

## Supporting Information

### Pd-Catalyzed One-Pot Synthesis of Vinylsilanes via a Three-Component Tandem Reaction

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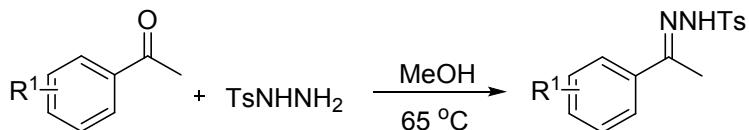
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## 1) General Information

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker ARX500 spectrometer (FT, 500 MHz for <sup>1</sup>H; 126 MHz for <sup>13</sup>C) at room temperature, unless otherwise noted. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> and referenced to residual CHCl<sub>3</sub> at 7.26 ppm and <sup>13</sup>C NMR spectra were referenced to the central peak of CDCl<sub>3</sub> at 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC systemcoupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Unless otherwise noted, all starting materials were commercially available and were used without further purification.

## 2) Synthetic Methods of Starting Materials

*N*-tosylhydrazones were Prepared According the Literature Method<sup>1-2</sup> with Some Modification.

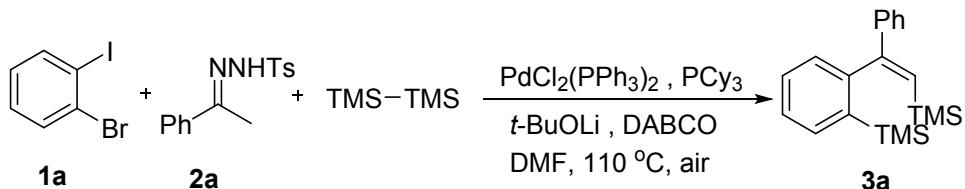


To a solution of *p*-toluenesulfonylhydrazide (4.4 mmol) in 16 mL MeOH, acetophenone derivatives (4.0 mmol) was added dropwise. The solution was stirred at 65 °C for 3 hours. There are two ways to get the target product: 1) First, the reaction liquid is transferred to the round bottom flask, evaporated and concentrated. The crude product was purified by silica gel column chromatography (Petroleum Ether/EtOAc) to give the corresponding *N*-tosylhydrazones. 2) The reaction mixture was cooled to 0 °C. The solid in solution was filtrated and washed by a little PE

(Petroleum Ether). Then *N*-tosylhydrazone was synthesized.

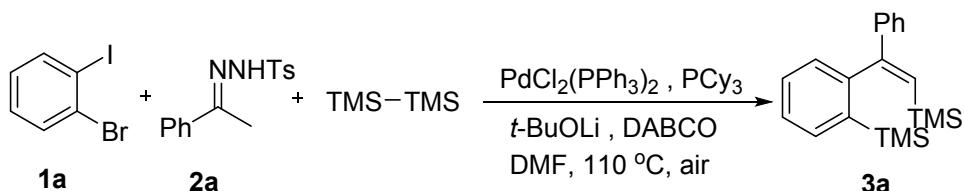
### 3) Typical Experimental Procedures

#### a) Synthesis of (*Z*)-Trimethyl(2-phenyl-2-(2-(trimethylsilyl)phenyl)vinyl)silane



The stirred mixture of 1-bromo-2-iodobenzene **1a** (0.2 mmol), *N*-tosylhydrazone (1.2 equiv), hexamethyldisilane (5.0 equiv),  $\text{PdCl}_2(\text{PPh}_3)_2$  (10 mol %),  $\text{PCy}_3$  (20 mol %), *t*-BuOLi (3.0 equiv) and DABCO (2.0 equiv) in DMF (2 mL) at  $110^\circ\text{C}$  for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted by EtOAc and the organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether unless otherwise noted) to provide the desired products **3a** as a colorless oil.

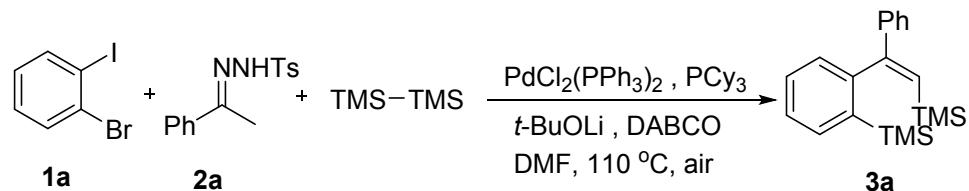
b) General Procedure for the Synthesis of (*Z*)-Trimethyl(2-phenyl-2-(2-(trimethylsilyl)phenyl)vinyl)silane (**3a**) from 1 mmol Scale of 1-Bromo-2-iodobenzene



To a schlenk tube were added 1-bromo-2-iodobenzene **1a** (1.0 mmol, 1.0 equiv), *N*-tosylhydrazone **2a** (1.2 mmol, 1.2 equiv), hexamethyldisilane (5.0 mmol, 5.0 equiv),  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.1 mmol, 10 mol %),  $\text{PCy}_3$  (0.2 mmol, 20 mol %), *t*-BuOLi (3.0 mmol, 3.0 equiv), and DABCO (2.0 mmol, 2.0 equiv) in DMF (10 mL) at  $110^\circ\text{C}$  (oil bath temperature) for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted by EtOAc, the organic layer was washed by water and the organic layer was evaporated under reduced pressure and the crude

product was purified by column chromatography (petroleum ether, unless otherwise noted) to provide the desired products **3a** (**213.8 mg, 66% yield**) as a colorless oil.

**Table S1. Screening of Optimal Reaction Conditions<sup>a</sup>**

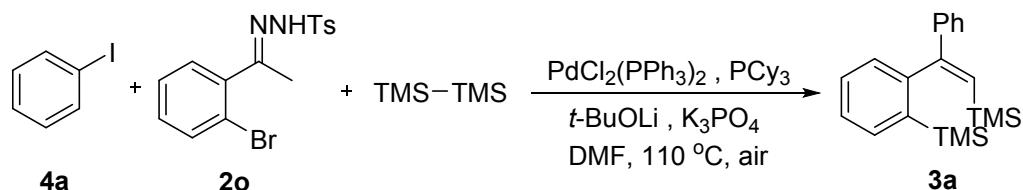


Entry	Catalyst	Ligand	Base 1	Base 2	Solvent	Yield/% <sup>b</sup>
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	ND	<i>t</i> -BuOLi		DMF	35
2	Pd(OAc) <sub>2</sub>	ND	<i>t</i> -BuOLi		DMF	12
3	Pd(dba) <sub>2</sub>	ND	<i>t</i> -BuOLi		DMF	13
4	Pd (PPh <sub>3</sub> ) <sub>4</sub>	ND	<i>t</i> -BuOLi		DMF	19
5	PdCl <sub>2</sub>	ND	<i>t</i> -BuOLi		DMF	16
6	ND	ND	<i>t</i> -BuOLi		DMF	0
7	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PPh <sub>3</sub>	<i>t</i> -BuOLi		DMF	32
8	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	P <sup>t</sup> Bu <sub>3</sub>	<i>t</i> -BuOLi		DMF	53
9	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi		DMF	60
10	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	K <sub>3</sub> PO <sub>4</sub>		DMF	trace
11	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>		DMF	trace
12	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	DABCO		DMF	0
13	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>3</sub> PO <sub>4</sub>	DMF	46
14	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>2</sub> CO <sub>3</sub>	DMF	45
15	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	Et <sub>3</sub> N	DMF	62
16	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	75
17	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	dioxane	0
18	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	Toluene	0
19	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	CH <sub>3</sub> CN	0
20 <sup>c</sup>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	54

21 <sup>d</sup>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	20
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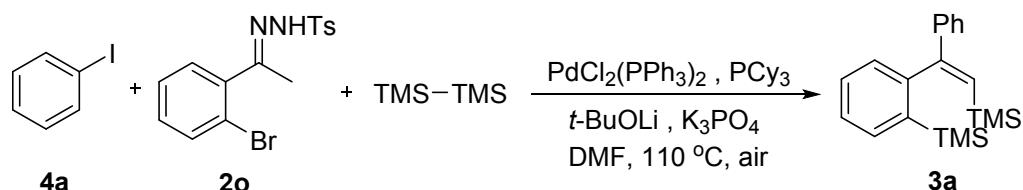
<sup>a</sup> Conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), TMS-TMS (5 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol %), PCy<sub>3</sub> (20 mol %), Base 1 (3 equiv), Base 2 (2 equiv), and solvent (2 mL) at 110 °C under Air atmosphere for 24 h. <sup>b</sup> Isolated yields. <sup>c</sup> 130 °C. <sup>d</sup> 90 °C.

c) Synthesis of (*Z*)-Trimethyl(2-phenyl-2-(2-(trimethylsilyl)phenyl)vinyl)silane



The stirred mixture of iodobenzene **4a** (0.2 mmol), *N*-tosylhydrazone **2o** (1.2 equiv), hexamethyldisilane (5.0 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol %), PCy<sub>3</sub> (20 mol %), *t*-BuOLi (3.0 equiv) and K<sub>3</sub>PO<sub>4</sub> (5.0 equiv) in DMF (2 mL) at 110 °C for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted by EtOAc and the organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether unless otherwise noted) to provide the desired products **3a** as a colorless oil.

**Table S2. Screening of Optimal Reaction Conditions<sup>a</sup>**



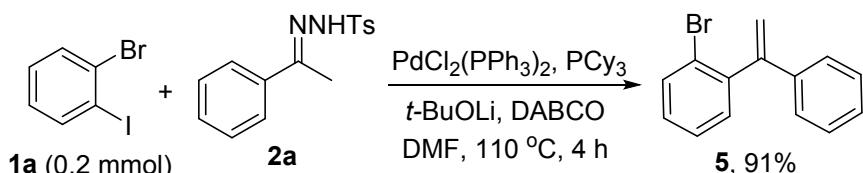
Entry	Catalyst	Ligand	Base	Additive	Solvent	Yield/% <sup>b</sup>
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	40
2	Pd(OAc) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	12
3	Pd (PPh <sub>3</sub> ) <sub>4</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	8
4	Pd(dba) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	11
5	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PtBu <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	trace
6	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PPh <sub>3</sub>	<i>t</i> -BuOLi	DABCO	DMF	14

7	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	<i>t</i> -Bu-X-Phos	<i>t</i> -BuOLi	DABCO	DMF	trace
8	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>2</sub> CO <sub>3</sub>	DMF	24
9	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	Cs <sub>2</sub> CO <sub>3</sub>	DMF	trace
10	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>3</sub> PO <sub>4</sub>	DMF	45
11 <sup>c</sup>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>3</sub> PO <sub>4</sub>	DMF	77
12 <sup>d</sup>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>3</sub> PO <sub>4</sub>	DMF	60
13	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>3</sub> PO <sub>4</sub>	CH <sub>3</sub> CN	0
14	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>3</sub> PO <sub>4</sub>	dioxane	0
15	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	PCy <sub>3</sub>	<i>t</i> -BuOLi	K <sub>3</sub> PO <sub>4</sub>	Toluene	0

<sup>a</sup> Conditions: **4a** (0.2 mmol), *N*-tosylhydrazone **2o** (0.24 mmol), TMS-TMS (5 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol %), PCy<sub>3</sub> (20 mol %), *t*-BuOLi (3 equiv), DABCO (2 equiv), and DMF (2 mL) at 110 °C under Air for 24 h. <sup>b</sup> Isolated yields. <sup>c</sup> K<sub>3</sub>PO<sub>4</sub> (5 equiv). <sup>d</sup> K<sub>3</sub>PO<sub>4</sub> (7 equiv). *t*-Bu-X-Phos = 2-di-tert-butylphosphino-2',4',6'-triisopropylbiphenyl.

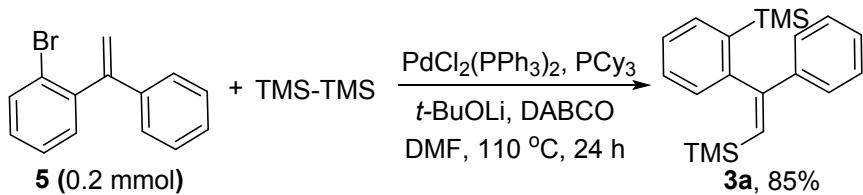
#### d) The Control Experiments

##### (1) Synthesis of *ortho*-Vinyl Bromobenzene



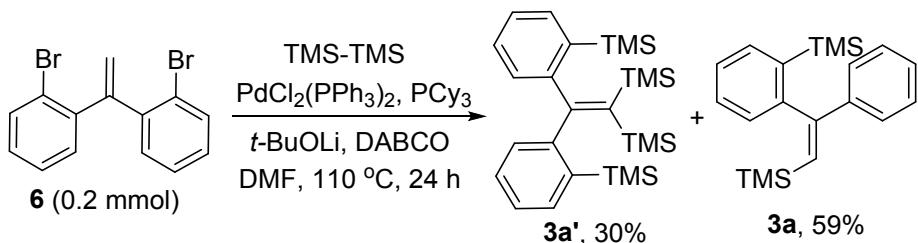
The stirred mixture of 1-bromo-2-iodobenzene **1a** (0.2 mmol), *N*-tosylhydrazone (1.2 equiv), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (10 mol %), PCy<sub>3</sub> (20 mol %), *t*-BuOLi (3.0 equiv) and DABCO (2.0 equiv) in DMF (2 mL) at 110 °C for 4 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted by EtOAc and the organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography to provide the desired products **5** as a pale yellow oil, up to 91% yield.

##### (2) The Procedure for the Synthesis of (*Z*)-Trimethyl(2-phenyl-2-(trimethylsilyl)phenyl)vinylsilane (**3a**) from *ortho*-Vinyl Bromobenzene



To a schlenk tube were added *ortho*-vinyl bromobenzene **5** (0.2 mmol), hexamethyldisilane (1.0 mmol, 5.0 equiv),  $\text{PdCl}_2(\text{PPh}_3)_2$  (10 mol %),  $\text{PCy}_3$  (20 mol %), *t*-BuOLi (0.6 mmol, 3.0 equiv), and DABCO (0.4 mmol, 2.0 equiv) in DMF (2 mL) at 110 °C (oil bath temperature) for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted by EtOAc, the organic layer was washed by water and the organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether, unless otherwise noted) to provide the desired products **3a** as a colorless oil.

(3) The Synthesis of (*Z*)-Trimethyl(2-phenyl-2-(trimethylsilyl)phenyl)vinylsilane (**3a**) and (2,2'-Bis(2-(trimethylsilyl)phenyl)ethene-1,1-diyl)bis(trimethylsilane) (**3a'**) from 2,2'-(Ethene-1,1-diyl)bis(bromobenzene) (**6**).



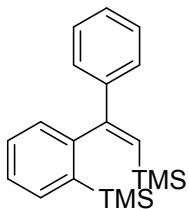
To a schlenk tube were added 2,2'-(ethene-1,1-diyl)bis(bromobenzene) **6** (0.2 mmol), hexamethyldisilane (2.0 mmol, 10.0 equiv),  $\text{PdCl}_2(\text{PPh}_3)_2$  (20 mol %),  $\text{PCy}_3$  (40 mol %), *t*-BuOLi (1.2 mmol, 6.0 equiv), and DABCO (0.8 mmol, 4.0 equiv) in DMF (5 mL) at 110 °C (oil bath temperature) for 24 h. After the completion of the reaction (monitored by TLC), the reaction mixture was extracted by EtOAc, the organic layer was washed by water and the organic layer was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether, unless otherwise noted) to provide the desired products **3a** as a colorless oil and products **3a'** as a white solid, respectively.

#### e) Crystal Culture Procedure of Product **3i**

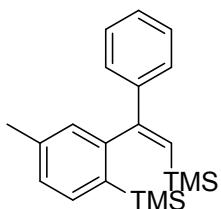
To a round-bottom flask (25 mL) was added (*Z*)-(4-methoxy-2-(1-phenyl-2-

(trimethylsilyl)vinyl)phenyl)trimethylsilane **3i** (10 mg). Dichloromethane (1.0 mL) were added slowly to make it dissolve completely. Then petroleum ether (5.0 mL) were added. Finally, the round-bottom flask was sealed with a rubber stopper, and connected the air with a syringe needle. Putting the flask in a dry and ventilated place to make the organic solvent volatilize slowly. After a few days, the crystal of **3i** were separated out.

#### 4) Characterization Data

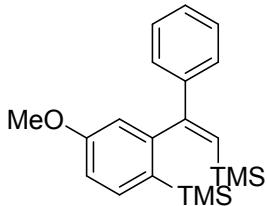


**(Z)-trimethyl(2-phenyl-2-(trimethylsilyl)phenyl)vinylsilane (3a):** colorless oil, isolated yield 75% (49 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.3$  Hz, 1H), 7.38 (dd,  $J = 7.4$  Hz, 1.2 Hz, 1H), 7.35-7.32 (m, 1H), 7.26 (s, 1H), 7.25 (s, 3H), 7.23-7.20 (m, 1H), 7.17 (d,  $J = 7.4$  Hz, 1H), 6.38 (s, 1H), -0.05 (s, 9H), -0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6, 147.9, 142.9, 138.6, 134.8, 131.0, 129.4, 128.3, 128.0, 127.6, 127.1, 126.5, 0.2, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{28}\text{Si}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  325.1802, found 325.1803.



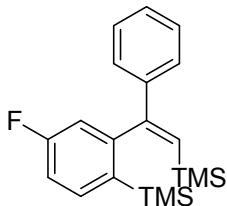
**(Z)-trimethyl(4-methyl-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)vinylsilane (3b):** colorless oil, isolated yield 80% (54 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 7.6$  Hz, 1H), 7.28-7.21 (m, 5H), 7.16 (d,  $J = 7.5$  Hz, 1H), 7.01 (s, 1H), 6.37 (s, 1H), 2.39 (s, 3H), -0.05(s, 9H), -0.15 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0, 147.8, 142.9, 138.0, 134.9, 132.0, 129.1, 128.0, 128.0, 127.6, 127.2, 127.1, 21.2, 0.3, -0.4.

HRMS (ESI) m/z calcd for  $C_{21}H_{30}Si_2^+$  ( $M+H$ )<sup>+</sup> 339.1959, found 339.1960.



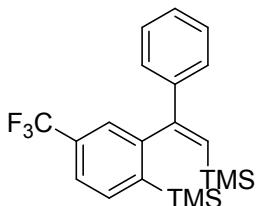
**(Z)-(4-methoxy-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3c):**

colorless oil, isolated yield 45% (32 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 8.3 Hz, 1H), 7.28-7.26 (m, 2H), 7.26-7.19 (m, 3H), 6.88 (dd, *J* = 8.3 Hz, 2.6 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.36 (s, 1H), 3.85 (s, 3H), -0.08 (s, 9H), -0.14 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.8, 157.4, 149.5, 142.6, 136.3, 129.6, 129.2, 128.1, 127.6, 127.0, 116.9, 111.9, 55.0, 0.3, -0.4. HRMS (ESI) m/z calcd for  $C_{21}H_{30}OSi_2^+$  ( $M+H$ )<sup>+</sup> 355.1908, found 355.1909.



**(Z)-(4-fluoro-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3d):**

colorless oil, isolated yield 63% (43 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.52 (t, *J* = 7.2 Hz, 1H), 7.28-7.24 (m, 5H), 7.04 (td, *J* = 8.3 Hz, 2.4 Hz, 1H), 6.92 (dd, *J* = 9.7 Hz, 1.9 Hz, 1H), 6.39 (s, 1H), -0.06 (s, 9H), -0.14 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 163.1 (d, *J* = 249.6 Hz), 156.3, 150.4 (d, *J* = 6.7 Hz), 142.3, 136.8 (d, *J* = 7.5 Hz), 134.4, 130.1, 128.2, 127.9, 127.0, 118.0 (d, *J* = 19.4 Hz), 113.3 (d, *J* = 18.8 Hz), 0.3, -0.4. HRMS (ESI) m/z calcd for  $C_{20}H_{27}FSi_2^+$  ( $M+H$ )<sup>+</sup> 343.1708, found 343.1709.

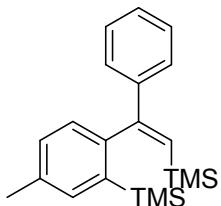


**(Z)-trimethyl(2-phenyl-2-(5-(trifluoromethyl)-2-(trimethylsilyl)phenyl)vinyl)silane (3e):**

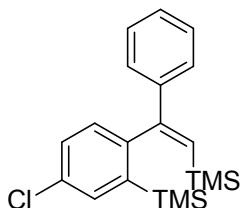
colorless oil, isolated yield 92% (72 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.61 (dd, *J* = 7.8 Hz, 1.1 Hz,

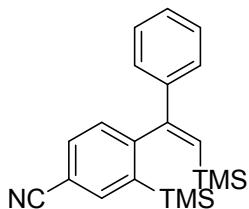
1H), 7.47 (s, 1H), 7.32-7.29 (m, 1H), 7.29-7.27 (m, 2H), 7.25-7.22 (m, 2H), 6.48 (s, 1H), 0.01 (s, 9H), -0.15 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 148.6, 143.9, 142.2, 135.4, 130.7, 130.5 (q,  $J = 32.4$  Hz), 128.2, 128.0, 127.3 (q,  $J = 3.7$  Hz), 127.0, 124.2 (q,  $J = 272.5$  Hz), 123.0 (q,  $J = 3.6$  Hz), 0.0, -0.5. HRMS (ESI) m/z calcd for  $\text{C}_{21}\text{H}_{27}\text{F}_3\text{Si}_2^+$  ( $\text{M}+\text{H})^+$  393.1676, found 393.1657.



