Palladium-Catalyzed Cross-Coupling of Monochlorosilanes And Grignard Reagents

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Supporting Information

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1. General Experimental Details:

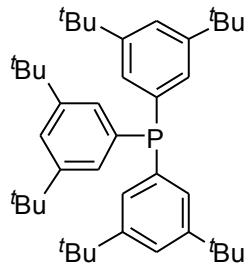
Bu_2O, Et_2O, methyl *tert*-butyl ether (MTBE), triethylamine, dichloromethane (DCM), acetonitrile (MeCN), and tetrahydrofuran (THF) were dried on alumina according to published procedures.[1] Cyclopentylmethyl ether (CPME) was dried over CaH_2, distilled under N_2, and stored in a Straus flask. The following reagents were purchased from commercial suppliers and used as received: Palladium(II) iodide (Strem), palladium(II) chloride (Strem), bis(acetonitrile)dichloropalladium(II) (Strem), 1-bromo-3,5-di-*tert*-butylbenzene (Combi Blocks), 2-chloropropane (Alfa) 2-bromopropane (Aldrich), 2-iodopropane (Oakwood), bromocyclopentane (Acros), 1-bromobutane (Acros), 3-bromopentane (Alfa Aesar), exo-2-bromonorbornane (Aldrich), (1-bromoethyl)benzene (Aldrich), (2-bromopropyl)benzene (Aldrich), dimethylphenylsilane (Gelest), iodomethane (Acros), magnesium turnings (Oakwood). All chlorosilanes were generously donated by Gelest Inc. and used as received. The following Grignard reagents were purchased from commercial suppliers and titrated with iodine before use: Phenylmagnesium bromide [3 M] in Et_2O (Aldrich), *ortho*-tolylmagnesium bromide [2 M] in Et_2O (Aldrich), 2-mesitylmagnesium bromide [1 M] in Et_2O (Aldrich), isopropylmagnesium bromide [1 M] in THF (Aldrich), isopropylmagnesium chloride [2 M] in THF (Acros), isopropylmagnesium chloride lithium chloride complex [1.3 M] in THF (Acros), cyclopentylmagnesium bromide [2 M] in Et_2O (Acros), (trimethylsilyl)methylmagnesium chloride [1 M] in Et_2O (Aldrich), and 2-methyl-2-phenylpropylmagnesium chloride [0.5 M] in Et_2O (Acros). (3-bromobutyl)benzene,[2] 1-(3-bromobutyl)-4-chlorobenzene,[3] and 1-(3-bromobutyl)-4-methoxybenzene,[4] were prepared according to the published procedures. Vials used in the glovebox were dried in a gravity oven at 140 °C for a minimum of 12 h, transferred into the glovebox hot, and then stored at rt in the glovebox prior to use. All hot glassware was oven dried for a minimum of four hours or flame-dried under vacuum prior to use. “Double manifold” refers to a standard Schlenk-line gas manifold equipped with nitrogen and vacuum (ca. 0.100 mm Hg). All optimization reactions (0.25 mmol scale) were charged in a nitrogen-filled glovebox and alkyl zinc halide was added on the bench via syringe then stirred on a magnetic stir plate. All yields and branched:linear (B:L) ratios in optimization reactions were determined by GC of the unpurified products with 1,3,5-trimethoxybenzene and *n*-nonane as internal standards. All other reactions were set up using standard Schlenk technique and heated with stirring in temperature controlled oil baths. **Note:** Any product yields listed in the main text that do not match those listed in the supporting information are the average of multiple isolated yields. The procedures listed below reflect yields from specific experimental runs.

2. Instrumentation and Chromatography:

400 MHz ^{1}H, 101 MHz ^{13}C and 376 MHz ^{19}F spectra were obtained on a 400 MHz FT-NMR spectrometer equipped with a Bruker CryoPlatform. 600 MHz ^{1}H, 151 MHz ^{13}C, 119 MHz ^{29}Si, and 243 ^{31}P spectra were obtained on a 600 MHz FT-NMR spectrometer equipped with a Bruker SMART probe. All samples were analyzed in the indicated deutero-solvent and were recorded at ambient temperatures. All chemical shifts are reported in ppm. ^{1}H NMR spectra were calibrated using the residual protio-signal in deutero-solvents as a standard. ^{13}C NMR spectra were calibrated using the deutero-solvent as a standard. Product ^{29}Si spectra were calibrated using a hexamethyldisiloxane capillary standard at 7.32ppm. IR spectra were recorded on a Nicolet Magma-IR 560 FT-IR spectrometer as thin films on KBr plates. High resolution MS data was obtained on a Waters GCT Premier spectrometer using chemical ionization (CI), electron ionization (EI), or liquid injection field desorption ionization (LIFDI). Unless otherwise noted, column chromatography was performed either by hand or by use of Isolera 4 Biotage unit with 40-63 μm silica gel, and the eluent reported in parentheses. Analytical thin-layer chromatography (TLC) was performed on silica gel (60 F_{254} Merck) pre-coated glass plates and visualized by UV or by staining with iodine, $KMnO_4$, or ceric ammonium molybdate.

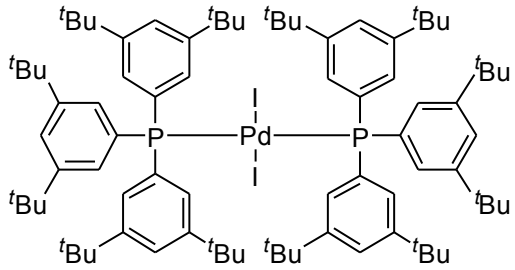
3. Synthesis of Ligand and Catalysts:

Ligand and Catalyst Synthesis:[5]



DrewPhos

DrewPhos: An oven-dried 500 mL round bottom flask equipped with a magnetic stir bar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the rubber septum was removed, 1-bromo-3,5-di-*tert*-butylbenzene (32.4 g, 120 mmol, 3.01 equiv) was added, and the septum replaced. The flask was then purged with N_2 for 15 minutes. THF (240 mL, [0.5 M]) was added and the flask was cool to –78 °C in a dry ice/acetone bath. While stirring, *n*BuLi (48.2 mL, 120 mmol, 3 equiv, [2.49 M] in hexanes) was added dropwise via syringe pump over 30 minutes. (**Note:** A large amount of solids can form and stall reaction stirring. Swirl flask by hand to break up clumps). PCl_3 (3.5 mL, 40 mmol, 1 equiv) was added dropwise via syringe pump over 15 minutes. (**Note:** Initial addition will begin to consume the aryl lithium and stirring will become easier, manual swirling may be necessary at the start of addition). After the addition was complete, the flask was warmed to 0 °C in an ice/water bath and stirred for 4 h. Flask was allowed to warm to rt, the septum was removed and the reaction was quenched by adding brine (100 mL). The reaction was poured into a separatory funnel and the product was extracted 2X with Et_2O (100 mL). The organic layer was dried over $MgSO_4$, filtered through a glass frit, and the solvent removed *in vacuo*. The product was purified by recrystallization from hot EtOH (200 mL), cooled under ambient conditions, then placed in a –20 °C freezer overnight. Collection of the solid via filtration and washing with EtOH resulted in white crystals (10.6 g, 44% yield): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (t, *J* = 1.8 Hz, 3H), 7.12 (dd, *J* = 8.5, 1.8 Hz, 6H), 1.22 (s, 54H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6 (d, *J* = 6.7 Hz), 137.3 (d, *J* = 9.4 Hz), 128.1 (d, *J* = 19.3 Hz), 122.4 , 35.0 , 31.5; ^{31}P NMR (243 MHz, $CDCl_3$) δ -3.59; FTIR (cm^{-1}): 2963, 1589, 1577, 1362, 1249, 1130, 875, 710; mp = 145–147 °C. HRMS (LIFDI) m/z, calcd for $[C_{42}H_{63}P]^+$: 598.4667; found: 598.4688.



(DrewPhos) $_2$PdI$_2$

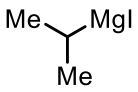
(DrewPhos)$_2$PdI$_2$: A 50 mL round bottom flask equipped with a magnetic stirbar was charged with palladium(II) iodide (1.08 g, 3 mmol, 1.0 equiv) and DrewPhos (3.59 g, 6 mmol, 2.0 equiv). The flask was sealed with a rubber septum and purged 10 min with N_2. Toluene (24 mL) was added via syringe and the reaction was stirred for 24 hours at 85 °C. The reaction was cooled to rt, transferred to a 250 mL round bottom flask and the solvent evaporated *in vacuo*. The resulting solid was recrystallized from hot 3:1 ethanol:toluene (100 mL), cooled under ambient conditions, then placed in a –20 °C freezer overnight. Collection of the solid via filtration resulted in a stable, red solid (3.52 g, 75% yield). A second crop of product was obtained by subsequent recrystallization with same solvent system resulted in red crystals (900 mg, 19%). Total 4.42 g, 95%: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 12H), 7.29 (s, 6H), 1.21 (s, 108H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2 (t, *J* = 5.1 Hz), 134.5 (t, *J* = 24.9 Hz), 129.9 (t, *J* = 6.2 Hz), 123.2, 35.1, 31.6; ^{31}P NMR (243 MHz, $CDCl_3$) δ 18.90 ; FTIR (cm^{-1}): 2953, 1589, 1384, 1247, 1087, 702, 584; mp = >250 °C. HRMS (LIFDI) m/z, calcd for $[C_{84}H_{126}P_2PdI]^+$:1429.7414; found: 1429.7373.

4. Synthesis of Alkylmagnesium Halides:

General Procedure A:

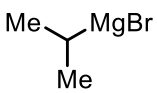
An oven dried round bottom flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the septum removed, magnesium turnings (1.5 equiv) and a single chip of I_2 (~20–30 mg) were added. The septum was replaced; the flask was attached to a double manifold and purged with N_2 for 10 min. The flask was held under positive N_2 then Et_2O [3 M] was added. The solution was stirred until clarity was reached (disappearance of brown I_2 color). An initial amount of alkyl halide (~200–400 µL) was added to start the reaction as evidenced by a minor exotherm. If reaction does not initiate, gentle warming (for example with a heating mantle) may be necessary. Once initiated, the alkyl halide was added dropwise so as to keep the mixture warm, but below full reflux. If desired, a reflux condenser may be used as well. After full addition of the alkyl halide, the flask was allowed to stir at rt for an additional 1-4 h. The excess magnesium was allowed to settle and the mixture was filtered via cannula to a Schlenk tube. If insoluble particles persist, filtration through a 0.2 µm PTFE syringe filter was employed. Solutions were then titrated according to the literature procedure by Knochel.[6]

Note: Titration concentrations used in the isolation runs in Section 5 may differ from those reported here. The procedures listed below reflect titrations from specific experimental runs.



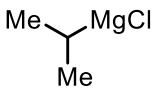
S1

(**S1**) According to general procedure A, magnesium turnings (1.1 mg, 45 mmol, 1.5 equiv), diethyl ether (10 mL), I_2 chip , and isopropyl iodide (3.0 mL, 5.1 g, 30 mmol, 1 equiv) were combined under nitrogen and stirred for 2 h at rt. Filtration and titration resulted in a [1.84 M] solution of isopropylmagnesium iodide.



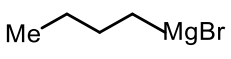
S2

(**S2**) According to general procedure A, magnesium turnings (1.1 mg, 45 mmol, 1.5 equiv), diethyl ether (10 mL), I_2 chip , and isopropyl bromide (2.8 mL, 3.69 g, 30 mmol, 1 equiv) were combined under nitrogen and stirred for 2 h at rt. Filtration and titration resulted in a [2.23 M] solution of isopropylmagnesium bromide.



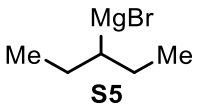
S3

(**S3**) According to general procedure A, magnesium turnings (1.1 mg, 45 mmol, 1.5 equiv), diethyl ether (10 mL), no iodine, and isopropyl chloride (2.7 mL, 2.36 g, 30 mmol) were combined under nitrogen and stirred for 4 h at rt. Filtration and titration resulted in a [2.65 M] solution of isopropylmagnesium chloride.



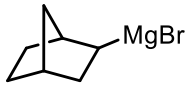
S4

(**S4**) According to general procedure A, magnesium turnings (730 mg, 30 mmol), diethyl ether (7 mL), no iodine, and a solution of *n*-butyl bromide (2.7 mL, 3.4 g, 25 mmol) in diethyl ether (5 mL) were combined under nitrogen and stirred for 4 h at rt.. Filtration and titration resulted in a [1.93 M] solution of *n*-butylmagnesium bromide.



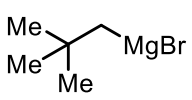
S5

(**S5**) According to general procedure A, magnesium turnings (300 mg, 12 mmol), diethyl ether (3 mL), I_2 chip, and solution of 3-bromopentane (1.2 mL, 1.5 g, 10 mmol) in diethyl ether (2 mL) were combined under nitrogen and stirred for 4 h at rt. Filtration and titration resulted in a [0.67 M] solution of 3-pentylmagnesium bromide.



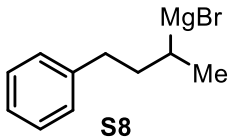
S6

(**S6**) According to general procedure A, magnesium turnings (730 mg, 30 mmol, 1.5 equiv), diethyl ether (6.7 mL), I_2 chip, and (1*S*,4*R*)-2-bromobicyclo[2.2.1]heptane (2.6 mL, 3.5 g, 20 mmol, 1 equiv) were combined under nitrogen and stirred 3 h at rt. Filtration and titration resulted in a [1.21 M] solution of bicyclo[2.2.1]heptan-2-ylmagnesium bromide in an *exo:endo* ratio of 41:59 by NMR matching literature reports.[7]



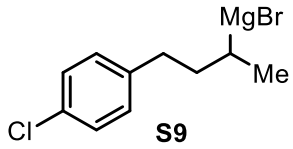
S7

(**S7**) According to general procedure A, magnesium turnings (730 mg, 30 mmol), diethyl ether (7 mL), I_2 chip, and solution of neopentyl bromide (3 mL, 3.6 g, 24 mmol) in diethyl ether (5 mL). Filtration and titration resulted in a [0.95 M] solution of neopentylmagnesium bromide.



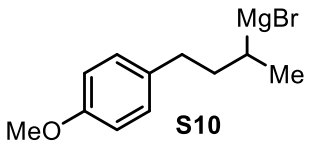
S8

(**S8**) According to general procedure A, magnesium turnings (1.1 g, 45 mmol, 1.5 equiv), I_2 chip, Et_2O (10 mL), and (3-bromobutyl)benzene (6.4 g, 30 mmol, 1 equiv) were combined under nitrogen and stirred for 1 h at rt. Filtration and iodometric titration resulted in a [1.34 M] solution of (4-phenylbutan-2-yl)magnesium bromide.



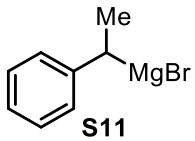
S9

(**S9**) According to general procedure A, magnesium turnings (292 mg, 12 mmol, 1.2 equiv), I_2 chip, Et_2O (3.3 mL), and 1-(3-bromobutyl)-4-chlorobenzene (2.48 g, 10 mmol, 1 equiv) were combined under nitrogen and stirred for 2 h at rt. Filtration and iodometric titration resulted in a [0.85 M] solution of (4-(4-chlorophenyl)butan-2-yl)magnesium bromide.



S10

(**S10**) According to general procedure A, magnesium turnings (292 mg, 12 mmol, 1.2 equiv), I_2 chip, Et_2O (3.3 mL), and 1-(3-bromobutyl)-4-methoxybenzene (2.43 g, 10 mmol, 1 equiv) were combined under nitrogen and stirred for 2 h at rt. Filtration and iodometric titration resulted in a [0.85 M] solution of (4-(4-methoxyphenyl)butan-2-yl)magnesium bromide.



S11

(**S11**) According to a modified version of general procedure A, magnesium turnings (1.1 g, 45 mmol, 1.5 equiv), diethyl ether (10 mL), and I_2 chip were added. Once clarity of the solution was reached, the flask was cooled to 0 °C in an ice/water bath. Stirring at 0 °C, (1-bromoethyl)benzene (5.6 g, 4.1 mL, 30 mmol, 1 equiv) was added dropwise via syringe pump over ~1 h. After addition, the flask was allowed to stir at rt ~3 h. Filtration and titration resulted in a [0.55 M] solution of (1-phenylethyl)magnesium bromide.

5. General Procedure for the Silyl-Kumada Reaction:

Note: Reactions are run at [0.5 M] overall concentration based on the sum of all liquid reagents.

General Procedure B (rt Coupling):

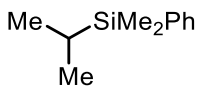
An oven dried 10 mL Schlenk flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the rubber septum was removed, and $(DrewPhos)_2PdI_2$ (0.01 equiv) was added. The septum was replaced and the flask purged with N_2 for 10 minutes. Et_2O, silyl chloride (1.2 equiv), and alkylmagnesium halide (1 equiv) were added sequentially via syringe. The solution was then stirred at rt for 24 h. A vent needle was added and the reaction was quenched with EtOAc (3 mL) then H_2O (3 mL) via syringe. The mixture was washed 2 times with brine (20 mL) and extracted using EtOAc or Et_2O. The combined organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The crude material was purified via silica gel flash chromatography in the indicated solvent.

General Procedure C (50 °C Coupling):

An oven dried 10 mL Schlenk flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the rubber septum was removed, and $(DrewPhos)_2PdI_2$ (0.01 equiv) was added. The septum was replaced and the flask purged with N_2 for 10 minutes. Bu_2O, silyl chloride (2 equiv), and alkylmagnesium halide (1 equiv) were added sequentially via syringe. The solution was then stirred in an oil bath at 50 °C for 24 h. The flask was cooled to rt, a vent needle was added and the reaction was quenched with EtOAc (3 mL) then H_2O (3 mL) via syringe. The mixture was washed 2 times with brine (20 mL) and extracted using EtOAc or Et_2O. The combined organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The crude material was purified via silica gel flash chromatography in the indicated solvent.

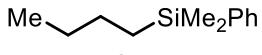
General Procedure D (Solid Silyl Chlorides):

An oven dried 10 mL Schlenk flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the rubber septum was removed, $(DrewPhos)_2PdI_2$ (0.01 equiv) and silyl chloride (2 equiv) were added. The septum was replaced and the flask purged with N_2 for 10 minutes. Bu_2O and alkylmagnesium halide (1 equiv) were added sequentially via syringe. The solution was then stirred in an oil bath at the indicated temperature for 24 h. The flask was cooled to rt, a vent needle was added and the reaction was quenched with EtOAc (3 mL) then H_2O (3 mL) via syringe. The mixture was washed 2 times with brine (20 mL) and extracted using EtOAc or Et_2O. The combined organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The crude material was purified via silica gel flash chromatography in the indicated solvent.



1

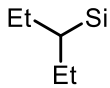
(**1**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (1.36 mL), dimethylphenylsilyl chloride (200 µL, 1.2 mmol), and [2.29 M] isopropylmagnesium bromide **S2** (440 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 1 h. After workup, the crude product was purified via silica gel flash chromatography (hexanes) to afford **1** as a clear oil (178 mg, 99%): ^1H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.39 – 7.33 (m, 3H), 1.01 – 0.94 (m, 7H), 0.26 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.8, 134.1, 128.9, 127.8, 17.7, 13.9, -5.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ 0.4. Spectra in agreement with previously reported literature.[5]



3

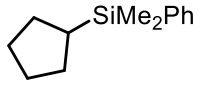
(**3**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (1.32 mL), dimethylphenylsilyl chloride (200 µL, 1.2 mmol), and [2.1 M] *n*-butylmagnesium bromide **S4** (480 µL, 1.0 mmol) were

combined under N_2 and stirred at rt for 1 h. After workup, the crude product was purified via silica gel flash chromatography (hexanes) to afford **3** as a clear oil (192 mg, 99%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.39 – 7.32 (m, 3H), 1.37 – 1.26 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.78 – 0.73 (m, 2H), 0.26 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.9, 133.7, 128.9, 127.8, 26.7, 26.2, 15.6, 13.9, -2.9. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -3.1. Spectra in agreement with previously reported literature.[5, 8]



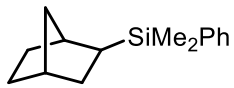
4

(**4**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), diethyl ether (0.3 mL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.67 M] 3-pentylmagnesium bromide **S5** (1.50 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, the crude product was purified via silica gel flash chromatography (hexanes) to afford **4** as a clear oil (203 mg, 99%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.38 – 7.34 (m, 3H), 1.54 (dqd, *J* = 14.7, 7.5, 5.3 Hz, 2H), 1.38 (dp, *J* = 14.7, 7.4 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 6H), 0.72 (tt, *J* = 7.5, 5.1 Hz, 1H), 0.29 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.8, 134.0, 128.8, 127.8, 29.04, 21.9, 13.8, -3.4. ^{29}Si NMR (119 MHz, $CDCl_3$) δ 1.0. Spectra in agreement with previously reported literature.[5]

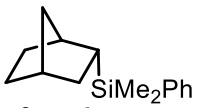


5

(**5**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), diethyl ether (1.24 mL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [1.77 M] cyclopentylmagnesium bromide (0.56 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **5** as a clear oil (200 mg, 99%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.40 – 7.32 (m, 3H), 1.83 – 1.72 (m, 2H), 1.58 – 1.49 (m, 4H), 1.39 – 1.27 (m, 2H), 1.13 (tt, *J* = 10.8, 8.2 Hz, 1H), 0.26 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 134.0, 128.8, 127.8, 28.4, 27.2, 25.6, -4.3. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -2.0. Spectra in agreement with previously reported literature.[5]



6-*exo* 73:27

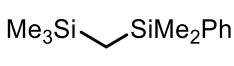


6-*endo*

(**6**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (970 μL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [1.21 M] (1*S*,4*R*)-bicyclo[2.2.1]heptan-2-ylmagnesium bromide **S6** (830 μL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **6** as an inseparable mixture of *exo:endo* (73:27) diastereomers as a clear oil (150 mg, 65%): Useful diagnostic peaks for each compound are listed, mixture matches previously reported spectra.[4-5, 9]

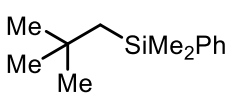
6-*exo*: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.22 – 2.20 (m, 2H), 1.06 – 1.05 (m, 2H), 0.83 – 0.79 (m, 1H), 0.24 (s, 3H), 0.22 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.5, 134.0, 128.8, 127.8, 38.1, 37.9, 37.1, 34.5, 32.9, 29.0, 28.7, -3.9, -3.9, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -3.20.

6-*endo*: ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.31 (s, 1H), 2.27 (t, *J* = 4.3 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.02 (tdd, *J* = 11.0, 4.9, 2.0 Hz, 1H), 0.31 (s, 3H), 0.28 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 133.9, 128.7, 127.8, 41.9, 39.7, 37.3, 32.0, 30.0, 28.5, 27.6, -2.7, -3.0, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -2.78.



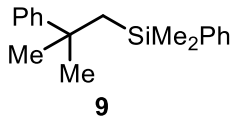
7

(**7**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), diethyl ether (0.76 mL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.96 M] (trimethylsilyl)methylmagnesium chloride (1.04 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **7** as a clear oil (122 mg, 55%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H), 7.38 – 7.33 (m, 3H), 0.31 (s, 6H), 0.02 (s, 2H), -0.01 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.5, 133.4, 128.86, 127.8, 3.4, 1.4, 0.0. ^{29}Si NMR (119 MHz, $CDCl_3$) δ 0.5, -4.2. FTIR (cm^{-1}): 2953, 2897, 1426, 1250, 1113, 1051, 836, 698. HRMS (CI) m/z, calcd for $C_{11}H_{19}Si_2^+$ $[M\text{-}CH_3]^+$: 207.1025; found: 207.1027.



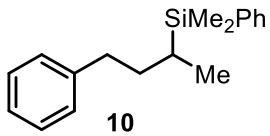
8

(**8**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (750 μL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.95 M] neopentylmagnesium bromide **S7** (1.05 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **8** as a clear oil (205 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.52 (m, 2H), 7.42 – 7.29 (m, 3H), 0.95 (s, 11H), 0.35 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 133.6, 128.7, 127.8, 33.2, 33.2, 31.3, -0.4. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -5.7. FTIR (cm^{-1}): 2954, 2893, 2869, 1465, 1427, 1363, 1249, 1113, 832, 707. HRMS (CI) m/z, calcd for $C_{13}H_{22}Si^+$ $[M]^+$: 206.1491; found: 206.1501.



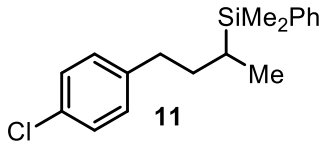
9

(**9**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (50 μL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.40 M] 2-methyl-2-phenylpropylmagnesium chloride (2.50 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **9** as a clear oil (136.2 mg, 51%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.33 – 7.32 (m, 2H), 7.30 – 7.27 (m, 3H), 7.27 – 7.22 (m, 2H), 7.15 – 7.13 (m, 1H), 1.37 (s, 2H), 1.32 (s, 6H), 0.01 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.1, 140.8, 133.6, 128.7, 128.1, 127.8, 125.7, 125.6, 37.5, 34.2, 32.6, -1.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -5.7. FTIR (cm^{-1}): 2959, 2360, 2339, 1652, 1558, 1456, 1110, 826. 668. HRMS (CI) m/z, calcd for $C_{17}H_{21}Si^+$ $[M\text{-}CH_3]^+$: 253.1413; found: 253.1417.



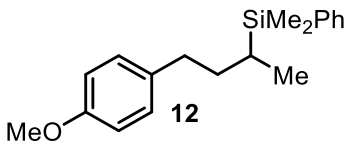
10

(**10**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), diethyl ether (1.1 mL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 μL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes gradient to hexanes:dichloromethane = 95:5) to afford **10** as a clear oil (264 mg, 98%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.50 – 7.47 (m, 2H), 7.37 – 7.31 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.17 – 7.13 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.76 (ddd, *J* = 14.0, 10.4, 4.9 Hz, 1H), 2.46 (ddd, *J* = 13.6, 10.1, 6.7 Hz, 1H), 1.79 (dddd, *J* = 13.7, 10.3, 6.7, 3.6 Hz, 1H), 1.41 (dtd, *J* = 13.6, 10.3, 4.9 Hz, 1H), 1.02 (d, *J* = 7.2 Hz, 3H), 0.96 – 0.89 (m, 1H), 0.26 (s, 3H), 0.25 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 138.7, 134.1, 128.9, 128.6, 128.4, 127.8, 125.7, 35.0, 33.9, 19.0, 14.1, -4.6, -4.8, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -0.05. Spectra in agreement with previously reported literature.[5, 10]



11

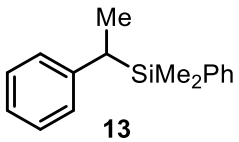
(**11**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), diethyl ether (0.52 mL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.79 M] 4-(4-(chloro)phenyl)butan-2-yl)magnesium bromide **S9** (1.28 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then by reverse phase chromatography on C18 modified silica (gradient from acetonitrile:water = 50:50 to acetonitrile:water 100:0) to afford **11** as a clear oil (272 mg, 89%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.40 – 7.32 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 2.76 – 2.69 (m, 1H), 2.44 (ddd, *J* = 13.7, 9.7, 7.0 Hz, 1H), 1.77 (dddd, *J* = 13.5, 10.2, 7.0, 3.5 Hz, 1H), 1.40 (dtd, *J* = 13.9, 10.1, 4.9 Hz, 1H), 1.02 (d, *J* = 7.3 Hz, 3H), 0.94 – 0.83 (m, 1H), 0.27 (s, 3H), 0.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 138.6, 134.1, 131.5, 129.9, 129.0, 128.5, 127.8, 34.3, 33.8, 18.9, 14.1, -4.6, -4.9. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -0.05. Spectra in agreement with previously reported literature.[5]



12

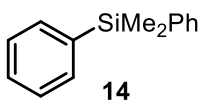
(**12**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), diethyl ether (620 μL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.85 M] (4-(4-methoxyphenyl)butan-2-yl)magnesium bromide **S10** (1.18 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes gradient to hexanes:dichloromethane = 90:10) to afford **12** as a clear oil (283 mg, 95%): ^{1}H NMR

(600 MHz, CD_2Cl2) δ 7.50 – 7.46 (m, 2H), 7.36 – 7.31 (m, 3H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.75 (s, 3H), 2.70 (ddd, *J* = 14.5, 10.2, 4.9 Hz, 1H), 2.40 (ddd, *J* = 13.6, 10.0, 6.8 Hz, 1H), 1.74 (dddd, *J* = 13.6, 10.2, 6.8, 3.5 Hz, 1H), 1.40 – 1.33 (m, 1H), 1.00 (d, *J* = 7.3 Hz, 3H), 0.90 (dqd, *J* = 11.0, 7.6, 7.2, 3.5 Hz, 1H), 0.25 (s, 3H), 0.24 (s, 3H), ^{13}C NMR (151 MHz, CD_2Cl2) δ 158.3, 139.2, 135.5, 134.5, 129.8, 129.3, 128.1, 114.1, 55.7, 34.6, 34.4, 19.3, 14.3, -4.5, -4.7, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -0.17. Spectra in agreement with previously reported literature.[4-5]



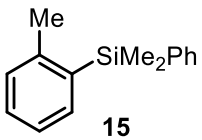
13

(**13**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (100 μL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.55 M] (1-phenylethyl)magnesium bromide **S11** (1.8 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then by reverse phase chromatography on C18 modifed silica (gradient from acetonitrile:water = 50:50 to acetonitrile:water = 75:25) to afford **13** as a clear oil (129 mg, 54%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 2H), 2.38 (q, *J* = 7.5 Hz, 1H), 1.33 (d, *J* = 7.5 Hz, 3H), 0.24 (s, 3H), 0.19 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.2, 137.5, 134.1, 129.0, 127.9, 127.5, 127.3, 124.4, 29.5, 15.1, -4.4, -5.5, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -1.03. Spectra in agreement with previously reported literature.[5]



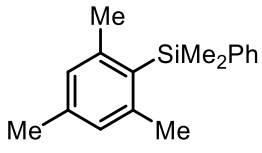
14

(**14**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (1.40 mL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [2.62 M] phenylmagnesium bromide (400 μL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then by reverse phase chromatography on C18 modifed silica (gradient from acetonitrile:water = 50:50 to acetonitrile:water = 100:0) to afford **14** as a clear oil (215 mg, 97%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.50 (m, 4H), 7.40 – 7.35 (m, 6H), 0.59 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 134.4, 129.2, 128.0, -2.2.^{29}Si NMR (119 MHz, $CDCl_3$) δ -8.1. Spectra in agreement with previously reported literature.[11]



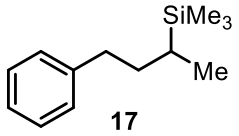
15

(**15**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (1.3 mL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [2.0 M] *ortho*-tolylmagnesium bromide (0.500 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **15** as a clear oil (210 mg, 93%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.51 – 7.47 (m, 3H), 7.38 – 7.31 (m, 3H), 7.29 (td, *J* = 7.5, 1.3 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 2.25 (s, 3H), 0.58 (s, 6H), ^{13}C NMR (151 MHz, CD_2Cl2) δ 144.7, 139.7, 136.8, 135.9, 134.6, 130.4, 130.1, 129.5, 128.4, 125.5, 23.5, -1.0, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -8.1, FTIR (cm^{-1}): 3067, 3050, 3003, 2956, 1589, 1428, 1250, 1130, 1112, 817, 775, 701, 642, 474. HRMS (CI) m/z, calcd for $C_{14}H_{15}Si^+$ $[M]^+$: 211.0943; found: 211.0952. Spectra in agreement with previously reported literature.[12]



16

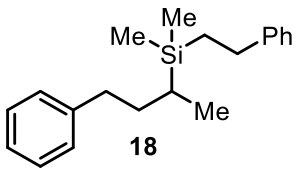
(**16**) According to general procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (720 μL), dimethylphenylsilyl chloride (200 μL, 1.2 mmol), and [0.93 M] 2-mesitylmagnesium bromide (1.08 mL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **16** as a clear oil (250 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.35 – 7.29 (m, 3H), 6.84 (s, 2H), 2.30 (s, 6H), 2.29 (s, 3H), 0.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 141.7, 139.2, 133.5, 130.8, 129.3, 128.7, 128.0, 25.1, 21.1, 3.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -9.0. FTIR (cm^{-1}): 2954, 1605, 1450, 1427, 1250, 1105, 816, 701, 667. HRMS (CI) m/z, calcd for $C_{17}H_{22}Si^+$ $[M]^+$: 254.1491; found: 254.1495.



17

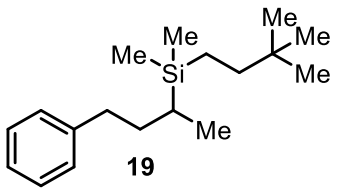
(**17**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (1.04 mL), trimethylsilyl chloride (150 μL, 1.2 mmol), and [1.43 M] (4-

phenylbutan-2-yl)magnesium bromide **S8** (700 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **17** as a clear oil (154 mg, 75%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.16 (m, 3H), 2.81 (ddd, *J* = 14.8, 10.6, 4.9 Hz, 1H), 2.51 (ddd, *J* = 13.5, 10.3, 6.6 Hz, 1H), 1.79 (dddd, *J* = 13.9, 10.3, 6.5, 3.7 Hz, 1H), 1.49 – 1.33 (m, 1H), 1.01 (d, *J* = 7.4 Hz, 3H), 0.65 (dqd, *J* = 10.9, 7.4, 3.7 Hz, 1H), -0.03 (s, 9H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 128.6, 128.4, 125.7, 35.2, 34.1, 19.6, 14.0, -3.1, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 4.53, FTIR (cm^{-1}): 3027, 2953, 2865, 1604, 1496, 1454, 1248, 856, 834, 745, 698. HRMS (CI) m/z, calcd for $[C_{13}H_{21}Si]^+$: 205.1413; found: 205.1418.



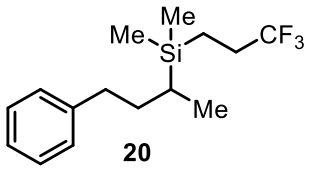
18

(**18**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (950 µL), phenethyldimethylsilyl chloride (240 µL, 1.2 mmol), and [1.23 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (810 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then by reverse phase chromatography on C18 modifed silica (gradient from acetonitrile:water = 75:25 to acetonitrile:water = 95:0) to afford **18** as a clear oil (280 mg, 94%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.29 – 7.23 (m, 4H), 7.22 – 7.12 (m, 6H), 2.82 (ddd, *J* = 14.3, 10.5, 4.8 Hz, 1H), 2.59 (dd, *J* = 11.4, 6.1 Hz, 2H), 2.50 (ddd, *J* = 13.6, 10.1, 6.7 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.47 – 1.39 (m, 1H), 1.04 (d, *J* = 7.4 Hz, 3H), 0.90 – 0.85 (m, 2H), 0.78 – 0.70 (m, 1H), -0.01 (s, 6H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.5, 143.1, 128.6, 128.4, 127.9, 125.8, 125.7, 35.2, 34.1, 30.2, 18.5, 16.1, 14.0, -4.98, -5.00, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 5.5. HRMS (CI) m/z, calcd for $[C_{19}H_{25}Si]^+$: 281.1726; found: 281.1716.



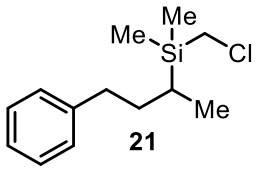
19

(**19**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (930 µL), (3,3-dimethylbutyl)dimethylsilyl chloride (250 µL, 1.2 mmol), and [1.23 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (810 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then by reverse phase chromatography on C18 modified silica (gradient from acetonitrile:water = 75:25 to acetonitrile:water = 100:0) to afford **19** as a clear oil (255 mg, 92%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.16 (m, 3H), 2.82 (ddd, *J* = 14.1, 10.4, 4.8 Hz, 1H), 2.50 (ddd, *J* = 13.5, 10.1, 6.7 Hz, 1H), 1.78 (dddd, *J* = 13.7, 10.3, 6.7, 3.5 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.11 (ddd, *J* = 12.7, 5.8, 2.1 Hz, 2H), 1.01 (d, *J* = 7.4 Hz, 3H), 0.84 (s, 9H), 0.74 – 0.66 (m, 1H), 0.45 – 0.40 (m, 2H), -0.07 (s, 3H), -0.07 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 128.6, 128.4, 125.7, 38.0, 35.2, 34.1, 31.2, 29.0, 18.4, 14.1, 7.8, -5.1, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 6.14, FTIR (cm^{-1}): 3027, 2952, 2913, 2865, 1604, 1466, 1454, 1363, 1248, 1159, 886, 835, 745, 698. HRMS (CI) m/z, calcd for $[C_{17}H_{29}Si]^+$: 261.2039; found: 261.2038.

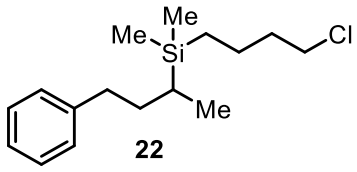


20

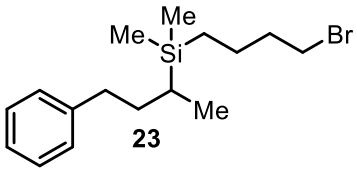
(**20**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (1.23 mL), (3,3,3-trifluoropropyl)dimethylsilyl chloride (210 µL, 1.2 mmol), and [1.78 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (560 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **20** as a clear oil (234 mg, 81%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 – 7.15 (m, 3H), 2.83 (ddd, *J* = 14.2, 10.1, 4.8 Hz, 1H), 2.51 (ddd, *J* = 13.6, 9.8, 6.9 Hz, 1H), 2.03 – 1.89 (m, 2H), 1.77 (dddd, *J* = 13.6, 10.2, 6.9, 3.3 Hz, 1H), 1.49 – 1.39 (m, 1H), 1.03 (d, *J* = 7.4 Hz, 3H), 0.78 – 0.66 (m, 3H), -0.01 (s, 3H), -0.01 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 128.5, 128.5, 127.80 (q, *J* = 276.7 Hz) 125.9, 34.9, 33.8, 28.95 (q, *J* = 29.8 Hz), 18.0, 13.8, 5.5, -5.3, -5.4, ^{19}F NMR (565 MHz, $CDCl_3$) δ 68.78, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 6.11, FTIR (cm^{-1}): 3028, 2953, 2867, 1604, 1497, 1364, 1264, 1212, 1125, 1067, 900, 844, 699. HRMS (CI) m/z, calcd for $[C_{15}H_{24}F_3Si]^+$: 289.1599; found: 289.1587.



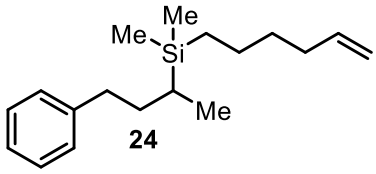
(**21**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (1.1 mL), chloromethyldimethylsilyl chloride (160 µL, 1.2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **21** as a clear oil (154 mg, 64%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.21 – 7.16 (m, 3H), 2.81 (s, 3H), 2.52 (ddd, *J* = 13.5, 10.3, 6.5 Hz, 1H), 1.80 (dddd, *J* = 13.9, 10.3, 6.5, 3.6 Hz, 1H), 1.51 – 1.42 (m, 1H), 1.05 (d, *J* = 7.4 Hz, 3H), 0.90 (dqd, *J* = 11.1, 7.3, 3.6 Hz, 1H), 0.10 (s, 3H), 0.09 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.7, 128.5, 128.5, 125.9, 35.0, 33.8, 29.5, 17.6, 13.9, -6.0, -6.1, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 6.21, FTIR (cm^{-1}): 3027, 2954, 2927, 2865, 1604, 1496, 1454, 1251, 842, 746, 699. HRMS (CI) m/z, calcd for $[C_{13}H_{22}ClSi]^+$: 241.1179; found: 241.1182.



(**22**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (970 µL), 4-chlorobutyldimethylsilyl chloride (220 µL, 1.2 mmol), and [1.23 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (810 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **22** as a clear oil (247 mg, 87%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.21 – 7.14 (m, 3H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.81 (ddd, *J* = 13.6, 10.3, 4.8 Hz, 1H), 2.50 (ddd, *J* = 13.5, 10.1, 6.7 Hz, 1H), 1.82 – 1.73 (m, 3H), 1.46 – 1.36 (m, 3H), 1.01 (d, *J* = 7.4 Hz, 3H), 0.69 (dqd, *J* = 10.8, 7.3, 3.5 Hz, 1H), 0.55 – 0.48 (m, 2H), -0.05 (s, 3H), -0.05 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 128.6, 128.4, 125.7, 44.9, 36.4, 35.1, 34.1, 21.4, 18.5, 14.0, 13.1, -4.98, -5.01, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 5.45, FTIR (cm^{-1}): 3026, 2952, 2931, 2864, 1603, 1496, 1454, 1248, 834, 747, 699. HRMS (CI) m/z, calcd for $[C_{16}H_{28}ClSi]^+$: 283.1649; found: 283.1658.

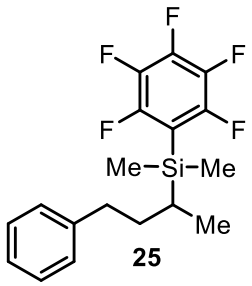


(**23**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (810 µL), 4-bromobutyldimethylsilyl chloride (220 µL, 1.2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then reverse phase chromatography on C18 modified silica (gradient from acetonitle:water = 70:30 to acetonitrile:water = 100:0) to afford **23** as a clear oil (302 mg, 92%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 6.4 Hz, 3H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.82 (ddd, *J* = 14.7, 10.4, 4.8 Hz, 1H), 2.49 (ddd, *J* = 13.5, 10.1, 6.7 Hz, 1H), 1.85 (p, *J* = 6.9 Hz, 2H), 1.77 (dddd, *J* = 13.7, 10.2, 6.7, 3.4 Hz, 1H), 1.41 (dddd, *J* = 14.7, 10.3, 6.8, 3.5 Hz, 3H), 1.01 (d, *J* = 7.3 Hz, 3H), 0.69 (dqd, *J* = 10.8, 7.4, 3.4 Hz, 1H), 0.53 – 0.47 (m, 2H), -0.05 (s, 6H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 128.6, 128.4, 125.7, 36.6, 35.1, 34.1, 33.8, 22.6, 18.4, 14.0, 12.9, -4.98, -5.01, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 5.42, FTIR (cm^{-1}): 3026, 2951, 2930, 2864, 1603, 1496, 1454, 1248, 835, 748, 699. HRMS (CI) m/z, calcd for $[C_{15}H_{24}BrSi]^+$: 311.0831; found: 311.0842.



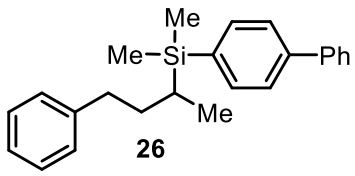
(**24**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Et_2O (950 µL), 5-hexenyldimethylsilyl chloride (240 µL, 1.2 mmol), and [1.23 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (810 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then reverse phase chromatography on C18 modified silica (gradient from acetonitle:water = 70:30 to acetonitrile:water = 100:0) to afford **24** as a clear oil (251 mg, 91%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.20 – 7.15 (m, 3H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (dq, *J* = 17.1, 1.5 Hz, 1H), 4.95 – 4.91 (m, 1H), 2.84 – 2.77 (m, 1H), 2.49 (ddd, *J* = 13.5, 10.2, 6.6 Hz, 1H), 2.04 (q, *J* = 7.0 Hz, 2H), 1.77 (dddd, *J* = 13.7, 10.2, 6.6, 3.5 Hz, 1H), 1.45 – 1.35 (m, 3H), 1.31 – 1.24 (m, 2H), 1.00 (d, *J* = 7.4 Hz, 3H), 0.68 (dqd, *J* = 10.8, 7.4, 3.5 Hz, 1H), 0.53 – 0.47 (m, 2H), -0.07 (s, 3H), -0.07 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 139.3, 128.6, 128.4, 125.7, 114.3,

35.2, 34.1, 33.6, 33.1, 23.6, 18.6, 14.1, 13.7, -4.9, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 5.31. FTIR (cm^{-1}): 3063, 3027, 2923, 2854, 1641, 1604, 1496, 1454, 1248, 909, 834, 746, 698. HRMS (CI) m/z, calcd for $[C_{17}H_{27}Si]^+$: 259.1882; found: 259.1882.



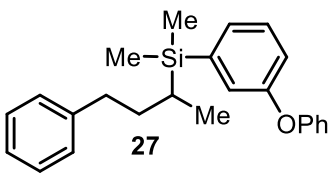
25

(**25**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (1.0 mL), pentafluorophenyldimethylsilyl chloride (230 μL, 1.2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 μL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **25** as a clear oil (227 mg, 63%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.25 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 2.80 (ddd, *J* = 14.6, 10.3, 4.9 Hz, 1H), 2.49 (ddd, *J* = 13.5, 10.0, 6.7 Hz, 1H), 1.76 (dddd, *J* = 13.7, 10.2, 6.7, 3.4 Hz, 1H), 1.45 (dddd, *J* = 16.9, 12.2, 8.5, 3.5 Hz, 1H), 1.09 (dp, *J* = 12.3, 4.7, 4.1 Hz, 1H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.39 (s, 3H), 0.38 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.2 (dddt, *J* = 241.4, 17.4, 8.7, 4.0 Hz), 142.5, 142.0 (dtt, *J* = 254.3, 12.9, 5.7 Hz), 138.3 – 136.2 (m), 128.5, 125.9, 110.0 – 109.3 (m), 34.9, 33.6, 19.0, 13.8, -3.34 (dt, *J* = 14.4, 3.7 Hz), ^{19}F NMR (565 MHz, CD_2Cl2) δ -126.48 – -126.61 (m), -152.97 (t, *J* = 19.8 Hz), -162.37 (td, *J* = 22.6, 8.6 Hz), ^{29}Si NMR (119 MHz, $CDCl_3$) δ 4.07, FTIR (cm^{-1}): 3028, 2955, 2868, 1642, 1517, 1457, 1374, 1283, 1256, 1086, 969, 841, 802, 747, 699. HRMS (CI) m/z, calcd for $[C_{17}H_{16}F_5Si]^+$: 343.0941; found: 343.0945.



