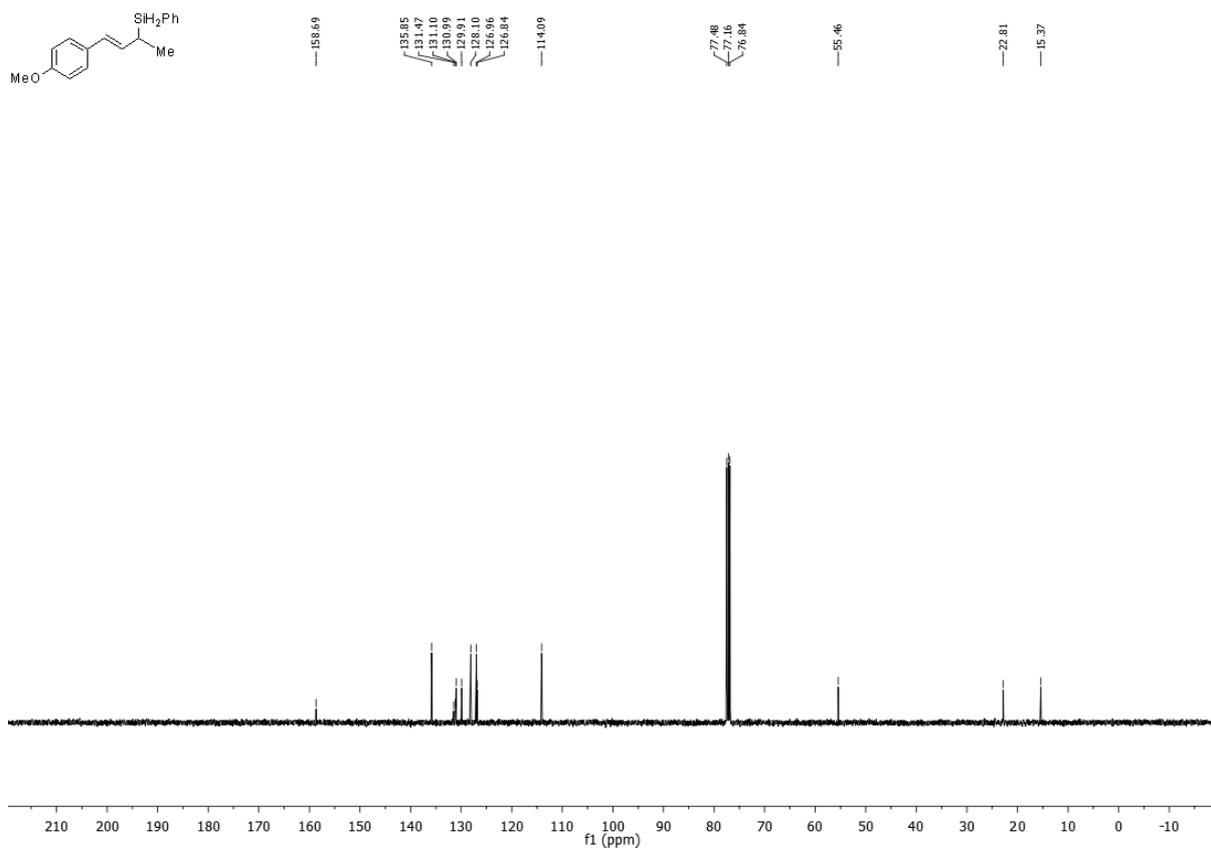
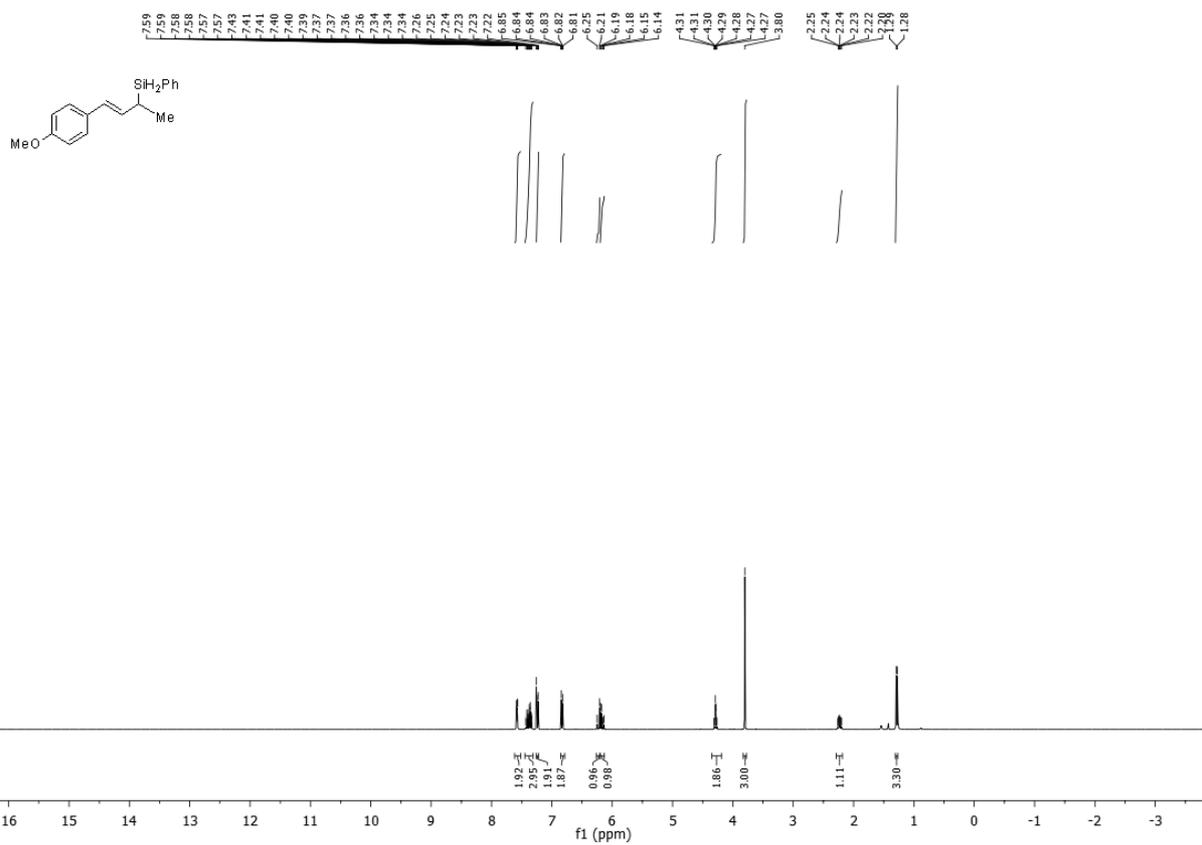


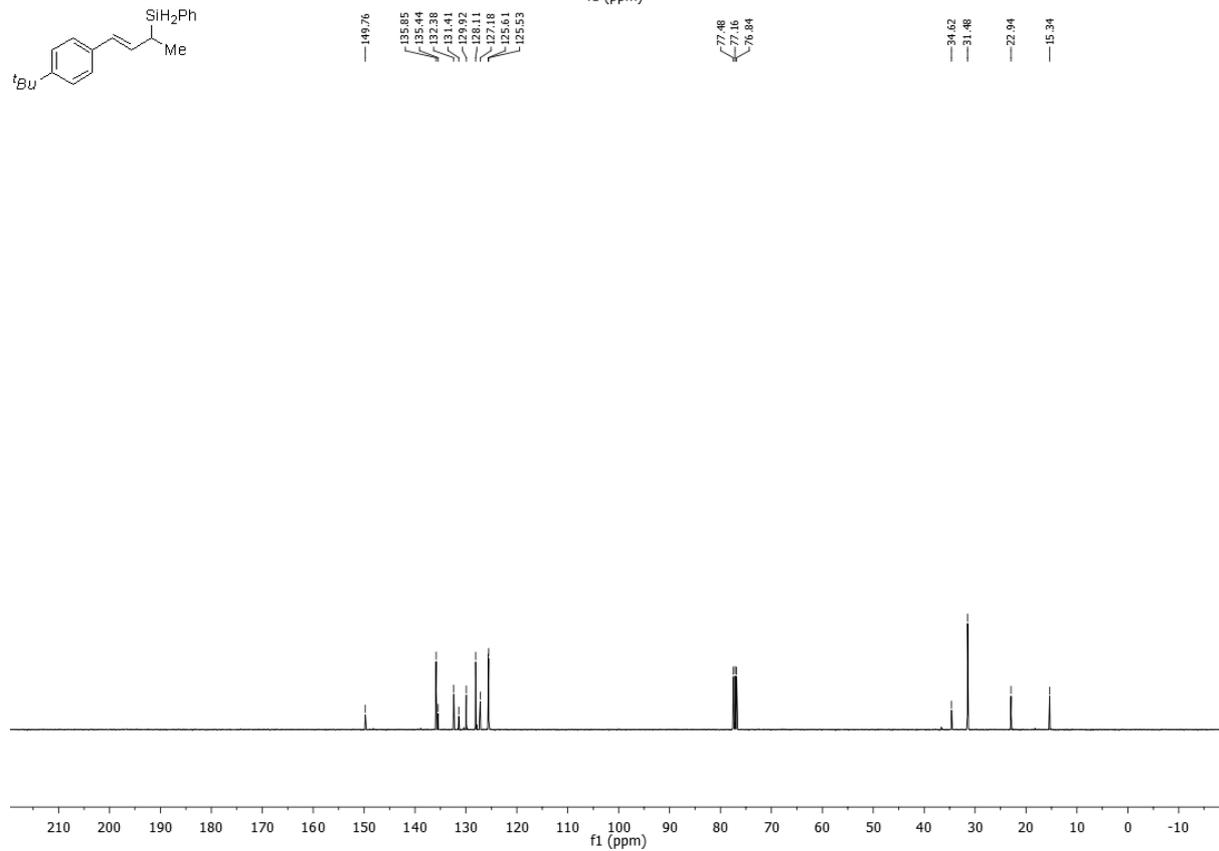