**(Z)-trimethyl(5-methyl-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)silane (3f):**  
colorless oil, isolated yield 65% (44 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (s, 1H), 7.26-7.25 (m, 4H), 7.24-7.21 (m, 1H), 7.19 (d,  $J = 7.5$  Hz, 1H), 7.07 (d,  $J = 7.6$  Hz, 1H), 6.36 (s, 1H), 2.41 (s, 3H), -0.05 (s, 9H), -0.16 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 144.9, 143.1, 138.2, 135.7, 135.5, 131.0, 129.3, 129.0, 128.0, 127.5, 127.1, 21.4, 0.2, -0.3. HRMS (ESI) m/z calcd for  $\text{C}_{21}\text{H}_{30}\text{Si}_2^+$  ( $\text{M}+\text{H})^+$  339.1959, found 339.1960.

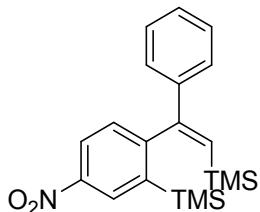


**(Z)-(5-chloro-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3g):**  
colorless oil, isolated yield 70% (50 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 2.3$  Hz, 1H), 7.36 (dd,  $J = 8.1$  Hz, 2.3 Hz, 1H), 7.28-7.26 (m, 1H), 7.26-7.24 (m, 2H), 7.23-7.21 (m, 2H), 7.11 (d,  $J = 8.1$  Hz, 1H), 6.39 (s, 1H), -0.04 (s, 9H), -0.15 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 146.2, 142.5, 141.5, 134.6, 133.0, 132.4, 130.1, 128.3, 128.1, 127.8, 127.0, 0.0, -0.3. HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{27}\text{ClSi}_2^+$  ( $\text{M}+\text{Na})^+$  381.1232, found 381.1233.



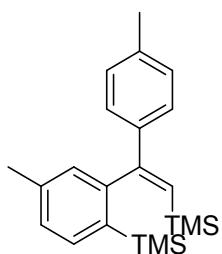
**(Z)-4-(1-phenyl-2-(trimethylsilyl)vinyl)-3-(trimethylsilyl)benzonitrile (3h):**

colorless oil, isolated yield 72% (50 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 1.6$  Hz, 1H), 7.65 (dd,  $J = 7.8$  Hz, 1.8 Hz, 1H), 7.26-7.23 (m, 2H), 7.15-7.13 (m, 2H), 7.29-7.27 (m, 2H), 6.41 (s, 1H), -0.06 (s, 9H), -0.20 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.8, 152.7, 141.6, 141.1, 138.5, 131.7, 131.3, 130.5, 128.3, 128.1, 126.8, 119.2, 110.8, -0.1, -0.5. HRMS (ESI) m/z calcd for  $\text{C}_{21}\text{H}_{27}\text{NSi}_2^+$  ( $\text{M}+\text{Na}$ ) $^+$  372.1574, found 372.1576.



**(Z)-(4-methoxy-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3i):**

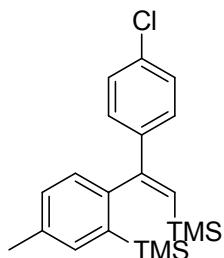
White solid, isolated yield 61% (45 mg), mp: 65.6-67.6 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (d,  $J = 2.3$  Hz, 1H), 8.24 (dd,  $J = 8.3$  Hz, 2.3 Hz, 1H), 7.36 (d,  $J = 8.3$  Hz, 1H), 7.30-7.26 (m, 3H), 7.19-7.17 (m, 2H), 6.48 (s, 1H), -0.02 (s, 9H), -0.15 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 155.0, 146.7, 141.9, 141.6, 131.8, 130.8, 129.6, 128.3, 128.2, 126.8, 123.3, -0.1, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{27}\text{NO}_2\text{Si}_2^+$  ( $\text{M}$ ) $^+$  369.1580, found 369.1576.



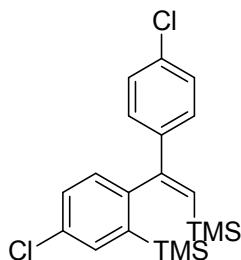
**(Z)-trimethyl(4-methyl-2-(1-(p-tolyl)-2-(trimethylsilyl)vinyl)phenyl)silane (3j):**

colorless oil, isolated yield 65% (46 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 7.6$  Hz, 1H), 7.17-7.15 (m, 3H), 7.07 (d,  $J = 8.1$  Hz, 2H), 6.99 (s, 1H), 6.31 (s, 1H),

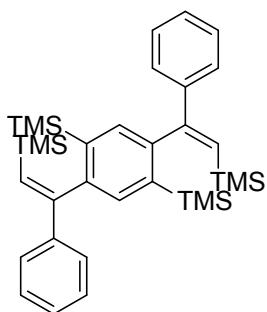
6.39 (s, 3H), 6.33 (s, 3H), -0.04 (s, 9H), -0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.8, 148.0, 140.1, 137.9, 137.4, 134.9, 134.8, 131.8, 128.7, 127.8, 127.1, 127.0, 21.2, 21.1, 0.3, -0.3. HRMS (ESI) m/z calcd for  $\text{C}_{22}\text{H}_{32}\text{Si}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  353.2115, found 353.2117.



**(Z)-(2-(4-chlorophenyl)-2-(4-methyl-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (3k):** colorless oil, isolated yield 72% (54 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (s, 1H), 7.21 (d,  $J = 8.7$  Hz, 2H), 7.19 (s, 2H), 7.17 (d,  $J = 2.3$  Hz, 1H), 7.03 (d,  $J = 7.6$  Hz, 1H), 6.34 (s, 1H), 2.40 (s, 3H), -0.03 (s, 9H), -0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 144.3, 141.6, 138.3, 135.9, 135.7, 133.4, 130.9, 130.0, 129.1, 128.3, 128.1, 21.4, 0.4, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{21}\text{H}_{29}\text{ClSi}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  373.1569, found 373.1571.

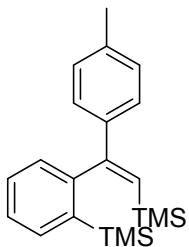


**(Z)-(5-chloro-2-(1-(4-chlorophenyl)-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3l):** colorless oil, isolated yield 74% (58 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 2.3$  Hz, 1H), 7.36 (dd,  $J = 8.1$  Hz, 2.3 Hz, 1H), 7.23 (dd,  $J = 6.9$  Hz, 1.8 Hz, 2H), 7.16-7.14 (m, 2H), 7.09 (d,  $J = 8.1$  Hz, 1H), 6.38 (s, 1H), -0.02 (s, 9H), -0.15 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.1, 145.6, 141.5, 141.0, 134.7, 133.7, 133.2, 132.3, 130.8, 128.5, 128.3, 128.2, 0.1, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{Si}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  393.1023, found 393.1083.

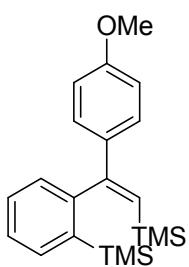


**(2,5-bis((Z)-1-phenyl-2-(trimethylsilyl)vinyl)-1,4-phenylene)bis(trimethylsilane)**

**(3m):** White solid, isolated yield 57% (65 mg), mp: 70.6-71.5 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (s, 2H), 7.30 (t, *J* = 7.8 Hz, 4H), 7.28-7.26 (m, 3H), 7.26-7.23 (m, 3H), 6.39 (d, *J* = 4.2 Hz, 2H), -0.04 (s, 18H), -0.09 (s, 18H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.0, 146.1, 143.0, 138.5, 137.3, 129.4, 128.1, 127.6, 127.2, 0.0, -0.3. HRMS (ESI) m/z calcd for C<sub>34</sub>H<sub>50</sub>Si<sub>4</sub><sup>+</sup> (M)<sup>+</sup> 570.2990, found 570.2986.



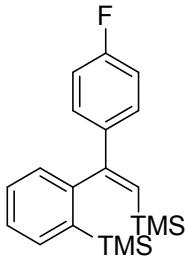
**(Z)-trimethyl(2-(p-tolyl)-2-(trimethylsilyl)phenyl)vinylsilane (3n):** colorless oil, isolated yield 69% (47 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.16-7.13 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.33 (s, 1H), 2.32 (s, 3H), -0.03 (s, 9H), -0.18 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.4, 148.0, 140.1, 138.6, 137.4, 134.7, 130.9, 128.7, 128.3, 128.1, 126.9, 126.4, 21.1, 0.3, -0.4. HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>30</sub>Si<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 339.1959, found 339.1960.



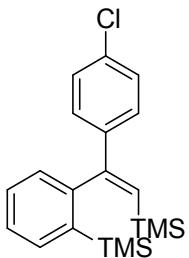
**(Z)-(2-(4-methoxyphenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3o):**

colorless oil, isolated yield 75% (53 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 6.9 Hz, 1H), 7.32 (t, *J* = 6.9 Hz, 1H), 7.18 (s, 1H), 7.17 (s,

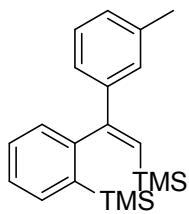
1H), 7.15 (d,  $J$  = 7.6 Hz, 1H), 6.80 (s, 1H), 6.78 (s, 1H), 6.24 (s, 1H), 3.79 (s, 3H), -0.02(s, 9H), -0.19 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3, 157.0, 148.1, 138.6, 135.8, 134.8, 130.8, 128.3, 128.3, 126.8, 126.4, 113.3, 55.3, 0.3, -0.3. HRMS (ESI) m/z calcd for  $\text{C}_{21}\text{H}_{30}\text{OSi}_2^+$  ( $\text{M}+\text{H}$ )<sup>+</sup> 355.1908, found 355.1909.



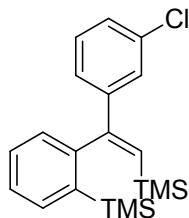
**(Z)-(2-(4-fluorophenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3p):**  
colorless oil, isolated yield 81% (55 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (dd,  $J$  = 7.2 Hz, 0.7 Hz, 1H), 7.39 (td,  $J$  = 7.4 Hz, 1.2 Hz, 1H), 7.36-7.35 (m, 1H), 7.23 (dd,  $J$  = 8.8 Hz, 5.6 Hz, 2H), 7.17 (d,  $J$  = 7.4 Hz, 1H), 6.97-6.93 (m, 2H), 6.32 (s, 1H), -0.01(s, 9H), -0.16 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d,  $J$  = 248.3 Hz), 156.5, 147.6, 139.2 (d,  $J$  = 2.8 Hz), 138.6, 134.9, 130.9, 129.2, 128.7 (d,  $J$  = 8.0 Hz), 128.5, 126.7, 114.9 (d,  $J$  = 21.6 Hz), 0.3, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{27}\text{FSi}_2^+$  ( $\text{M}+\text{H}$ )<sup>+</sup> 343.1708, found 343.1709.



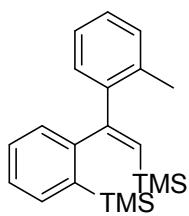
**(Z)-(2-(4-chlorophenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3q):**  
colorless oil, isolated yield 73% (52 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J$  = 7.3 Hz, 1H), 7.38 (t,  $J$  = 7.4 Hz, 1H), 7.34 (t,  $J$  = 7.3 Hz, 1H), 7.22 (d,  $J$  = 7.9 Hz, 2H), 7.17 (d,  $J$  = 8.1 Hz, 2H), 7.14 (d,  $J$  = 7.3 Hz, 1H), 6.37 (s, 1H), -0.02(s, 9H), -0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 147.3, 141.4, 138.6, 135.0, 133.5, 130.9, 130.1, 128.5, 128.3, 128.2, 126.7, 0.4, -0.5. HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{27}\text{ClSi}_2^+$  ( $\text{M}+\text{Na}$ )<sup>+</sup> 381.1232, found 381.1233.



**(Z)-trimethyl(2-(m-tolyl)-2-(trimethylsilyl)phenyl)vinylsilane (3r):** colorless oil, isolated yield 52% (35 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J = 7.2$  Hz, 1H), 7.38 (t,  $J = 6.5$  Hz, 1H), 7.34-7.31 (m, 1H), 7.17-7.13 (m, 2H), 7.05 (t,  $J = 8.7$  Hz, 3H), 6.37 (s, 1H), 2.3 (s, 3H), -0.03 (s, 9H), -0.18 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.6, 148.0, 142.8, 138.6, 137.5, 134.7, 131.0, 129.1, 128.4, 128.3, 127.9, 127.6, 126.4, 124.3, 21.5, 0.3, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{21}\text{H}_{30}\text{Si}_2^+$  ( $\text{M}+\text{H}$ ) $^+$  339.1959, found 339.1960.

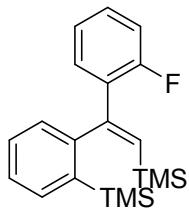


**(Z)-(2-(3-chlorophenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3s):** colorless oil, isolated yield 88% (63 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 7.2$  Hz, 1H), 7.38 (t,  $J = 7.3$  Hz, 1H), 7.34 (t,  $J = 7.3$  Hz, 1H), 7.24 (s, 1H), 7.19 (dd,  $J = 15.3$  Hz, 7.9 Hz, 2H), 7.12 (dd,  $J = 13.4$  Hz, 7.3 Hz, 2H), 6.41 (s, 1H), -0.02 (s, 9H), -0.17 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 147.0, 144.7, 138.6, 135.0, 134.2, 131.1, 130.9, 129.2, 128.5, 127.5, 126.9, 126.8, 125.2, 0.3, -0.5. HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{27}\text{ClSi}_2^+$  ( $\text{M}+\text{Na}$ ) $^+$  381.1232, found 381.1233.

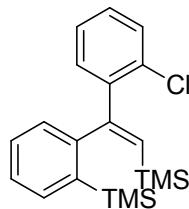


**(Z)-trimethyl(2-(o-tolyl)-2-(trimethylsilyl)phenyl)vinylsilane (3t):** colorless oil, isolated yield 40% (27 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.3$  Hz, 1H), 7.39-7.30 (m, 3H), 7.15-7.11 (m, 3H), 7.11-7.08 (m, 1H), 6.12 (s, 1H), 2.22 (s, 3H), -0.06(s, 9H), -0.13 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 149.9, 143.0, 137.7,

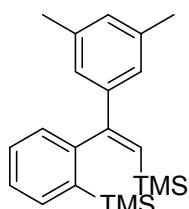
135.9, 135.2, 134.8, 132.7, 131.6, 130.6, 128.2, 127.3, 126.5, 125.5, 22.4, -0.2, -0.3.  
 HRMS (ESI) m/z calcd for  $C_{21}H_{30}Si_2^+$  ( $M+H$ )<sup>+</sup> 339.1959, found 339.1960.



**(Z)-(2-(2-fluorophenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3u):**  
 colorless oil, isolated yield 45% (31 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 6.0 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.17 (dd, *J* = 13.2 Hz, 7.2 Hz, 1H), 7.04 (dd, *J* = 12.0 Hz, 8.3 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 4.5 Hz, 1H), 6.51 (s, 1H), -0.03(s, 9H), -0.17 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.5 (d, *J* = 251.6 Hz), 152.3, 148.4, 138.2, 135.9 (d, *J* = 7.2 Hz), 134.8, 131.5, 131.2 (d, *J* = 36.1 Hz), 131.0 (d, *J* = 9.2 Hz), 128.8 (d, *J* = 8.6 Hz), 128.3, 126.6, 123.58 (d, *J* = 3.7 Hz), 116.43 (d, *J* = 24.0 Hz), -0.06, -0.47. HRMS (ESI) m/z calcd for  $C_{20}H_{27}FSi_2^+$  ( $M+H$ )<sup>+</sup> 343.1708, found 343.1709.

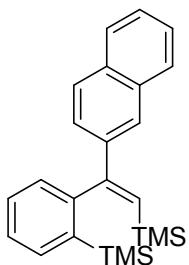


**(Z)-(2-(2-chlorophenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3v):**  
 pale yellow oil, isolated yield 60% (43 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.13-7.06 (m, 2H), 7.01 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 6.62 (s, 1H), -0.02(s, 9H), -0.15 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.4, 148.7, 141.2, 137.9, 137.6, 134.9, 133.0, 132.3, 131.7, 131.3, 128.3, 128.1, 126.6, 126.3, -0.2, -0.6. HRMS (ESI) m/z calcd for  $C_{20}H_{27}ClSi_2^+$  ( $M+Na$ )<sup>+</sup> 381.1232, found 381.1233.



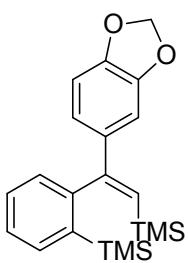
**(Z)-(2-(3,5-dimethylphenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane**

**(3w):** colorless oil, isolated yield 40% (28 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.55 (m, 1H), 7.37 (td,  $J = 7.3$  Hz, 1.3 Hz, 1H), 7.33 (td,  $J = 7.3$  Hz, 1.3 Hz, 1H), 7.15 (d,  $J = 7.2$  Hz, 1H), 6.87 (d,  $J = 4.4$  Hz, 3H), 6.36 (s, 1H), 2.25 (s, 6H), -0.02 (s, 9H), -0.18 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 148.1, 142.7, 138.6, 137.4, 134.6, 130.9, 129.3, 128.8, 128.3, 126.4, 124.9, 21.3, 0.3, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{22}\text{H}_{32}\text{Si}_2^+$  ( $\text{M}+\text{H})^+$  353.2115, found 353.2116.



**(Z)-trimethyl(2-(naphthalen-2-yl)-2-(trimethylsilyl)phenyl)vinylsilane (3x):**

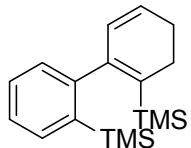
colorless oil, isolated yield 54% (40 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80-7.78 (m, 2H), 7.69-7.67 (m, 2H), 7.61 (d,  $J = 7.3$  Hz, 1H), 7.45-7.38 (m, 5H), 7.23 (d,  $J = 7.3$  Hz, 1H), 6.56 (s, 1H), -0.05 (s, 9H), -0.13 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  157.3, 147.7, 139.9, 138.9, 134.9, 133.2, 132.8, 131.0, 129.9, 128.5, 128.4, 127.7, 127.4, 127.0, 126.6, 126.0, 126.0, 124.3, 0.4, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{24}\text{H}_{30}\text{Si}_2^+$  ( $\text{M}+\text{H})^+$  375.1959, found 375.1960.



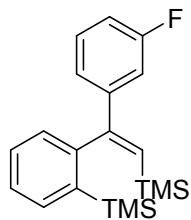
**(Z)-(2-(benzo[d][1,3]dioxol-5-yl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane**

**(3y):** colorless oil, isolated yield 42% (31 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (dd,  $J = 7.2$  Hz, 1.3 Hz, 1H), 7.36 (td,  $J = 7.4$  Hz, 1.5 Hz, 1H), 7.32 (td,  $J = 7.4$  Hz, 1.5 Hz, 1H), 7.14-7.12 (m, 1H), 6.89 (d,  $J = 1.7$  Hz, 1H), 6.67 (d,  $J = 8.2$  Hz, 1H), 6.60 (dd,  $J = 8.2$  Hz, 1.8 Hz, 1H), 6.22 (s, 1H), 5.94 (dd,  $J = 8.0$  Hz, 1.1 Hz, 2H), 0.01 (s, 9H), -0.19 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 147.9, 147.7, 147.2,

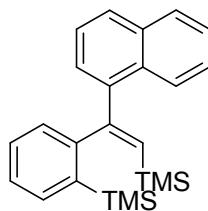
138.6, 137.7, 134.8, 130.8, 128.3, 127.6, 126.5, 121.7, 107.6, 106.9, 101.1, 0.3, -0.4. HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>Si<sub>2</sub><sup>+</sup> (M)<sup>+</sup> 368.1628, found 368.1624.



**(3,4-dihydro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (3z):** colorless oil, isolated yield 30% (18 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53 (dd, *J* = 7.1 Hz, 1.2 Hz, 1H), 7.29-7.26 (m, 1H), 7.25-7.22 (m, 1H), 7.00-6.97 (m, 1H), 6.14-6.12 (m, 1H), 5.85-5.81 (m, 1H), 2.41-2.36 (m, 1H), 2.36-2.33 (m, 1H), 2.31-2.25 (m, 1H), 2.23-2.18 (m, 1H), 0.30 (s, 9H), -0.25 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 151.3, 149.8, 137.2, 134.7, 130.6, 128.9, 128.4, 127.9, 126.0, 123.1, 32.2, 22.4, 0.9, -0.7. HRMS (ESI) m/z calcd for C<sub>18</sub>H<sub>28</sub>Si<sub>2</sub><sup>+</sup> (M+Na)<sup>+</sup> 323.1622, found 323.1625.

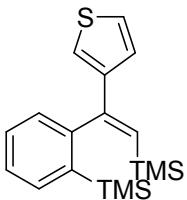


**(Z)-(2-(3-fluorophenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3aa):** colorless oil, isolated yield 72% (49 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.41-7.33 (m, 2H), 7.24-7.19 (m, 1H), 7.16-7.14 (m, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.98-6.91 (m, 2H), 6.41 (s, 1H), -0.01 (s, 9H), -0.16 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 163.9, 161.9, 156.3, 147.2, 145.3 (d, *J* = 6.9 Hz), 138.6, 134.9, 130.9 (d, *J* = 5.3 Hz), 129.4 (d, *J* = 8.3 Hz), 128.5, 126.8, 122.7 (d, *J* = 2.5 Hz), 114.3 (d, *J* = 21.7 Hz), 113.7 (d, *J* = 22.3 Hz), 0.3, -0.5. HRMS (ESI) m/z calcd for C<sub>20</sub>H<sub>27</sub>FSi<sub>2</sub><sup>+</sup> (M+H)<sup>+</sup> 343.1708, found 343.1709.

