

**Supporting Information**

**Heterogeneous Allylsilylation of Aromatic and Aliphatic Alkenes  
Catalyzed by Proton-Exchanged Montmorillonite**

Ken Motokura, Shigekazu Matsunaga, Akimitsu Miyaji, Yasuharu Sakamoto, and  
Toshihide Baba\*

*Interdisciplinary Graduate School of Science and Engineering, Department of  
Environmental Chemistry and Engineering, Tokyo Institute of Technology, 4259  
Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan*

Characterization Procedures	S2
Materials	S2
Proton Affinity Calculation	S3
Typical Procedure for Allylsilylation	S5
Product Characterization Data	S6
Allylsilylation Using Brönsted Acids	S20
Solid-State NMR Spectra	S21
References	S23

**Characterization Procedures:**

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR), carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR), were recorded in  $\text{CDCl}_3$  with a JNM-AL300 spectrometer operating at 300 and 75 MHz, respectively. Solid-state  $^{13}\text{C}$  and  $^{29}\text{Si}$  MAS NMR spectra were recorded on a ECA400 spectrometer operating at 99.5 and 78.7 MHz, rotor spin rate of 10 and 12 kHz, respectively. The delay time was 0.2 s.  $^{13}\text{C}$  and  $^{29}\text{Si}$  MAS NMR spectra with cross polarization (CP) were acquired at a contact time of 0.5 and 1.0 ms, respectively. External standard was used as an external standard for the calibration of chemical shifts. The accumulation number was fixed at about 200000 ( $^{13}\text{C}$ ) and 400000 ( $^{29}\text{Si}$ ). Analytical GLC was measured using a Shimadzu GC-7A equipped with a Silicon SE-30 column and a flame ionization detector. Shimadzu QP5000 was used as GC-MS equipped with DB-1 column. FT-IR spectra were recorded on a FT/IR 6100 with TGS detector. The products were confirmed by comparison with reported NMR, MS, and IR data.

**Materials:**

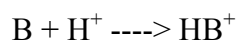
$\text{Na}^+$ -montmorillonite ( $\text{Na}_{0.66}(\text{OH})_4\text{Si}_8(\text{Al}_{3.34}\text{Mg}_{0.66}\text{Fe}_{0.19})\text{O}_{20}$ ; Kunipia F) was obtained from Kunimine Industry. Proton-exchanged montmorillonite was prepared from  $\text{Na}^+$ -montmorillonite using reported ion exchange procedure with aqueous hydrogen chloride.[1] MontK10 was purchased from Aldrich.  $\text{H}^+$ -Beta ( $\text{SiO}_2/\text{Al}_2\text{O}_3=25$ ),  $\text{H}^+$ -Mordenite ( $\text{SiO}_2/\text{Al}_2\text{O}_3=18.0$ ) was purchased from Nikki Chemical Co..  $\text{H}^+$ -ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=23.8$ ) was obtained from Toso Co.. These zeolites were treated at 500 °C under air before use. Amberlyst was purchased from Organo Co. as Amberlyst® 15DRY. Nafion was purchased from Aldrich Inc. as Nafion® NR50.

Unless otherwise noted, materials were purchased from Wako Pure Chemicals,

Tokyo Kasei Co., Kanto kagaku Co. and Aldrich Inc. 1,3-Di(trimethylsilyl)propan-2-ol were purchased from NARD Institute. Allyltriethylsilane was synthesized using reported procedure.[2]

### Proton Affinity Calculation:

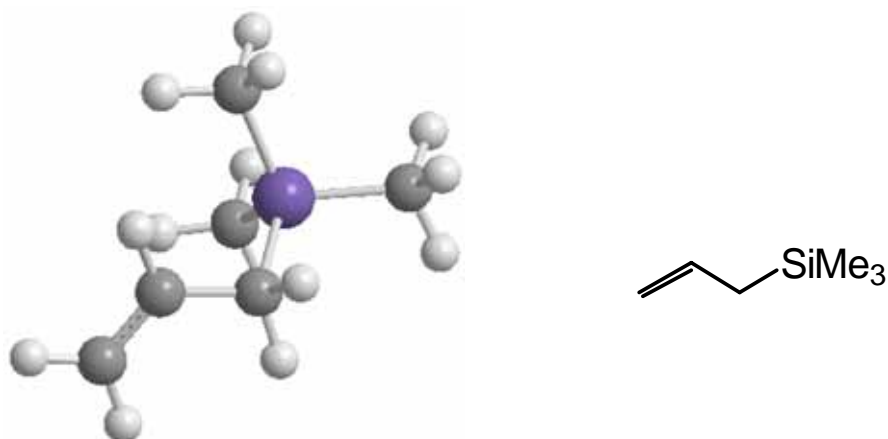
Proton affinity (PA) was theoretically calculated by reported AM1 method.[3] The PA of a compound (B) is defined as minus the heat of reaction for its combination with a proton ( $H^+$ ).



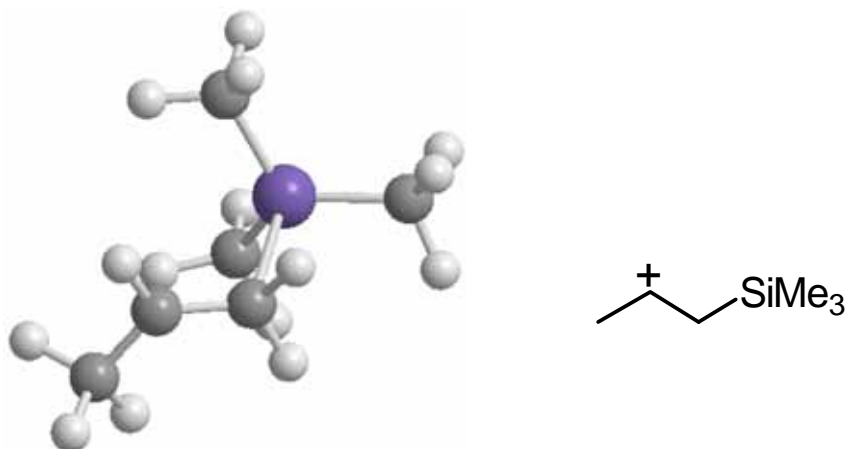
$$PA(B) = \Delta H_f(H^+) + \Delta H_f(B) - \Delta H_f(HB^+)$$

where  $\Delta H_f$  is heat of formation.

Experimental value of heat of formation of  $H^+$  ( $\Delta H_f(H^+) = 367.2$  kcal/mol) was used.[3]



**Figure 1S.** Optimized structure of allyltrimethylsilane with AM1. C: gray, H: white, Si: purple. Calculated heat of formation was -34.89 kcal/mol.



**Figure 2S.** Optimized structure of protonated allyltrimethylsilane with AM1. C: gray, H: white, Si: purple. Calculated heat of formation was 127.03 kcal/mol.

PA(Allyltrimethylsilane)

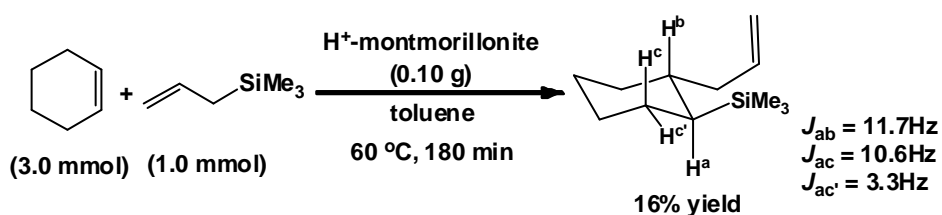
$$\begin{aligned}
 &= \Delta H_f(\text{H}^+) + \Delta H_f(\text{Allyltrimethylsilane}) - \Delta H_f(\text{Protonated Allyltrimethylsilane}) \\
 &= 367.2 + (-34.89) - 127.03 \\
 &= \mathbf{205.3 \text{ kcal/mol}}
 \end{aligned}$$

This PA(Allyltrimethylsilane) value is ~4 kcal/mol higher than that for the reported PA(Styrene) (201.4 kcal/mol)[4].

