Generation of cations from alkoxides allylation of propargyl alcohols

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Supporting information

General Remarks: All reagents were used as received. Column chromatography was performed using silica gel (60 Å, 230–400 mesh, ICN Biomedicals GmbH, Eschwege, Germany). Analytical thin-layer chromatography was performed using 250 μm silica (Analtech, Inc., Newark, DE). ^{1}H NMR and ^{13}C NMR spectra were recorded at 250.13 and 62.89 MHz, respectively. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra were referenced to TMS and measured with respect to the residual protons in the deuterated solvents. Microanalysis was performed by Atlantic Microlab, Inc. Norcross, Georgia.

Typical experimental procedure for preparation of compounds 1a-l, 2a-e and 3: A solution of alcohol (1.5 mmol) in dry dichloromethane (10 mL) was treated with *n*-butyllithium (1.0 mL of a 1.6 *M* solution in hexanes) at 0 °C and the mixture warmed to room temperature. After stirring at room temperature for 30 min, allyltrimethylsilane (1.8 mmol) and boron trichloride (1.5 mL of a 1.0 *M* solution in dichloromethane) were added. The reaction mixture was allowed to stir 10 hours at room temperature. Water (20 mL) was added to quench the reaction. The reaction mixture was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the product purified by silica gel column chromatography.

Product 1a: Known compound.[1]

Product 1b: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.13–7.29 (m, 10H), 5.80–5.91 (m, 1H), 5.03–5.10 (m, 2H), 3.86 (t, J = 7. 01 Hz, 1H), 2.50–2.56 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 139.8, 134.9, 132.5, 131.6, 128.9, 128.5, 128.2, 127.9, 123.4, 117.4, 90.3, 84.1, 42.6, 37.9. Anal. Calcd for $C_{18}H_{15}Cl$: C, 81.04; H, 5.67. Found: C, 80.52; H, 5.53.

Product 1c: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.07–7.44 (m, 8H), 5.79–5.95 (m, 1H), 5.04–5.10 (m, 2H), 3.87 (t, J = 6.97 Hz, 1H), 2.52–2.57 (m, 2H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.9, 137.9, 135.0, 132.5, 131.5, 128.9, 128.7, 128.5, 120.3, 117.3, 89.5, 84.1, 42.6, 37.9, 21.4. Anal. Calcd for $C_{19}H_{17}Cl$: C, 81.27; H, 6.10. Found: C, 80.83; H, 5.82.

Product 1d: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.05–7.53 (m, 9H), 5.81–5.98 (m, 1H), 5.02–5.12 (m, 2H), 4.04 (t, J = 7.07 Hz, 2H), 2.46–2.52 (m, 2H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.5, 135.6, 134.8, 131.6, 130.4, 128.3, 127.7, 126.9, 126.3, 125.6, 124.9, 116.9, 91.3, 83.1, 41.2, 5.0, 19.3. HR-MS Calcd for $C_{19}H_{18}$: 246.1409. Found: 246.1404.

Product 1e: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.07–7.58 (m, 8H), 5.88–6.02 (m, 1H), 5.05–5.16 (m, 2H), 4.08 (t, J = 7.03 Hz, 2H), 2.50–2.56 (m, 2H), 2.37 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.7, 137.7, 135.7, 134.7, 131.5, 130.4, 128.9, 127.7, 126.7, 126.3, 116.9, 90.5, 83.1, 41.3, 35.0, 21.4, 19.3. Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.62.

Product 1f: ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.81–7.58 (m, 8H), 5.89–6.03 (m, 1H), 5.07–5.17 (m, 2H), 4.09 (t, J = 7.07 Hz, 2H), 3.80 (s, 3H), 2.46–2.60 (m, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.5, 135.6, 130.5, 129.2, 127.6, 126.8, 126.3, 124.8, 124.2, 117.0, 116.6, 114.3, 91.2, 83.0, 55.2, 41.2, 35.0, 19.3. Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.39; H, 7.25.

Product 1g: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.24–7.66 (m, 5H), 6.68 (s, 2H), 5.87–5.97 (m, 1H), 5.08–5.18 (m, 2H), 3.82–4.02 (m, 7H), 3.68 (s, 3H), 2.56–2.61 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 153.1, 137.1, 135.4, 131.6, 128.5, 128.2, 127.8, 123.5, 117.1, 104.6, 90.8, 83.9, 60.8, 56.1, 42.7, 38.8. Anal. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88. Found: C, 78.14; H, 6.71.

Product 1h: ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.99–7.37 (m, 4H), 6.64 (s, 2H), 5.84–5.97 (m, 1H), 5.09–5.18 (m, 2H), 3.63–3.91 (m, 7H), 3.61 (s, 3H), 2.56–2.61 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 164.3,

160.4, 153.2, 136.9, 135.5, 131.5, 129.8, 129.7, 127.4, 118.2, 117.2, 116.8, 115.4, 115.0, 105.7, 91.9, 82.8, 60.8, 56.1, 42.5, 38.8. HR-MS Calcd for $C_{21}H_{21}FO_3$: 340.1475. Found: 340.1469.

Product 1i: ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.98–7.45 (m, 9H), 5.83–5.94 (m, 1H), 5.05–5.13 (m, 2H), 3.89 (t, J = 7.00 Hz, 2H), 2.53–2.85 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 163.7, 159.8, 135.2, 131.6, 129.1, 129.0, 128.6, 128.5, 128.2, 127.9, 127.1, 123.5, 117.3, 115.4, 115.1, 90.7, 84.0, 42.8, 37.8. HR-MS Calcd for $C_{18}H_{15}F$: 250.1158. Found: 250.1150.

