Re-revised

Supporting Information

Lewis Acid Catalyzed Stereoselective Carbosilylation. Intramolecular *trans*-Vinylsilylation and *trans*-Arylsilylation of Unactivated Alkynes

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Table 1. Lewis Acid-Catalyzed Carbocyclization of **8**[a]

Entry	Substrate **8** n		Lewis acid (equiv)		Solvent		Yield (%)[b]
1	1	**8a**	$HfCl_4$	(0.1)	CH_2Cl_2	**9a**	48[c]
2	1	**8a**	$HfCl_4$	(0.2)	CH_2Cl_2	**9a**	70[c]
3	1	**8a**	$HfCl_4$	(0.5)	CH_2Cl_2	**9a**	63[c]
4	1	**8a**	$HfCl_4$	(1.0)	CH_2Cl_2	**9a**	-
5	1	**8a**	$HfCl_4$	(0.2)	toluene	**9a**	74[c]
6	1	**8a**	$HfCl_4$	(0.2)	$(ClCH_2)_2$	**9a**	23
7	1	**8a**	$HfCl_4$	(0.2)	hexane	**9a**	trace
8	1	**8a**	$ZrCl_4$	(0.2)	toluene	**9a**	16
9	1	**8a**	$AlCl_3$	(0.2)	toluene	**9a**	26
10	2	**8b**	$EtAlCl_2$	(0.2)	CH_2Cl_2	**9b**	45

[a]Reactions were conducted at -78° to 10°C for 1h. The reaction was quenched by adding excess amounts of Et_2NH and saturated aq. $NaHCO_3$ solution at 10°C. [b]Isolated yield. [c]Trace amounts of **10** were obtained.

(*E*)-1,1-Dimethyl-5-styryl-1,2,3,4-tetrahydro-siline (4b). Colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.43-7.16 (m, 5H), 6.78 (d, J = 16.5 Hz, 1H), 6.58 (d, J = 16.5 Hz, 1H), 5.83 (s, 1H), 2.38 (t, J = 6.0 Hz, 2H), 1.90 (tt, J = 6.0, 6.6 Hz, 2H), 0.69 (m, 2H), 0.10 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 154.5, 137.6, 135.2, 130.0, 128.6, 127.3, 127.0, 126.5, 29.5, 21.3, 11.7, -1.78. IR (neat) 3028-2855, 1598, 1558, 1246, 841 cm^{-1}. MS (EI) *m/z* 228 (M^+, 100), 213 (M^+ - CH_3, 51). HRMS calcd for $C_{15}H_{20}Si$ 228.1334, found 228.1338.

(*E*)-1,1-Dimethyl-5-propenyl-1,2,3,4-tetrahydro-siline (4c). Colorless oil: ^1H NMR ($CDCl_3$, 500 MHz) δ 5.85 (d, J = 11.7 Hz, 1H), 5.53 (s, 1H), 5.48 (dq, J = 11.7, 7.0 Hz, 1H), 2.16 (t, J = 5.3 Hz, 2H), 1.80 (m, 2H), 1.79 (dd, J = 2.0, 7.0 Hz, 3H), 0.63 (m, 2H), 0.07 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 155.1, 135.1, 125.5, 124.9, 34.4, 21.7, 15.0, 11.5, 1.57. IR (neat) 2953-2855, 1587, 1454, 1429, 1250, 839 cm^{-1}. MS (EI) *m/z* 166 (M^+, 70), 151 (M^+ -

CH_3, 100). HRMS calcd for $C_{10}H_{18}Si$ 166.1178, found 166.1190. Anal. calcd for $C_{10}H_{18}Si$: C, 72.21; H, 10.91. found: C, 72.60; H, 10.81.

***(E)*-(1-Trimethylsilyl) methylene-3,4-Dihydro-2*H*-naphthalene (9a):** colorless oil: ^1H NMR (C_6D_6, 300 MHz) δ 7.72-7.65 (m, 1H), 7.08-7.01 (m, 2H), 6.70-6.90 (m, 1H), 2.60-2.45 (m, 4H), 1.69-1.58 (m, 2H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 152.4, 137.6, 137.0, 129.3, 127.9, 126.3, 125.1, 121.7, 32.5, 30.5, 24.0, 0.3. IR (neat) 3061, 3015, 2953, 2864, 2837, 1609, 1589, 1566, 1485, 1454, 1248, 903, 849, 758 cm^{-1}. HRMS calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1357.

***(E)*-5-(1-Trimethylsilyl) methylene-6,7,8,9-tetrahydro-benzocycloheptene (9b):** colorless oil: ^1H NMR (C_6D_6, 300 MHz) δ 7.25-7.18 (m, 1H), 7.06-6.98 (m, 2H), 6.93-6.89 (m, 1H), 5.60 (s, 1H), 2.58 (m, 2H), 2.39 (m, 2H), 1.67-1.48 (m, 4H), 0.16 (s, 9H). ^{13}C NMR (C_6D_6, 75.45 MHz) δ 139.0, 128.9, 128.7, 128.1, 127.8, 127.8, 127.3, 126.6, 36.2, 35.3, 30.8, 27.7, 0.3. IR (neat) 3063, 3015, 2926, 2855, 1601, 1479, 1445, 1248, 866, 854, 839, 758cm^{-1}. HRMS calcd for $C_{15}H_{22}Si$ 230.1490, found 230.1508.