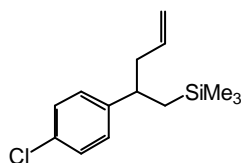
### Typical Procedure for Allylsilylation:

Typical procedure for allylsilylation of *p*-chlorostyrene (**1b**) with allyltrimethylsilane (**2a**) is as follows. Into a glass reactor were placed H<sup>+</sup>-montmorillonite (0.10 g), toluene (1.0 mL), **1b** (1.0 mmol), **2a** (3.0 mmol) in a dry Ar atmosphere using Schlenk technique. The resulting mixture was vigorously stirred at 100 °C. After 180 min, the catalyst was separated by filtration and GC analysis of the filtrate showed a 95 % yield of (2-(4-chlorophenyl)pent-4-enyl)trimethylsilane (**3ba**). The filtrate was evaporated and the crude product was purified by column chromatography using silica (*n*-hexane elute) to afford a pure product. The product was identified by <sup>1</sup>H and <sup>13</sup>C NMR and Mass data.

### Allylsilylation of cyclohexene with allyltrimethylsilane:

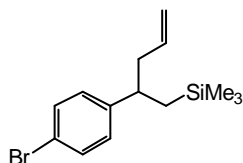


## Product Characterization Data:



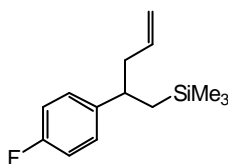
### 4-(4-chlorophenyl)-5-trimethylsilyl-1-pentene (3ba):

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.03 (s, 9H), 1.03-1.20 (m, 2H), 2.49 (t,  $J = 7.0\text{Hz}$ , 2H), 2.88-2.93 (m, 1H), 5.08-5.13 (m, 2H), 5.73-5.82 (m, 1H), 7.27 (d,  $J = 8.3\text{Hz}$ , 2H), 7.42 (d,  $J = 8.4\text{Hz}$ , 2H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ ): -1.07, 24.2, 41.7, 45.2, 116.2, 128.3, 128.9, 131.5, 136.8, 145.3; MS (EI)  $m/z$  (%): 252( $\text{M}^+$ ), 211, 195, 181, 169, 161, 138, 129, 115, 99, 73(100), 59, 45; IR (KBr):  $\nu_{\text{max}}$  3079, 2953, 2925, 2855, 1638, 1492, 1412, 1249, 1095, 1014, 914, 837, 692, 530.



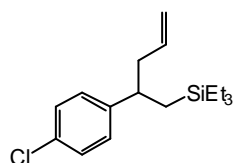
### 4-(4-bromophenyl)-5-trimethylsilyl-1-pentene (3ca):

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.16 (s, 9H), 0.86-1.04 (m, 2H), 2.32 (t,  $J = 6.8\text{Hz}$ , 2H), 2.68-2.78 (m, 1H), 4.91-4.98 (m, 2H), 5.51-5.67 (m, 1H), 7.06 (d,  $J = 8.4\text{Hz}$ , 2H), 7.40 (d,  $J = 8.4\text{Hz}$ , 2H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ ): -1.03, 24.1, 41.7, 45.1, 116.12, 119.5, 128.1, 131.24, 136.7, 145.9; MS (EI)  $m/z$  (%): 257( $\text{M}^+$ -allyl), 255, 215, 213, 184, 182, 161, 145, 115, 99, 73(100), 59, 45; IR (KBr):  $\nu_{\text{max}}$  3077, 2952, 2900, 1640, 1489, 1408, 1248, 1074, 914, 849, 692, 530.



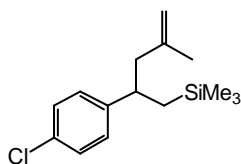
### 4-(4-fluorophenyl)-5-trimethylsilyl-1-pentene (3da):

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.03 (s, 9H), 1.06-1.24 (m, 2H), 2.53 (t,  $J = 7.1\text{Hz}$ , 2H), 2.90-3.00 (m, 1H), 5.11-5.17 (m, 2H), 5.78-5.89 (m, 1H), 7.13-7.21 (m, 2H), 7.30-7.34 (m, 2H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ ): -1.10, 24.4, 41.6, 45.5, 114.8, 116.0, 128.8, 137.0, 142.5, 159.7; MS (EI)  $m/z$  (%): 236( $\text{M}^+$ ), 221, 195, 153, 139, 122, 109, 99, 73(100), 59, 45; IR (KBr):  $\nu_{\text{max}}$  3077, 2953, 2901, 1639, 1605, 1509, 1417, 1248, 1226, 1158, 993, 914, 834, 691, 543.



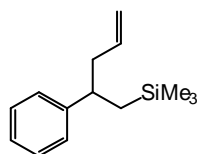
**4-(4-chlorophenyl)-5-triethylsilyl-1-pentene (3ab):**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.43-0.60 (m, 6H), 1.02 (t,  $J = 7.9\text{Hz}$ , 9H), 1.08-1.17 (m, 2H), 2.49 (t,  $J = 7.1\text{Hz}$ , 2H), 2.90 (m, 1H), 5.08-5.13 (m, 2H), 5.70-5.87 (m, 1H), 7.29 (d,  $J = 8.4\text{Hz}$ , 2H), 7.42 (d,  $J = 8.2\text{Hz}$ , 2H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ ): 3.62, 6.78, 18.9, 41.5, 45.4, 116.2, 128.3, 128.8, 131.5, 136.8, 145.7; MS (EI)  $m/z$  (%): 253( $\text{M}^+$ -allyl), 169, 167, 141, 127, 115(100), 99, 87, 71, 59, 43; IR (KBr):  $\nu_{\text{max}}$  3078, 2953, 2909, 2875, 1639, 1492, 1459, 1413, 1238, 1093, 1014, 913, 831, 750, 727, 534.



**(2-(4-chlorophenyl)-4-methylpent-4-enyl)trimethylsilane (3ac):**

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.03 (s, 9H), 0.95-1.16 (m, 2H), 1.78 (s, 3H), 2.42 (d,  $J = 7.6\text{Hz}$ , 2H), 2.95-3.05 (m, 1H), 4.70 (s, 1H), 4.82 (s, 1H), 7.25 (d,  $J = 8.5\text{Hz}$ , 2H), 7.38 (d,  $J = 8.4\text{Hz}$ , 2H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ ): -1.10, 22.3, 24.3, 39.8, 49.5, 112.4, 128.3, 128.8, 131.4, 143.6, 145.7; MS (EI)  $m/z$  (%): 211( $\text{M}^+$ -methallyl), 181, 179, 138, 113, 108, 85, 73(100), 59, 45; IR (KBr):  $\nu_{\text{max}}$  3074, 2953, 2900, 1647, 1492, 1411, 1249, 1093, 1014, 886, 837, 695, 540.