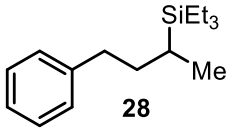
26

(**26**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (1.3 mL), 4-biphenyldimethylsilyl chloride (300 mg, 1.2 mmol), and [1.43 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (700 μL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then reverse phase chromatography on C18 modified silica (gradient from acetonitle:water = 80:20 to acetonitrile:water = 90:10) to afford **26** as a clear oil (287 mg, 83%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.64 – 7.61 (m, 2H), 7.61 – 7.55 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.14 (t, *J* = 6.3 Hz, 3H), 2.84 – 2.76 (m, 1H), 2.53 – 2.44 (m, 1H), 1.87 – 1.78 (m, 1H), 1.48 – 1.39 (m, 1H), 1.06 (t, *J* = 5.9 Hz, 3H), 1.00 – 0.92 (m, 1H), 0.31 – 0.27 (m, 6H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 141.7, 141.3, 137.4, 134.6, 128.9, 128.6, 128.4, 127.5, 127.3, 126.5, 125.7, 35.0, 33.9, 19.0, 14.2, -4.5, -4.7, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -0.04, FTIR (cm^{-1}): 3062, 3025, 2952, 2863, 1597, 1496, 1485, 1454, 1384, 1250, 1115, 1007, 826, 811, 756, 697. HRMS (CI) m/z, calcd for $[C_{23}H_{25}Si]^+$: 329.1726; found: 329.1731.



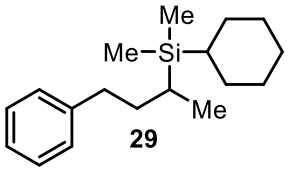
27

(**27**) According to procedure B, $(DrewPhos)_2PdI_2$ (16 mg, 10 μmol), Et_2O (1.0 mL), 3-phenoxydimethylsilyl chloride (285 μL, 1.2 mmol), and [1.43 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (700 μL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) then reverse phase chromatography on C18 modified silica (gradient from acetonitle:water = 80:20 to acetonitrile:water = 90:10) to afford **27** as a clear oil (314 mg, 87%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.32 (q, *J* = 7.5 Hz, 3H), 7.26 – 7.22 (m, 3H), 7.18 – 7.13 (m, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.95 (m, 3H), 2.76 (ddd, *J* = 14.9, 10.4, 4.9 Hz, 1H), 2.46 (ddd, *J* = 13.5, 10.2, 6.6 Hz, 1H), 1.78 (dddd, *J* = 13.8, 10.3, 6.6, 3.6 Hz, 1H), 1.40 (dtd, *J* = 13.6, 10.2, 4.9 Hz, 1H), 1.02 (d, *J* = 7.3 Hz, 3H), 0.96 – 0.87 (m, 1H), 0.25 (s, 3H), 0.24 (s, 3H), ^{13}C NMR (151 MHz, CD_2Cl2) δ 158.2, 157.0, 143.5, 141.7, 130.3, 129.7, 129.6, 128.9, 128.8, 126.1, 125.1, 123.5, 120.0, 118.9, 35.4, 34.4, 19.4, 14.3, -4.5, -4.8, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 0.34, FTIR (cm^{-1}): 3061, 3026, 2952, 2864, 1566, 1489, 1476, 1401, 1226, 1110, 812, 771, 697. HRMS (CI) m/z, calcd for $[C_{23}H_{25}SiO]^+$: 345.1675; found: 345.1685.



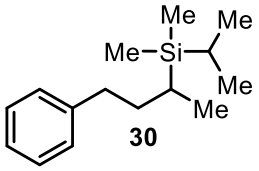
28

(**28**) According to procedure C, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Bu_2O (910 µL), triethylsilyl chloride (340 µL, 2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **28** as a clear oil (249 mg, 99%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.15 (m, 3H), 2.84 (ddd, *J* = 14.1, 10.5, 4.8 Hz, 1H), 2.48 (ddd, *J* = 13.5, 10.2, 6.7 Hz, 1H), 1.80 (dddd, *J* = 13.6, 10.0, 6.6, 3.1 Hz, 1H), 1.50 – 1.41 (m, 1H), 1.04 (d, *J* = 7.4 Hz, 3H), 0.93 (t, *J* = 8.0 Hz, 9H), 0.81 (dqd, *J* = 10.6, 7.4, 3.3 Hz, 1H), 0.54 (q, *J* = 8.0 Hz, 6H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 128.6, 128.4, 125.7, 35.3, 34.3, 16.7, 14.3, 7.8, 2.3, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 8.21, FTIR (cm^{-1}): 3027, 2952, 2909, 2874, 1604, 1496, 1454, 1416, 1238, 1016, 730, 698. HRMS (CI) m/z, calcd for $[C_{16}H_{27}Si]^+$: 247.1882; found: 247.1884.



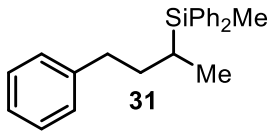
29

(**29**) According to procedure C, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Bu_2O (880 µL), cyclohexyldimethylsilyl chloride (370 µL, 2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **29** as a clear oil (210 mg, 90%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.15 (m, 3H), 2.82 (ddd, *J* = 14.3, 10.5, 4.8 Hz, 1H), 2.48 (ddd, *J* = 13.5, 10.2, 6.7 Hz, 1H), 1.78 (dddd, *J* = 13.6, 10.1, 6.6, 3.2 Hz, 1H), 1.74 – 1.67 (m, 3H), 1.61 (dd, *J* = 26.0, 13.0 Hz, 2H), 1.46 – 1.36 (m, 1H), 1.24 – 1.15 (m, 3H), 1.13 – 1.03 (m, 2H), 1.01 (d, *J* = 7.4 Hz, 3H), 0.74 (dqd, *J* = 10.7, 7.4, 3.3 Hz, 1H), 0.68 (tt, *J* = 12.7, 3.0 Hz, 1H), -0.11 (s, 3H), -0.12 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 128.6, 128.4, 125.7, 35.2, 34.2, 28.37, 28.36, 27.9, 27.8, 27.2, 24.3, 17.2, 14.2, -6.9, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 5.66, FTIR (cm^{-1}): 3026, 2919, 2847, 1604, 1496, 1446, 1246, 1099, 996, 888, 833, 799, 767, 698. HRMS (CI) m/z, calcd for $[C_{18}H_{29}Si]^+$: 273.2039; found: 273.2031.



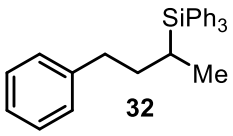
30

(**30**) According to procedure C, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Bu_2O (950 µL), isopropyldimethylsilyl chloride (310 µL, 2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **30** as a clear oil (210 mg, 90%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.15 (m, 3H), 2.83 (ddd, *J* = 14.8, 10.6, 4.8 Hz, 1H), 2.49 (ddd, *J* = 13.5, 10.3, 6.6 Hz, 1H), 1.78 (dddd, *J* = 13.7, 10.1, 6.6, 3.2 Hz, 1H), 1.41 (ddt, *J* = 14.0, 10.5, 5.3 Hz, 1H), 1.02 (d, *J* = 7.4 Hz, 3H), 0.95 – 0.90 (m, 6H), 0.88 – 0.81 (m, 1H), 0.76 (dqd, *J* = 10.7, 7.4, 3.3 Hz, 1H), -0.10 (s, 3H), -0.11 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 128.6, 128.4, 125.7, 35.2, 34.3, 18.0, 17.9, 17.5, 14.2, 12.1, -7.20, -7.23, FTIR (cm^{-1}): 3027, 2953, 2864, 1604, 1496, 1454, 1249, 997, 883, 832, 808, 765, 697. HRMS (CI) m/z, calcd for $[C_{14}H_{23}Si]^+$: 219.1569; found: 219.1559.



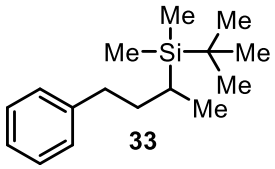
31

(**31**) According to procedure C, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Bu_2O (850 µL), diphenylmethylsilyl chloride (410 µL, 2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at rt for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **31** as a clear oil (315 mg, 95%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.50 – 7.47 (m, 4H), 7.39 – 7.31 (m, 6H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 2.80 (ddd, *J* = 14.1, 9.9, 4.8 Hz, 1H), 2.50 (ddd, *J* = 13.5, 9.5, 7.2 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.51 – 1.43 (m, 1H), 1.41 – 1.33 (m, 1H), 1.09 (d, *J* = 7.3 Hz, 3H), 0.53 (s, 3H), ^{13}C NMR (151 MHz, CD_2Cl2) δ 143.4, 137.4, 137.2, 135.40, 135.37, 129.7, 129.6, 129.1, 128.8, 128.37, 128.35, 126.2, 35.4, 34.5, 17.8, 14.5, -6.2, ^{29}Si NMR (119 MHz, $CDCl_3$) δ -4.7, FTIR (cm^{-1}): 3068, 2953, 2856, 1603, 1495, 1427, 1251, 1110, 788, 737, 698, 476. HRMS (CI) m/z, calcd for $[C_{22}H_{23}Si]^+$: 315.1569; found: 315.1579.



32

(**32**) According to procedure D, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Bu_2O (1.25 mL), triphenylsilyl chloride (590 mg, 2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at 50 °C for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes:DCM 100:0 to hexanes:DCM 90:10) to afford **32** as a viscous clear oil (267 mg, 68%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.50 (dd, *J* = 8.0, 1.4 Hz, 6H), 7.42 – 7.37 (m, 3H), 7.37 – 7.31 (m, 6H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 2H), 2.86 (ddd, *J* = 13.8, 9.3, 4.7 Hz, 1H), 2.57 (dt, *J* = 13.5, 8.3 Hz, 1H), 2.09 – 2.02 (m, 1H), 1.75 – 1.68 (m, 1H), 1.52 – 1.44 (m, 1H), 1.21 (d, *J* = 7.3 Hz, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 136.5, 135.2, 129.9, 129.2, 128.8, 128.4, 126.3, 35.3, 34.7, 16.7, 14.8, ^{29}Si NMR (119 MHz, CD_2Cl2) δ -8.7, FTIR (cm^{-1}): 3067, 3024, 2935, 2856, 1602, 1495, 1428, 1189, 1108, 998, 741, 698, 575, 510. HRMS (CI) m/z, calcd for $[C_{22}H_{23}Si]^+$: 315.1569; found: 315.1578.

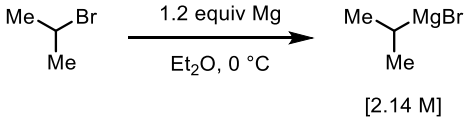


33

(**33**) According to procedure D, $(DrewPhos)_2PdI_2$ (16 mg, 10 µmol), Bu_2O (1.25 mL), *tert*-butyldimethylsilyl chloride (300 mg, 2 mmol), and [1.34 M] (4-phenylbutan-2-yl)magnesium bromide **S8** (750 µL, 1.0 mmol) were combined under N_2 and stirred at 100 °C for 24 h. After workup, crude product was purified via silica gel flash chromatography (hexanes) to afford **33** as a clear oil (74 mg, 30%): ^{1}H NMR (600 MHz, CD_2Cl2) δ 7.26 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.14 (m, 3H), 2.83 (ddd, *J* = 13.7, 10.5, 4.8 Hz, 1H), 2.48 (ddd, *J* = 13.4, 10.2, 6.6 Hz, 1H), 1.85 (dddd, *J* = 13.5, 10.2, 6.6, 2.9 Hz, 1H), 1.48 – 1.39 (m, 1H), 1.07 (d, *J* = 7.4 Hz, 3H), 0.89 (s, 9H), 0.85 (ddq, *J* = 15.0, 7.5, 4.5, 3.6 Hz, 1H), -0.070 (s, 3H), -0.075 (s, 3H), ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 128.6, 128.4, 125.7, 35.2, 35.0, 27.6, 17.6, 17.4, 15.2, -7.0, ^{29}Si NMR (119 MHz, $CDCl_3$) δ 9.7, FTIR (cm^{-1}): 3027, 2928, 2856, 1604, 1470, 1250, 828, 765, 697. HRMS (CI) m/z, calcd for $[C_{15}H_{25}Si]^+$: 233.1726; found: 233.1722.

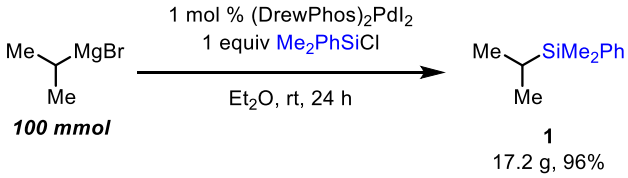
6. Scale Up and Catalyst Recovery:

Grignard Synthesis:



An oven dried 200 mL round bottom flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the septum removed, magnesium turnings (5.8 g, 240 mmol, 1.2 equiv) and two chips of I_2 (~50–70 mg) were added. The septum was replaced; the flask was attached to a double manifold and purged with N_2 for 10 min. The flask was held under positive N_2 then Et_2O (67 mL, [3 M]) was added. The solution was stirred until clarity was reached (disappearance of brown I_2 color). An initial amount of isopropyl bromide (1.5 mL) was added to start the reaction as evidenced by a minor exotherm. If reaction does not initiate, gentle warming (for example with a heating mantle) may be necessary. Once initiated, the flask was cooled to 0 °C in an ice/water bath and the remaining isopropyl bromide was added dropwise over 30 minutes for a total addition of 18.8 mL (24.6 g, 200 mmol, 1 equiv). After full addition of isopropyl bromide, the flask was allowed to stir at rt for an additional 2 h. The excess magnesium was allowed to settle and the mixture was filtered via cannula to a Schlenk tube. If insoluble particles persist, filtration through a 0.2 µm PTFE syringe filter may be employed. Titrated according to the literature procedure by Knochel[6] resulted in a [2.14 M] solution.

Silyl-Kumada Reaction:

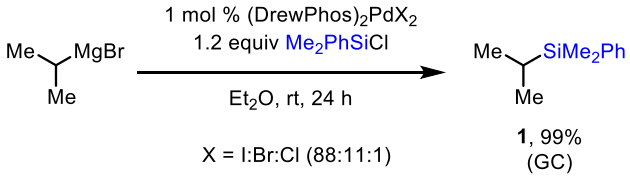


An oven dried 500 mL Schlenk flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the rubber septum was removed, and $(DrewPhos)_2PdI_2$ (1.558 g, 1 mmol, 0.01 equiv) was added. The septum was replaced and the flask purged with N_2 for 15 minutes. Et_2O (136 mL), silyl chloride (17.9 g, 17.6 mL, 105 mmol, 1 equiv), and [2.12 M] isopropylmagnesium bromide (47.2 mL, 100 mmol, 1 equiv) were added sequentially via syringe. The solution was then stirred at rt for 24 h. The flask was then placed in a room temperature water bath. The septum was removed and EtOAc (20 mL) was added followed by a slow addition of water. (**Note:** Water quenching results in an exotherm.) Water was added until the salts formed were completely solubilized. The mixture was then poured into a separatory funnel and washed with 100 mL brine. The aqueous layer was back extracted with 75 mL EtOAc. The combined organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. EtOH (50 mL) was then added and thoroughly swirled to ensure even mixing. This flask was then placed in a –20 °C freezer for 24 h. Red solid precipitated from the solution and was then collected via suction filtration, rinsing with EtOH as necessary. This yielded 1.12 g of $(DrewPhos)_2PdX_2$ (X = I:Br:Cl 88:11:1) as determined by ^{31}P NMR. The filtrate was then concentrated *in vacuo* then distilled at 10 mm Hg / 79 °C to afford **1** as a clear oil (17.2 g, 96%): ^1H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.38 – 7.33 (m, 3H), 0.98 – 0.95 (m, 7H), 0.25 (s, 6H).

Activity of Recovered Catalyst Mixture:

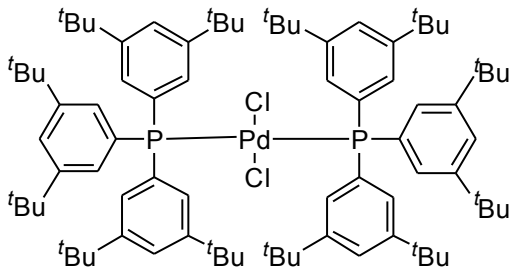
Note: The recovered catalyst from the scale up reaction was obtained as a mixture of palladium halide salts (as determined by ^{31}P NMR), with the iodo-complex being the predominant constituent. The fact that this mixed halide catalyst has similar reactivity to the pure iodo-complex was established using the following study:

In a nitrogen filled glovebox, a 1-dram vial equipped with a magnetic stirbar was charged with $(DrewPhos)_2PdX_2$ (88:11:1, I:Br:Cl) (4 mg, 2.5 µmol, 0.01 equiv), Et_2O (340 µL), and dimethylphenylsilyl chloride (50 µL, 51 mg, 300 µmol, 1.2 equiv). Vial was then sealed with a septum cap and removed from GB. Isopropylmagnesium bromide [2.29 M] (109 µL, 250 µmol, 1 equiv) was then added via syringe and the vial was then stirred at rt for 24 h. The reaction was quenched with Et_2O (1 mL) then H_2O (0.5 mL) via syringe. *n*-Nonane (32 mg, 45 µL, 0.25 mmol, 1 equiv) and 1,3,5-trimethoxybenzene (TMB) (14 mg, 0.25 mmol, 0.33 equiv) were added as GC internal standards. Brine (1 mL) and Et_2O (1 mL) were then added and the vials shaken. An aliquot was then filtered through a $MgSO_4$ and silica plug. The solution was directly analyzed by GC. These results are similar to other test scale reactions using pure $(DrewPhos)_2PdI_2$.



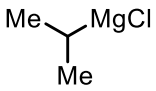
7. All Chloride Experiments:

Synthesis of Chloride Reagents:



(DrewPhos)$_2$PdCl$_2$

(DrewPhos)$_2$PdCl$_2$: A 100 mL round bottom flask equipped with a magnetic stirbar was charged with bis(acetonitrile)dichloropalladium(II) (259 mg, 1 mmol, 1.0 equiv) and DrewPhos (1.2 g, 2 mmol, 2.0 equiv). The flask was sealed with a rubber septum and purged 10 min with N_2. CH_2Cl_2 (20 mL) was added via syringe and the solution was stirred for 6 hours at rt. The solvent was then removed *in vacuo*. EtOAc (15 mL) was added and the flask sat overnight at rt. The solid was collected via vacuum filtration and rinsing with EtOH resulted in a stable, yellow solid (905 mg, 66% yield): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 12H), 7.38 (s, 6H), 1.19 (s, 108H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.69 (t, J = 5.0 Hz), 130.41 (t, J = 23.9 Hz), 129.87 (t, J = 6.4 Hz), 123.83 , 35.01 , 31.54,^{31}P NMR (243 MHz, $CDCl_3$) δ 26.82; FTIR (cm^{-1}): 2963, 2903, 2868, 1590, 1477, 1421, 1363, 1266, 1249, 1138, 731, 705, 586; mp = >250 °C. HRMS (LIFDI) m/z, calcd for $[C_{84}H_{126}P_2PdCl_2]^+$:1372.7747; found: 1372.7599.



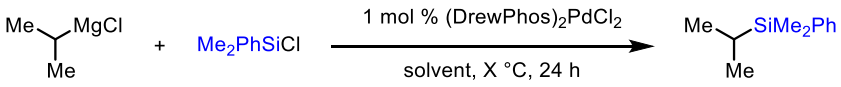
S3

An oven-dried 25 mL round-bottom flask equipped with a magnetic stirbar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the septum removed, magnesium turnings (1.1 g, 45 mmol, 1.5 equiv) were added. The septum was replaced; the flask was attached to a double manifold and purged with N_2 for 10 min. The flask was held under positive N_2 then Et_2O (10 mL, [3 M]) was added. An initial amount of alkyl halide (~200–400 µL) was added and the reaction to start the reaction as evidenced by a minor exotherm. If reaction does not initiate, gentle warming (for example with a heating mantle) may be necessary. Once initiated, the flask was placed in a rt water bath and the remaining alkyl halide (2.74 mL, 2.36 g, 30 mmol, 1 equiv, total addition amount) was added dropwise over ~30 min. After full addition of the alkyl halide, the mixture was allowed to stir at rt for an additional 4 h. The excess magnesium was allowed to settle and the mixture was filtered via cannula to a Schlenk tube. Titration resulted in a [2.65 M] solution of isopropylmagnesium chloride. **Note:** In this preparation, I_2 was not used to activate the magnesium turnings.

All Chloride Reactions:

In a nitrogen filled glovebox, a 1-dram vial equipped with a magnetic stirbar was charged with (DrewPhos)$_2$PdCl$_2$ (3.4 mg, 2.5 µmol, 0.01 equiv), Et_2O (350 µL) or Bu_2O (350 µL), and dimethylphenylsilyl chloride (50 µL, 51 mg, 300 µmol, 1.2 equiv). Vial was then sealed with a septum cap and removed from the glovebox. Isopropylmagnesium chloride [2.65 M] (94 µL, 250 µmol, 1 equiv) was then added via syringe and the vial was then stirred at the indicated temperature for 24 h. The reaction was quenched with Et_2O (1 mL) then H_2O (0.5 mL) via syringe. *n*-Nonane (32 mg, 45 µL, 0.25 mmol, 1 equiv) and 1,3,5-trimethoxybenzene (TMB) (14 mg, 0.25 mmol, 0.33 equiv) were added as GC internal standards. Brine (1 mL) and Et_2O (1 mL) were then added and the vials shaken. An aliquot was then filtered through a $MgSO_4$ and silica plug. The solution was directly analyzed by GC.

Table S1. All Chloride Conditions



1

Entry	Solvent	Temp	Additive	Yield (%)[a]
1	Et_2O	rt	---	6
2	Bu_2O	50 °C	---	70
3	Et_2O	rt	0.25 equiv TMEDA	52

[a]Yields determined by GC. All reactions gave >99:1 B:L selectivity by GC.

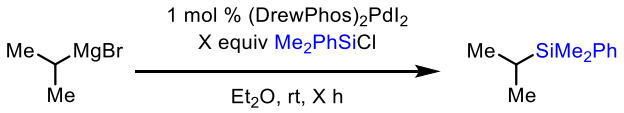
8. Additional Optimization Data:

Note: All reactions in this section were performed on 0.25 mmol in a nitrogen-filled glovebox with a [0.5 M] overall concentration based on the sum of all liquid reagents.

Examination of Stoichiometry:

In a nitrogen filled glovebox, a 1-dram vial equipped with a magnetic stirbar was charged with $(DrewPhos)_2PdI_2$ (4 mg, 2.5 µmol, 0.01 equiv), Et_2O (330 µL), and dimethylphenylsilyl chloride (52 µL, 53 mg, 313 µmol, 1.25 equiv, or 46 µL, 47 mg, 275 µmol, 1.1 equiv, or 42 µL, 43 mg, 250 µmol, 1 equiv). Vial was then sealed with a septum cap and removed from the glovebox. Isopropylmagnesium bromide [2.13 M] (117 µL, 250 µmol, 1 equiv, or 129 µL, 275 µL, 1.1 equiv, or 147 µL, 313 µmol, 1.25 equiv) was then added via syringe and the vial was then stirred at rt for the indicated time. The reaction was quenched with Et_2O (1 mL) then H_2O (0.5 mL) via syringe. *n*-Nonane (32 mg, 45 µL, 0.25 mmol, 1 equiv) and 1,3,5-trimethoxybenzene (TMB) (14 mg, 0.25 mmol, 0.33 equiv) were added as GC internal standards. Brine (1 mL) and Et_2O (1 mL) were then added and the vials shaken. An aliquot was then filtered through a $MgSO_4$ and Silica plug. The solution was directly analyzed by GC.

Table S2. Effect of Stoichiometry



1

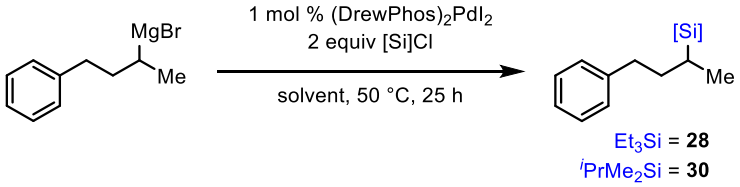
Entry	Mg:Si	4 h (%)[a]	8 h (%)[a]	24 h (%)[a]
1	1:1.25	99	99	99
2	1:1.1	78	96	99
3	1:1	73	90	97
4	1.1:1	74	88	93
5	1.25:1	71	86	93

[a]Yields determined by GC. All reactions gave >99:1 B:L selectivity by GC.

Examination of Ethereal Solvents:

In a nitrogen filled glovebox, a 1-dram vial equipped with a magnetic stirbar was charged with $(DrewPhos)_2PdI_2$ (4 mg, 2.5 µmol, 0.01 equiv), MTBE or CPME (280 µL), and triethylsilyl chloride (84 µL, 75 mg, 500 µmol, 2 equiv) or iso-propyldimethylsilyl chloride (78 µL, 68 mg, 500 µmol, 2 equiv). Vial was then sealed with a septum cap and removed from the glovebox. (4-phenylbutan-2-yl)magnesium bromide [1.78 M] (140 µL, 250 µmol, 1 equiv) was then added via syringe and the vial was then stirred at 50 °C for the indicated time. The reaction was quenched with Et_2O (1 mL) then H_2O (0.5 mL) via syringe. *n*-Nonane (32 mg, 45 µL, 0.25 mmol, 1 equiv) and 1,3,5-trimethoxybenzene (TMB) (14 mg, 0.25 mmol, 0.33 equiv) were added as GC and NMR internal standards. Brine (1 mL) and Et_2O (1 mL) were then added and the vials shaken. An aliquot was then filtered through a $MgSO_4$ and Silica plug. The solution was directly analyzed by GC then concentrated in vacuo and analyzed by NMR.

Table S3. Examination of Ethereal Solvents



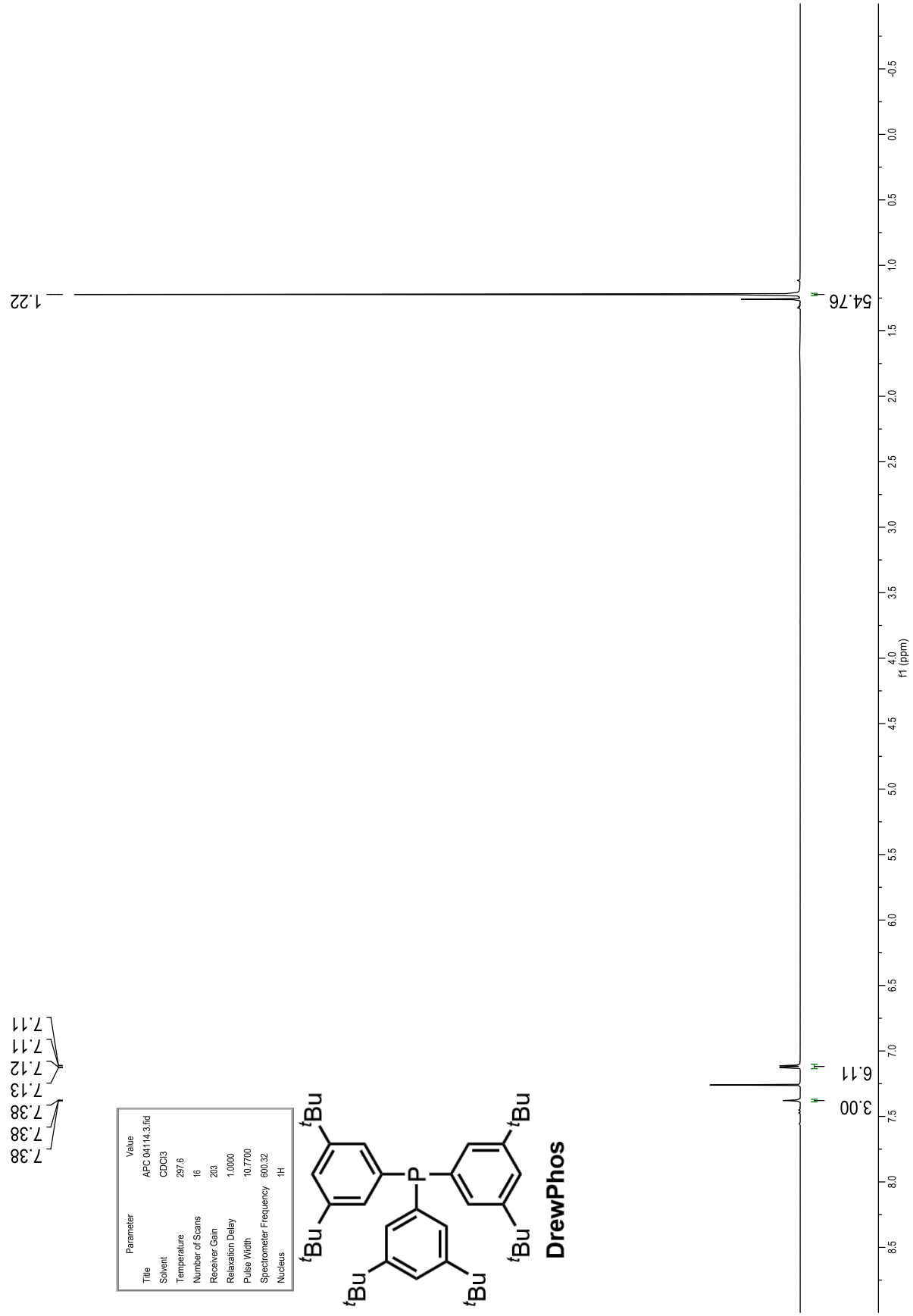
Entry	[Si]	MTBE[a]	CPME[a]
1	Et_3Si	99	99
2	$^{i}PrMe_2Si$	97	90

[a]Yields determined by NMR. All reactions gave >99:1 B:L selectivity by GC.

9. References:

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996,** *15*, 1518-1520.
(2) Denmark, S. E.; Cresswell, A. J. *J. Org. Chem.* **2013,** *78*, 12593-12628.
(3) Powell, D. A.; Fu, G. C. *J. Am. Chem. Soc.* **2004,** *126*, 7788-7789.
(4) Chu, C. K.; Liang, Y.; Fu, G. C. *J. Am. Chem. Soc.* **2016,** *138*, 6404-6407.
(5) Jensen, F. R.; Nakamaye, K. L. *J. Am. Chem. Soc.* **1966,** *88*, 3437-3438.
(6) Krasovskiy, A.; Knochel, P. *Synthesis* **2006,** *2006*, 890-891.
(7) Morita, E.; Murakami, K.; Iwasaki, M.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2009,** *82*, 1012-1014.
(8) (a) Inubushi, H.; Kondo, H.; Lesbani, A.; Miyachi, M.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2013,** *49*, 134-136; (b) Negishi, E.; Akiyoshi, K. *J. Am. Chem. Soc.* **1988,** *110*, 646-647.
(9) Nakamura, S.; Uchiyama, M. *J. Am. Chem. Soc.* **2007,** *129*, 28-29.
(10) Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.; Sanderson, P. E. J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 317-337.
(11) Murakami, K.; Hirano, K.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2008,** *47*, 5833-5835.
(12) Murakami, K.; Yorimitsu, H.; Oshima, K. *J. Org. Chem.* **2009,** *74*, 1415-1417.

10. Spectral Data: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54.76
6.11
3.00
7.38
7.38
7.38
7.13
7.12
7.11
7.11
Parameter Value
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Temperature 297.6
Number of Scans 16
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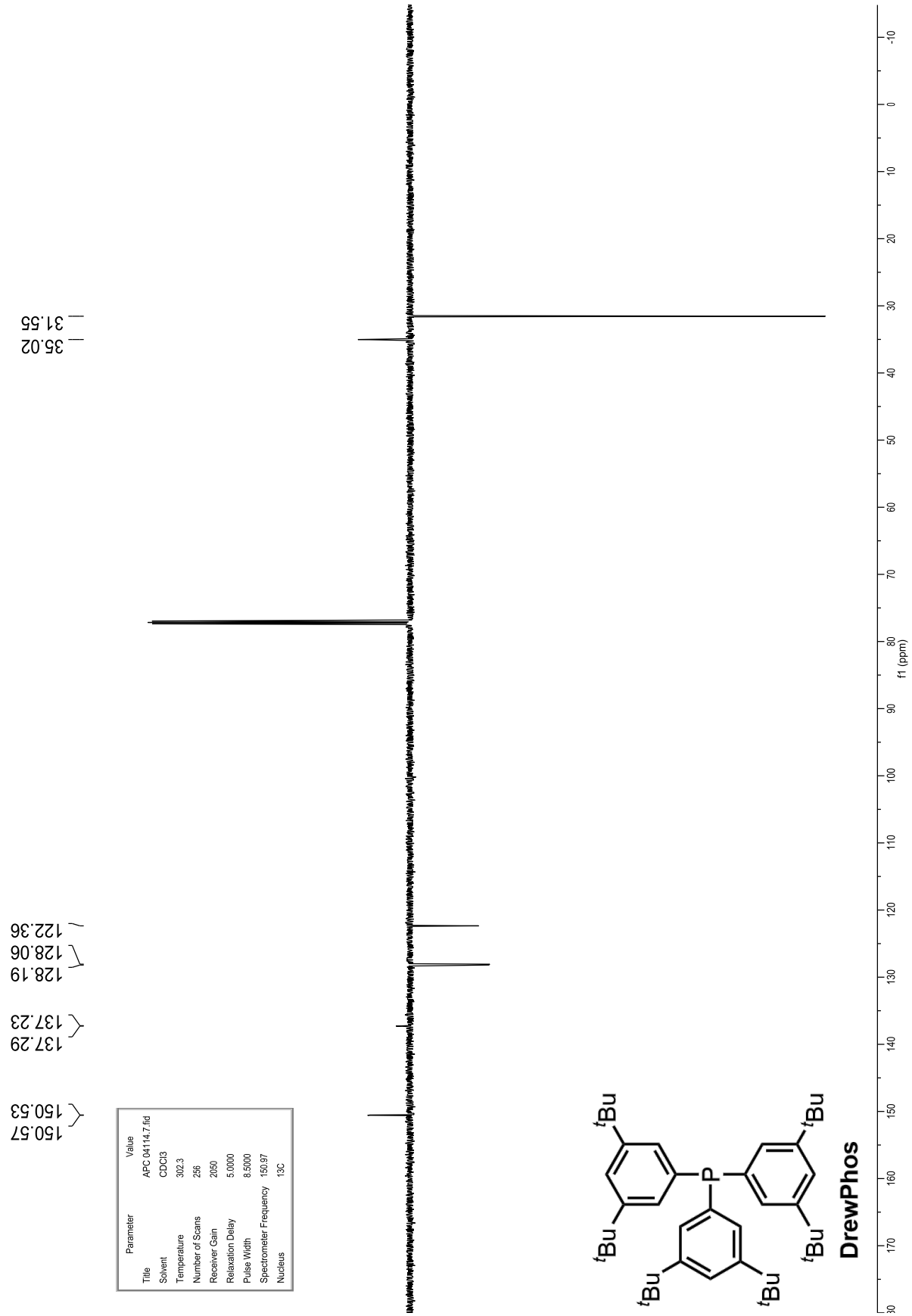
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150.53
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128.06
122.36
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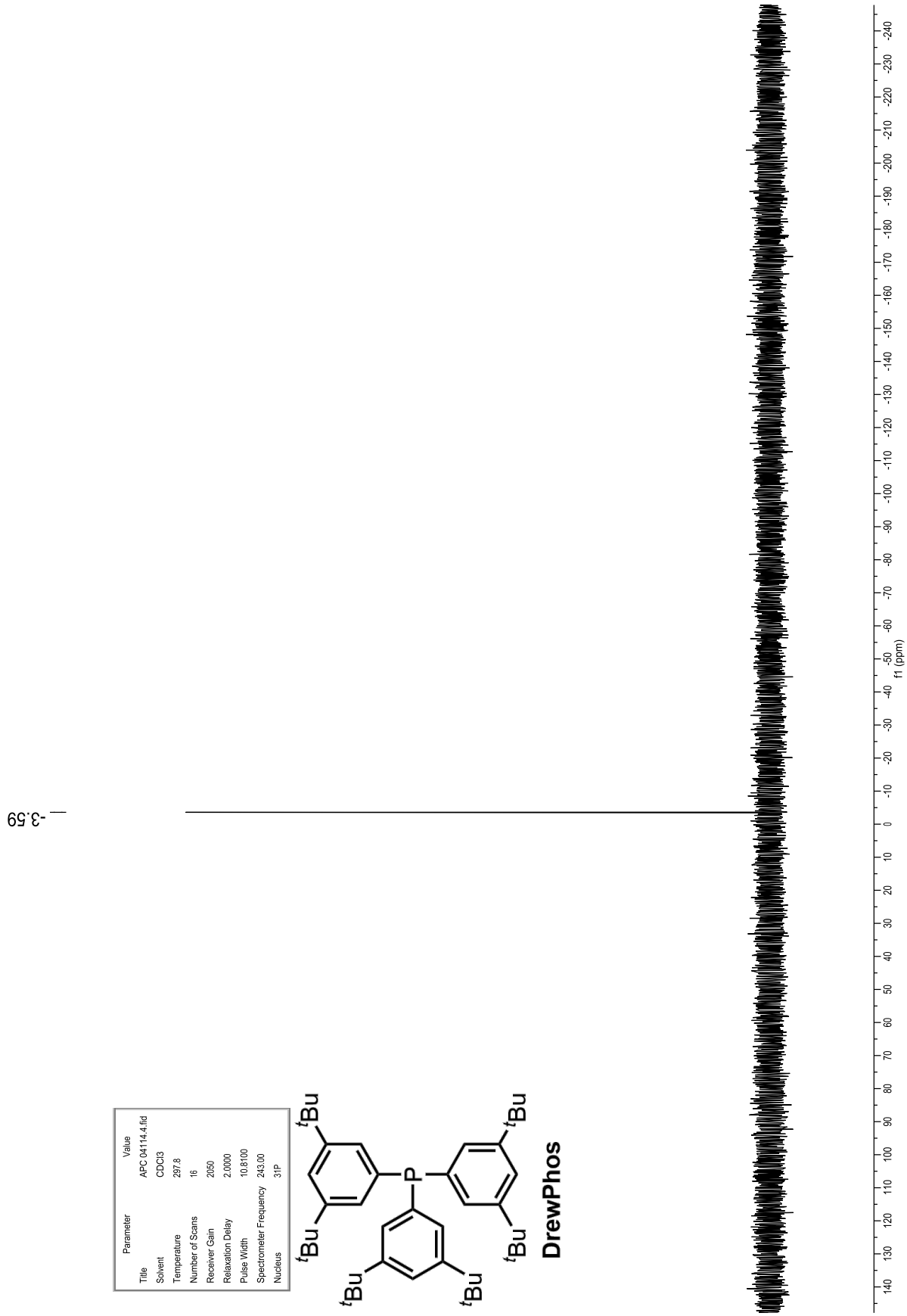
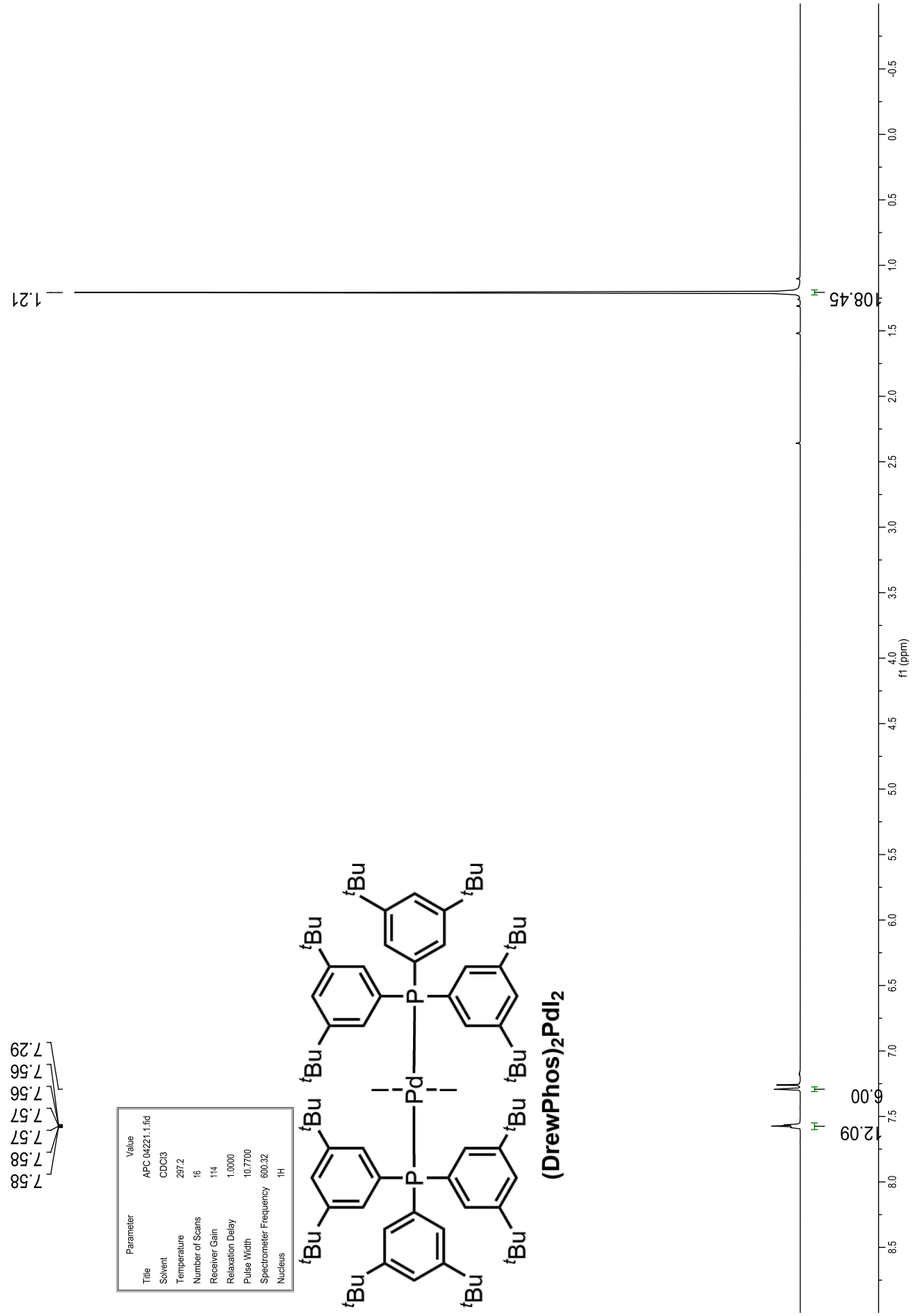
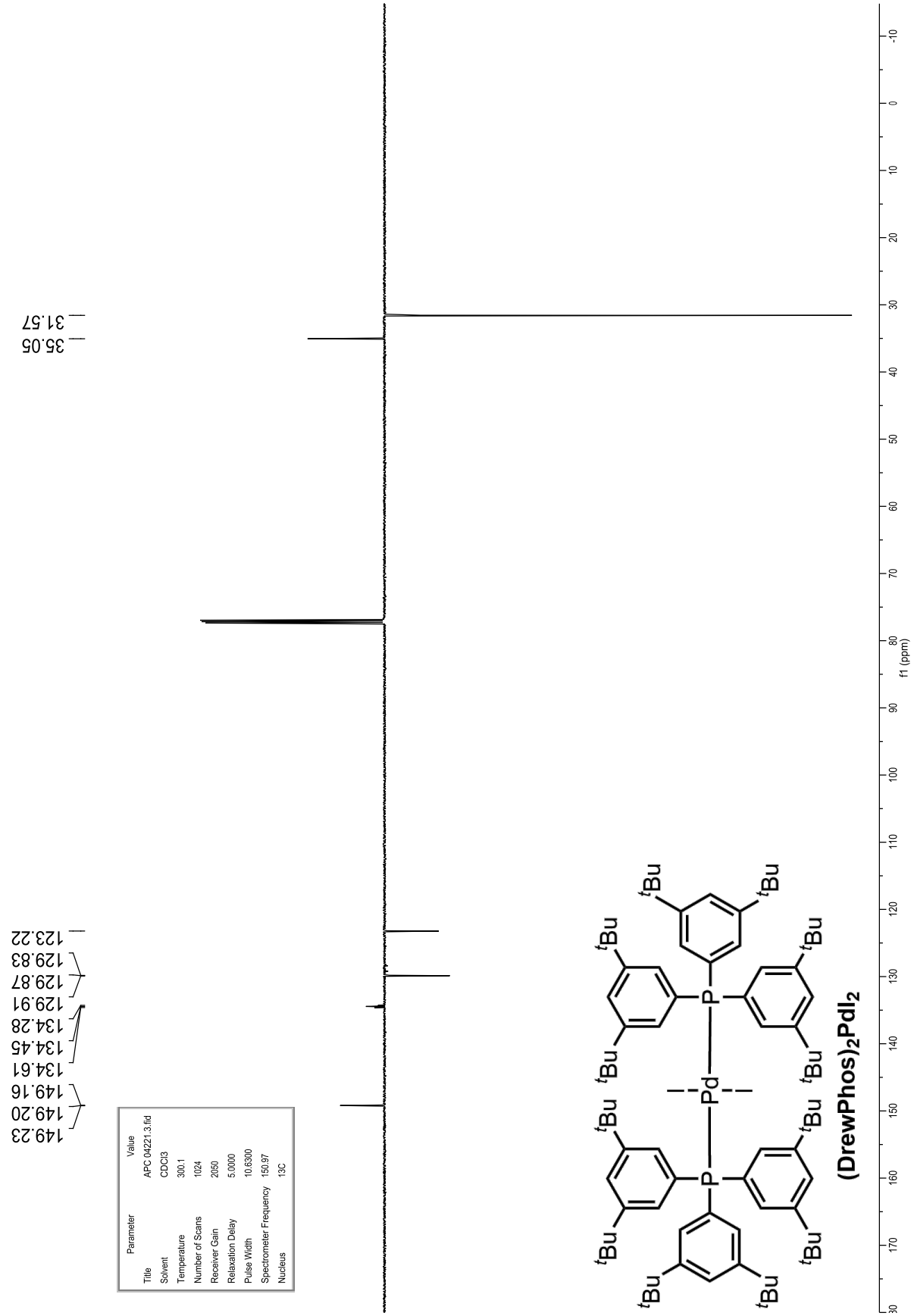
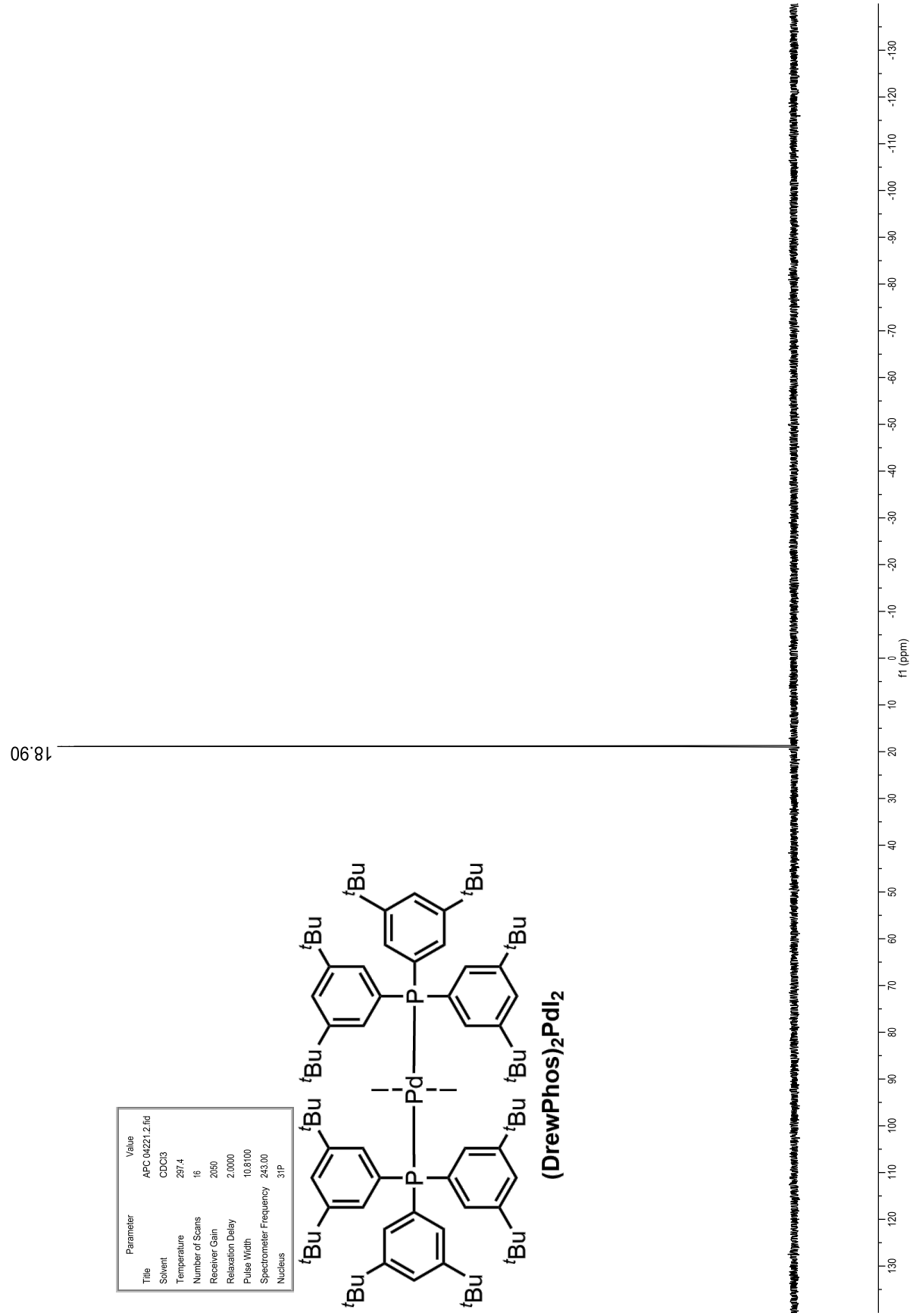
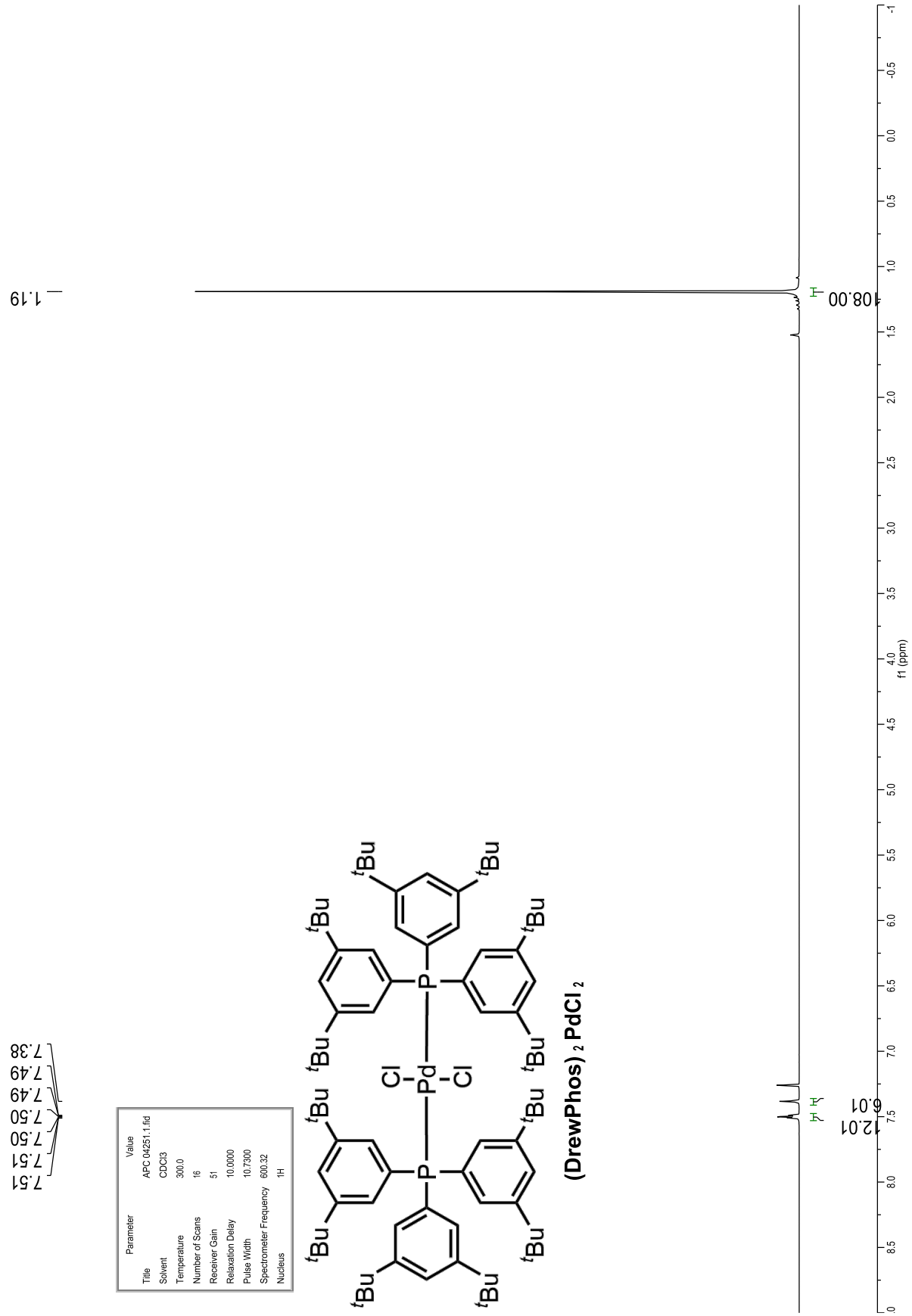
31.55
Parameter Value
Title APC 04114.7.fid
Solvent CDCl3
Temperature 302.3
Number of Scans 256
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 8.5000
Spectrometer Frequency 150.97
Nucleus 13C
tBu
tBu
tBu
P
tBu
tBu
DrewPhos
f1 (ppm)