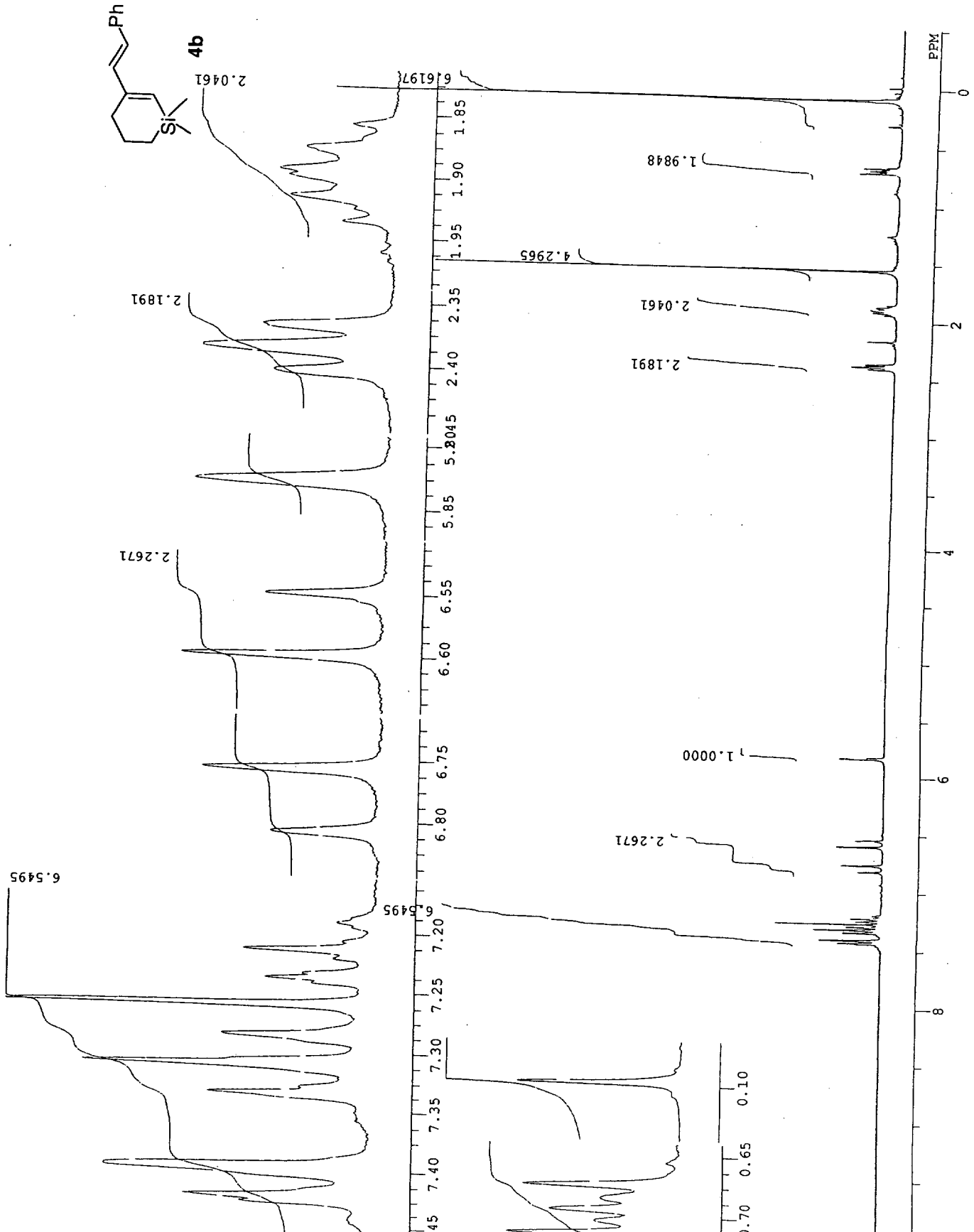
5-Trimethylsilyl-1-(1-trimethylsilylmethylene)-1,2,3,4-tetrahydro-naphthalene (10): colorless oil: ^1H NMR (C_6D_6, 300 MHz) δ 7.61 (d, J = 8.2 Hz, 1H), 7.30 (m, 1H), 6.98 (m, 1H), 6.05 (s, 1H), 2.67 (t, J = 6.5 Hz, 2H), 2.40 (dt, J = 6.5, 1.6 Hz, 2H), 1.57 (tt, J = 6.5, 6.5 Hz, 2H), 0.15 (s, 9H), 0.12 (s, 9H). ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 138.2, 134.6, 128.4, 128.1, 127.8, 126.9, 122.4, 32.2, 31.6, 24.1, 0.3 (x2); IR (neat) 3053, 2953, 1591, 1406, 1248, 849, 787, 754 cm^{-1}. HRMS calcd for $C_{17}H_{28}Si_2$ 288.1729, found 288.1739.