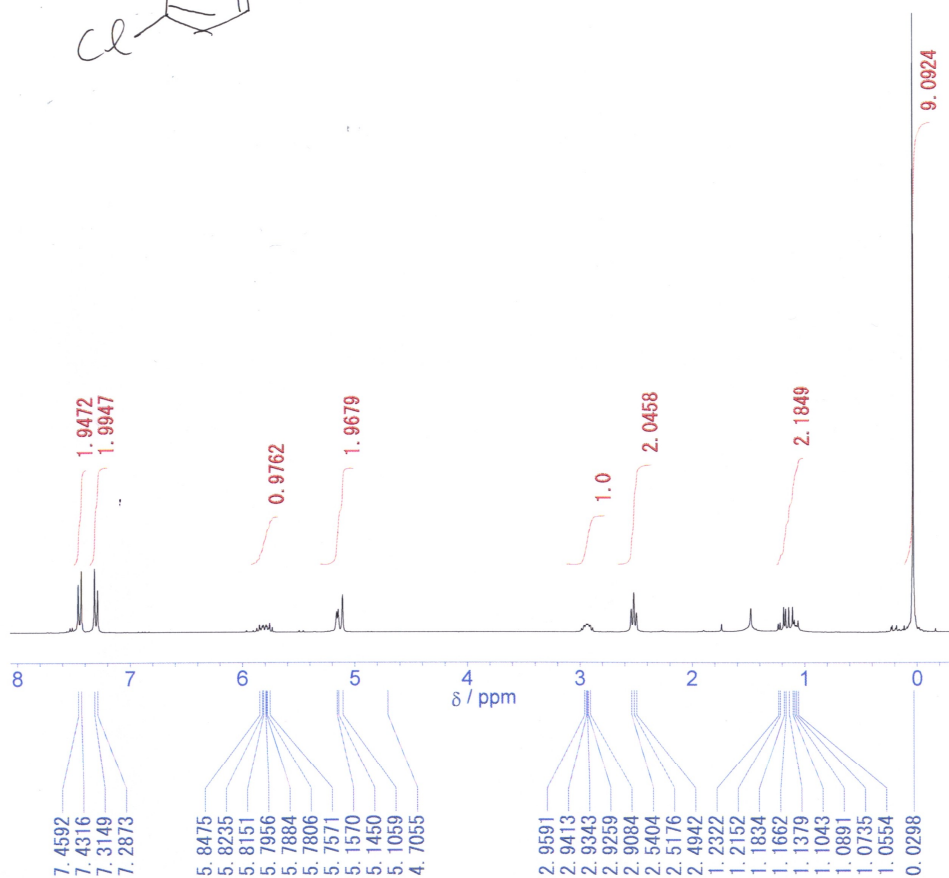
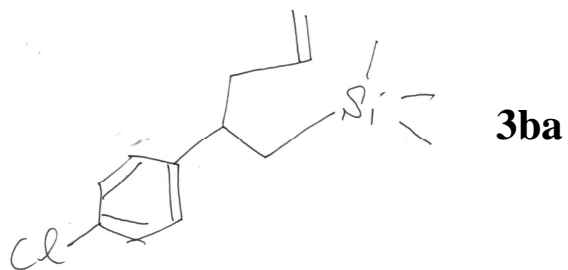


**4-phenyl-5-trimethylsilyl-1-pentene (3aa):**

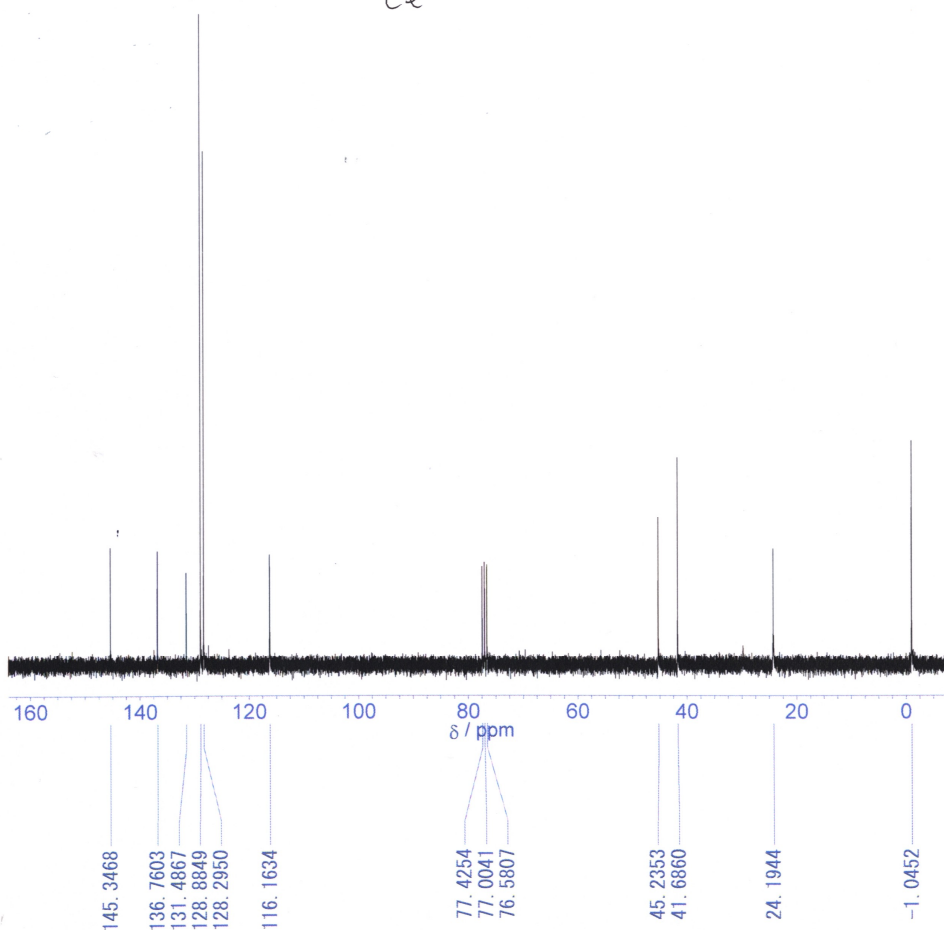
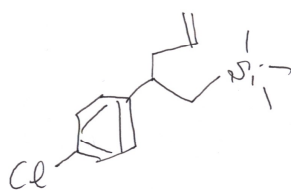
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.07 (s, 9H), 1.01-1.16 (m, 2H), 2.47 (t,  $J = 6.6\text{ Hz}$ , 2H), 2.84-2.90 (m, 1H), 5.03-5.10 (m, 2H), 5.71-6.81 (1H), 7.28-7.42 (m, 5H);  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (75.45 MHz,  $\text{CDCl}_3$ ): -1.12, 24.2, 42.2, 45.3, 115.8, 126.0, 127.5, 128.2, 137.3, 146.9; MS (EI)  $m/z$  (%): 218( $\text{M}^+$ ), 177, 145, 135, 121, 99, 73(100), 56, 45; IR (KBr):  $\nu_{\text{max}}$  3076, 3063, 3028, 2954, 2900, 1639, 1603, 1493, 1415, 1247, 1181, 996, 912, 859, 838, 760, 700.

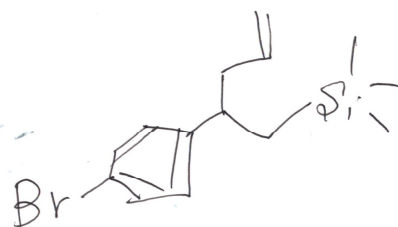
**trimethyl[2-(2-propen-1-yl)hexyl]silane (3ea): CAS[165059-54-1]** <sup>[5]</sup>