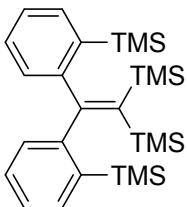


**(Z)-trimethyl(2-(naphthalen-1-yl)-2-(trimethylsilyl)phenyl)vinylsilane (3ab):** colorless oil, isolated yield 55% (41 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.59 (d, *J* =

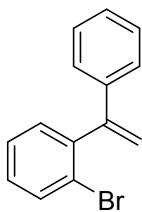
8.3 Hz, 1H), 7.87 (d,  $J$  = 7.1 Hz, 1H), 7.73 (d,  $J$  = 8.1 Hz, 1H), 7.59 (d,  $J$  = 7.3 Hz, 1H), 7.53-7.48 (m, 2H), 7.47-7.44 (m, 1H), 7.41 (d,  $J$  = 7.0 Hz, 1H), 7.37 (t,  $J$  = 7.4 Hz, 1H), 7.31 (t,  $J$  = 7.7 Hz, 1H), 7.11 (d,  $J$  = 7.3 Hz, 1H), 6.48 (s, 1H), -0.06 (s, 9H), -0.08 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 149.9, 141.6, 138.0, 137.0, 135.2, 134.7, 132.7, 131.0, 128.7, 128.4, 128.0, 127.6, 126.6, 126.4, 125.8, 125.3, 124.8, 0.0, -0.3. HRMS (ESI) m/z calcd for  $\text{C}_{24}\text{H}_{30}\text{Si}_2^+$  ( $\text{M}^+$ ) 374.1886, found 374.1882.



**(Z)-trimethyl(2-(thiophen-3-yl)-2-(trimethylsilyl)phenyl)vinylsilane (3ac):** colorless oil, isolated yield 32% (21 mg).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (dd,  $J$  = 7.0 Hz, 1.3 Hz, 1H), 7.36-7.33 (m, 1H), 7.33-7.30 (m, 1H), 7.28 (d,  $J$  = 5.1 Hz, 1H), 7.26-7.25 (m, 1H), 7.14 (dd,  $J$  = 7.6 Hz, 1.6 Hz, 1H), 6.58-6.57 (m, 1H), 6.22 (s, 1H), 0.03 (s, 9H), -0.18 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.6, 147.8, 146.5, 138.6, 134.7, 130.0, 128.3, 127.4, 126.9, 125.6, 125.6, 123.9, 0.5, -0.4. HRMS (ESI) m/z calcd for  $\text{C}_{18}\text{H}_{26}\text{SSi}_2^+$  ( $\text{M}+\text{H}^+$ ) 331.1367, found 331.1368.

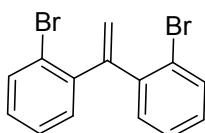


**(2,2-bis(2-(trimethylsilyl)phenyl)ethene-1,1-diyl)bis(trimethylsilane) (3a'): White solid, isolated yield 30% (28 mg), mp: 75.6-77.5 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.48 (m, 4H), 7.32 (td,  $J$  = 7.4 Hz, 1.6 Hz, 2H), 7.29-7.26 (m, 2H), -0.15 (s, 18H), -0.18 (s, 18H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 152.4, 148.9, 139.2, 135.7, 135.5, 128.1, 127.7, 2.8, 0.3. HRMS (ESI) m/z calcd for  $\text{C}_{26}\text{H}_{44}\text{Si}_4^+$  ( $\text{M}+\text{H}^+$ ) 469.2593, found 469.2595.**



**1-bromo-2-(1-phenylvinyl)benzene (5):** pale yellow oil, isolated yield 91% (47 mg).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.35-7.33 (m, 2H), 7.32-7.30 (m, 1H), 7.30-7.28 (m, 3H), 7.27-7.26 (m, 1H), 7.24-7.20 (m, 1H), 5.85 (s, 1H), 5.28 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.9, 142.7, 139.6, 133.0, 131.6, 129.0, 128.4, 127.8, 127.3, 126.6, 123.3, 116.1.



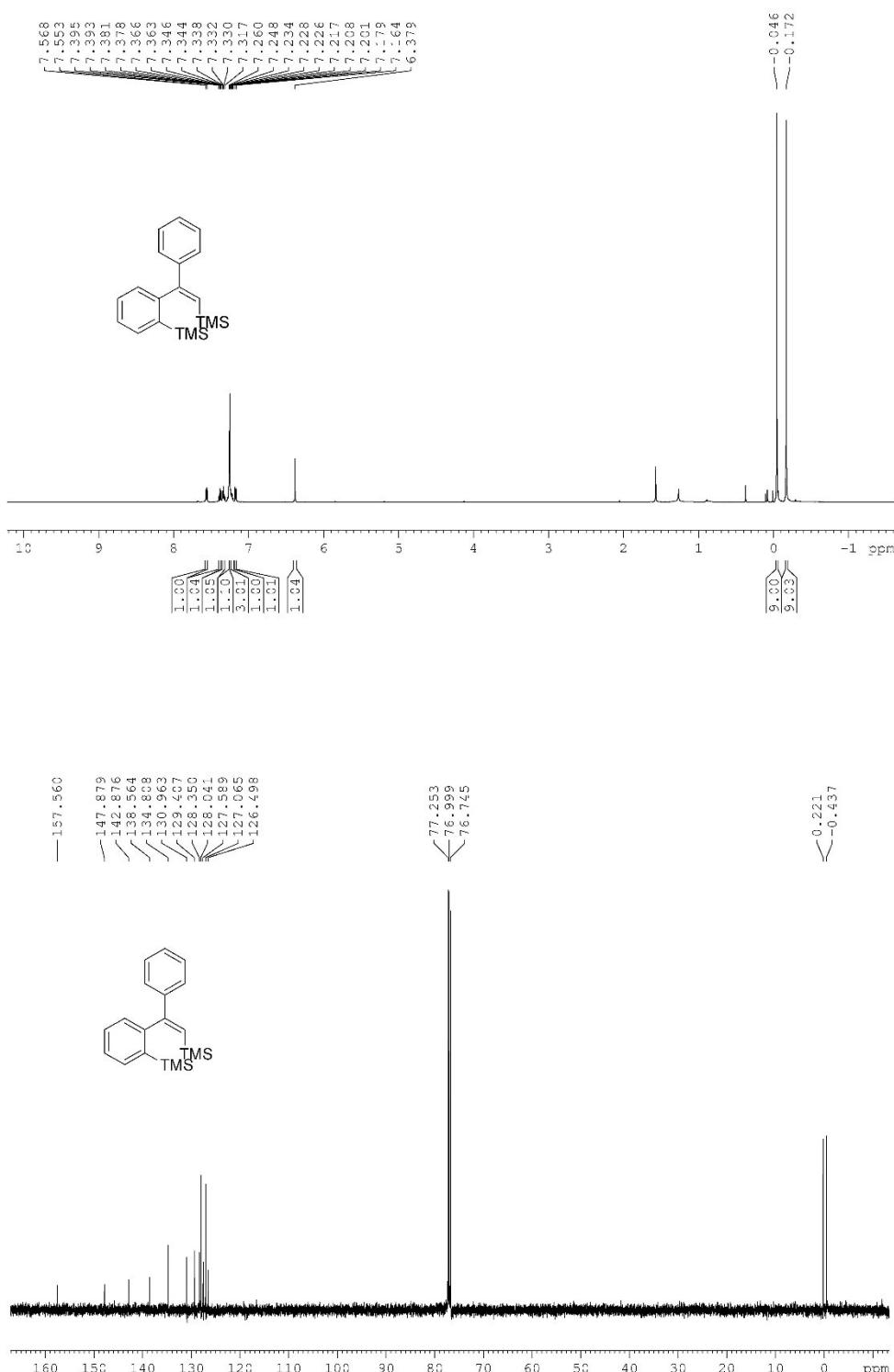
**2,2'-(ethene-1,1-diyl)bis(bromobenzene) (6):** pale yellow oil, isolated yield 90% (61 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.31-7.29 (dd, *J* = 7.7 Hz, 2.8 Hz, 3H), 7.27 (d, *J* = 0.7 Hz, 1H), 7.16-7.13 (m, 2H), 5.71 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.7, 141.8, 133.4, 131.7, 128.8, 127.1, 122.7, 122.6.

## 5) References

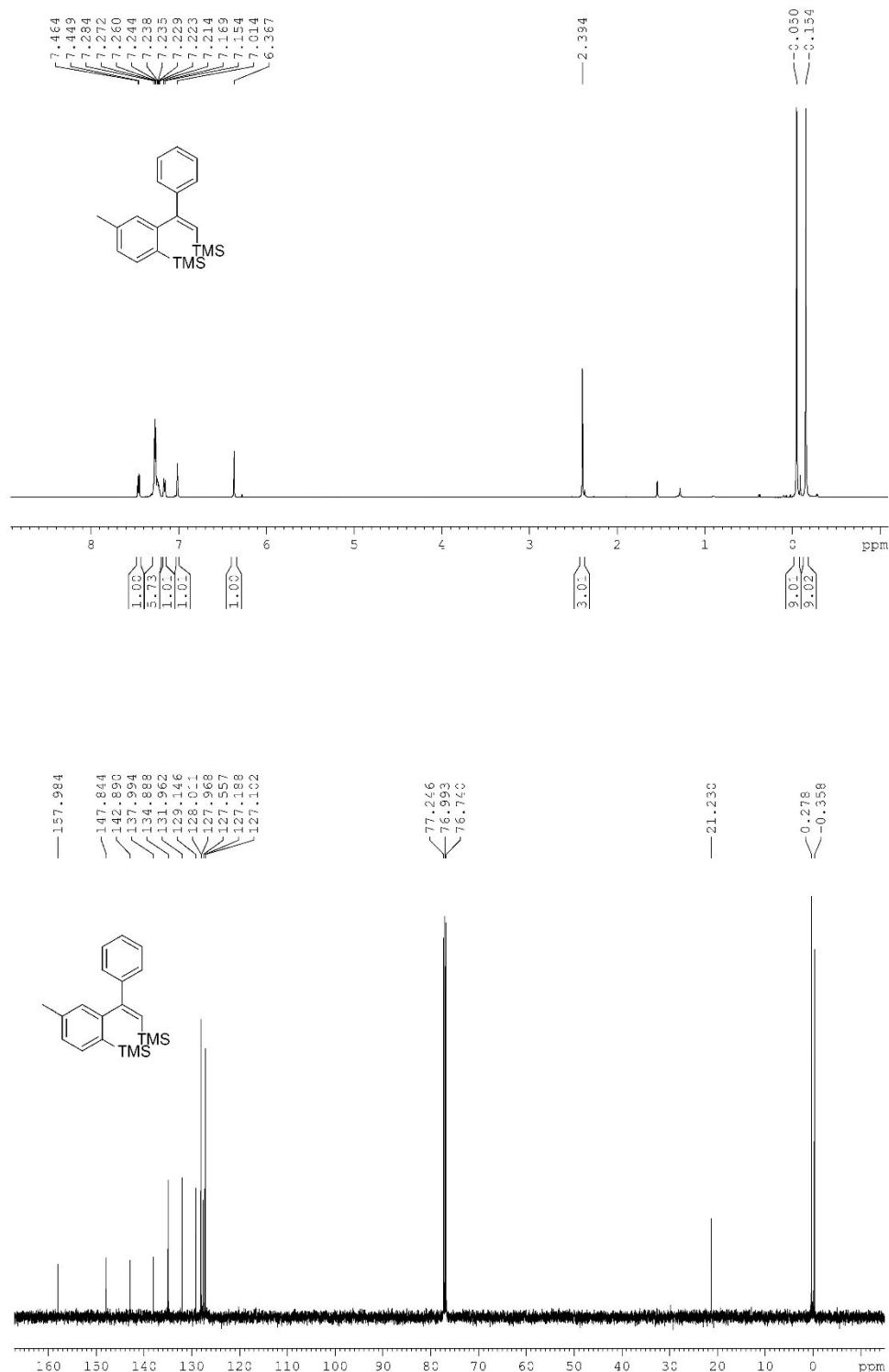
- (1) X. Zhao, J. Jing, K. Lu, Y. Zhang and J. Wang, *Chem. Commun.*, 2010, **46**, 1724.
- (2) T. Bzeih, K. Zhang, A. Khalaf, A. Hachem, M. Alami and A. Hamze, *J. Org. Chem.*, 2019, **84**, 228.

## 6) Scanned $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of All New Compounds.

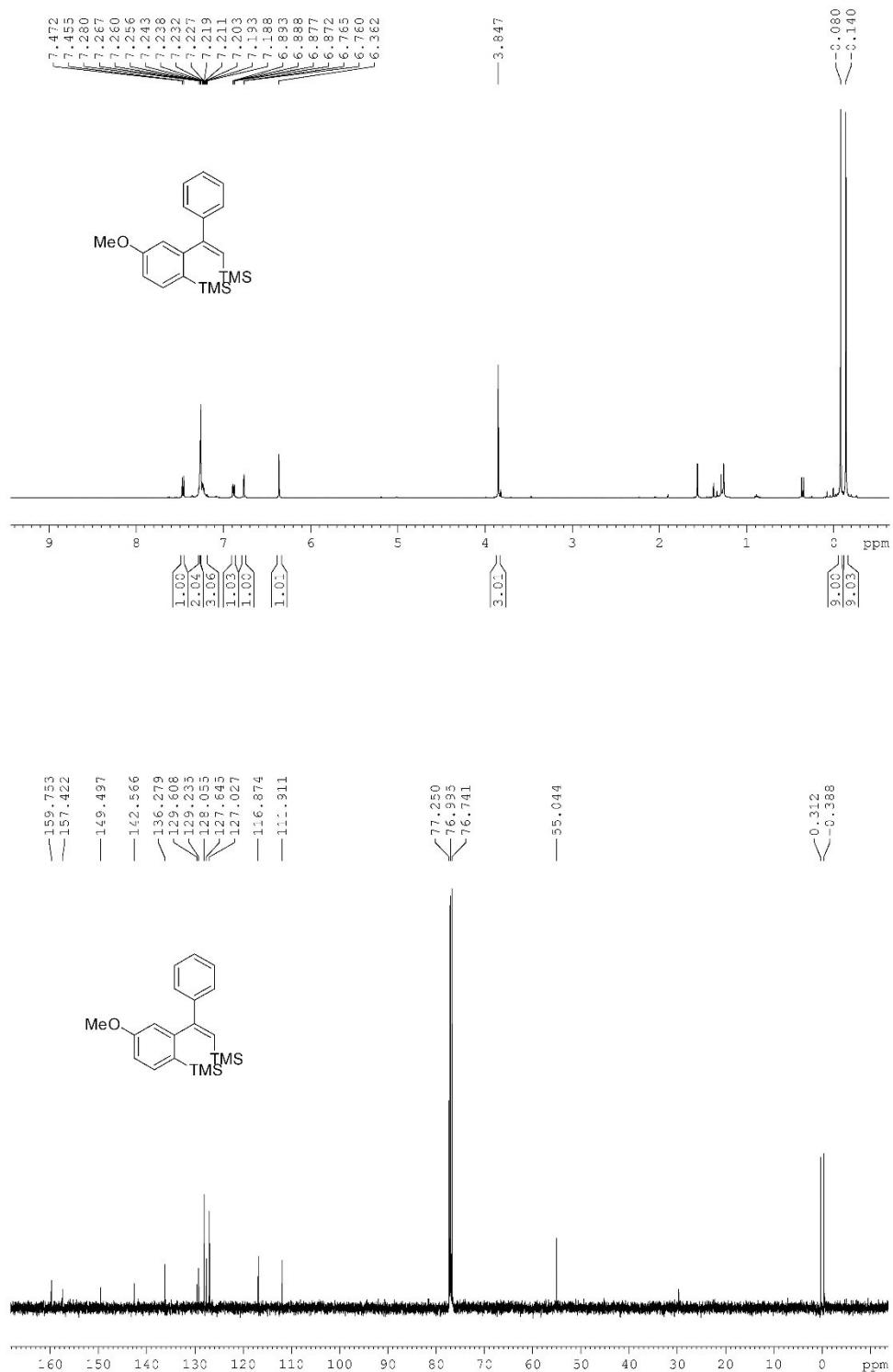
### (Z)-trimethyl(2-phenyl-2-(trimethylsilyl)phenyl)vinyl)silane (3a)



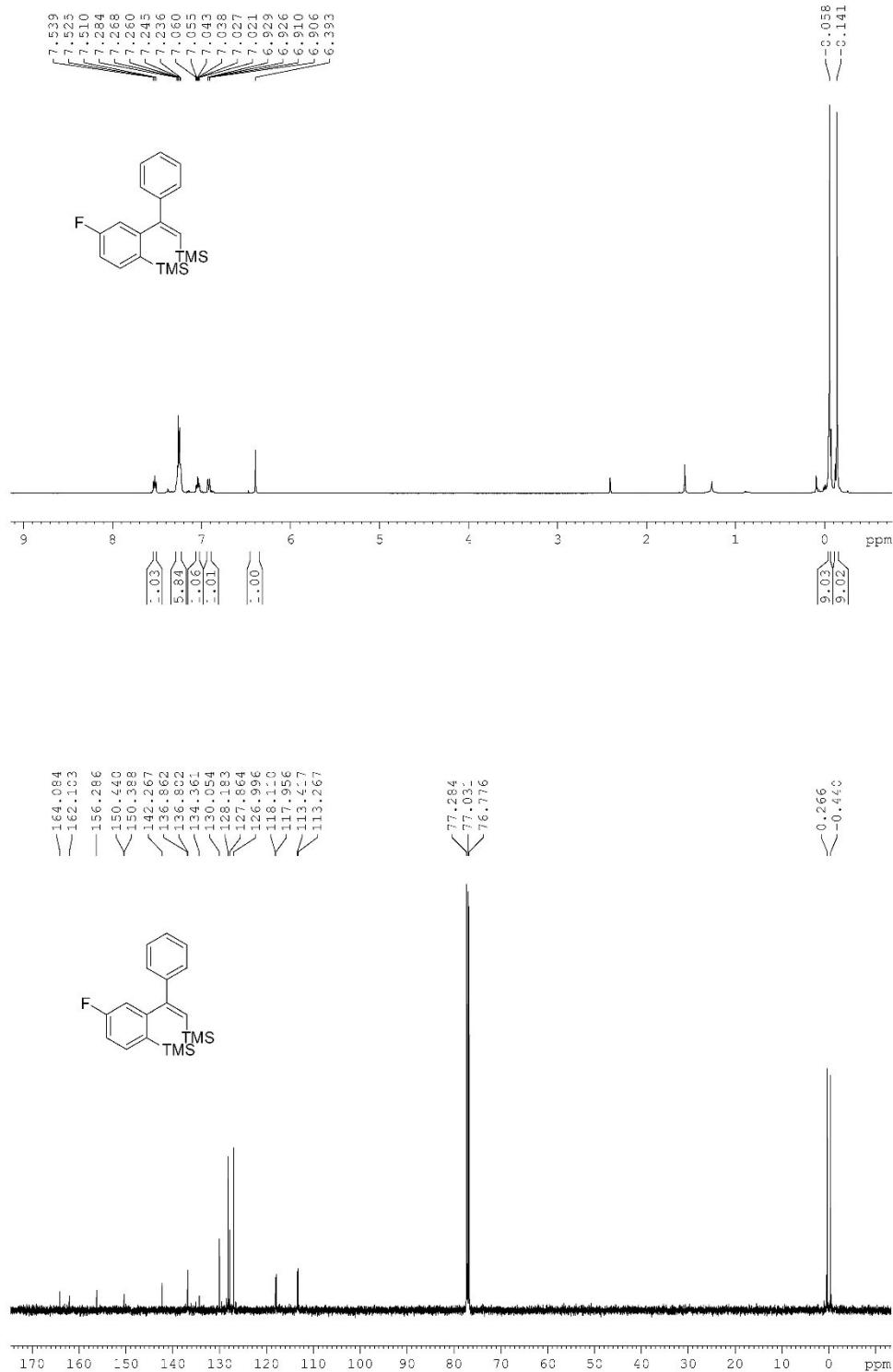
**(Z)-trimethyl(4-methyl-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)silane (3b)**