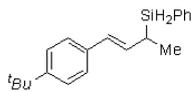
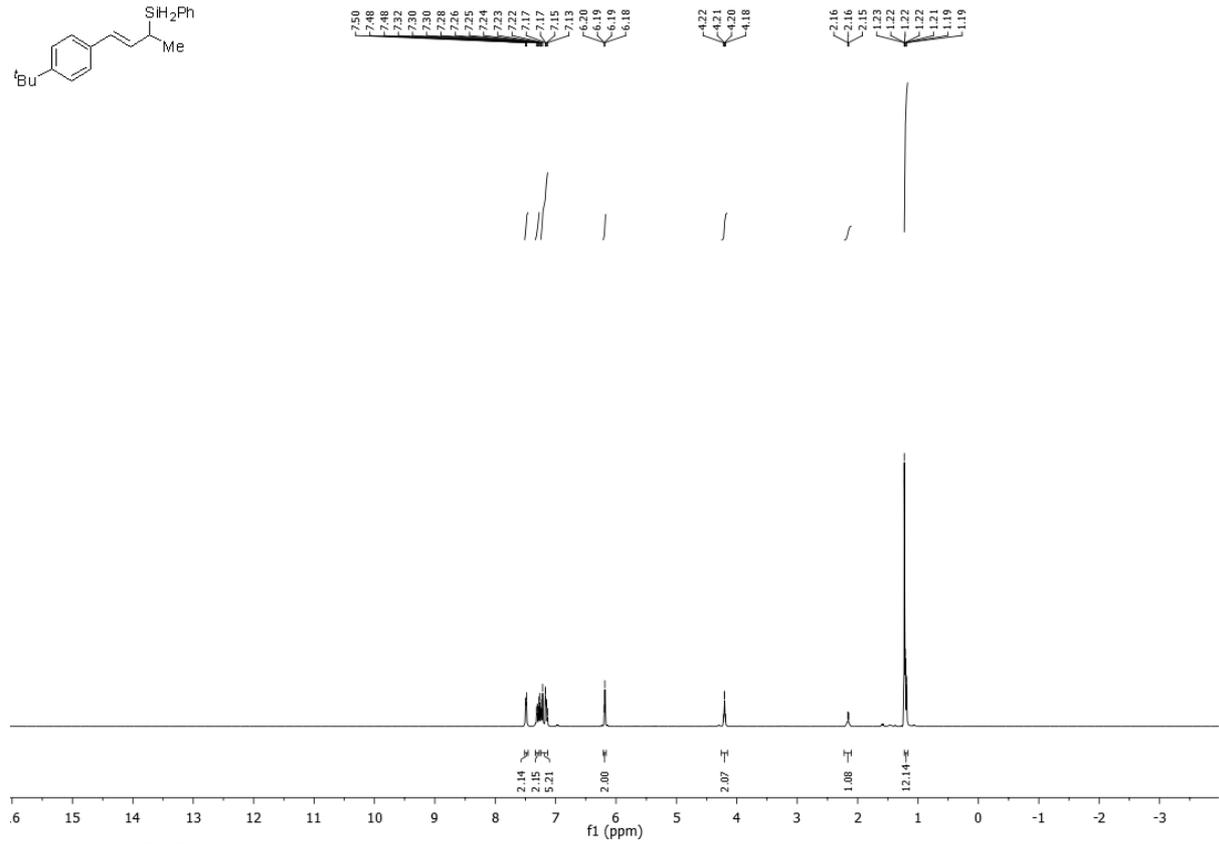
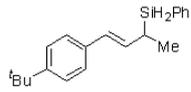