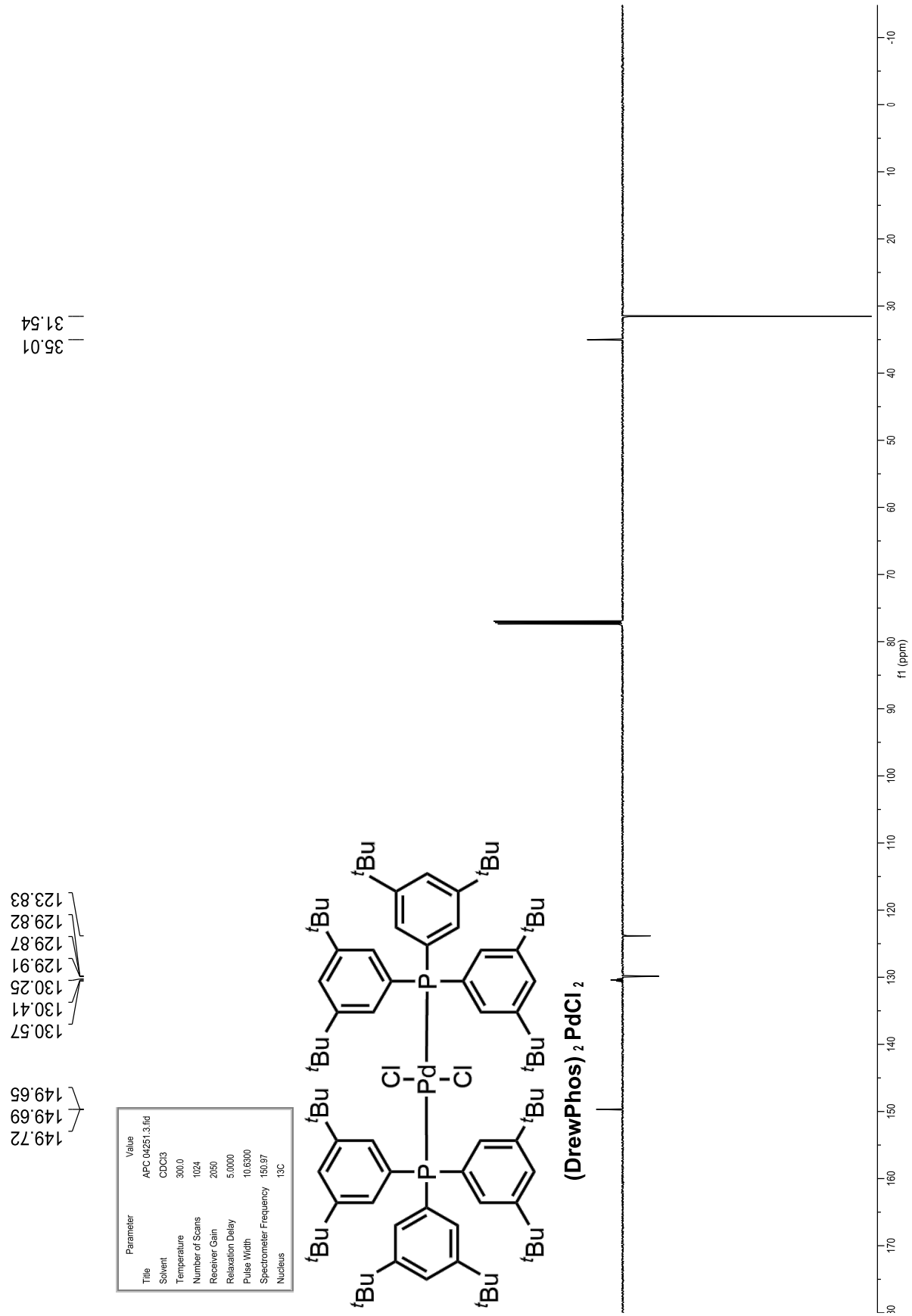

-3.59
Parameter Value
Title APC 04114.4.fid
Solvent CDCl3
Temperature 297.8
Number of Scans 16
Receiver Gain 2050
Relaxation Delay 2.0000
Pulse Width 10.8100
Spectrometer Frequency 243.00
Nucleus 31P
tBu
tBu
tBu
tBu
tBu
P
DrewPhos
f1 (ppm)


1.21
108.45
6.00
12.09
7.58
7.57
7.57
7.56
7.56
7.57
7.58
7.29
f1 (ppm)
Parameter Value
Title APC 04221.1.fid
Solvent CDCl3
Temperature 297.2
Number of Scans 16
Receiver Gain 114
Relaxation Delay 1.0000
Pulse Width 10.7700
Spectrometer Frequency 600.32
Nucleus 1H
(DrewPhos)2PdI2

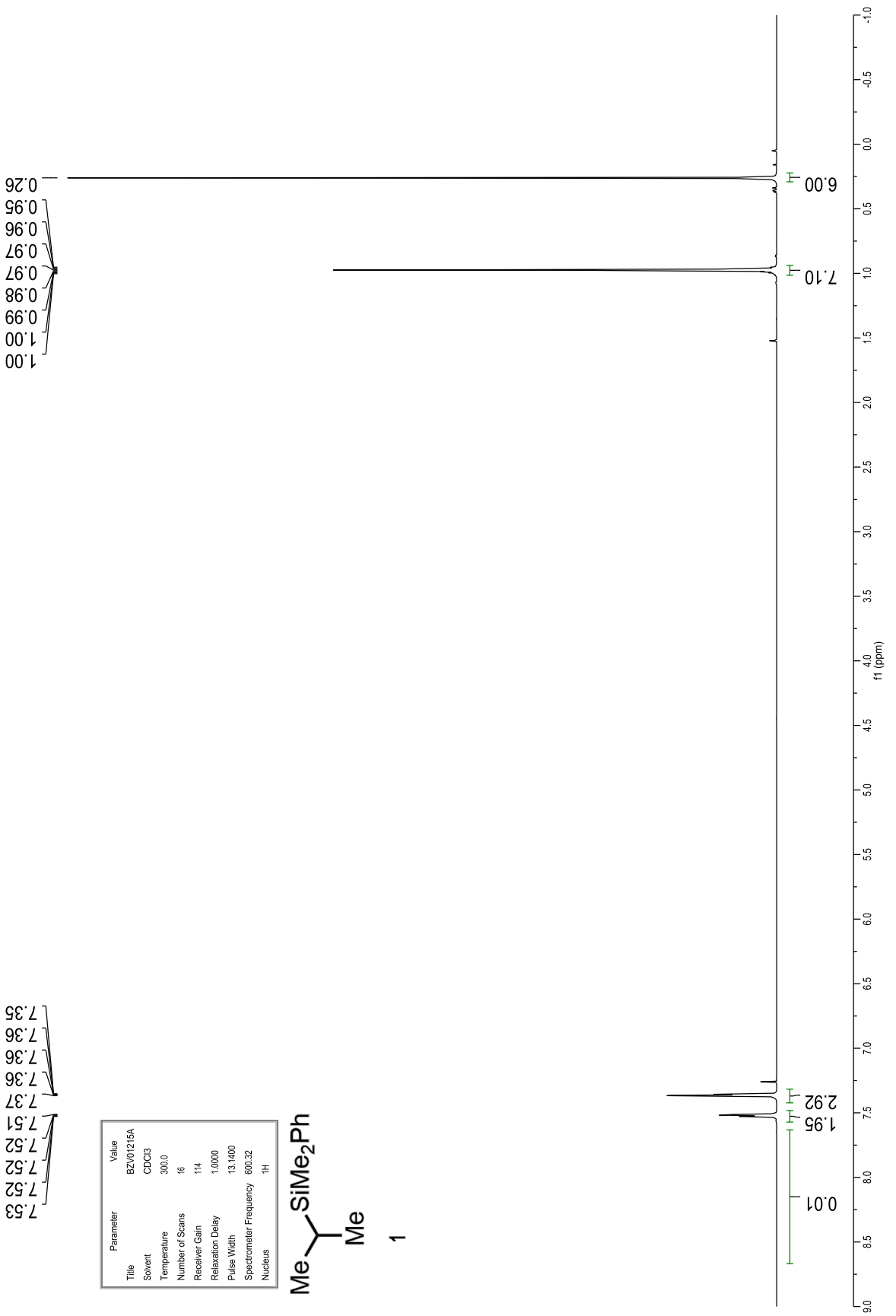

149.23
149.20
149.16
134.61
134.45
134.28
129.91
129.87
129.83
123.22
35.05
31.57
Parameter Value
Title APC 04221.3.fid
Solvent CDCl3
Temperature 300.1
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
tBu
P
Pd
(DrewPhos)2PdI2
f1 (ppm)

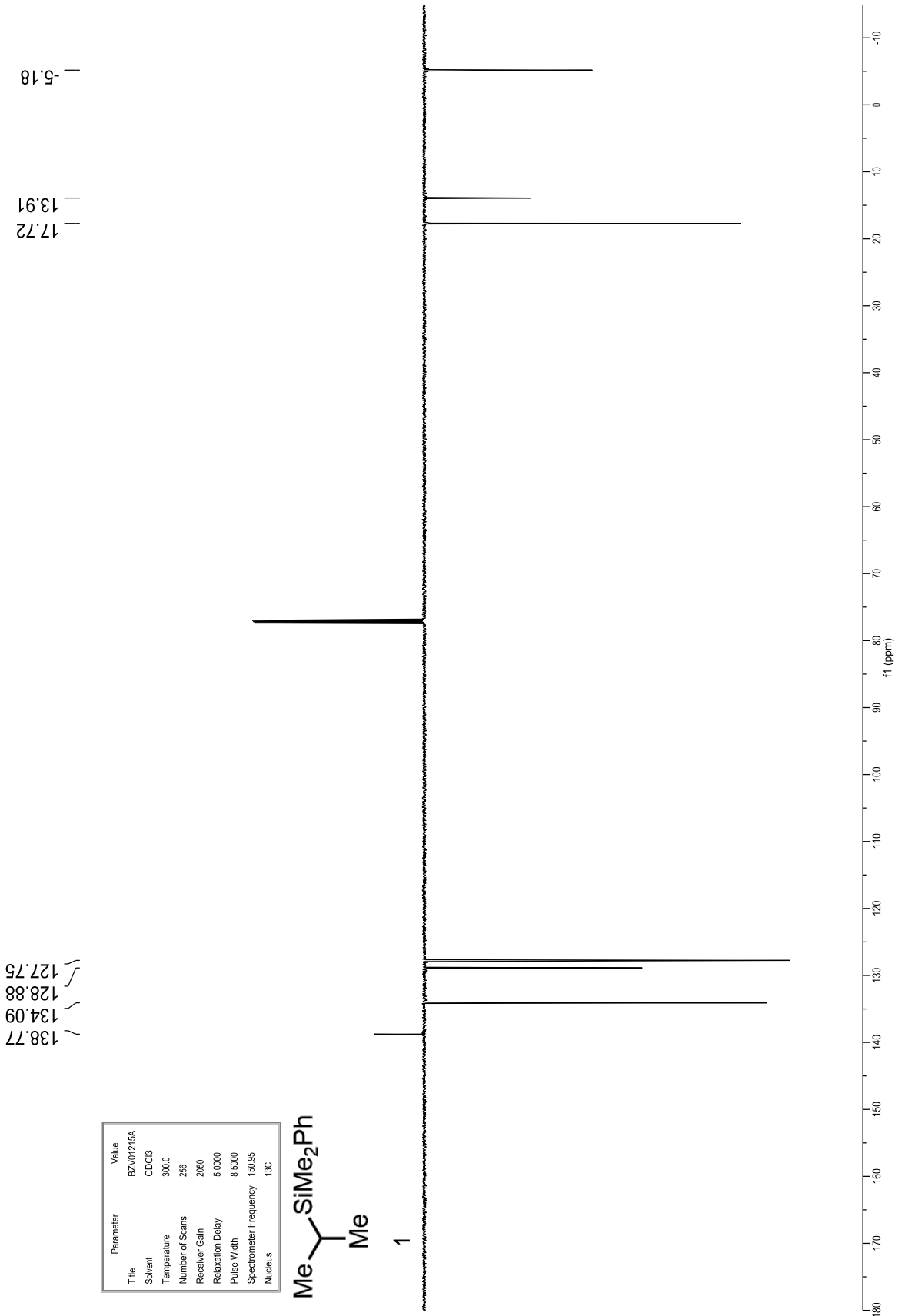

18.90
f1 (ppm)
(DrewPhos)2PdI2
Parameter Value
Title APC 04221.2.fid
Solvent CDCl3
Temperature 297.4
Number of Scans 16
Receiver Gain 2050
Relaxation Delay 2.0000
Pulse Width 10.8100
Spectrometer Frequency 243.00
Nucleus 31P

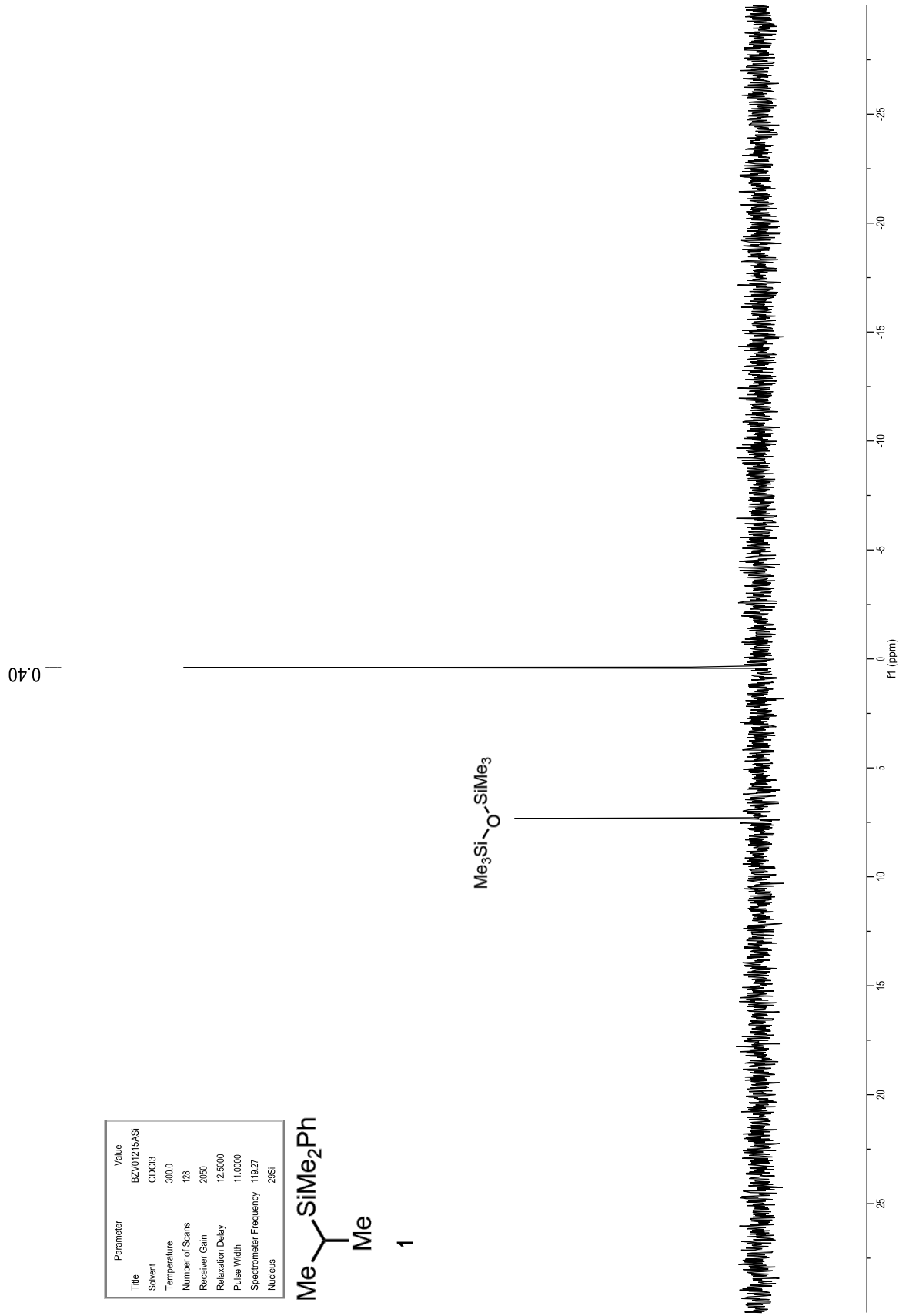

7.51
7.51
7.50
7.50
7.49
7.49
7.38
Parameter Value
Title APC 04251.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 51
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
(DrewPhos)2PdCl2
1.19
108.00
12.01
6.01
f1 (ppm)

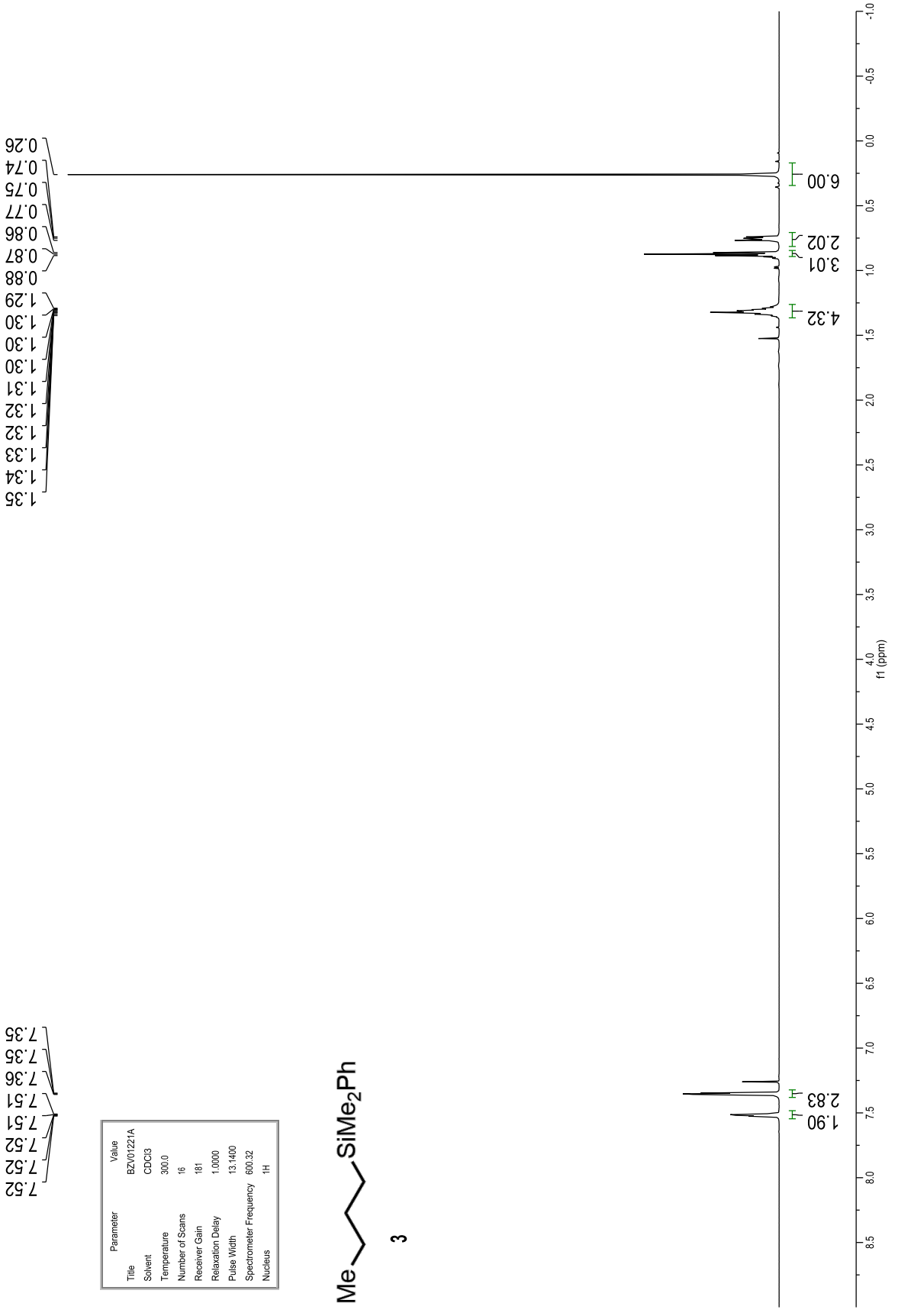

149.72
149.69
149.65
130.57
130.41
130.25
129.91
129.87
129.82
123.83
35.01
31.54
Parameter Value
Title APC 04251.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
(DrewPhos)2PdCl2
f1 (ppm)

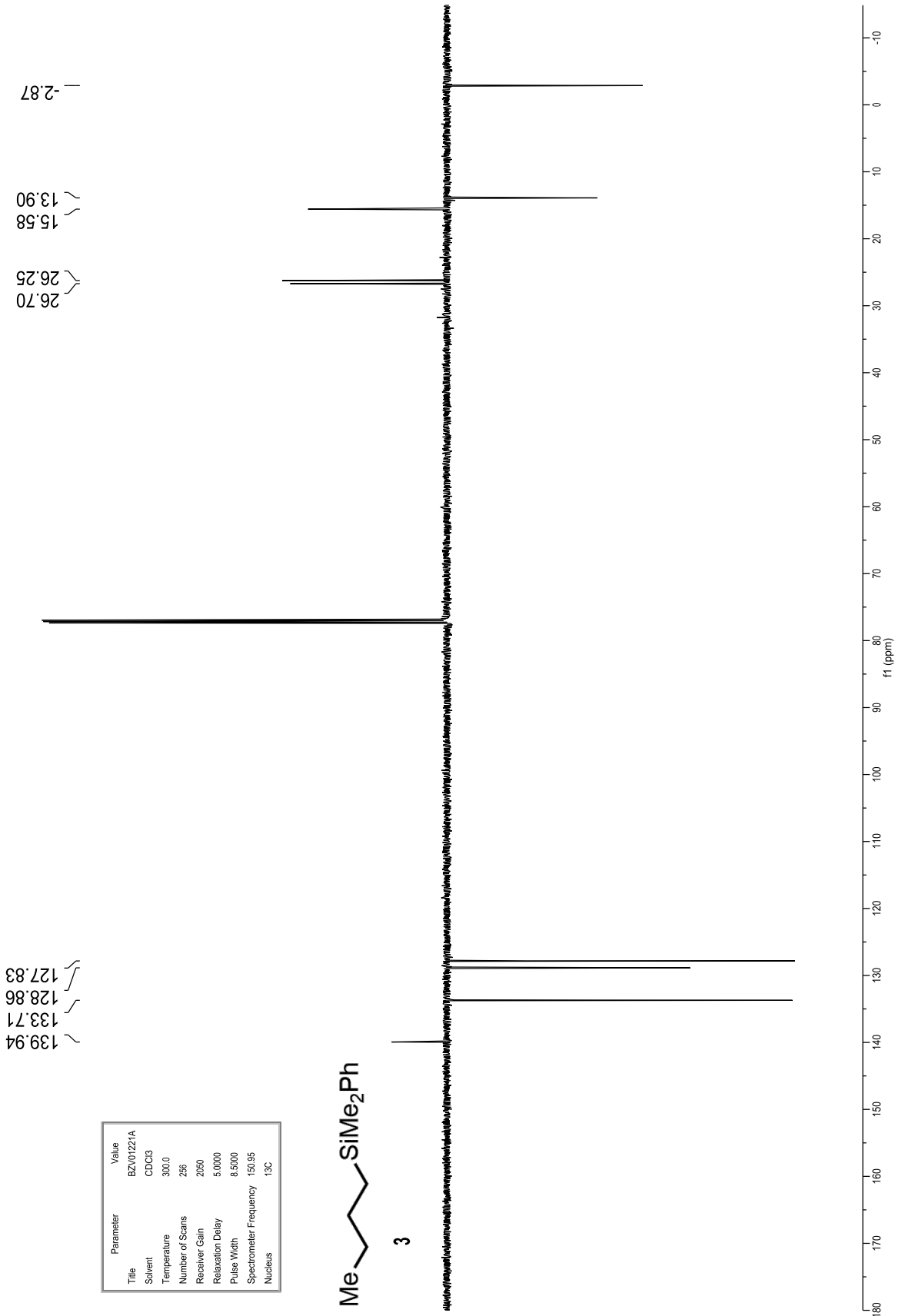
26.82
Parameter Value
Title APC 04251-2.fid
Solvent CDCl3
Temperature 300.2
Number of Scans 16
Receiver Gain 2050
Relaxation Delay 2.0000
Pulse Width 10.8000
Spectrometer Frequency 243.00
Nucleus 31P
tBu
P
Cl
Pd
Cl
(DrewPhos)2PdCl2
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
f1 (ppm)

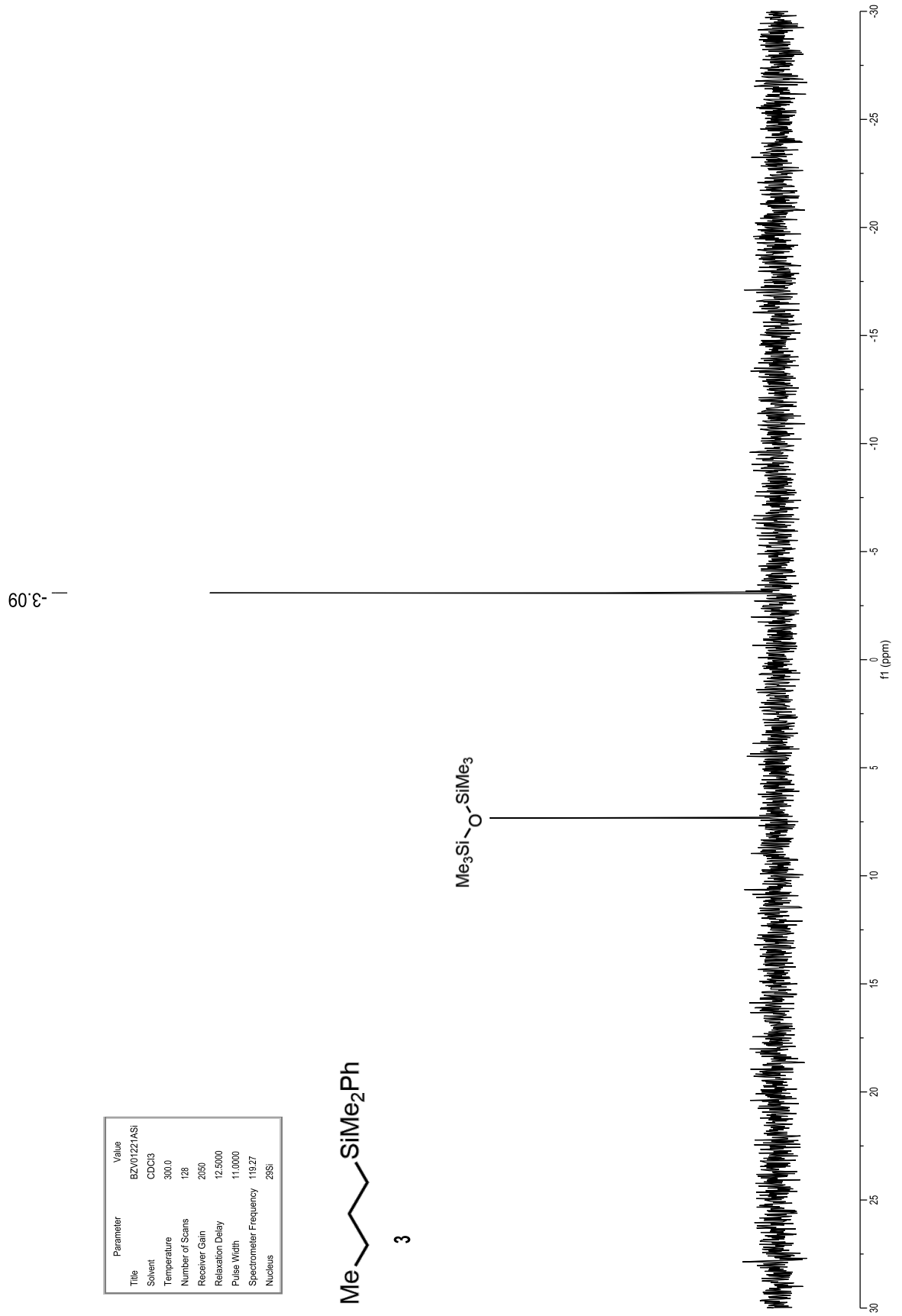

7.53
7.52
7.52
7.52
7.51
7.37
7.36
7.36
7.36
7.35
1.00
0.99
0.98
0.97
0.97
0.96
0.95
0.26
6.00
7.10
0.01
1.95
2.92
f1 (ppm)
Me
SiMe2Ph
Me
1
Parameter Value
Title BZV01215A
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 114
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H

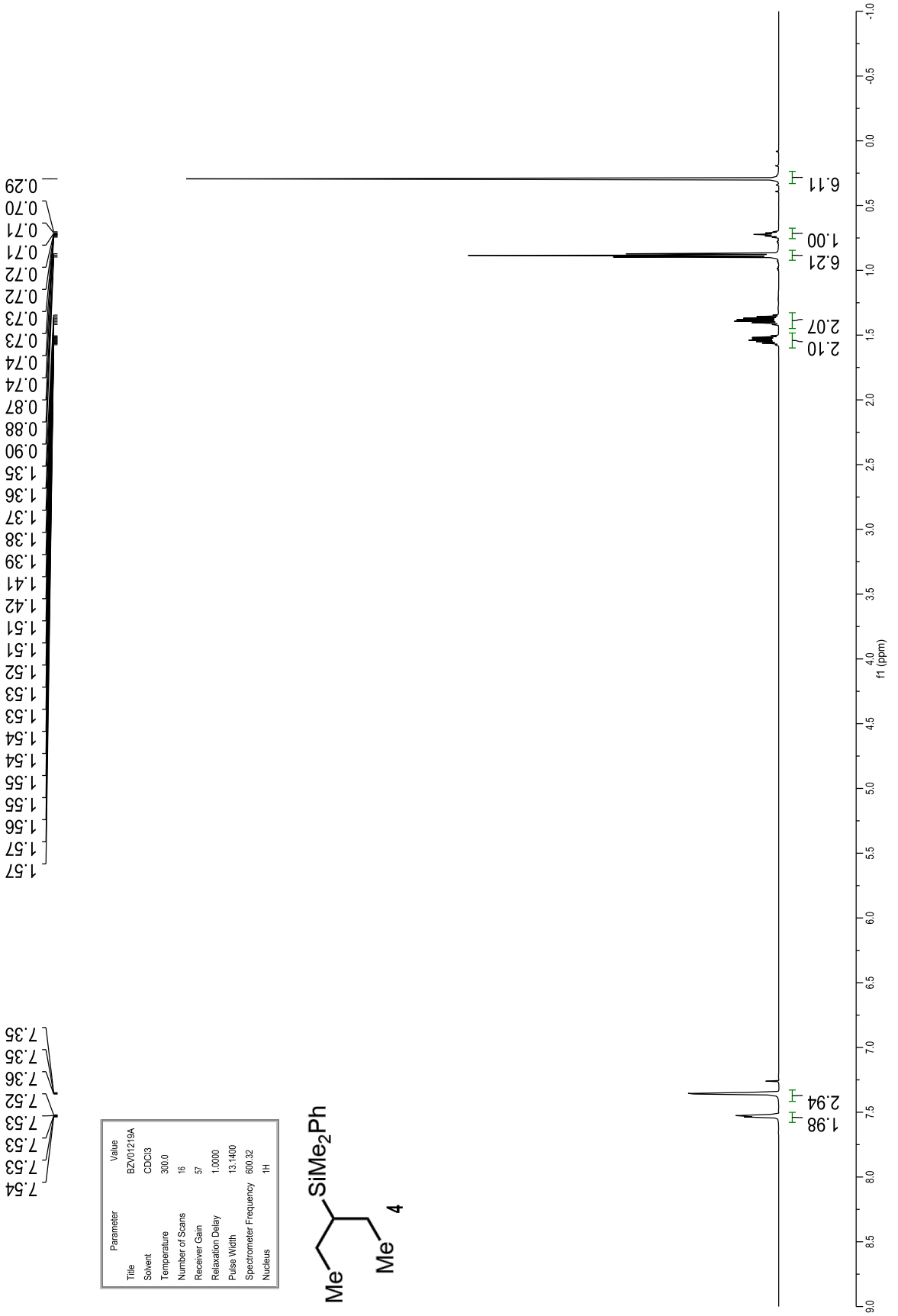

Parameter Value
Title BZV01215A
Solvent CDCl3
Temperature 300.0
Number of Scans 256
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 8.5000
Spectrometer Frequency 150.95
Nucleus 13C
Me SiMe2Ph Me
1
138.77
134.09
128.88
127.75
17.72
13.91
-5.18
f1 (ppm)

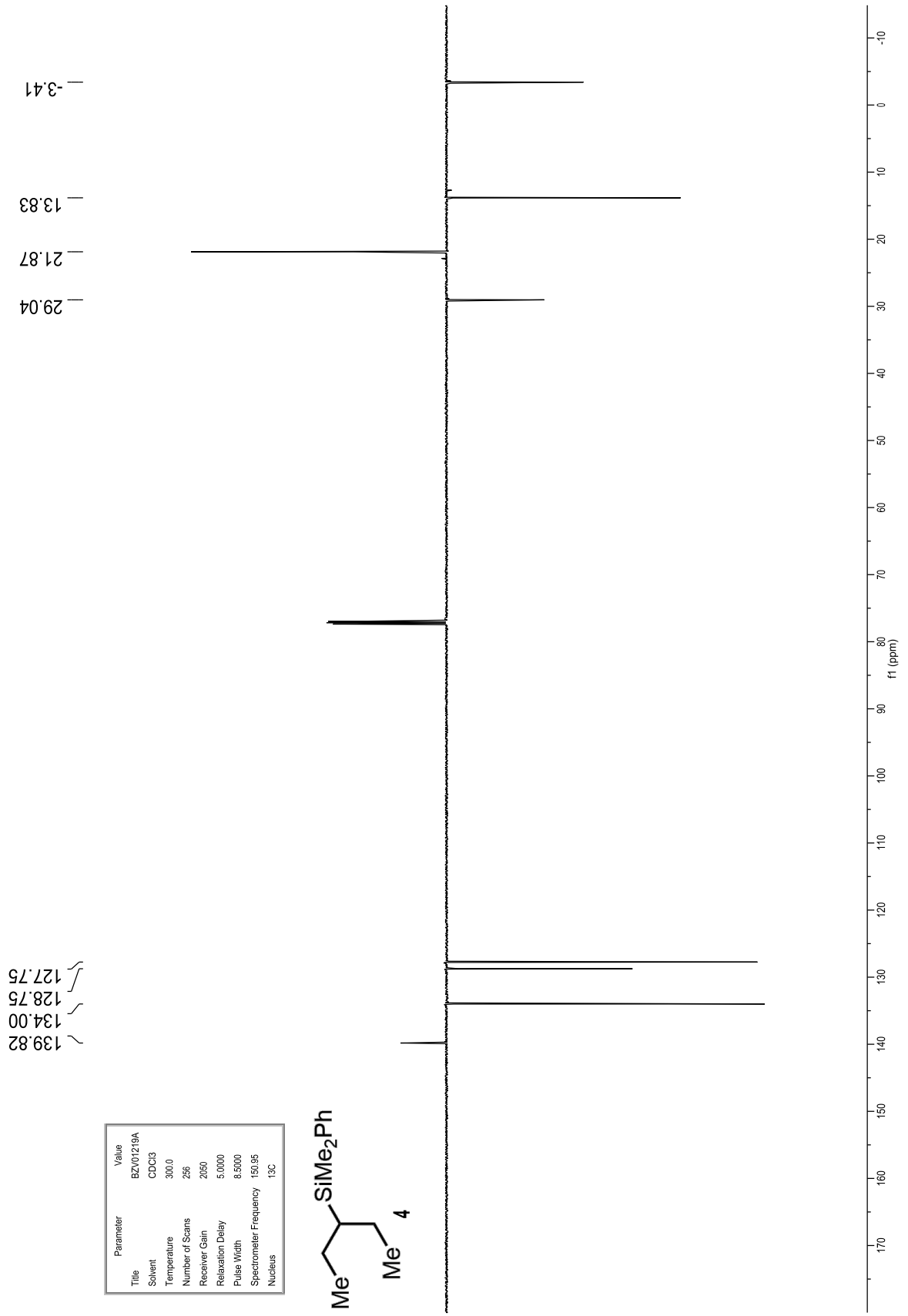

Parameter Value
Title BZV01215ASi
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
Me SiMe2Ph Me
1
Me3Si O SiMe3
0.40
25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)