Product 1j: ^{1}H NMR (250 MHz, $CDCl_3$): δ. 7.11–7.34 (m, 4H), 5.73–5.84 (m, 1H), 4.91–5.06 (m, 2H), 3.52-3.64 (m, 1H), 2.23–2.45 (m, 2H), 2.15–2.21 (m, 2H), 1.37–1.55 (m, 4H), 0.91 (t, J = 6.53 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 140.6, 135.3, 132.3, 128.9, 128.4, 116.9, 84.1, 80.6, 42.9, 37.4, 31.1, 21.9, 18.4, 13.6. Anal. Calcd for $C_{16}H_{19}Cl$: C, 77.87; H, 7.76. Found: C, 77.35; H, 7.64.

Product 1k: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.24–7.43 (m, 9H), 4.77-4.84 (m, 2H), 3.93–3.99 (m, 2H), 2.46–2.54 (m, 2H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.1, 140.3, 132.5, 131.6, 128.8, 128.5, 128.2, 127.8, 123.5, 113.4, 90.6, 83.9, 46.8, 36.7, 22.4. Anal. Calcd for $C_{19}H_{17}Cl$: C, 81.27; H, 6.10. Found: C, 81.03; H, 5.99.

Product 1l: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.07–7.37 (m, 8H), 4.75–4.83 (m, 2H), 3.93–3.99 (m, 2H), 2.39-2.59 (m, 2H), 2.32 (s, 3H), 1.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 142.2, 140.5, 137.9, 132.4, 131.5, 128.9, 128.8, 128.5, 113.3, 89.9, 83.9, 46.9, 36.8, 22.5, 21.4. Anal. Calcd for $C_{20}H_{19}Cl$: C, 81.48; H, 6.50. Found: C, 81.31; H, 6.36.

Product 2a: Known compound.[2]

Product 2b: Known compound.[3]

Product 2c: Known compound.[4]

Product 2d: Known compound.[2]

Product 2e: Known compound.[5]

Product 5: Known compound.[6]

The NMR study of reaction of allyltrimethylsilane with boron trichloride: A mixture of allyltrimethylsilane and boron trichloride (1.0 *M* solution in dichloromethane) was kept at room temperature for 6 hours. No reaction occurred as evidenced by the ^{1}H NMR (see attached).

Typical experimental procedure to preparation of compounds 6a-c and 7a-c: A solution of alcohol (1.5 mmol) in dry dichloromethane (10 mL) was treated with *n*-butyllithium (1.0 mL of a 1.6 *M* solution in hexanes) at 0 °C and subsequently warmed to room temperature. After stirring at room temperature for 30 min, phenylacetylene (1.8 mmol) and boron trichloride (1.5 mmol) were added at 0 ^{o}C. The reaction mixture was allowed to stir for 10 hours at room temperature. Water (20 mL) was added to quench the reaction. The reaction mixture was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the product purified by silica gel column chromatography.

Product 6a: Known compound.[7]

Product 7a: Known compound.[8]

Product 6b: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.11–7.36 (m, 9H), 6.73–6.81 (m, 2H), 6.57–6.65 (m, 2H), 6.38 (d, J = 10.8 Hz, 1H), 4.67 (d, J = 11.4 Hz, 1H), 4.20–423 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 138.1, 137.9, 137.7, 136.7, 131.4, 128.8, 128.6, 128.3, 128.0, 126.9, 121.0, 117.3, 116.9, 64.4, 64.3, 49.9. HR-MS Calcd for $C_{18}H_{18}O_2$: 266.1307. Found: 266.1295.

Product 6c: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.00–7.61 (m, 13H), 6.50 (d, J = 10.5 Hz, 1H), 4.73 (d, J = 10.8 Hz, 1H).

Product 7c: Known compound.[8]

Literatures:

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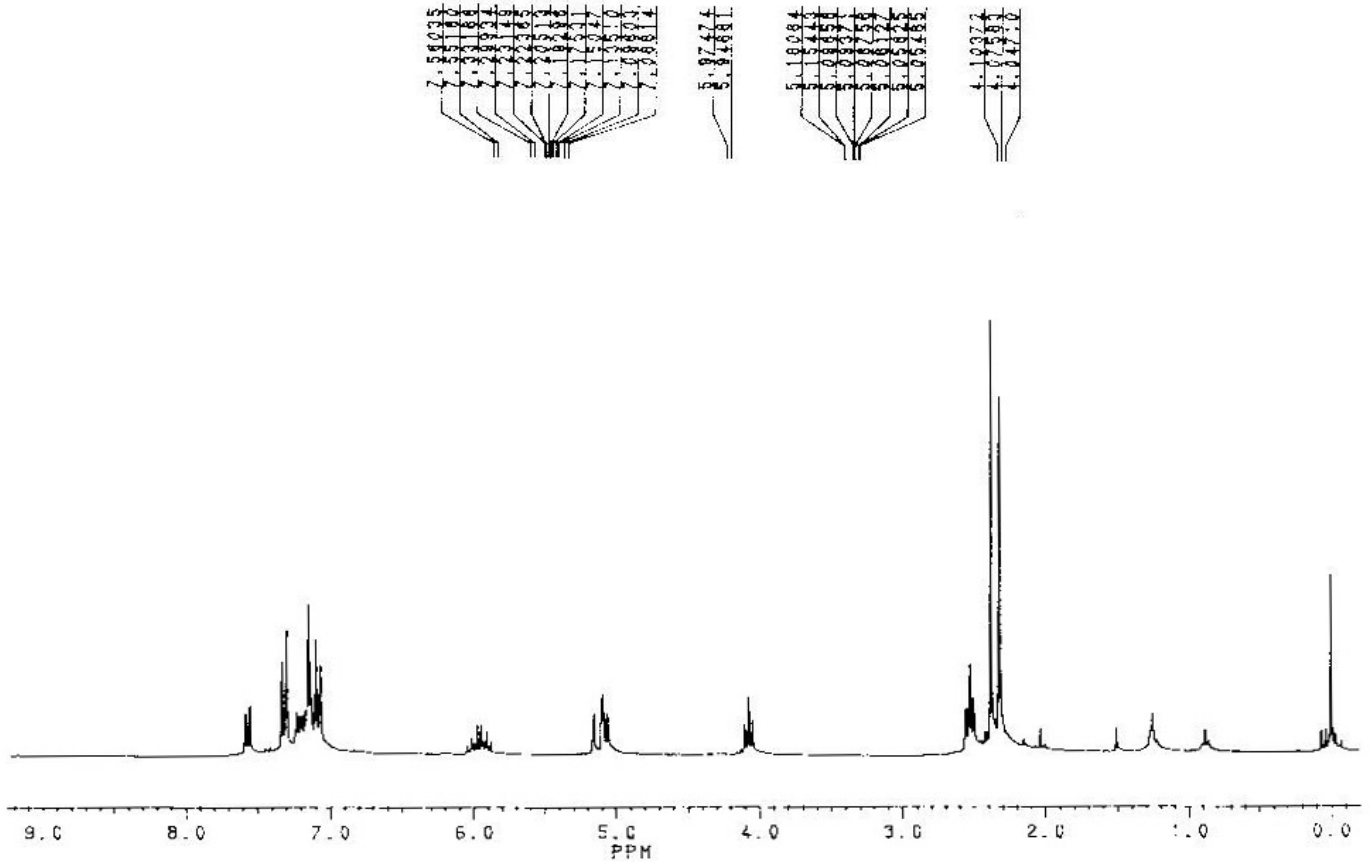
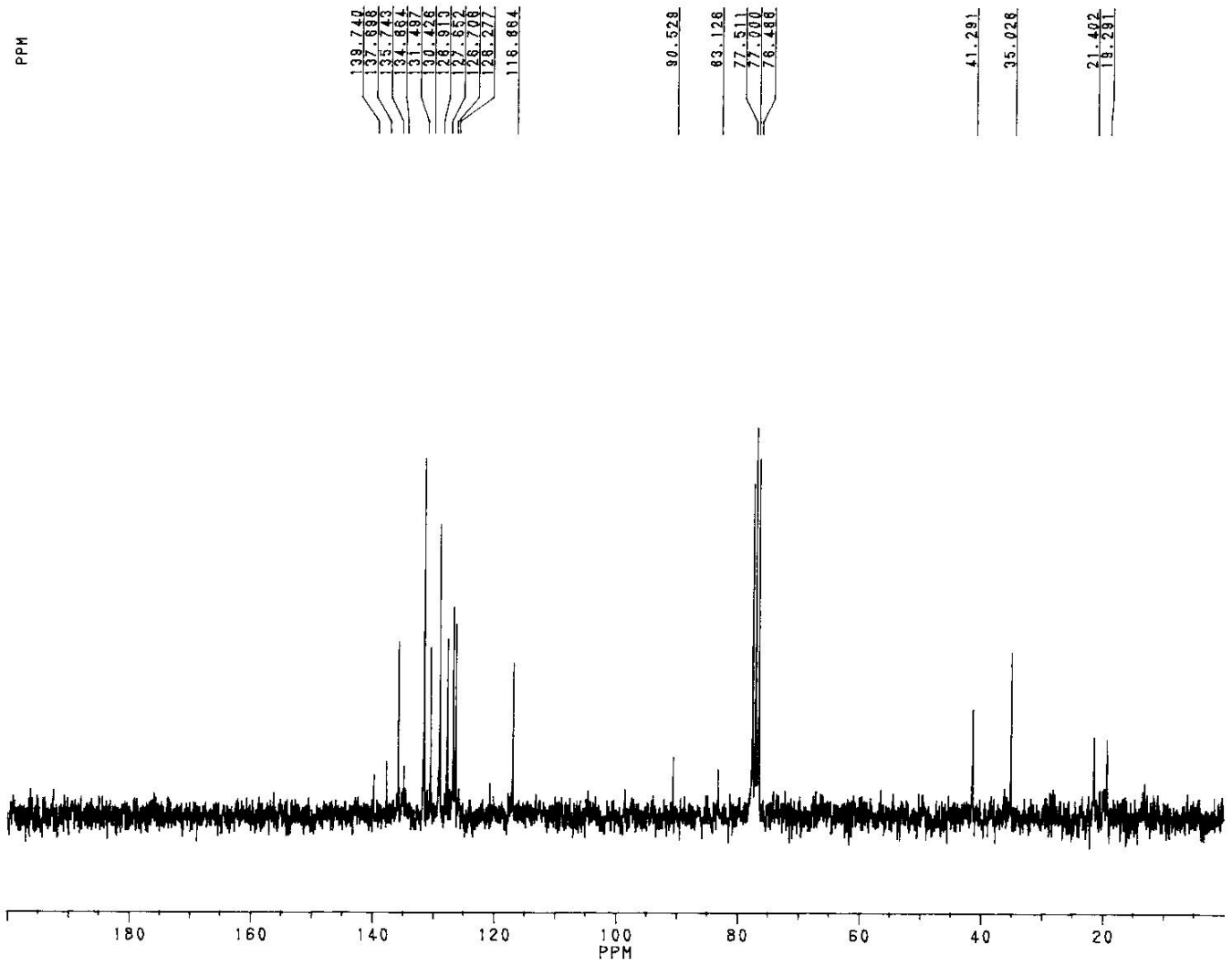
^{1}H NMR of 1e