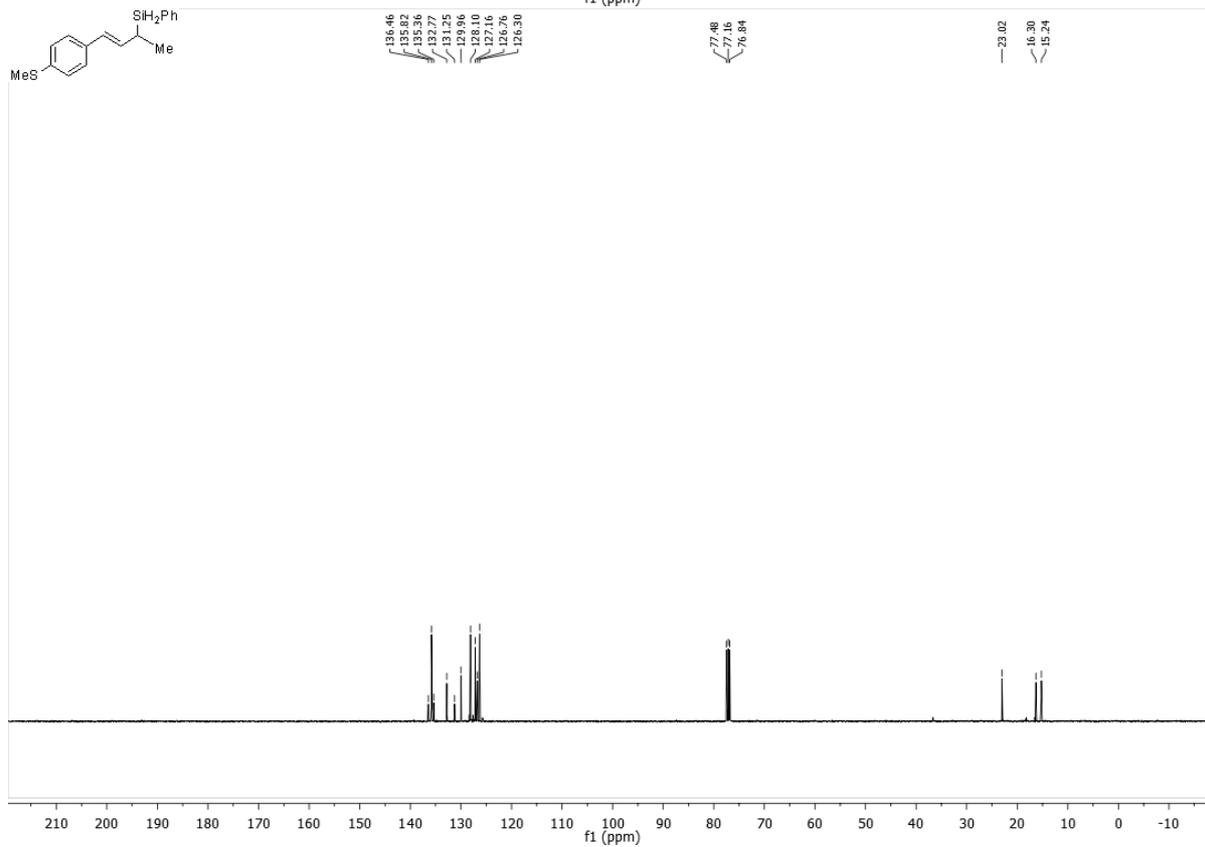
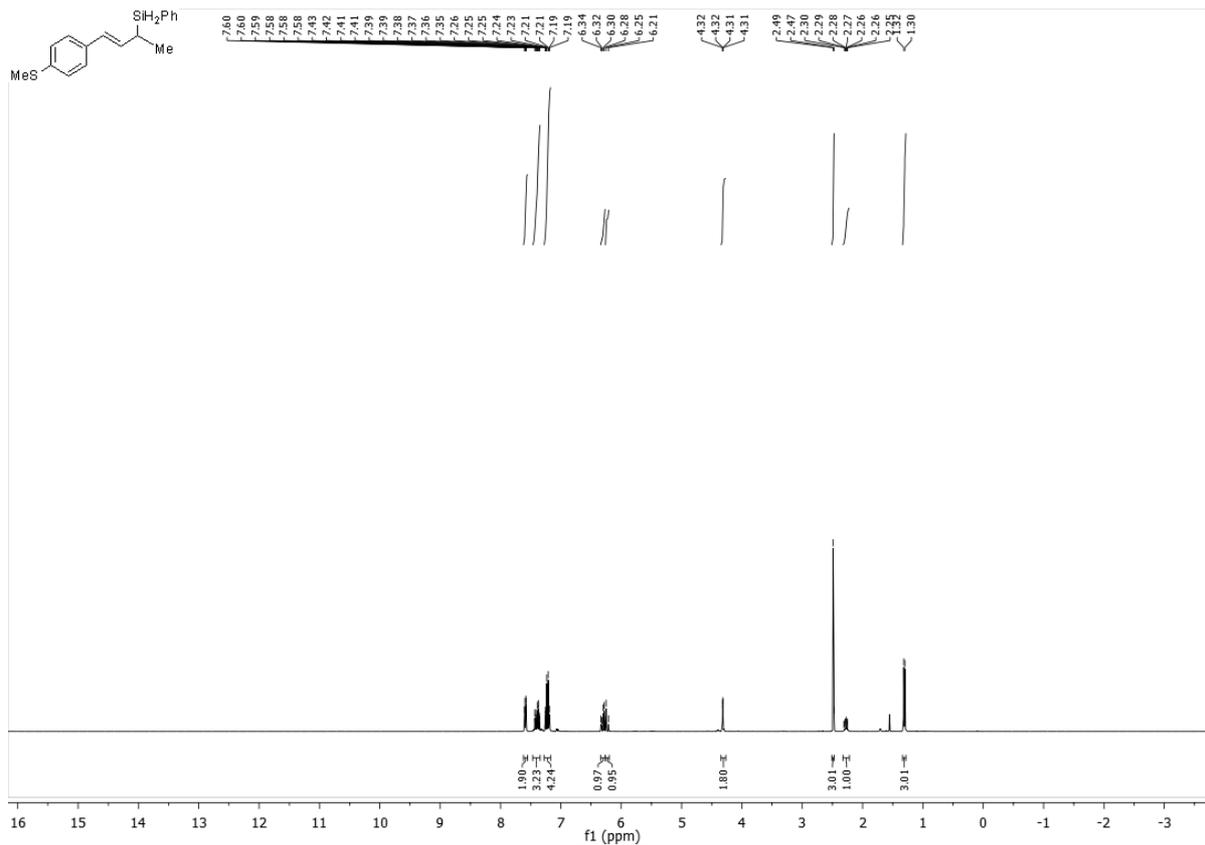


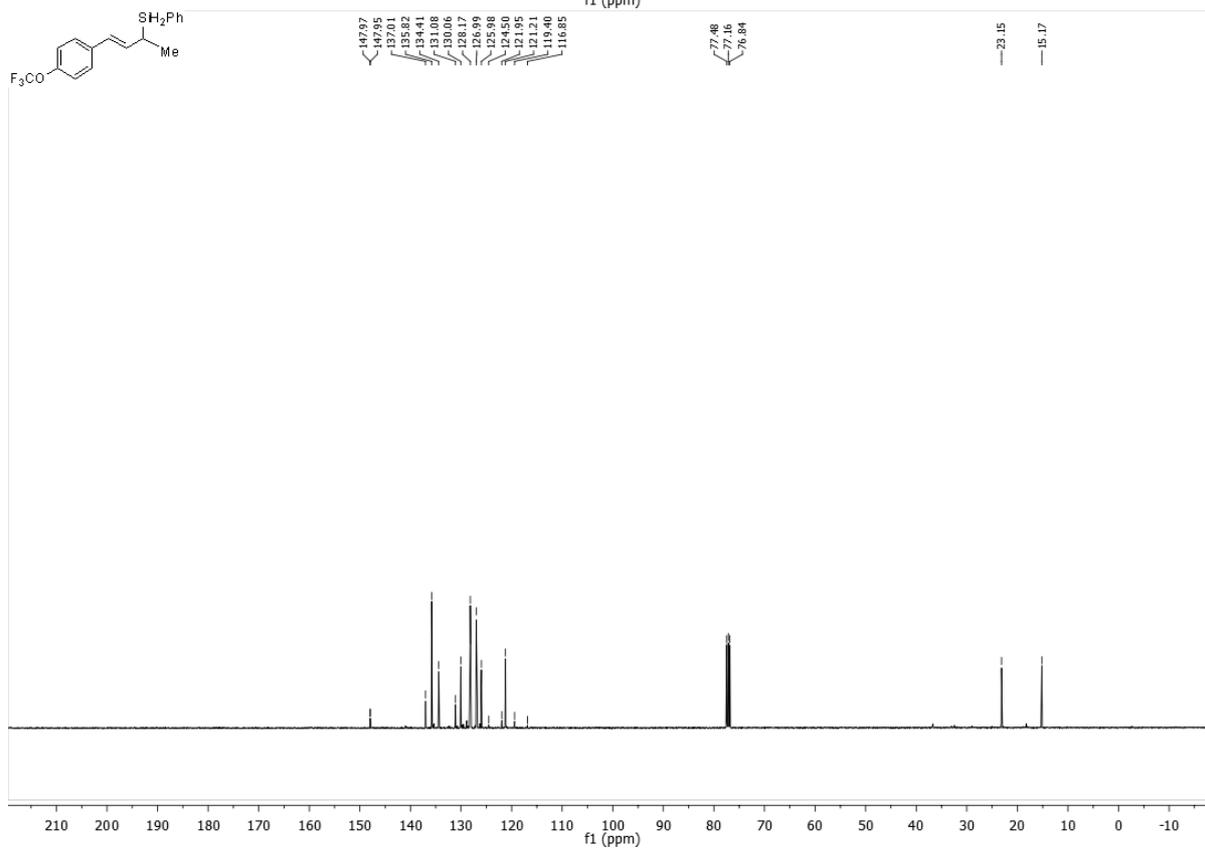