**trimethyl[2-(2-propen-1-yl)octyl]silane (3fa): CAS[165059-56-3]** <sup>[5]</sup>

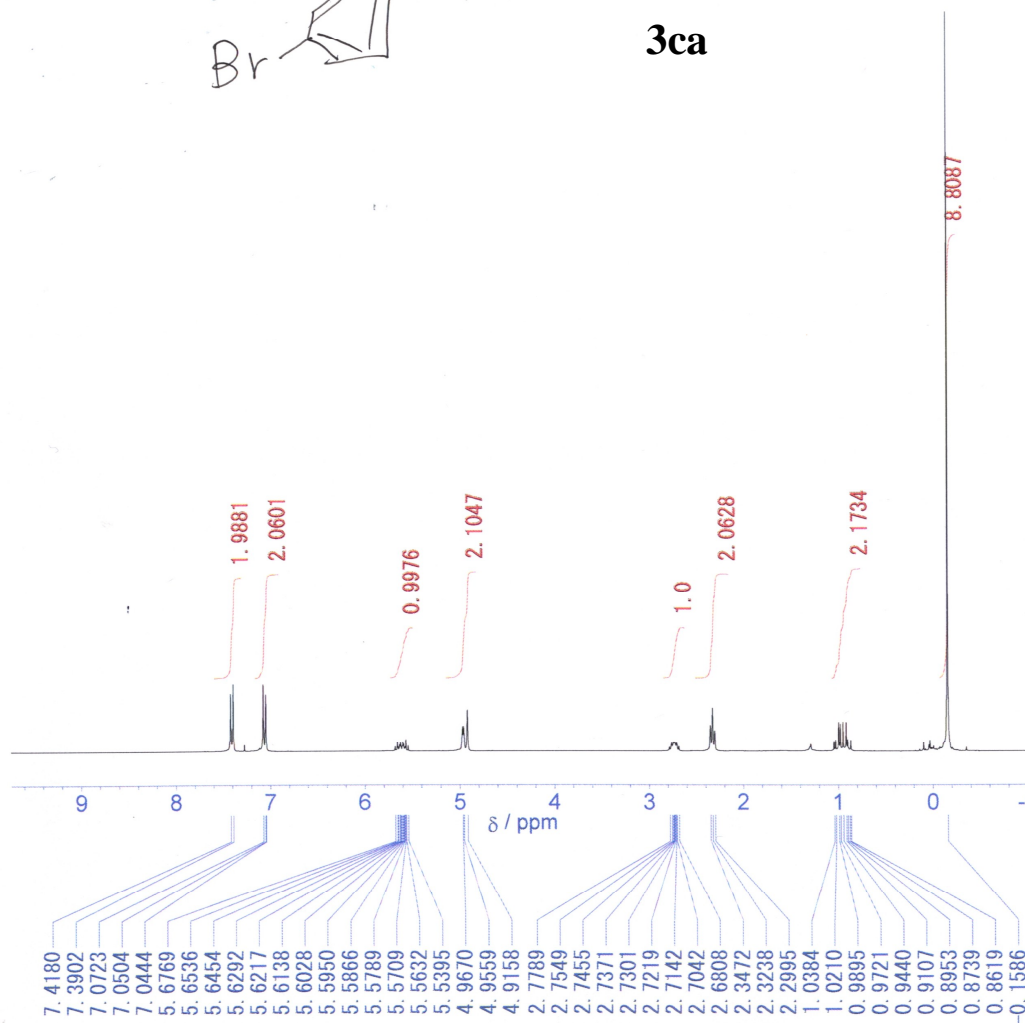




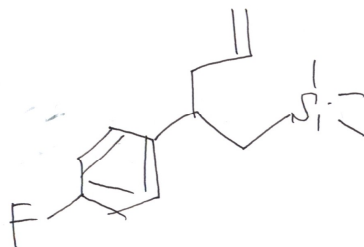




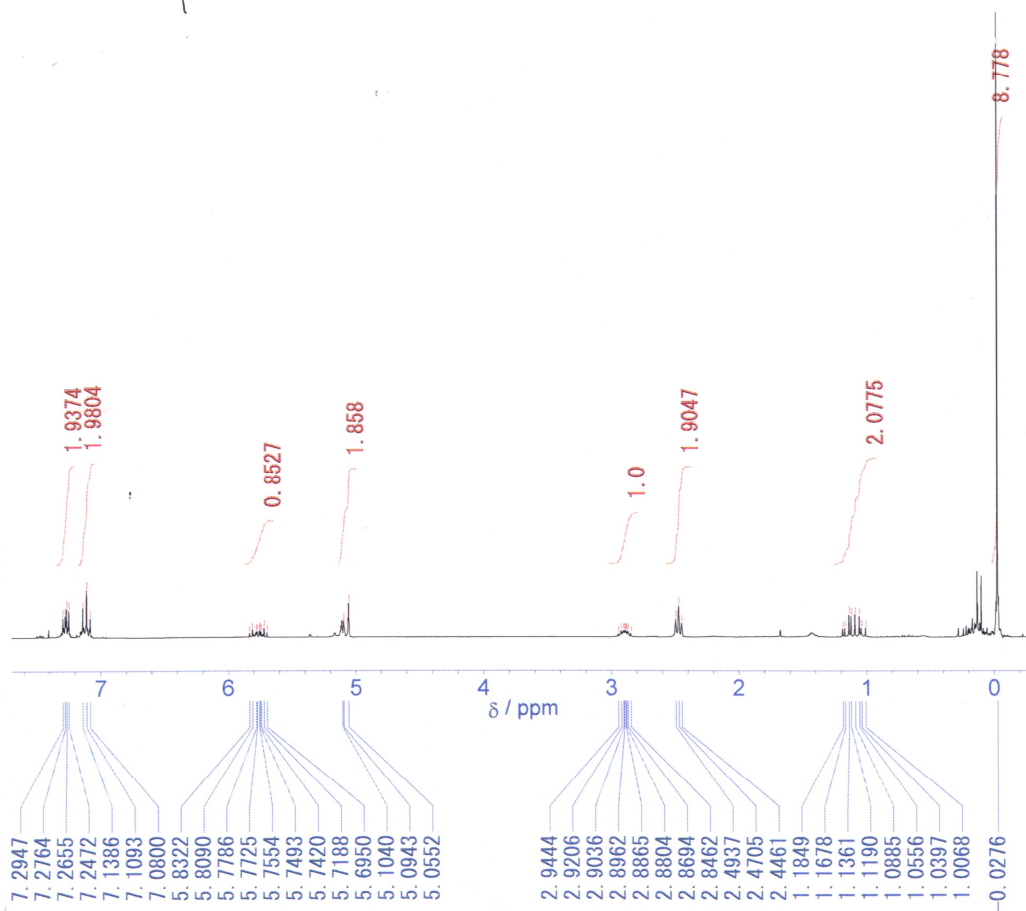
**3ca**

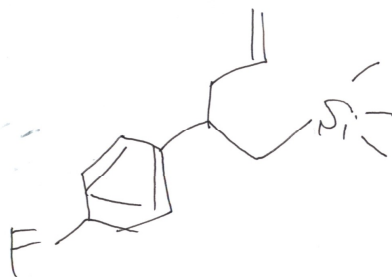




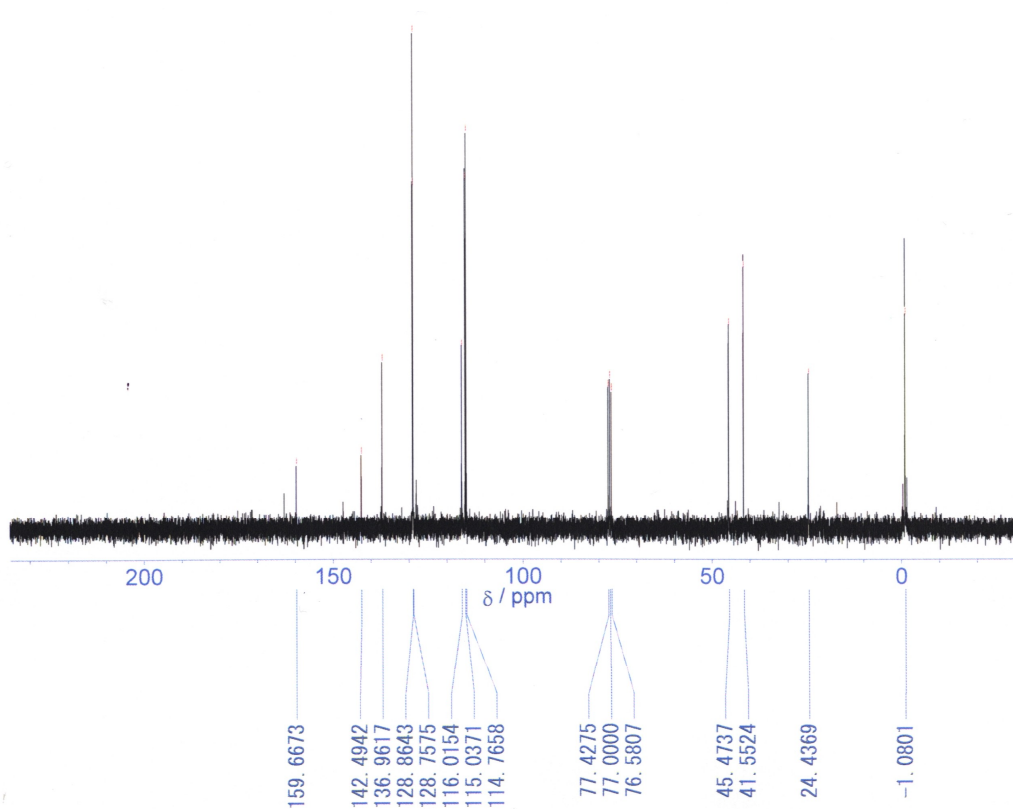


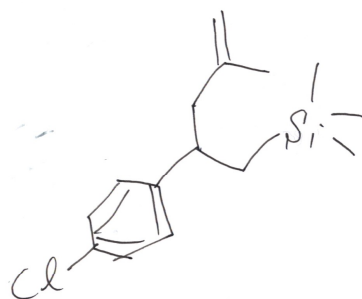
**3da**



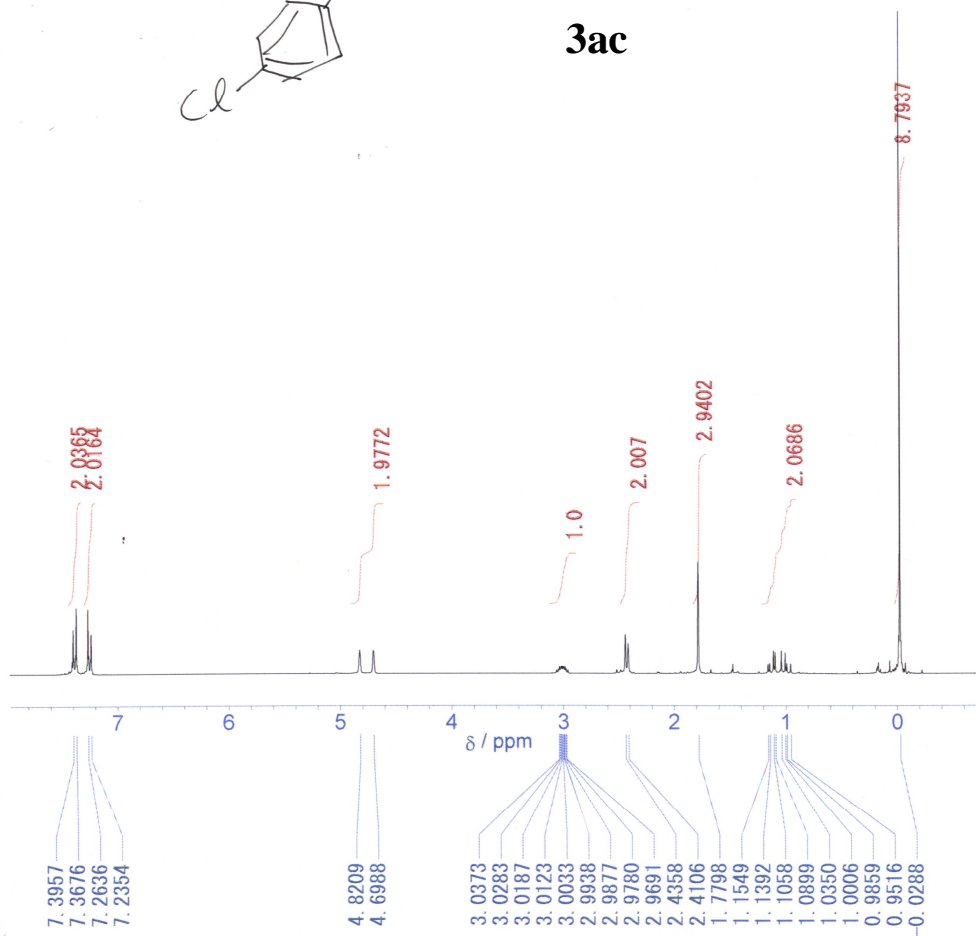


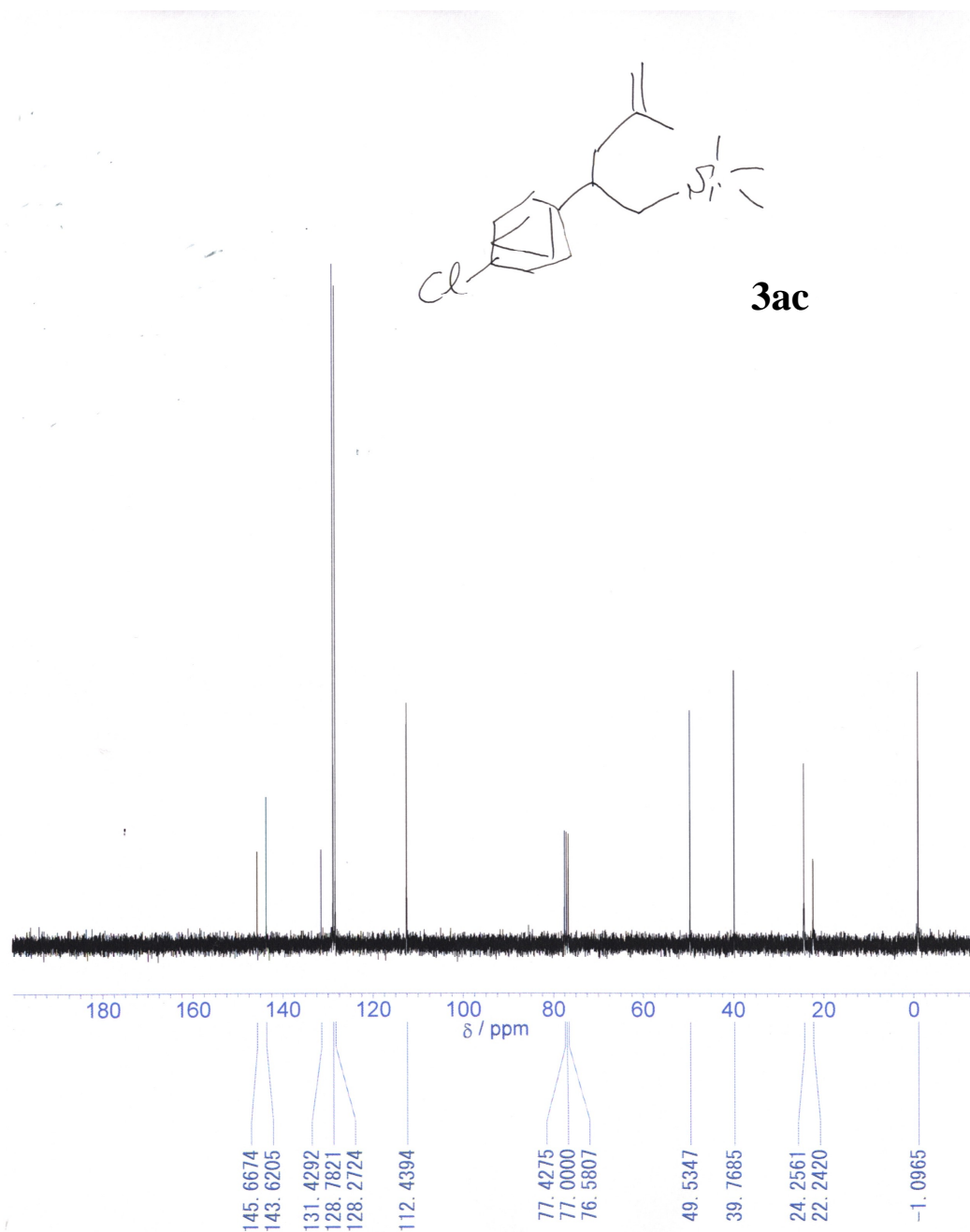
**3da**

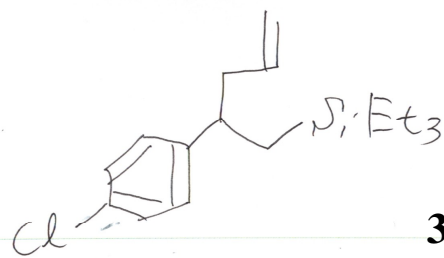




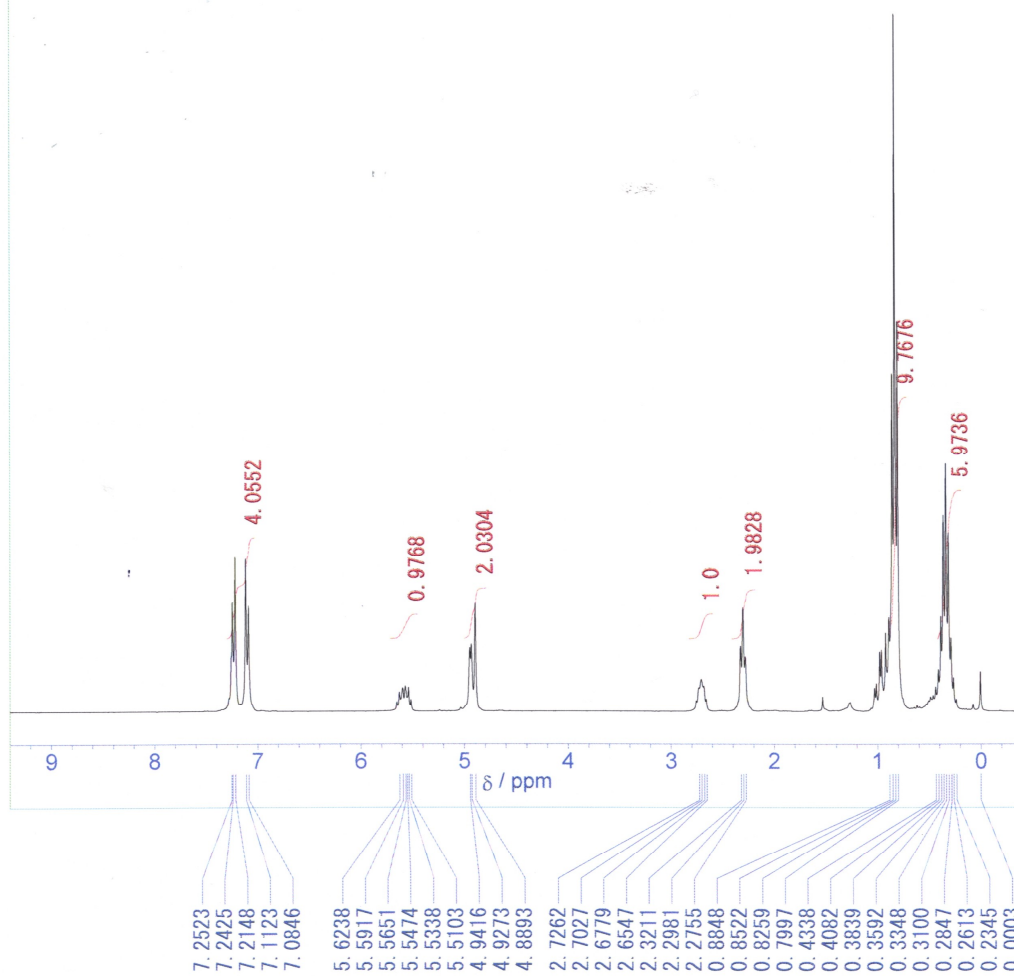
**3ac**



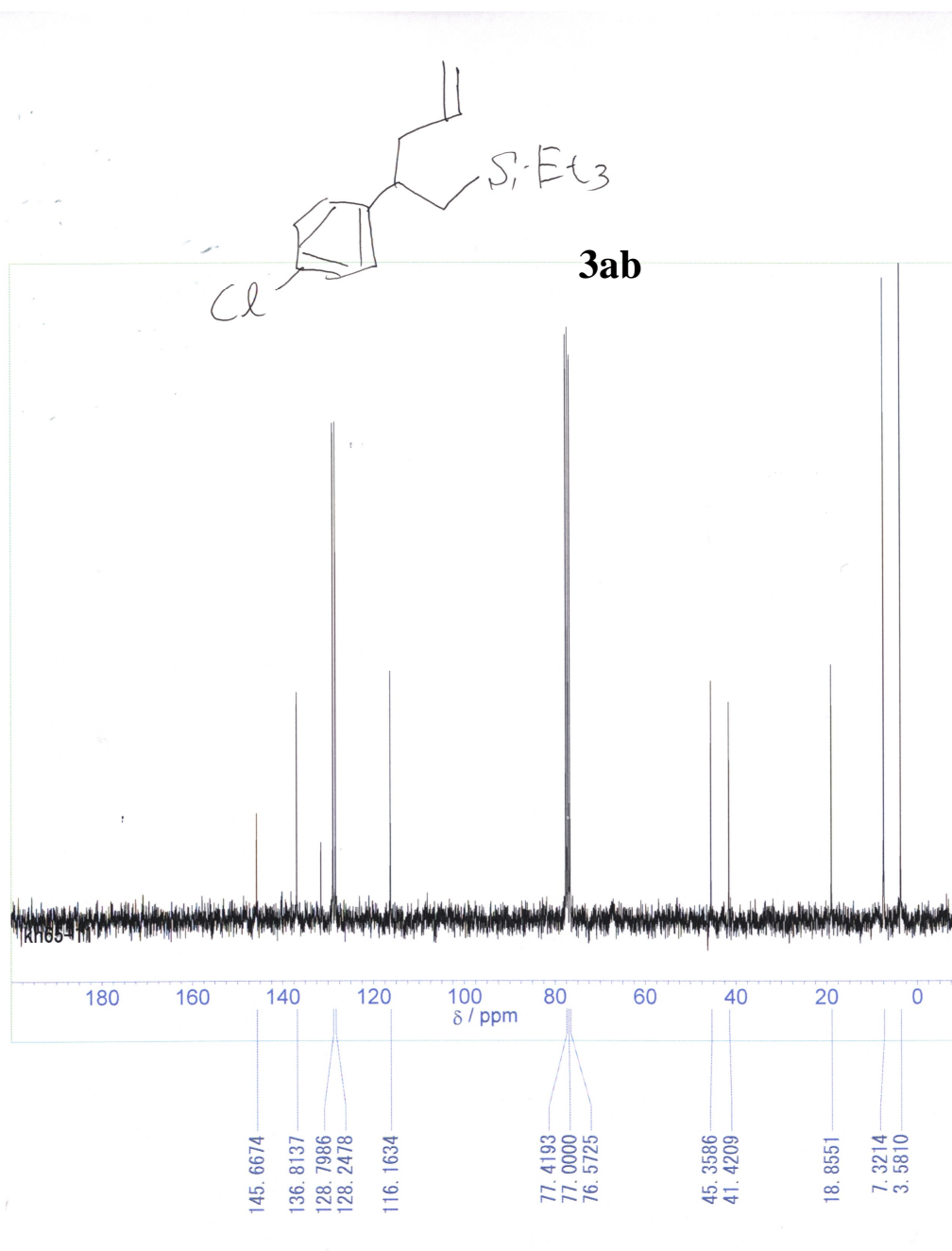


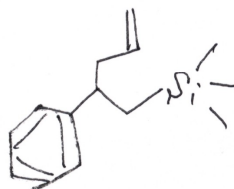


