Pd-Catalyzed Synthesis of Allylic Silanes from Allylic *Ethers*

Supporting Information

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I. General information

Unless otherwise noted, all reactions were performed in a glove-bag under an atmosphere of argon. A 2 % PTS/H_2O solution was prepared by dissolving 4 g PTS in 196 g water (HPLC grade), followed by degassing with argon. PTS (Polyoxyethanyl-α-tocopheryl sebacate) was obtained from Zymes, LLC (PTS is also available from Sigma-Aldrich, catalog # 698717)). $PdCl_2$(DPEphos) (catalog # Pd-117), $PdCl_2(PPh_3)_2$ (catalog # Pd-100), as well as other screened Pd-precursors were purchased from Johnson Matthey. Hexamethyldisilane (**2a**) (Alfa Aesar, Stock # A13155) and 1,2-diphenyltetramethyldisilane (**2b**) (Gelest, catalog # SID4584.0) were used as received without further purification. NEt_3 was distilled over CaH_2 and stored over potassium hydroxide. Analytical thin layer chromatography (TLC) was performed using Silica Gel 60 F_{254} plates (Merck, 0.25 mm thick). The developed chromatogram was analyzed by UV lamp (254 nm) or aqueous potassium permanganate ($KMnO_4$). Flash chromatography was either performed in glass columns using Silica Flash® P60 (SiliCycle, 40-63 μm), or on pre-packed SINGLE StEP^{TM} columns (standard silica, Thomson) using a BIOTAGE SP-4® system. GCMS data was recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies). As capillary column a HP-5MS cross-linked 5% phenylmethylpolysiloxanediphenyl column (30 m x 0.250 mm, 0.25 micron, Agilent Technologies) was employed. Helium was used as carrier gas at a constant flow of 1 mL/min. Retention times (t_R) refer to the following temperature program: 50°C for 5 min; heating rate 20°C/min; 300°C for 20 min; injection temperature 250°C; detection temperature 280°C. ^1H and ^{13}C spectra were recorded at 22°C on a Varian UNITY INOVA Avance 400 MHz or a Varian UNITY INOVA 500 MHz. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.23 ppm) on the δ scale. High resolution mass analyses were obtained using a VG70 double-focusing magnetic sector instrument (VG Analytical) for EI and a PE Sciex QStar Pulsar quadrupole/TOF instrument (API) for ESI.

II. Optimization of Pd-catalyzed silylation reactions (Table 1).

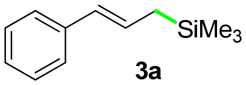
General procedure

A 1 dram vial containing a strong magnetic stir bar was loaded with catalyst (7.5 µmol, 3 mol%), cinnamyl phenyl ether (**1a**, 52.6 mg, 0.25 mmol) and brought into a glove-bag. After an atmosphere of argon was applied, hexamethyldisilane (**2a**, 77 µL, 0.38 mmol), NEt_3 (see table) and 2 % PTS/H_2O (1.5 mL) were added via syringe. The vial was immediately closed with a Teflon coated cap and vigorously stirred for 20 h at room temperature. The reaction mixture was poured into brine (2 mL) and extracted with EtOAc (3 x 2 mL). All organic phases were collected, dried over anhydrous Na_2SO_4, filtered through a short plug of silica gel and the solvent removed by a constant stream of argon. The residue was analyzed by GSMS and ^1H NMR. GCMS: t_R (cinnamyl phenyl ether (**1a**)) = 15.32 min, t_R (*linear-(E)*-cinnamyl trimethylsilane (**3a**)) = 12.24 min, (*linear-(Z)*-cinnamyl trimethylsilane) = 11.83 min, (*branched*-product) = 11.37 min. Ratio of *linear-(E)* vs. *linear-(Z)* as well as *linear* vs. *branched* confirmed by ^1H NMR analysis.[1]

III. Pd-catalyzed silylation reactions with hexamethyldisilane (2a) (Table 2).

General procedure

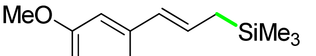
A 1 dram vial containing a strong magnetic stir bar was loaded with $PdCl_2$(DPEphos) (3 mol%: 5.4 mg, 7.5 µmol), allylic phenyl ether (0.25 mmol) and brought into a glove-bag. After an atmosphere of argon was applied, hexamethyldisilane (**2a**, 77 µL, 0.38 mmol), NEt_3 (139 µL, 1.0 mmol) and 2 % PTS/H_2O (1.5 mL) were added via syringe. The vial was *immediately* closed with a Teflon coated cap and vigorously stirred for 20 h at room temperature. The reaction mixture was poured into brine (2 mL) and extracted with EtOAc (3 x 2 mL). All organic phases were collected, dried over anhydrous Na_2SO_4, filtered through a short plug of silica gel and the solvent removed by a constant stream of argon. The residue was loaded on silica gel and purified by flash chromatography eluting with hexanes/EtOAc to afford the product.



3a

l:*b* ≥ 25:1; *E*:*Z* = 10:1

(Table 2, entry 1); Following the general procedure, using *(E)*-cinnamyl phenyl ether (**1a**, 52.6 mg, 0.25 mmol), hexamethyldisilane (**2a**, 77 µL, 0.38 mmol), $PdCl_2$(DPEphos) (5.4 mg, 7.5 µmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (139 µL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (hexanes) yielded cinnamyl trimethyl silane **3a** (43.3 mg, 91 %, as a 10:1 measure *E*:*Z* mixture[1]). The obtained NMR data for **3a** is identical with the literature values.[2] *(E)*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 0.09$ (s, 9H), 1.70 (dd, $J = 7.0, 2.5$ Hz, 2H), 6.24-6.32 (m, 2H), 7.19 (tt, $J = 7.0, 1.5$ Hz, 1H), 7.29-7.35 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -1.63$, 24.16, 125.71, 126.39, 128.05, 128.45, 128.65, 138.72. HR-MS (EI) calcd. for $C_{12}H_{18}Si$ (M^+): 190.1178; found: 190.1184.



3b

l:*b* ≥ 25:1; *E*:*Z* = 9:1

(Table 2, entry 3); Following the general procedure, using **1c** (60.1 mg, 0.25 mmol), hexamethyldisilane (**2a**, 77 µL, 0.38 mmol), $PdCl_2$(DPEphos) (10.8 mg, 15 µmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (139 µL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded allylic silane **3b** (49.9 mg, 90 %, as a 9:1 *E*:*Z* mixture[3]). *(E)*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 0.07$ (s, 9H), 1.69 (d, $J = 7.0$ Hz, 2H), 3.83 (s, 3H), 6.22 (d, $J = 16.0$ Hz, 1H), 6.28 (dt, $J = 16.0, 7.5$ Hz, 1H), 6.73-6.94 (m, 3H), 7.20-7.25 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = -1.63$, 24.15, 55.37, 111.25, 111.84, 118.43, 128.31, 128.48, 129.59, 140.22, 159.99. HR-MS (EI) calcd. for $C_{13}H_{20}OSi$ (M^+): 220.1283; found: 220.1290.

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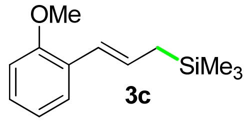
[1] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at $\delta = 1.70$ (*E*) and $\delta = 1.85$ (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

[2] Olsson, V. J.; Szabó, K. *Org. Lett.* **2008**, *10*, 3129-3131.

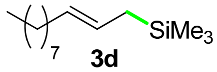
[3] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at $\delta = 1.69$ (*E*) and $\delta = 1.87$ (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.



3c

l:*b* ≥ 25:1; *E*:*Z* ≥ 25:1

(Table 2, entry 4); Following the general procedure, using **1d** (60.1 mg, 0.25 mmol), hexamethyldisilane (**2a**, 77 µL, 0.38 mmol), $PdCl_2$(DPEphos) (10.8 mg, 15 µmol), 2% PTS/H_2O (1.5 mL) and NEt_3 (139 µL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded allylic silane **3c** (47.8 mg, 86 %, as a ≥ 25:1 *E*:*Z* mixture[4]). *(E)*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.08 (s, 9H), 1.73 (dd, *J* = 8.5, 1.5 Hz, 2H), 3.86 (s, 3H), 6.26 (dt, *J* = 16.0, 8.0 Hz, 1H), 6.57 (d, *J* = 15.5 Hz, 1H), 6.86-6.94 (m, 2H), 7.16-7.19 (m, 1H), 7.39-7.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -1.63, 24.57, 55.70, 111.05, 120.83, 123.04, 126.24, 127.37, 127.93, 128.74, 156.20. HR-MS (EI) calcd. for $C_{13}H_{20}OSi$ (M^+): 220.1283; found: 220.1280.



3d

l:*b* ≥ 25:1; *E*:*Z* = 3:1

(Table 2, entry 5); Following the general procedure, using **1e** (61.6 mg, 0.25 mmol), hexamethyldisilane (**2a**, 77 µL, 0.38 mmol), $PdCl_2$(DPEphos) (2.7 mg, 3.8 µmol), $PdCl_2(PPh_3)_2$ (2.6 mg, 3.8 µmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (70 µL, 0.5 mmol), silica gel chromatography (hexanes) yielded allylic silane **3d** (48.1 mg, 85%, as a 3.6:1 *E*:*Z* mixture[5]). The obtained NMR data for **3d** was compared to spectra of similar reported compounds.[6] *(E)*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.01 (s, 9H), 0.89 (t, *J* =7.0 Hz, 3H), 1.27-1.34 (m, 12H), 1.40 (dd, *J* = 7.5, 1.5 Hz, 2H), 1.95-1.99 (m, 2H), 5.21-5.30 (m, 1H), 5.34-5.42 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -1.78, 14.34, 22.79, 22.91, 29.35, 29.57, 29.72, 30.25, 32.14, 33.02, 126.114, 129.29. HR-MS (EI) calcd. for $C_{14}H_{30}Si$ (M^+): 226.2114; found: 226.2117.

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[4] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.73 (*E*) and δ = 1.77 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

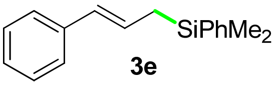
[5] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.40 (*E*) and δ = 1.47 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

[6] Desponds, O.; Franzini, L.; Schlosser, M. *Synthesis* **1997**, 150-152.

IV. Pd-catalyzed silylations with 1,2-diphenyltetramethyldisilane (2b) (Table 3).

General procedure

A 1 dram vial containing a strong magnetic stir bar was loaded with $PdCl_2$(DPEphos) (3 mol %: 5.4 mg, 7.5 μmol), allylic phenyl ether (0.25 mmol) and 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol). The vial was brought into a glove-bag, an atmosphere of argon was applied and NEt_3 (139 μL, 1.0 mmol) and 2 % PTS/H_2O (1.5 mL) were added via syringe. The vial was closed with a Teflon coated cap and vigorously stirred for 20 h at room temperature. The reaction mixture was poured into brine (2 mL) and extracted with EtOAc (3 x 2 mL). All organic phases were collected, dried over anhydrous Na_2SO_4, filtered through a short plug of silica gel and the solvent removed by a constant stream of argon. The residue was loaded on silica gel and purified by flash chromatography eluting with hexanes/EtOAc to afford the product.



3e

l:*b* ≥ 25:1; *E*:*Z* ≥ 25:1

(Table 3, entry 1); Following the general procedure, using *(E)*-cinnamyl phenyl ether (**1a**, 52.6 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), $PdCl_2$(DPEphos) (10.8 mg, 15 μmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (139 μL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (hexanes) yielded cinnamyl silane **3e** (55.5 mg, 88 %, as a ≥ 25:1 *E*:*Z* mixture[7]). The obtained NMR data for **3e** is identical with the literature values.[8] *(E)*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.32 (s, 6H), 1.90 (dd, *J* = 4.8, 2.0 Hz, 2H), 6.17-6.27 (m, 2H), 7.13-7.55 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = -3.11, 23.22, 125.76, 126.51, 127.33, 128.02, 128.65, 129.12, 129.30, 133.83, 138.56, 138.72. HR-MS (EI) calcd. for $C_{17}H_{20}Si$ (M^+): 252.1337; found: 252.1334.

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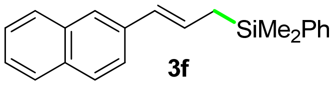
[7] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.90 (*E*) and δ = 2.04 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

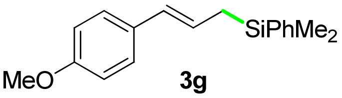
[8] Gómez, C *Tetrahedron* **2007**, *63*, 4655-4662.



3f

l:*b* ≥ 25:1; *E*:*Z* ≥ 25:1

(Table 3, entry 3); Following the general procedure, using **1f** (65.1 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), $PdCl_2$(DPEphos) (10.8 mg, 15 µmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (139 µL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (0-1 % EtOAc/hexanes) yielded **3f** (69.9 mg, 93 %, as a ≥ 25:1 *E*:*Z* mixture[9]). *(E)*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.37 (s, 6H), 1.98 (d, *J* = 7.5 Hz, 2H), 6.36 (dt, *J* = 16.0, 7.5 Hz, 1H), 6.43 (d, *J* =15.5 Hz, 1H), 7.37-7.79 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -3.07, 23.46, 123.68, 124.82, 125.43, 126.30, 127.81, 127.92, 128.04, 128.19, 129.26, 129.34, 132.62, 133.86, 133.99, 136.02, 138.72. HR-MS (EI) calcd. for $C_{21}H_{22}Si$ (M^+): 302.1493; found: 302.1491.



3g

l:*b* ≥ 25:1; *E*:*Z* ≥ 25:1

(Table 3, entry 4); Following the general procedure, using **1g** (60.1 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), $PdCl_2$(DPEphos) (10.8 mg, 15 µmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (139 µL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded **3g** (66.5 mg, 94 %, as a ≥ 25:1 *E*:*Z* mixture[10]). *(E)*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.34 (s, 6H), 1.90 (dd, *J* = 8.0, 1.0 Hz, 2H), 3.81 (s, 3H), 6.09 (dt, *J* = 15.5, 8.0 Hz, 1H), 6.22 (d, *J* = 16.0 Hz, 1H), 6.83-6.86 (m, 2H), 7.12-7.24 (m, 2H), 7.36-7.57 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -3.11, 22.97, 55.50, 114.10, 125.03, 126.80, 127.99, 128.51, 129.25, 131.50, 133.84, 138.89, 158.50. HR-MS (EI) calcd. for $C_{18}H_{22}OSi$ (M^+): 282.1440; found: 282.1436.

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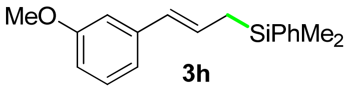
[9] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.98 (*E*) and δ = 2.15 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

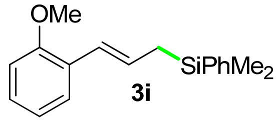
[10] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.90 (*E*) and δ = 2.07 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.



3h

l:*b* ≥ 25:1; *E*:*Z* = 24:1

(Table 3, entry 5); Following the general procedure, using **1c** (60.1 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), PdCl$_2$(DPEphos) (10.8 mg, 15 μmol), 2 % PTS/H$_2$O (1.5 mL) and NEt$_3$ (139 μL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded **3h** (63.9 mg, 91%, as a ≥ 25:1 *E*:*Z* mixture[11]). *(E)*-isomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ = 0.36 (s, 6H), 1.93 (dd, *J* = 5.0, 3.0 Hz, 2H), 3.83 (s, 3H), 6.24-6.26 (m, 2H), 6.74-6.92 (m, 3H), 7.21-7.24 (m, 1H), 7.38-7.58 (m, 5H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = -3.12, 23.22, 55.36, 111.28, 111.97, 118.47, 127.78, 128.01, 128.99, 129.30, 129.59, 133.83, 138.69, 140.07, 159.96. HR-MS (EI) calcd. for C$_{18}$H$_{22}$OSi (M$^+$): 282.1440; found: 282.1432.