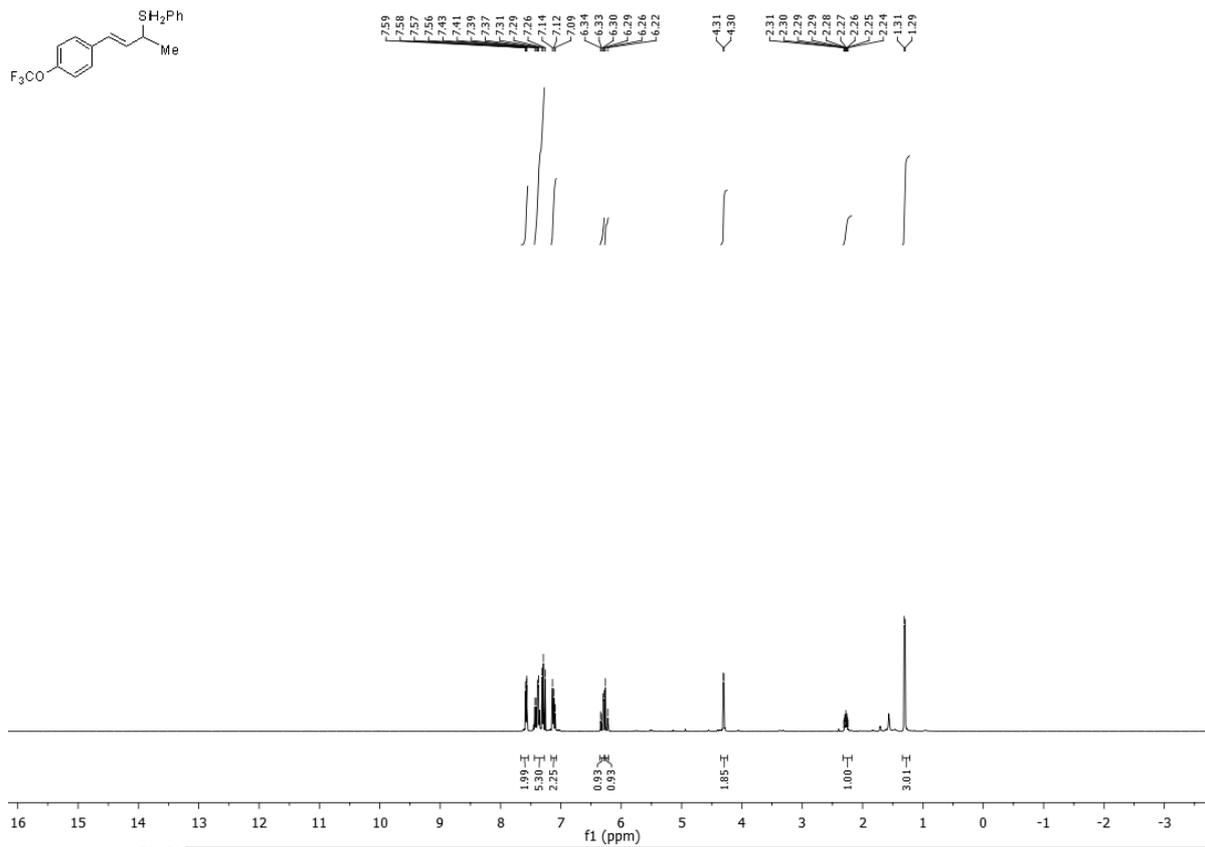
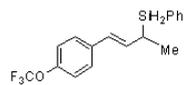


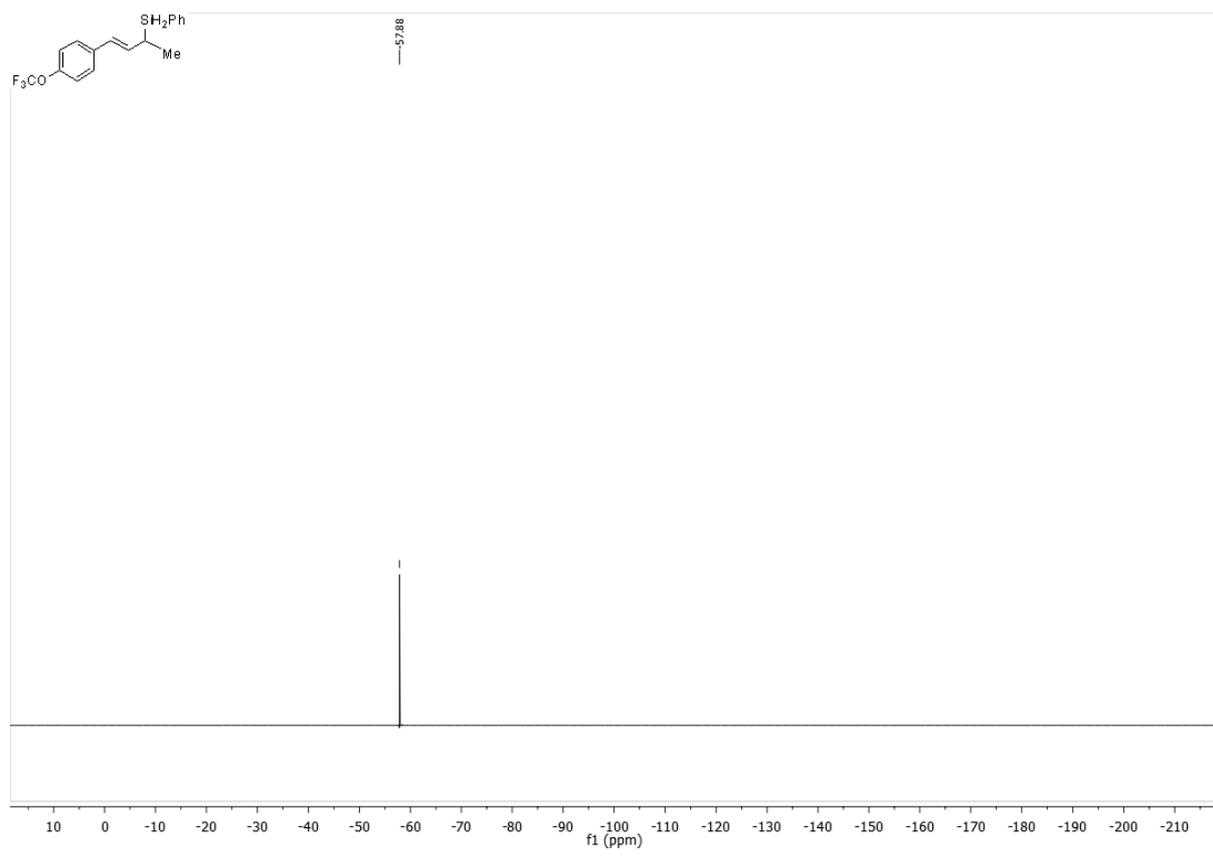


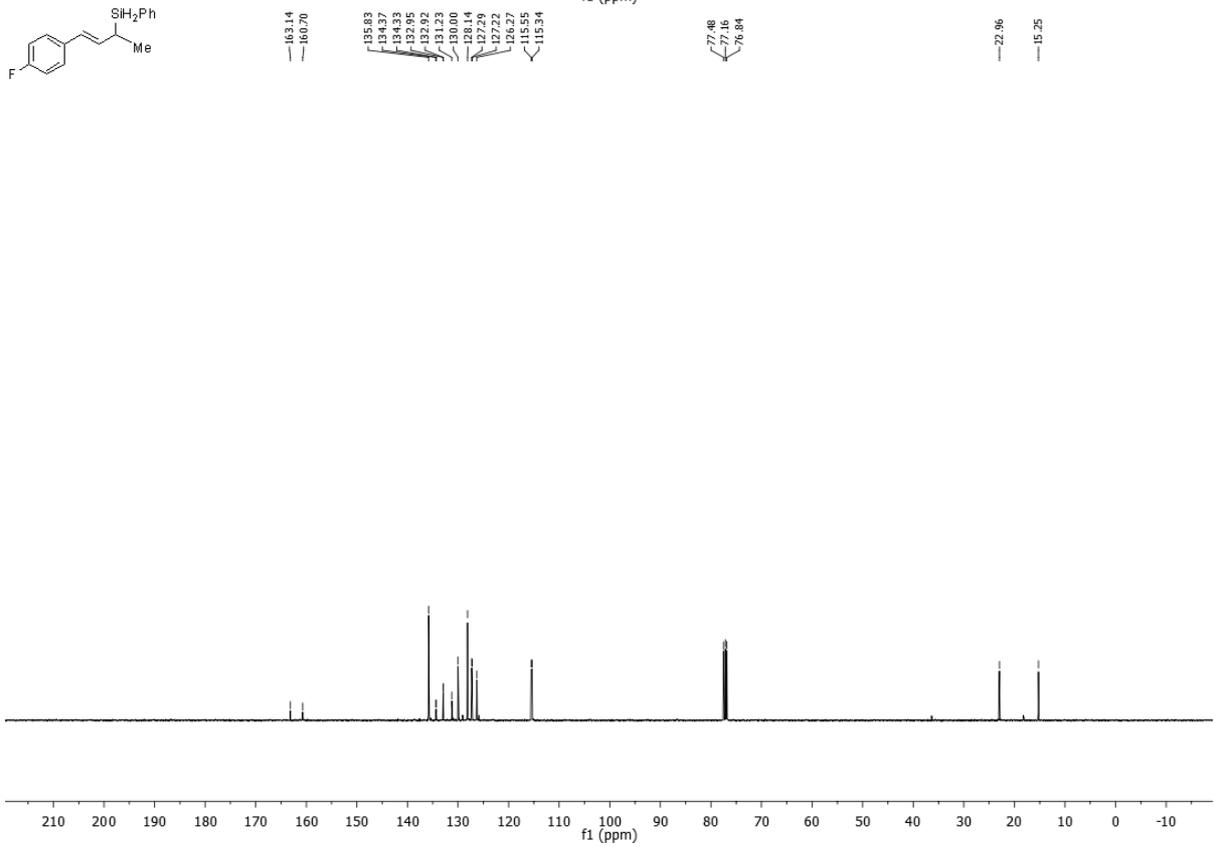