^{13}C NMR of 1e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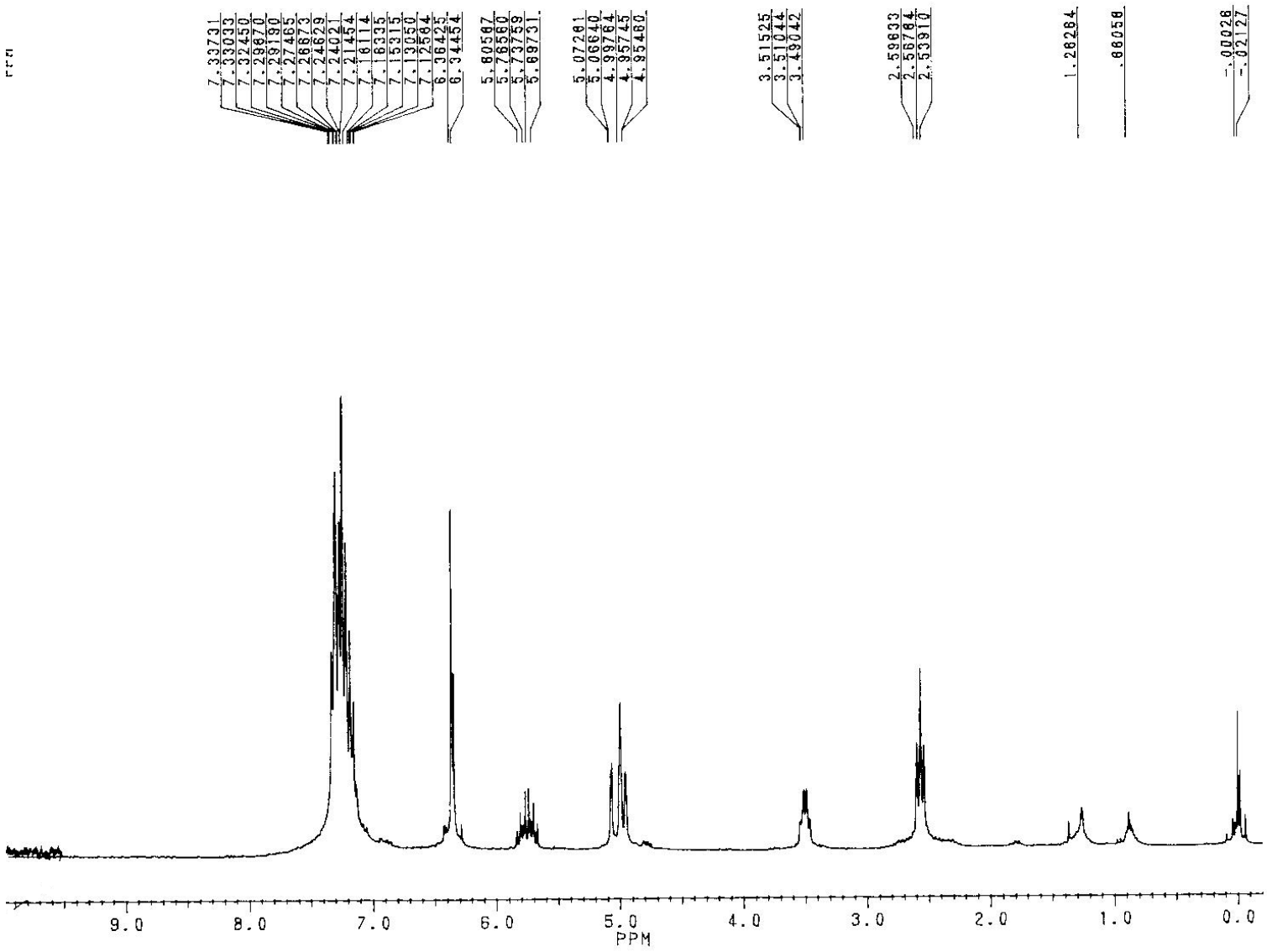