3i

l:*b* ≥ 25:1; *E*:*Z* ≥ 25:1

(Table 3, entry 6); Following the general procedure, using **1d** (60.1 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), PdCl$_2$(DPEphos) (10.8 mg, 15 μmol), 2 % PTS/H$_2$O (1.5 mL) and NEt$_3$ (139 μL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded **3i** (61.4 mg, 87 %, as a ≥ 25:1 *E*:*Z* mixture[12]). *(E)*-isomer: ^{1}H NMR (500 MHz, CDCl$_3$) δ = 0.35 (s, 6H), 1.96 (dd, *J* = 8.5, 1.5 Hz, 2H), 3.84 (s, 3H), 6.22 (dt, *J* = 15.5, 8.5 Hz, 1H), 6.59 (d, *J* = 15.5 Hz, 1H), 6.85-6.92 (m, 2H), 7.16-7.19 (m, 1H), 7.34-7.59 (m, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ = -3.09, 23.63, 55.70, 111.05, 120.83, 123.78, 126.35, 127.50, 127.81, 127.98, 128.08, 129.22, 133.86, 138.98, 156.25. HR-MS (EI) calcd. for C$_{18}$H$_{22}$OSi (M$^+$): 282.1440; found: 282.1449.

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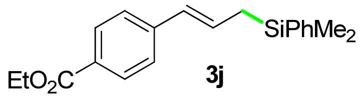
[11] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.93 (*E*) and δ = 2.11 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

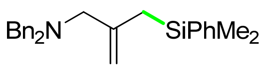
[12] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.96 (*E*) and δ = 2.09 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.



3j

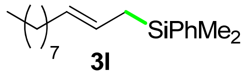
l:*b* ≥ 25:1; *E*:*Z* ≥ 25:1

(Table 3, entry 7); Following the general procedure, using **1h** (70.6 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), $PdCl_2$(DPEphos) (10.8 mg, 15 μmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (139 μL, 1.0 mmol), chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded **3j** (76.9 mg, 95 %, as a ≥ 25:1 *E*:*Z* mixture[13]). *(E)*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.36 (s, 6H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.96 (dd, *J* = 8.0, 0.5 Hz, 2H), 4.38 (q, *J* = 7.5 Hz, 2H), 6.27 (d, *J* = 15.5 Hz, 1H), 6.38 (dt, *J* = 16.0, 8.0 Hz, 1H), 7.31-7.56 (m, 7H), 7.95-7.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -3.11, 14.57, 23.77, 60.95, 125.47, 128.06, 128.31, 128.36, 129.41, 130.05, 130.65, 133.80, 138.37, 142.95, 166.77. HR-MS (EI) calcd. for $C_{20}H_{24}O_2Si$ (M^+): 324.1546; found: 324.1551.



3k

(Table 3, entry 8); Following the general procedure, using **1i** (85.9 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), $PdCl_2$(DPEphos) (18.0 mg, 25 μmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (139 μL, 1.0 mmol), preparative thin layer chromatography (10 % EtOAc/hexanes) yielded **3k** (70.4 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.12 (s, 6H), 1.90 (s, 2H), 2.79 (s, 2H), 3.48 (s, 4H), 4.68 (d, *J* = 1.5 Hz, 1H), 4.97 (d, *J* = 2.0 Hz, 1H), 7.24-7.45 (m, 15H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -3.05, 23.02, 58.08, 61.10, 110.82, 126.97, 127.84, 128.37, 128.87, 129.10, 133.83, 139.25, 140.06, 144.92. HR-MS (EI) calcd. for $C_{26}H_{31}NSi$ (M^+): 385.2226; found: 385.2232.



3l

l:*b* ≥ 25:1; *E*:*Z* = 5:1

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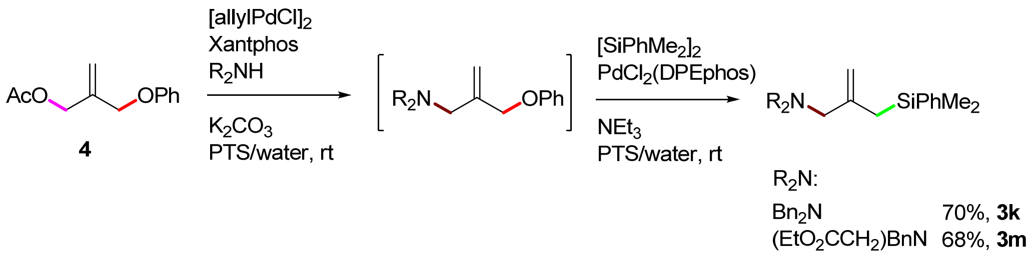
[13] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.96 (*E*) and δ = 2.09 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

(Scheme 2); Following the general procedure, using **1e** (61.6 mg, 0.25 mmol), 1,2-diphenyltetramethyldisilane (**2b**, 101.4 mg, 0.38 mmol), $PdCl_2$(DPEphos) (5.4 mg, 7.5 µmol), 2 % PTS/H_2O (1.5 mL) and NEt_3 (70 µL, 0.5 mmol), silica gel chromatography (hexanes) yielded **3l** (64.3 mg, 89 %, as a 4:1 *E*:*Z* mixture[14]). The obtained NMR data for **3l** was compared to spectra of similar reported compounds.[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.30 (s, 6H), 0.93 (t, *J* = 7.5 Hz, 3H), 1.30-1.36 (m, 12H), 1.69 (dd, *J* = 7.5, 1.0 Hz, 2H), 1.95-2.01 (m, 2H), 5.27-5.35 (m, 1H), 5.37-5.44 (m, 1H), 7.37-7.40 (m, 3H), 7.53, 7.57 (m,2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -3.18, 14.35, 21.81, 22.93, 29.35, 29.57, 29.73, 30.18, 32.15, 33.01, 125.44, 127.89, 129.08, 130.13, 133.86, 139.29. HR-MS (EI) calcd. for $C_{19}H_{32}Si$ (M^+): 288.2273; found: 288.2267.

V. Amination/silylation sequence in 1-pot (Scheme 3).

General procedure



A 5 mL microwave vial equipped with a strong stir bar was loaded with **4** (51.6 mg, 0.25 mmol), $[allylPdCl]_2$ (0.9 mg, 2.5 µmol), Xantphos (2.9 mg, 5.0 µmol), amine (0.28 mmol), K_2CO_3 (17.3 mg, 0.13 mmol) and capped with a septum. After argon substitution, 2 % PTS/H_2O (0.5 mL) was added and the reaction vigorously stirred at room temperature until TLC control indicated full conversion of the first step (10 % EtOAc/hexanes, $KMnO_4$). 1,2-diphenyltetramethyldisilane (**2b**, 87.8 mg, 0.33 mmol) and $PdCl_2$(DPEphos) (18.0 mg, 25 µmol) were added. The vial was closed with a septum and after argon substitution NEt_3 (139 µL, 1.00 mmol) and additional 2 % PTS/H_2O (0.5 mL) were introduced. The reaction mixture was vigorously stirred at room temperature until TLC control indicated full conversion of the

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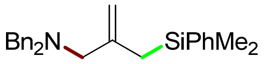
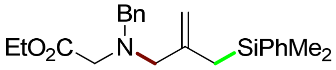
[14] Ratio of *E*- and *Z*-isomer was determined by the relative integral intensity of signals at δ = 1.69 (*E*) and δ = 1.75 (*Z*). ^{1}H NMR signals for the *branched* isomer could not be detected.

second step (5 % EtOAc/hexanes, $KMnO_4$). The reaction mixture was poured into brine (2 mL) and extracted with EtOAc (4 x 2 mL). All organic phases were collected, dried over anhydrous Na_2SO_4, filtered through a short plug of silica gel and the solvent removed by a constant stream of argon. The residue was loaded on silica gel and purified by flash chromatography eluting with hexanes/EtOAc to afford the product.



3k

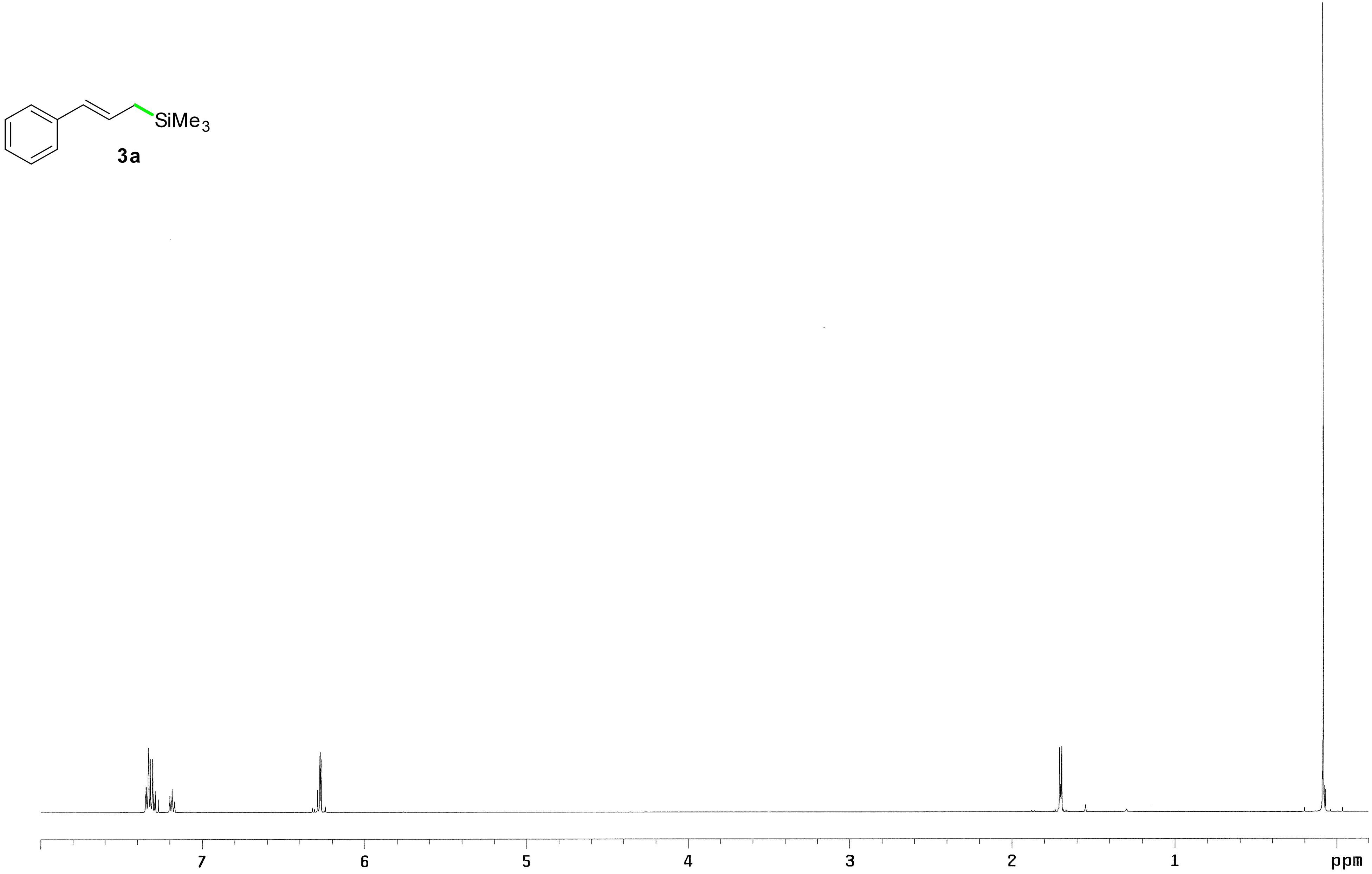
(Scheme 3, entry 1); Following the general procedure, using dibenzylamine (54.3 mg, 0.28 mmol) as amine, chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded **3k** (67.5 mg, 70 %). The obtained NMR data was consistent with the NMR data already obtained for this compound (see Table 3, entry 8).



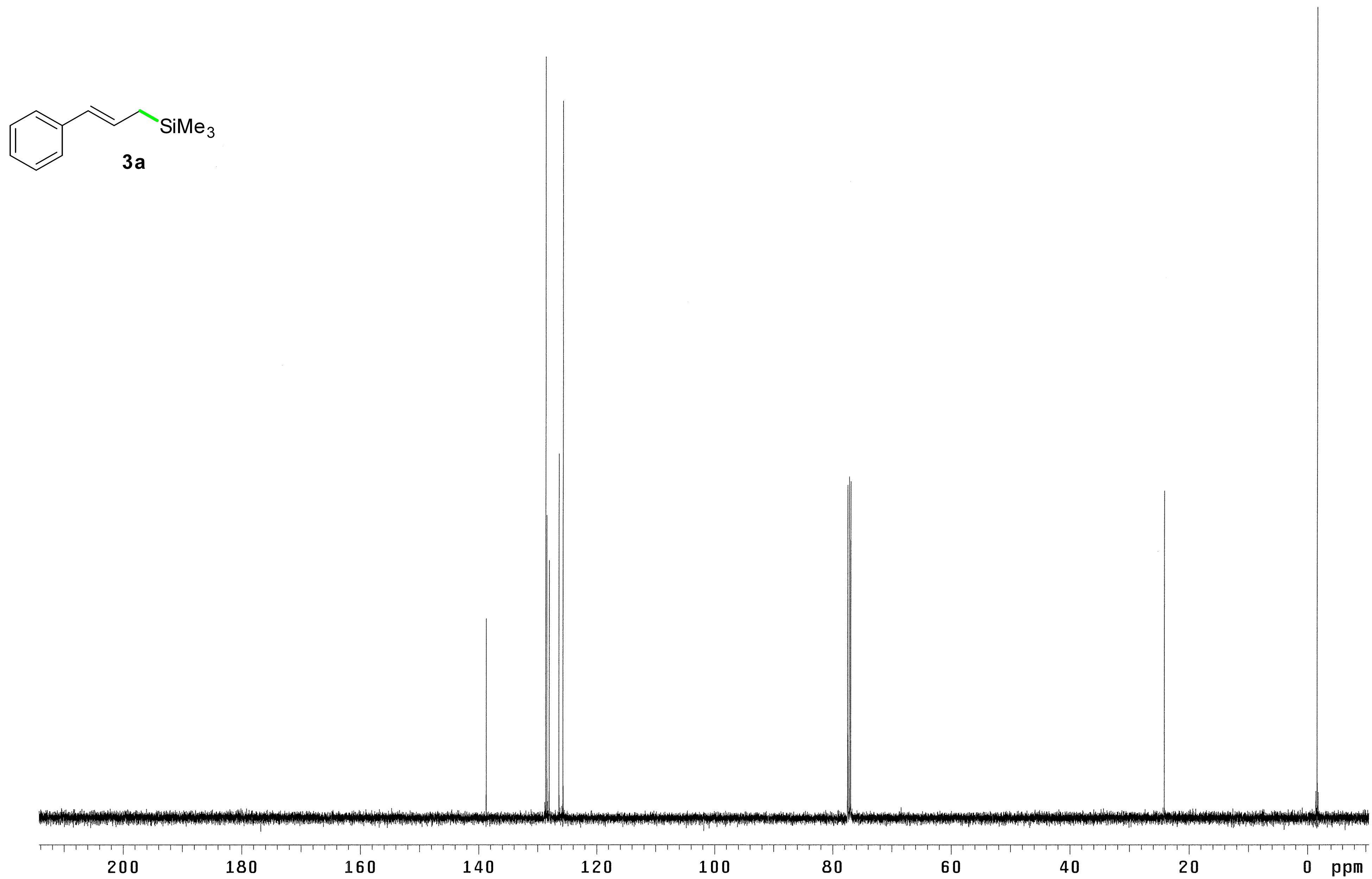
3m

(Scheme 3, entry 2); Following the general procedure, using ethyl 2-(benzylamino)acetate (53.1 mg, 0.28 mmol) as amine, chromatography on a 12 g SINGLE StEP® column (0-10 % EtOAc/hexanes) yielded **3m** (65.1 mg, 68 %). ^1H NMR (500 MHz, $CDCl_3$) δ = 0.23 (s, 6H), 1.28 (t, J = 7.0 Hz, 3H), 1.89 (s, 2H), 3.00 (s, 2H), 3.22 (s, 2H), 3.71 (s, 2H), 4.14 (q, J = 7.0 Hz, 2H), 4.67-4.68 (m, 1H), 4.90-4.91 (m, 1H), 7.27-7.50 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = -2.90, 14.49, 22.85, 53.40, 57.88, 60.20, 60.58, 111.32, 127.19, 127.86, 128.41, 129.09, 129.19, 133.81, 139.17, 139.46, 144.53, 171.73. HR-MS (ESI) calcd. for $C_{23}H_{31}NO_2NaSi$ (M+Na$^+$): 404.2022; found: 404.2022.