7.52
7.52
7.52
7.51
7.51
7.36
7.35
7.35
Parameter Value
Title BZV01221A
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 181
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H
Me SiMe2Ph
3
1.35
1.34
1.33
1.32
1.32
1.31
1.30
1.30
1.30
1.29
0.88
0.87
0.86
0.77
0.75
0.74
0.26
6.00
4.32
3.01
2.02
1.90
2.83
f1 (ppm)

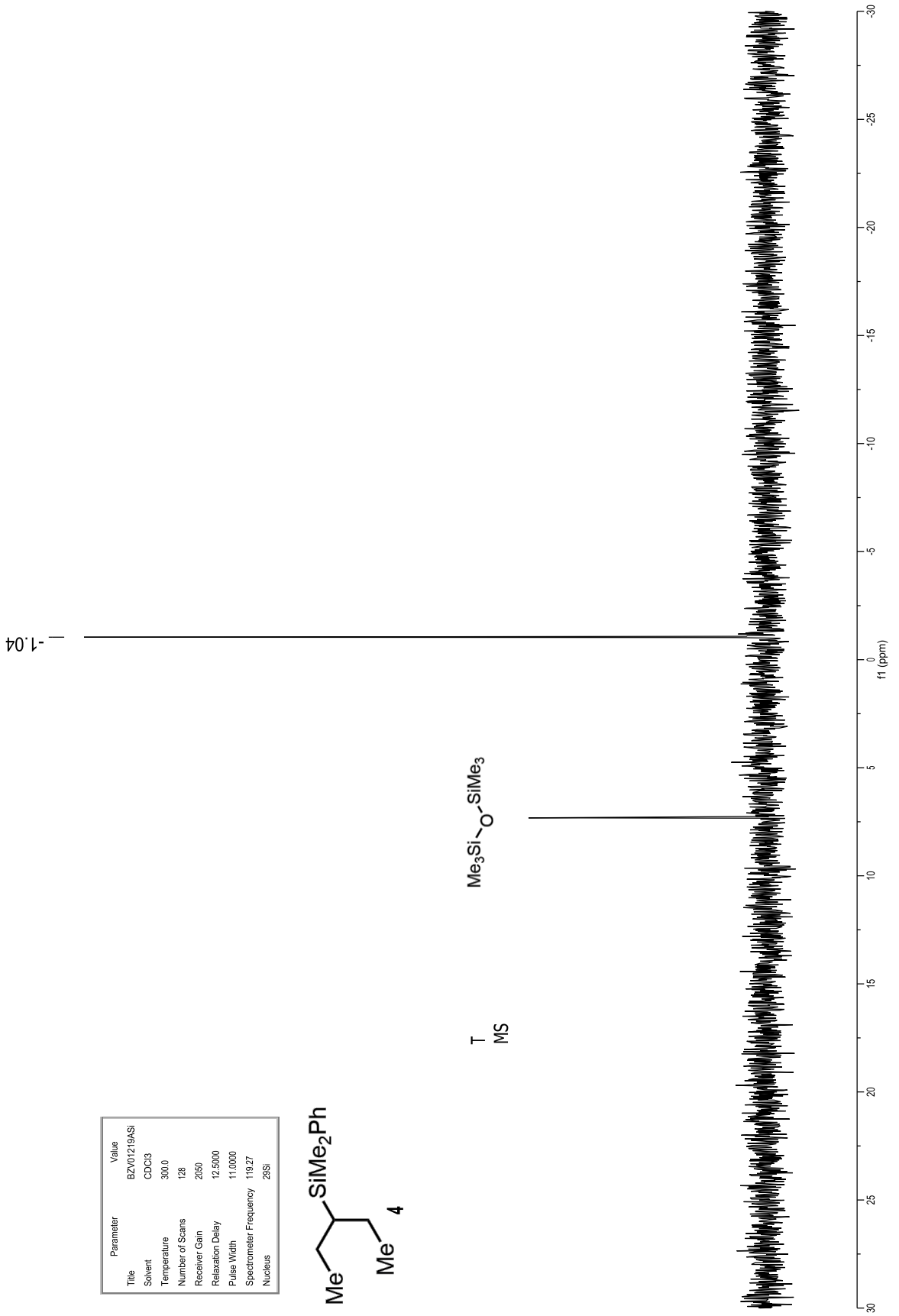

Me
SiMe2Ph
3
Parameter Value
Title BZV01221A
Solvent CDCl3
Temperature 300.0
Number of Scans 256
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 8.5000
Spectrometer Frequency 150.95
Nucleus 13C
139.94
133.71
128.86
127.83
26.70
26.25
15.58
13.90
-2.87
f1 (ppm)

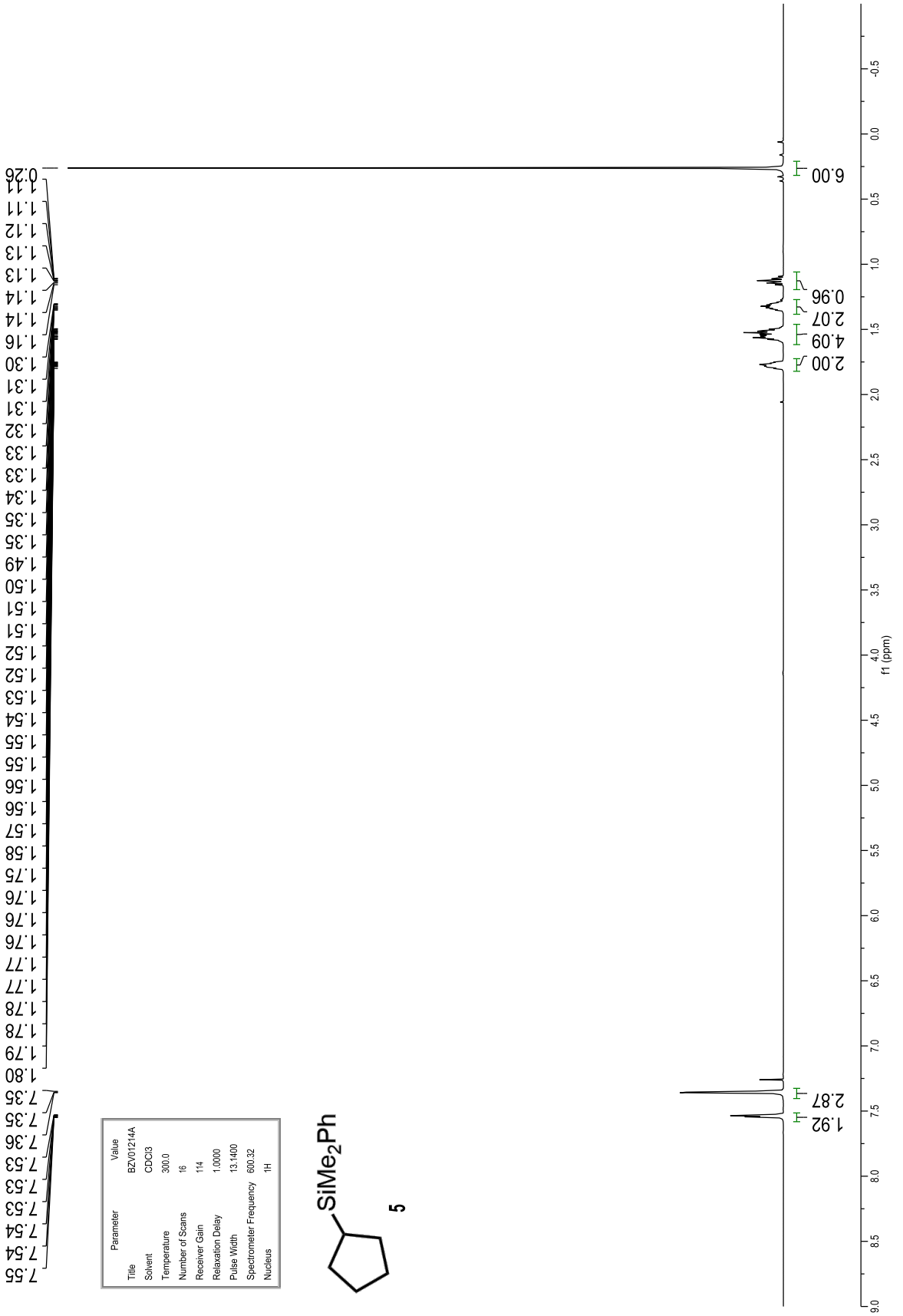

Parameter Value
Title BZV01221ASI
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
Me SiMe2Ph
3
Me3Si O SiMe3
-3.09
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
f1 (ppm)

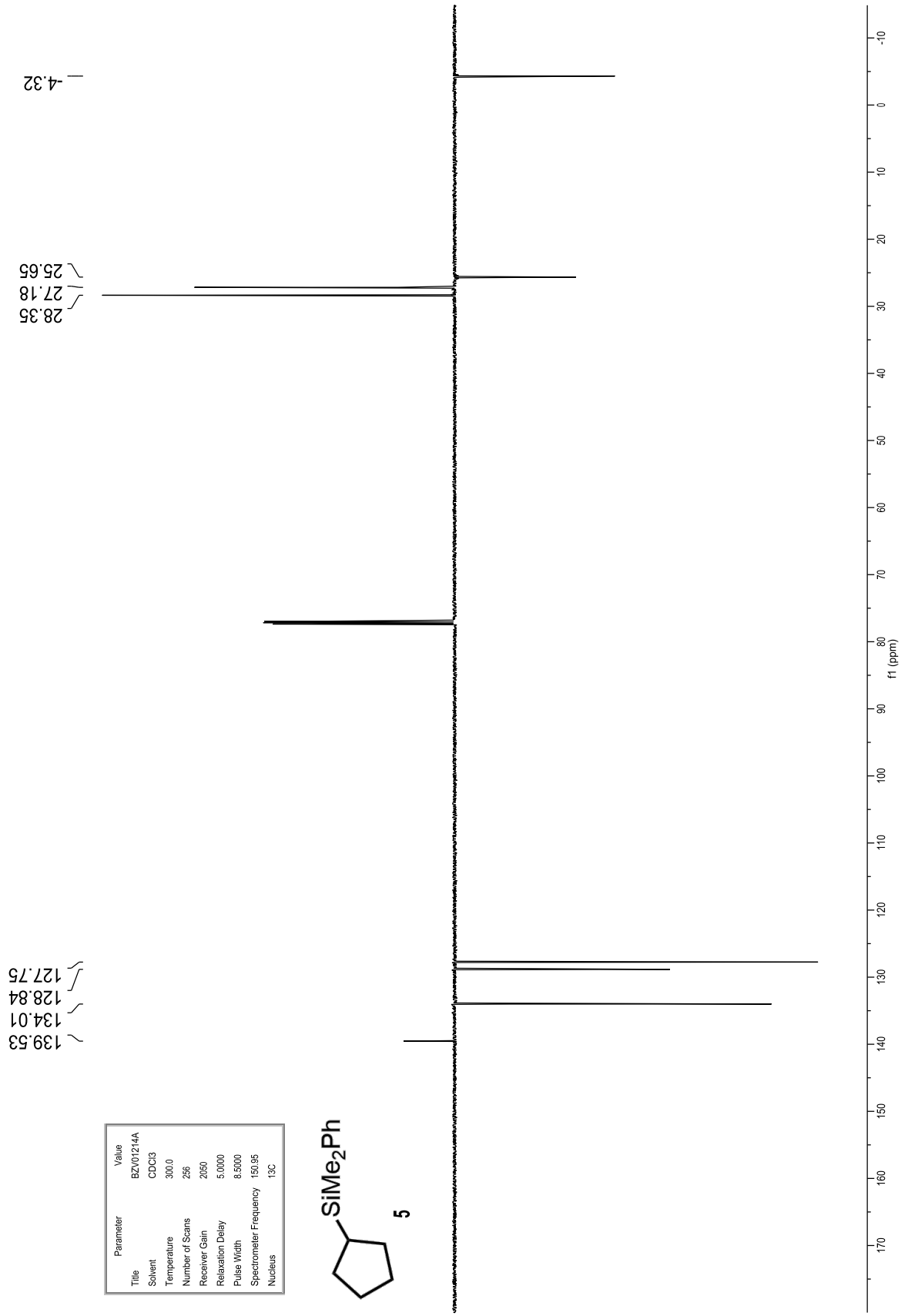

0.29
0.70
0.71
0.71
0.72
0.72
0.73
0.73
0.74
0.74
0.87
0.88
0.90
1.35
1.36
1.37
1.38
1.39
1.41
1.42
1.51
1.51
1.52
1.53
1.53
1.54
1.54
1.55
1.55
1.56
1.57
1.57
7.35
7.35
7.36
7.52
7.53
7.53
7.53
7.54
6.11
1.00
6.21
2.07
2.10
1.98
2.94
f1 (ppm)
Parameter Value
Title BZV01219A
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 57
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Ph
Me
Me
4

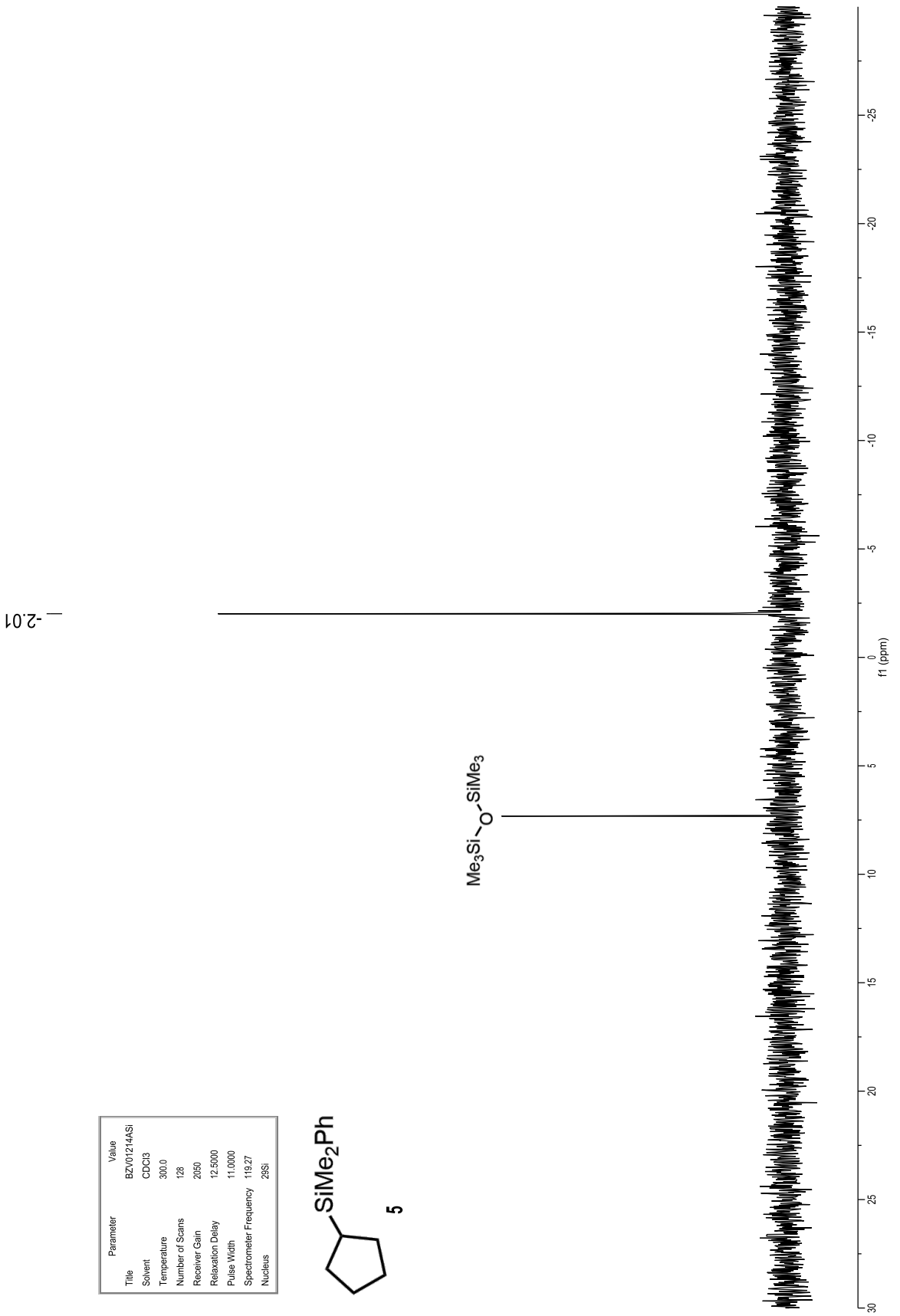


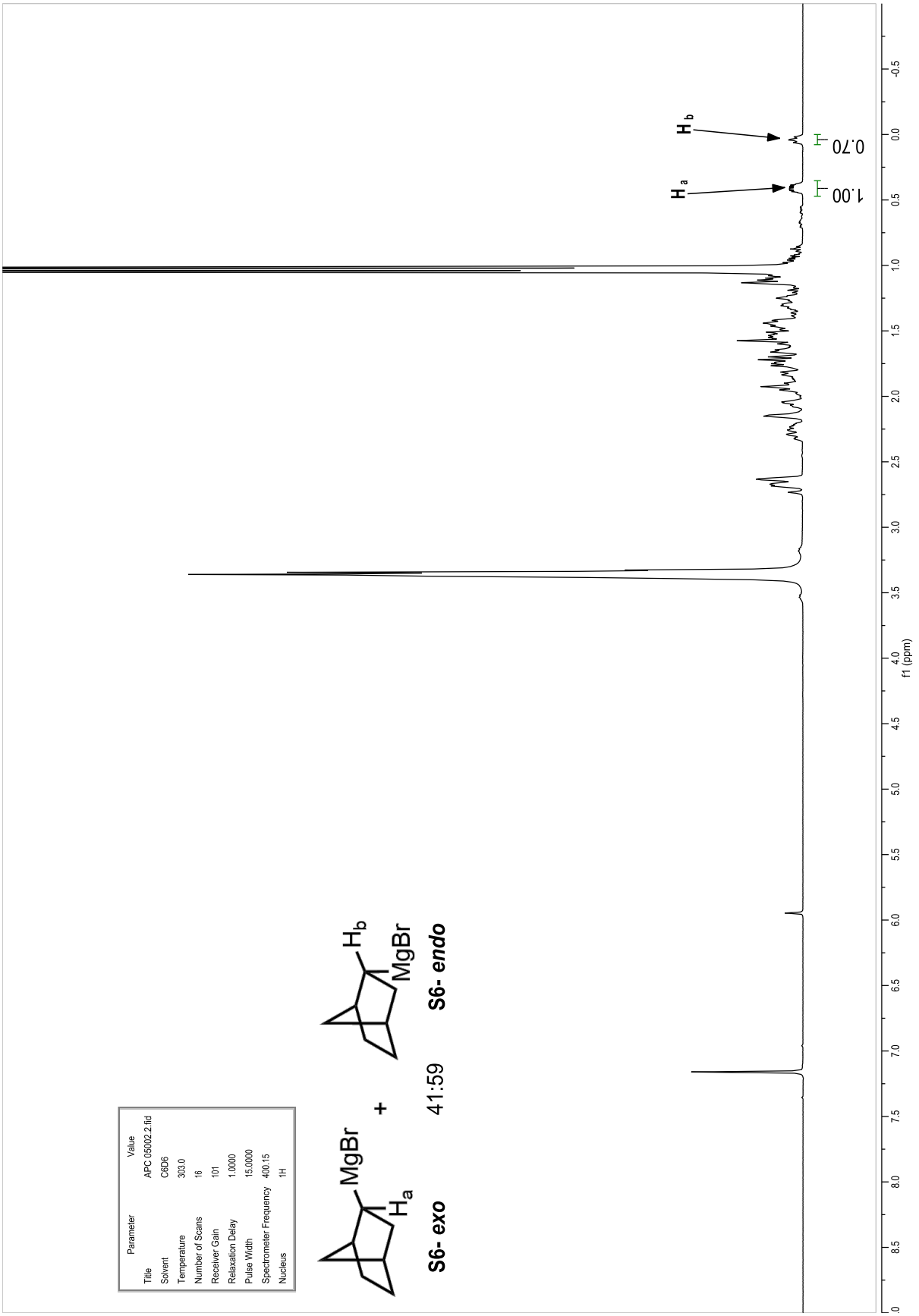
Parameter	Value
Title	BZV01219A
Solvent	CDCl3
Temperature	300.0
Number of Scans	256
Receiver Gain	2050
Relaxation Delay	5.0000
Pulse Width	8.5000
Spectrometer Frequency	150.95
Nucleus	13C

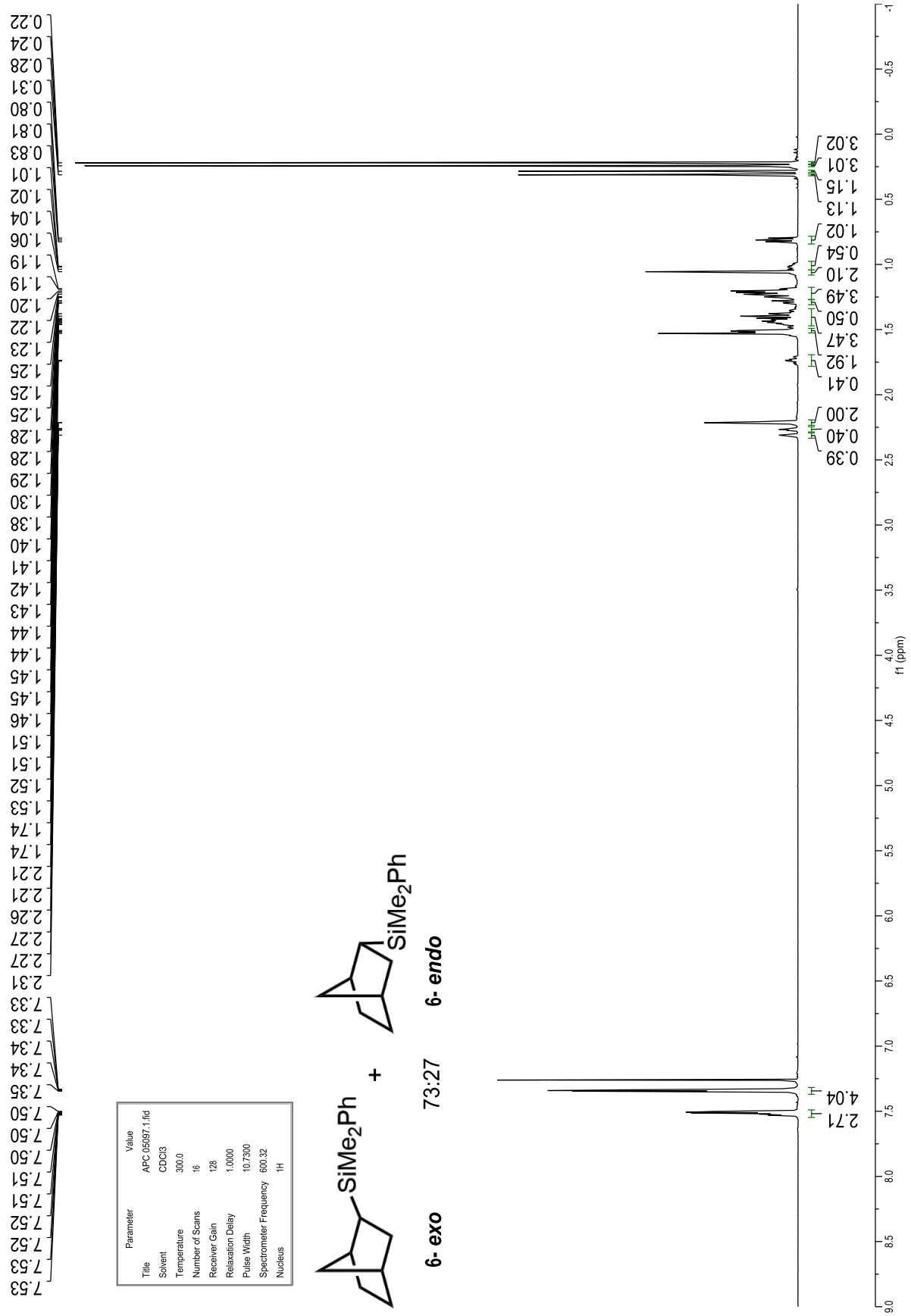

Parameter Value
Title BZV01219ASi
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
SiMe2Ph
Me
Me
4
T
MS
Me3Si
O
SiMe3
-1.04
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
f1 (ppm)

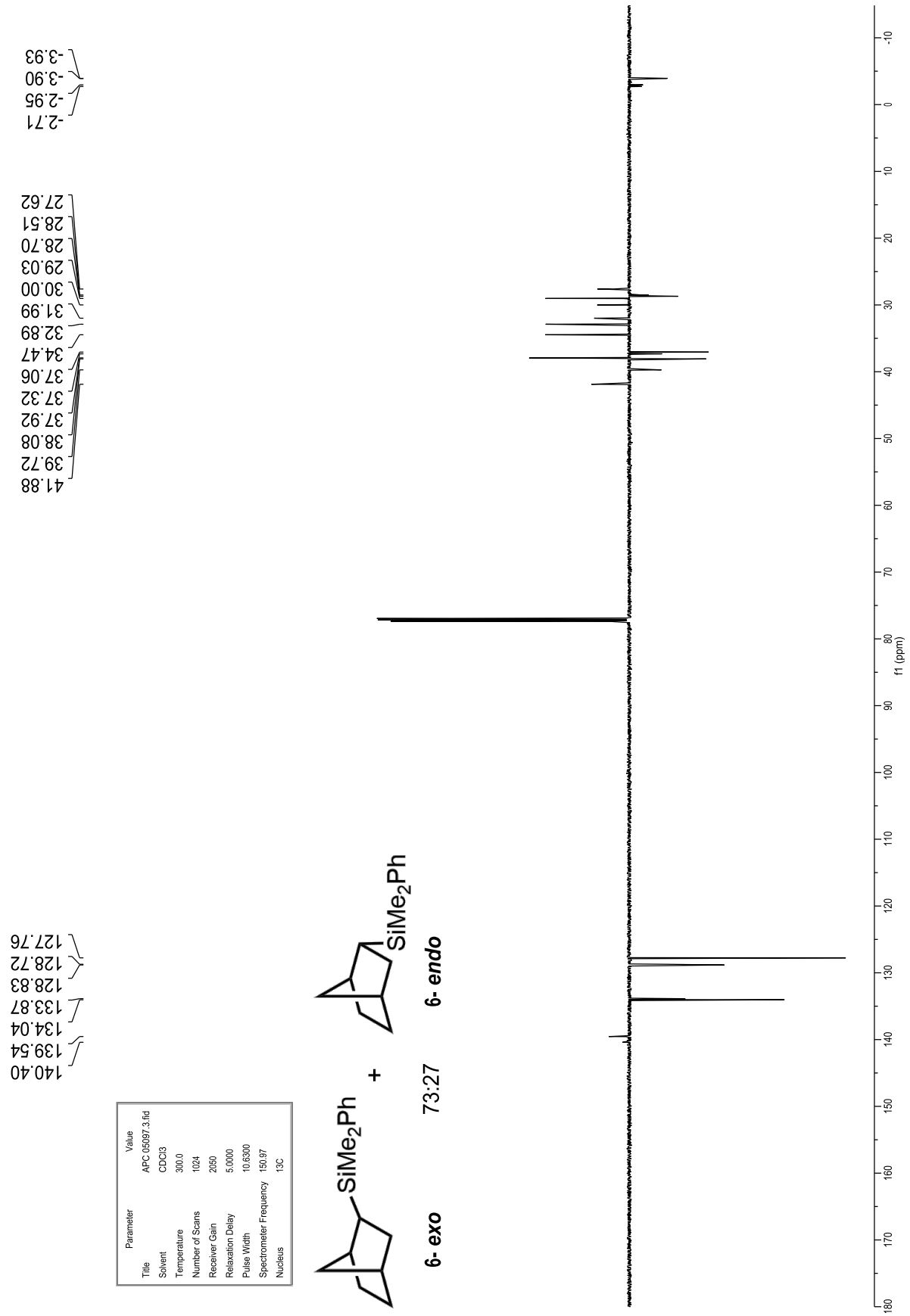

0.26
1.11
1.12
1.13
1.13
1.14
1.14
1.16
1.30
1.31
1.31
1.32
1.33
1.33
1.34
1.35
1.35
1.49
1.50
1.51
1.51
1.52
1.52
1.53
1.54
1.55
1.55
1.56
1.56
1.56
1.57
1.58
1.75
1.76
1.76
1.76
1.77
1.77
1.78
1.78
1.79
1.80
7.35
7.35
7.36
7.53
7.53
7.53
7.54
7.54
7.55
Parameter Value
Title BZV01214A
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 114
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Ph
5
6.00
0.96
2.07
4.09
2.00
1.92
2.87
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


139.53
134.01
128.84
127.75
28.35
27.18
25.65
-4.32
SiMe2Ph
5
Parameter Value
Title BZV01214A
Solvent CDCl3
Temperature 300.0
Number of Scans 256
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 8.5000
Spectrometer Frequency 150.95
Nucleus 13C
f1 (ppm)

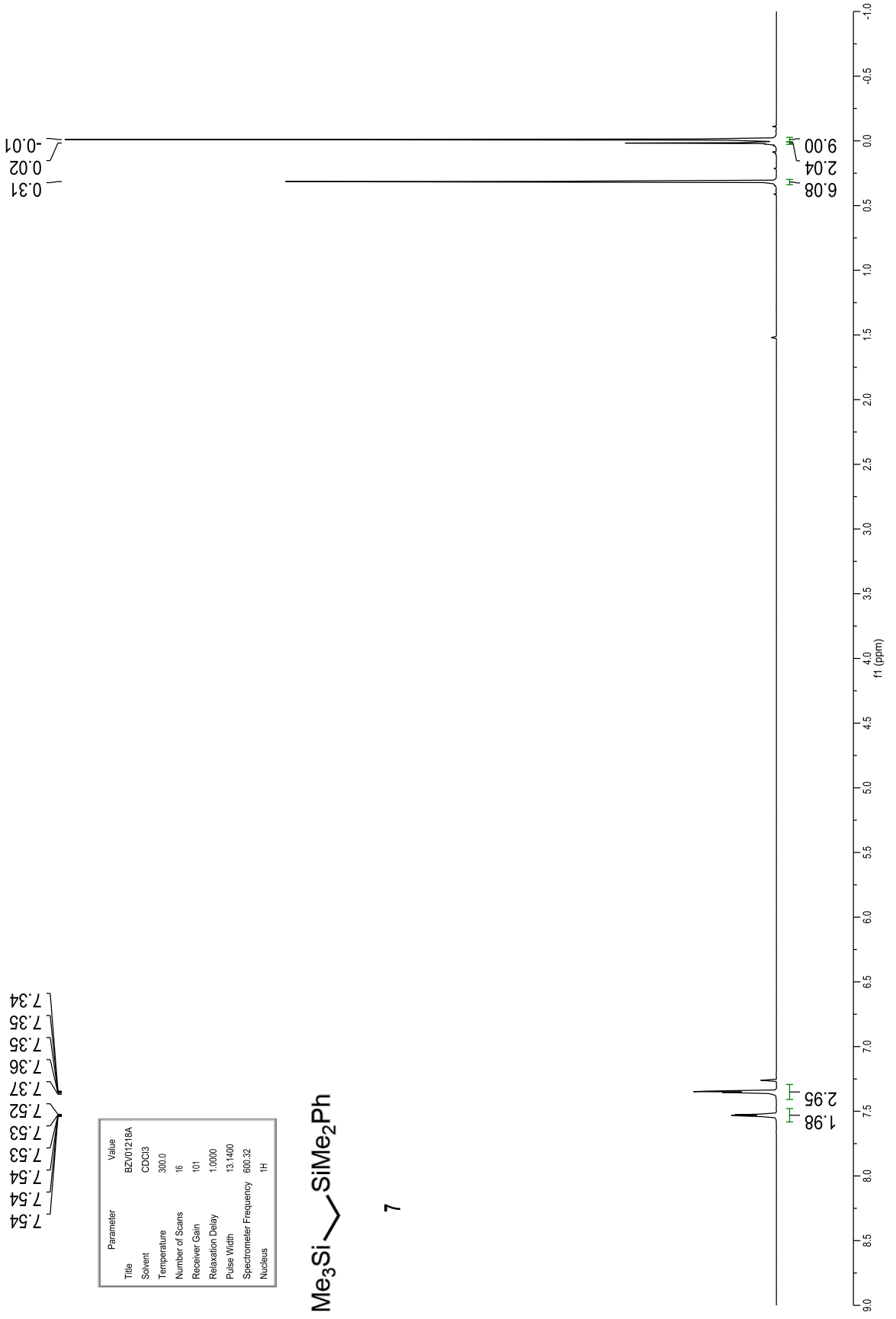

Parameter Value
Title BZV01214ASi
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
SiMe2Ph
5
Me3Si
O
SiMe3
-2.01
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

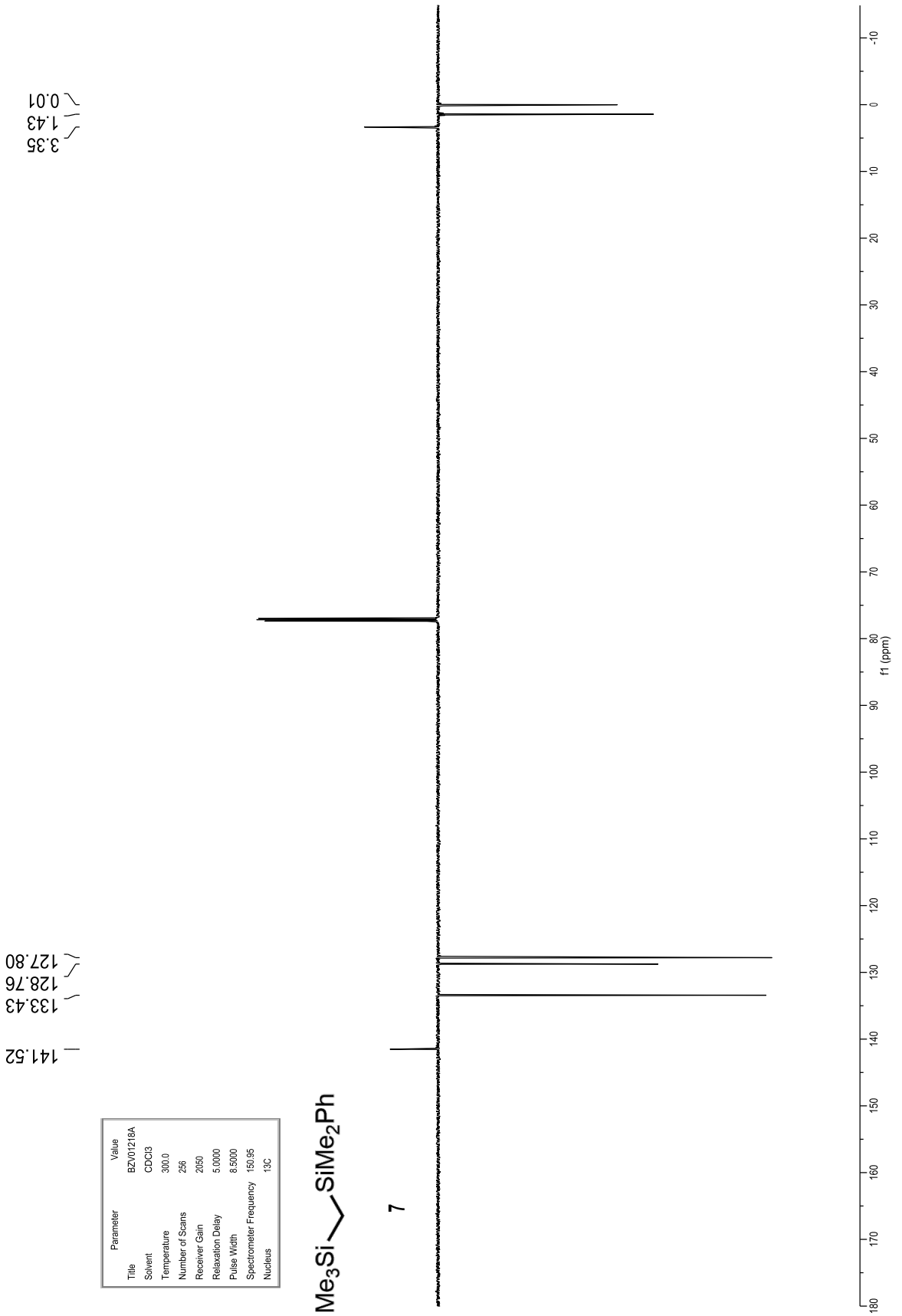

Parameter Value
Title APC 05002.2.fid
Solvent C6D6
Temperature 303.0
Number of Scans 16
Receiver Gain 101
Relaxation Delay 1.0000
Pulse Width 15.0000
Spectrometer Frequency 400.15
Nucleus 1H
MgBr
Ha
+
Hb
MgBr
41:59
S6- exo
S6- endo
Ha
Hb
1.00
0.70
f1 (ppm)

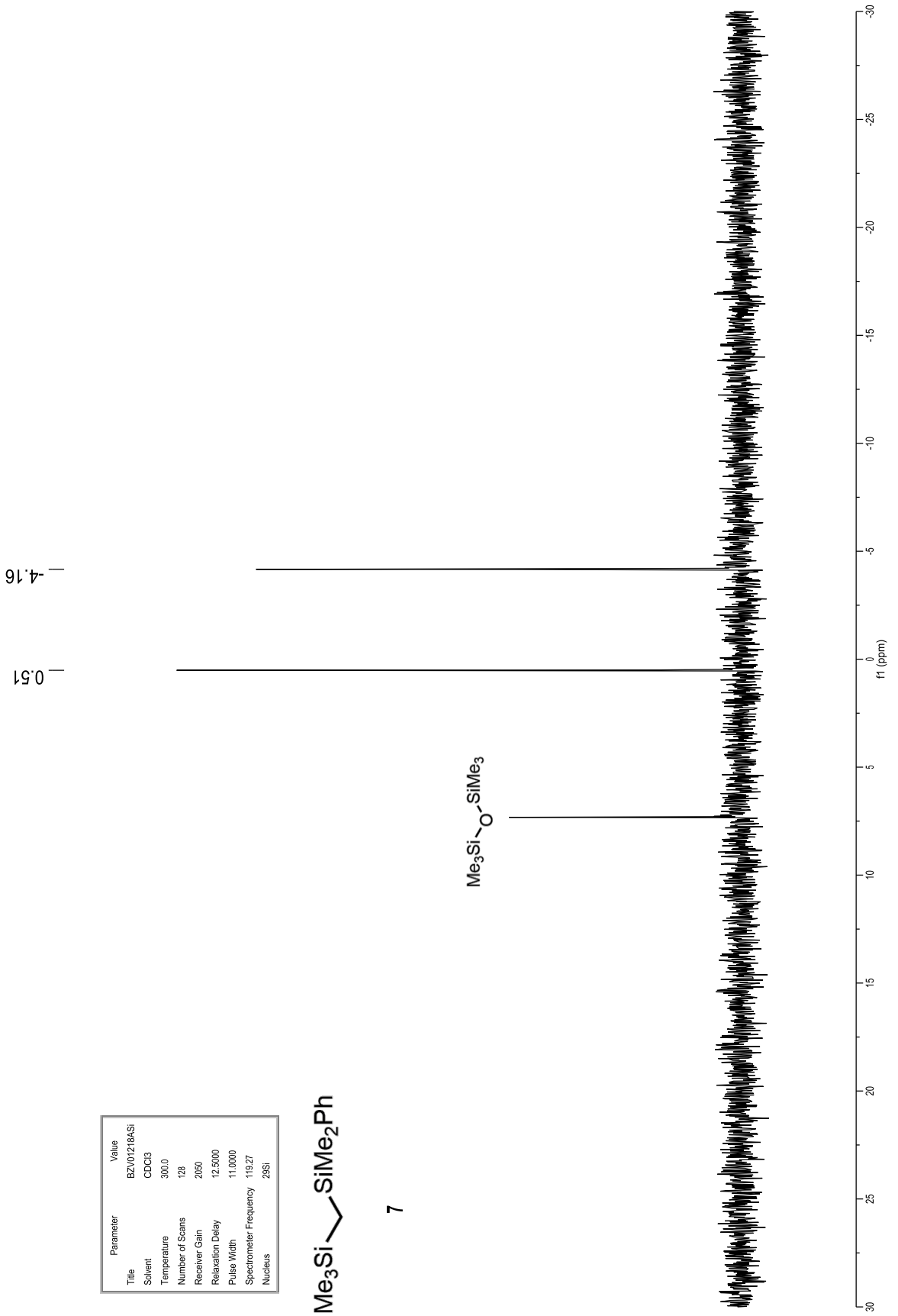

Parameter Value
Title APC 05097.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 128
Relaxation Delay 1.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Ph
+
SiMe2Ph
6- exo
73:27
6- endo
f1 (ppm)

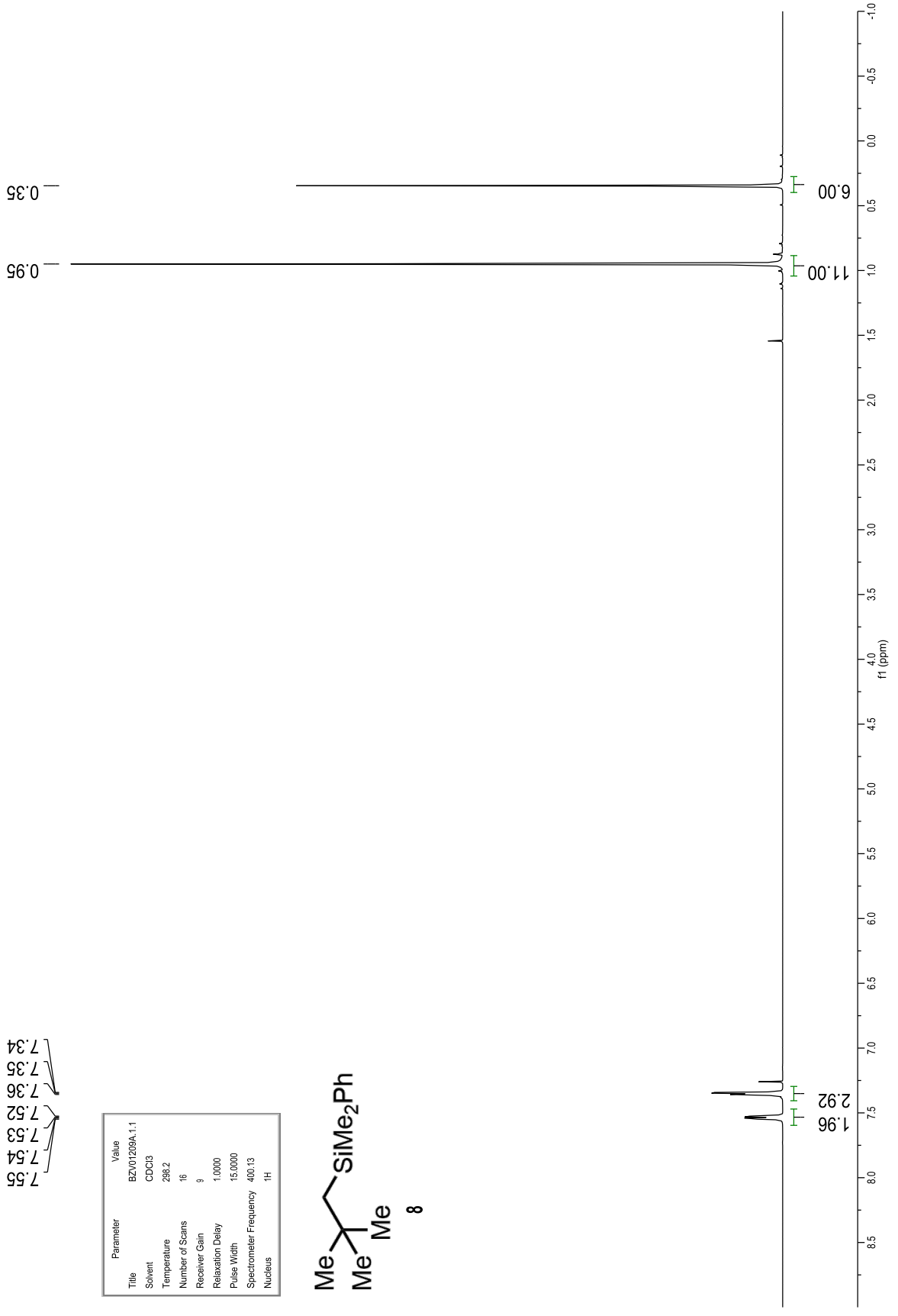

-2.71
-2.95
-3.90
-3.93
27.62
28.51
28.70
29.03
30.00
31.99
32.89
34.47
37.06
37.32
37.92
38.08
39.72
41.88
140.40
139.54
134.04
133.87
128.83
128.72
127.76
Parameter Value
Title APC 05097.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
SiMe2Ph
+
SiMe2Ph
6- exo
73:27
6- endo
f1 (ppm)