[1] H NMR of 2e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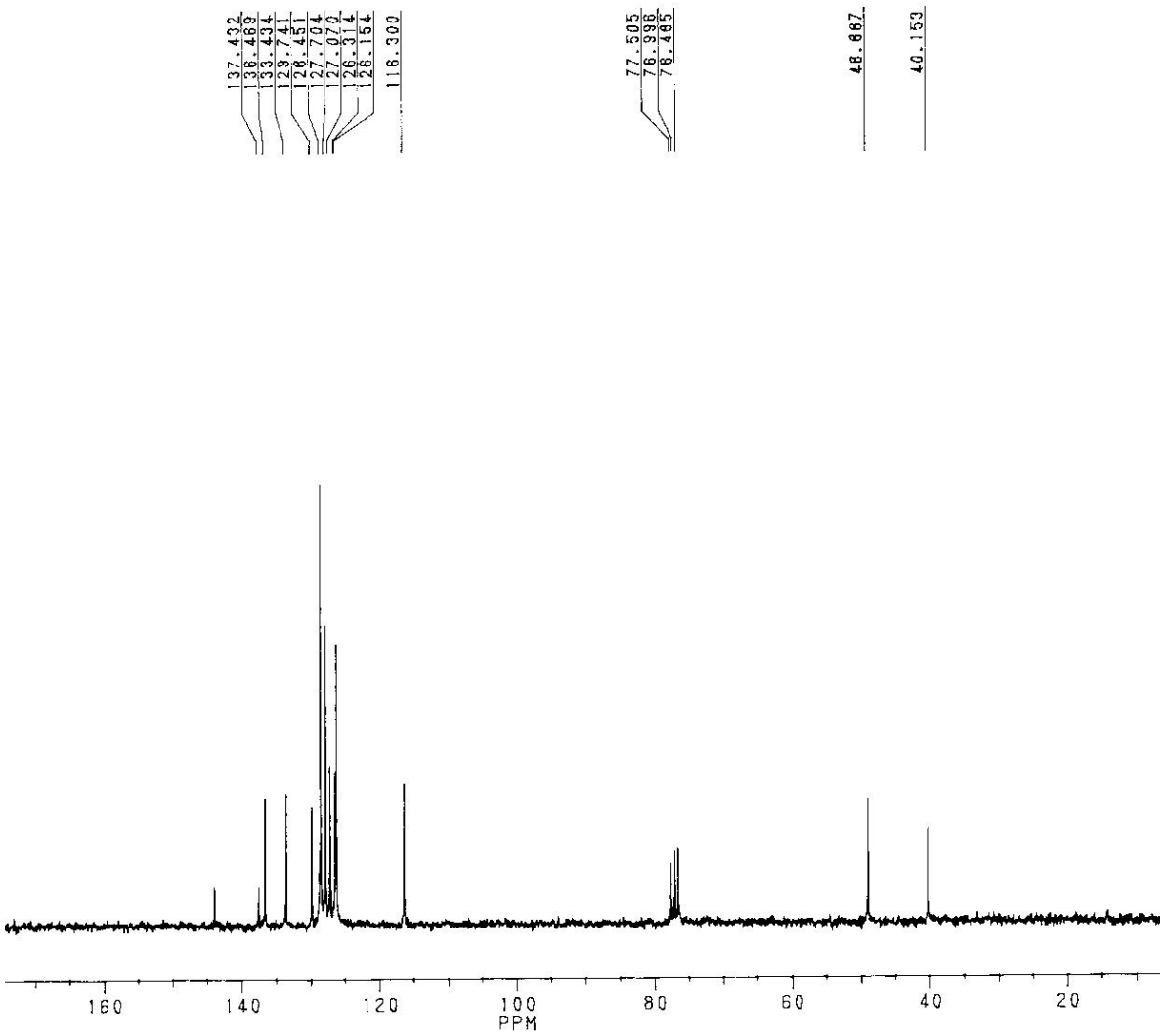
`^{13}C NMR of 