VI. Characterization data



3a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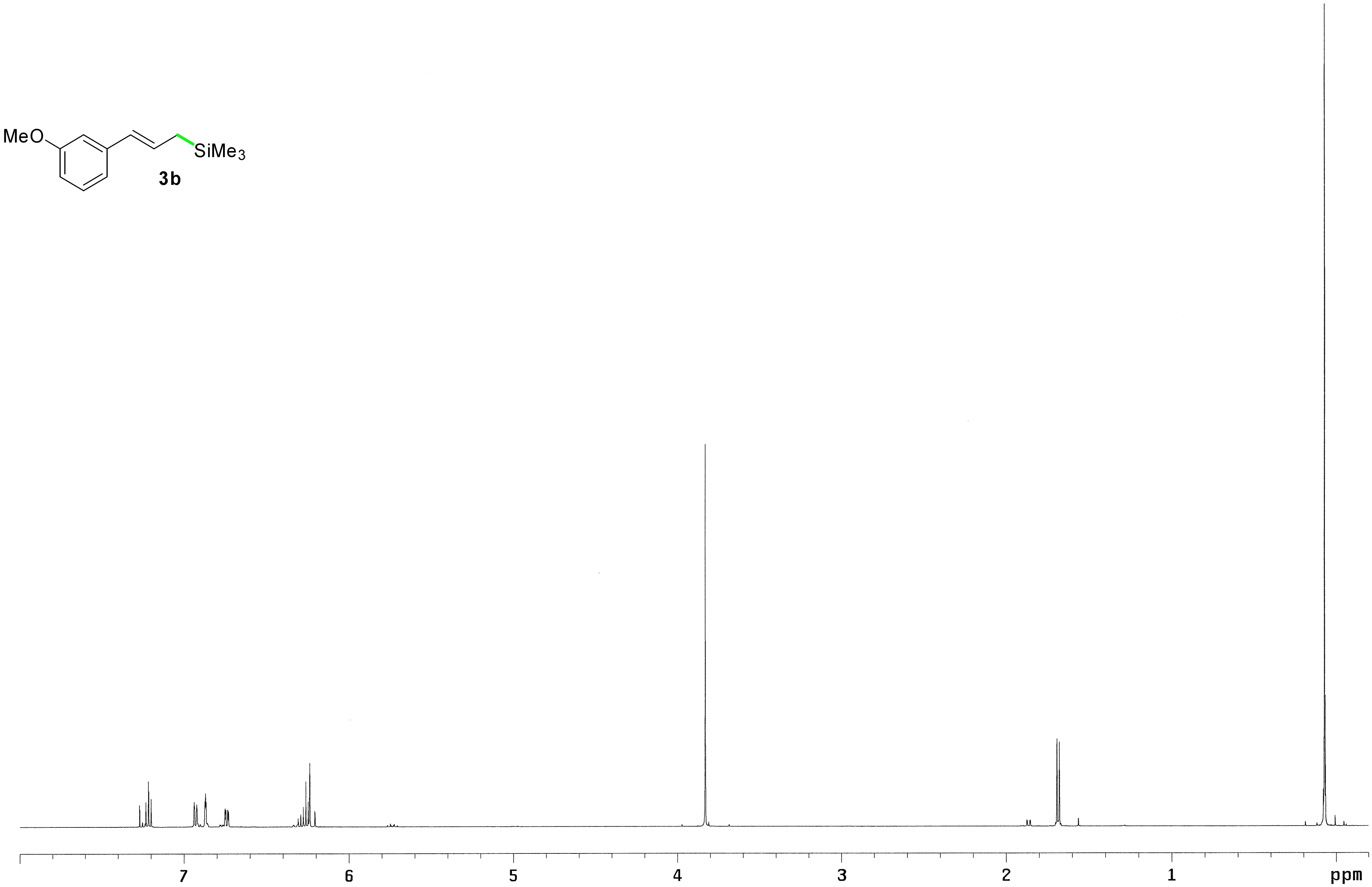
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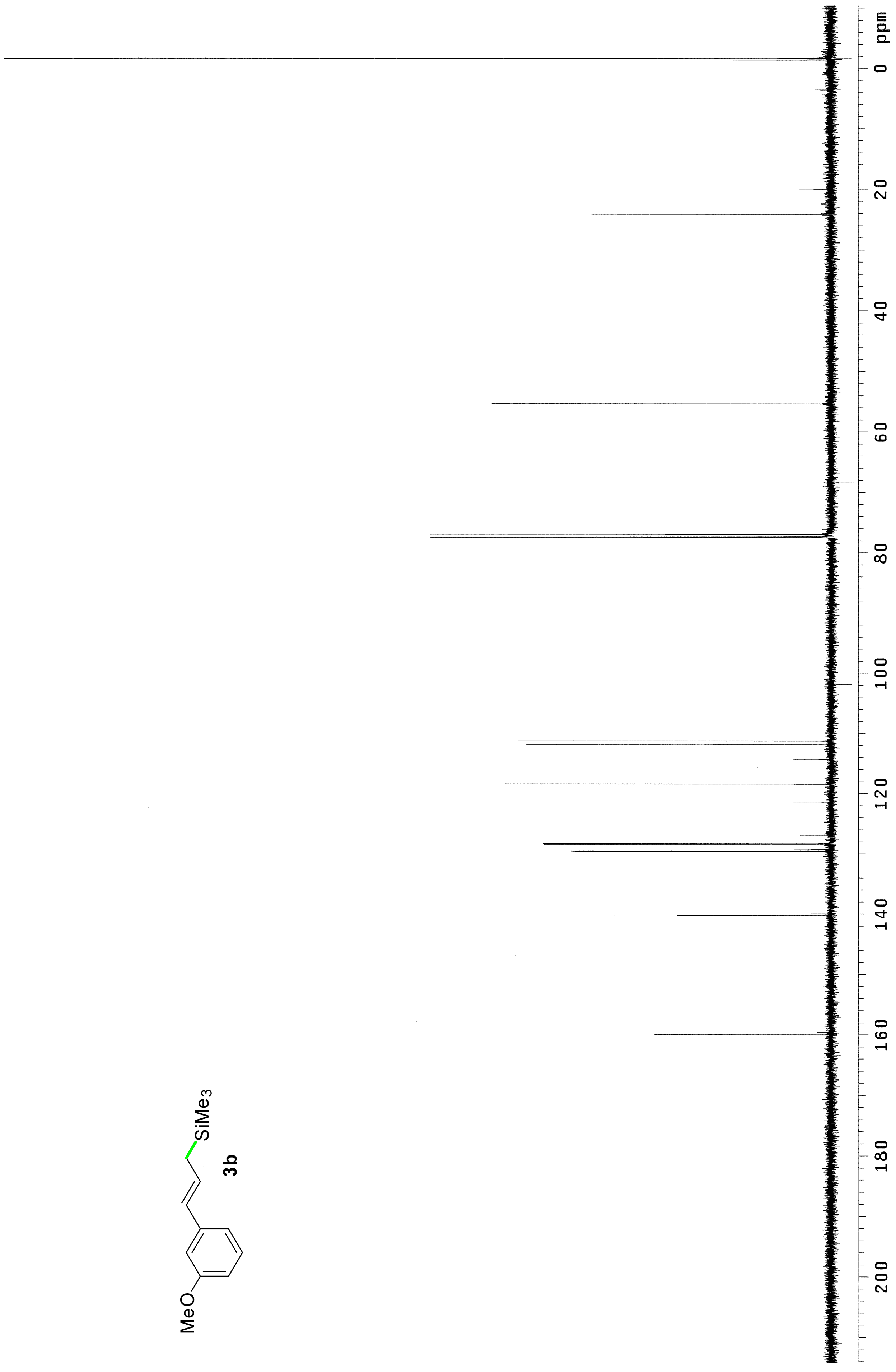
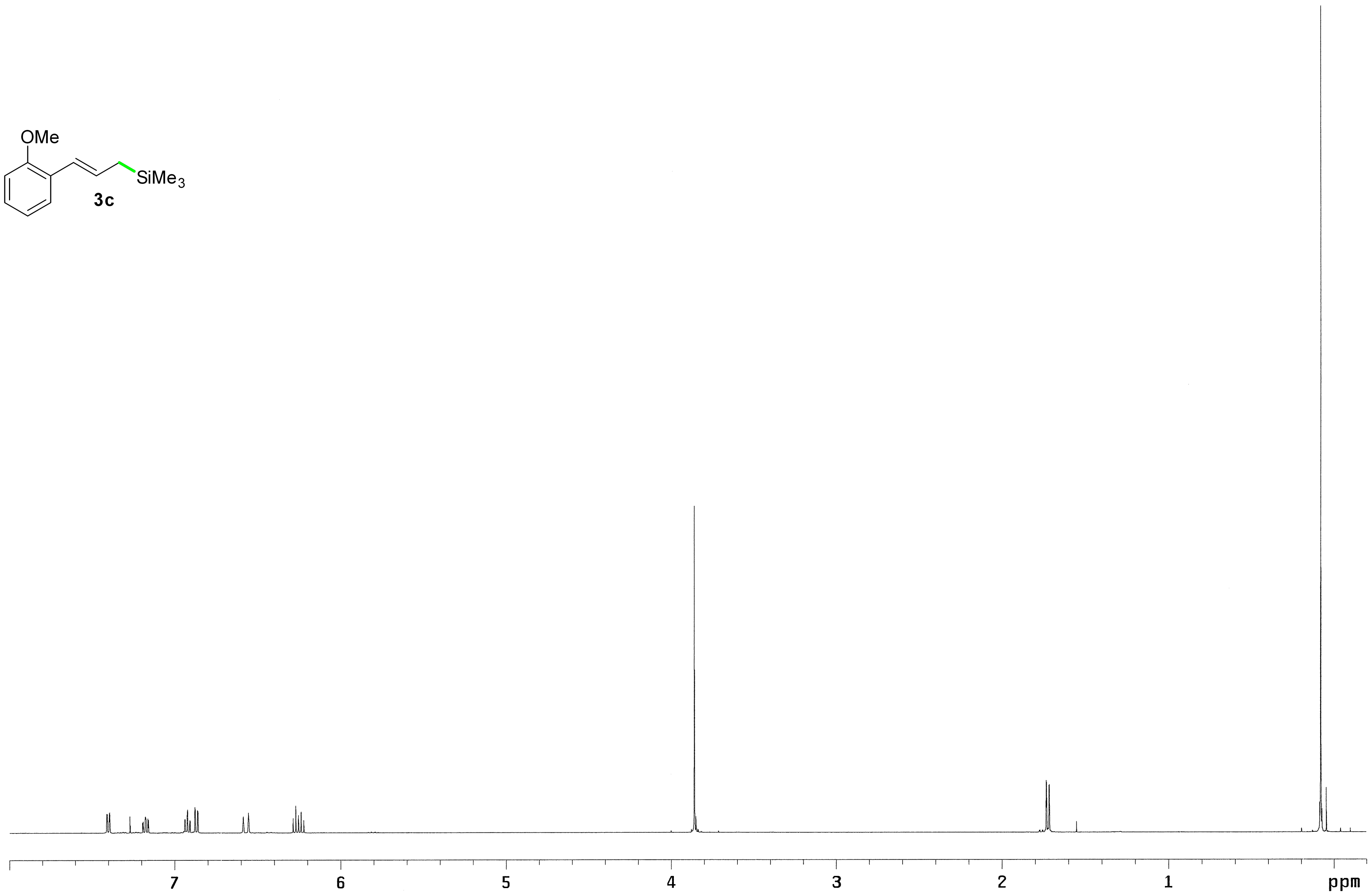