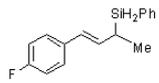
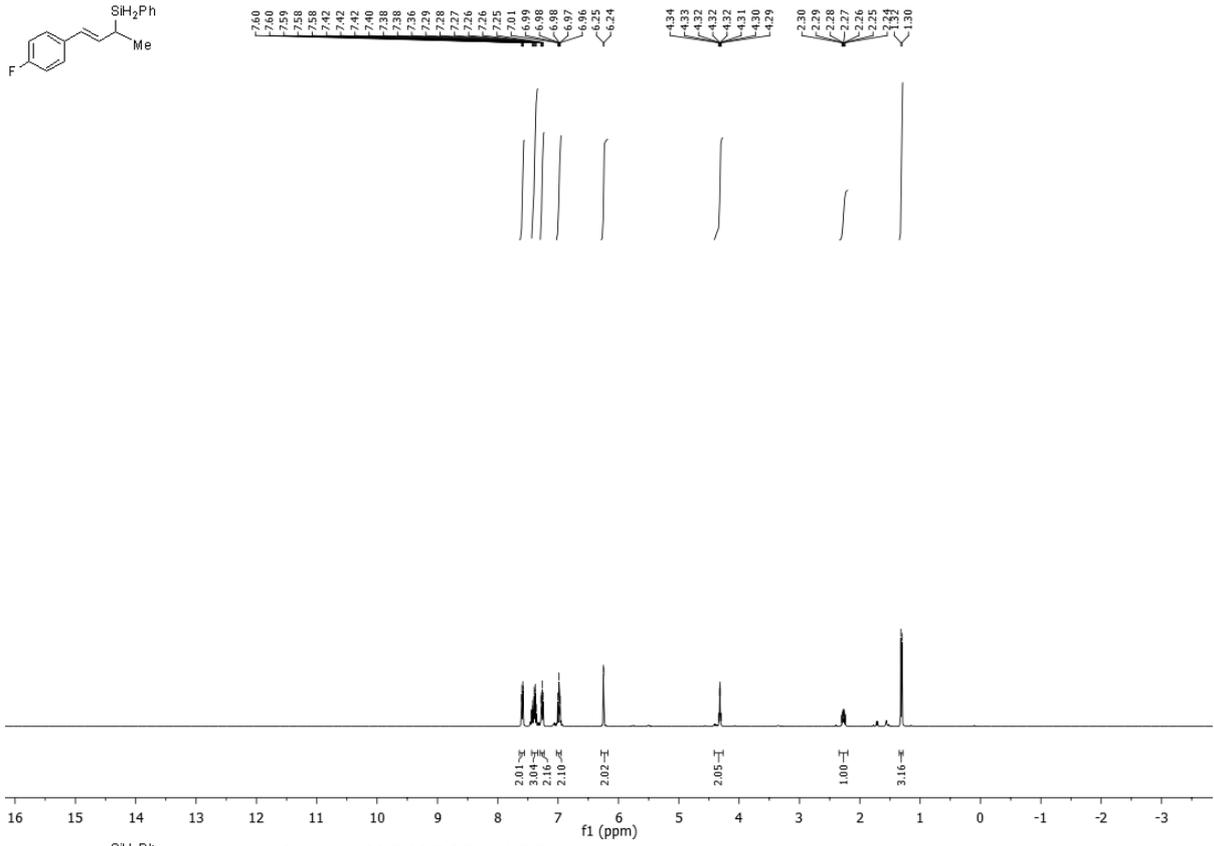
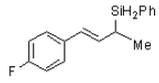