**3ab**

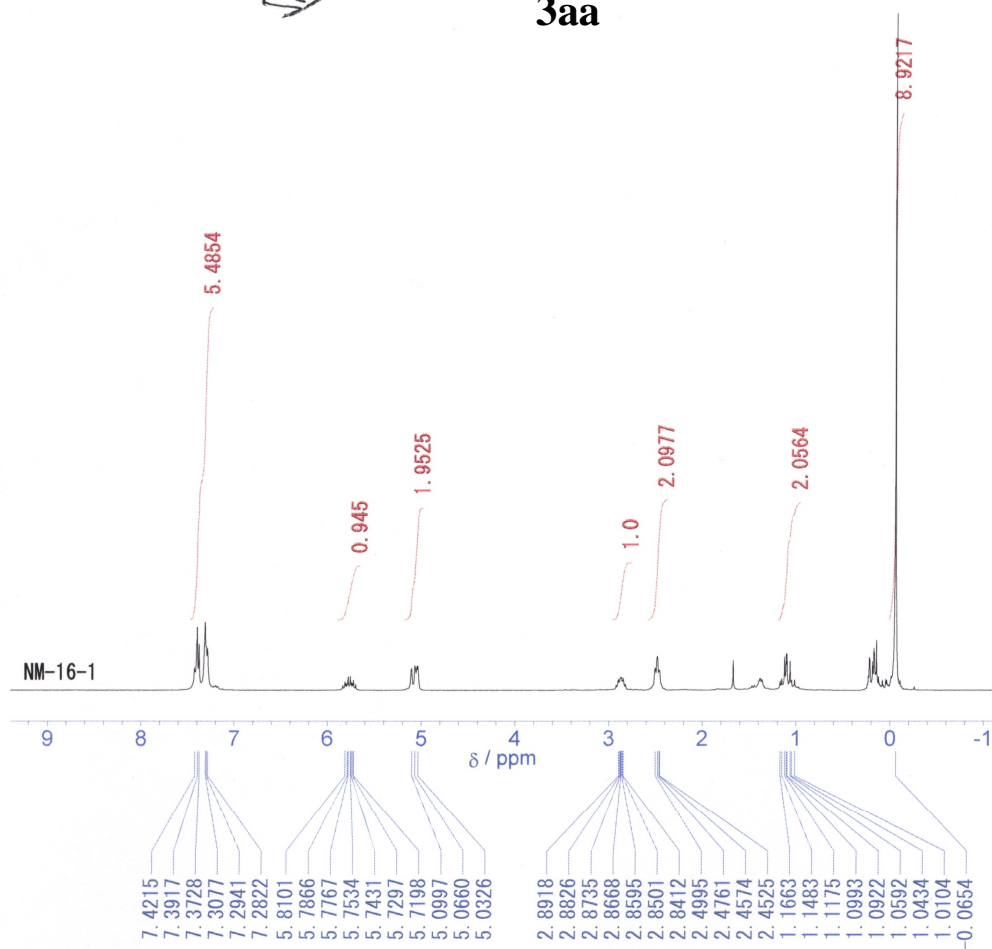


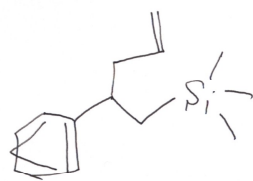




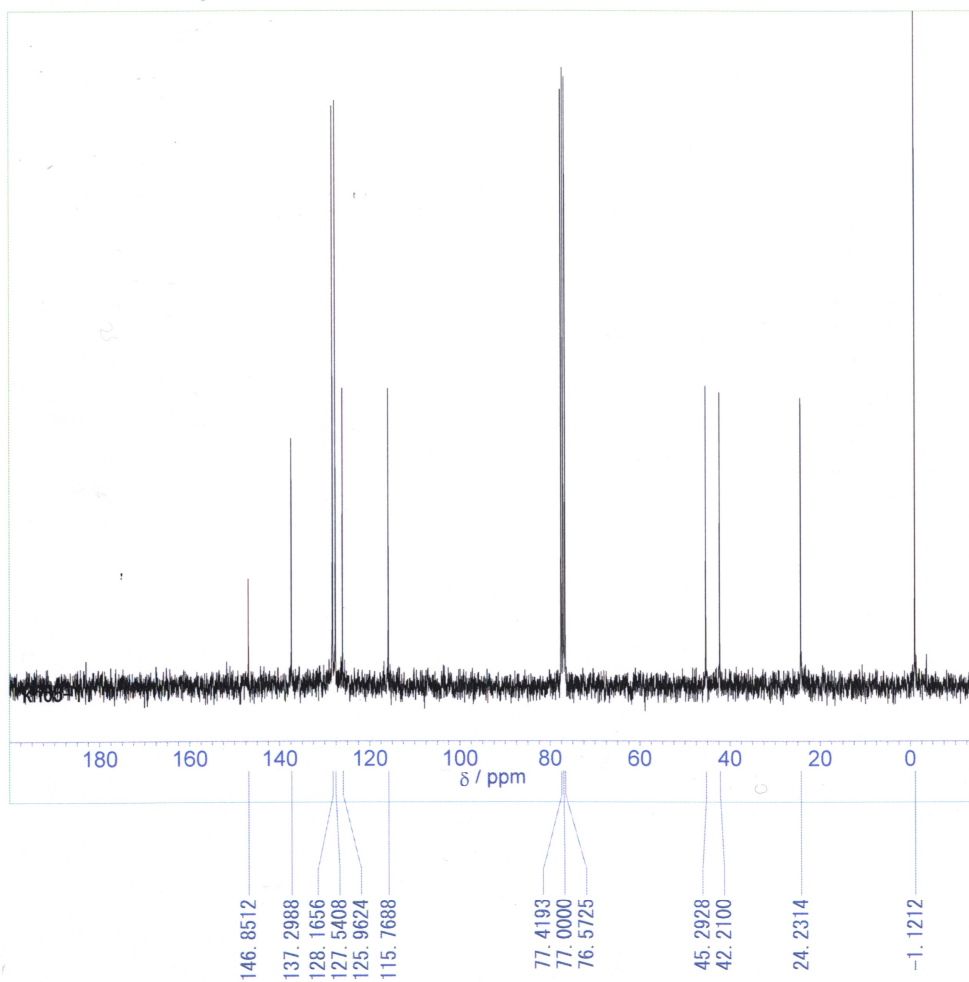


**3aa**

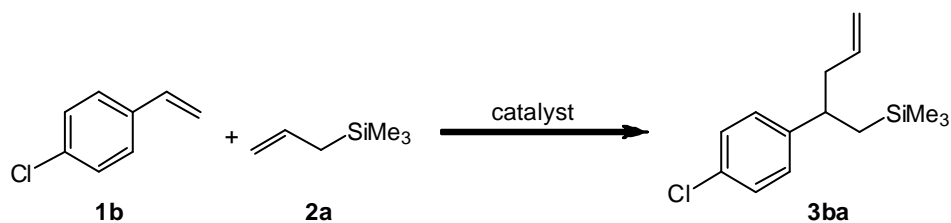




**3aa**



**Table 1S.** Allylsilylation of **1b** with **2a** using Brönsted acids.<sup>[a]</sup>



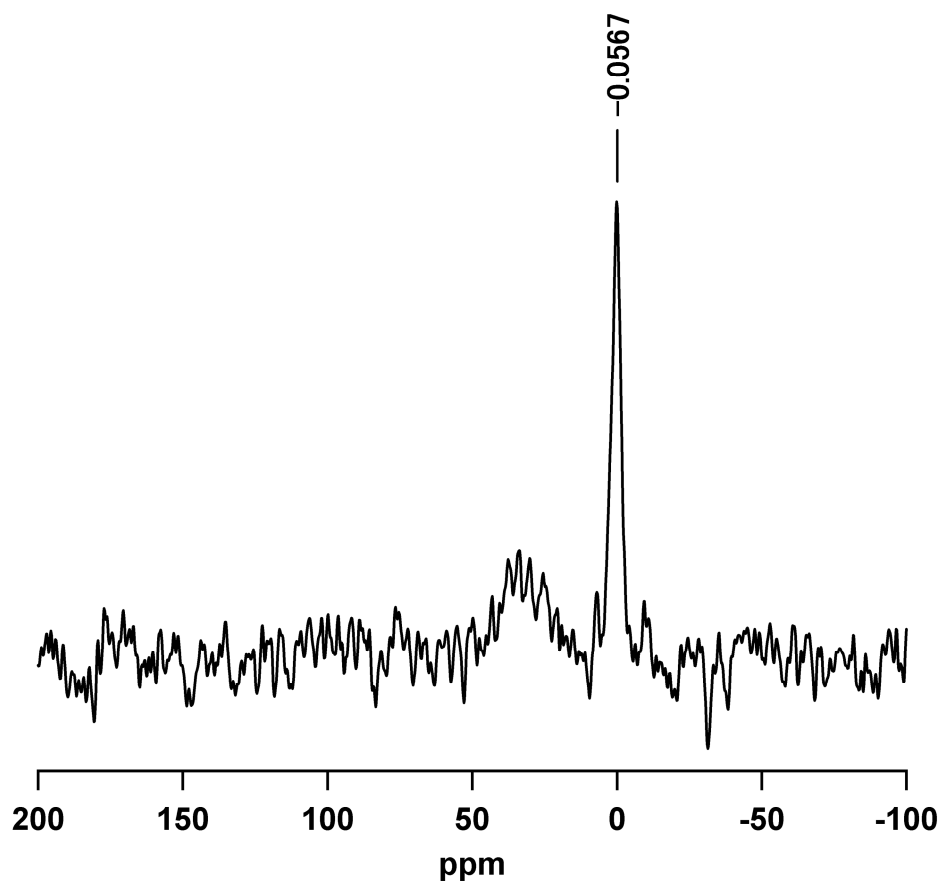
Entry	Brönsted acid	Conversion of <b>1b</b> [%] <sup>[b]</sup>	Conversion of <b>2a</b> [%] <sup>[b]</sup>	Yield of <b>3ba</b> [%] <sup>[b]</sup>
1	H <sup>+</sup> -montmorillonite	99	55	85
2	Mont K10	16	6.5	7.2
3	Na <sup>+</sup> -montmorillonite	20	3.6	<1.0
4	H <sup>+</sup> -ZSM-5	19	4.0	<1.0
5	H <sup>+</sup> -mordenite	6.8	7.5	<1.0