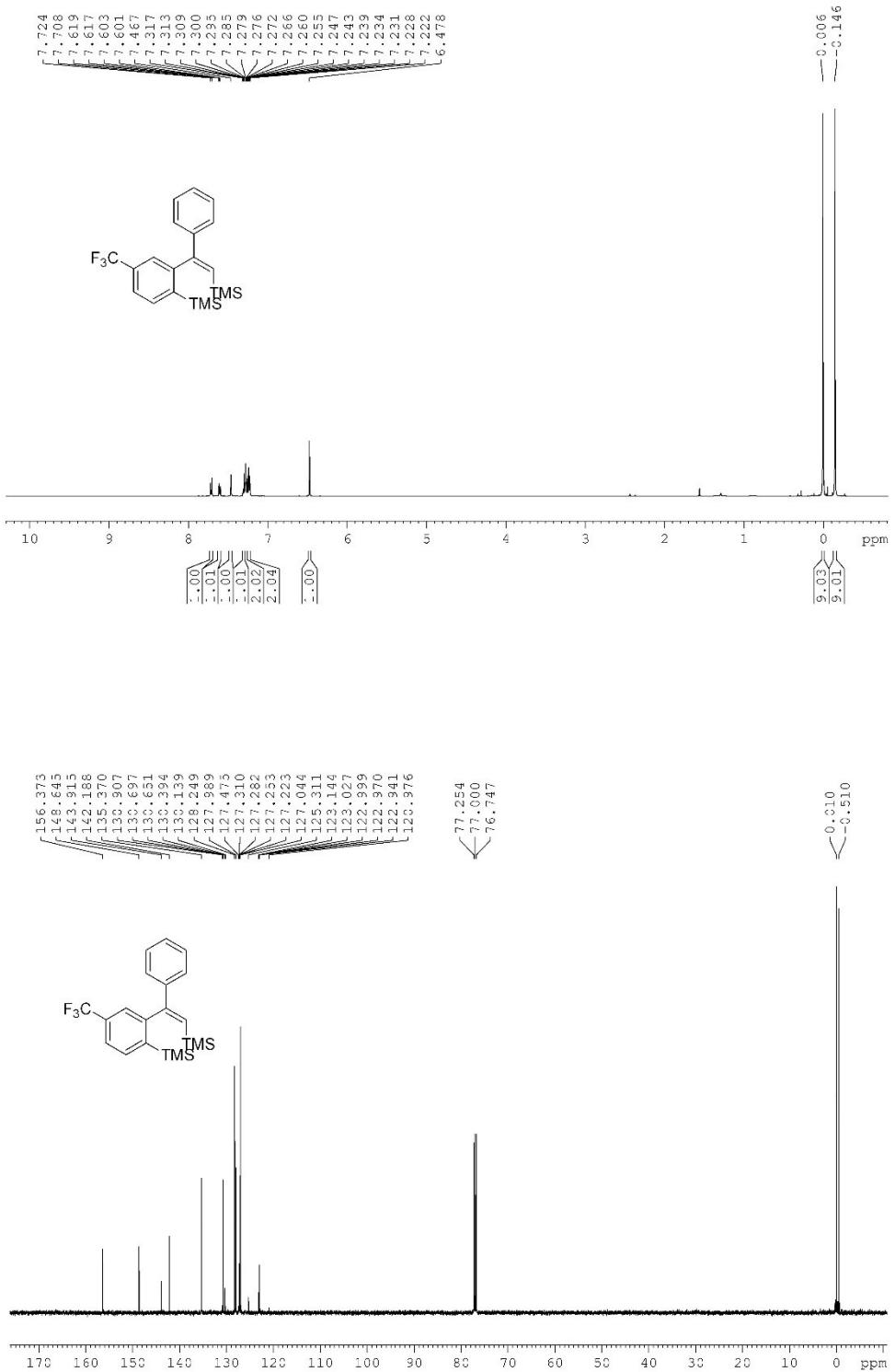
(Z)-(4-methoxy-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3c)



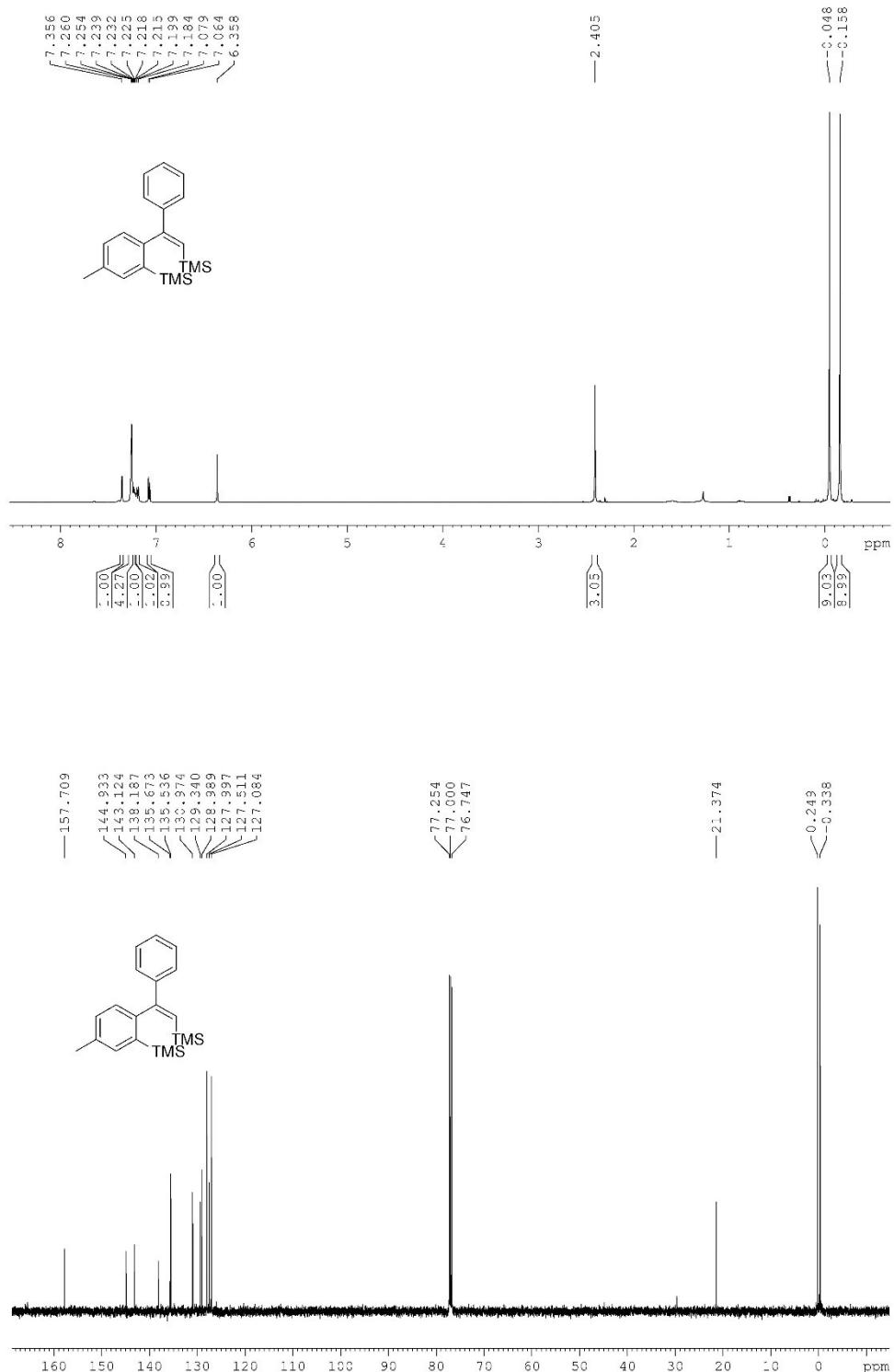
**(Z)-(4-fluoro-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3d)**



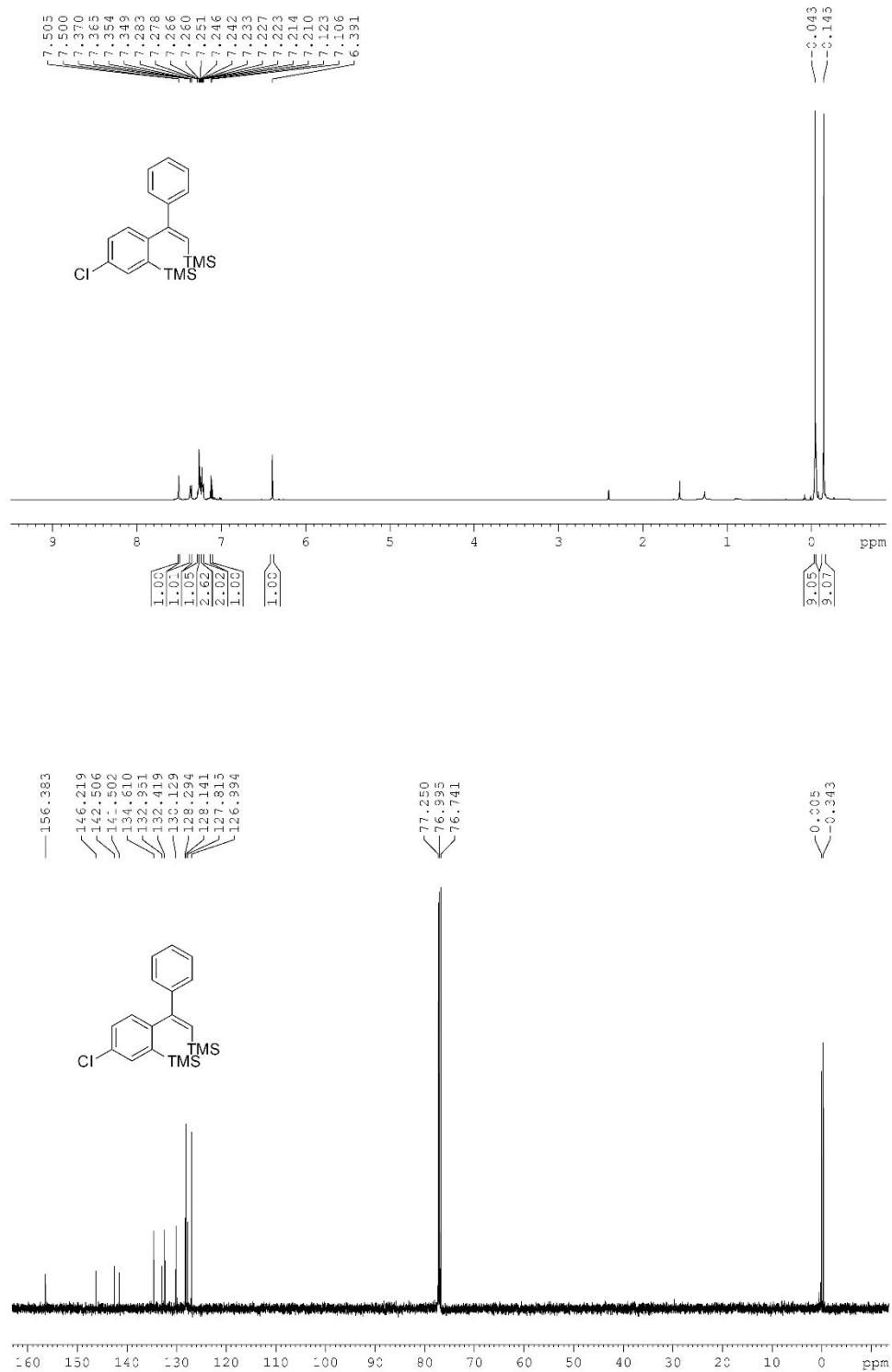
**(Z)-trimethyl(2-phenyl-2-(5-(trifluoromethyl)-2-(trimethylsilyl)phenyl)vinyl)silane (3e)**



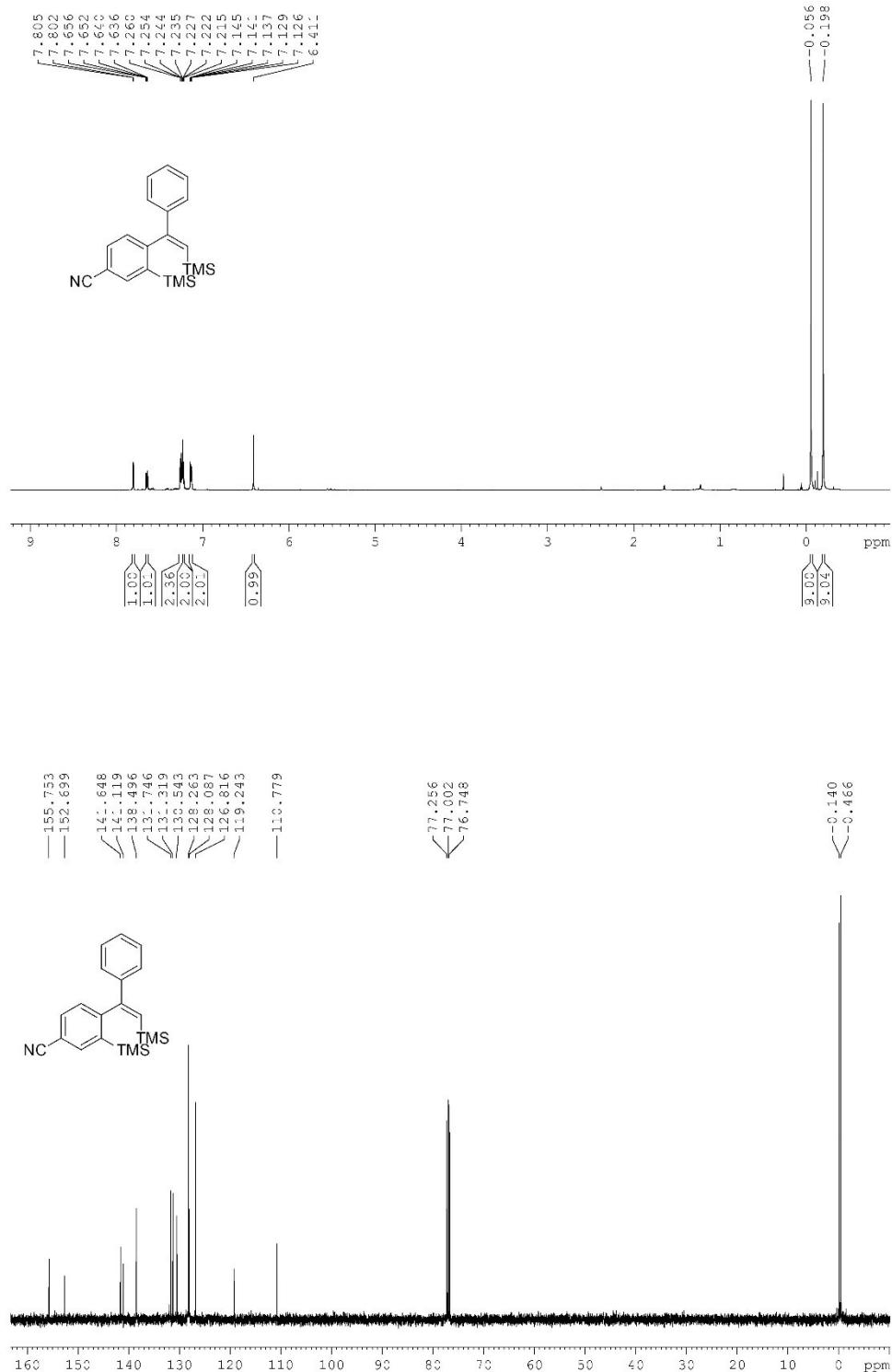
**(Z)-trimethyl(5-methyl-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)silane (3f)**



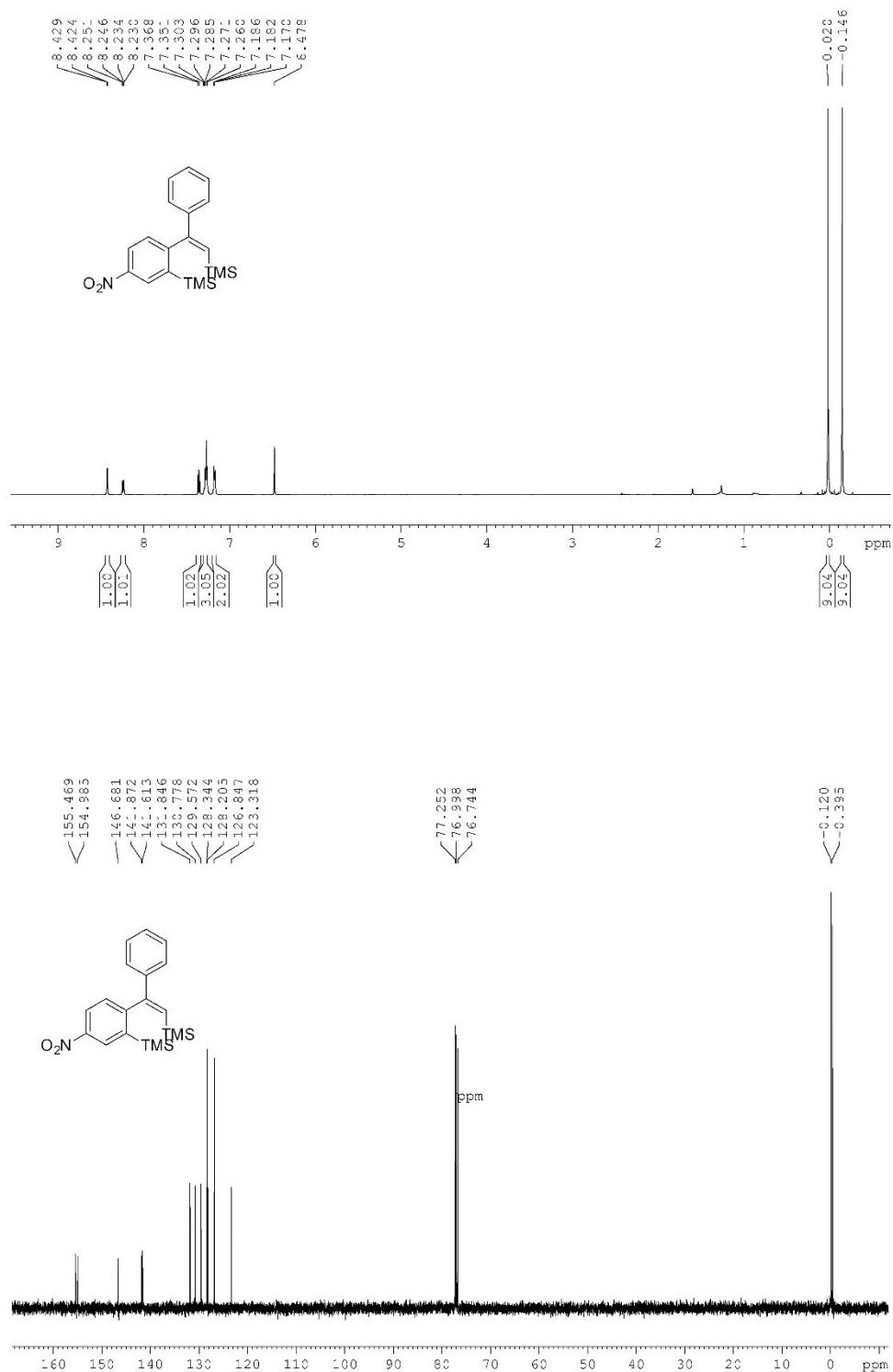
**(Z)-(5-chloro-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3g)**



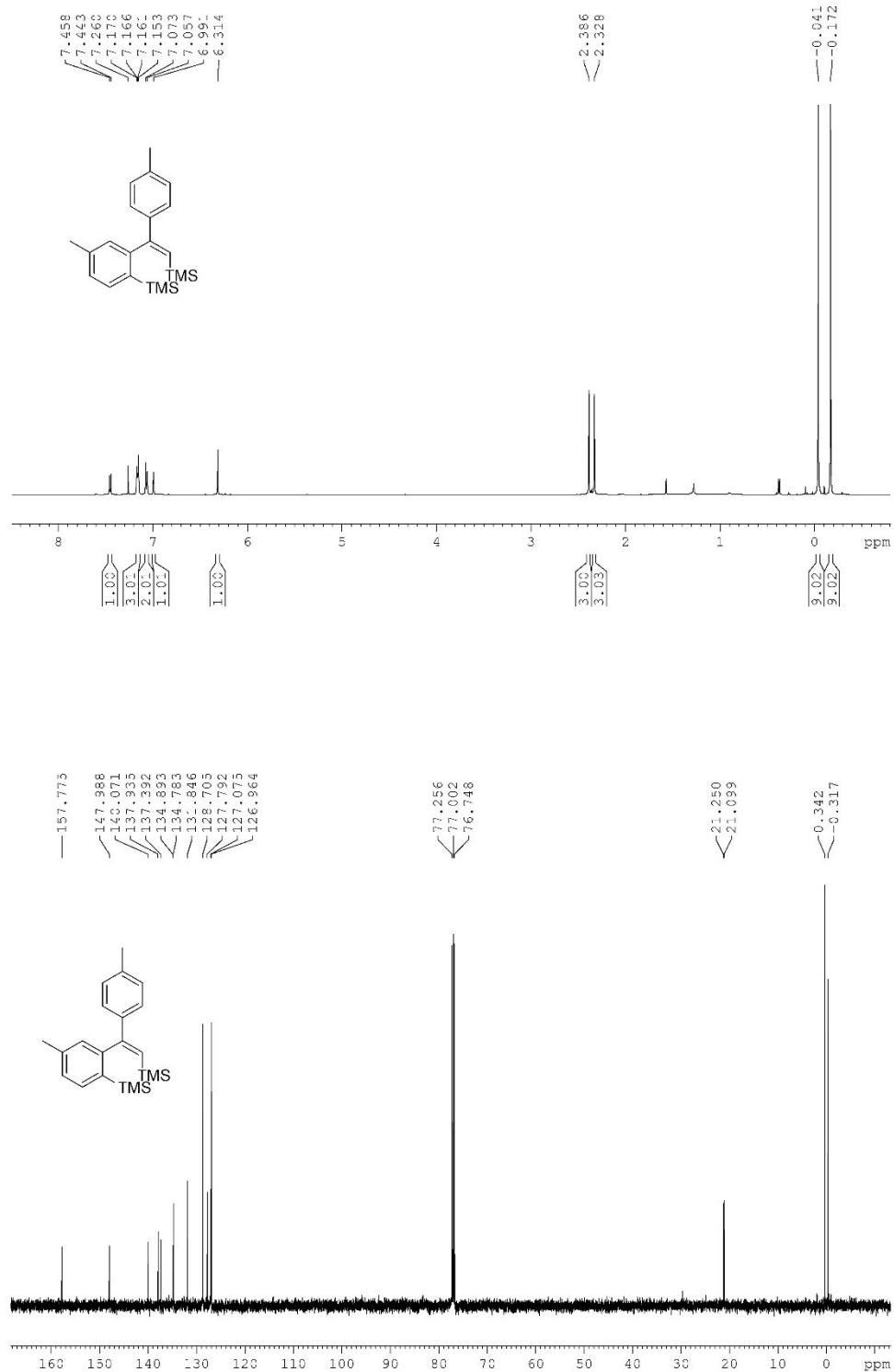
**(Z)-4-(1-phenyl-2-(trimethylsilyl)vinyl)-3-(trimethylsilyl)benzonitrile (3h)**