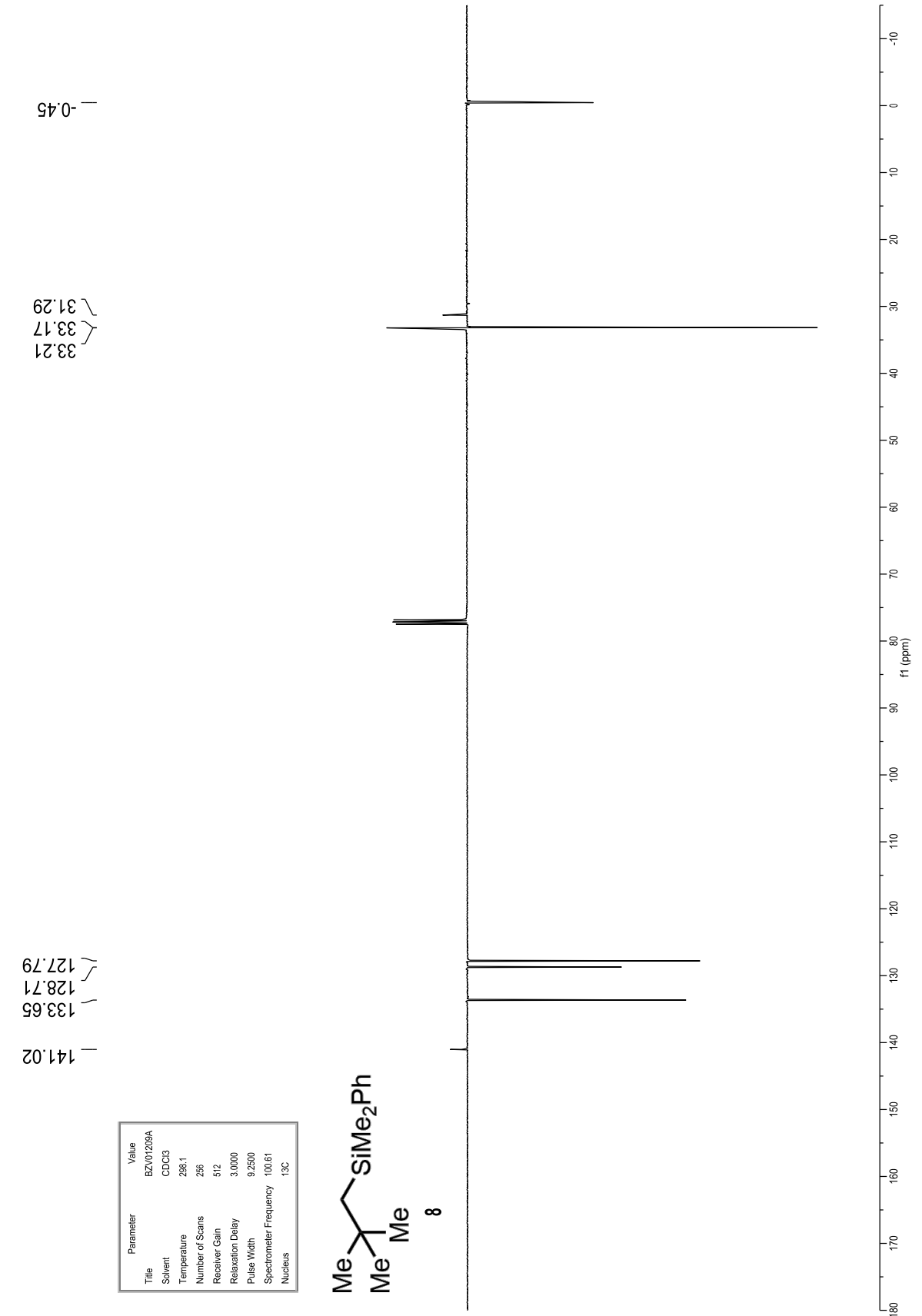
Parameter Value
Title APC 05097.4.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 1820
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
SiMe2Ph
+
SiMe2Ph
6- exo
73:27
6- endo
Me3Si
O
SiMe3
-2.78
-3.20
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

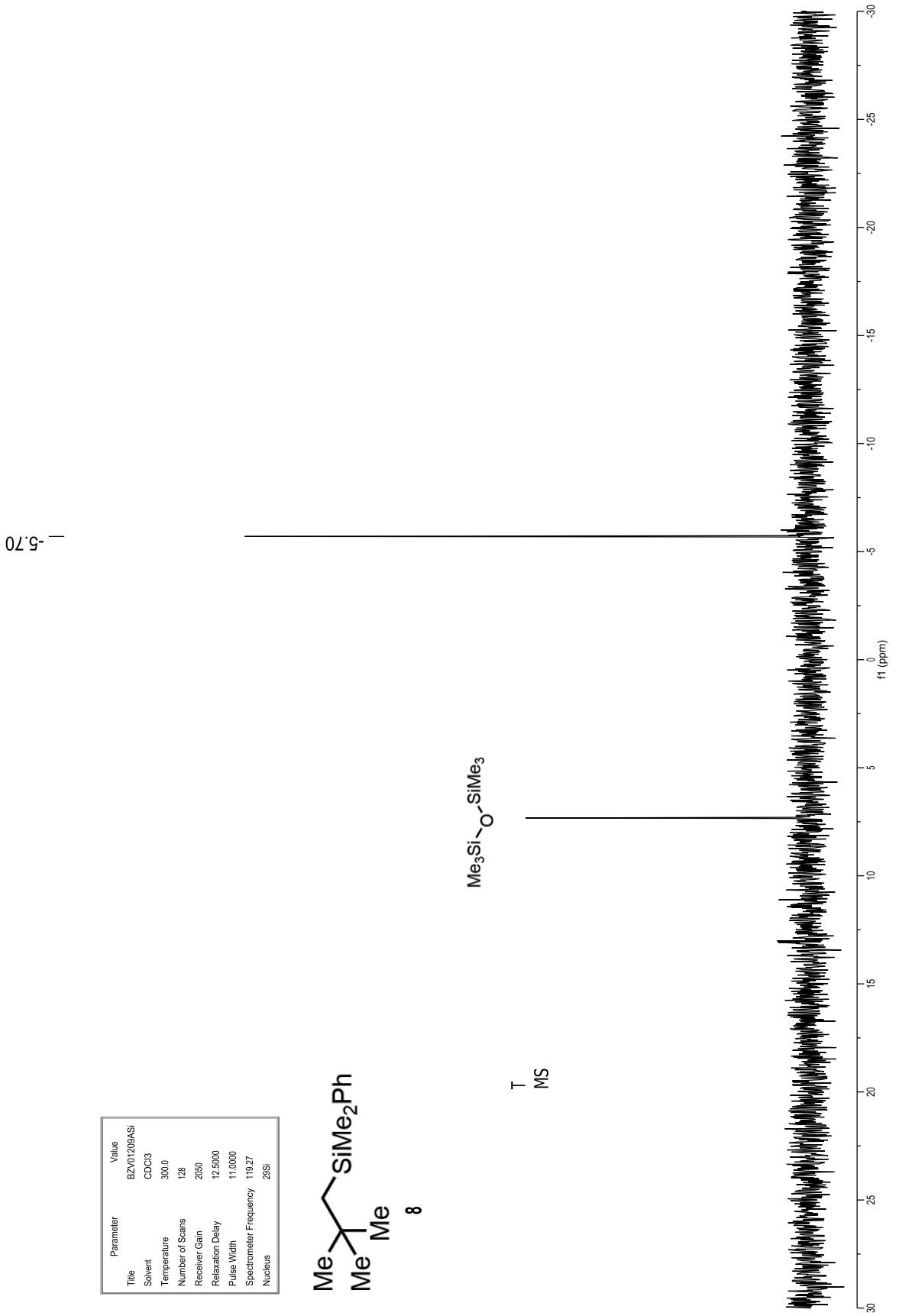

7.54
7.54
7.54
7.53
7.53
7.52
7.37
7.36
7.35
7.35
7.34
Parameter Value
Title BZV01218A
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 101
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H
Me3Si SiMe2Ph
7
0.31
0.02
-0.01
6.08
2.04
9.00
1.98
2.95
f1 (ppm)

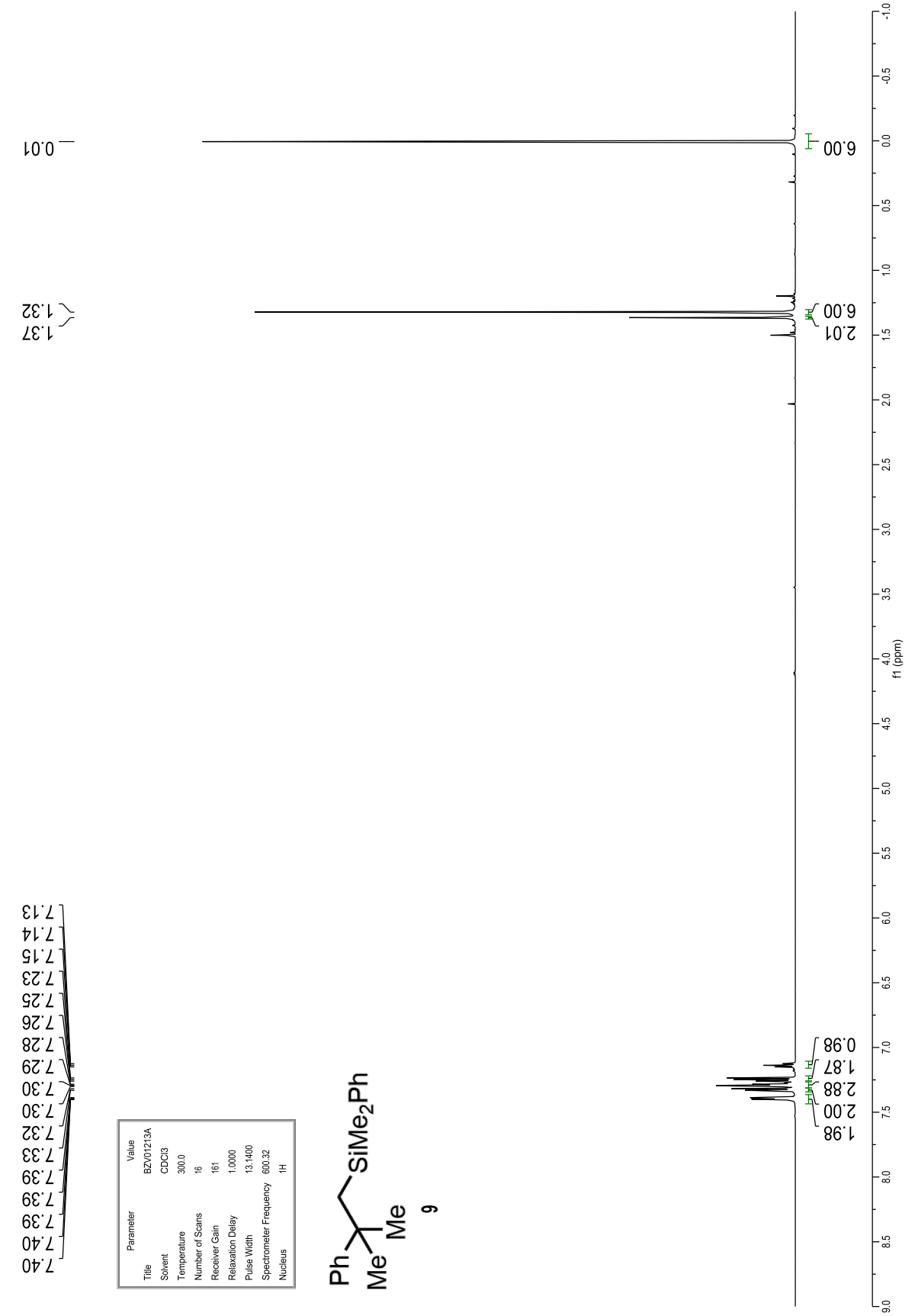

Me3Si SiMe2Ph
7
141.52
133.43
128.76
127.80
3.35
1.43
0.01
f1 (ppm)
Parameter Value
Title BZV01218A
Solvent CDCl3
Temperature 300.0
Number of Scans 256
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 8.5000
Spectrometer Frequency 150.95
Nucleus 13C

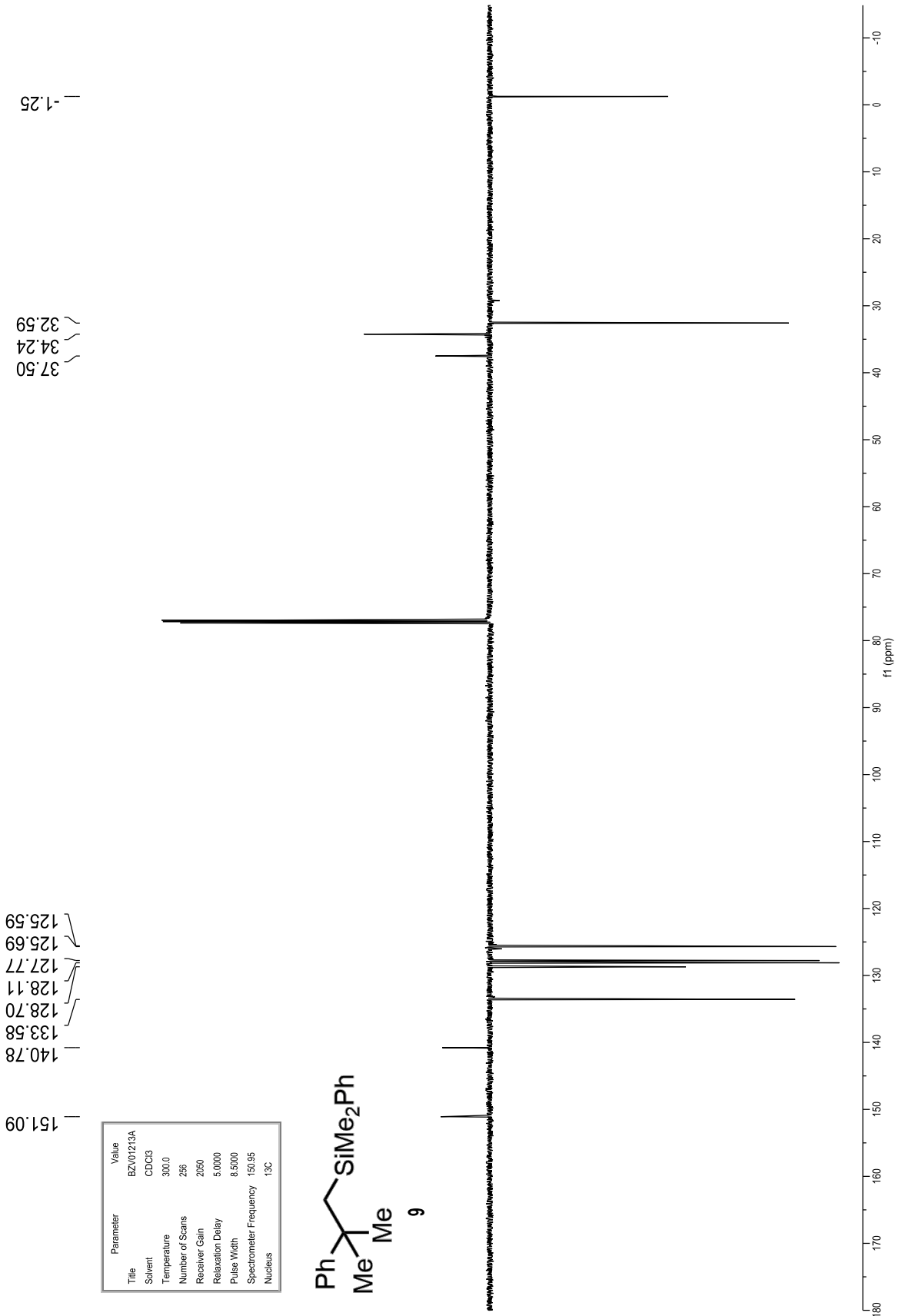

Parameter Value
Title BZV01218ASi
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
Me3Si SiMe2Ph
7
Me3Si O SiMe3
0.51
-4.16
30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
f1 (ppm)

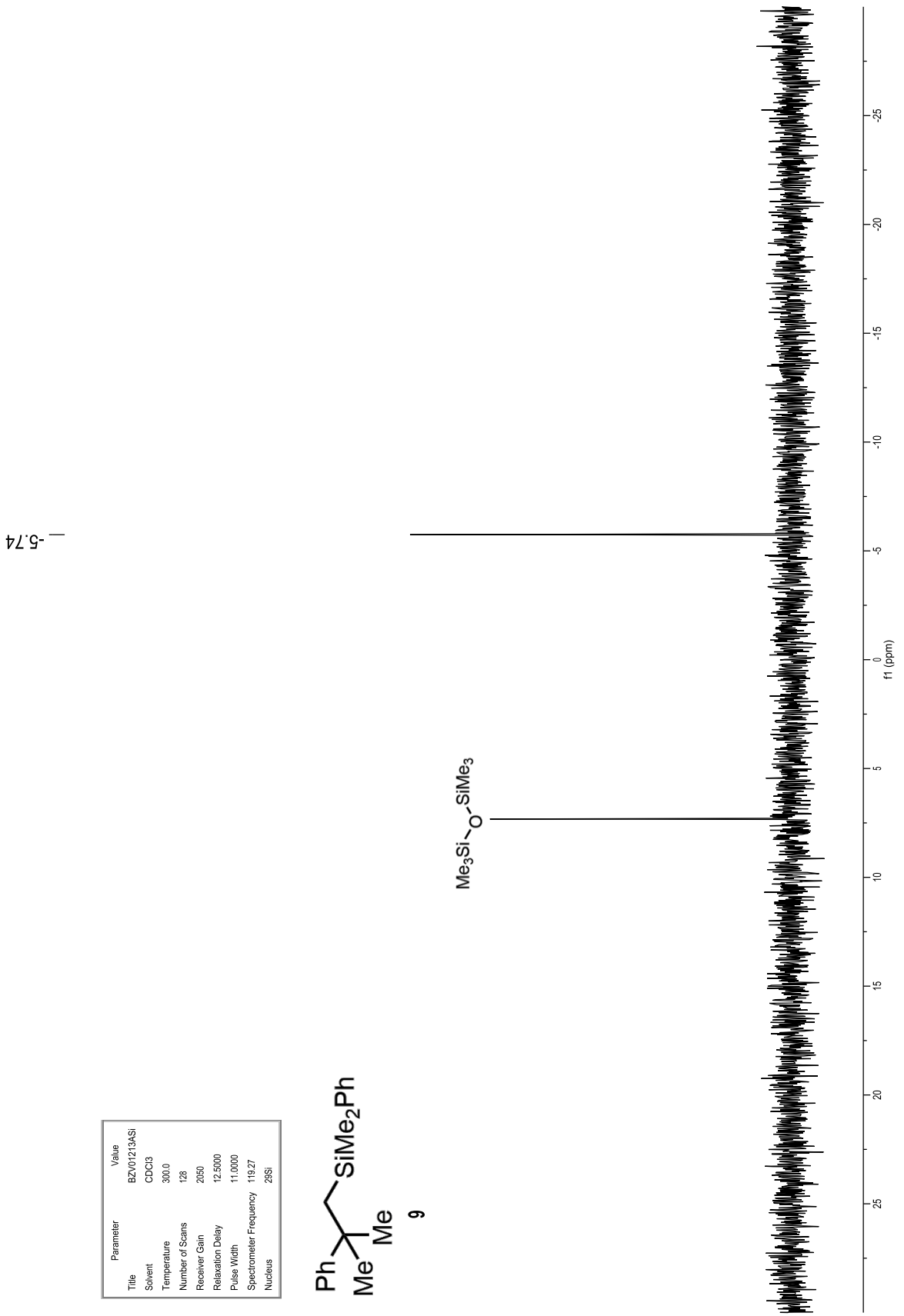

7.55
7.54
7.53
7.52
7.36
7.35
7.34
Parameter Value
Title BZV012209A.1.1
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 9
Relaxation Delay 1.0000
Pulse Width 15.0000
Spectrometer Frequency 400.13
Nucleus 1H
Me
Me
SiMe2Ph
8
0.95
0.35
11.00
6.00
2.92
1.96
f1 (ppm)

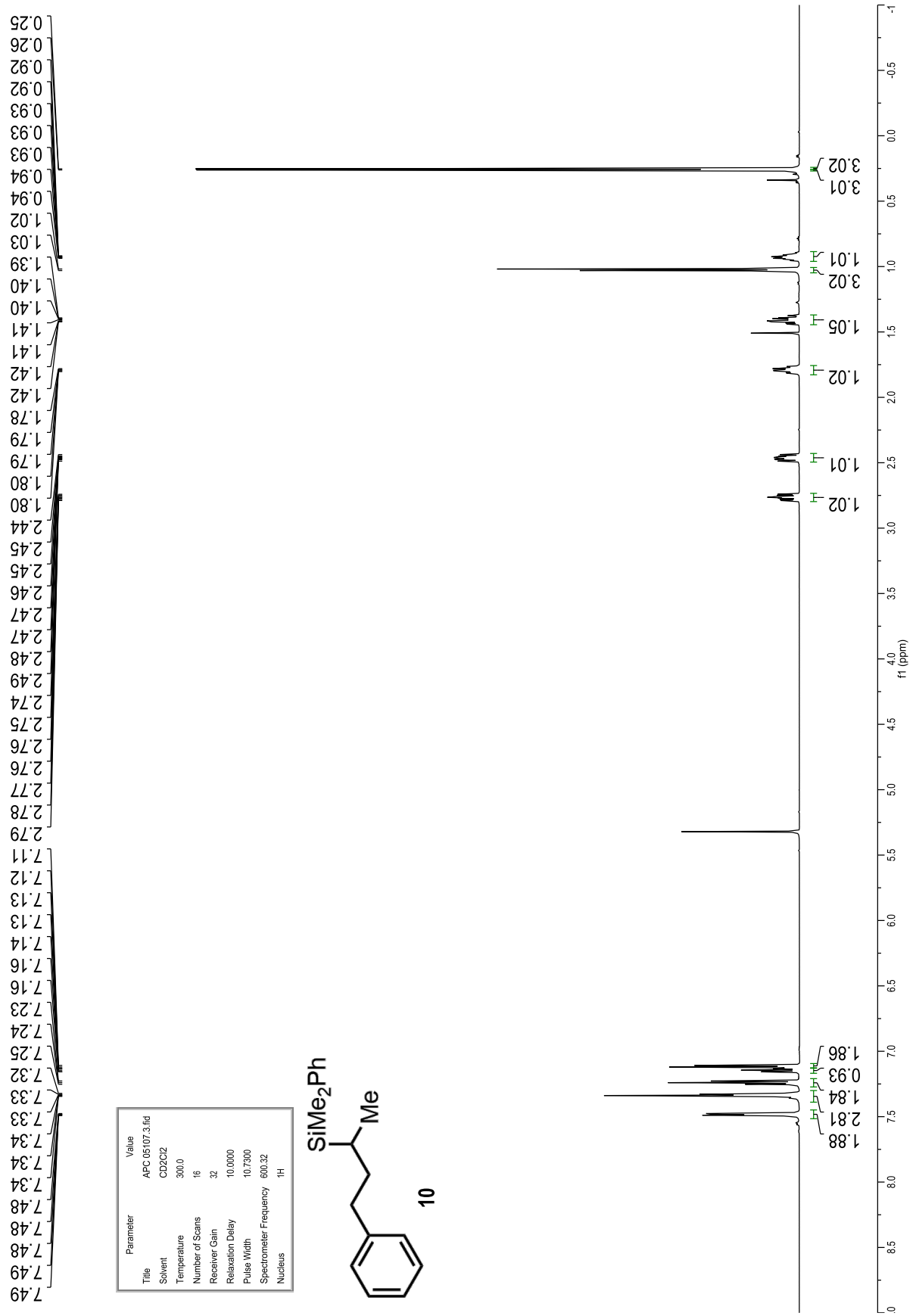

Parameter Value
Title BZV01209A
Solvent CDCl3
Temperature 298.1
Number of Scans 256
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Spectrometer Frequency 100.61
Nucleus 13C
141.02
133.65
128.71
127.79
33.21
33.17
31.29
-0.45
Me
Me
SiMe2Ph
8
f1 (ppm)

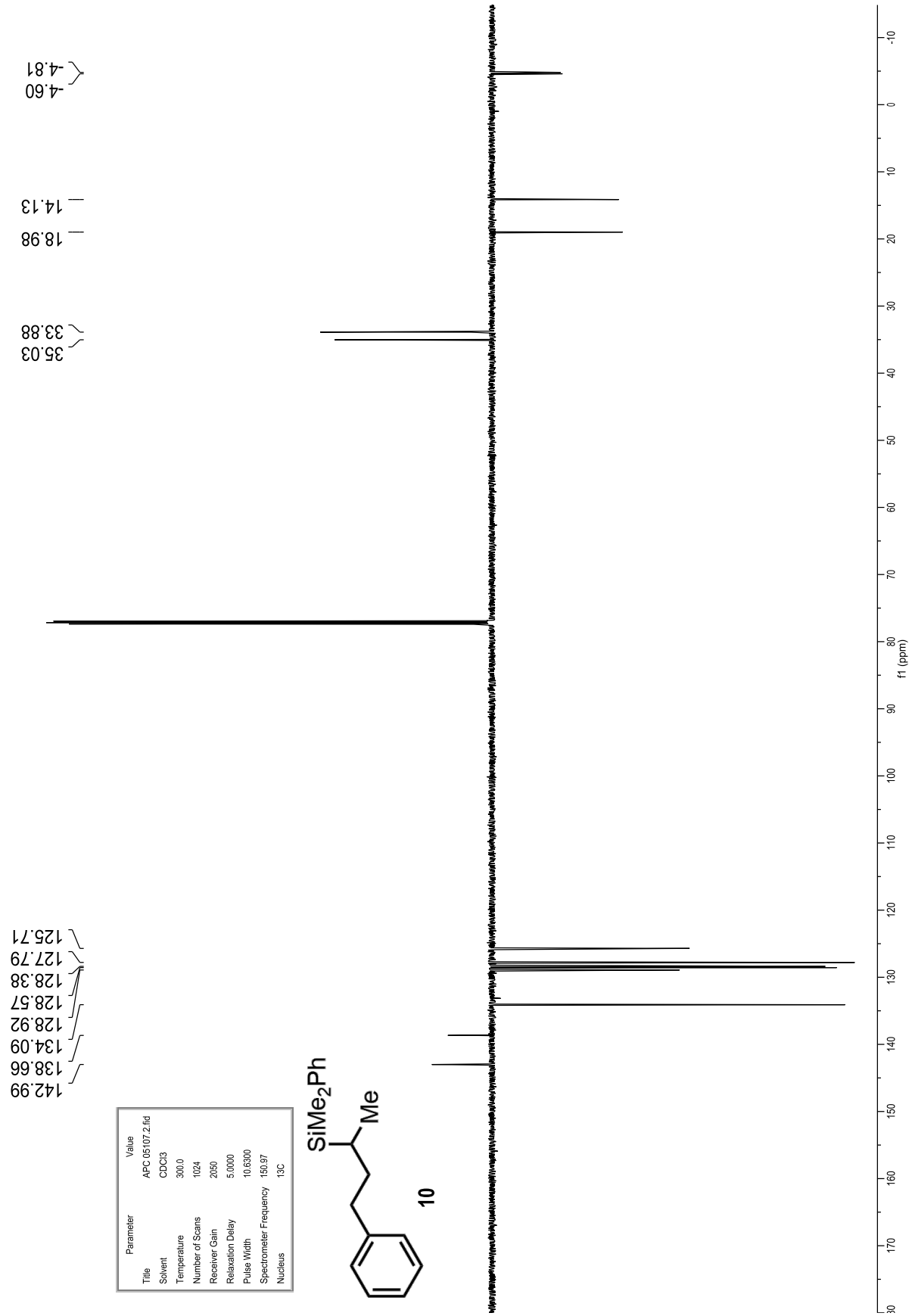

Parameter Value
Title BZV01209ASi
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
Me
Me
SiMe2Ph
8
Me3Si
O
SiMe3
T
MS
-5.70
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
f1 (ppm)


7.40
7.40
7.39
7.39
7.39
7.33
7.32
7.30
7.30
7.29
7.28
7.26
7.25
7.23
7.15
7.14
7.13
Parameter Value
Title BZV01213A
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 161
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H
Ph
Me
Me
SiMe2Ph
6
0.01
1.32
1.37
6.00
2.01
6.00
0.98
1.87
2.88
2.00
1.98
f1 (ppm)

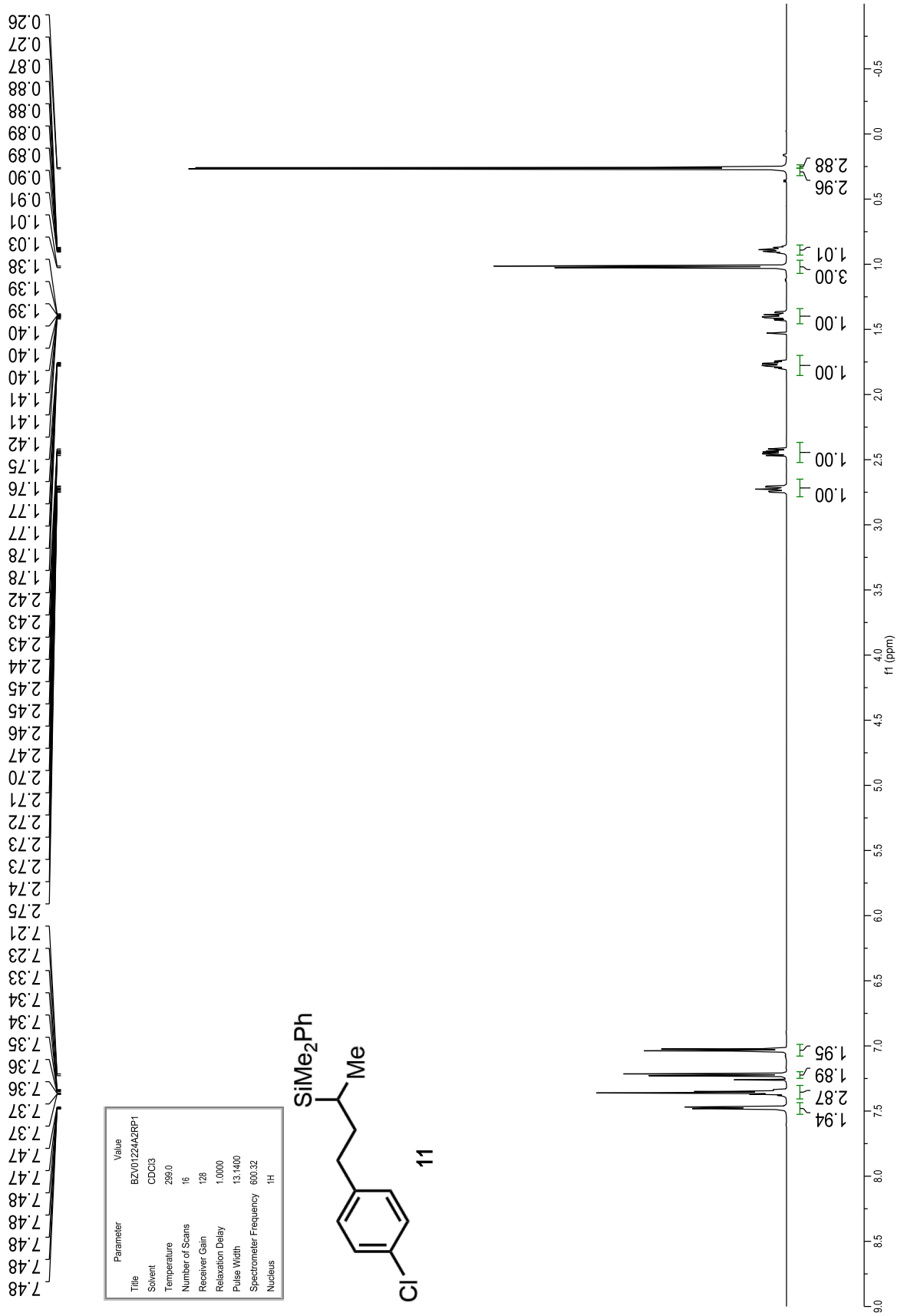

Parameter Value
Title BZV01213A
Solvent CDCl3
Temperature 300.0
Number of Scans 256
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 8.5000
Spectrometer Frequency 150.95
Nucleus 13C
Ph
Me
Me
SiMe2Ph
9
151.09
140.78
133.58
128.70
128.11
127.77
125.69
125.59
37.50
34.24
32.59
-1.25
f1 (ppm)

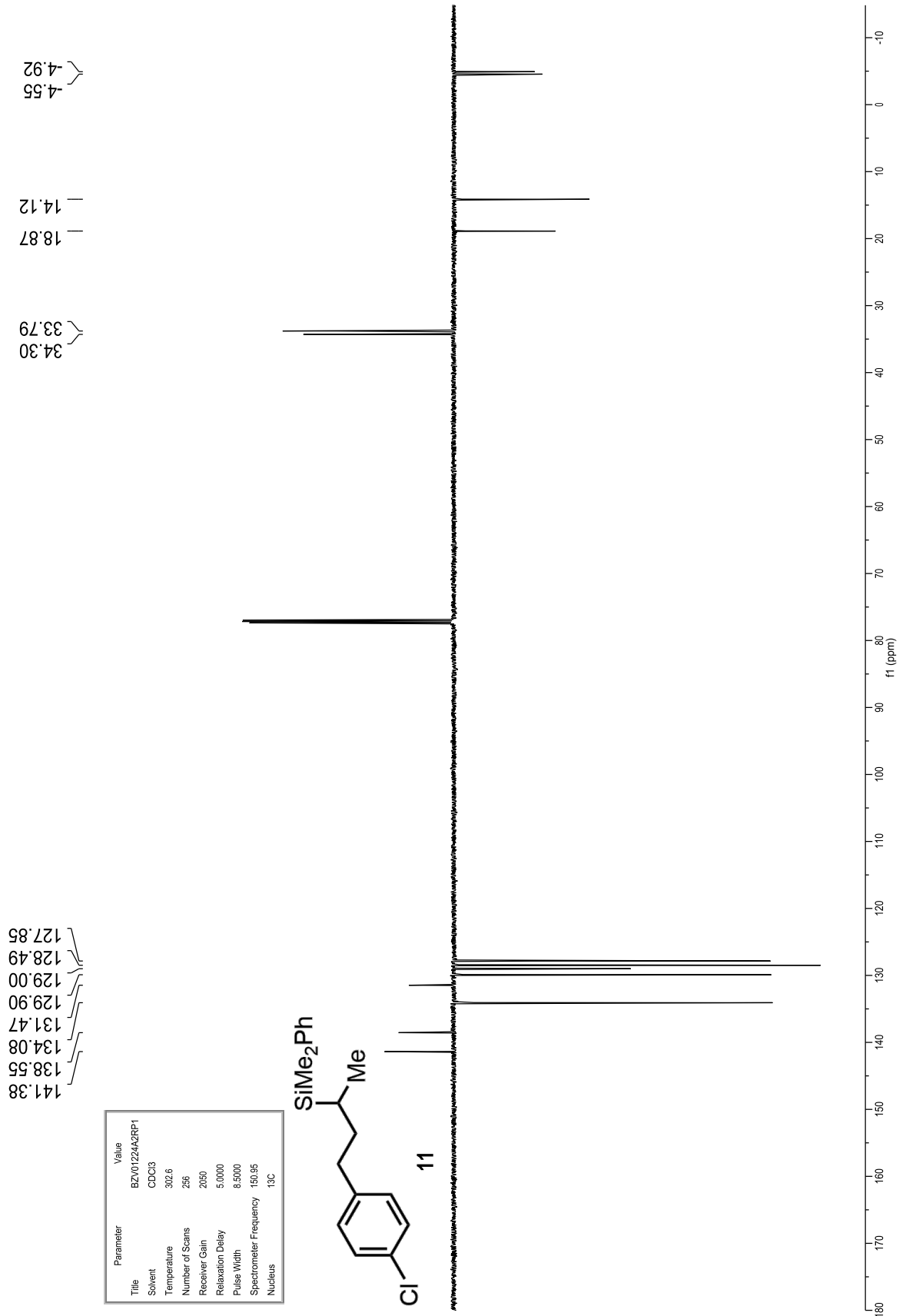

Parameter Value
Title BZV01213ASi
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
Ph
Me
SiMe2Ph
Me
6
Me3Si
O
SiMe3
-5.74
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)


Parameter Value
Title APC 05107.3.fid
Solvent CD2Cl2
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Ph
Me
10
1.88
2.81
1.84
0.93
1.86
1.02
1.01
1.02
1.05
3.02
1.01
3.02
3.01
f1 (ppm)

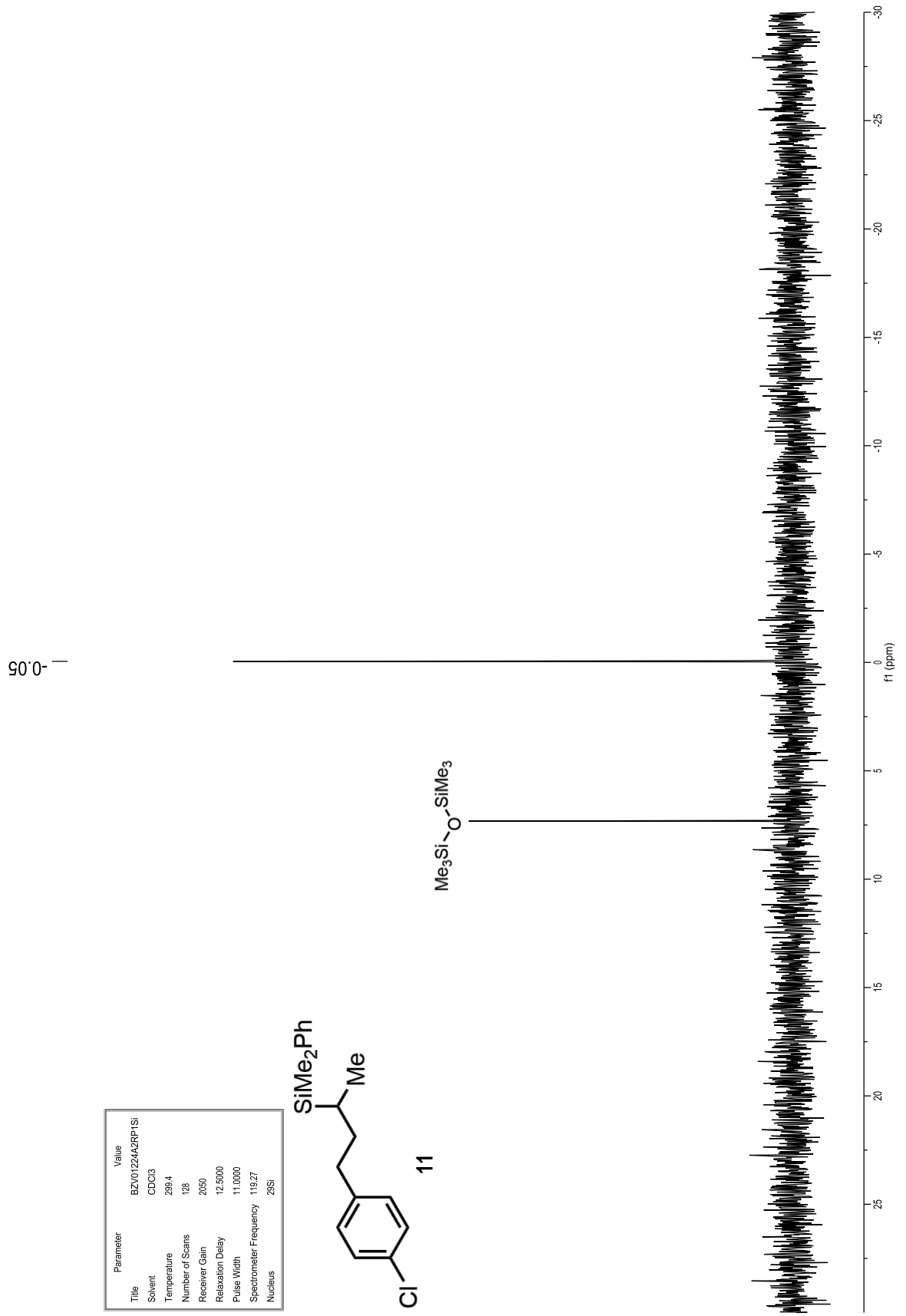

142.99
138.66
134.09
128.92
128.57
128.38
127.79
125.71
35.03
33.88
18.98
14.13
-4.60
-4.81
SiMe2Ph
Me
10
Parameter Value
Title APC 05107.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

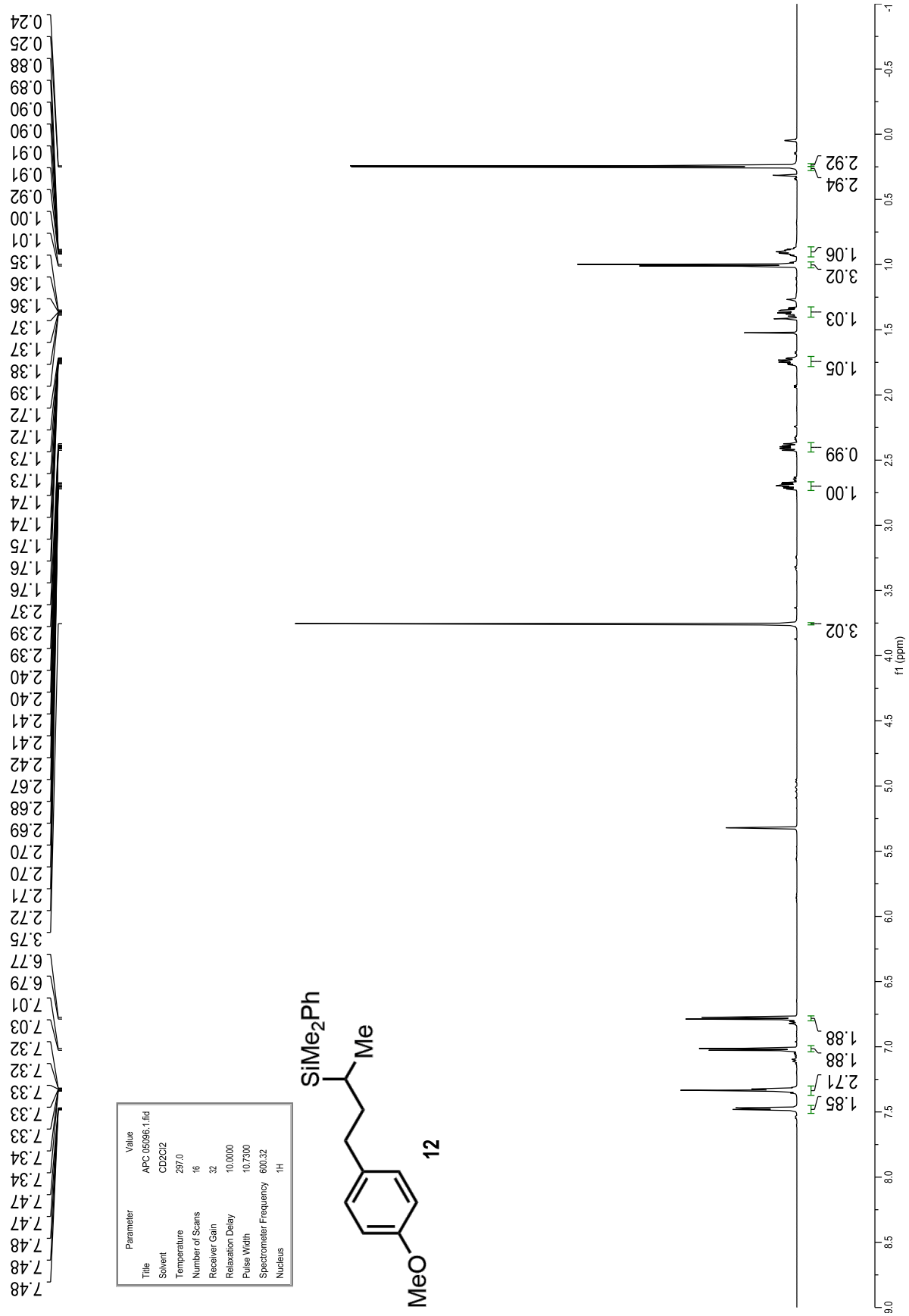
Parameter Value
Title APC 05107.4.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
SiMe2Ph
Me
10
Me3Si
O
SiMe3
-0.05
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