6	Amberlyst	20	25	<1.0
7	CF <sub>3</sub> SO <sub>3</sub> H <sup>[c]</sup>	6.8	13	3.7
8	<i>p</i> -TsOH·H <sub>2</sub> O <sup>[c]</sup>	15	11	<1.0
9	H <sub>2</sub> SO <sub>4</sub> <sup>[c]</sup>	5.4	8.7	<1.0

[a] Reaction conditions: **1b** (1.0 mmol), **2a** (3.0 mmol), catalyst (0.10 g), *n*-heptane (1.0 mL), 100 °C, 30 min.

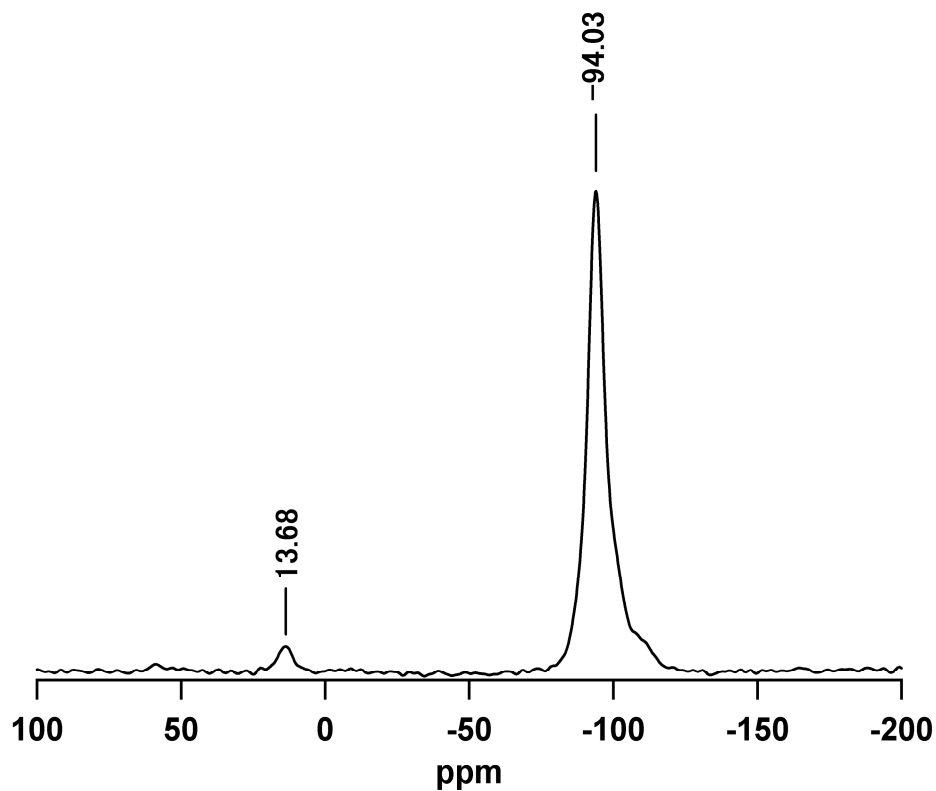
[b] Determined by GC using internal standards. Yield was based on **1a** used.

[c] 0.1 mmol of acid was used.

**Solid-State NMR Analyses for SiMe<sub>3</sub> Species on Montmorillonite Surface:**



**Figure 3S.