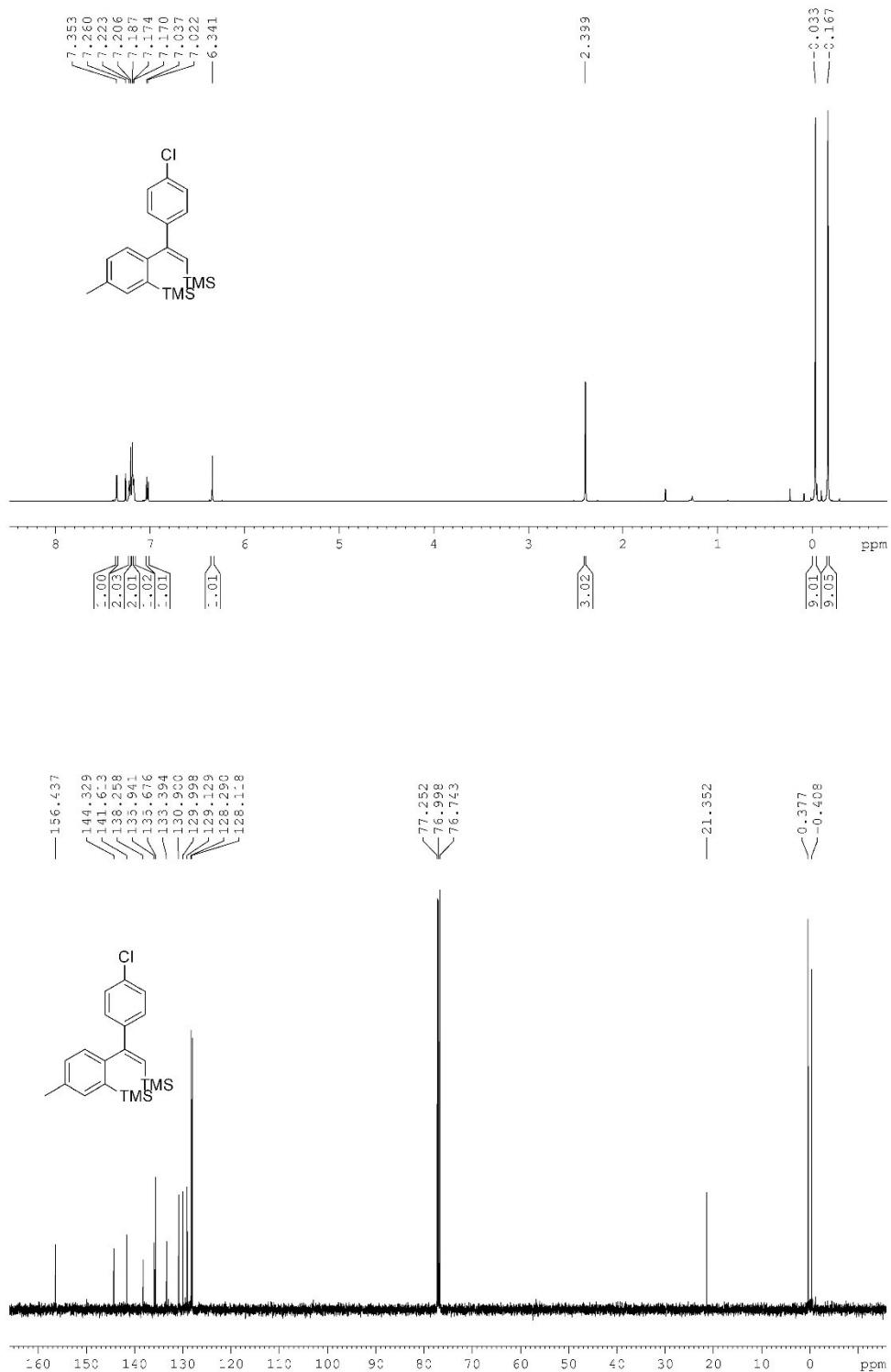
**(Z)-(4-methoxy-2-(1-phenyl-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3i)**



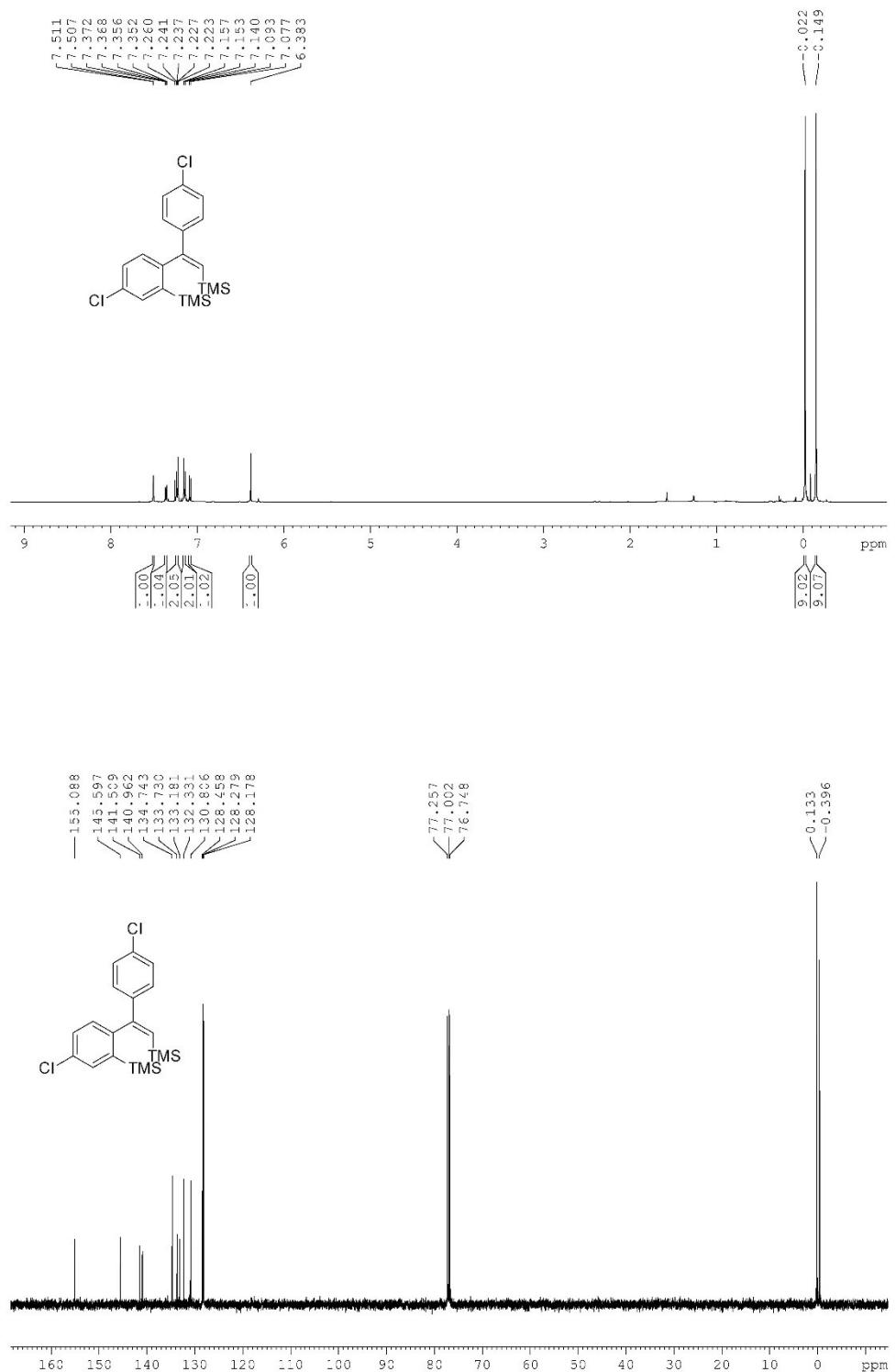
**(Z)-trimethyl(4-methyl-2-(1-(p-tolyl)-2-(trimethylsilyl)vinyl)phenyl)silane (3j)**



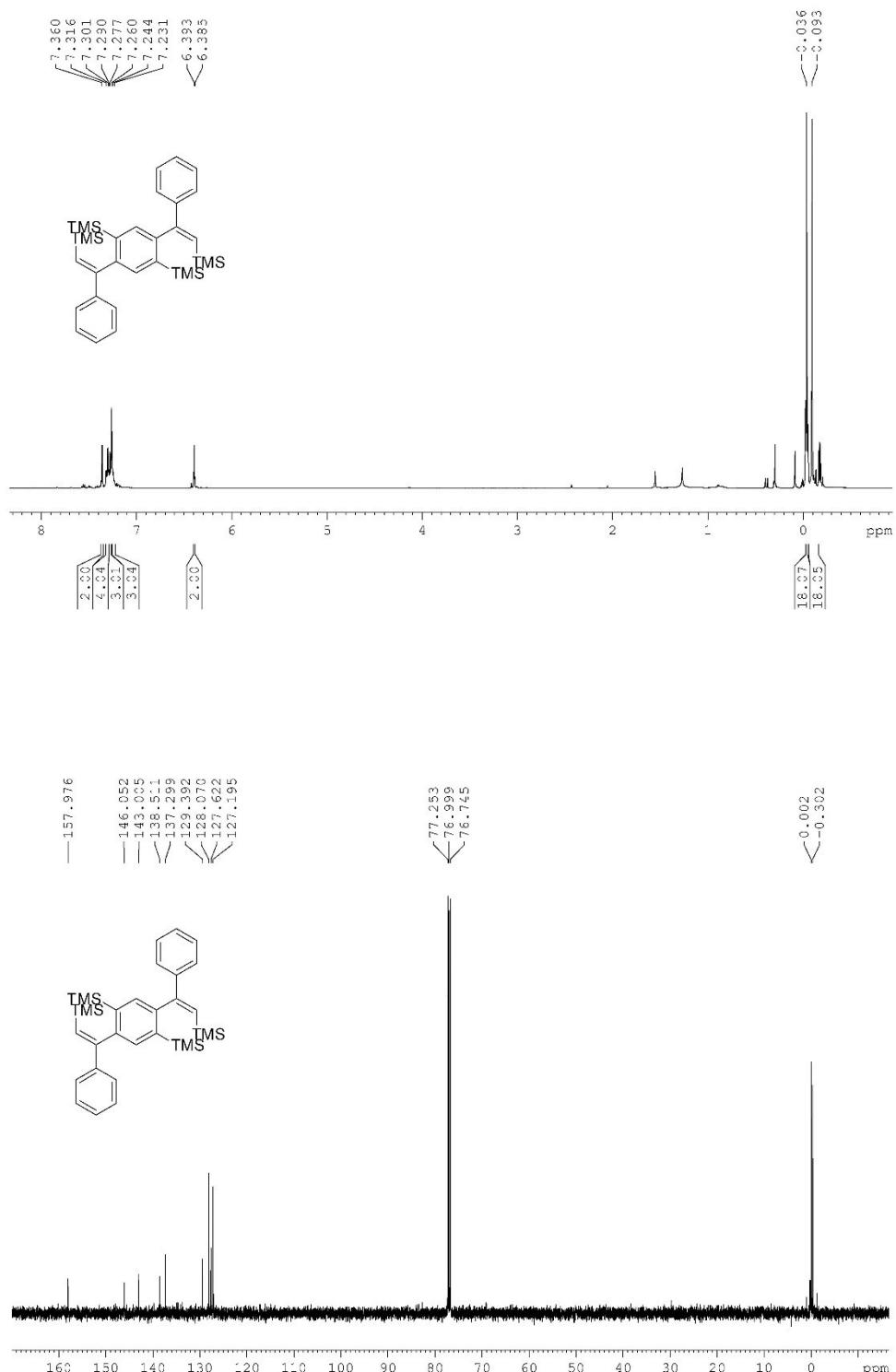
**(Z)-(2-(4-chlorophenyl)-2-(4-methyl-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (3k)**



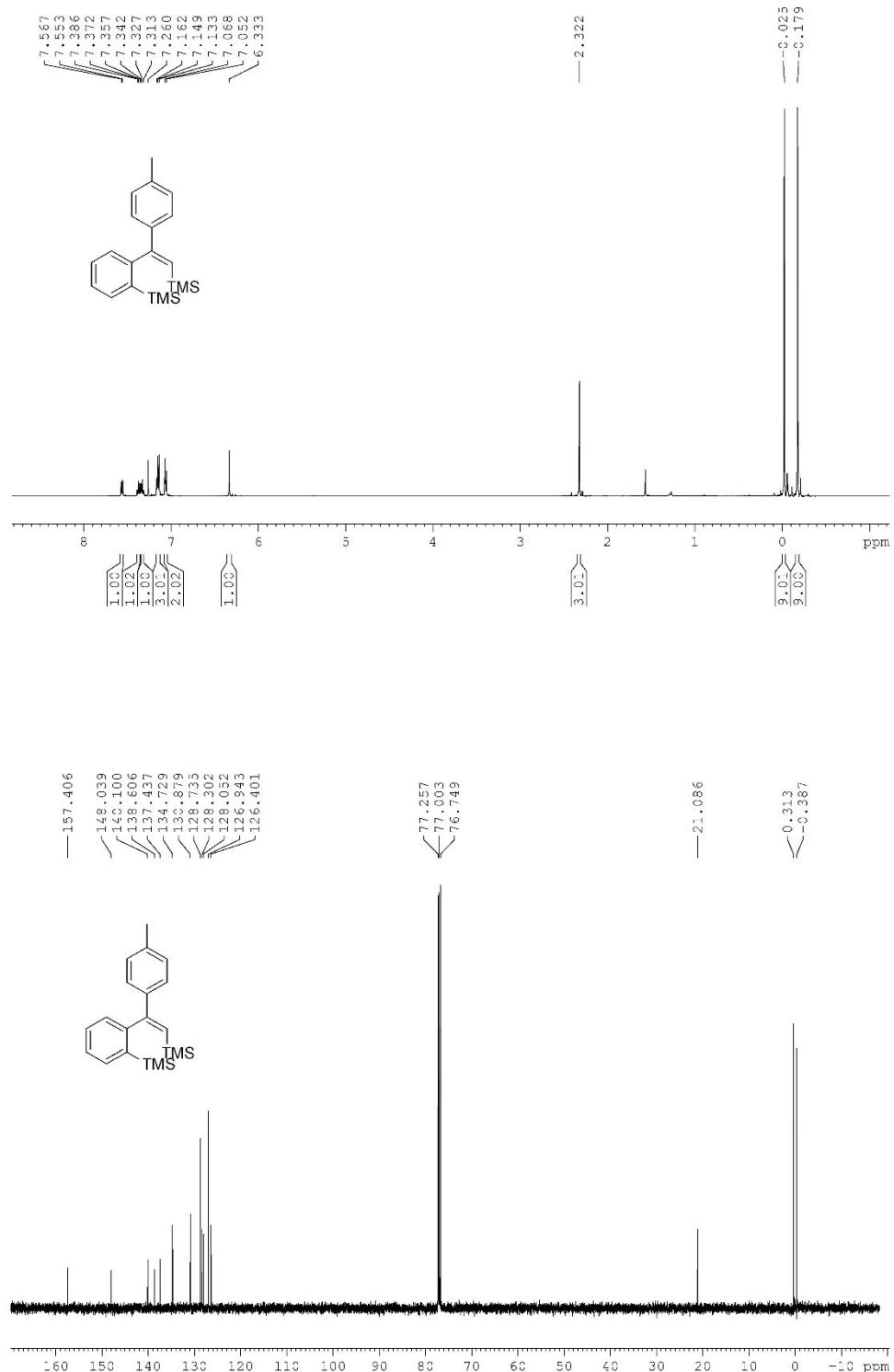
**(Z)-(5-chloro-2-(1-(4-chlorophenyl)-2-(trimethylsilyl)vinyl)phenyl)trimethylsilane (3l)**



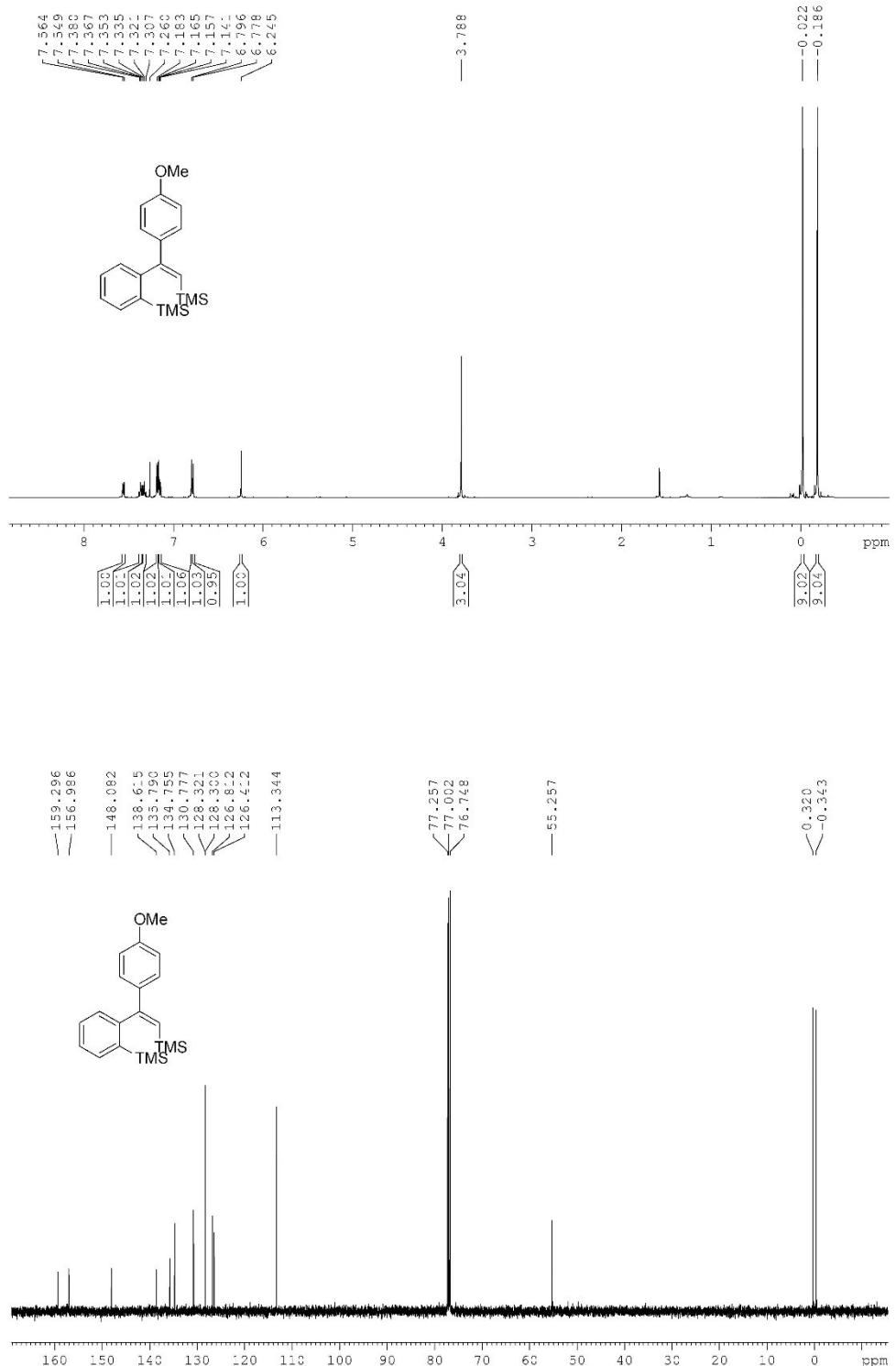
**(2,5-bis((Z)-1-phenyl-2-(trimethylsilyl)vinyl)-1,4-phenylene)bis(trimethylsilane)  
(3m)**