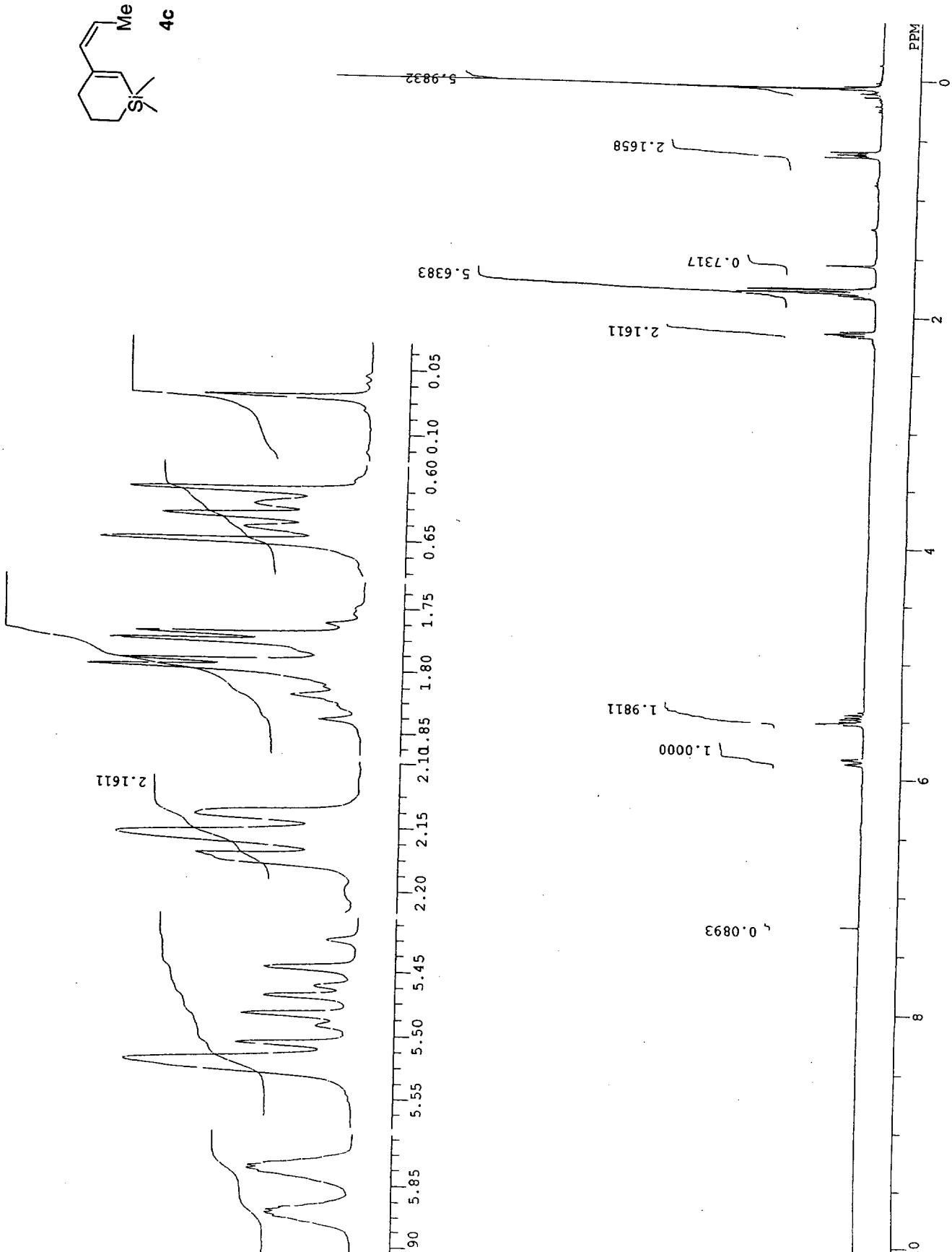
1,1-Dimethyl-3-phenylsilacyclopent-2-ene (14a): colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (m, 2H), 7.36-7.23 (m, 3H), 6.35 (s, 1H), 2.95-2.87 (m, 2H), 0.98-0.90 (m, 2H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.45 MHz) 161.2, 139.8, 128.2, 127.7, 126.2, 125.9, 32.6, 10.1, -0.9. IR (neat) 3084, 3057, 3024, 2951, 2905, 1558, 1493, 1445, 1246, 1190, 862, 843, 783, 756 cm^{-1}. HRMS calcd for $C_{12}H_{16}Si$ 188.1022, found 188.1011.