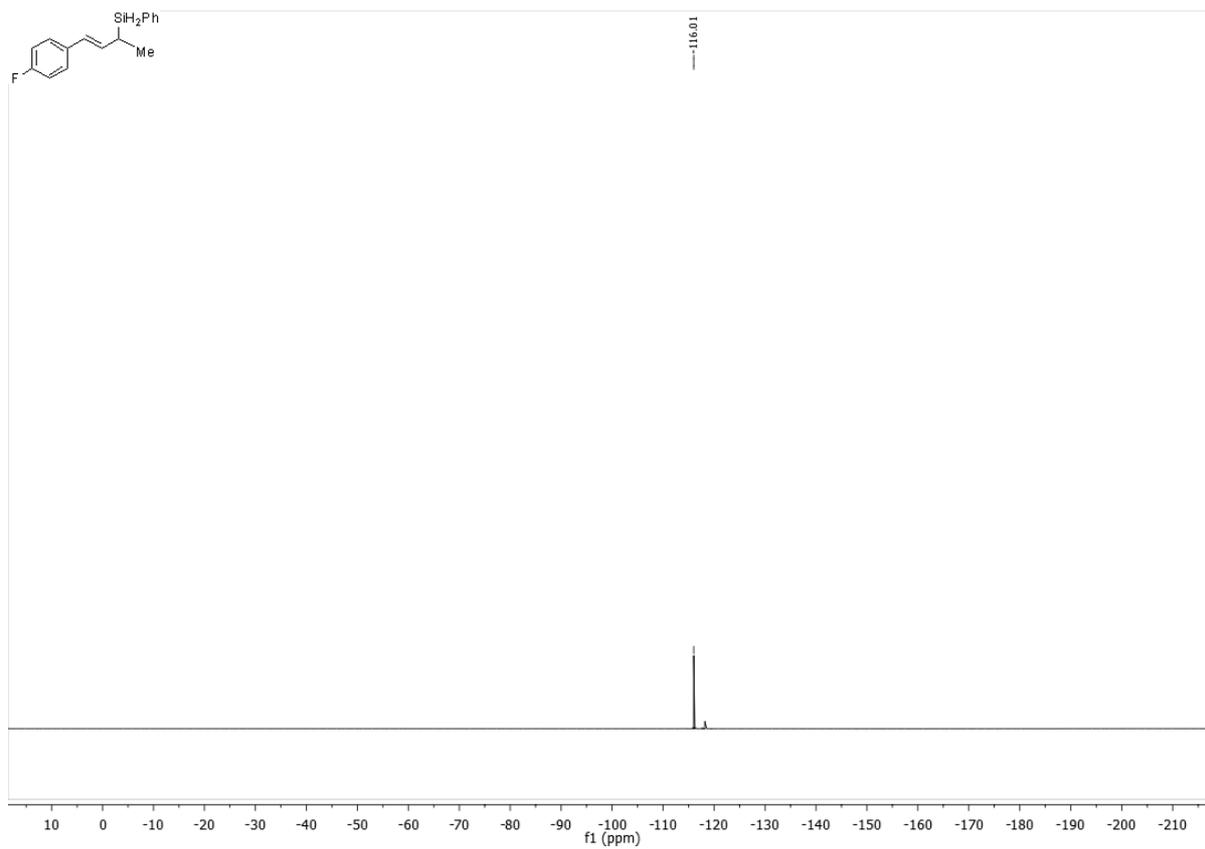


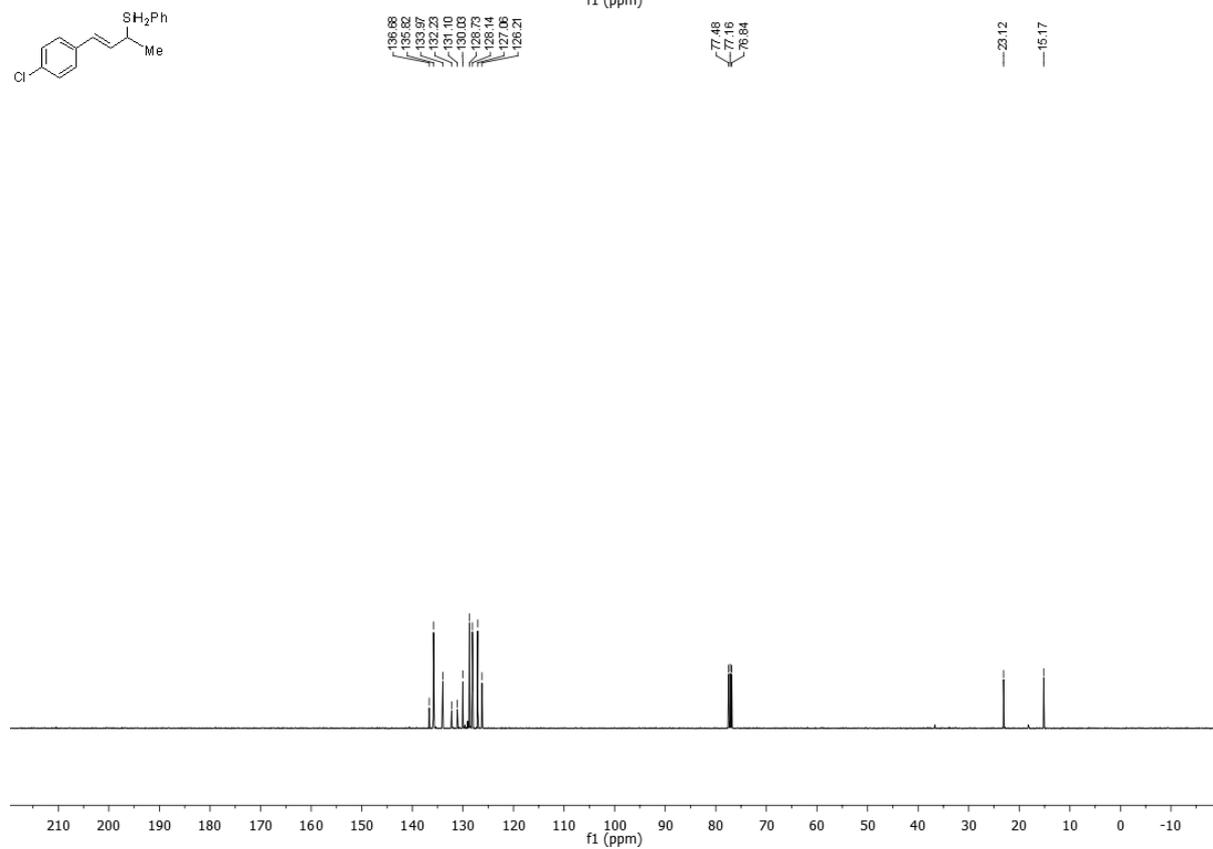
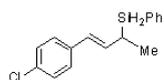