3b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3
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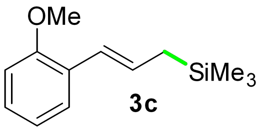
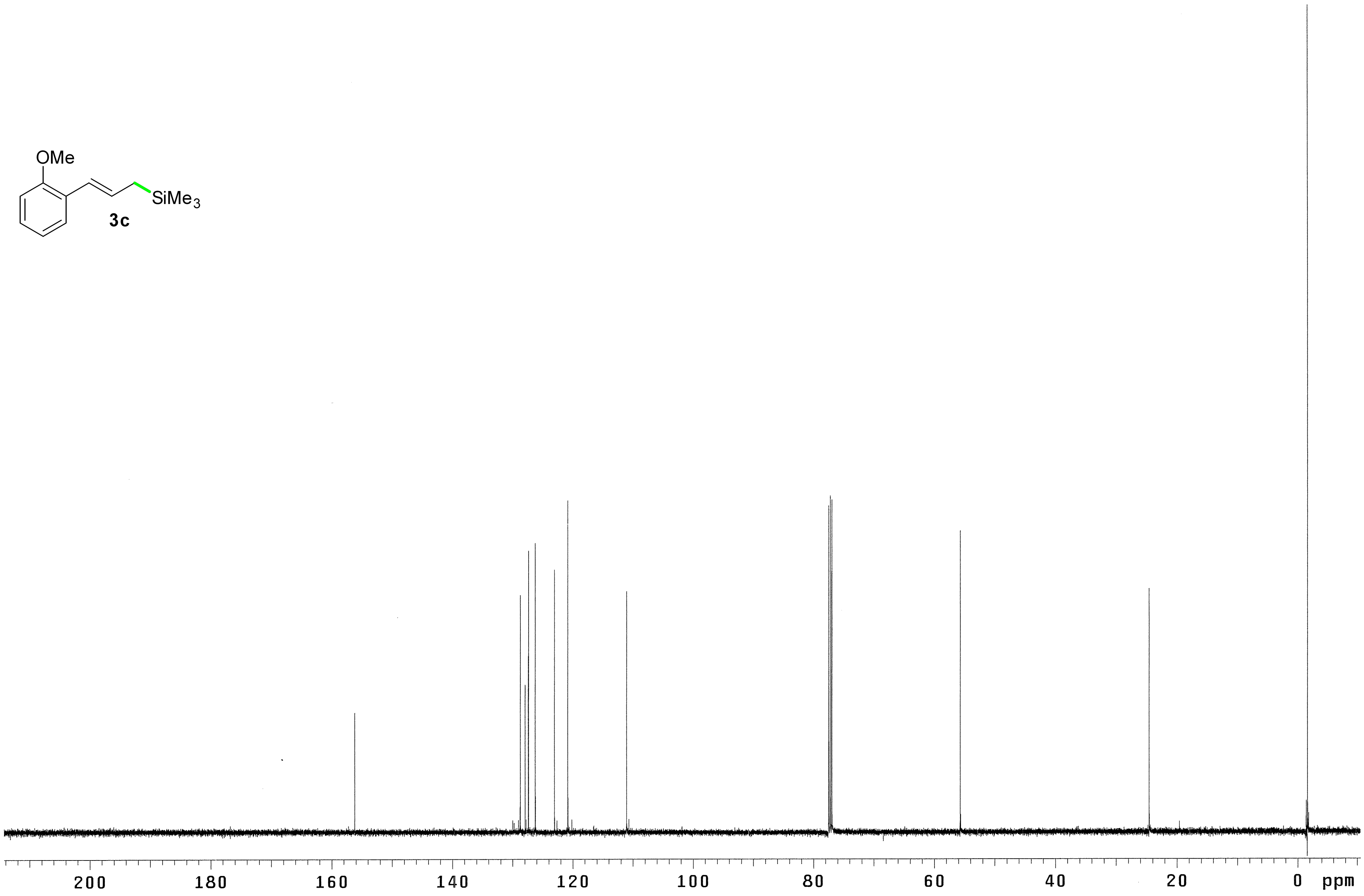
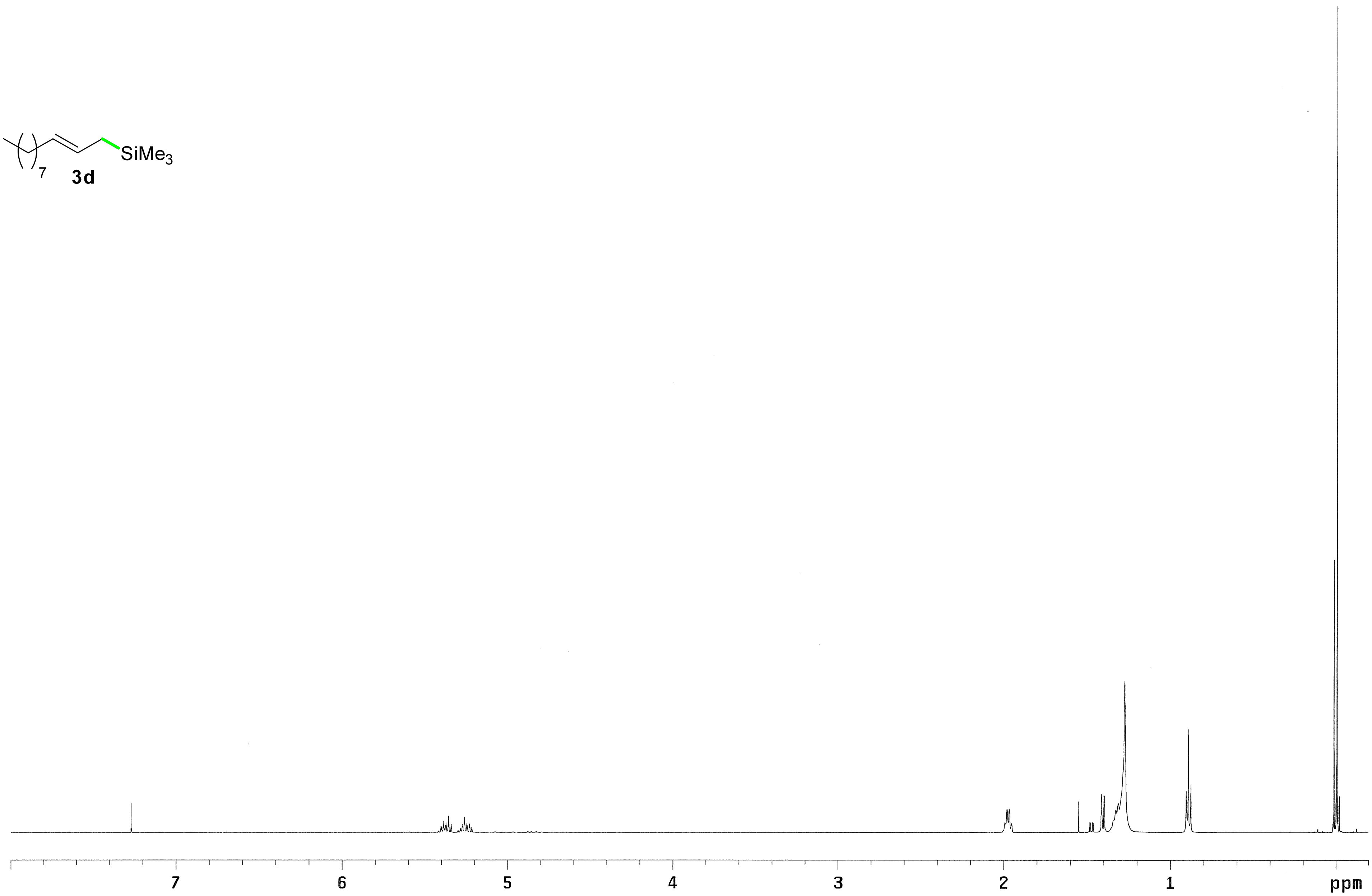
1
ppm



3c





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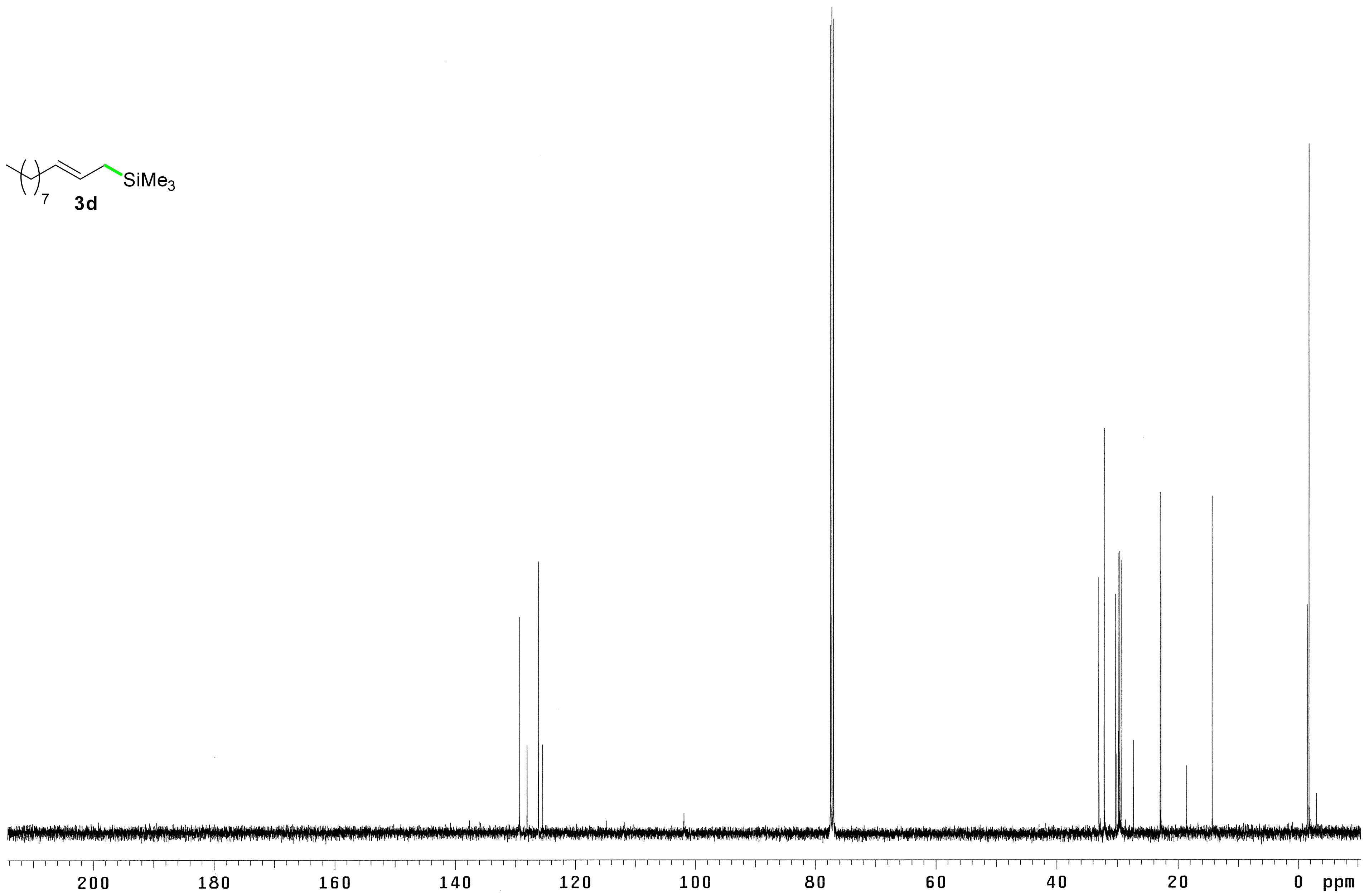

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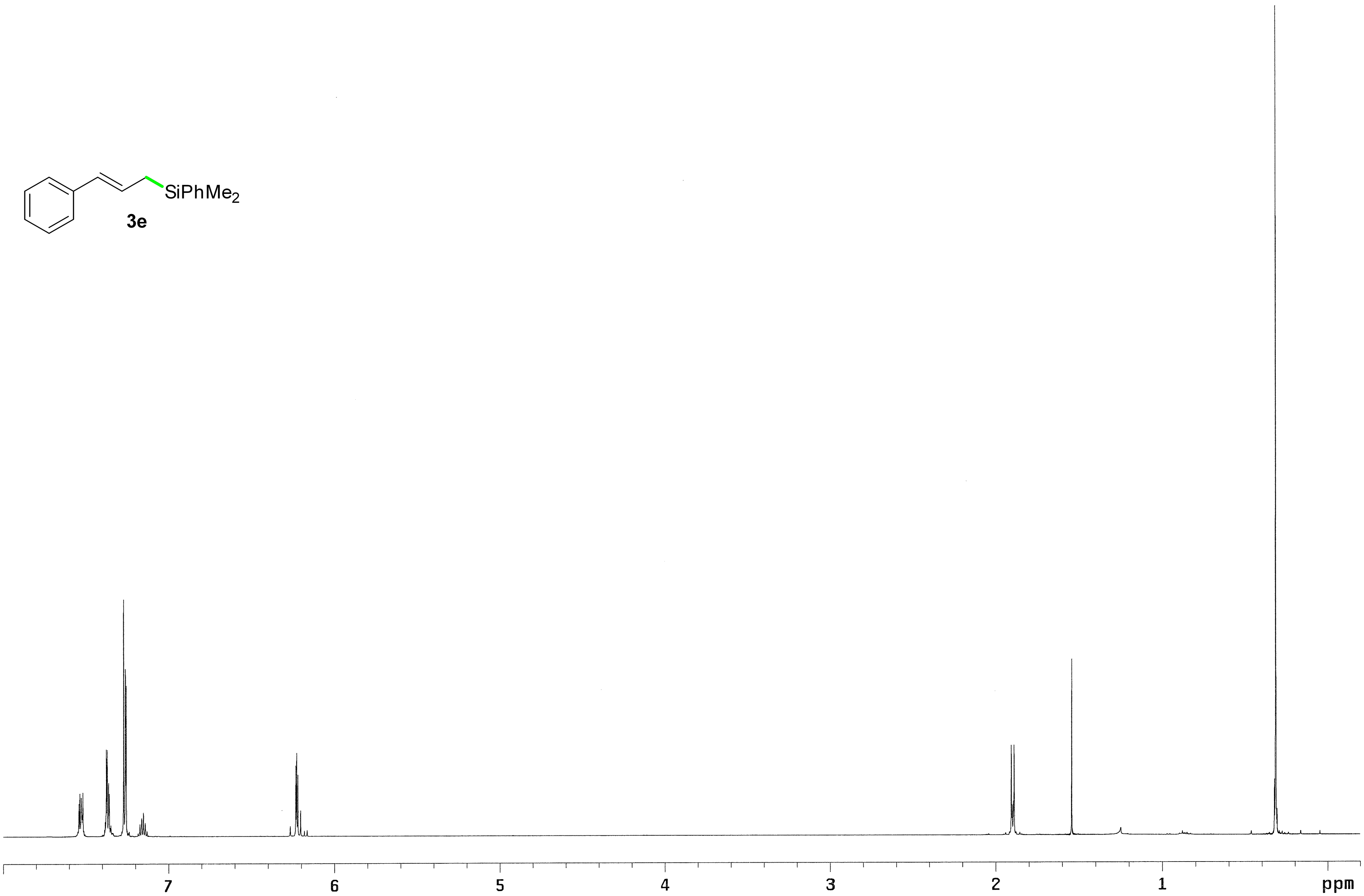

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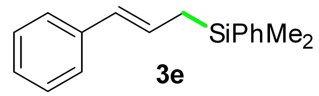

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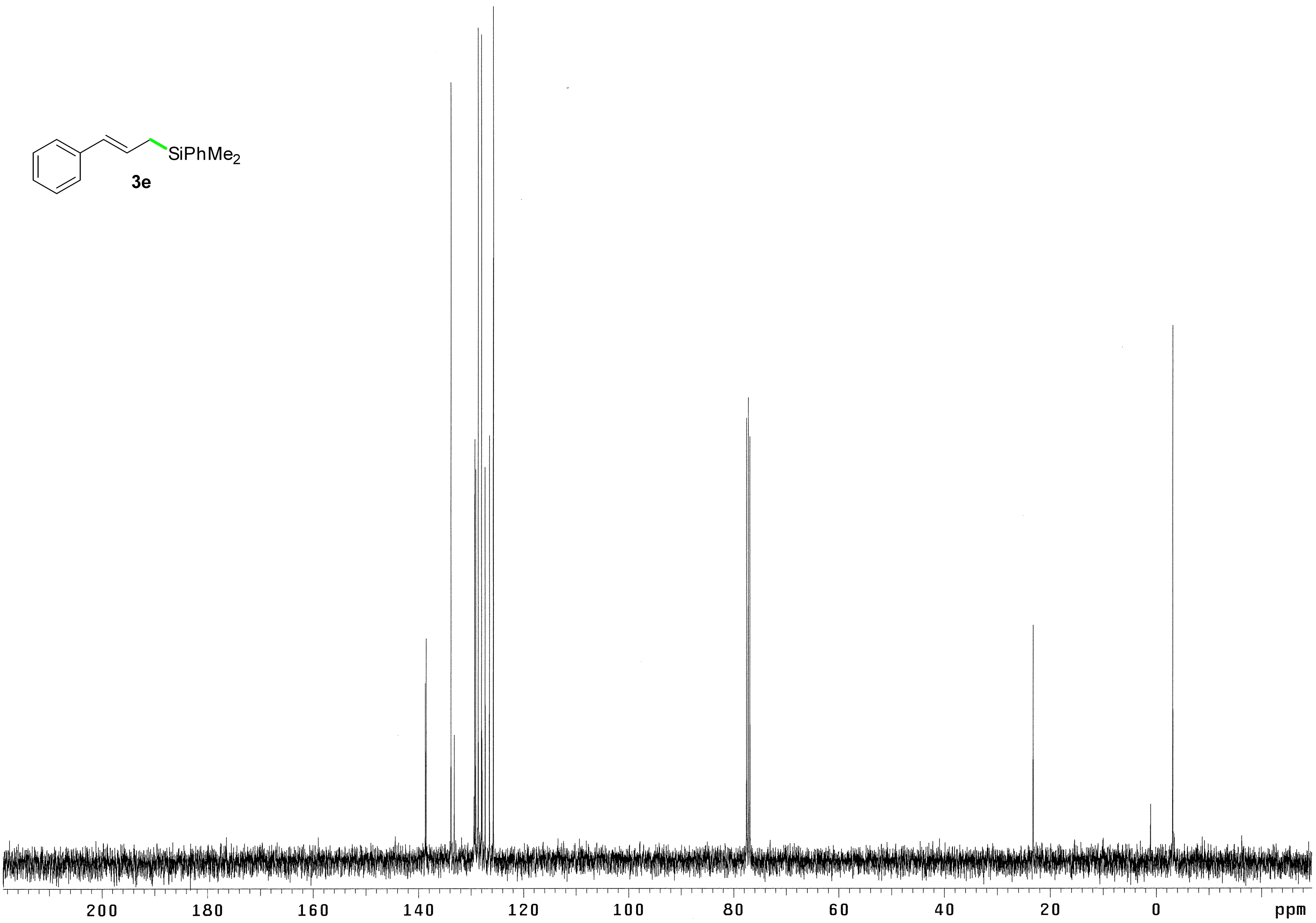