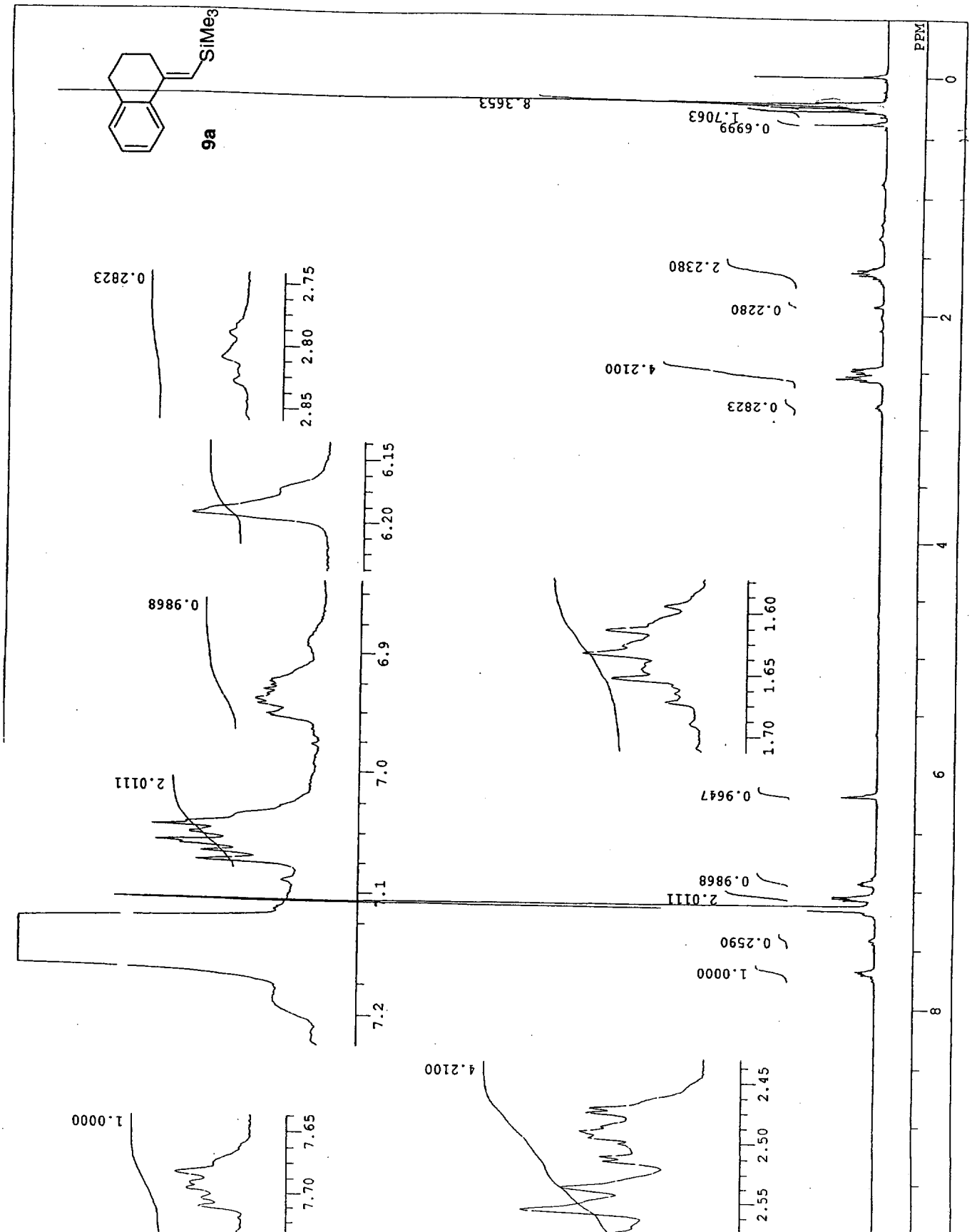
1,1-Dimethyl-3-(4-methylphenyl)silacyclopent-2-ene (14b): colorless oil. ^1H NMR (C_6D_6, 300 MHz) δ 7.57 (d, J = 7.6 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 6.49 (s, 1H), 3.00-2.92 (m, 2H), 2.24 (s, 3H), 1.01-0.95 (m, 2H), 0.31 (s, 6H). ^{13}C NMR (C_6D_6, 75.45 MHz) δ 161.9, 137.6, 137.5, 129.2, 126.3, 124.8, 33.0, 21.1, 10.2, -0.8. IR (neat) 3022, 2951, 2900, 1553, 1510, 1439, 1408, 1246, 1186, 862, 842, 802, 785 cm^{-1}. HRMS calcd for $C_{13}H_{18}Si$ 202.1178, found 202.1195.