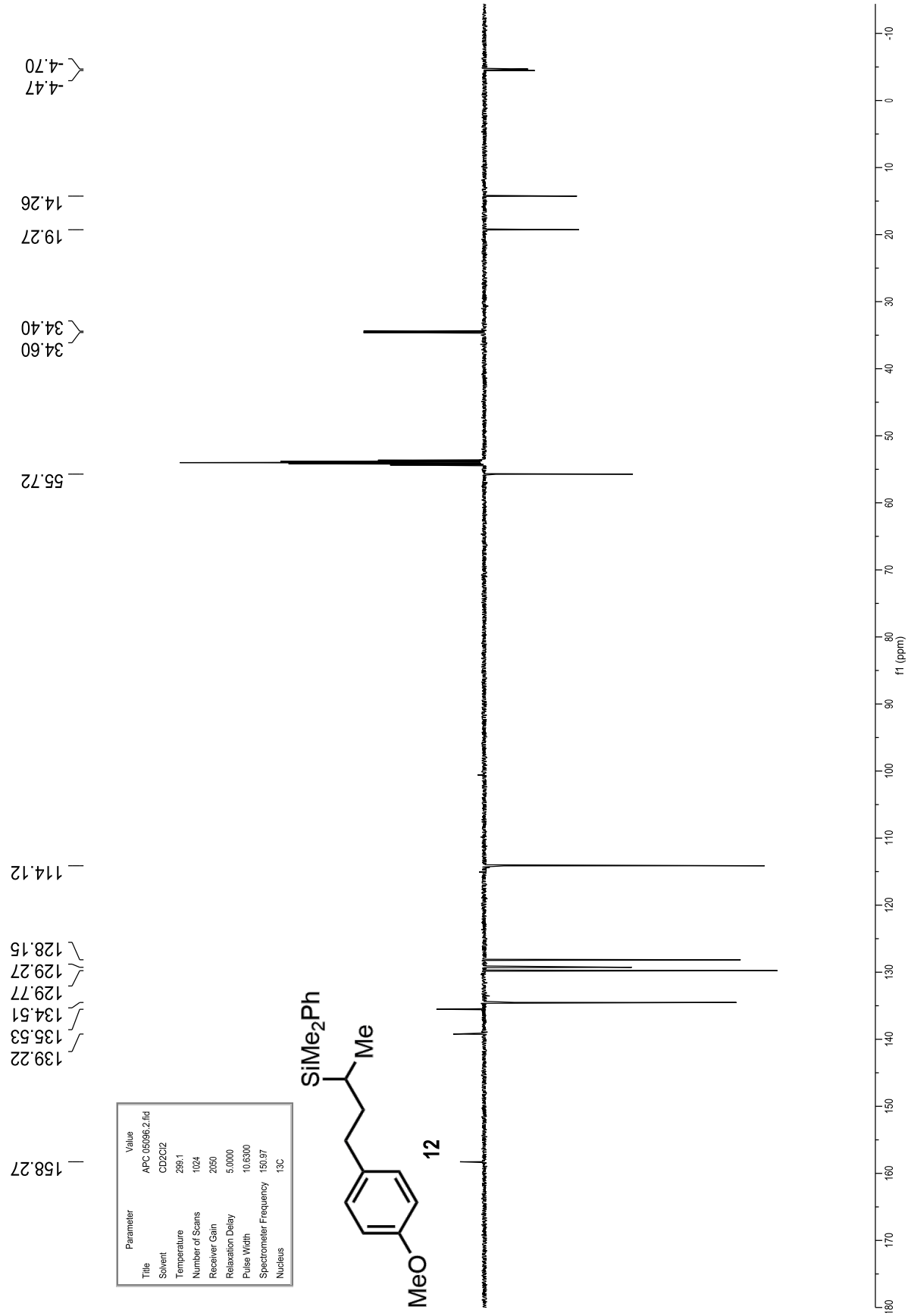

Parameter Value
Title BZV01224A2RP1
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Receiver Gain 128
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Ph
Me
Cl
11
1.94
2.87
1.89
1.95
1.00
1.00
1.00
1.00
3.00
1.01
2.96
2.88
f1 (ppm)



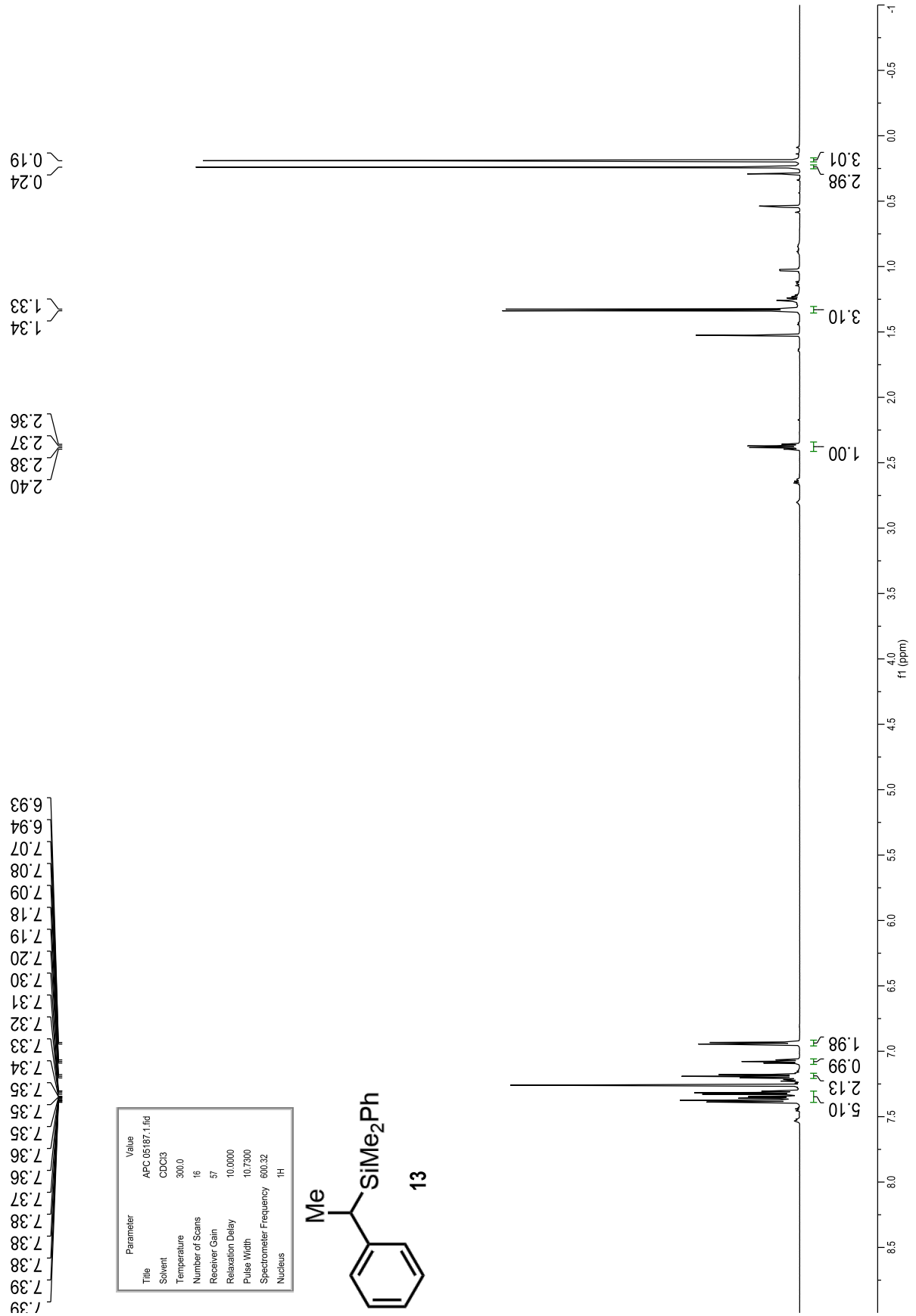
Parameter	Value
Title	BZV01224A2RP1
Solvent	CDCl3
Temperature	302.6
Number of Scans	256
Receiver Gain	2050
Relaxation Delay	5.0000
Pulse Width	8.5000
Spectrometer Frequency	150.95
Nucleus	13C

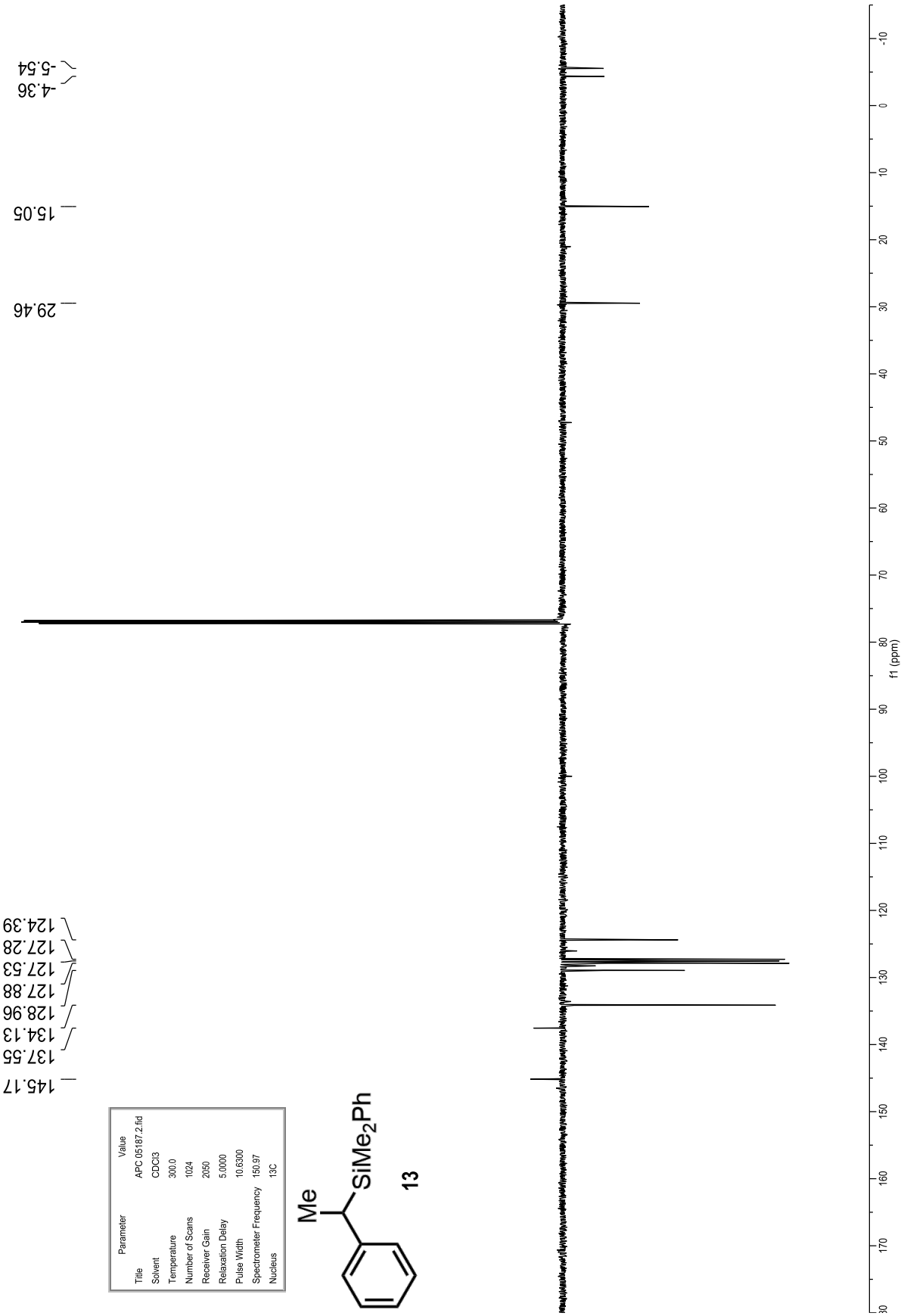

Parameter Value
Title BZV01224A2RP1Si
Solvent CDCl3
Temperature 299.4
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 11.0000
Spectrometer Frequency 119.27
Nucleus 29Si
SiMe2Ph
Me
Cl
11
Me3Si
O
SiMe3
-0.05
f1 (ppm)

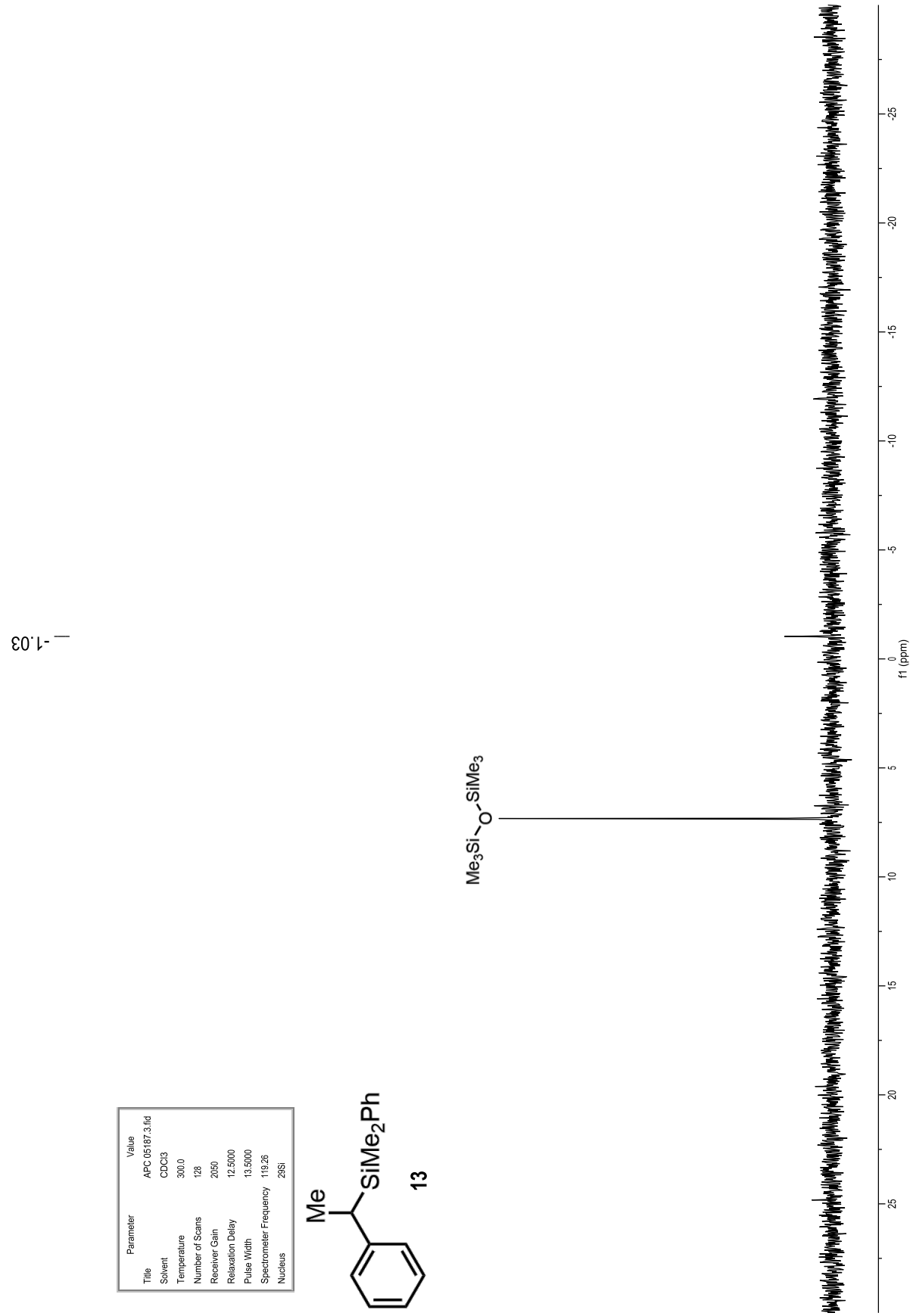

Parameter Value
Title APC 05096.1.fid
Solvent CD2Cl2
Temperature 297.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Ph
Me
MeO
12
3.02
1.00
0.99
1.05
1.03
3.02
1.06
2.94
2.92
1.85
1.88
2.71
1.88
f1 (ppm)


-4.70
-4.47
14.26
19.27
34.60
34.40
55.72
114.12
128.15
129.27
129.77
134.51
135.53
139.22
158.27
Parameter Value
Title APC 05096.2.fid
Solvent CD2Cl2
Temperature 299.1
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
SiMe2Ph
Me
MeO
12
f1 (ppm)

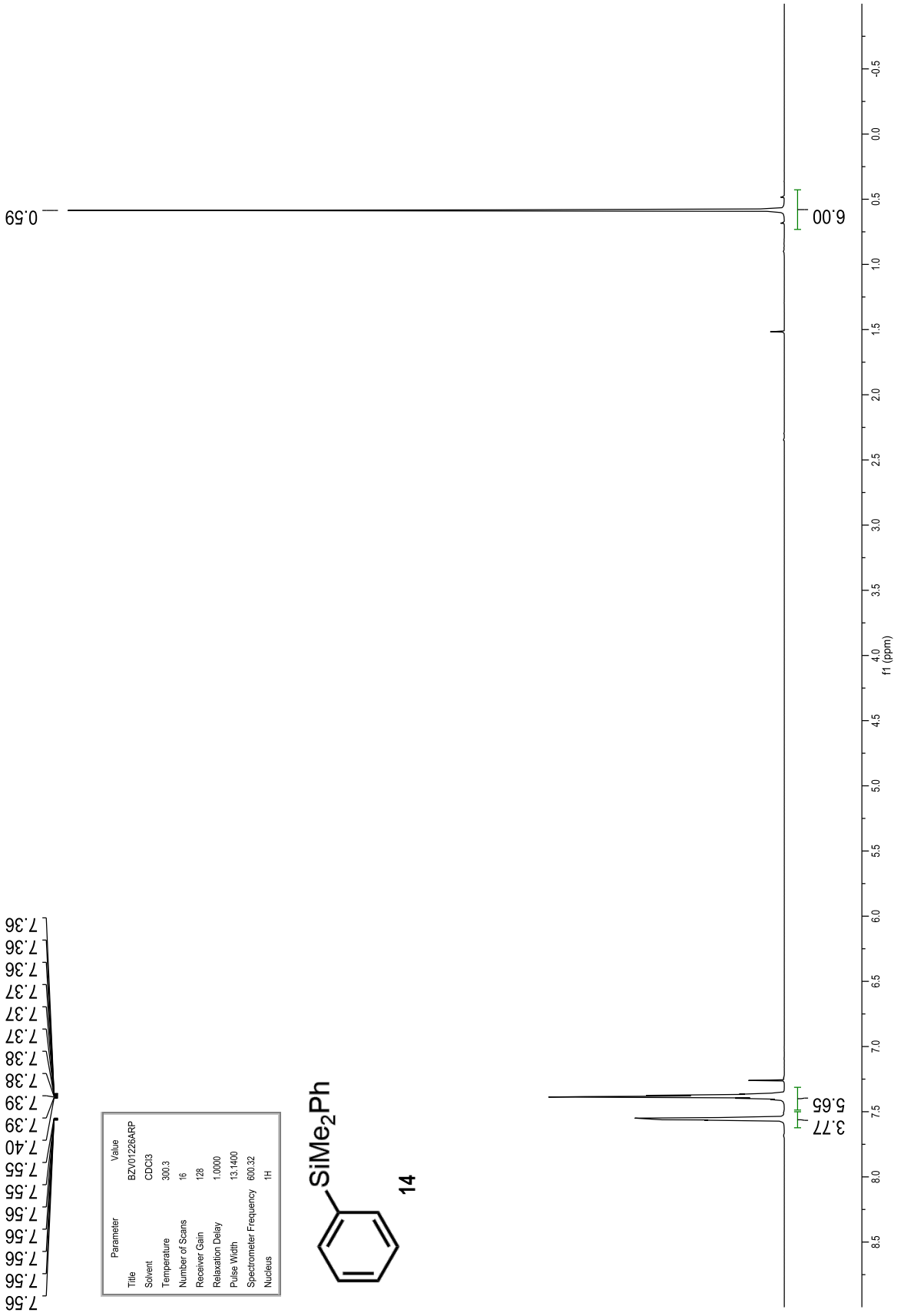
-0.17
Parameter Value
Title APC 05096_3.fid
Solvent CD2Cl2
Temperature 297.0
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
SiMe2Ph
Me
MeO
12
Me3Si
O
SiMe3
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

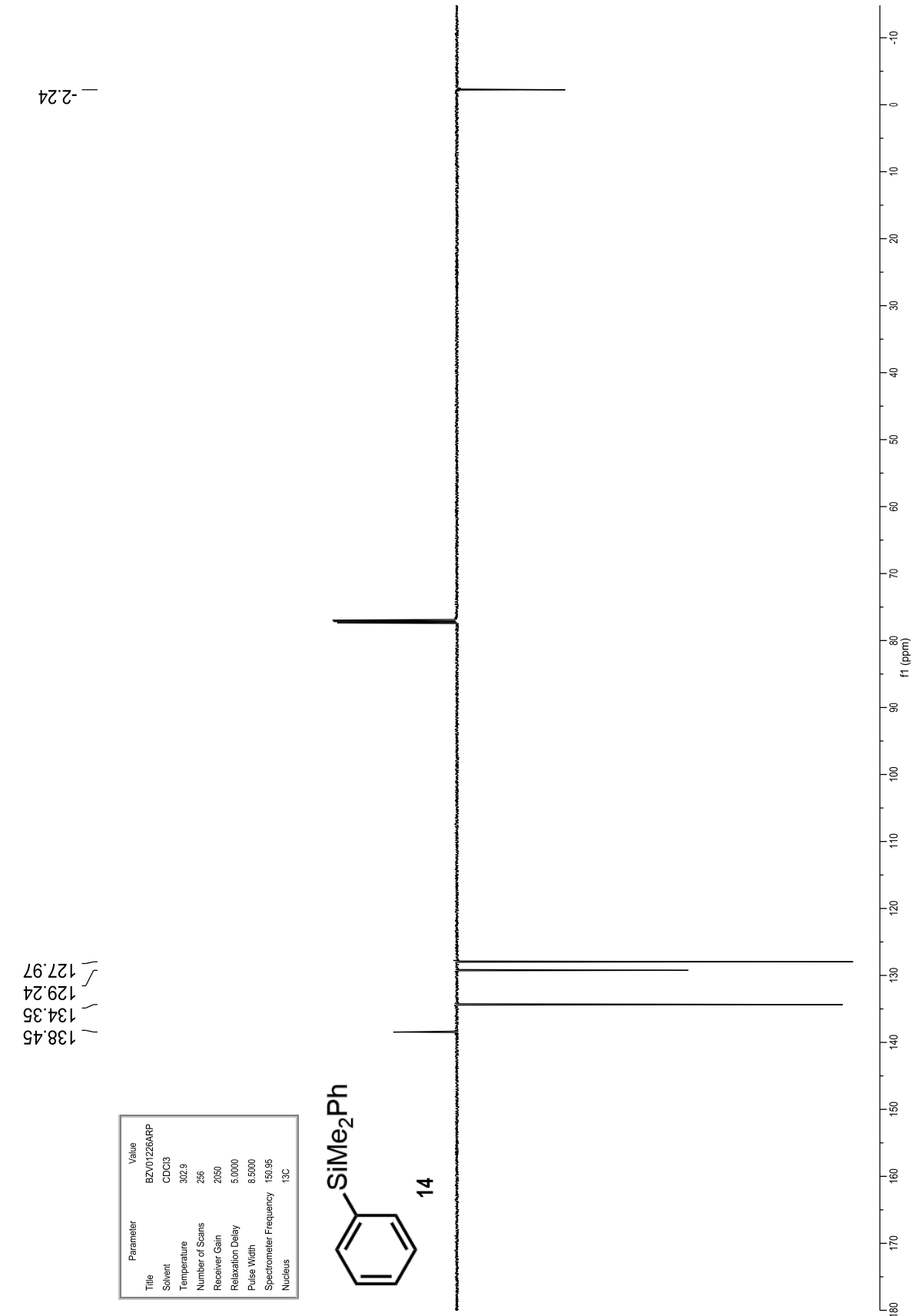

Parameter Value
Title APC 05187_1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 57
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
SiMe2Ph
13
5.10
2.13
0.99
1.98
1.00
3.10
2.98
3.01
f1 (ppm)

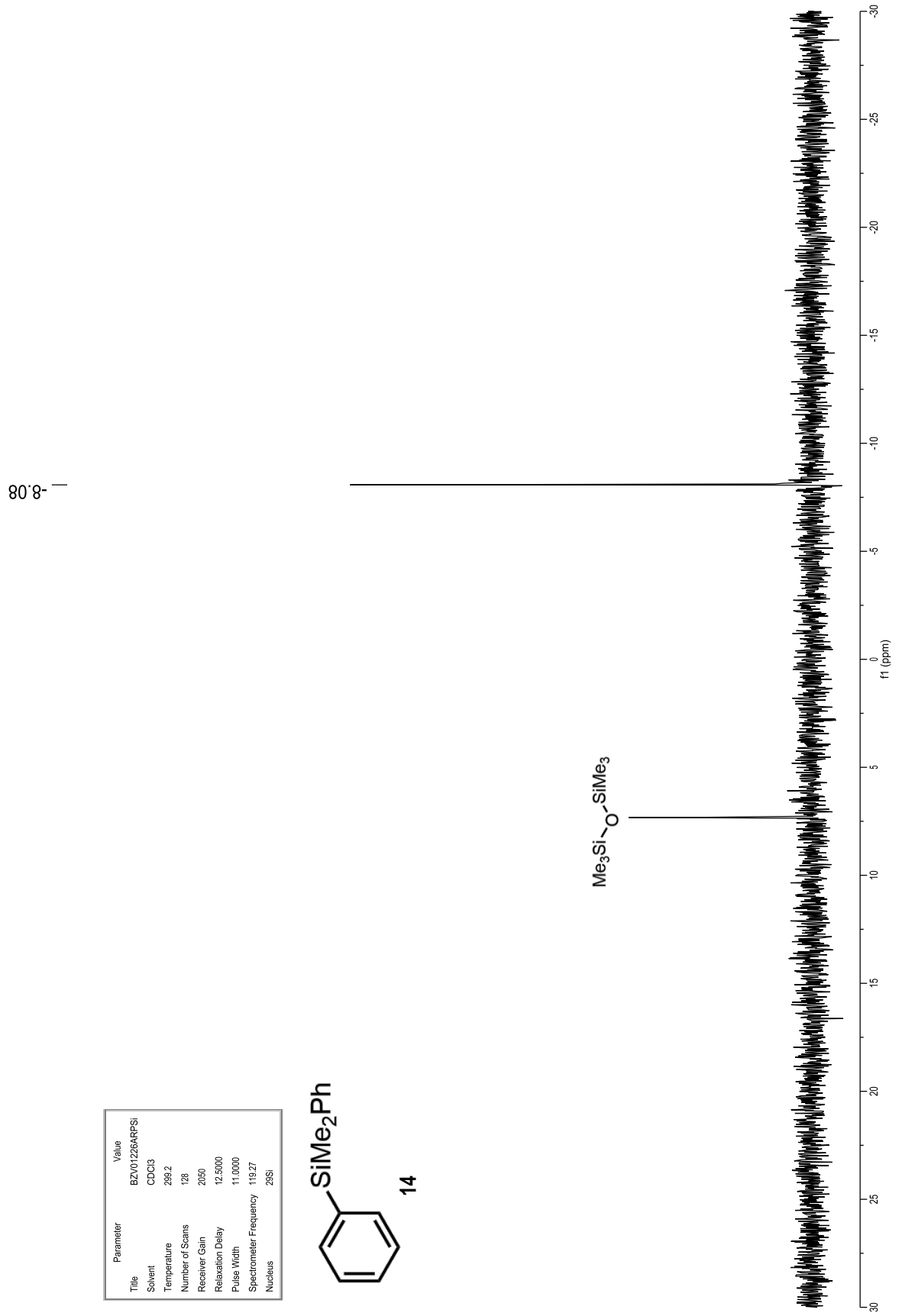

-5.54
-4.36
15.05
29.46
124.39
127.28
127.53
127.88
128.96
134.13
137.55
145.17
Me
SiMe2Ph
13
Parameter Value
Title APC 05187.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)



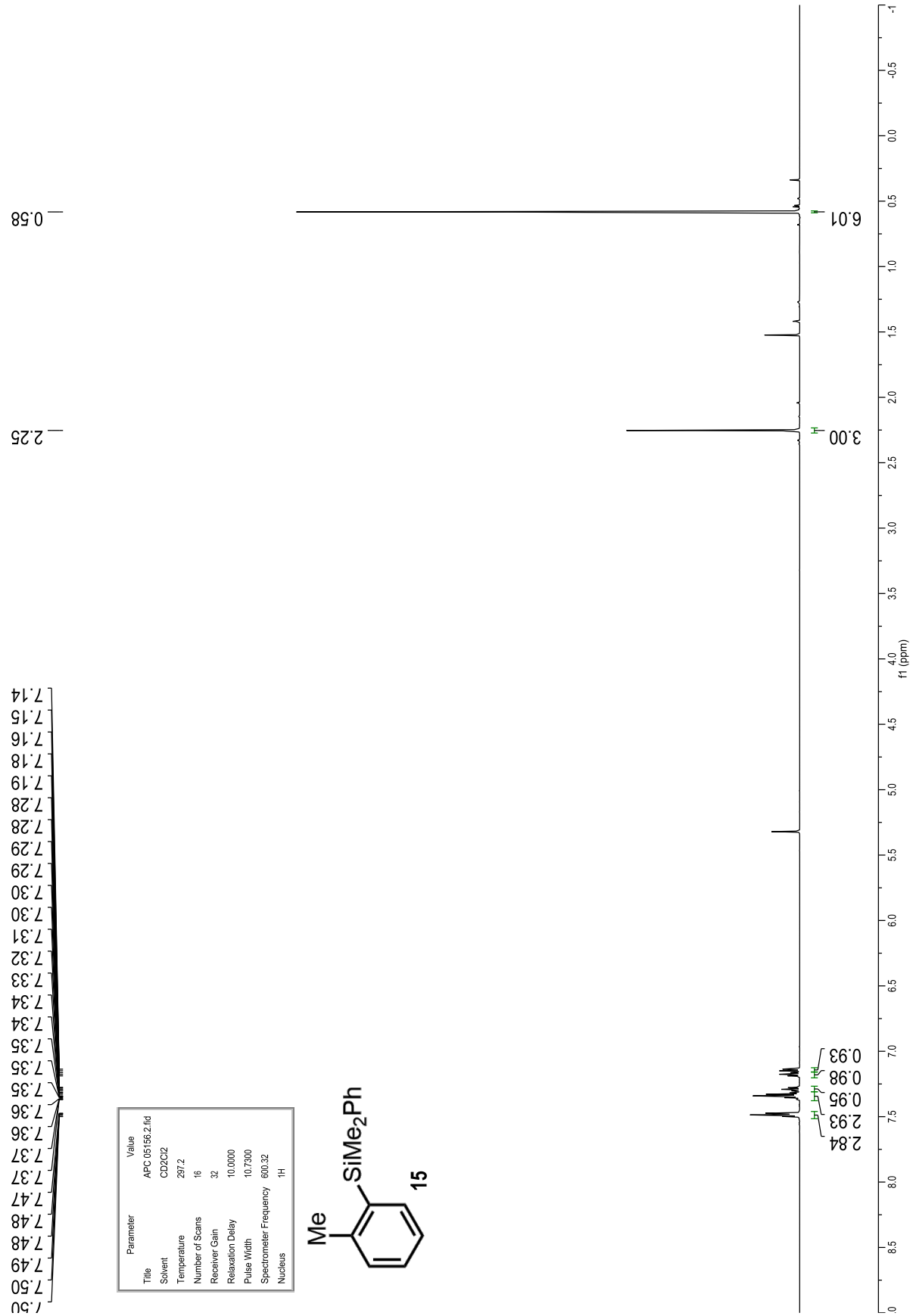
Parameter	Value
Title	APC 05187.3.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	128
Receiver Gain	2050
Relaxation Delay	12.5000
Pulse Width	13.5000
Spectrometer Frequency	119.26
Nucleus	29Si

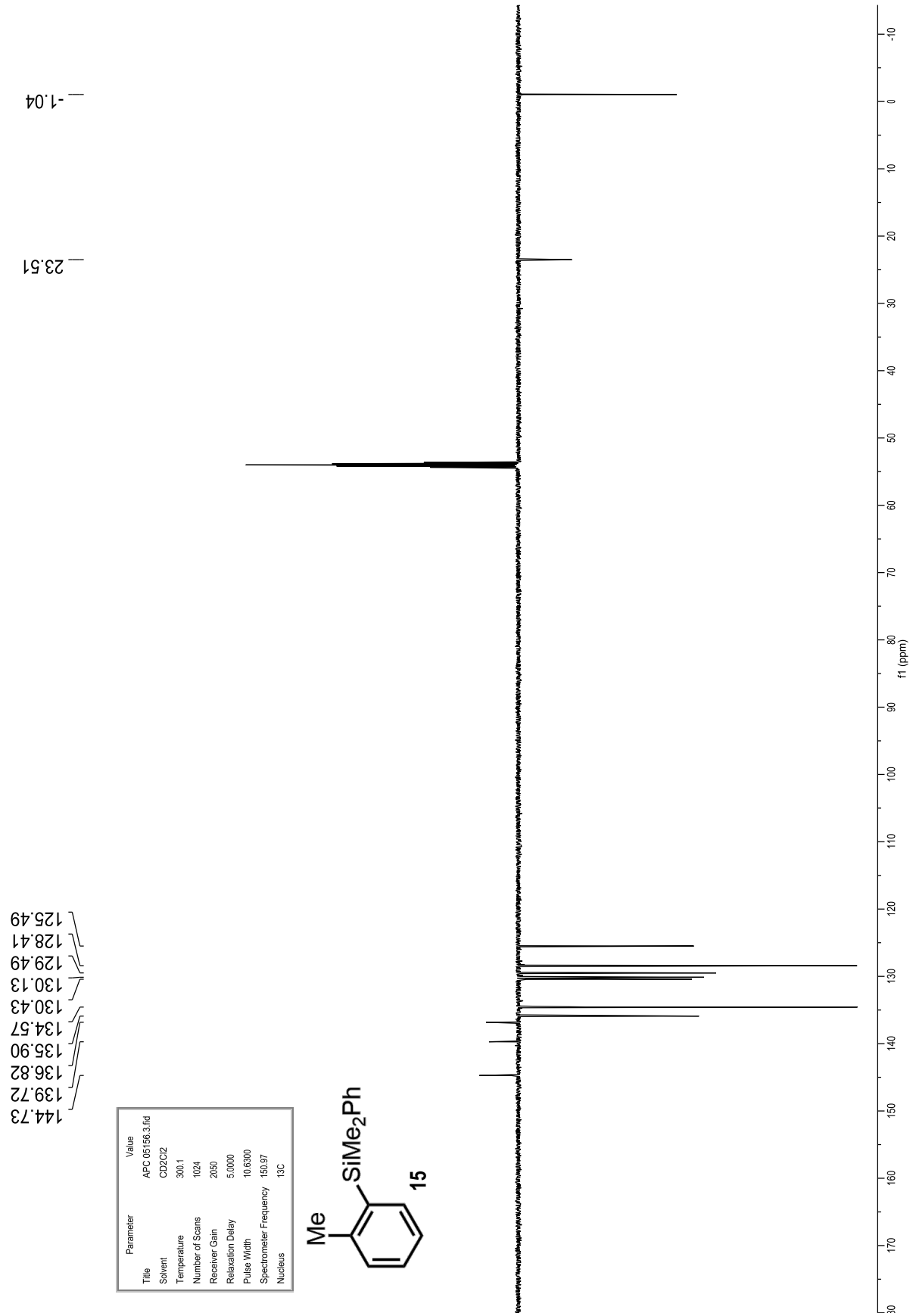

0.59
6.00
5.65
3.77
f1 (ppm)
7.56
7.56
7.56
7.56
7.56
7.55
7.55
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.36
Parameter Value
Title BZV01226ARP
Solvent CDCl3
Temperature 300.3
Number of Scans 16
Receiver Gain 128
Relaxation Delay 1.0000
Pulse Width 13.1400
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Ph
14


138.45
134.35
129.24
127.97
-2.24
SiMe2Ph
14
Parameter Value
Title BZV01226ARP
Solvent CDCl3
Temperature 302.9
Number of Scans 256
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 8.5000
Spectrometer Frequency 150.95
Nucleus 13C
f1 (ppm)

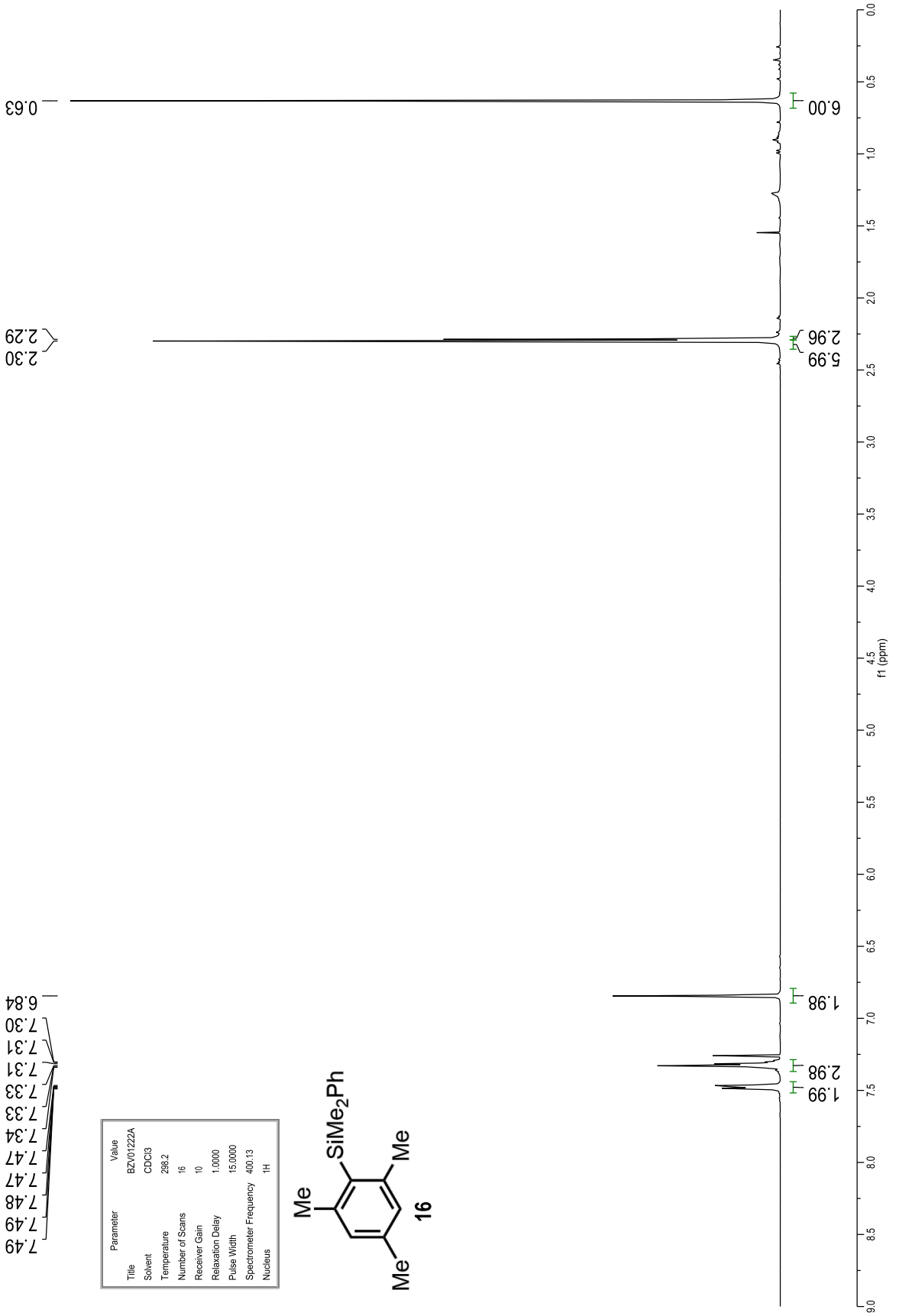


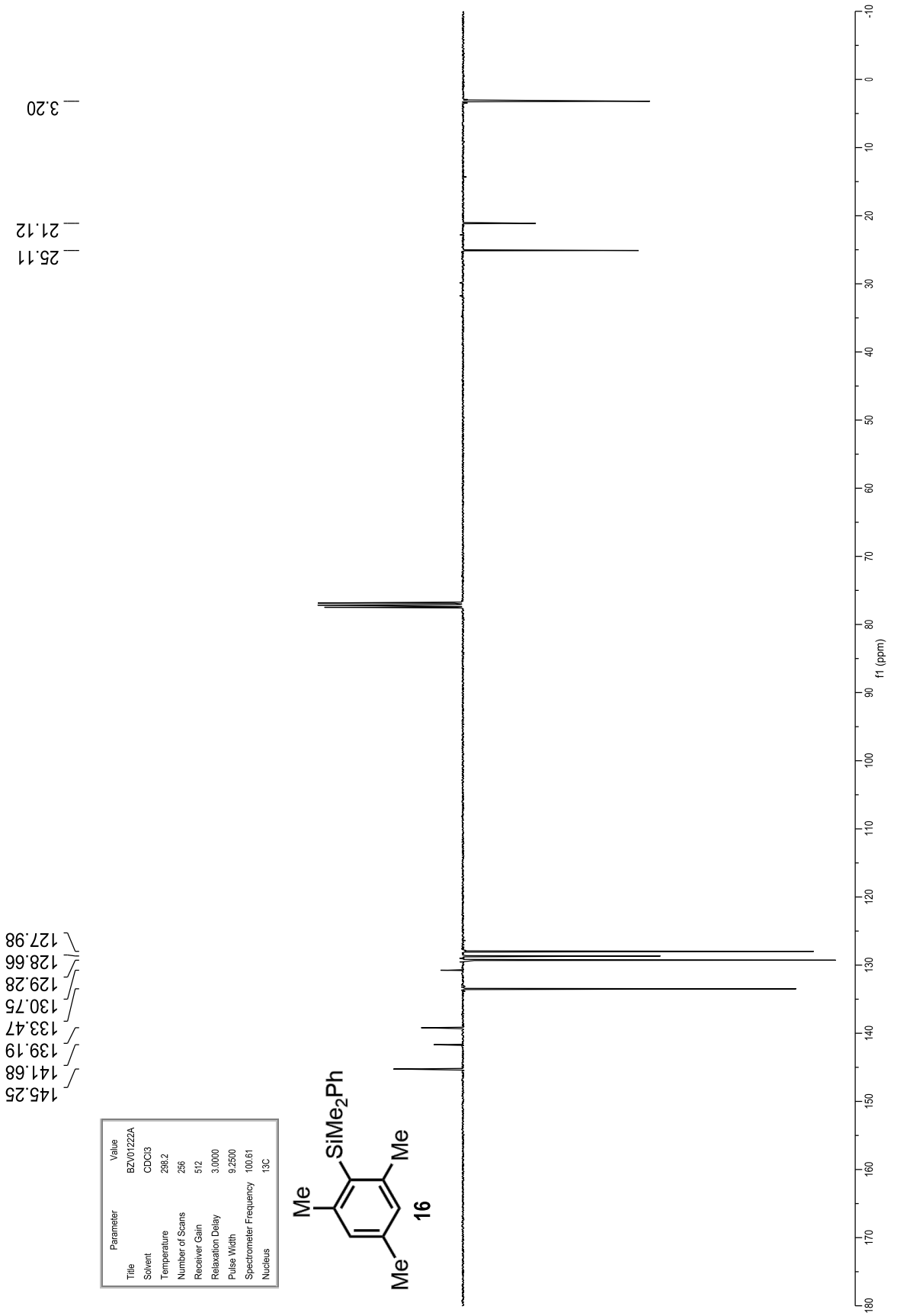
Parameter	Value
Title	BZV01226ARPSi
Solvent	CDCl3
Temperature	299.2
Number of Scans	128
Receiver Gain	2050
Relaxation Delay	12.5000
Pulse Width	11.0000
Spectrometer Frequency	119.27
Nucleus	29Si