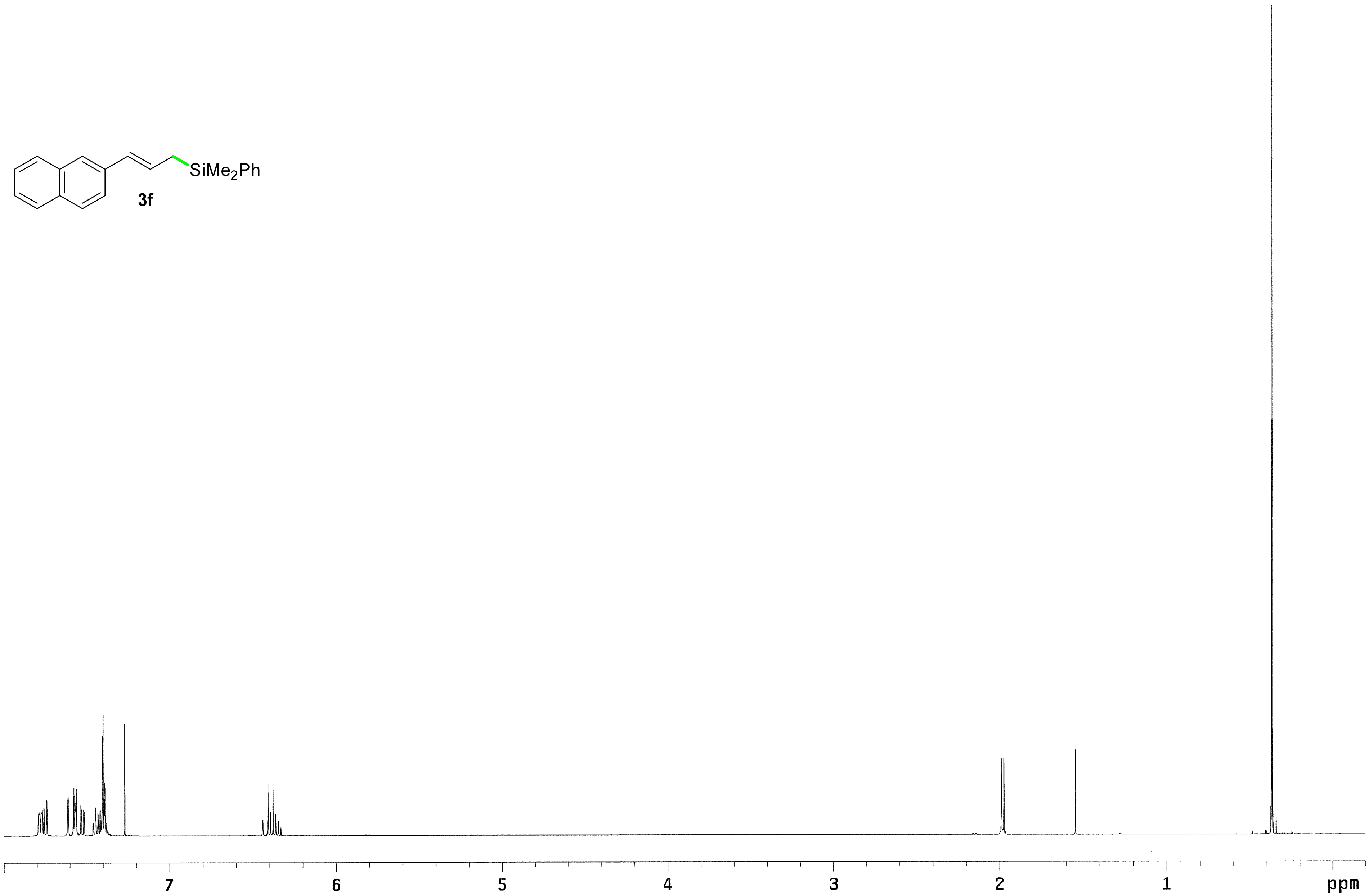

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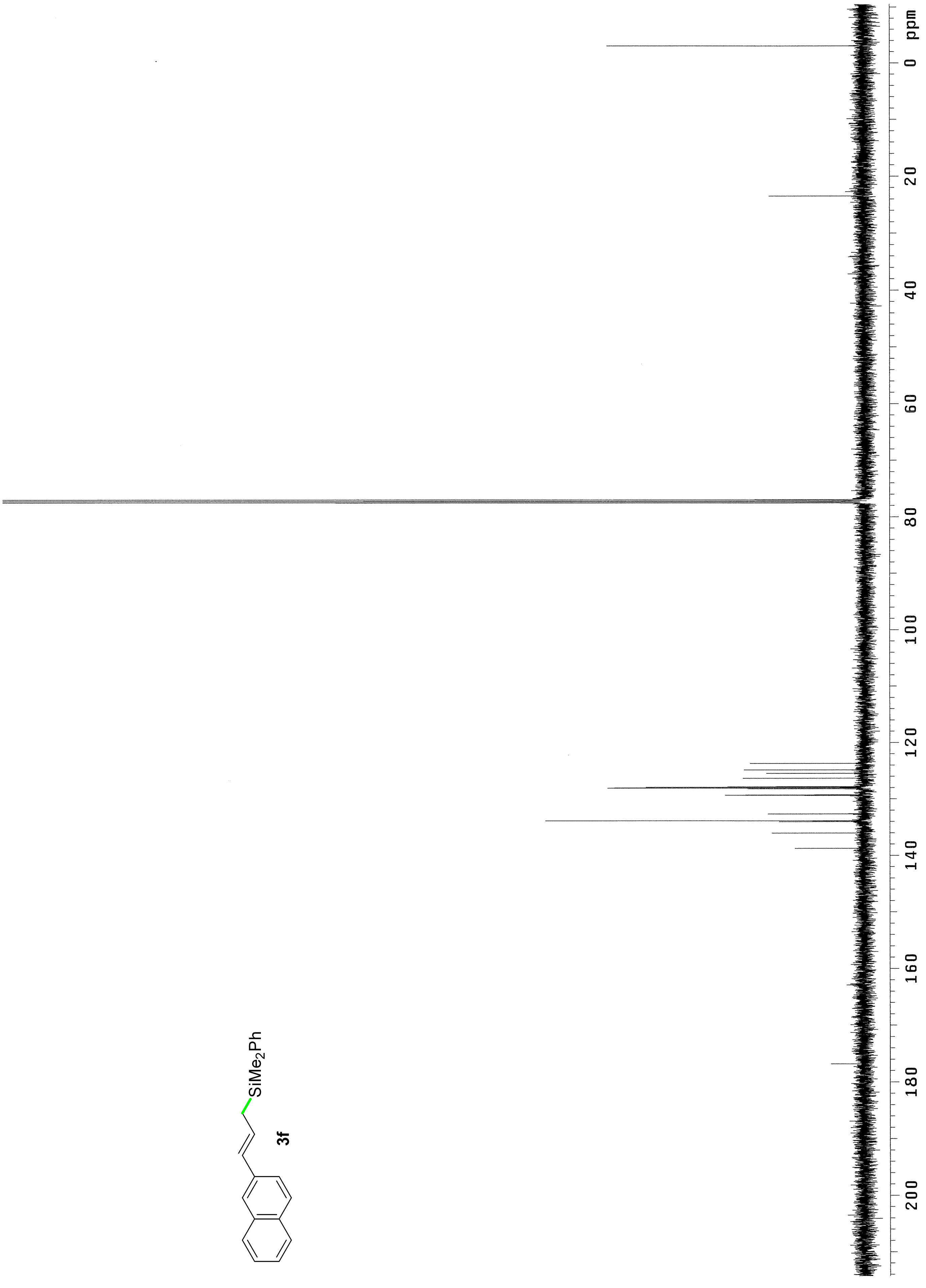
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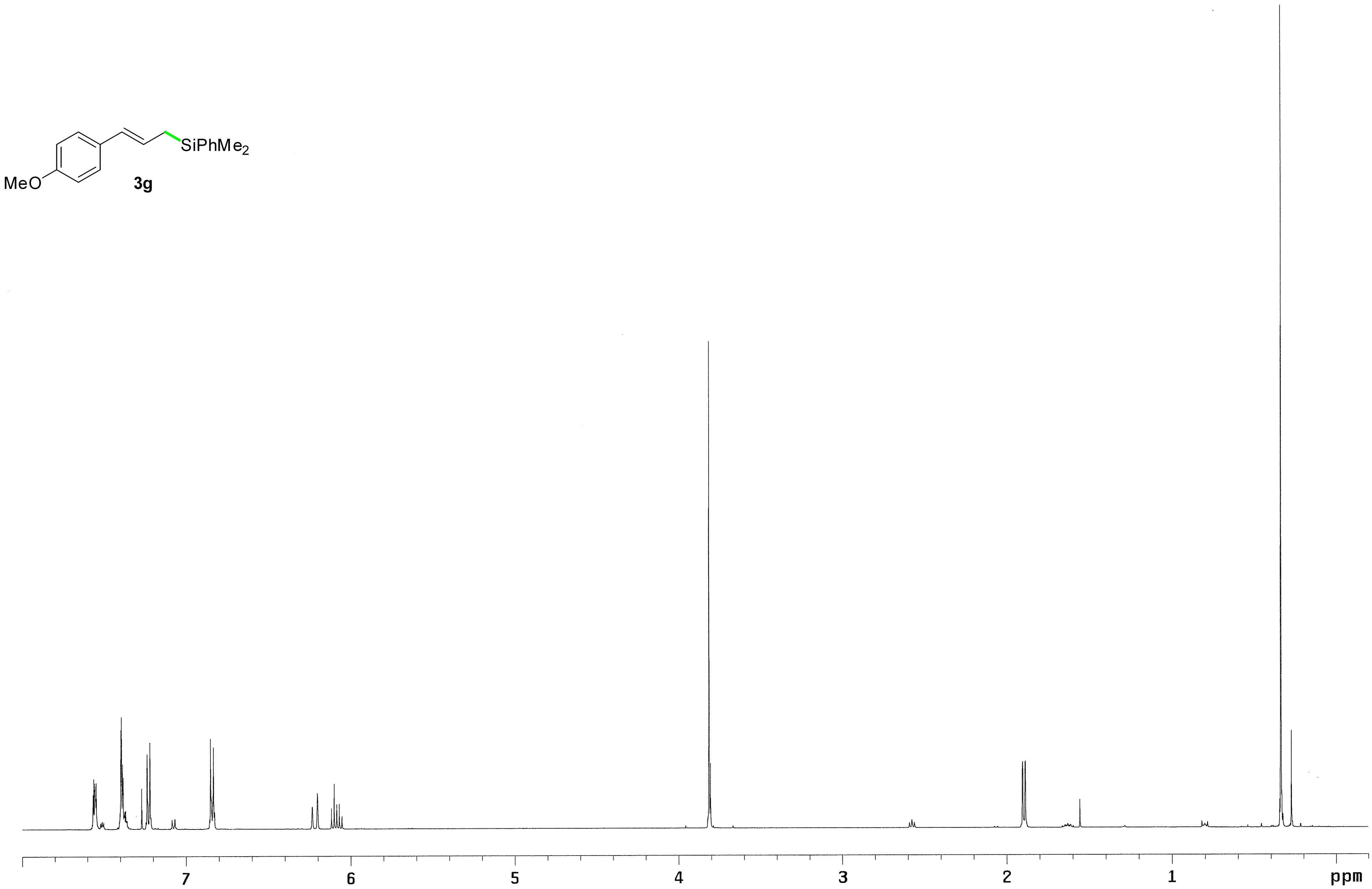