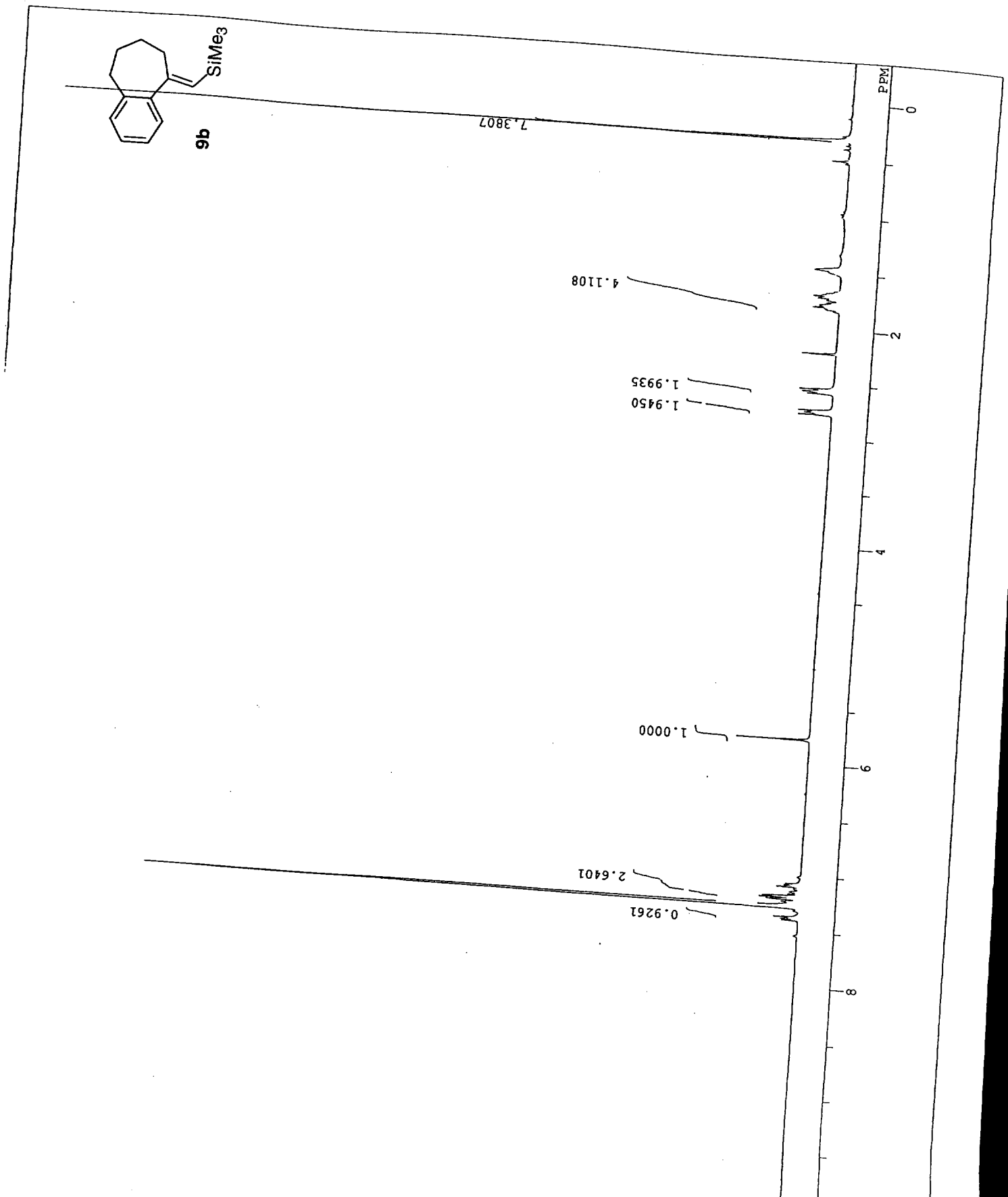
1,1-Dimethyl-3-(2-methylphenyl)silacyclopent-2-ene (14c): colorless oil: ^1H NMR (C_6D_6, 300 MHz) δ 7.26-7.13 (m, 4H), 5.96 (s, 1H), 2.86-2.79 (m, 2H), 2.33 (s, 3H), 1.00-0.94 (m, 2H), 0.31 (s, 6H). ^{13}C NMR (C_6D_6, 75.45 MHz) δ 134.2, 130.5, 129.2, 128.1, 127.9, 127.5, 127.1, 125.8, 36.7, 20.1, 10.7, -0.8. IR (neat) 2953, 2924, 1578, 1483, 1246, 1182, 860, 843, 785, 758, 746 cm^{-1}. HRMS calcd for $C_{13}H_{18}Si$ 202.1178, found 202.1152.

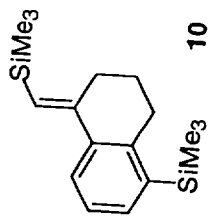
1,1-Dimethyl-3-phenylsilacyclohex-2-ene (14d): colorless oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.38-7.32 (m, 2H), 7.20-7.06 (m, 3H), 6.07 (s, 1H), 2.39 (td, J = 6.0, 1.6 Hz, 2H), 1.87-1.78 (m, 2H), 0.68-0.62 (m, 2H), 0.13 (s, 6H). ^{13}C NMR ($CDCl_3$, 125.65 MHz) δ 157.2, 145.1, 128.1, 127.2, 125.4, 124.5, 33.0, 22.0, 11.3, -1.6. IR (neat) 2953, 2907, 2853, 1591, 1570, 1493, 1442, 1246, 1138, 918, 862, 845, 795, 752 cm^{-1}. HRMS calcd for $C_{13}H_{18}Si$ 202.1178, found 202.1189.