**(Z)-trimethyl(2-(p-tolyl)-2-(trimethylsilyl)phenyl)vinyl)silane (3n)**



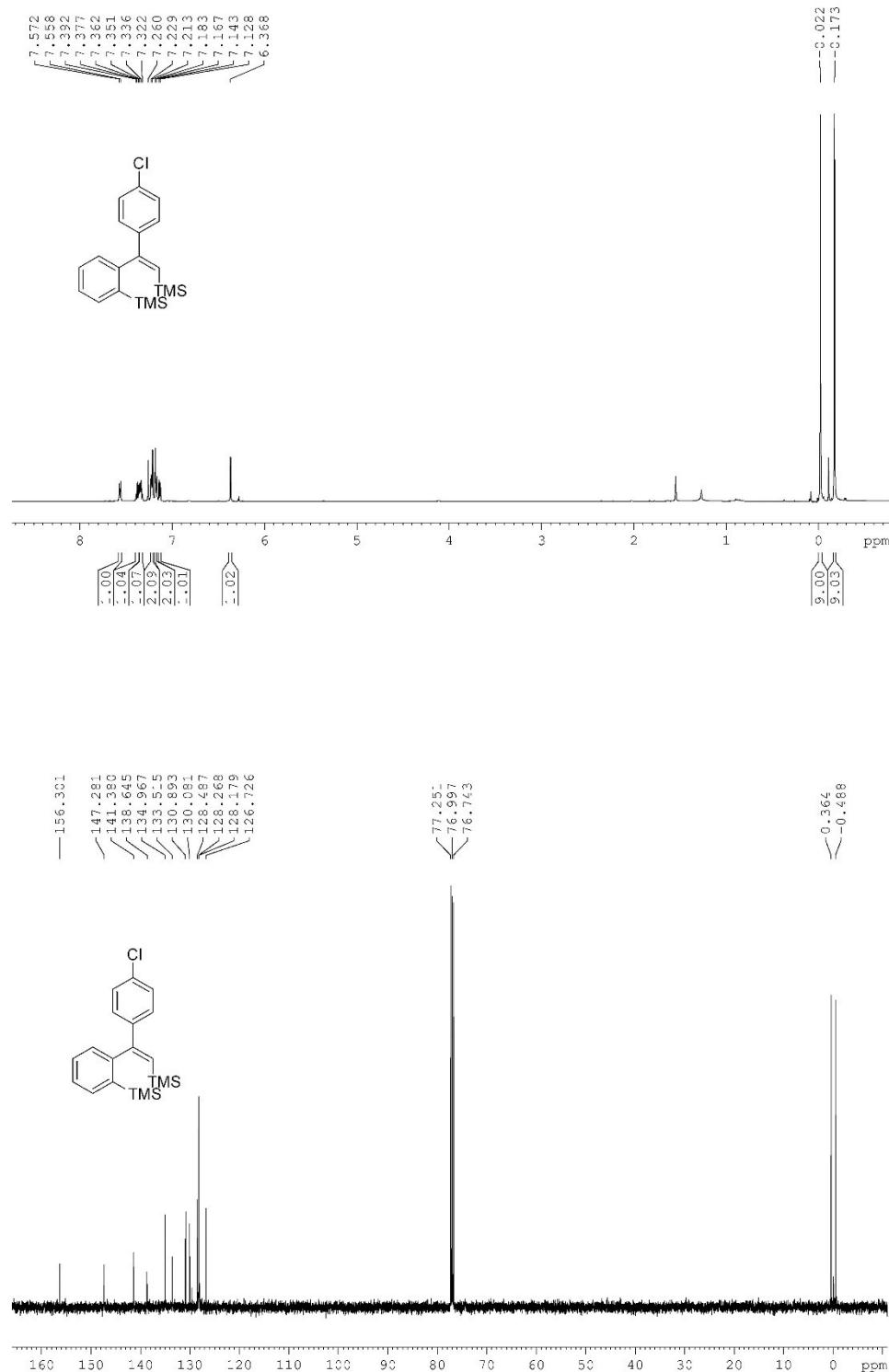
(Z)-(2-(4-methoxyphenyl)-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (3o)



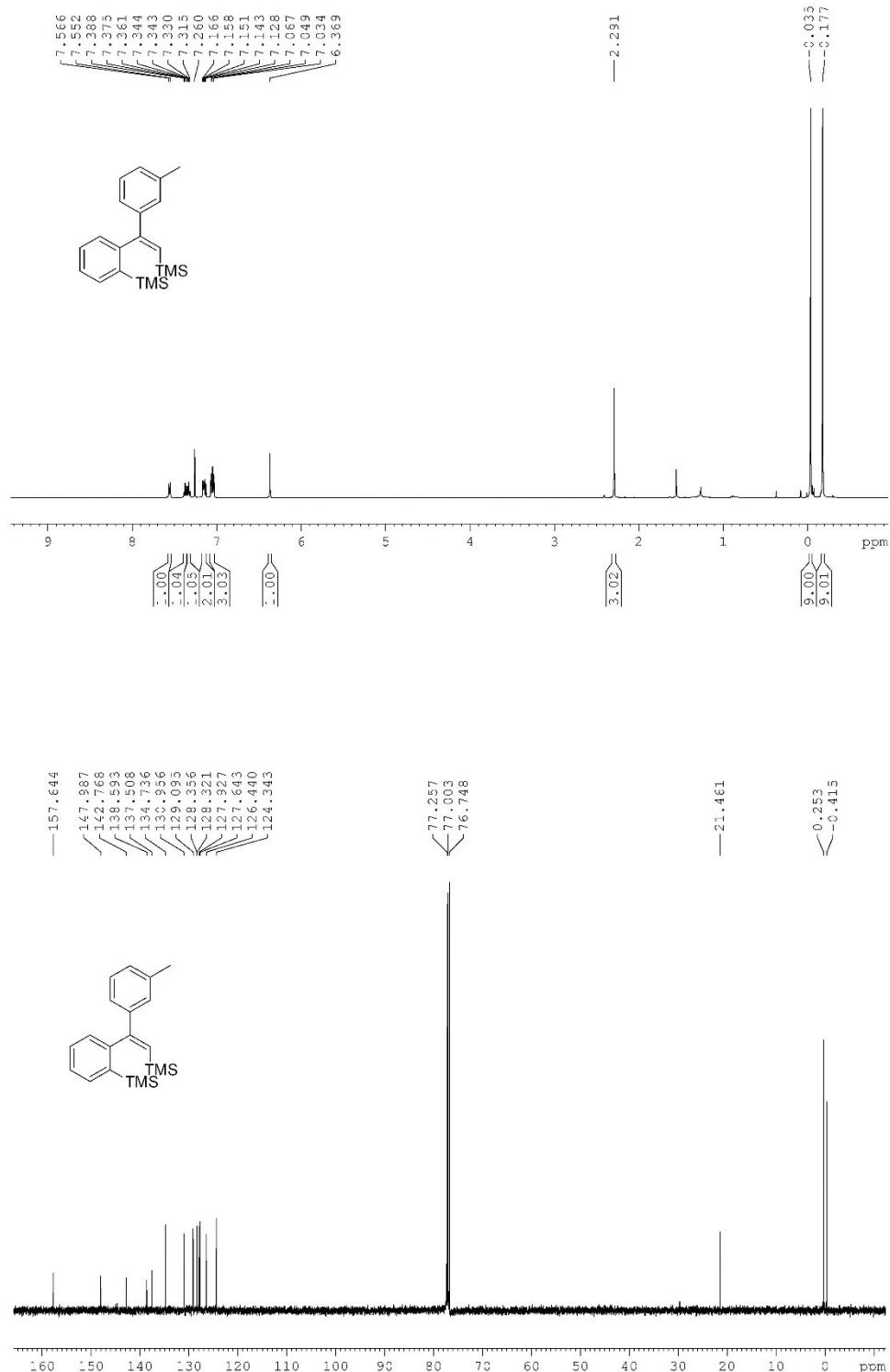
**(Z)-(2-(4-fluorophenyl)-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (3p)**



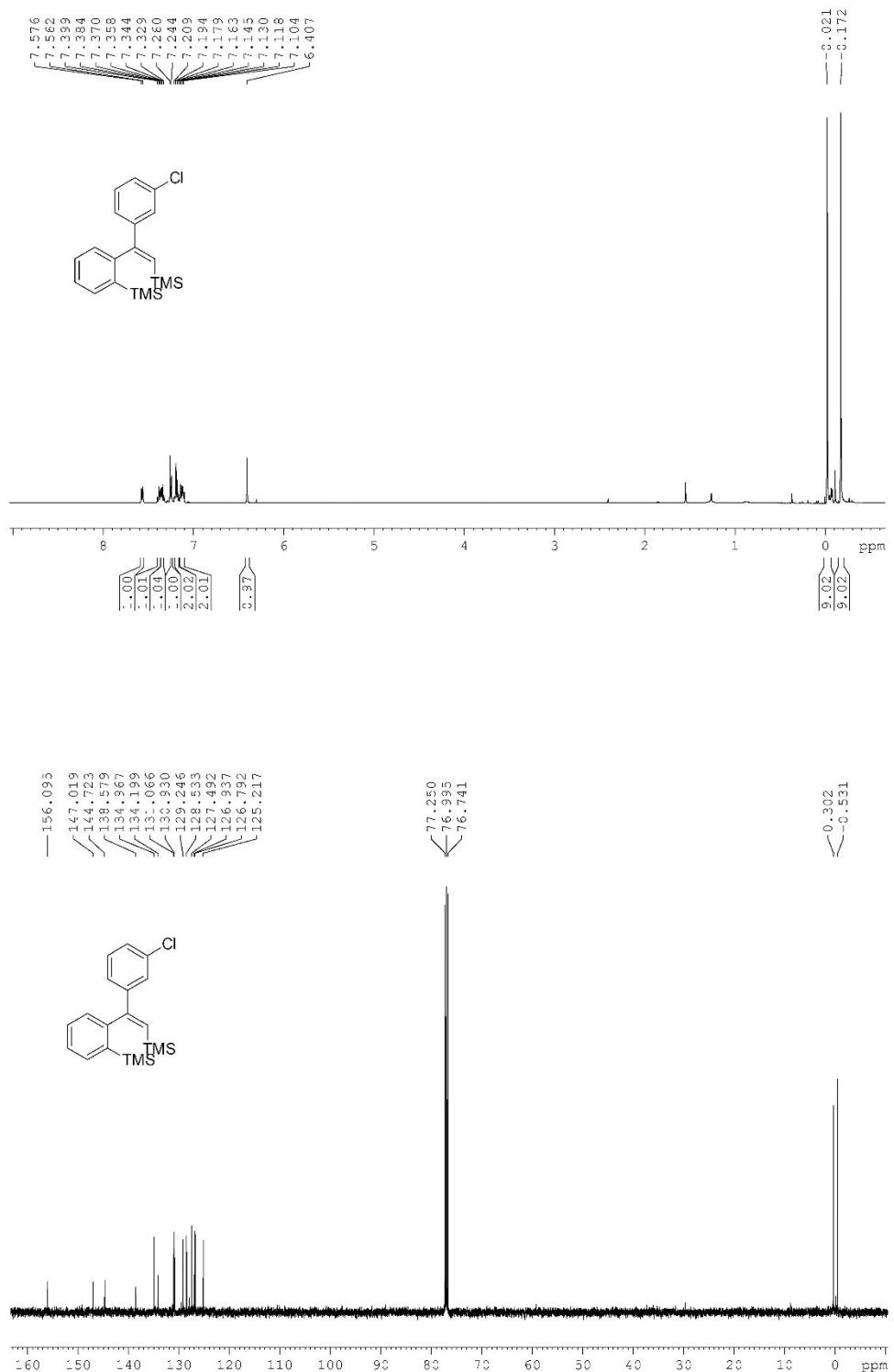
**(Z)-(2-(4-chlorophenyl)-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (3q)**



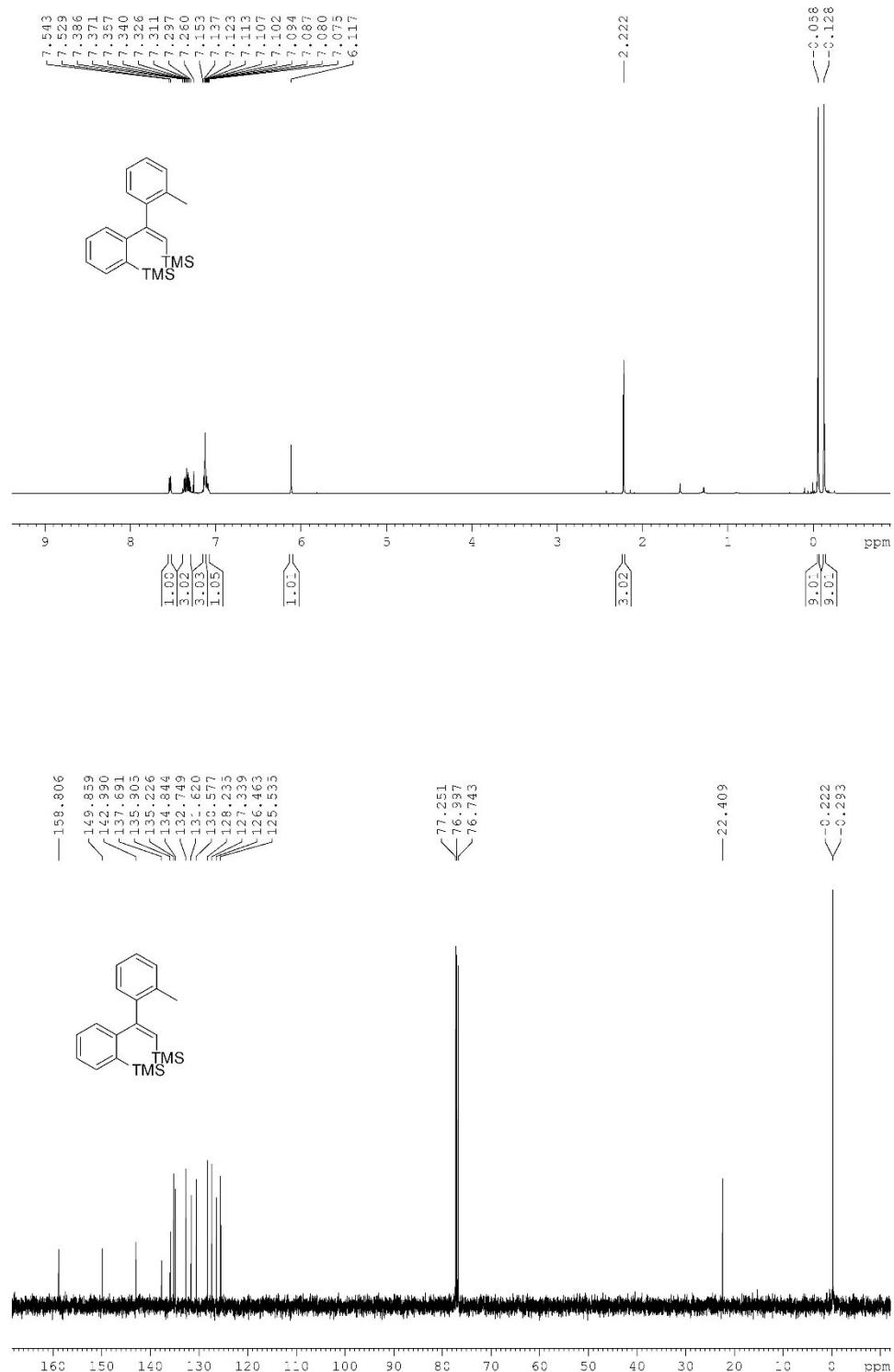
(Z)-trimethyl(2-(m-tolyl)-2-(trimethylsilyl)phenyl)vinyl)silane (3r)



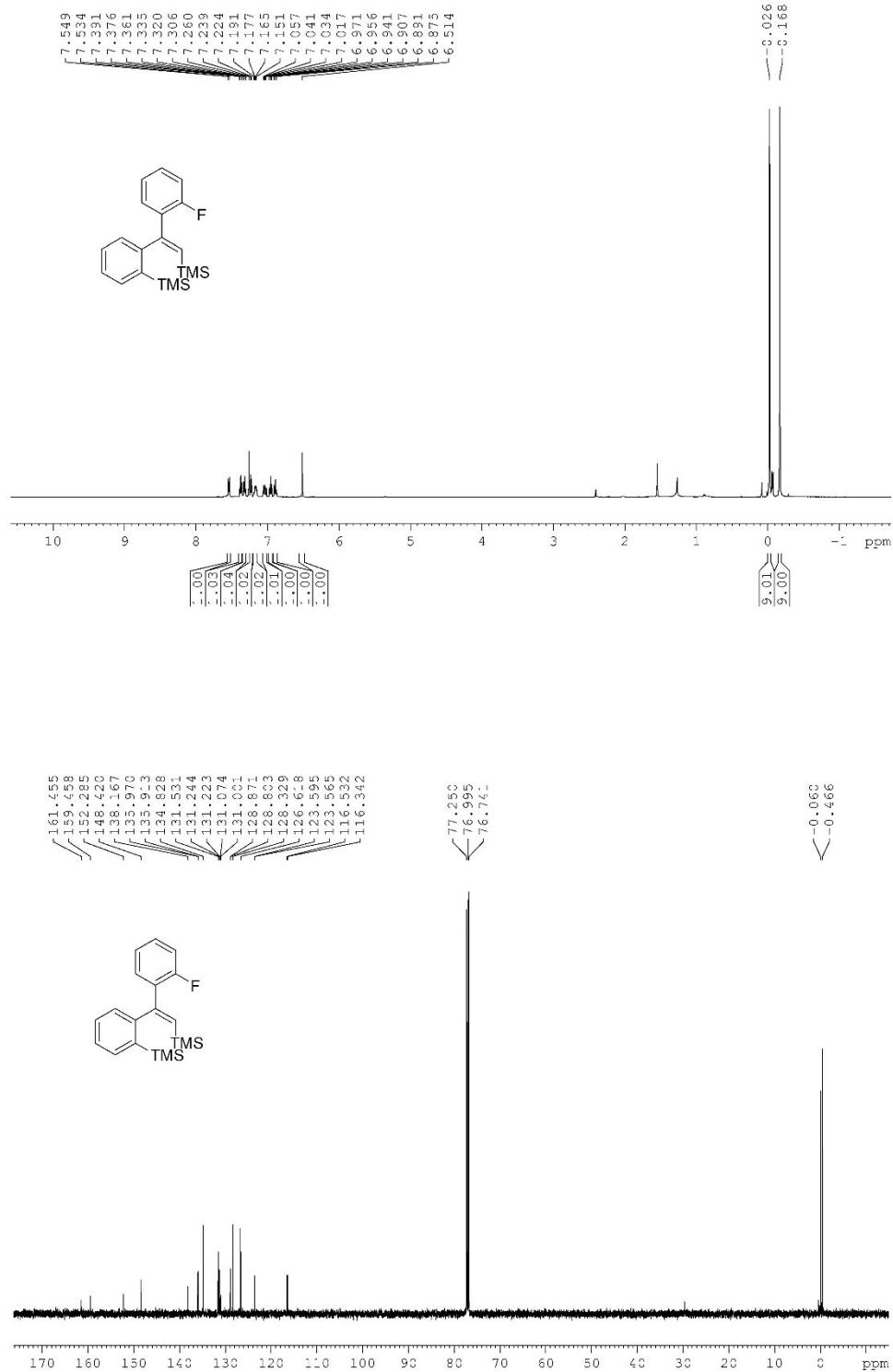
(Z)-(2-(3-chlorophenyl)-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (3s)



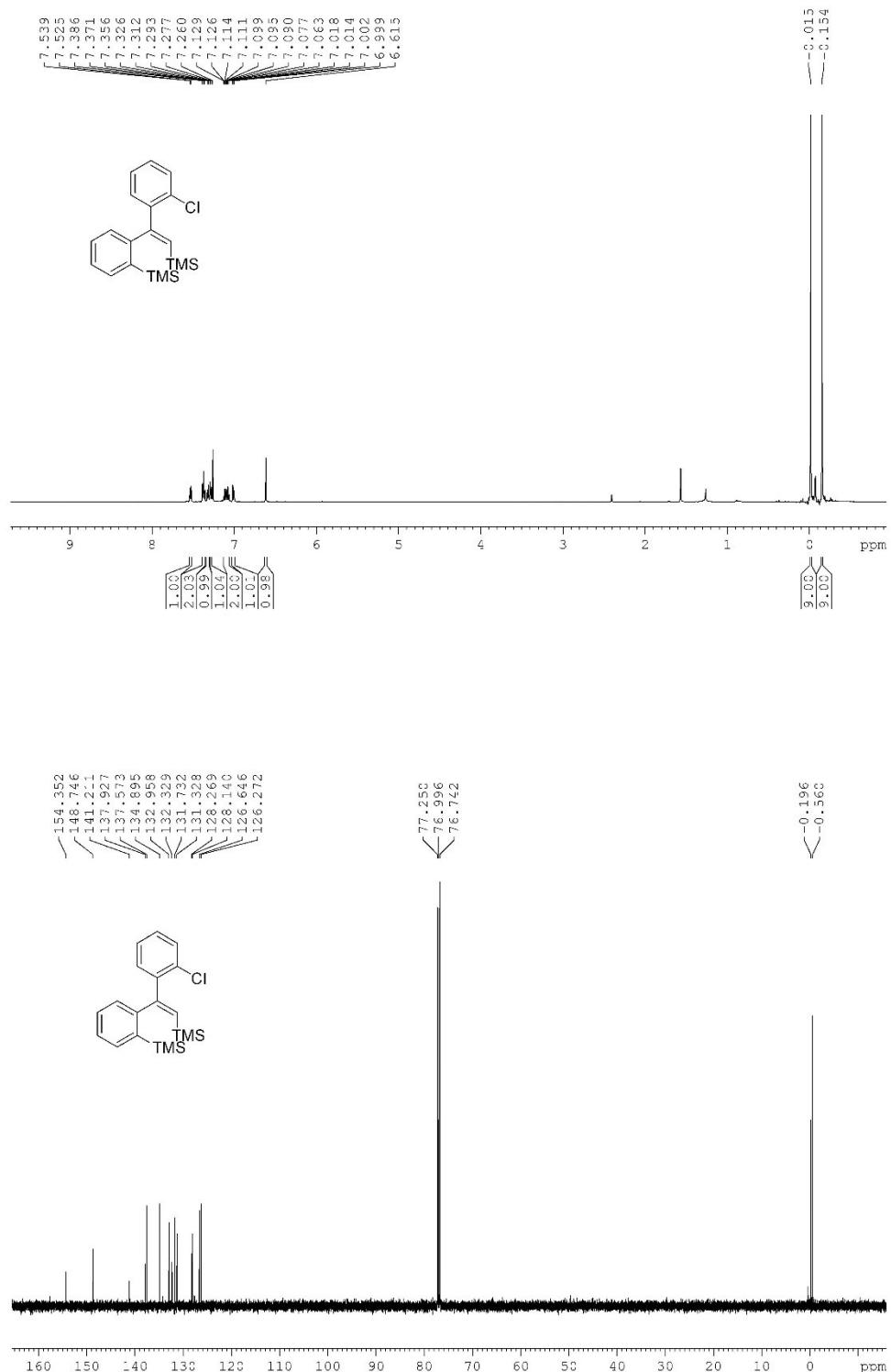
**(Z)-trimethyl(2-(o-tolyl)-2-(trimethylsilyl)phenyl)vinyl)silane (3t)**