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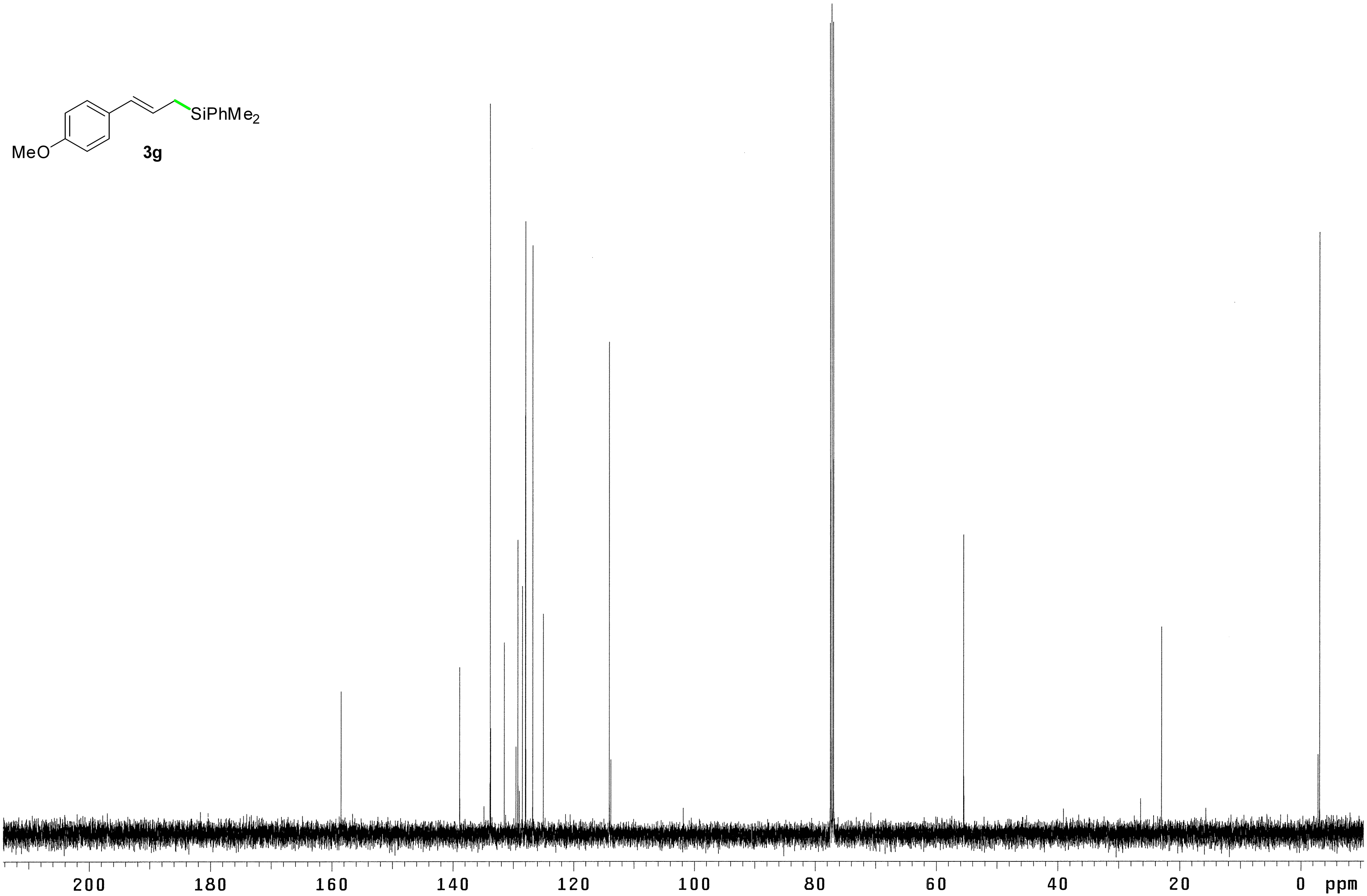
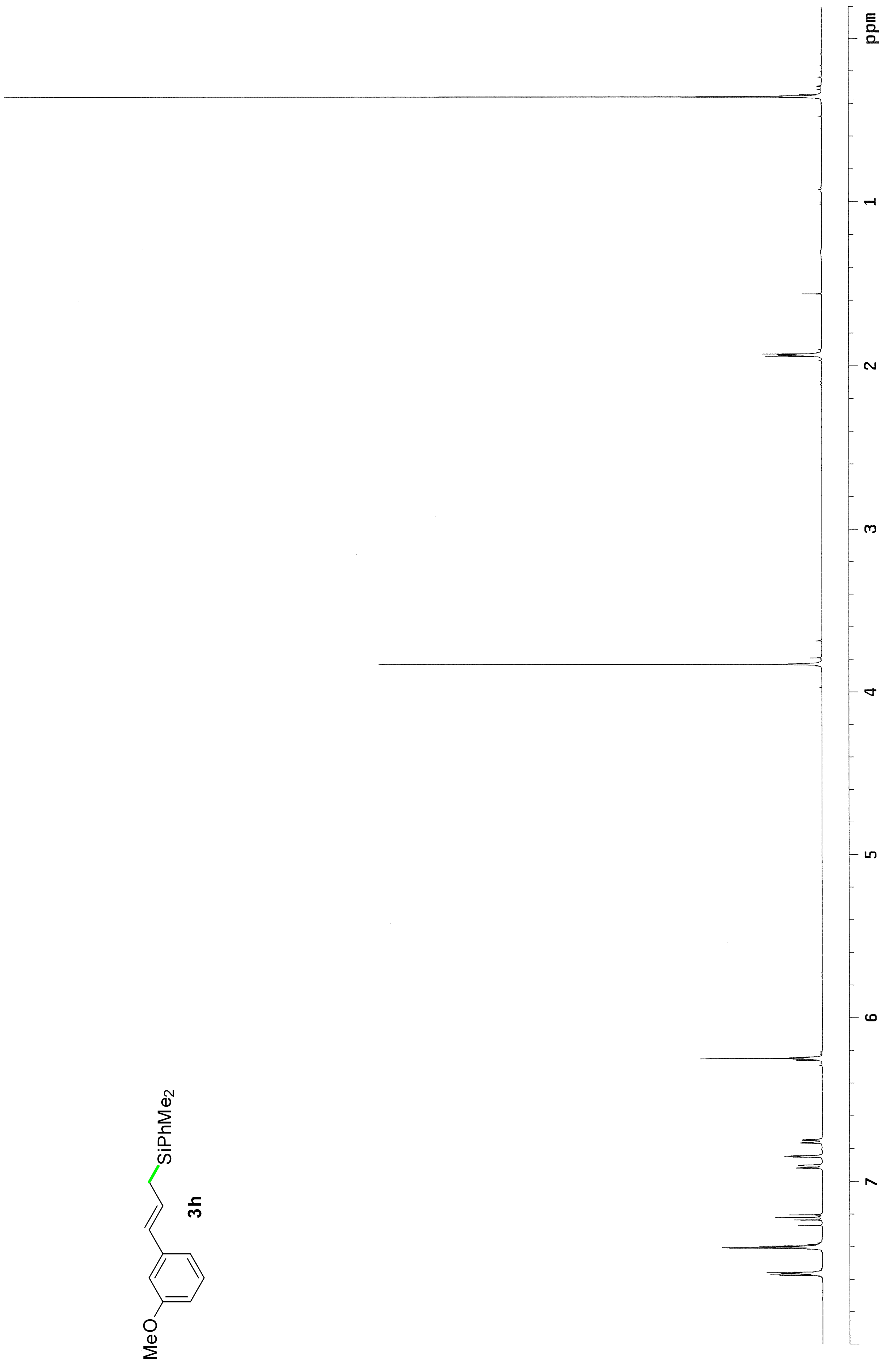

3g



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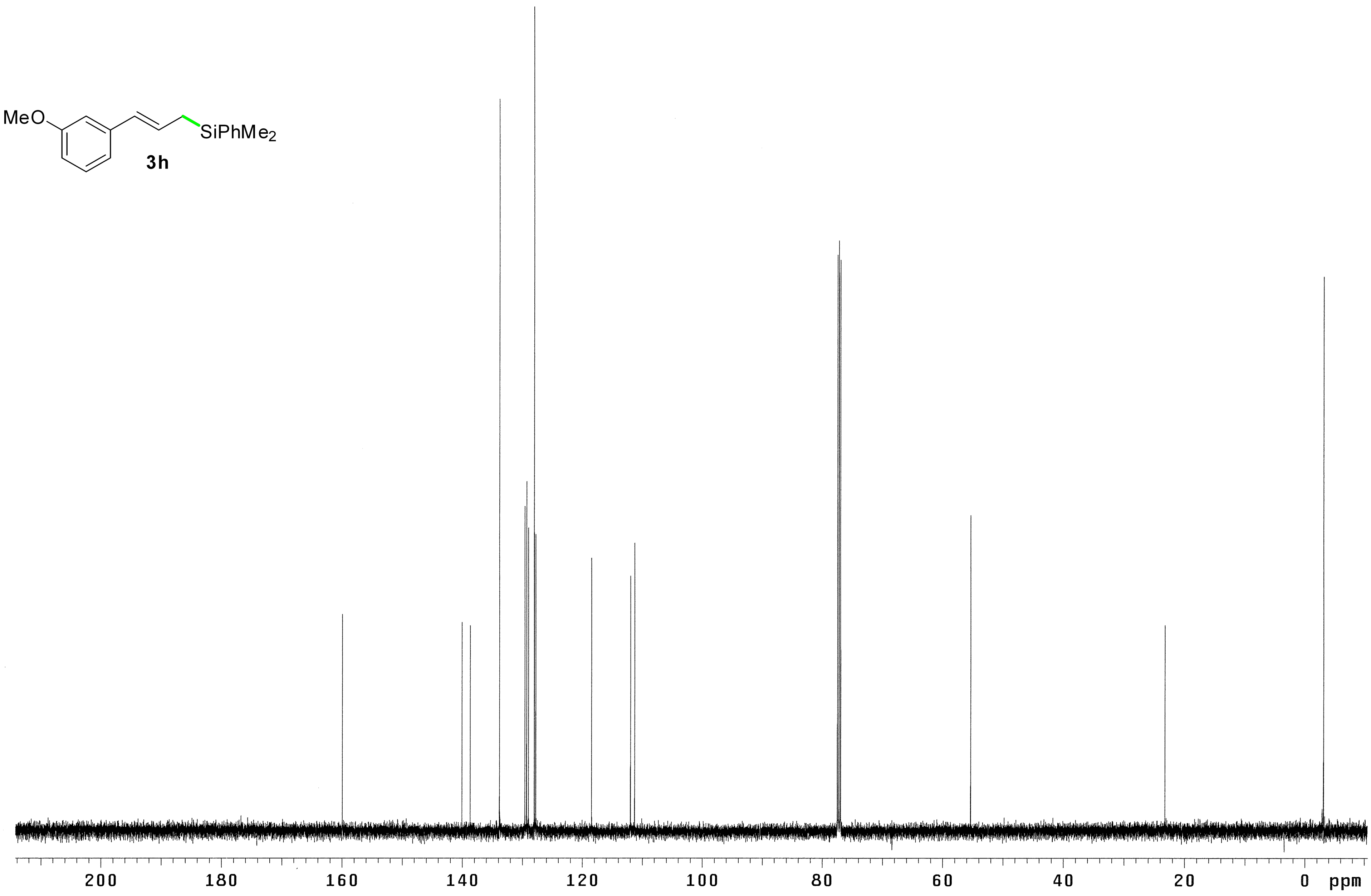
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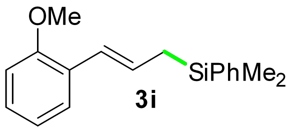
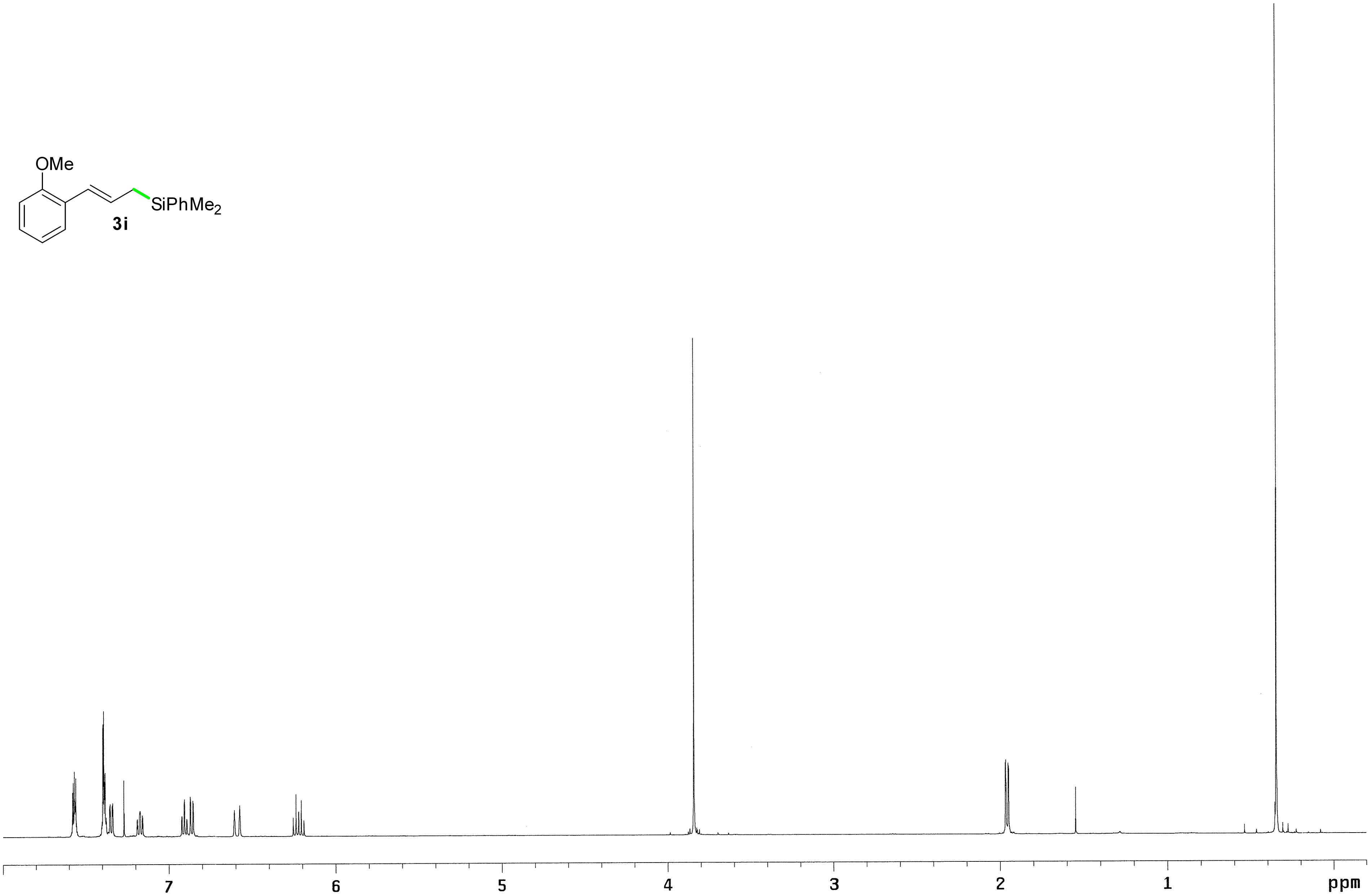
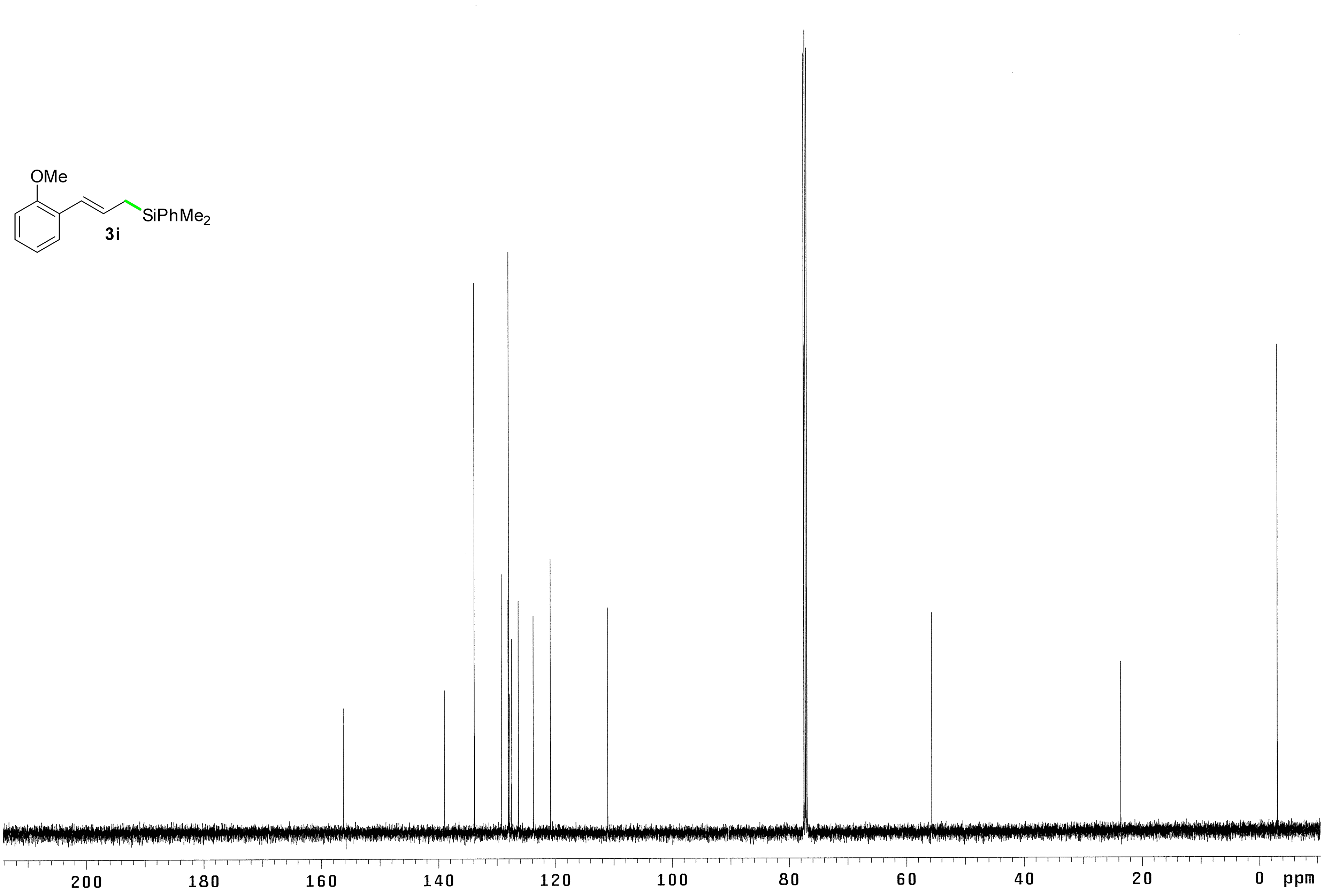