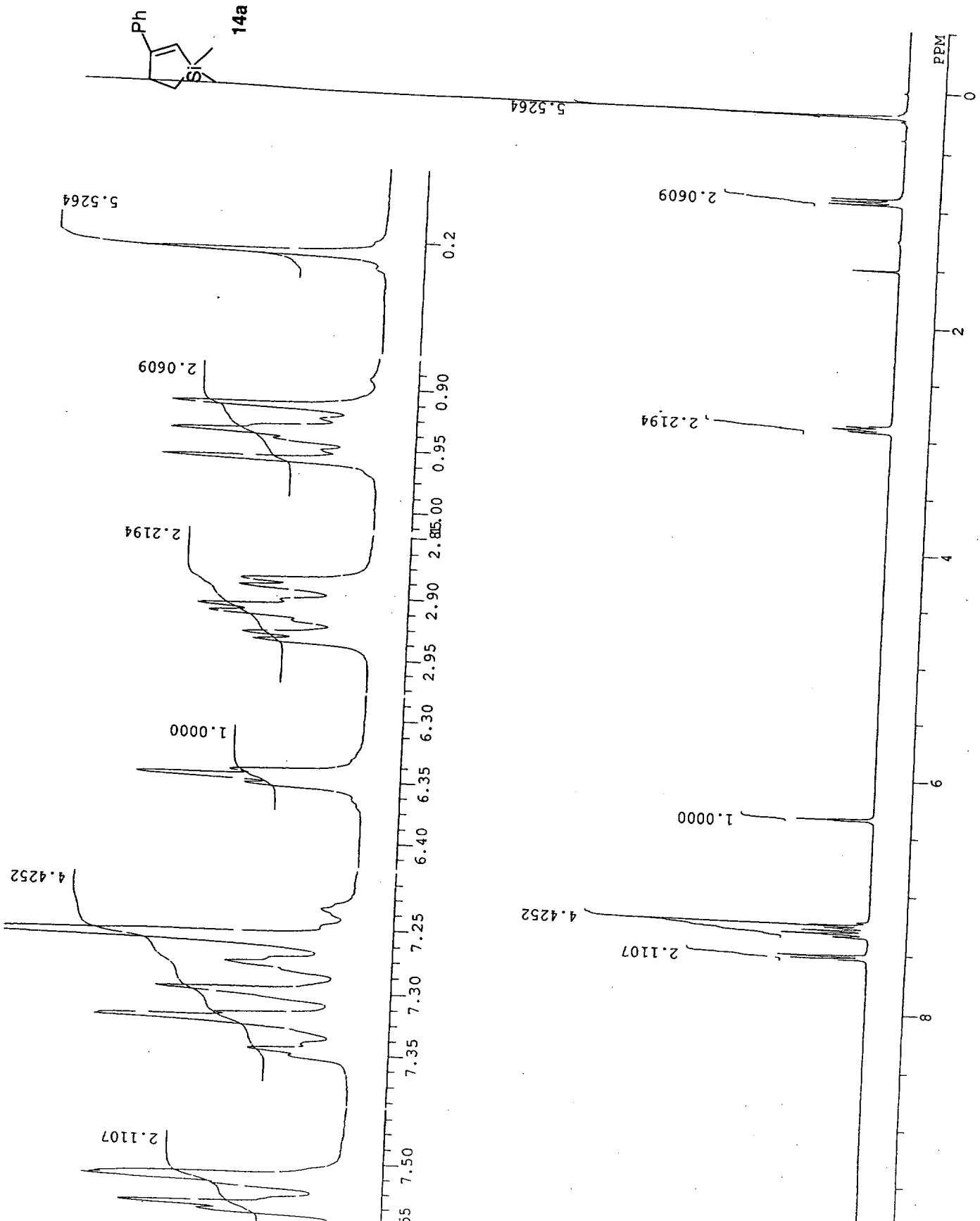


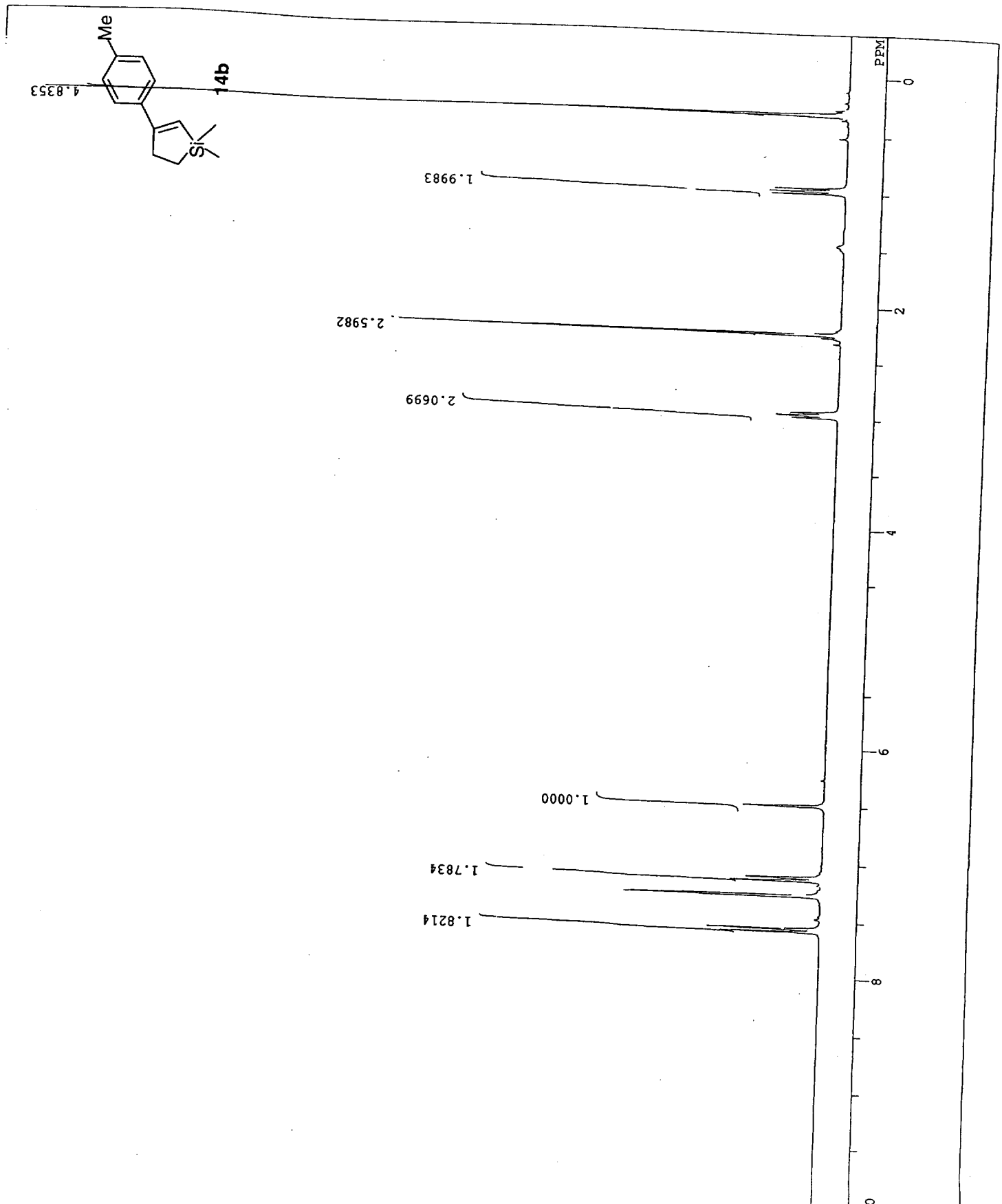


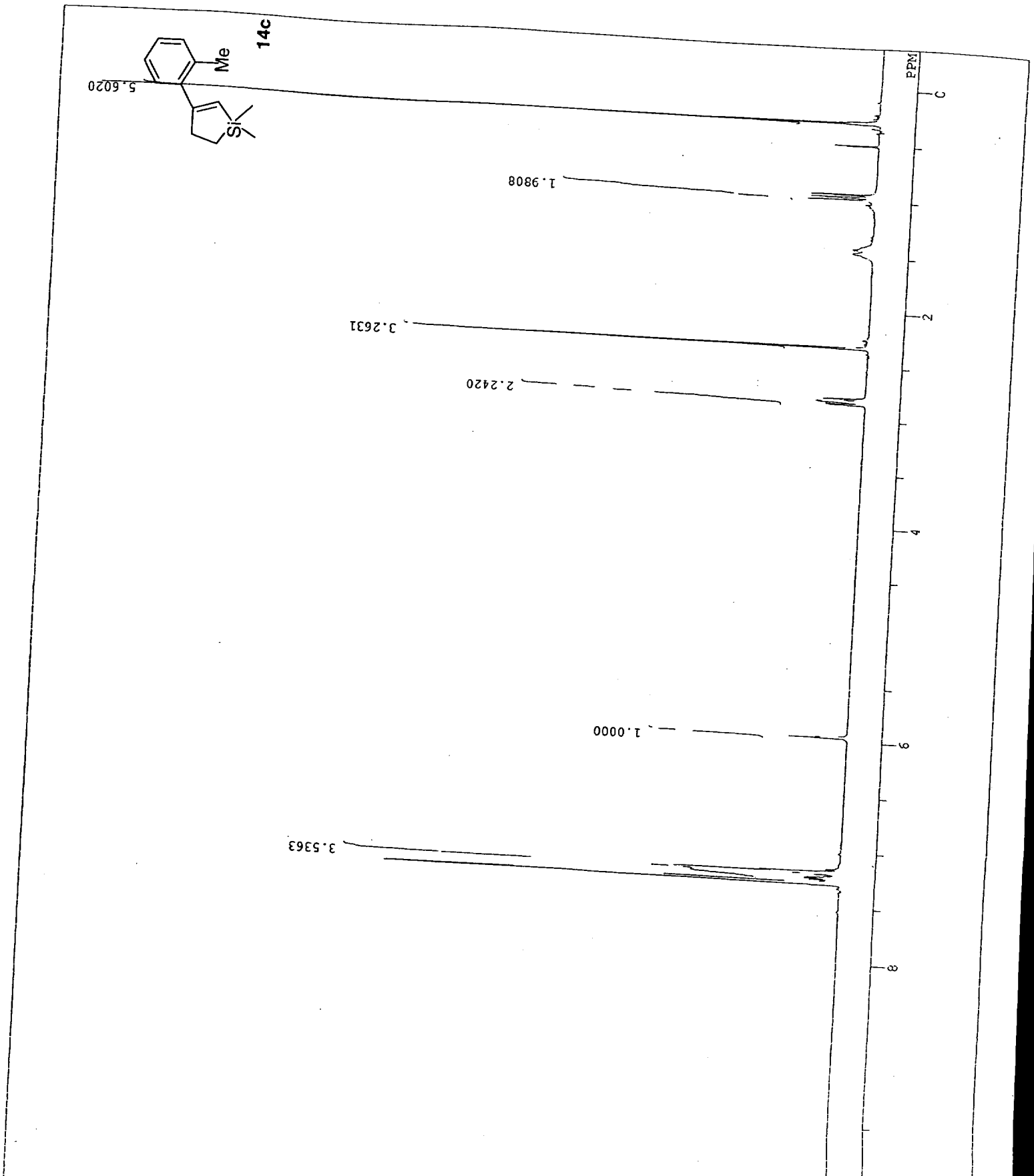