2e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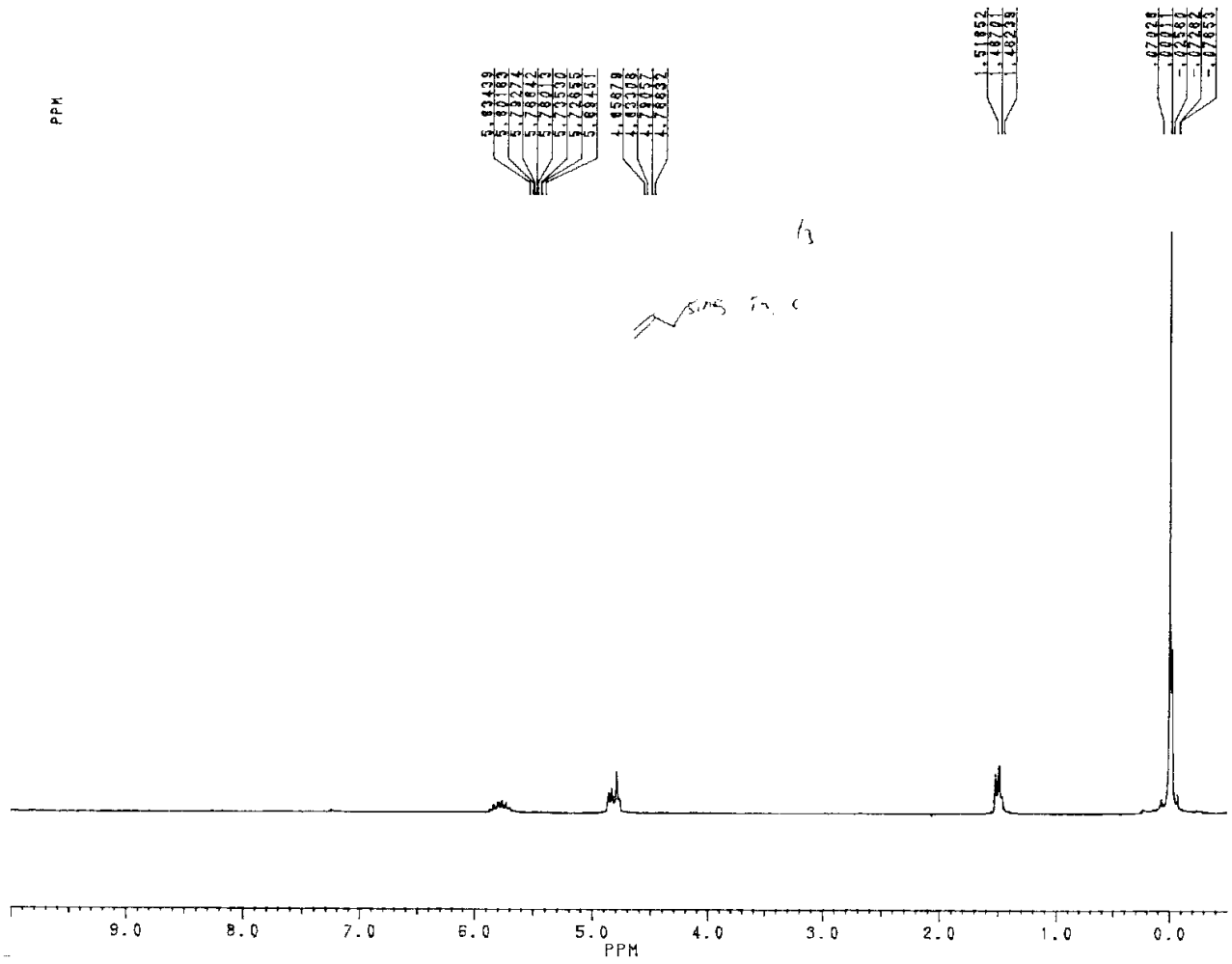
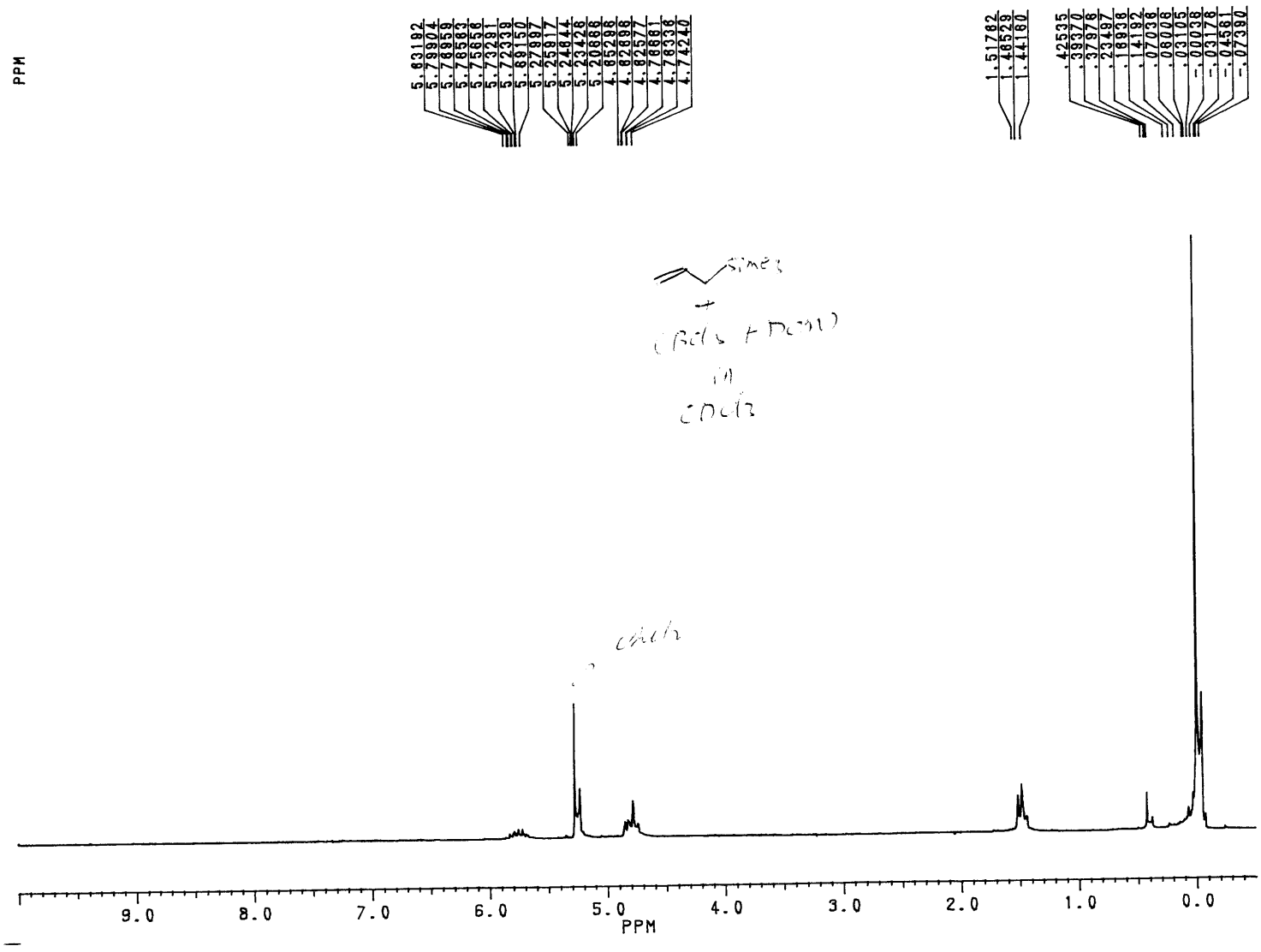
PPM