3i

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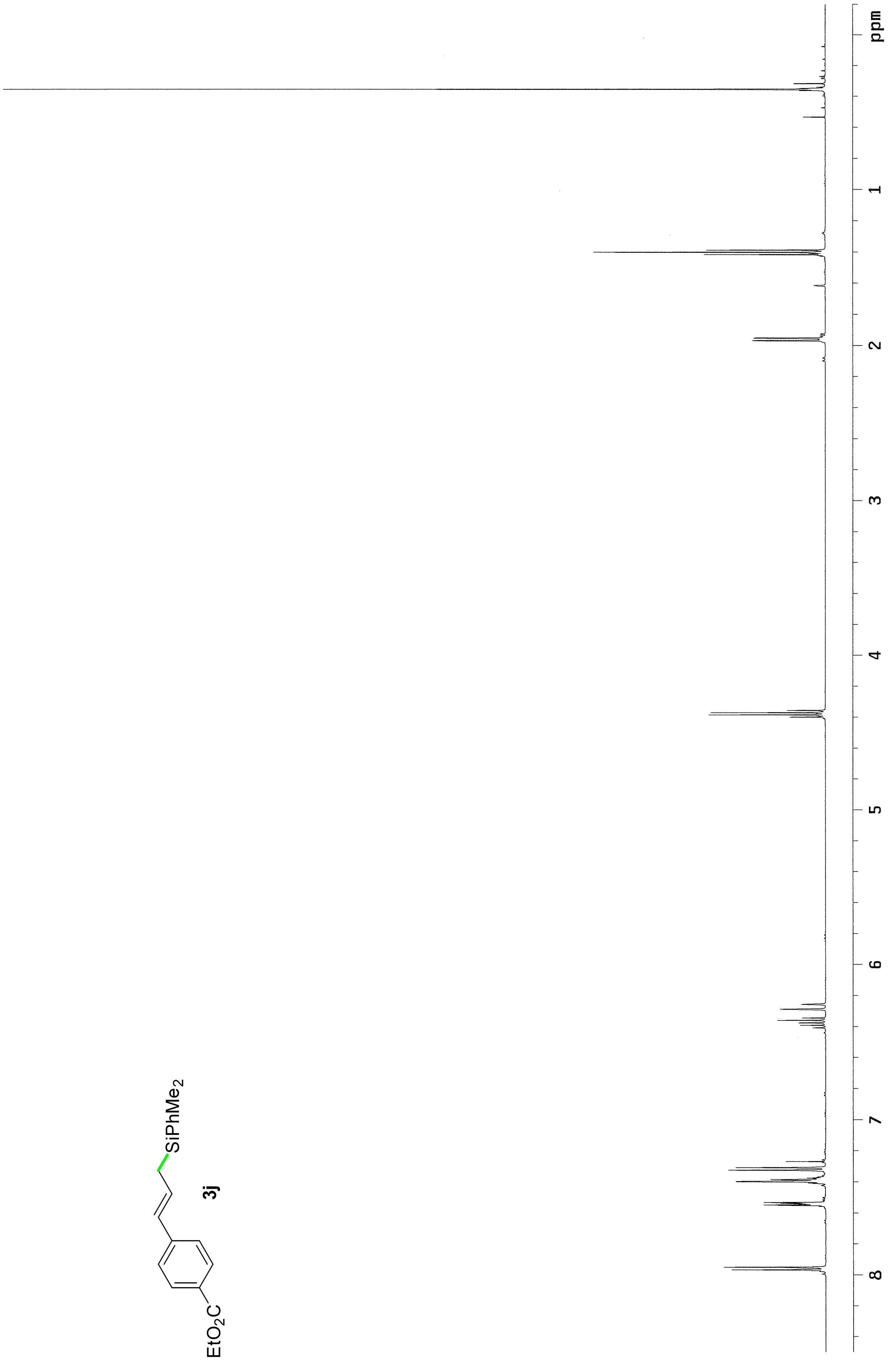
ppm



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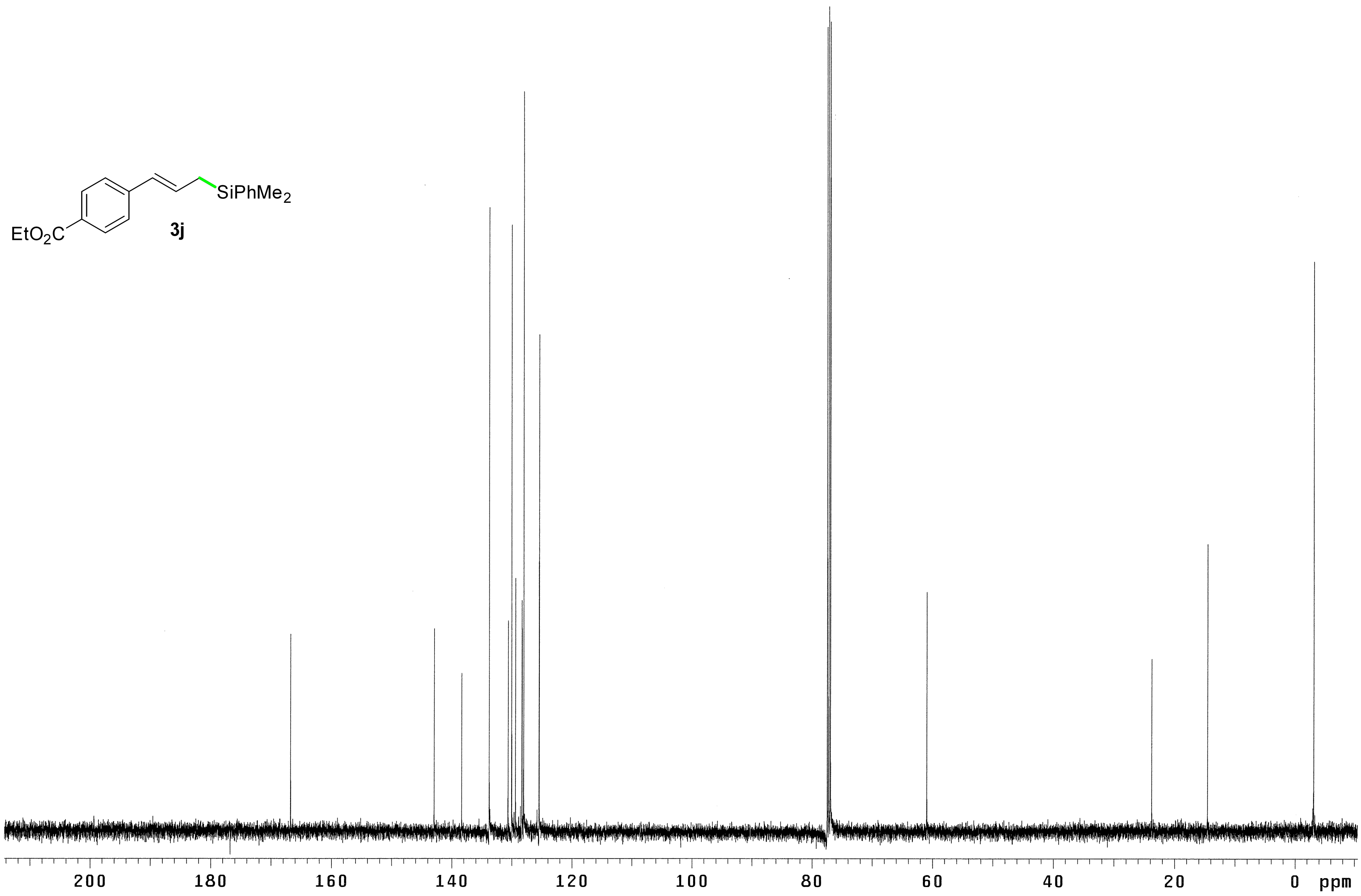

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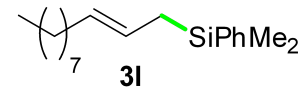

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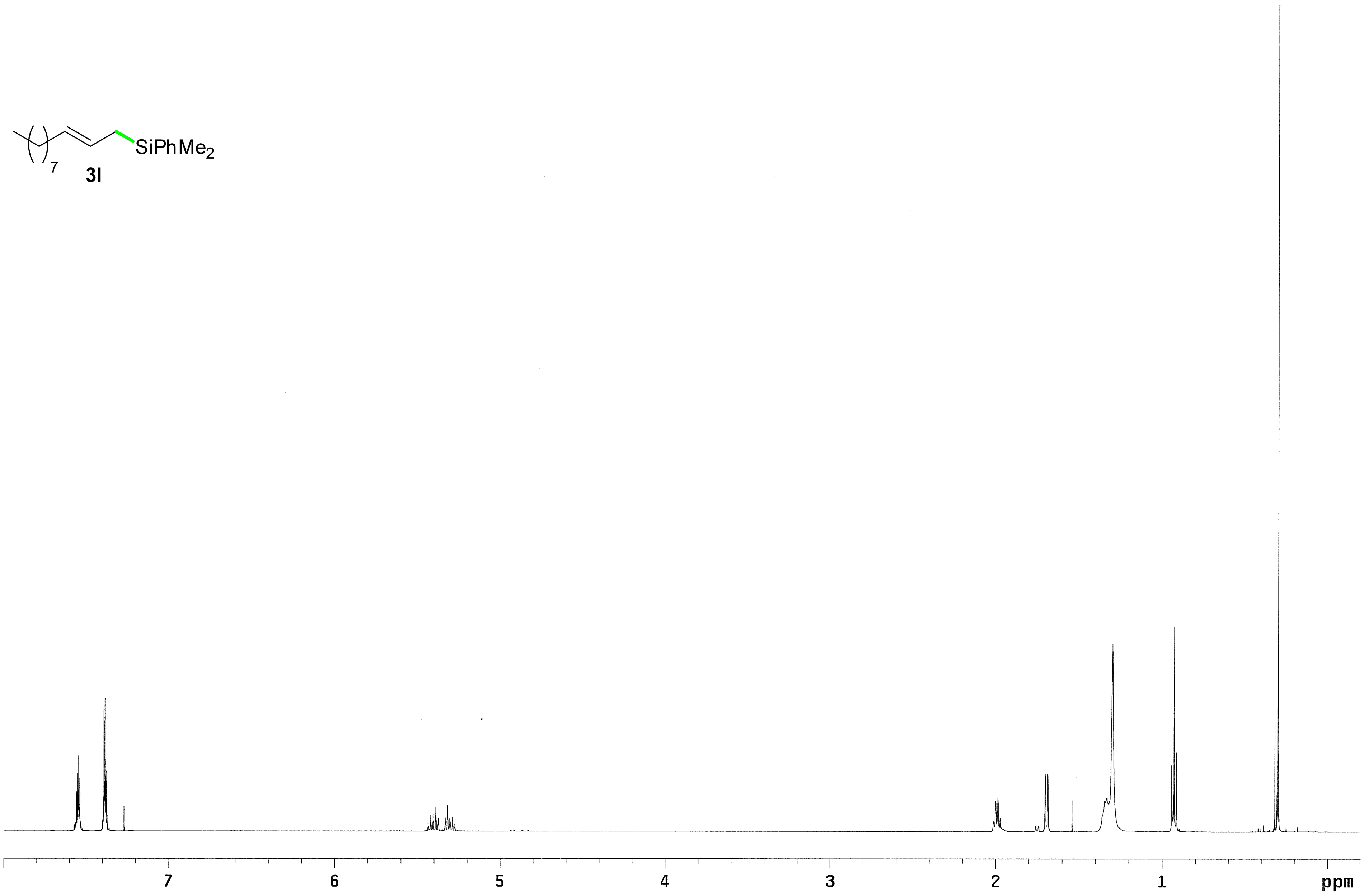