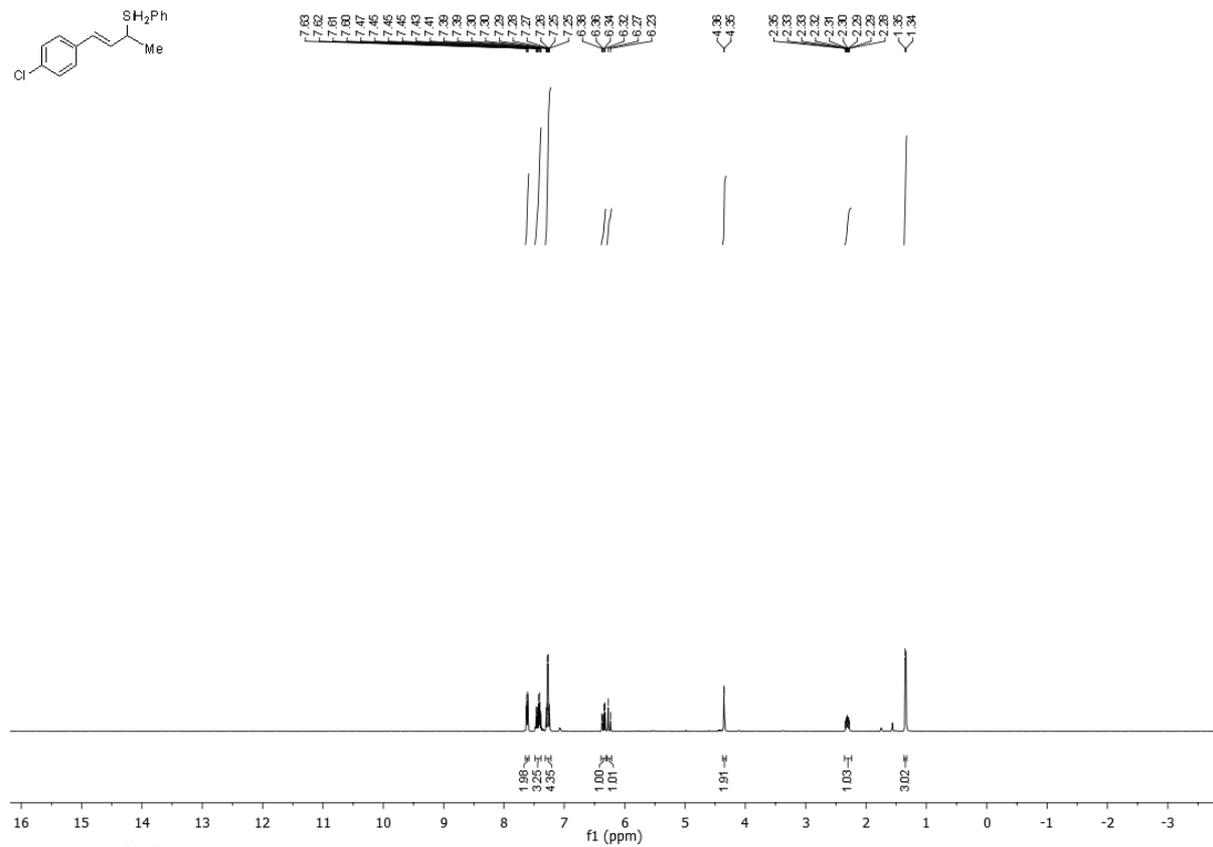
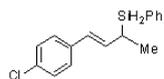


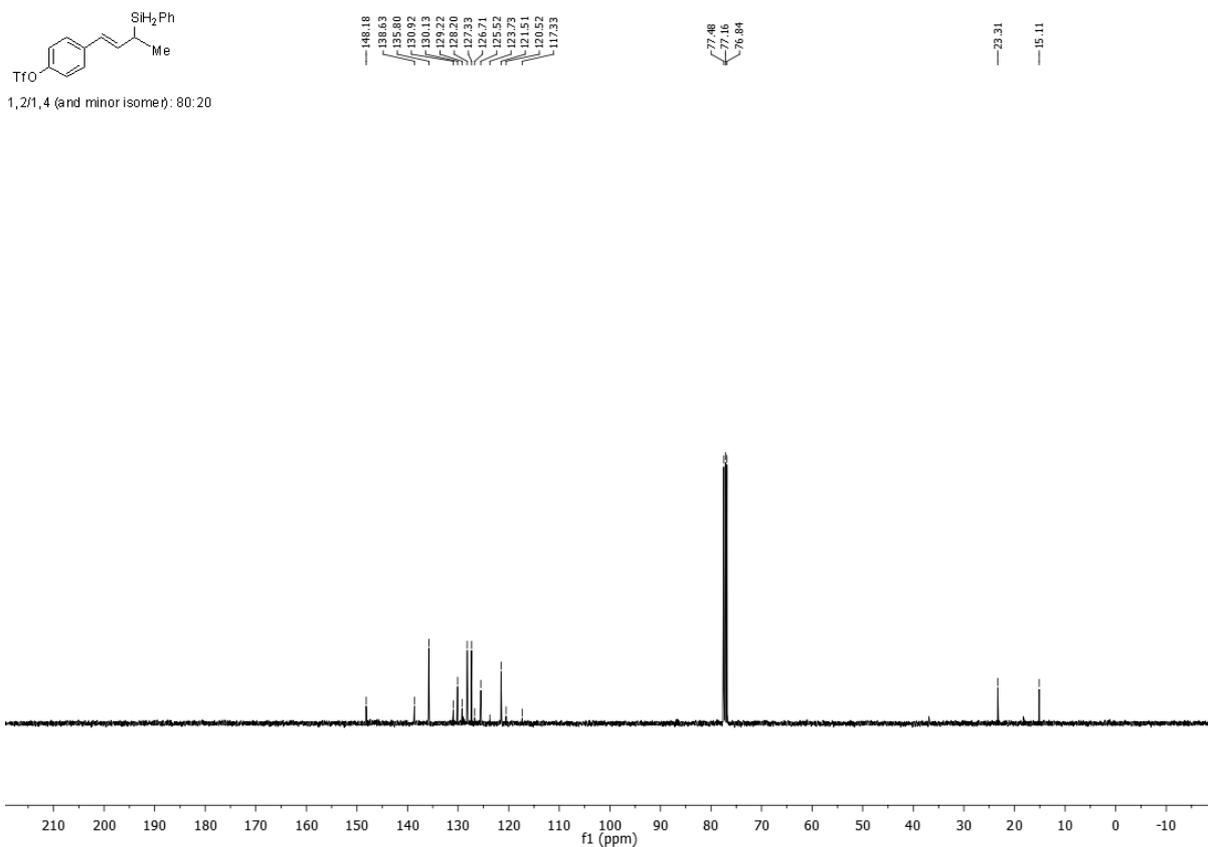