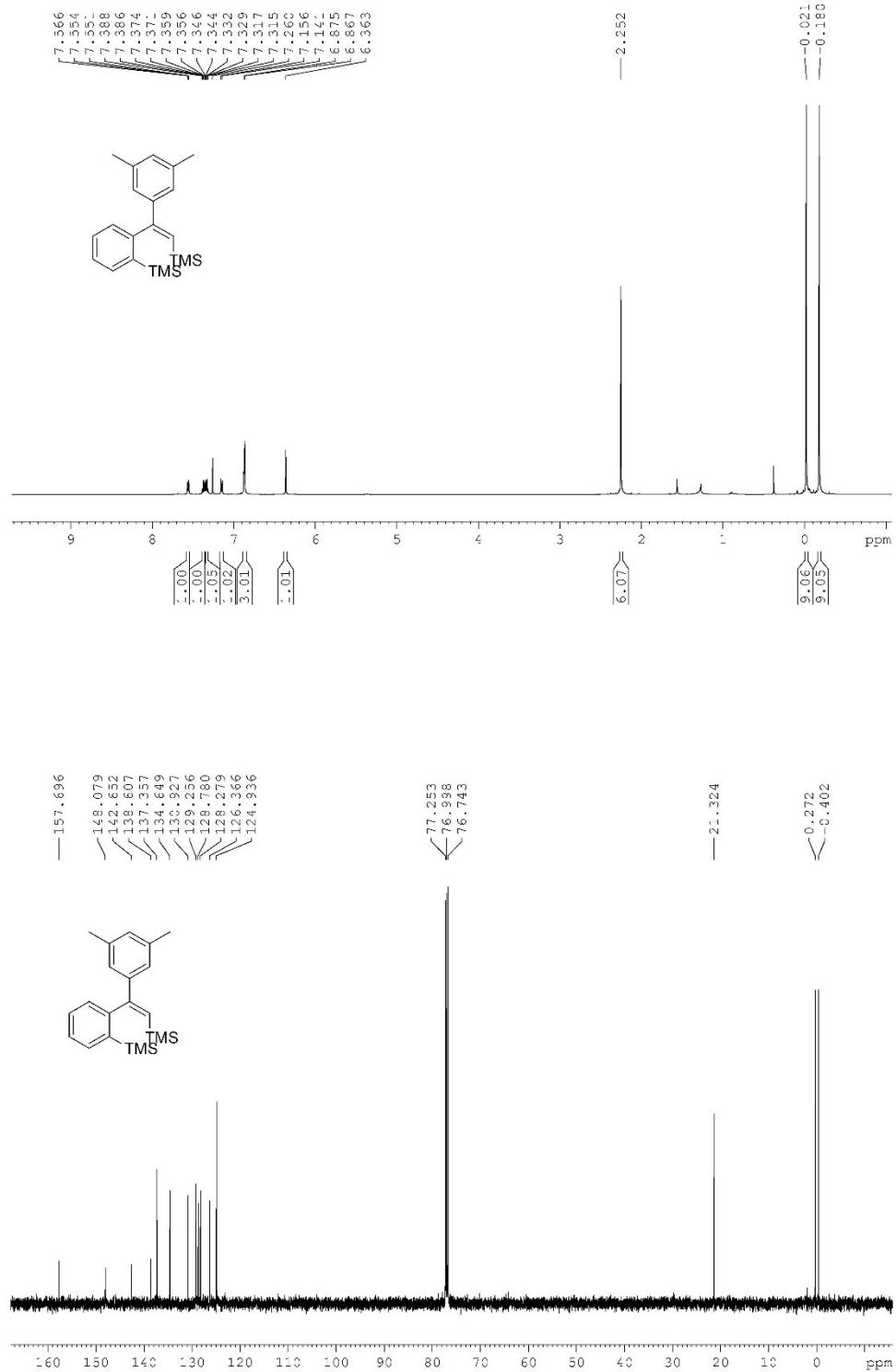
(Z)-(2-(2-fluorophenyl)-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (3u)



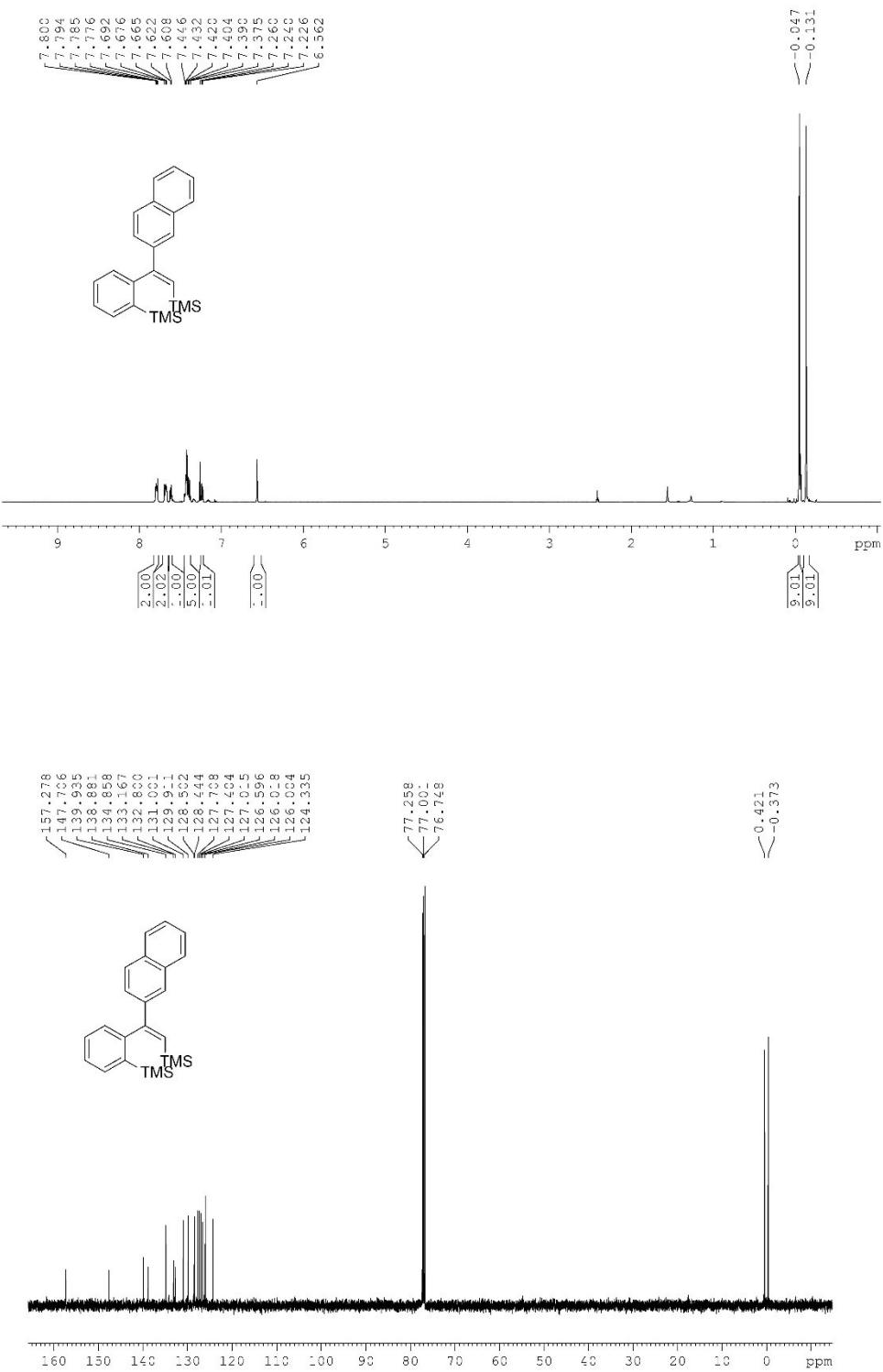
(Z)-(2-(2-chlorophenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3v)



**(Z)-(2-(3,5-dimethylphenyl)-2-(trimethylsilyl)phenyl)vinyltrimethylsilane (3w)**

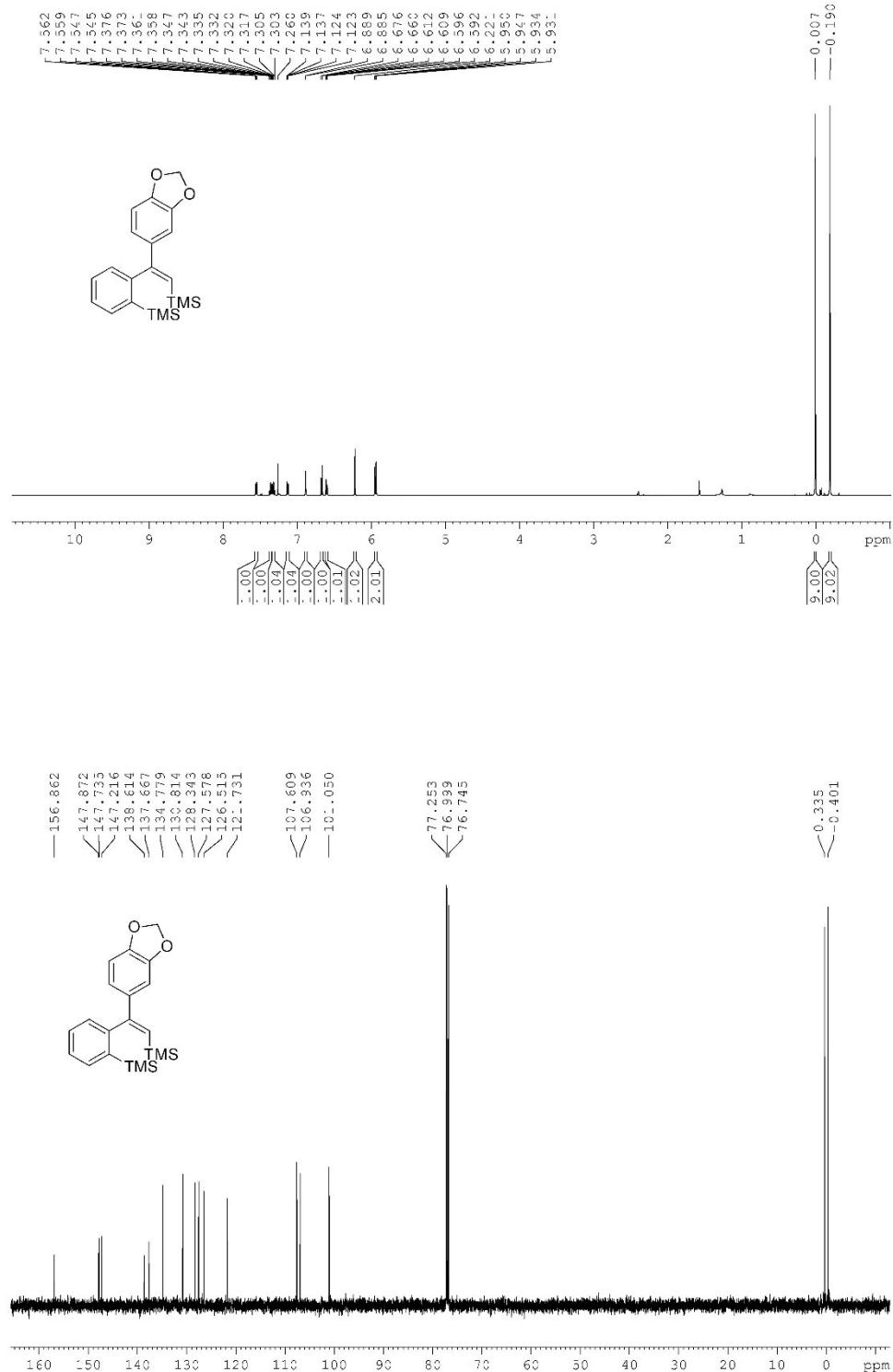


**(Z)-trimethyl(2-(naphthalen-2-yl)-2-(trimethylsilyl)phenyl)vinyl)silane (3x)**

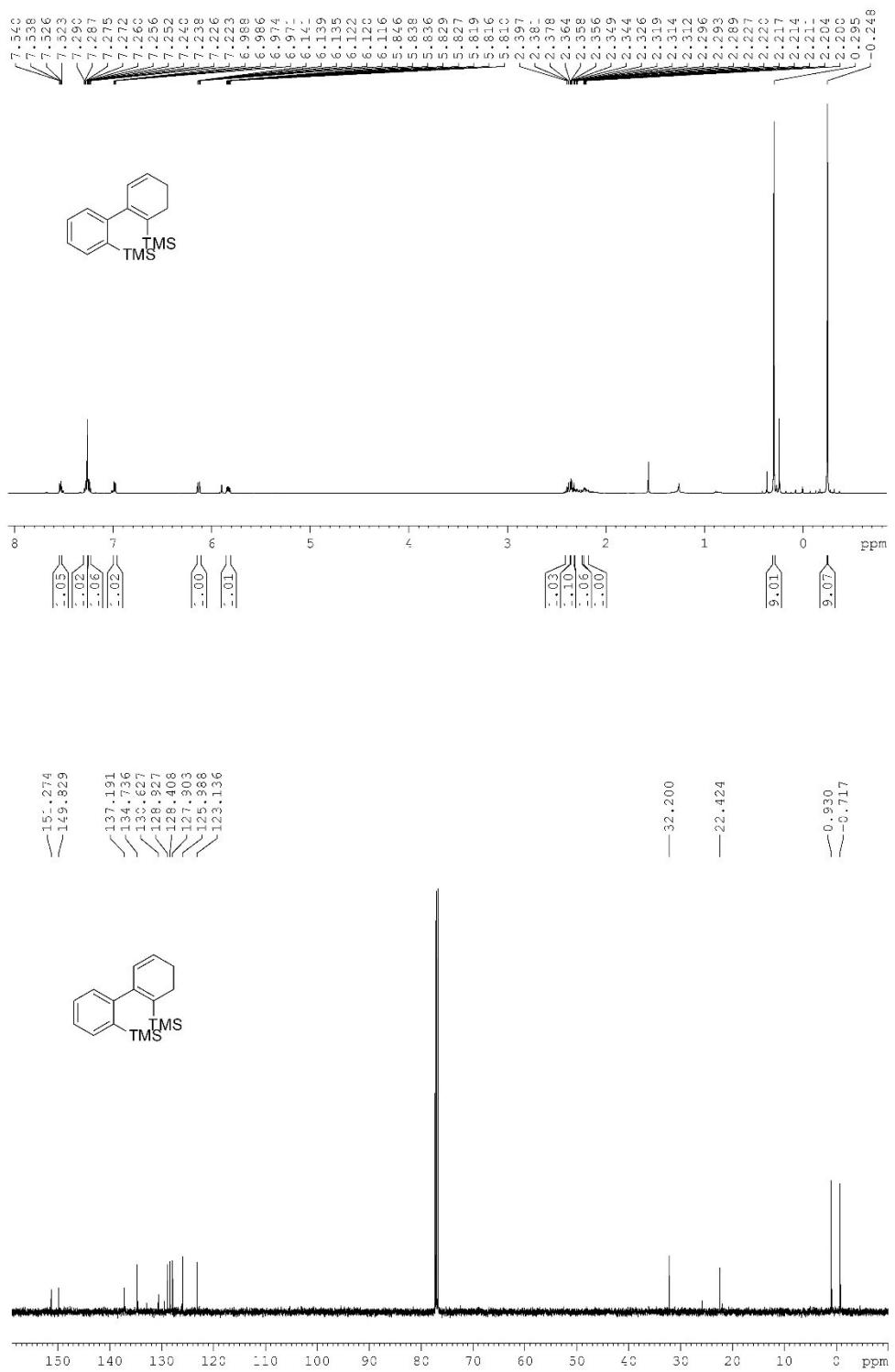


**(Z)-(2-(benzo[d][1,3]dioxol-5-yl)-2-(trimethylsilyl)phenyl)trimethylsilane**

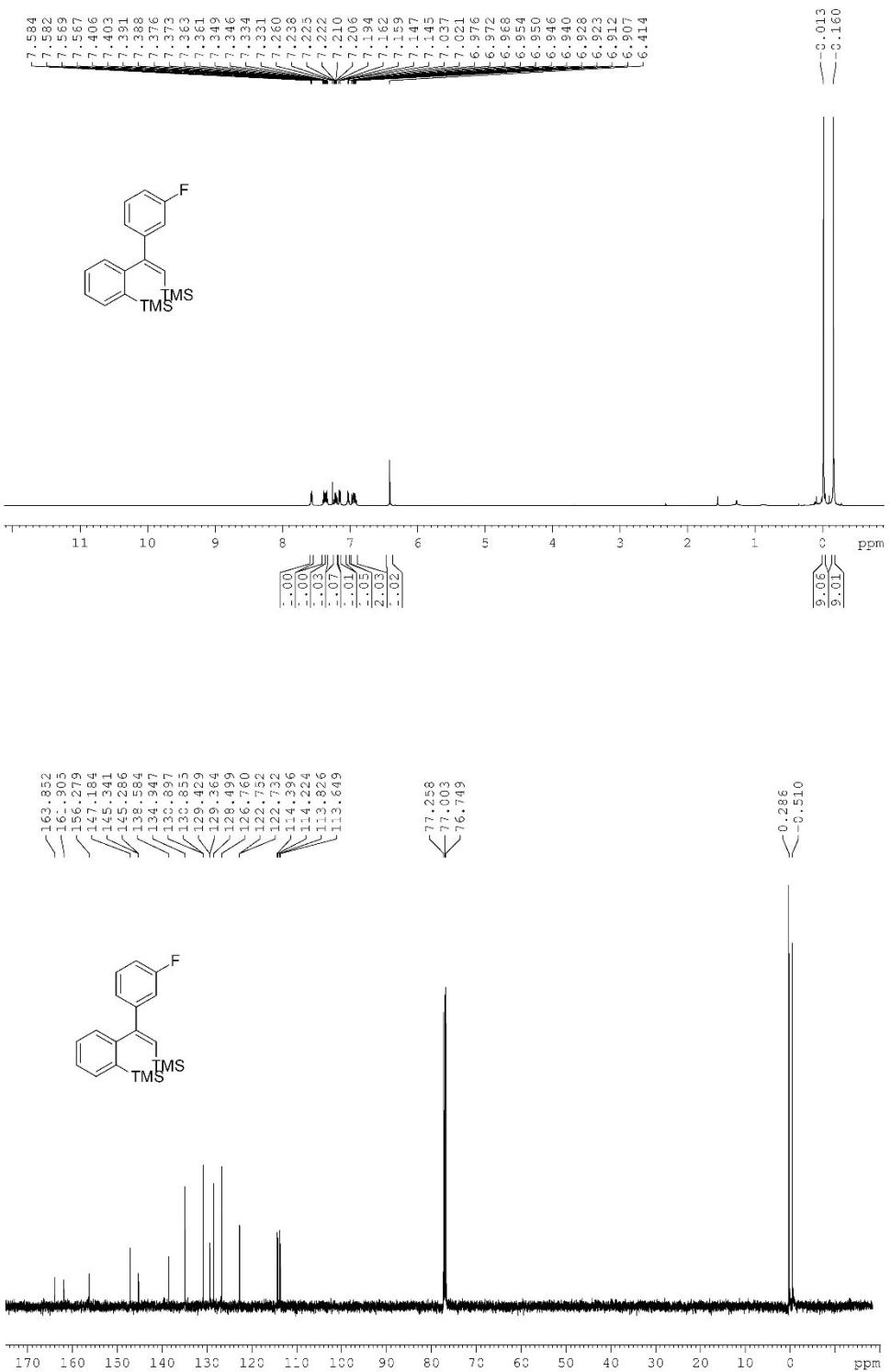
**(3y)**



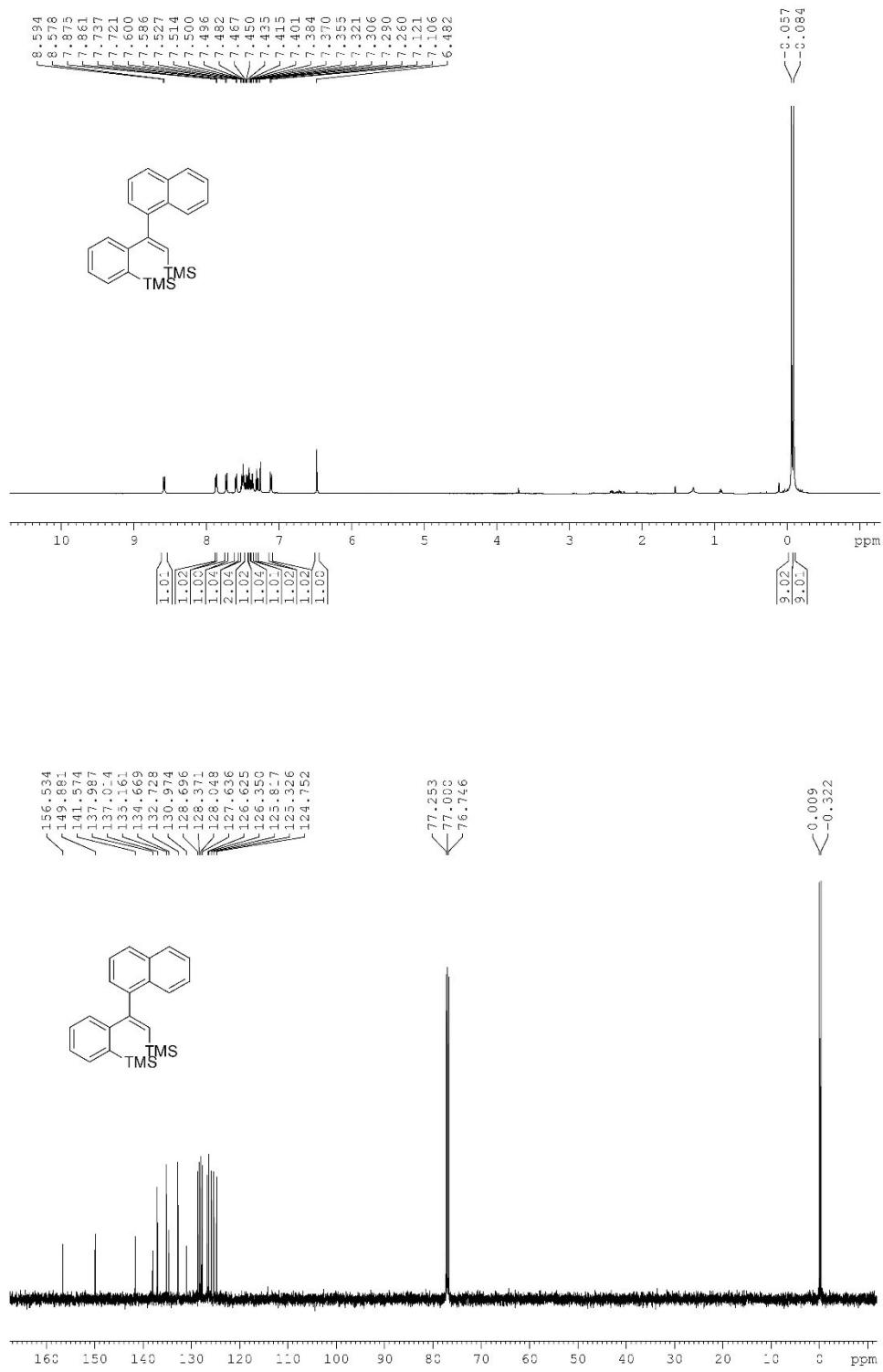
**(3,4-dihydro-[1,1'-biphenyl]-2,2'-diyl)bis(trimethylsilane) (3z)**