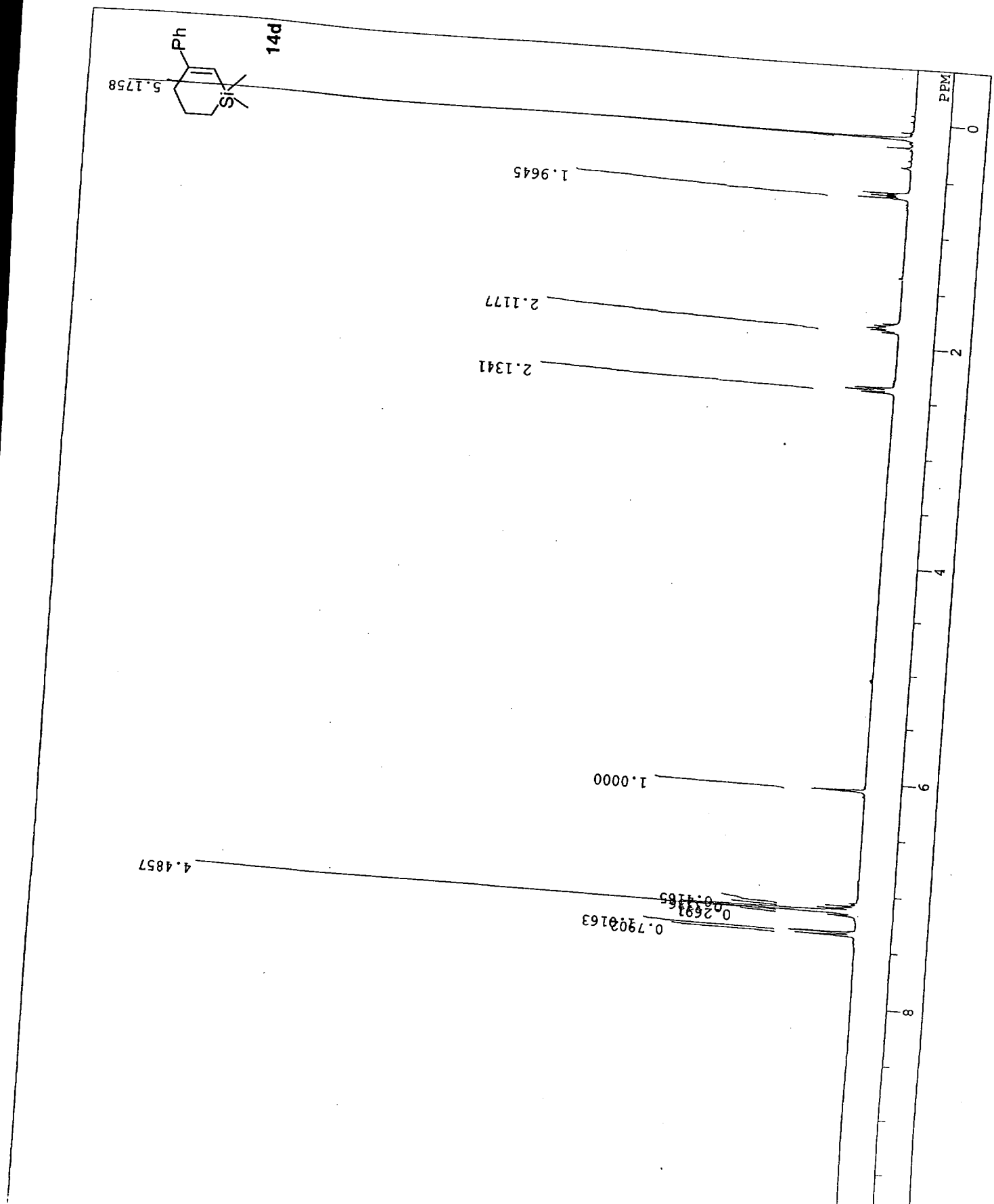


10

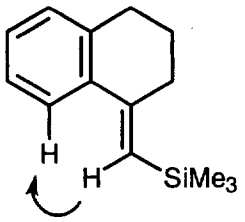




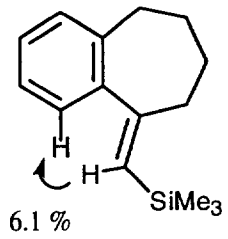




The results of NOE experiments of the cyclization products **9a**, and **9b**.



9a



9b