** Solid-state <sup>13</sup>C CP/MAS NMR spectrum of H<sup>+</sup>-montmorillonite treated with allyltrimethylsilane (SiMe<sub>3</sub>-montmorillonite). The signal at -0.057 ppm is assignable to methoxy group on montmorillonite surface attached by Si-O-Si covalent bonding.



**Figure 4S.** Solid-state  $^{29}\text{Si}$  CP/MAS NMR spectrum of  $\text{H}^+$ -montmorillonite treated with allyltrimethylsilane ( $\text{SiMe}_3$ -montmorillonite). The signal at -13.68 ppm is assignable to methoxy group on montmorillonite surface attached by Si-O-Si covalent bonding. The signal at -94.03 ppm is assignable to silicon atom in montmorillonite silicate layer.

## Reference

- [1] a) K. Motokura, N. Fujita, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Angew. Chem. Int. Ed.* **2006**, 45, 2605; b) K. Motokura, N. Nakagiri, K. Mori, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, *Org. Lett.* **2006**, 8, 4617; c) K. Motokura, N. Nakagiri, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Org. Chem.* **2007**, 72, 6006.
- [2] J. Terao, H. Watabe, H. Watanabe, N. Kambe, *Adv. Synth. Catal.* **2004**, 346, 1674.
- [3] Dewar, M. J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, 108, 8075.
- [4] Kafafi, S. A.; Meot-Ner, M.; Liebman, J. F. *Struct. Chem.* **1989**, 1, 101.
- [5] S.H. Yeon, B.W. Lee, B.R. Yoo, M.-Y. Suk, I.N. Jung, *Organometallics* **1995**, 14, 2361.