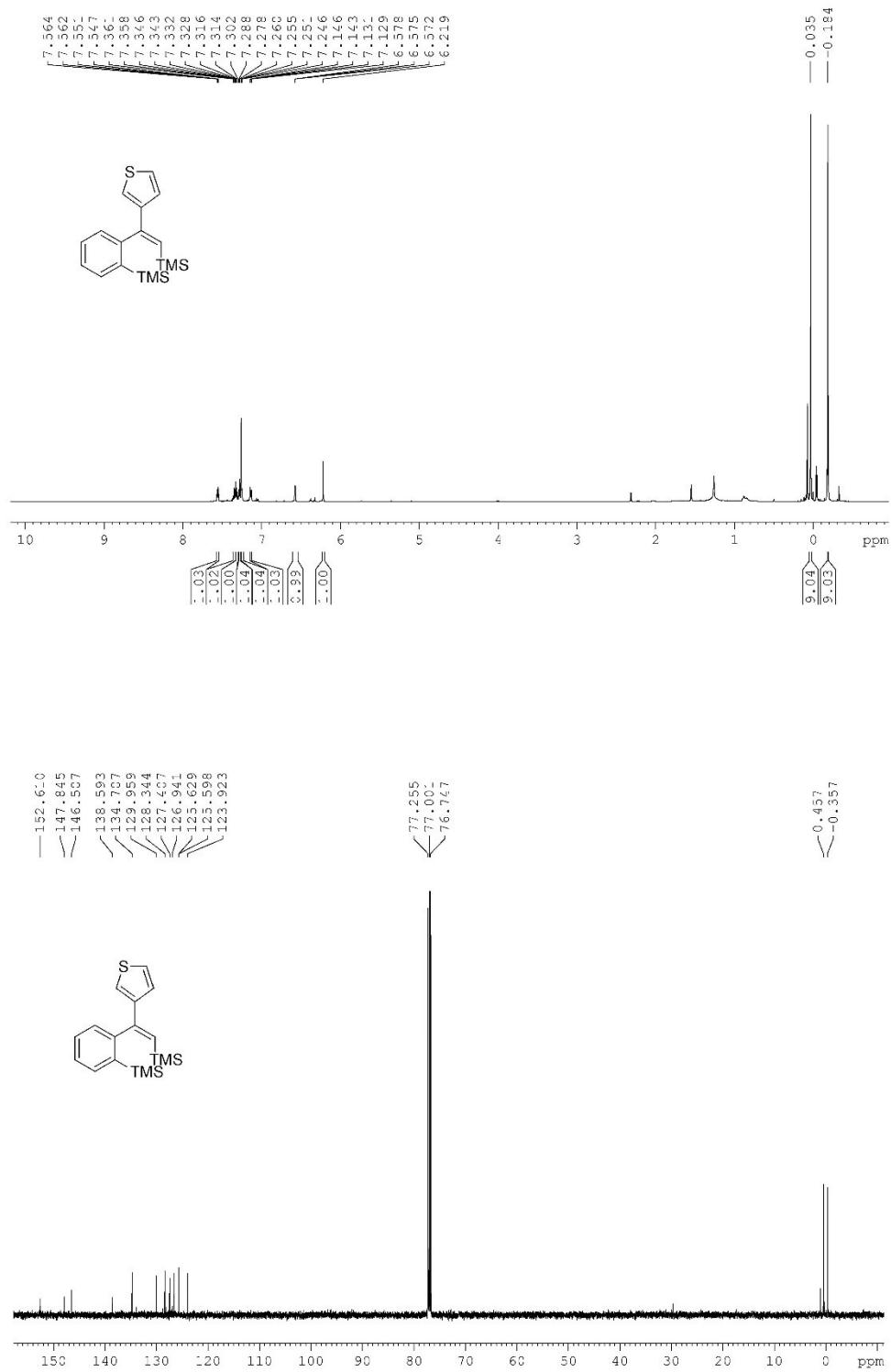
(Z)-(2-(3-fluorophenyl)-2-(trimethylsilyl)phenyl)vinyl)trimethylsilane (**3aa**)



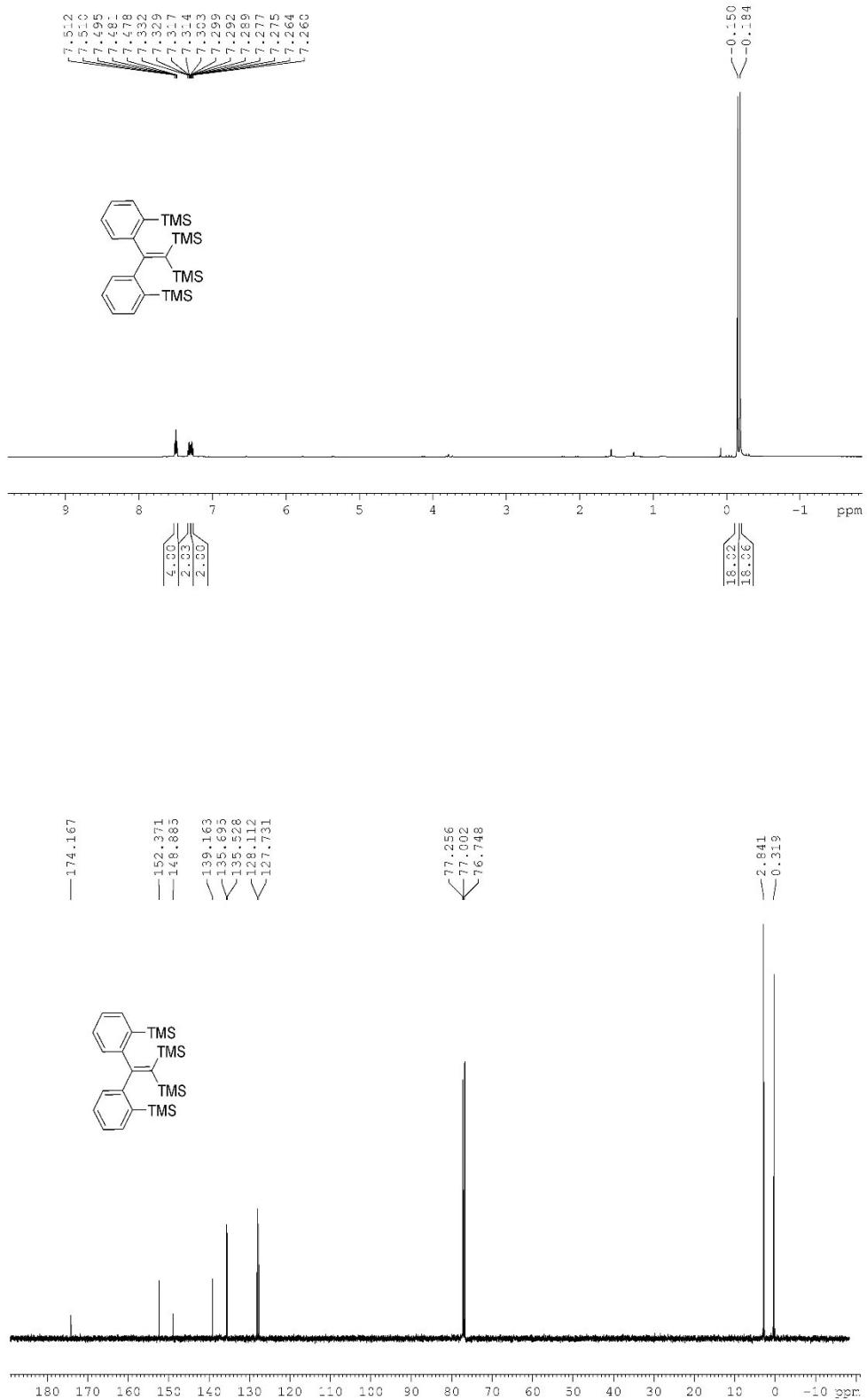
(Z)-trimethyl(2-(naphthalen-1-yl)-2-(trimethylsilyl)phenyl)vinyl)silane (**3ab**)



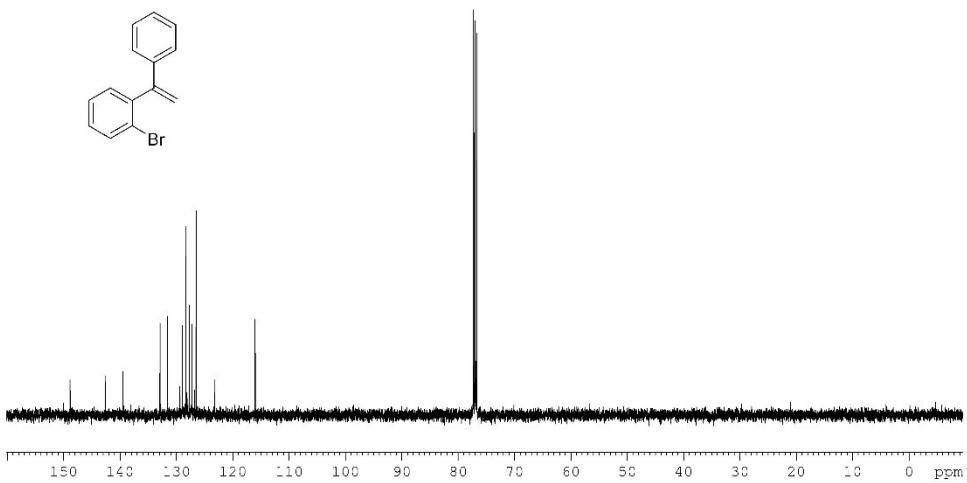
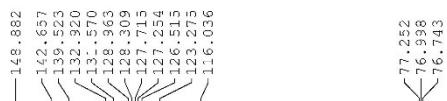
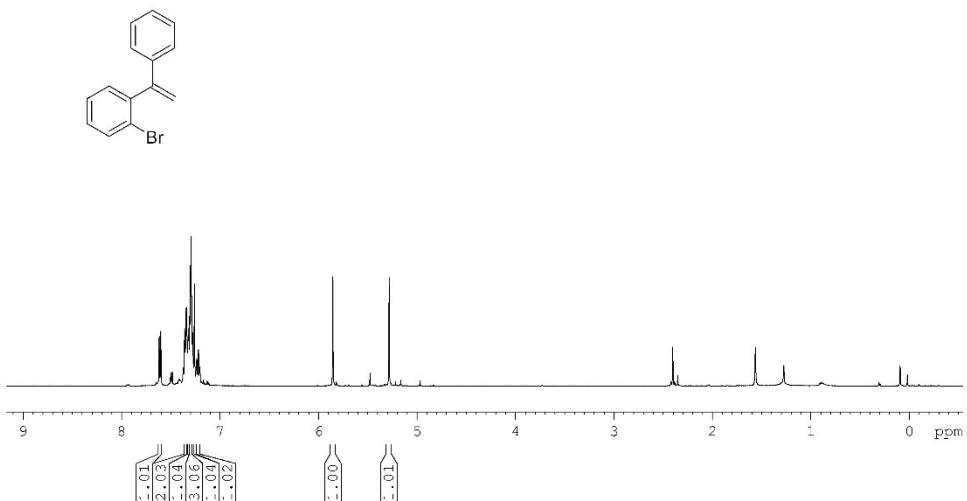
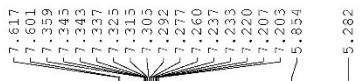
**(Z)-trimethyl(2-(thiophen-3-yl)-2-(trimethylsilyl)phenyl)vinyl)silane (3ac)**



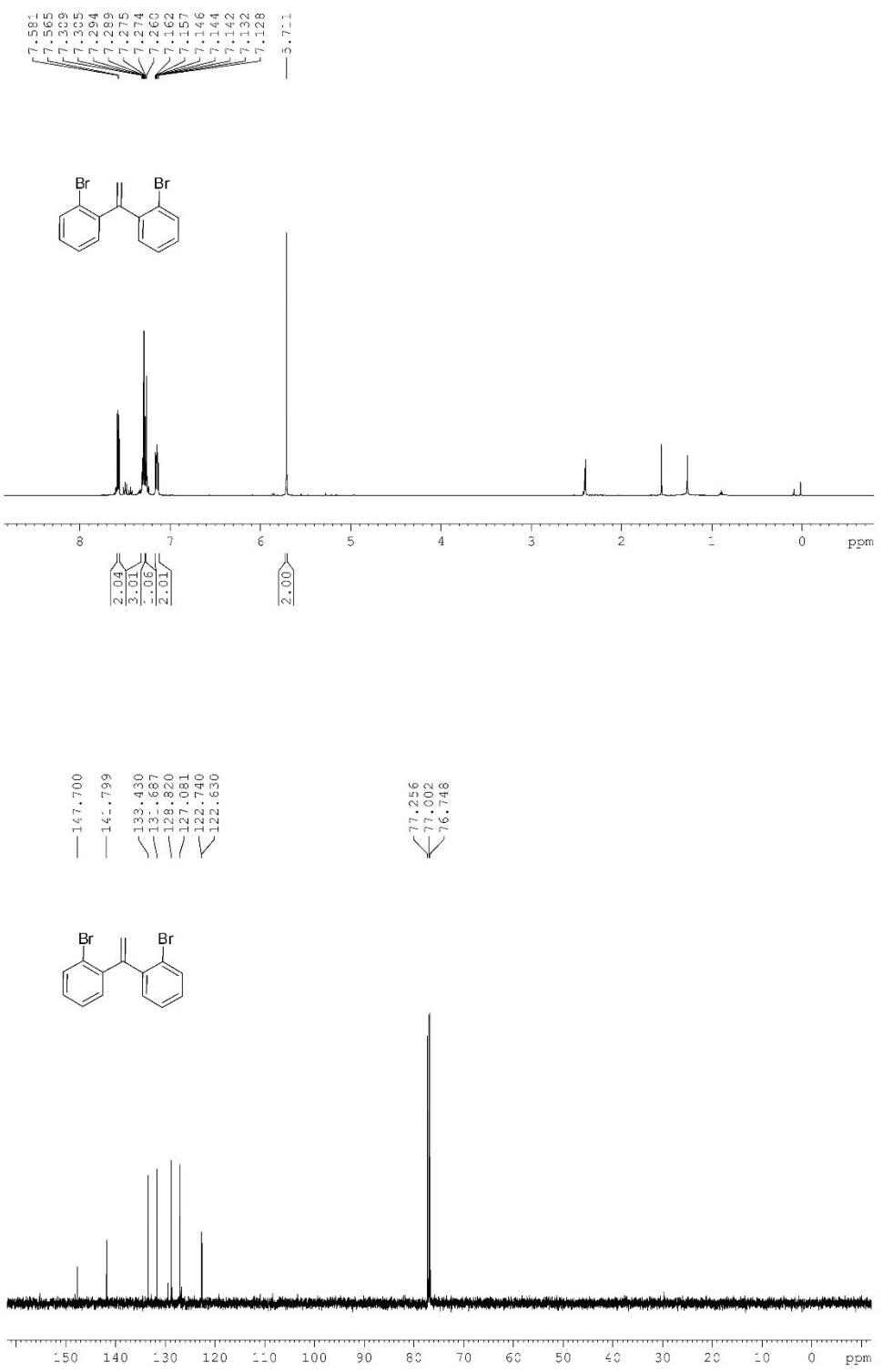
(2,2-bis(2-(trimethylsilyl)phenyl)ethene-1,1-diy)bis(trimethylsilane) (**3a'**)



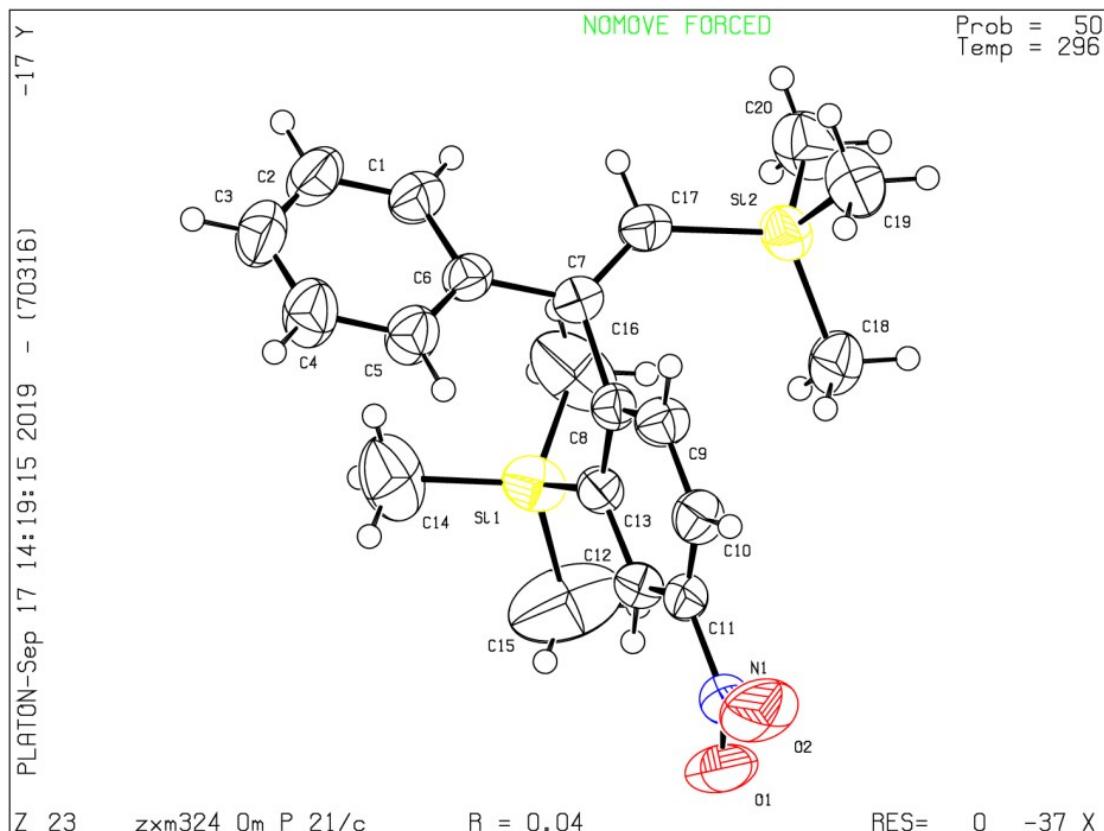
**1-bromo-2-(1-phenylvinyl)benzene (5)**



**2,2'-(ethene-1,1-diyl)bis(bromobenzene) (6)**



**7) The X-ray Single-Crystal Diffraction Analysis of 3i (CCDC: 1955948)**



**Table S3 Crystal data and structure refinement for Datablock zxm324\_0m**

Bond precision: C-C = 0.0023 Å Wavelength=0.71073

Cell: a=13.5803 (9) b=11.5718 (8) c=15.1255 (10)  
alpha=90 beta=114.050 (1) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	2170.6 (3)	2170.6 (3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C <sub>20</sub> H <sub>27</sub> N O <sub>2</sub> Si <sub>2</sub>	?
Sum formula	C <sub>20</sub> H <sub>27</sub> N O <sub>2</sub> Si <sub>2</sub>	C <sub>20</sub> H <sub>27</sub> N O <sub>2</sub> Si <sub>2</sub>
Mr	369.61	369.60

Dx, g cm <sup>-3</sup>	1.131	1.131
Z	4	4
Mu (mm <sup>-1</sup> )	0.175	0.175
F000	792.0	792.0
F000'	792.91	
h, k, lmax	16, 13, 17	16, 13, 17
Nref	3817	3817
Tmin, Tmax	0.959,	0.966
Tmin'	0.959	
Correction method=	Not given	
Data completeness=	1.000	Theta (max) = 25.009
R(reflections)=	0.0375 (3220)	wR2 (reflections)= 0.1099 (3817)
S =	1.070	Npar= 231