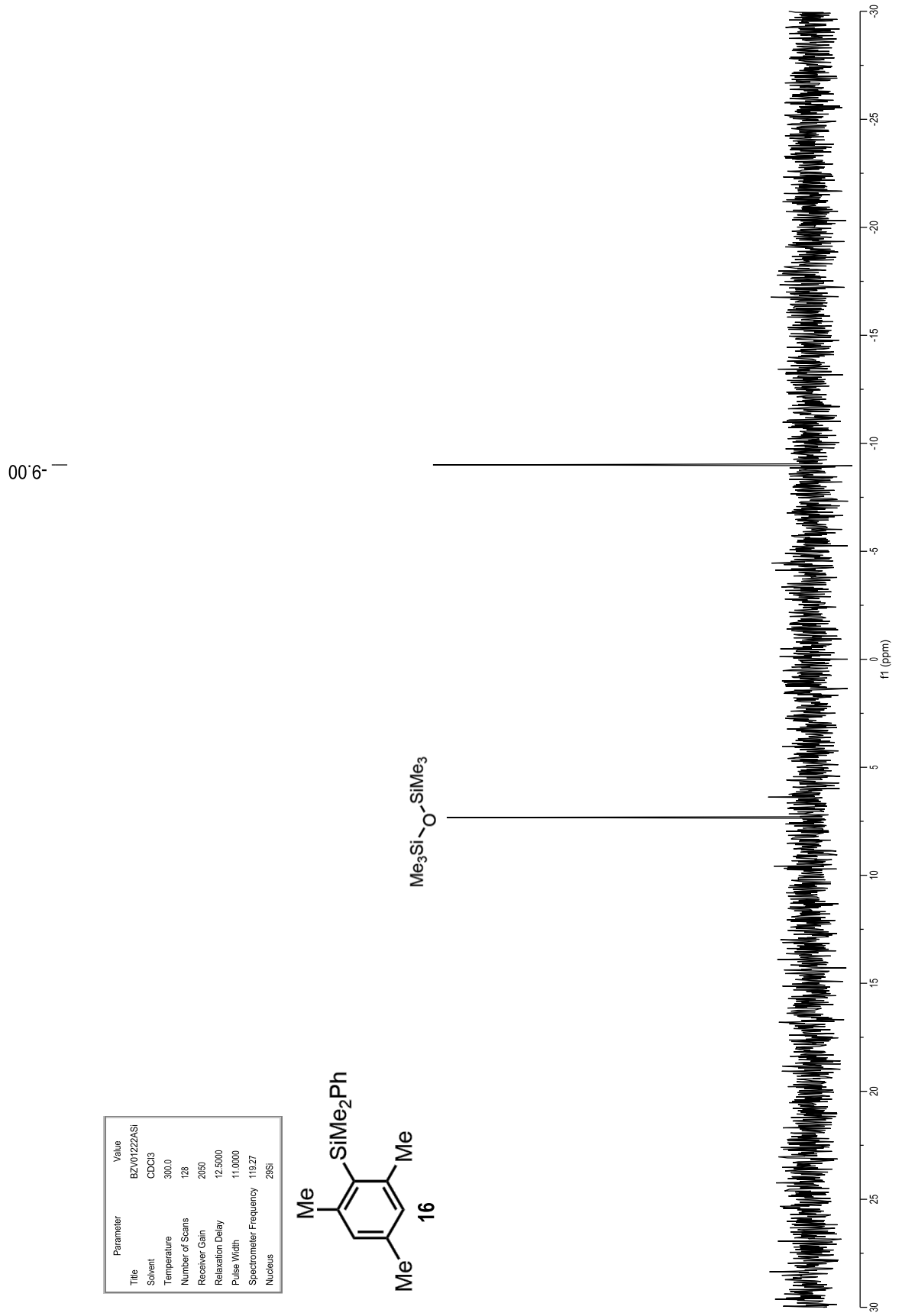

0.58
2.25
6.01
3.00
2.84
2.93
0.95
0.98
0.93
f1 (ppm)
Me
SiMe2Ph
15
Parameter Value
Title APC 05156.2.fid
Solvent CD2Cl2
Temperature 297.2
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H


-1.04
23.51
144.73
139.72
136.82
135.90
134.57
130.43
130.13
129.49
128.41
125.49
Parameter Value
Title APC 05156.3.fid
Solvent CD2Cl2
Temperature 300.1
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
Me
SiMe2Ph
15
f1 (ppm)

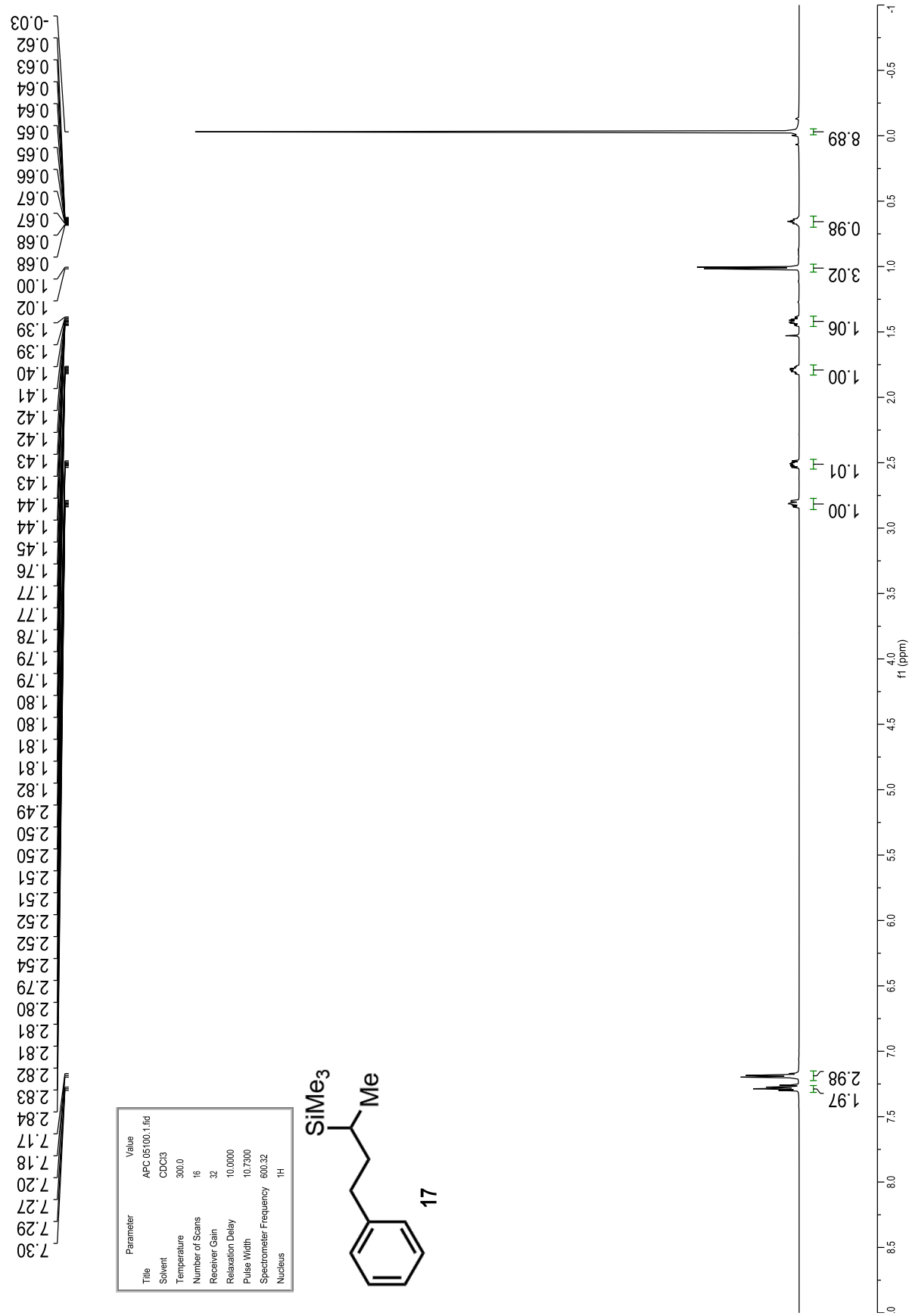
Parameter	Value
Title	APC 05156.4.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	128
Receiver Gain	1030
Relaxation Delay	12.5000
Pulse Width	13.5000
Spectrometer Frequency	119.26
Nucleus	29Si

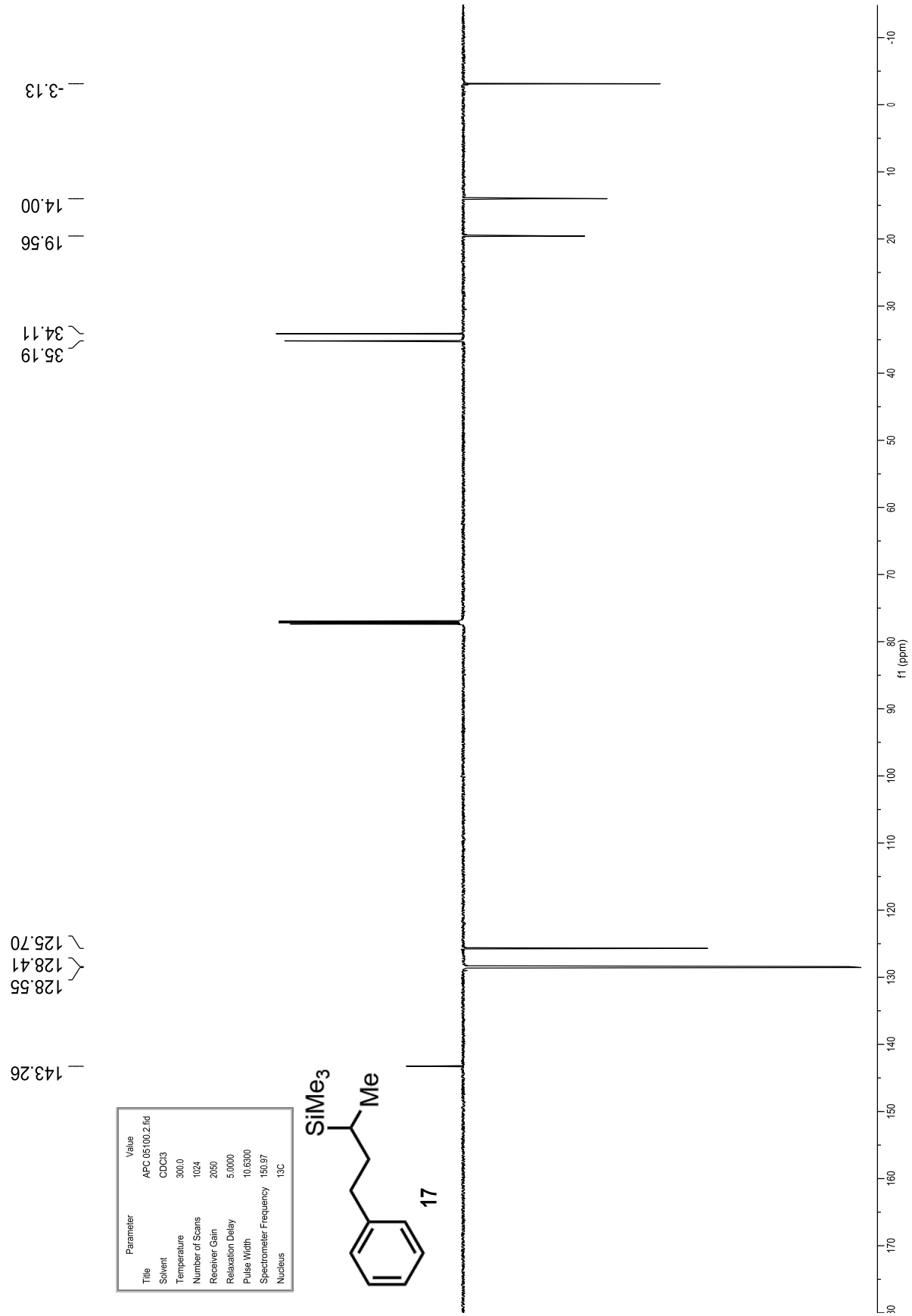

0.63
6.00
2.30
2.29
5.99
2.96
1.98
2.98
1.99
7.49
7.49
7.48
7.47
7.47
7.34
7.33
7.33
7.31
7.31
7.30
6.84
Parameter Value
Title BZV01222A
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 10
Relaxation Delay 1.0000
Pulse Width 15.0000
Spectrometer Frequency 400.13
Nucleus 1H
Me
SiMe2Ph
Me
Me
16
f1 (ppm)


145.25
141.68
139.19
133.47
130.75
129.28
128.66
127.98
25.11
21.12
3.20
Me
SiMe2Ph
Me
Me
16
f1 (ppm)
Parameter Value
Title BZV01222A
Solvent CDCl3
Temperature 298.2
Number of Scans 256
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Spectrometer Frequency 100.61
Nucleus 13C

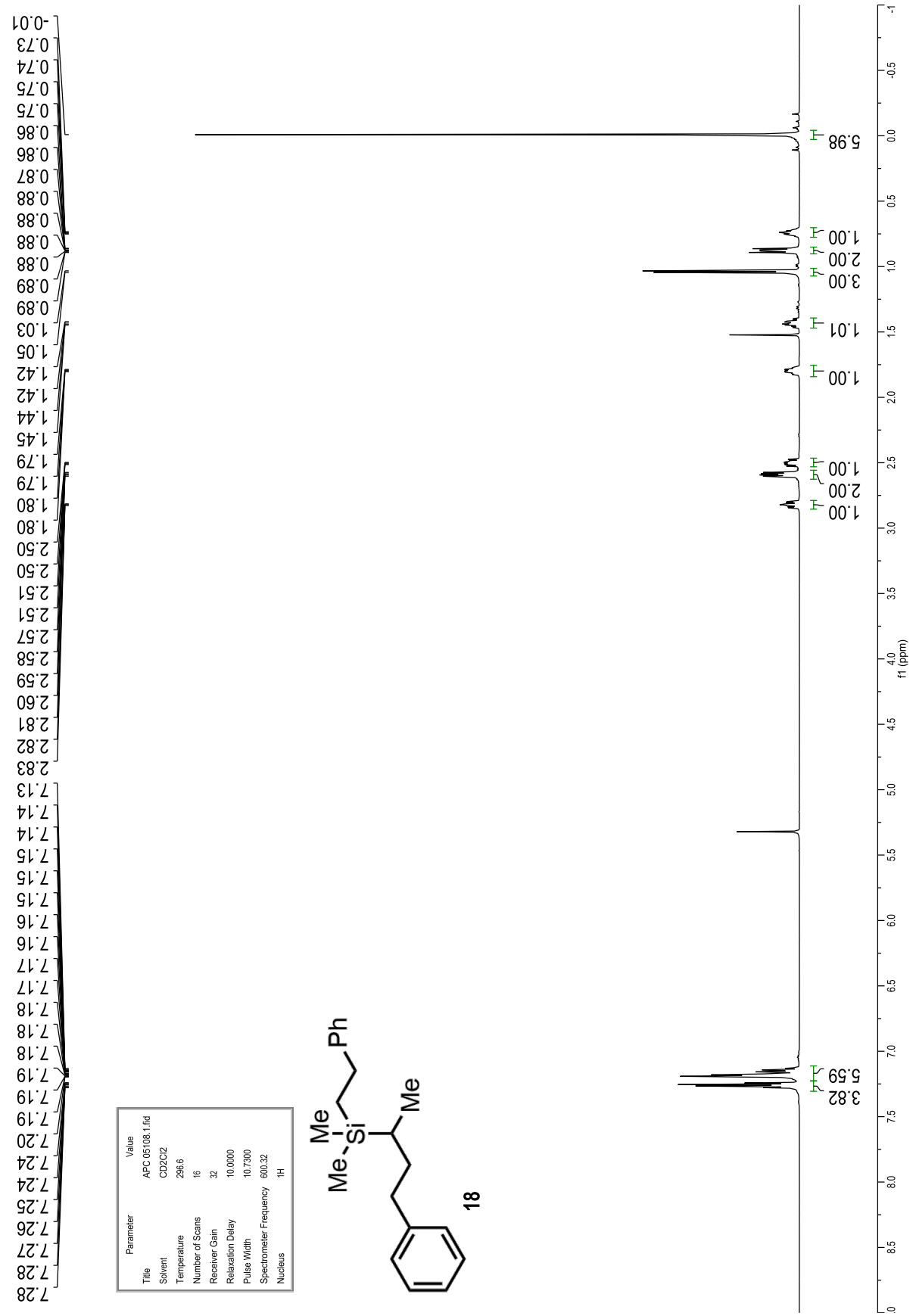


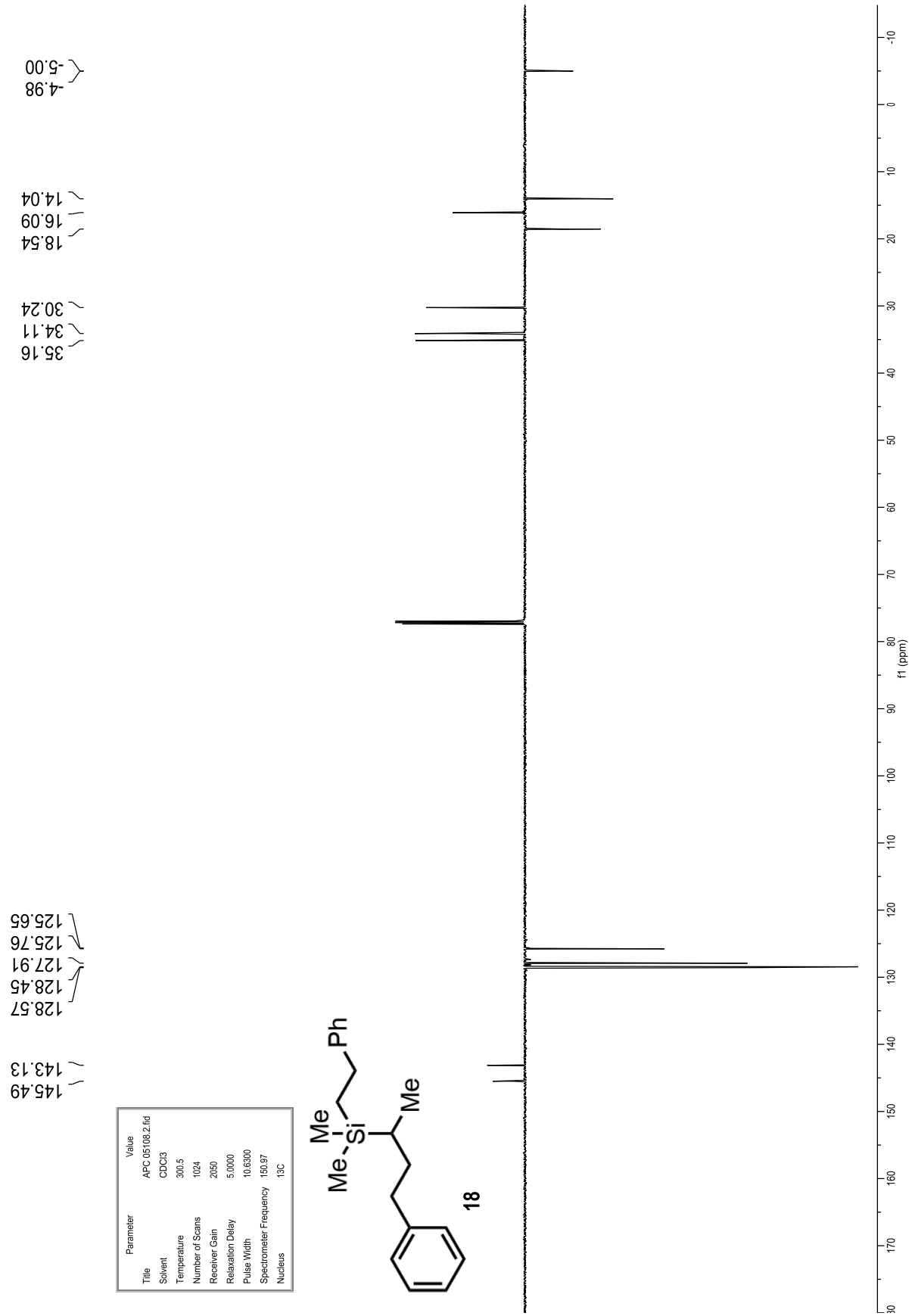
Parameter	Value
Title	BZV01222ASi
Solvent	CDCl3
Temperature	300.0
Number of Scans	128
Receiver Gain	2050
Relaxation Delay	12.5000
Pulse Width	11.0000
Spectrometer Frequency	119.27
Nucleus	29Si


8.89
0.98
3.02
1.06
1.00
1.01
1.00
1.97
2.98
f1 (ppm)
SiMe3
Me
17
Parameter Value
Title APC 05100_1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H

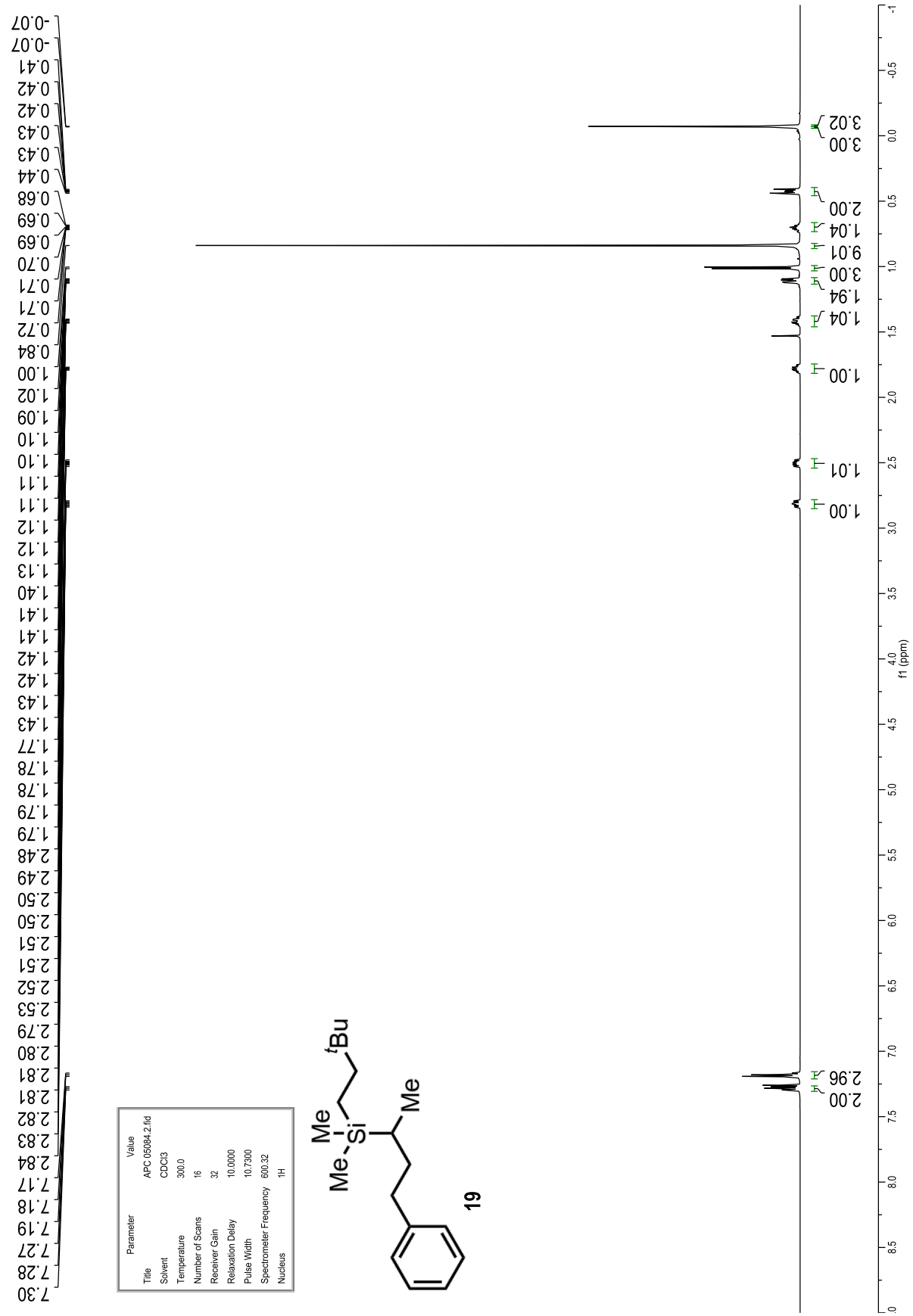

-3.13
14.00
19.56
34.11
35.19
128.55
128.41
125.70
143.26
SiMe3
Me
17
f1 (ppm)
Parameter Value
Title APC 05100.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C

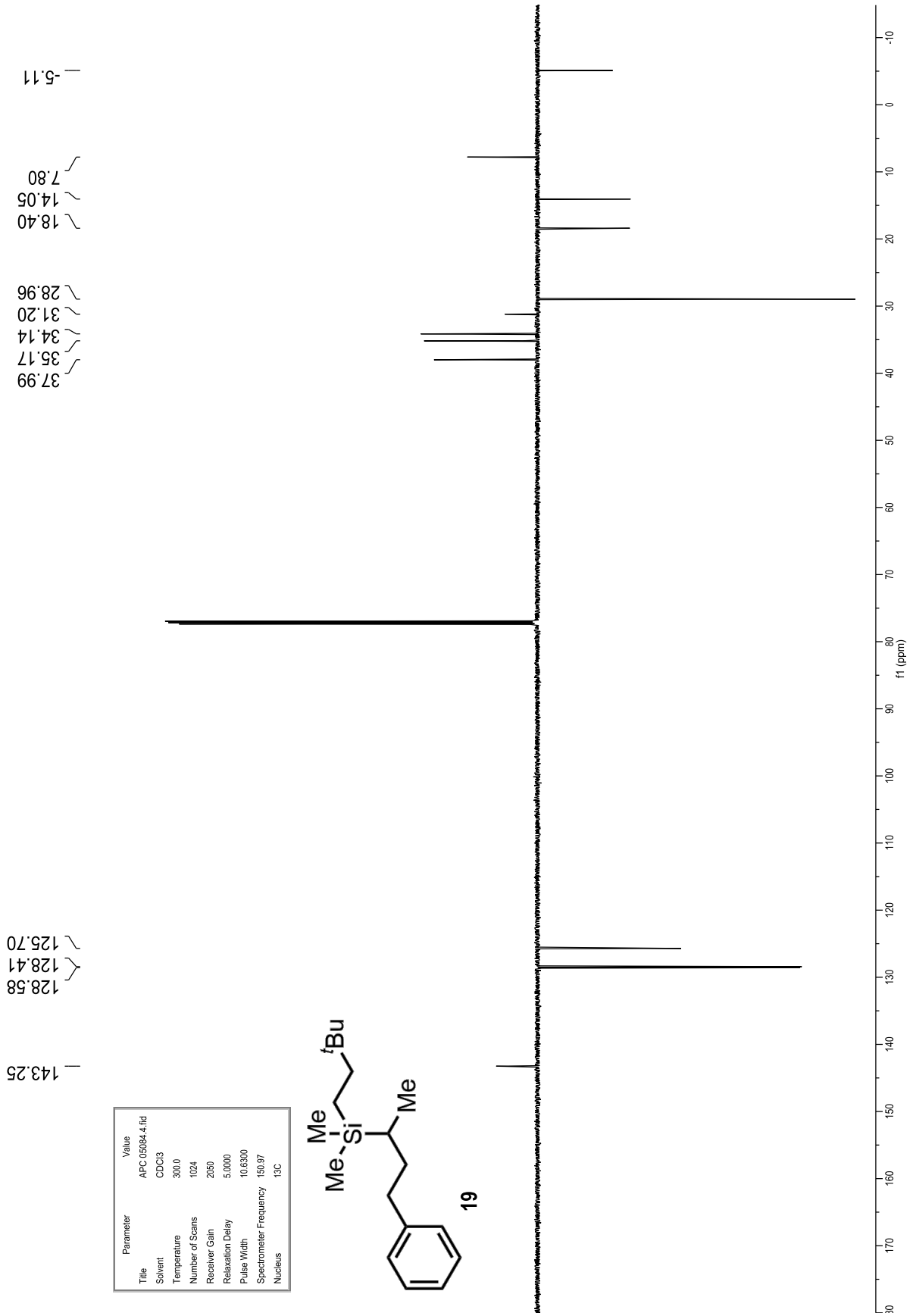
Parameter	Value
Title	APC 05100.3.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	128
Receiver Gain	1030
Relaxation Delay	12.5000
Pulse Width	13.5000
Spectrometer Frequency	119.26
Nucleus	29Si

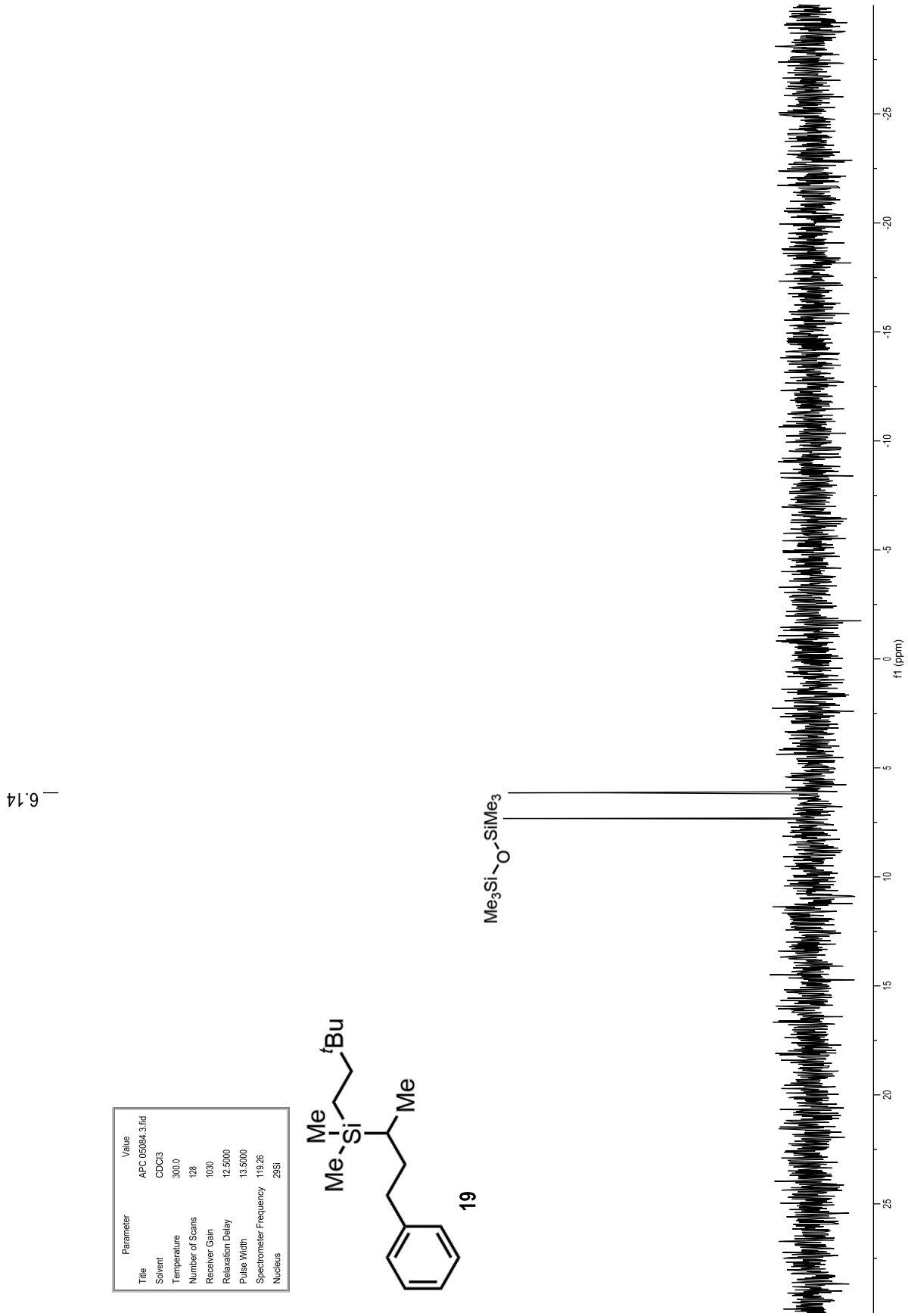

Parameter Value
Title APC 05108.1.fid
Solvent CD2Cl2
Temperature 296.6
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me
Si
Ph
Me
18
5.98
1.00
2.00
3.00
1.01
1.00
1.00
2.00
1.00
3.82
5.59
f1 (ppm)

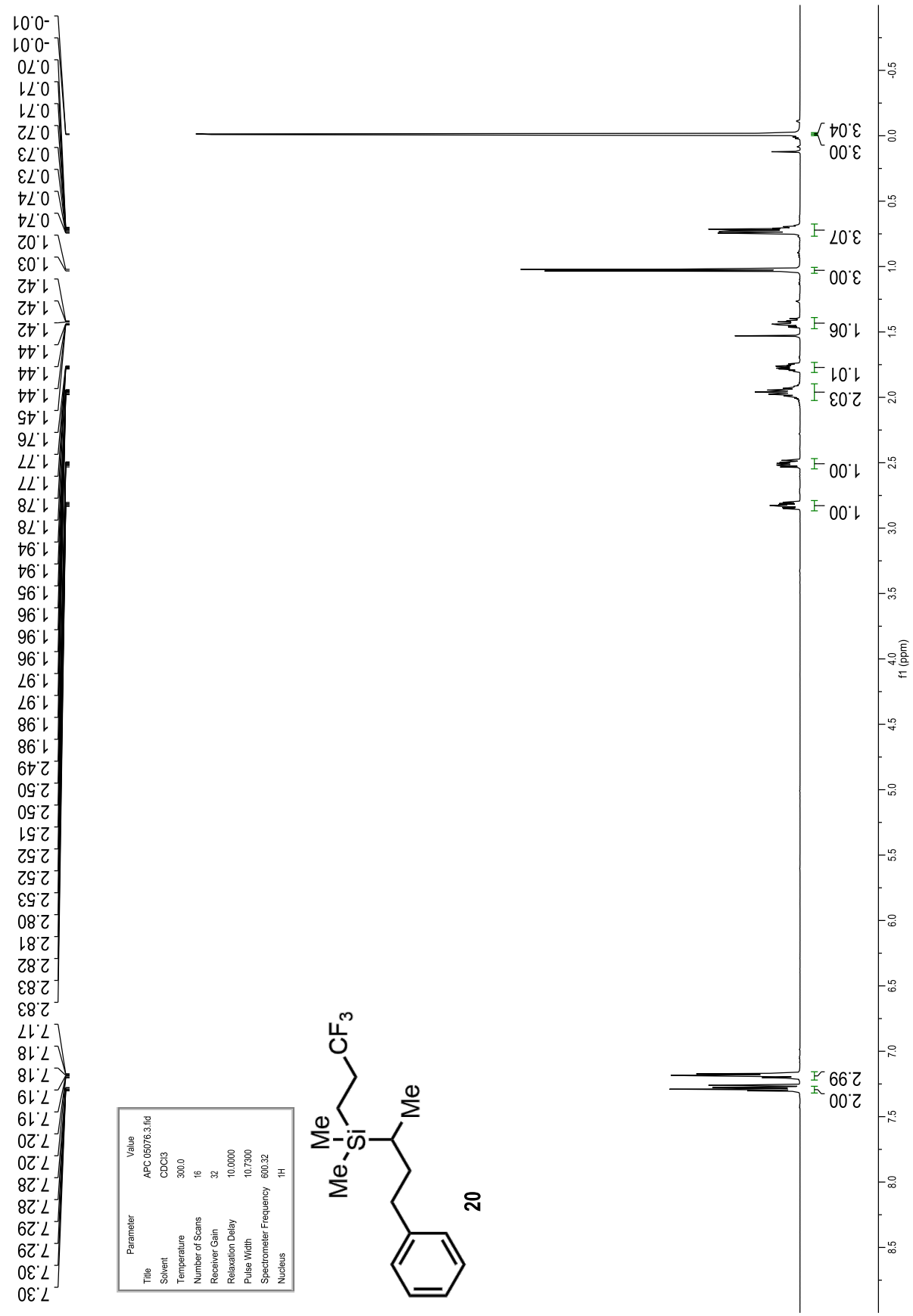

145.49
143.13
128.57
128.45
127.91
125.76
125.65
35.16
34.11
30.24
18.54
16.09
14.04
-4.98
-5.00
Me
Me
Si
Ph
Me
18
Parameter Value
Title APC 05108.2.fid
Solvent CDCl3
Temperature 300.5
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

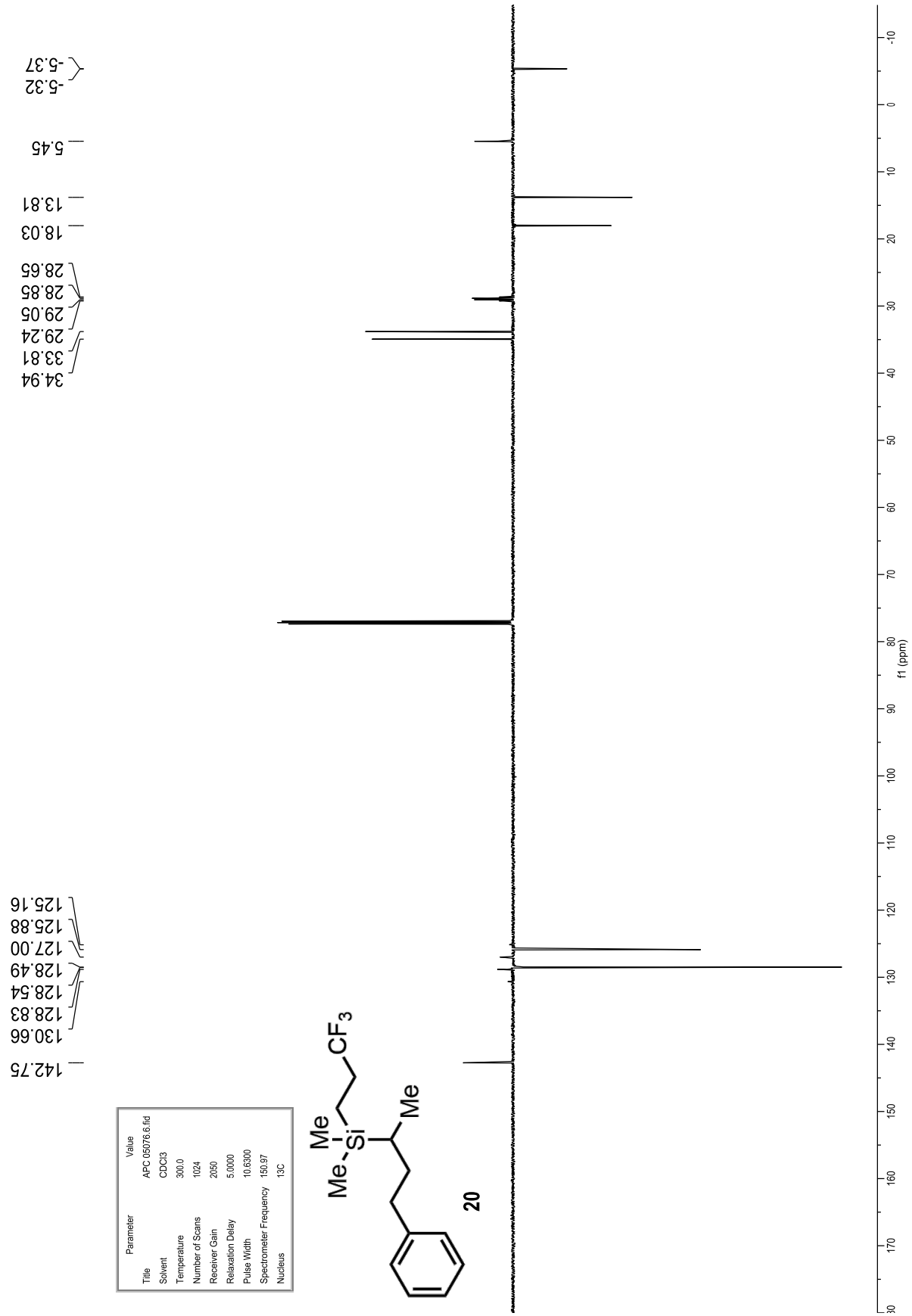
5.45
Parameter Value
Title APC 05108.3.fid
Solvent CDCl3
Temperature 297.3
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
Me
Me
Si
Ph
Me
18
Me3Si
O
SiMe3
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)


Parameter Value
Title APC 05084-2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me
Si
Me
tBu
19
3.02
3.00
2.00
1.04
9.01
3.00
1.94
1.04
1.00
1.01
1.00
2.00
2.96
f1 (ppm)

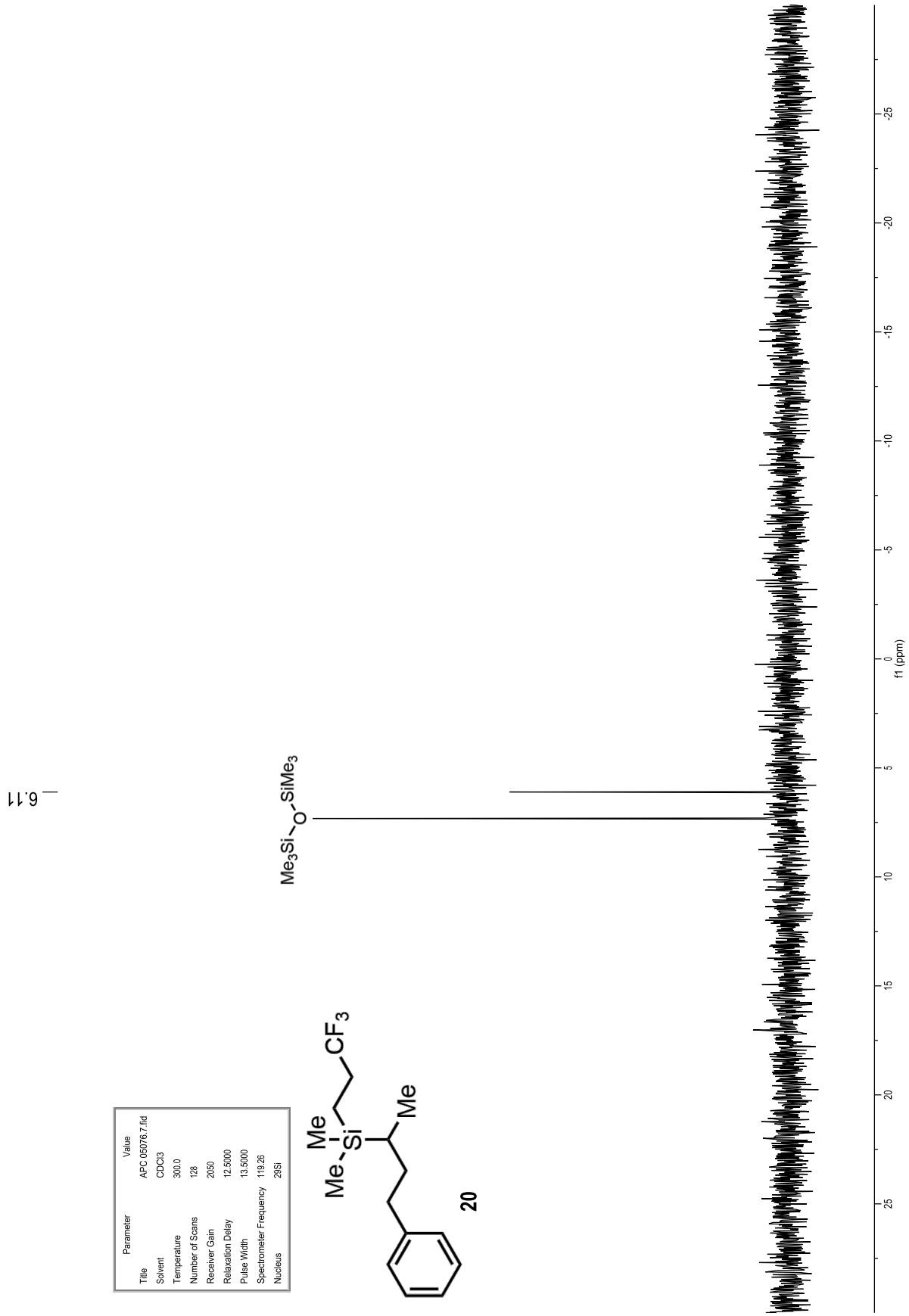

143.25
128.58
128.41
125.70
37.99
35.17
34.14
31.20
28.96
18.40
14.05
7.80
-5.11
Me
Me
Si
Me
tBu
19
Parameter Value
Title APC 05084.4.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

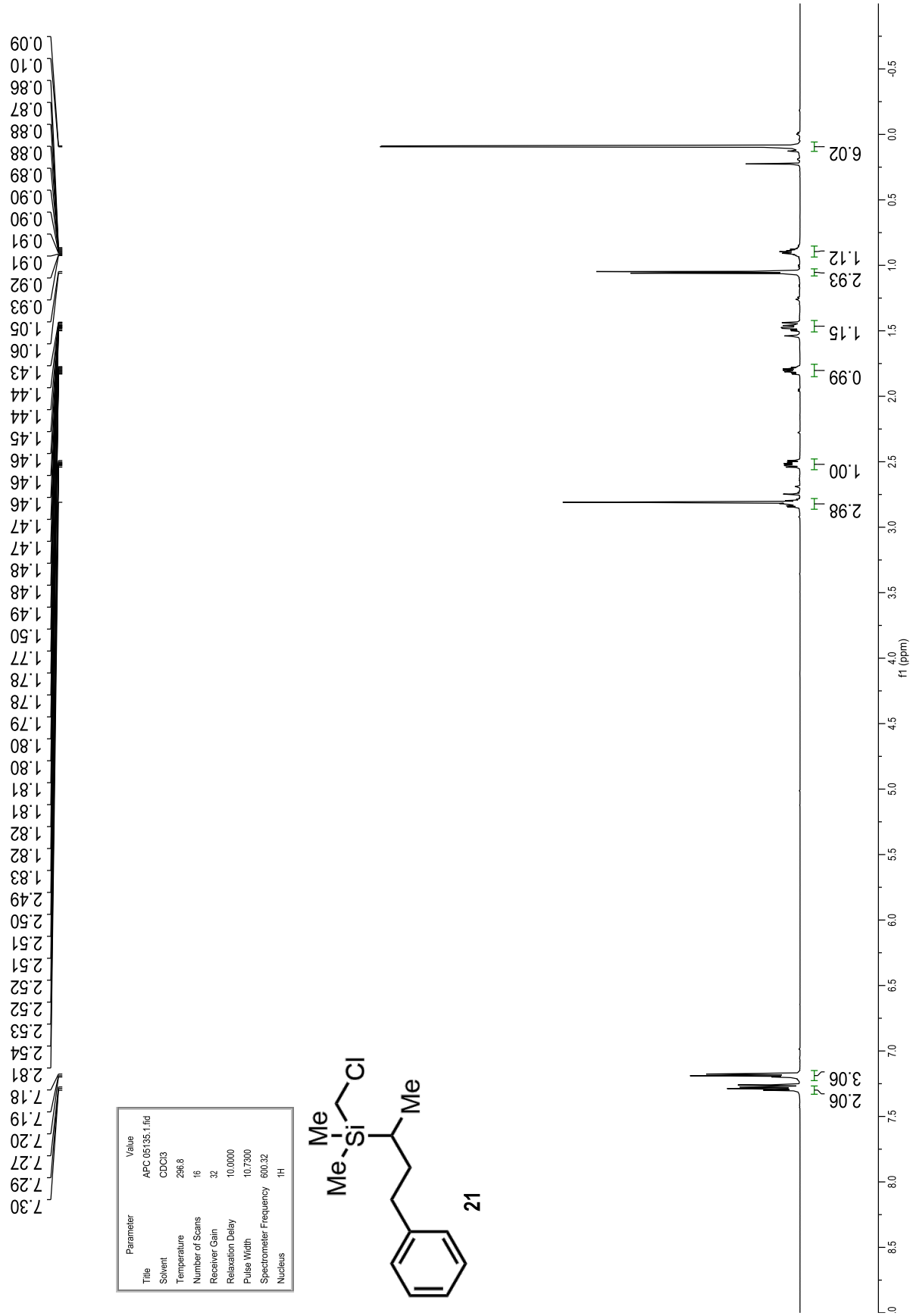

6.14
Parameter Value
Title APC 05084-3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
Me
Me
Si
tBu
Me
19
Me3Si
O
SiMe3
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