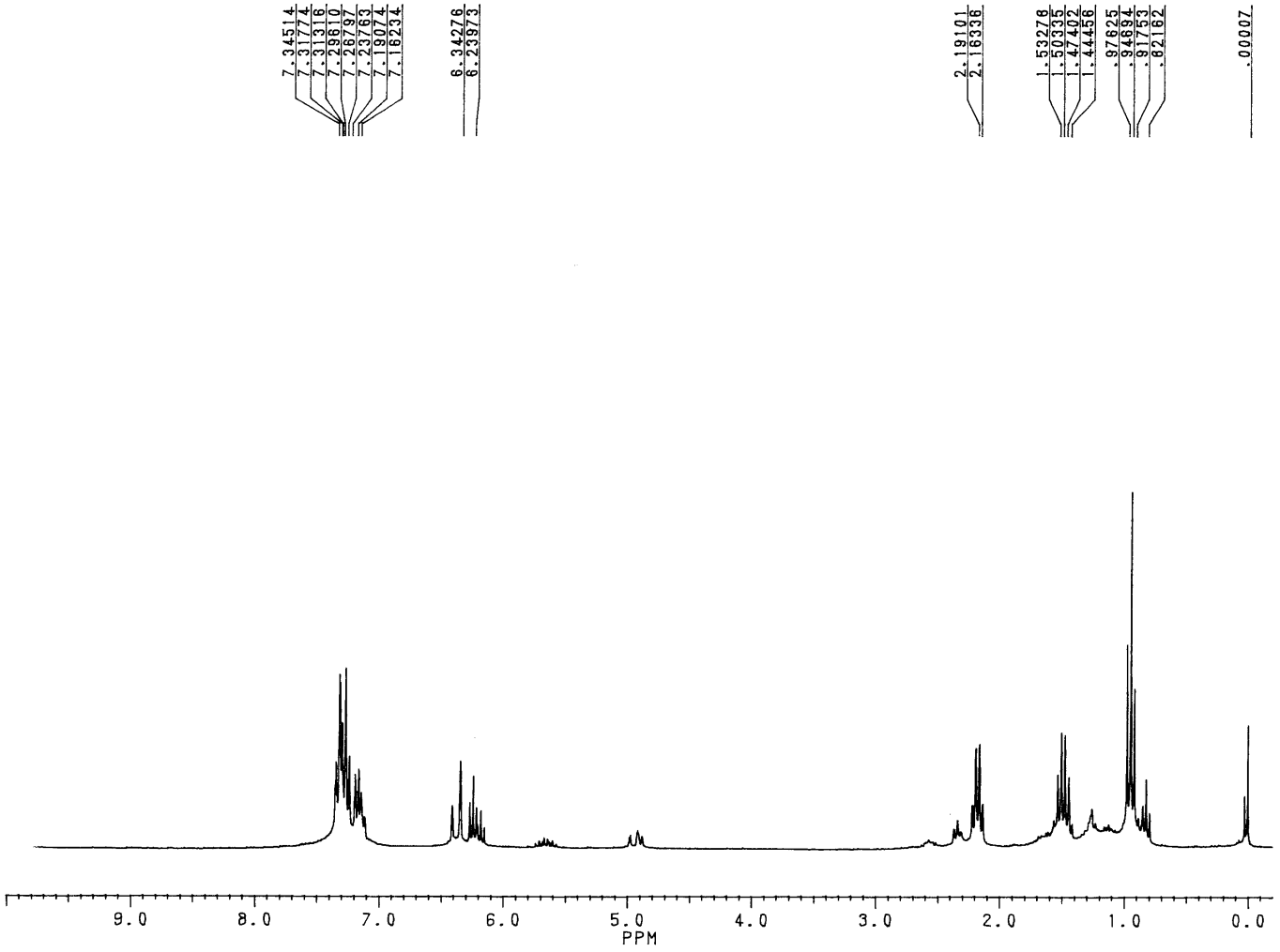
^{1}H NMR of Allyltrimethylsilane



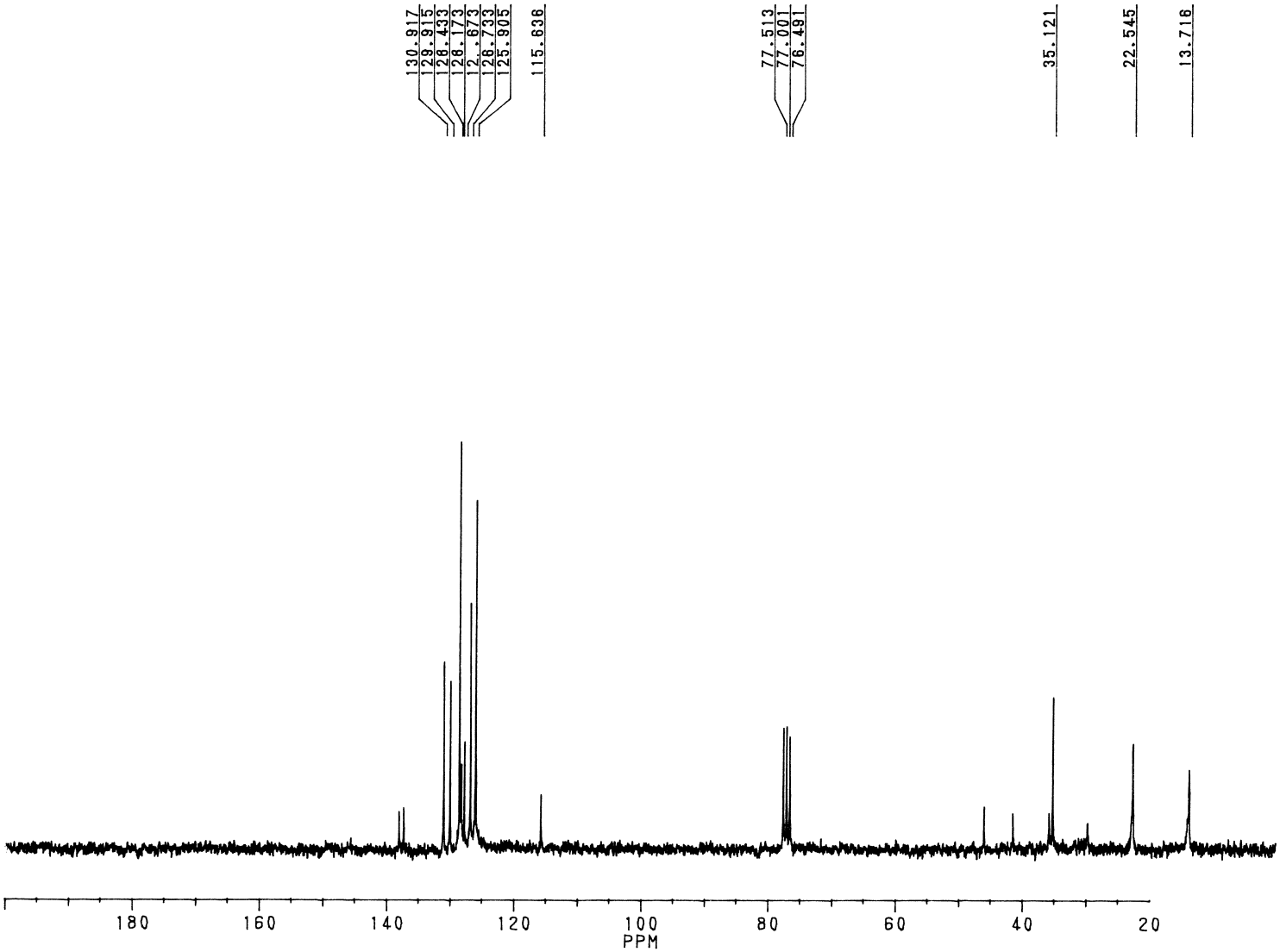
^{1}H NMR of reaction of allyltrimethylsilane with boron trichloride (after 6 hours standing)