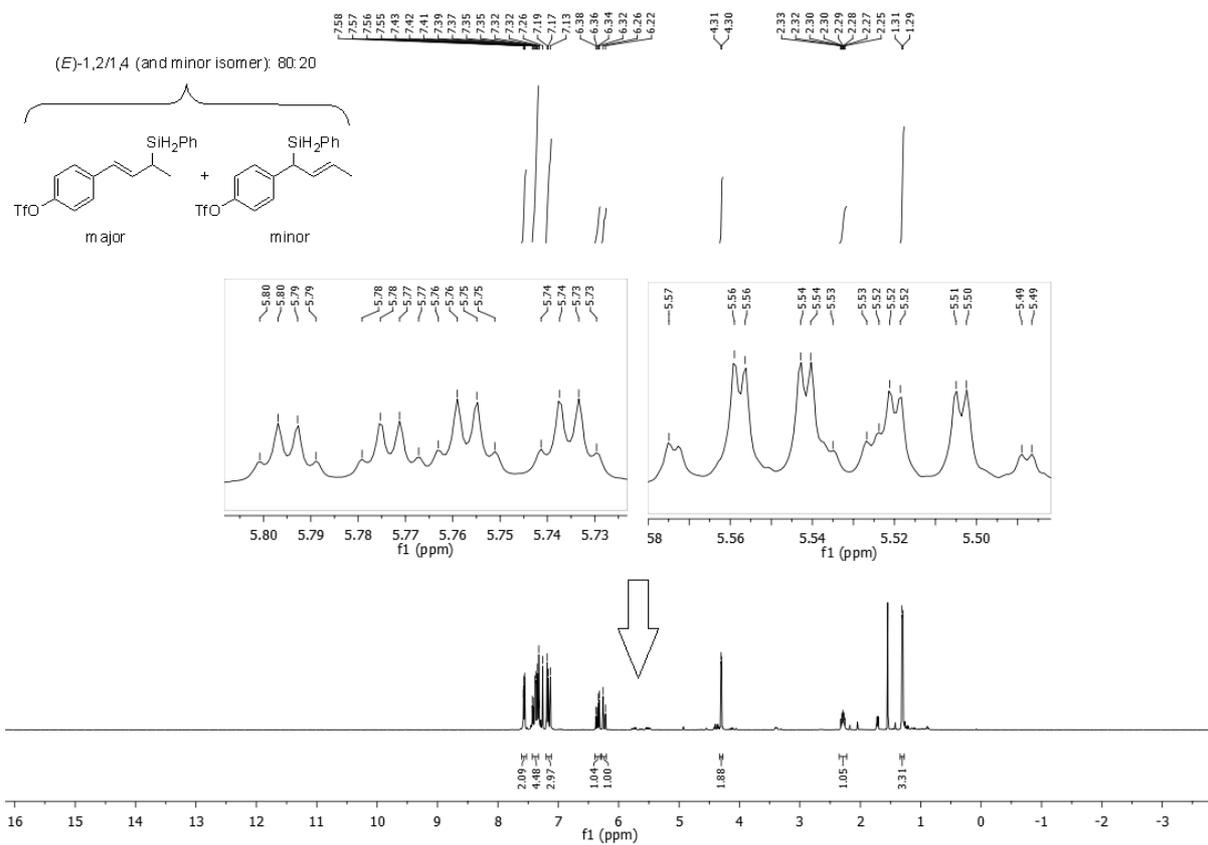


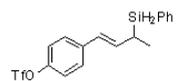












1,2/1,4 (and minor isomer) : 80:20