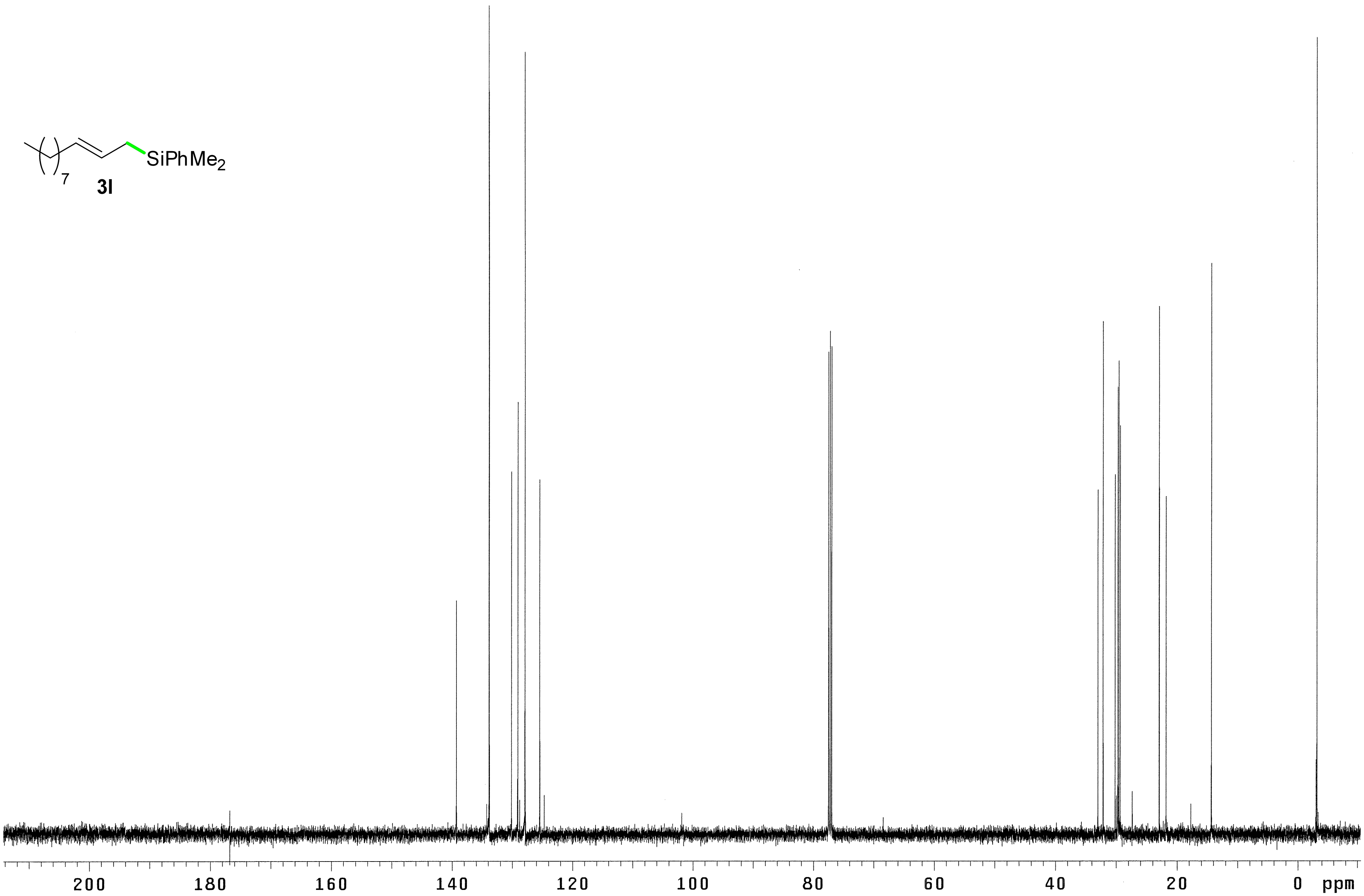
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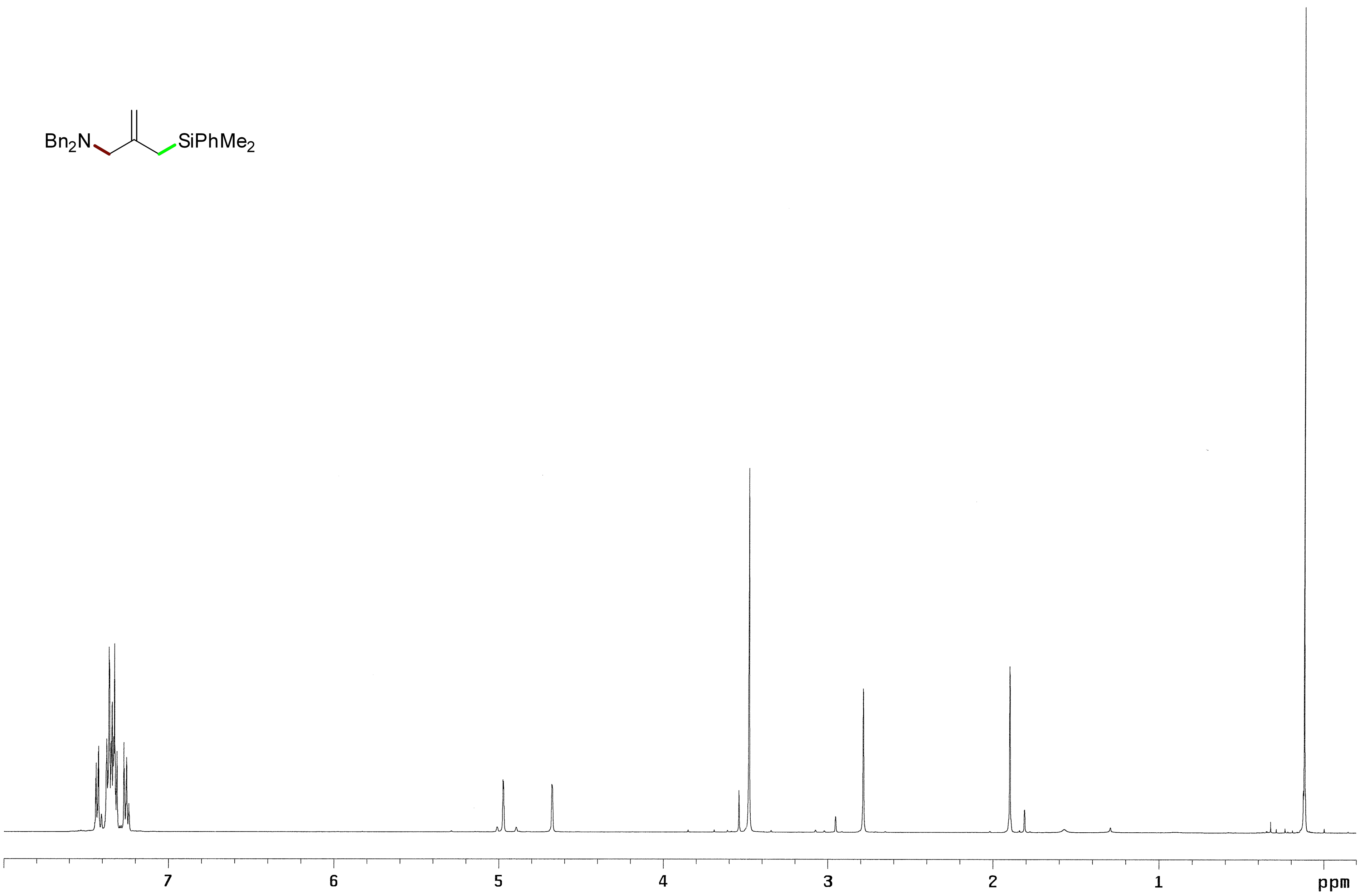
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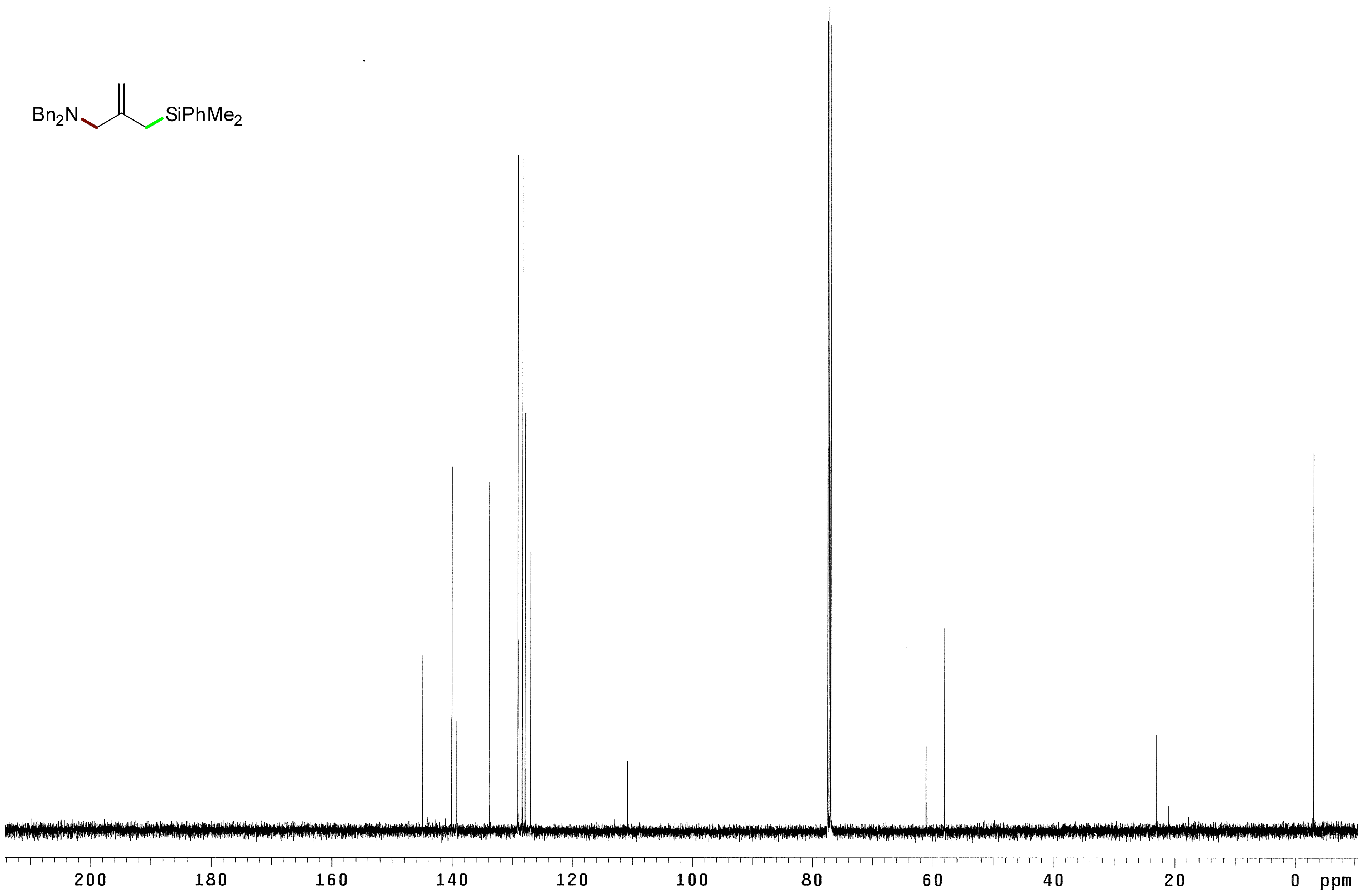
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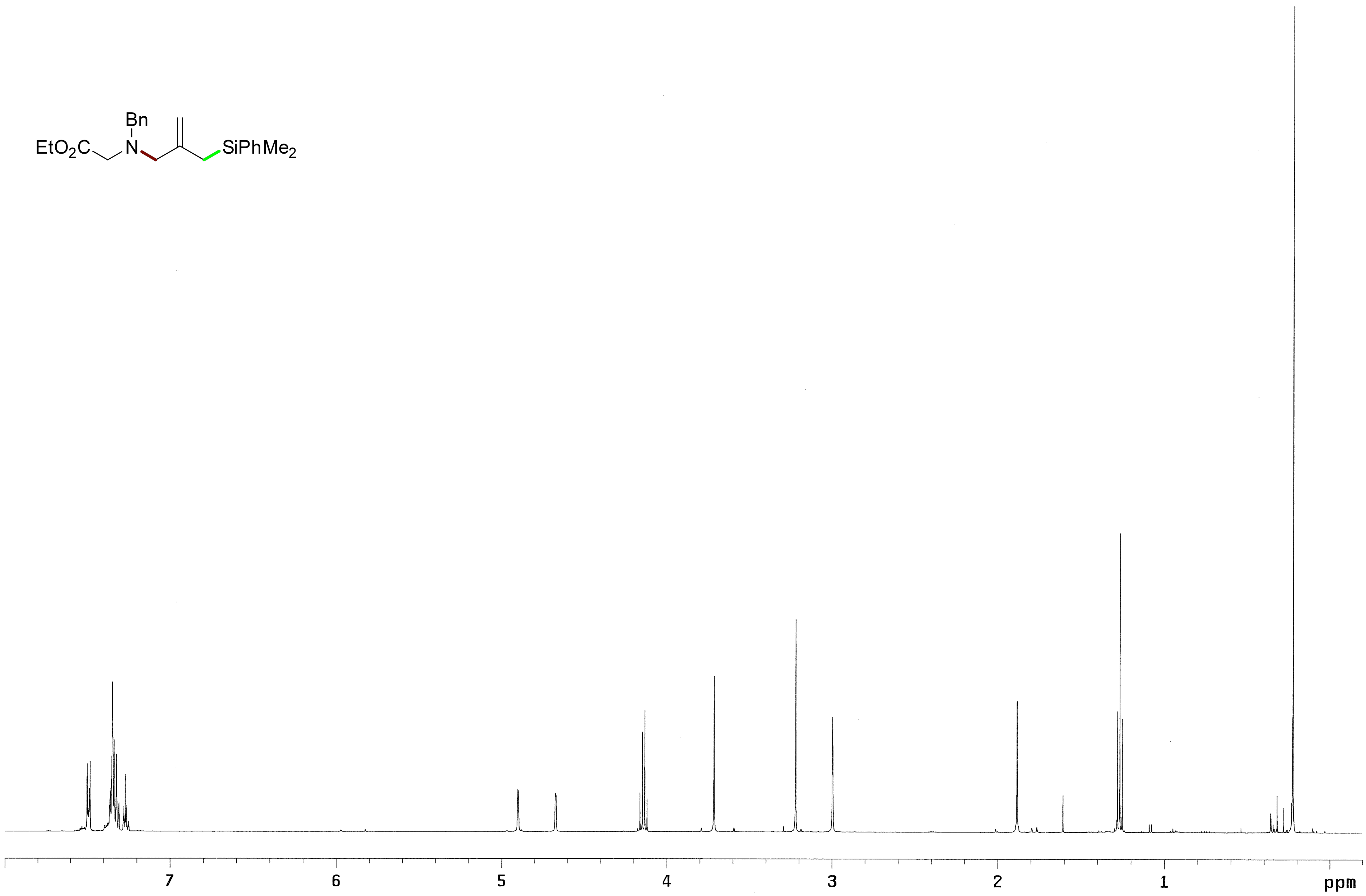
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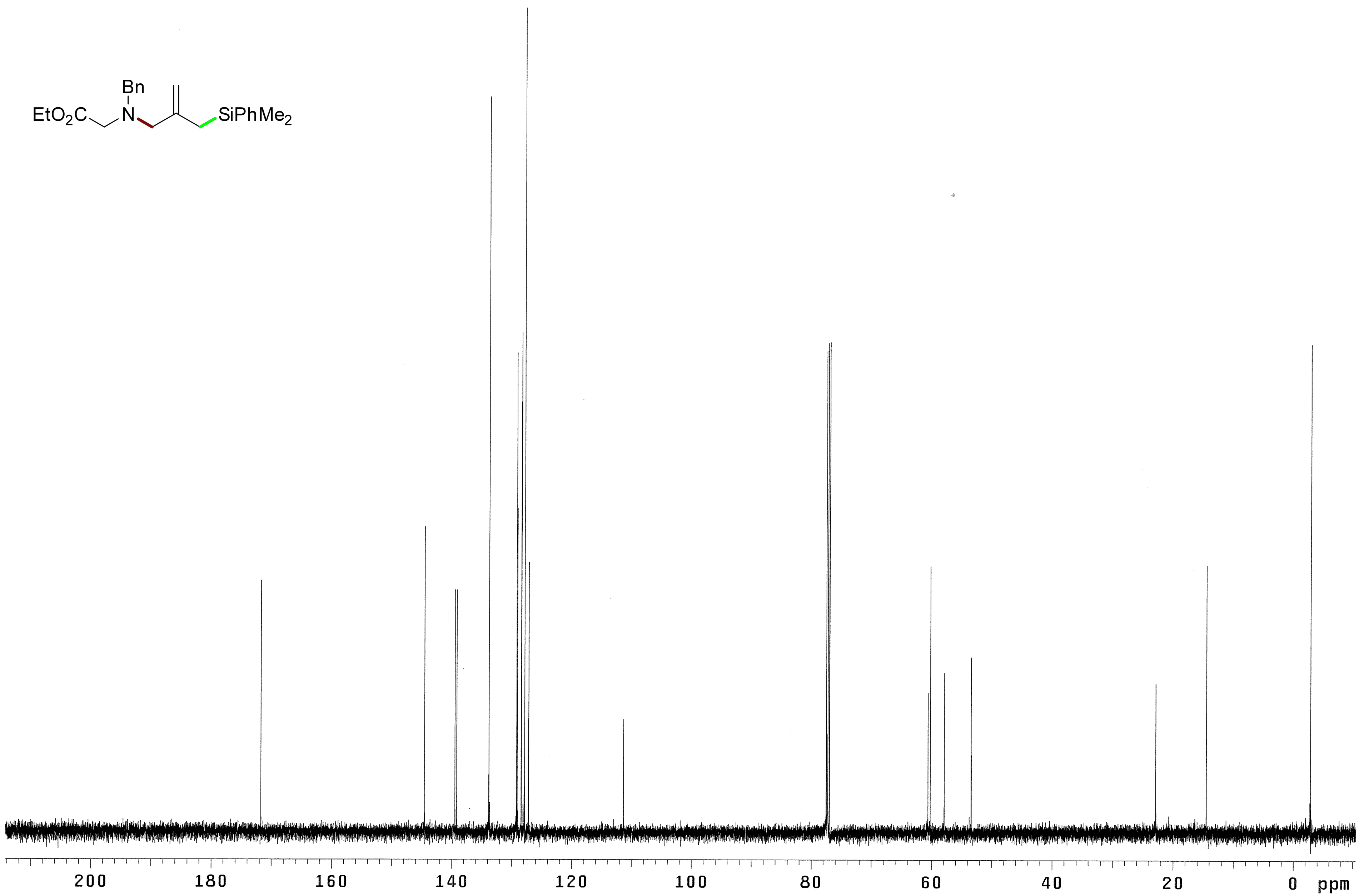
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