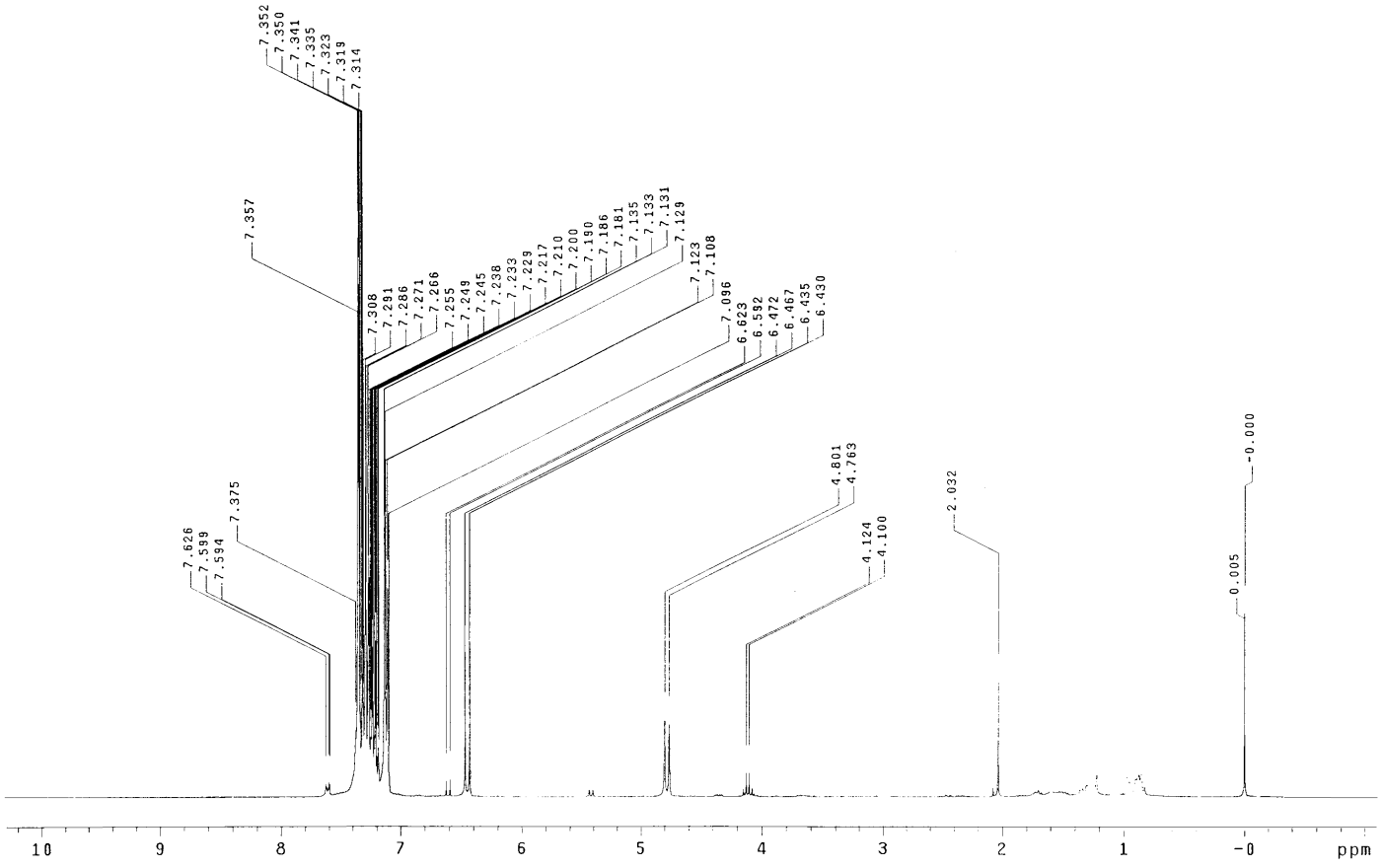
^{1}H- NMR spectrum of inseparable products 3 and 4



^{13}C-NMR spectrum of inseparable products 3 and 4



^{1}H NMR spectrum of inseparable products 6a and 7a



^{13}C NMR spectrum of inseparable products 6a and 7a