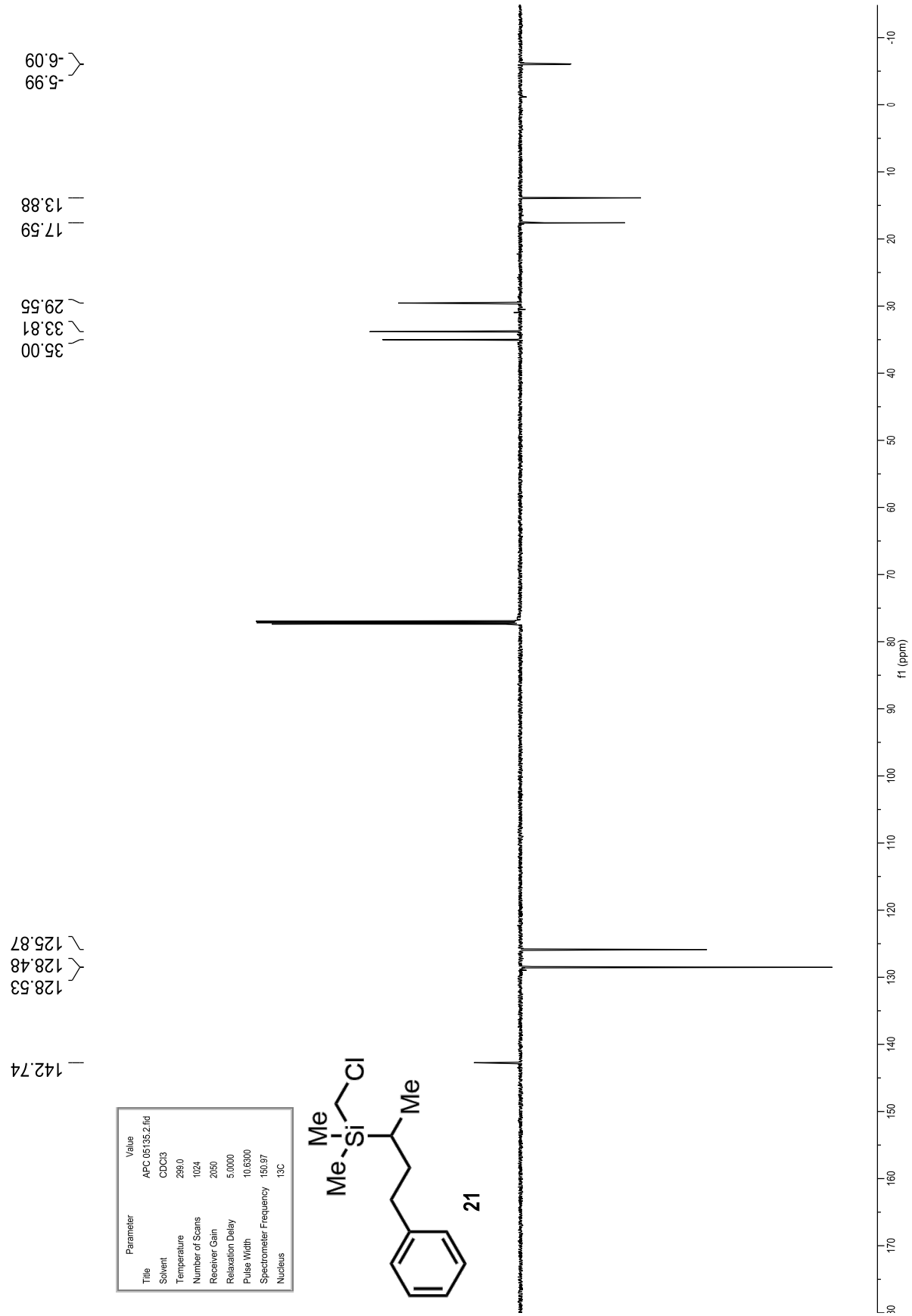

Parameter Value
Title APC 050763.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me
Si
CF3
Me
20
3.04
3.00
3.07
3.00
1.06
1.01
2.03
1.00
1.00
2.99
2.00
f1 (ppm)


142.75
130.66
128.83
128.54
128.49
127.00
125.88
125.16
34.94
33.81
29.24
29.05
28.85
28.65
18.03
13.81
5.45
-5.32
-5.37
Me
Me
Si
Me
CF3
20
Parameter Value
Title APC 050076.6.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

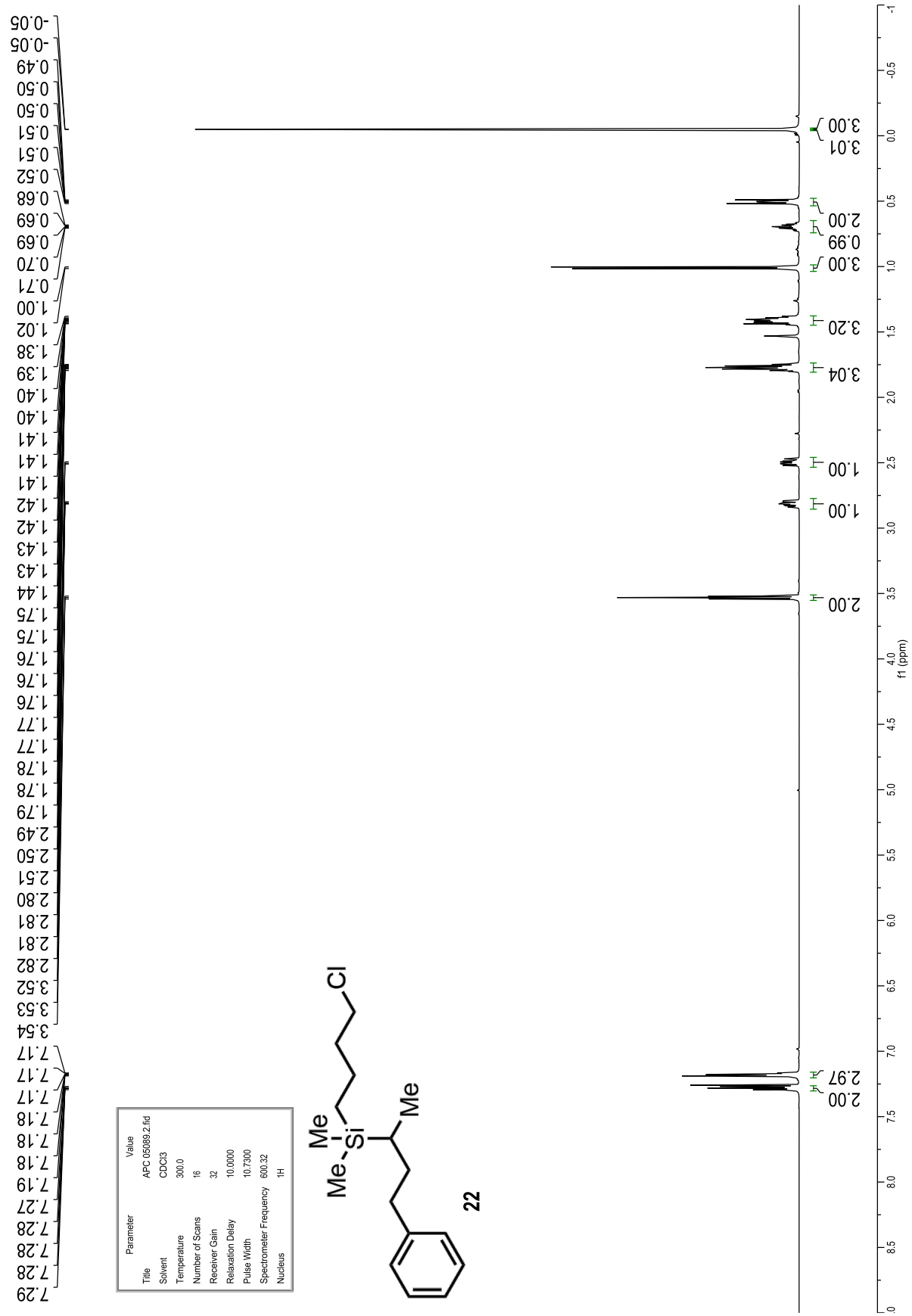
-68.78
Parameter Value
Title APC 05076.5.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 287
Relaxation Delay 3.0000
Pulse Width 11.6000
Spectrometer Frequency 564.81
Nucleus 19F
Me
Me
Si
CF3
Me
20
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

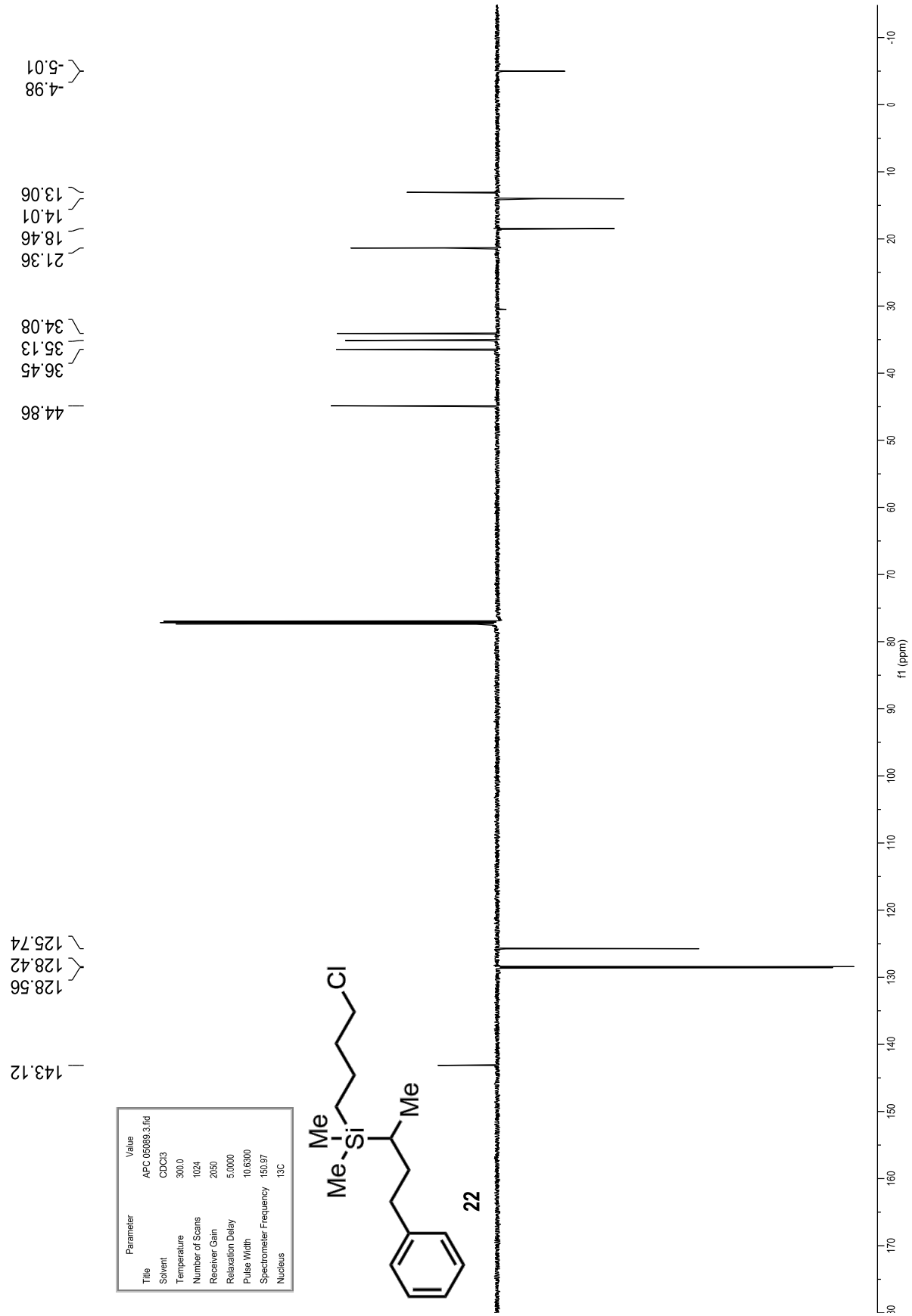

6.11
Me3Si
O
SiMe3
Me
Me
Si
CF3
Me
20
Parameter Value
Title APC 050776.7.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

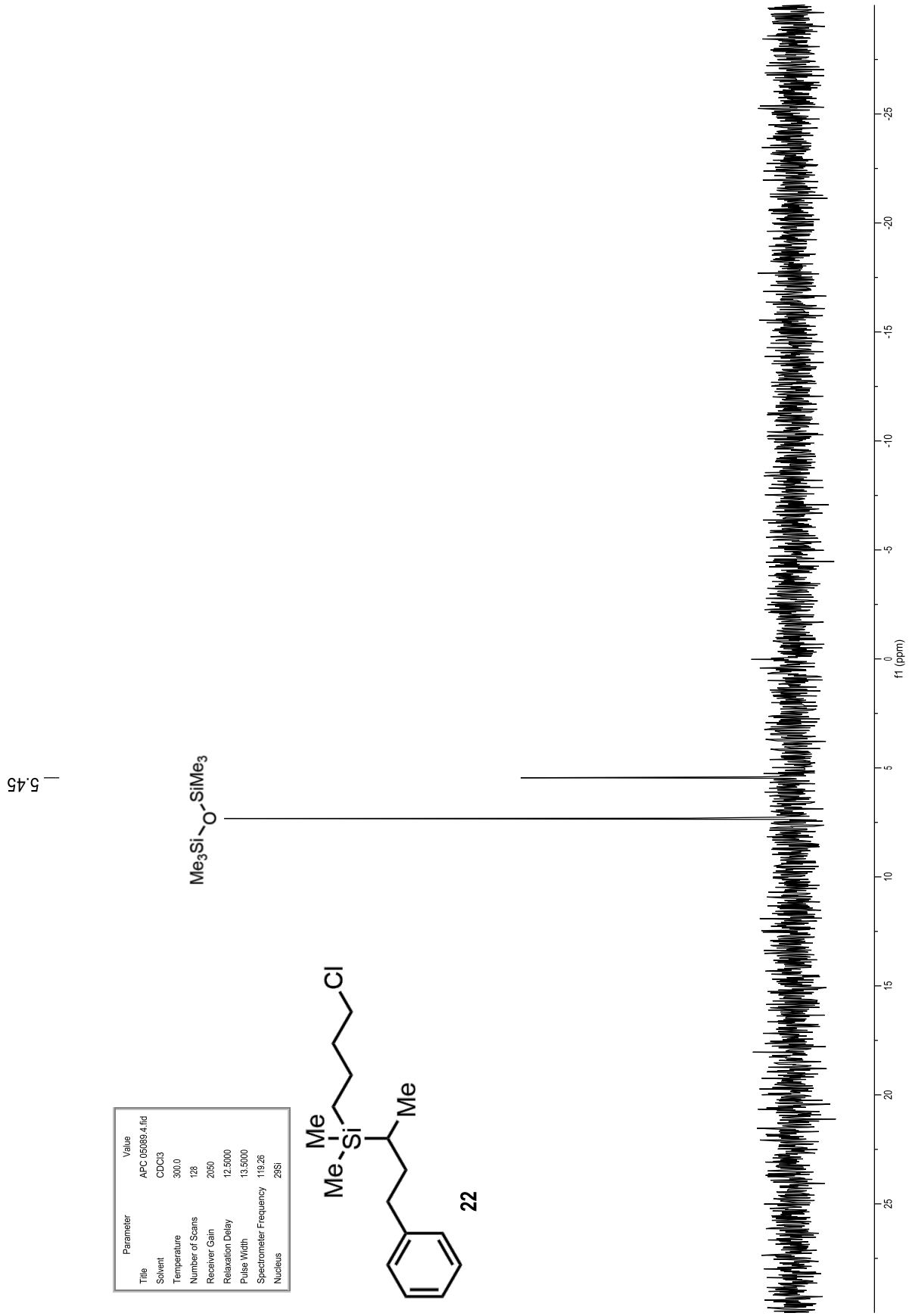

Parameter Value
Title APC 05135.1.fid
Solvent CDCl3
Temperature 296.8
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me
Si
Cl
Me
21
6.02
1.12
2.93
1.15
0.99
1.00
2.98
2.06
3.06
f1 (ppm)

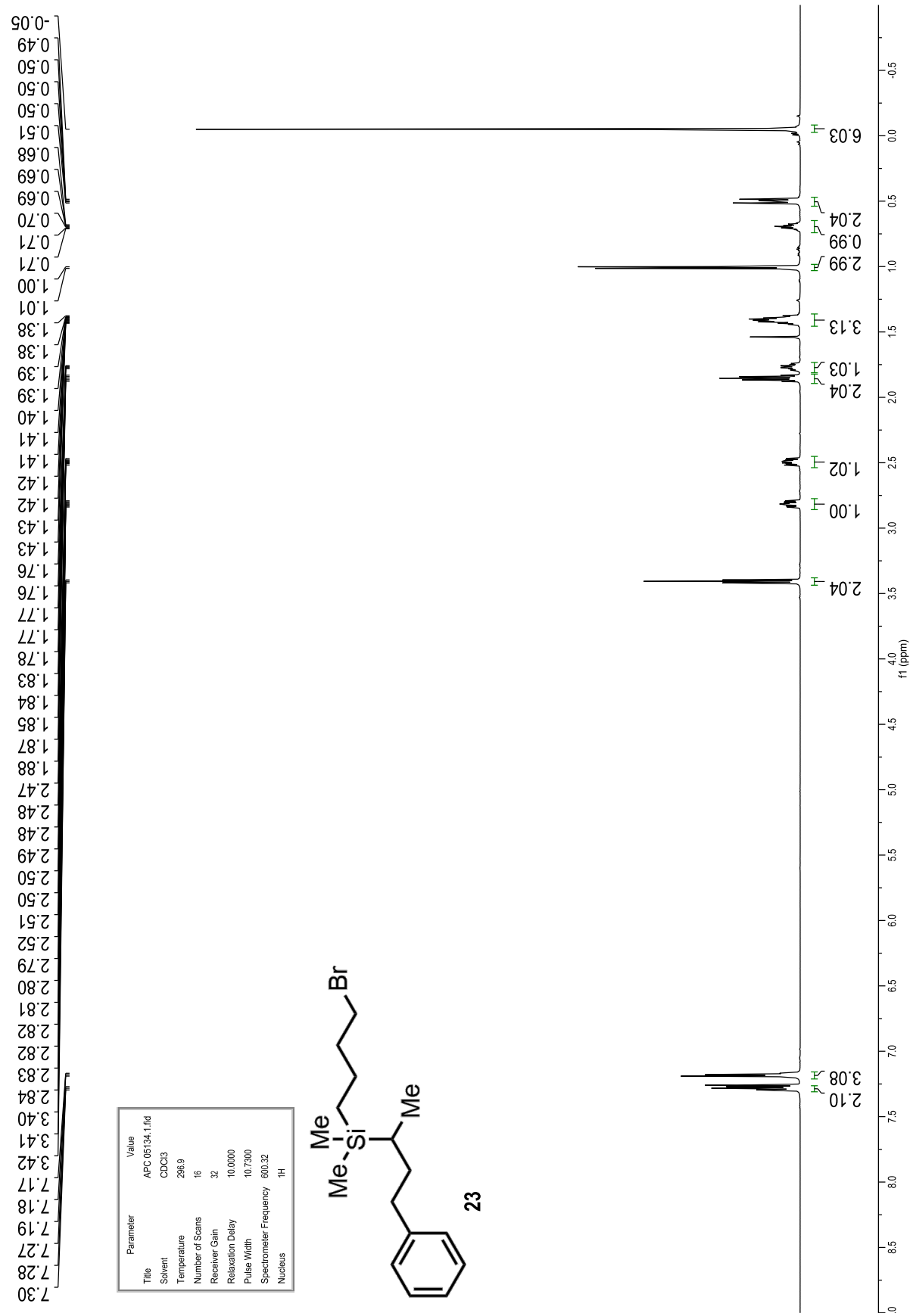

142.74
128.53
128.48
125.87
35.00
33.81
29.55
17.59
13.88
-5.99
-6.09
Me
Me
Si
Cl
Me
21
Parameter Value
Title APC 05135.2.fid
Solvent CDCl3
Temperature 299.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

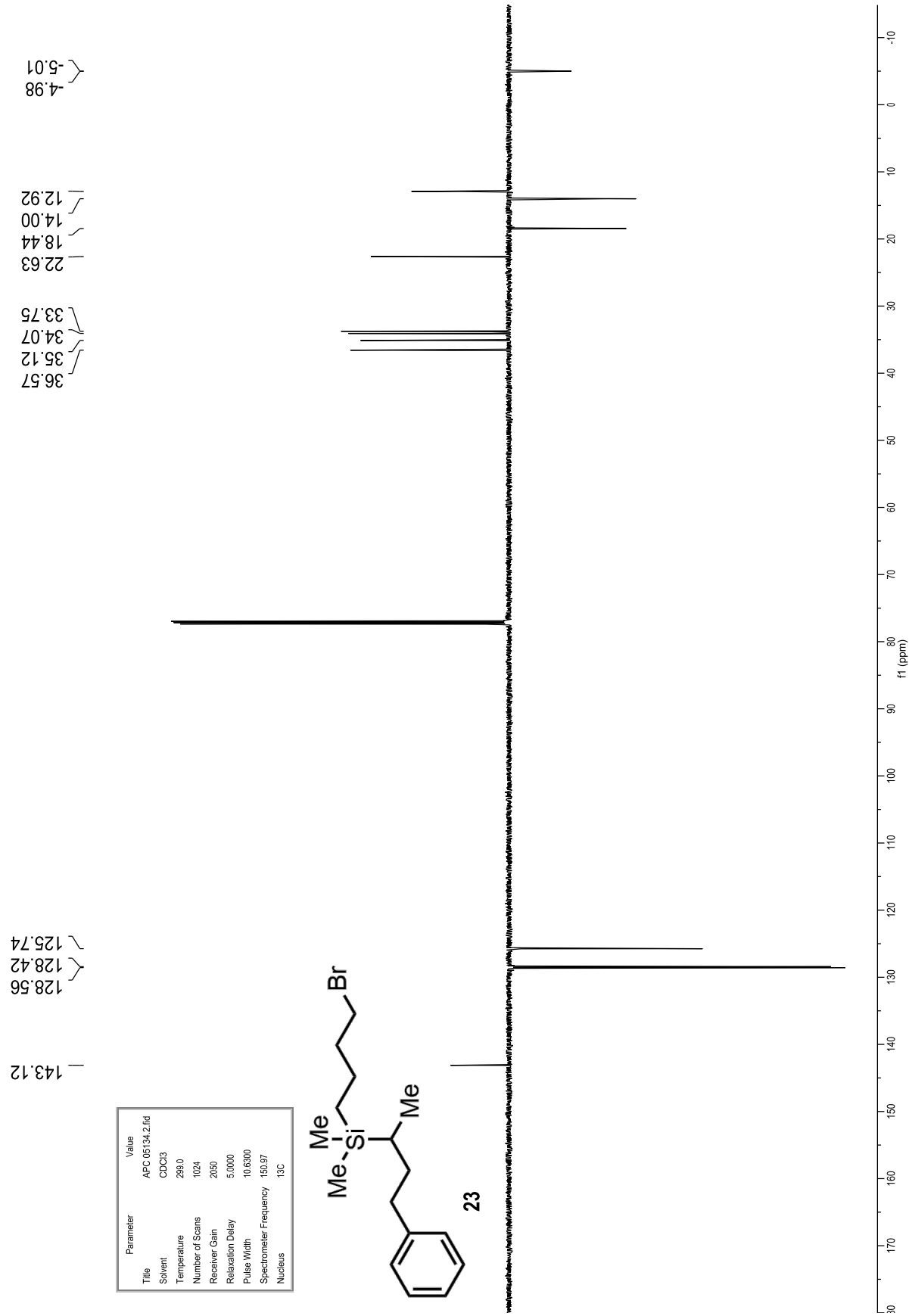
Parameter	Value
Title	APC 05135.3.fid
Solvent	CDCl3
Temperature	297.0
Number of Scans	128
Receiver Gain	1030
Relaxation Delay	12.5000
Pulse Width	13.5000
Spectrometer Frequency	119.26
Nucleus	29Si

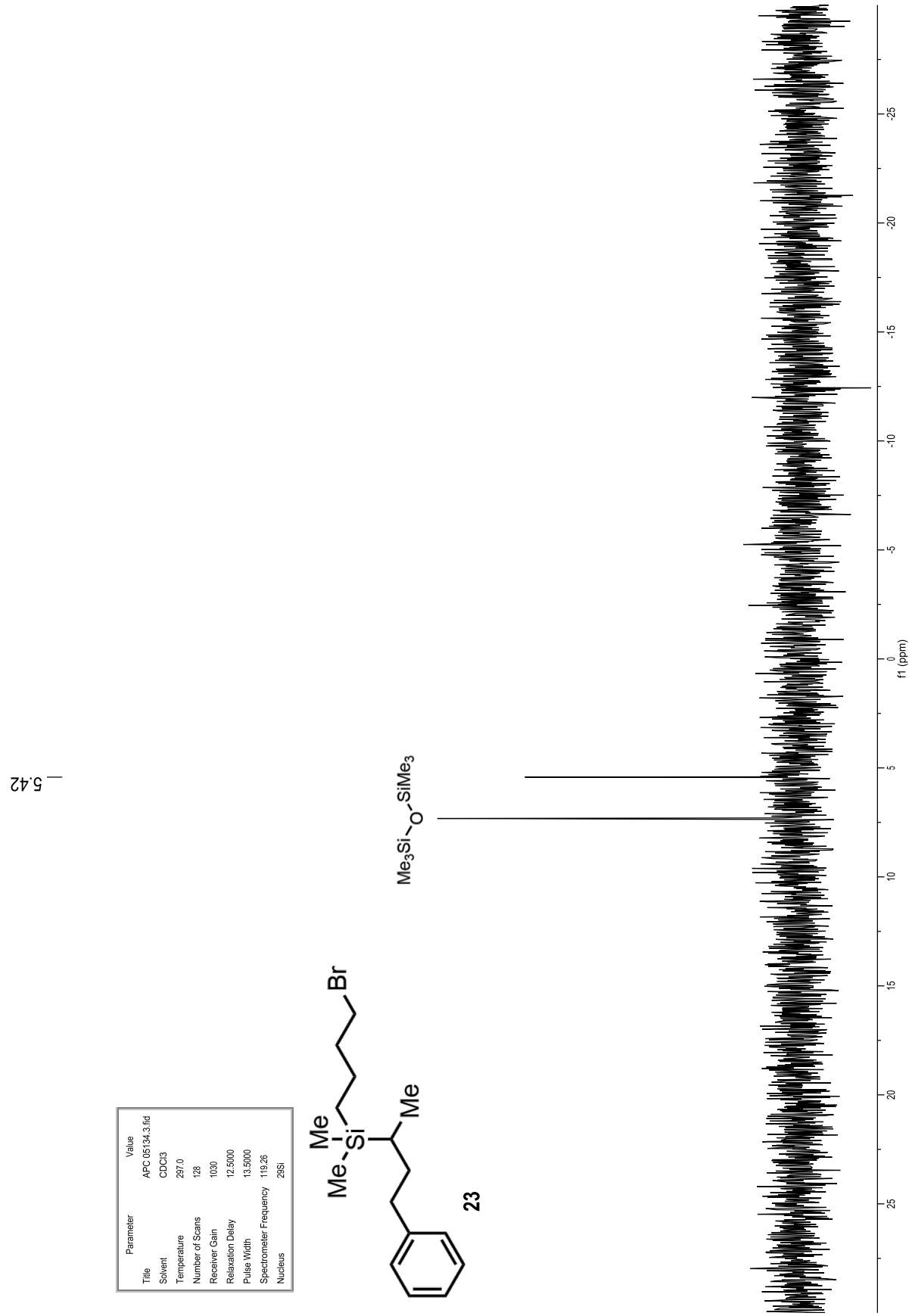

Parameter Value
Title APC 05089-2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me
Si
Cl
Me
22
f1 (ppm)

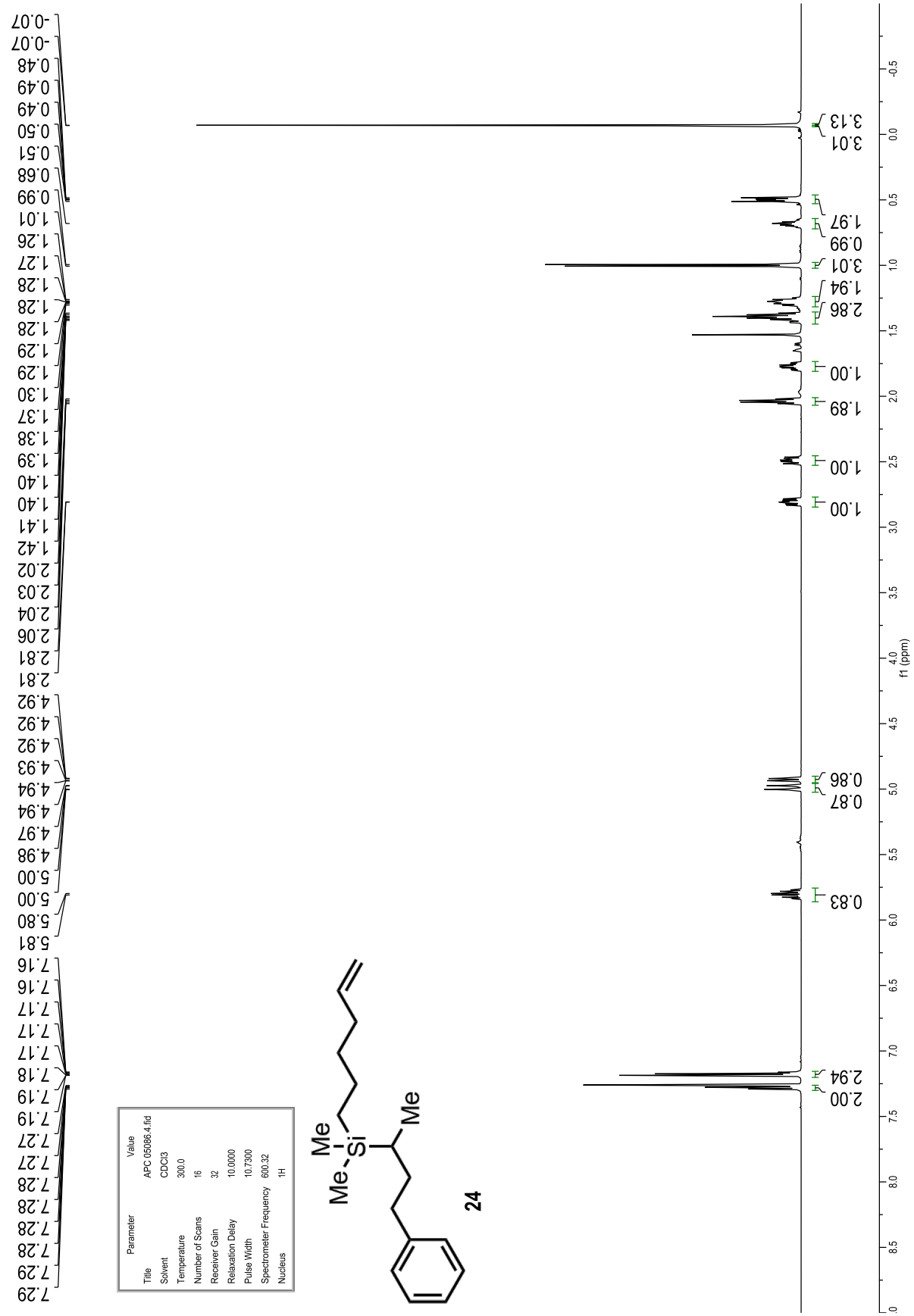

Parameter Value
Title APC 05089.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
143.12
128.56
128.42
125.74
44.86
36.45
35.13
34.08
21.36
18.46
14.01
13.06
-4.98
-5.01
Me
Me
Si
Me
Cl
22
f1 (ppm)

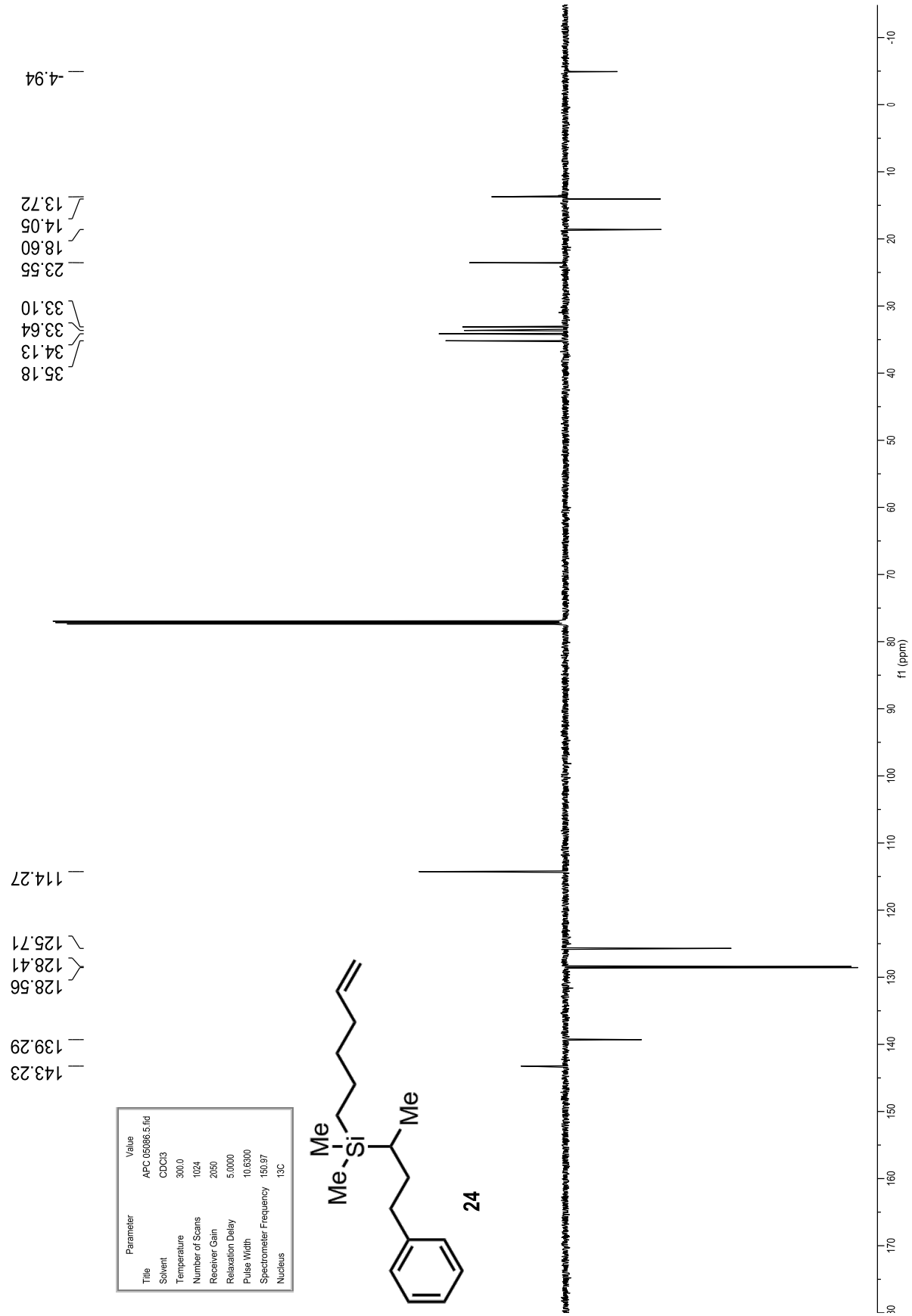

Parameter Value
Title APC 05089.4.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
5.45
Me3Si O SiMe3
Me
Me Si
Cl
Me
22
25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

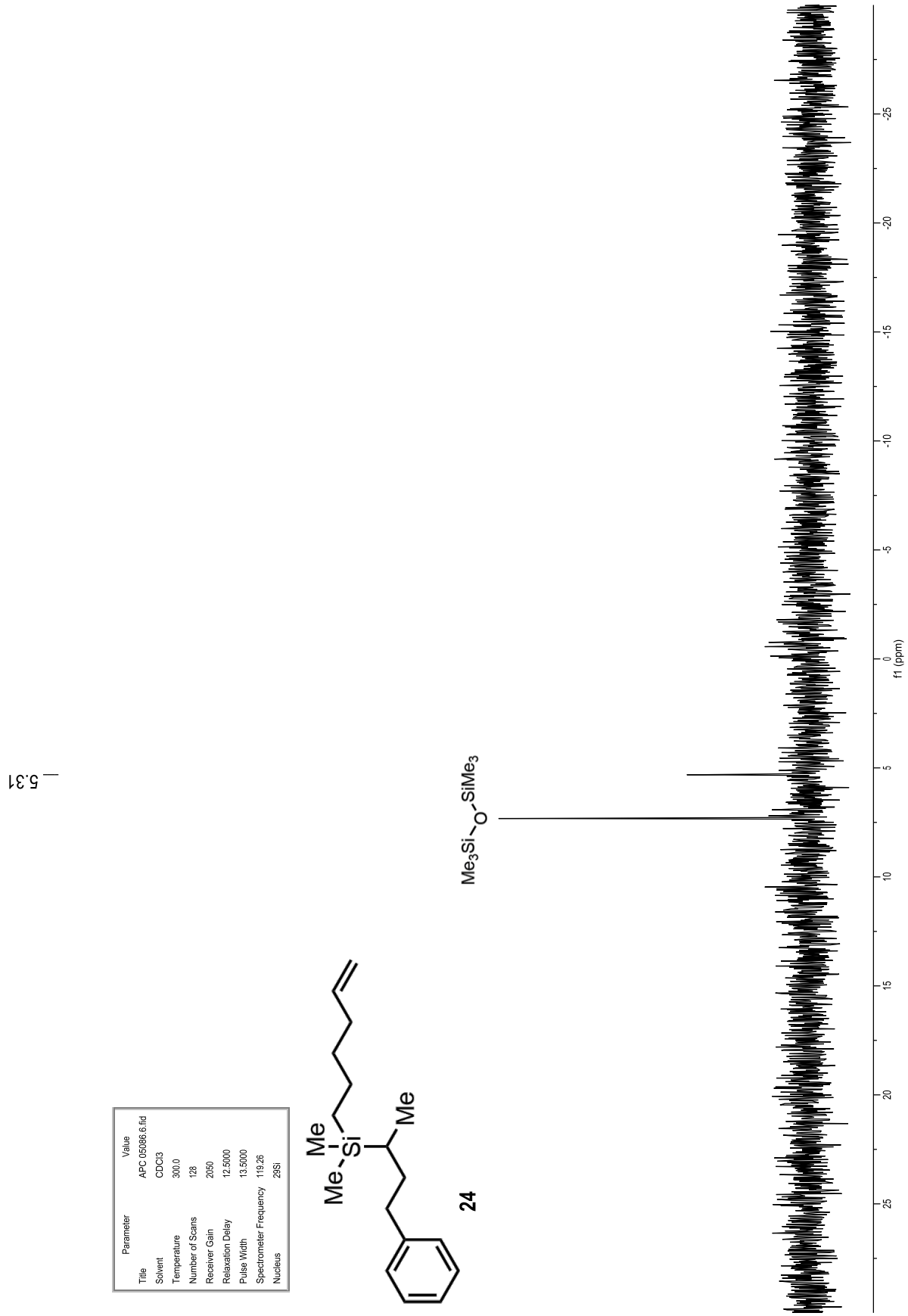

Parameter Value
Title APC 05134-1.fid
Solvent CDCl3
Temperature 296.9
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me
Si
Me
Br
23
6.03
2.04
0.99
2.99
3.13
1.03
2.04
1.02
1.00
2.04
3.08
2.10
f1 (ppm)

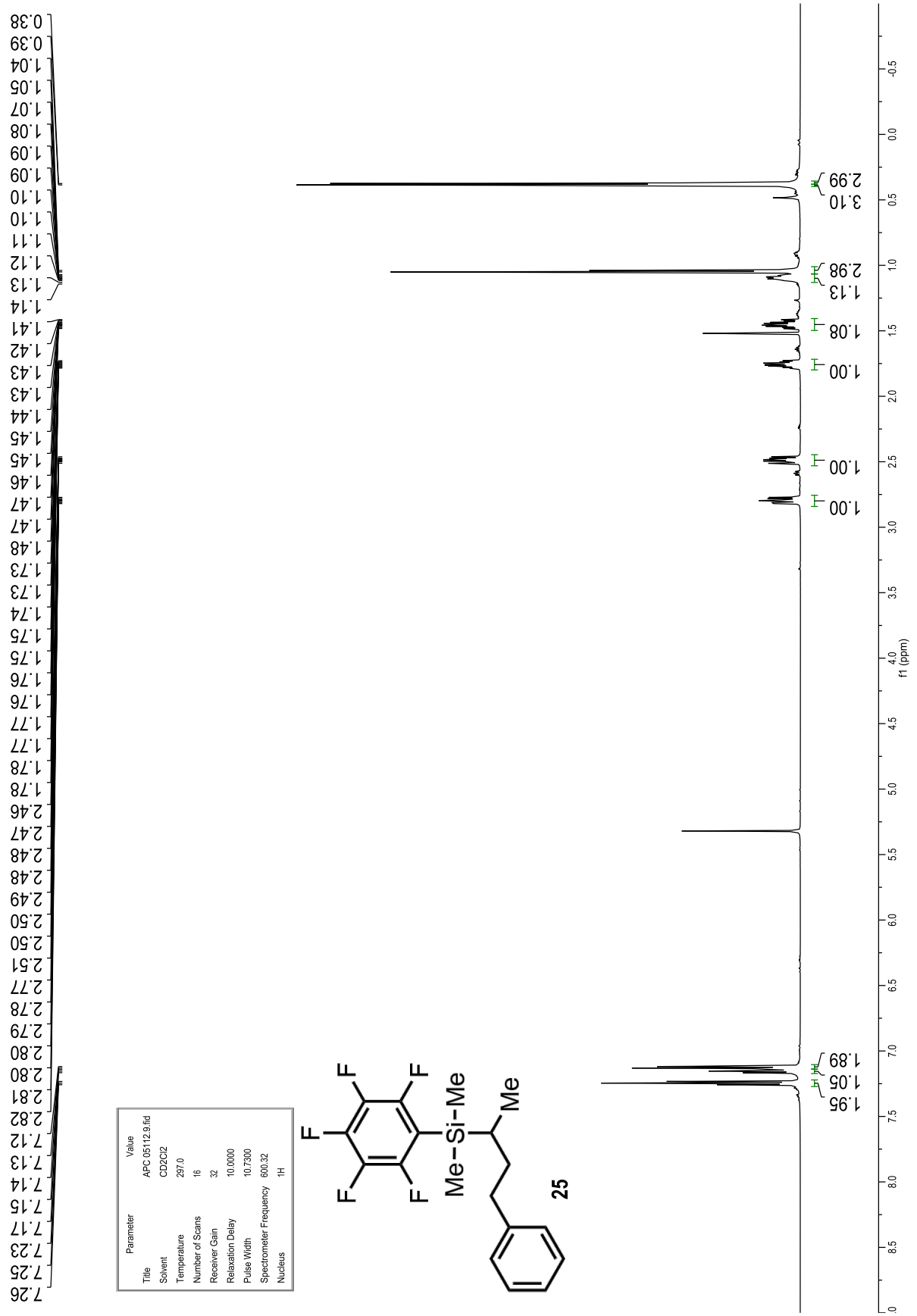

143.12
128.56
128.42
125.74
36.57
35.12
34.07
33.75
22.63
18.44
14.00
12.92
-4.98
-5.01
Me
Me
Si
Me
Br
23
Parameter Value
Title APC 05134-2.fid
Solvent CDCl3
Temperature 299.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

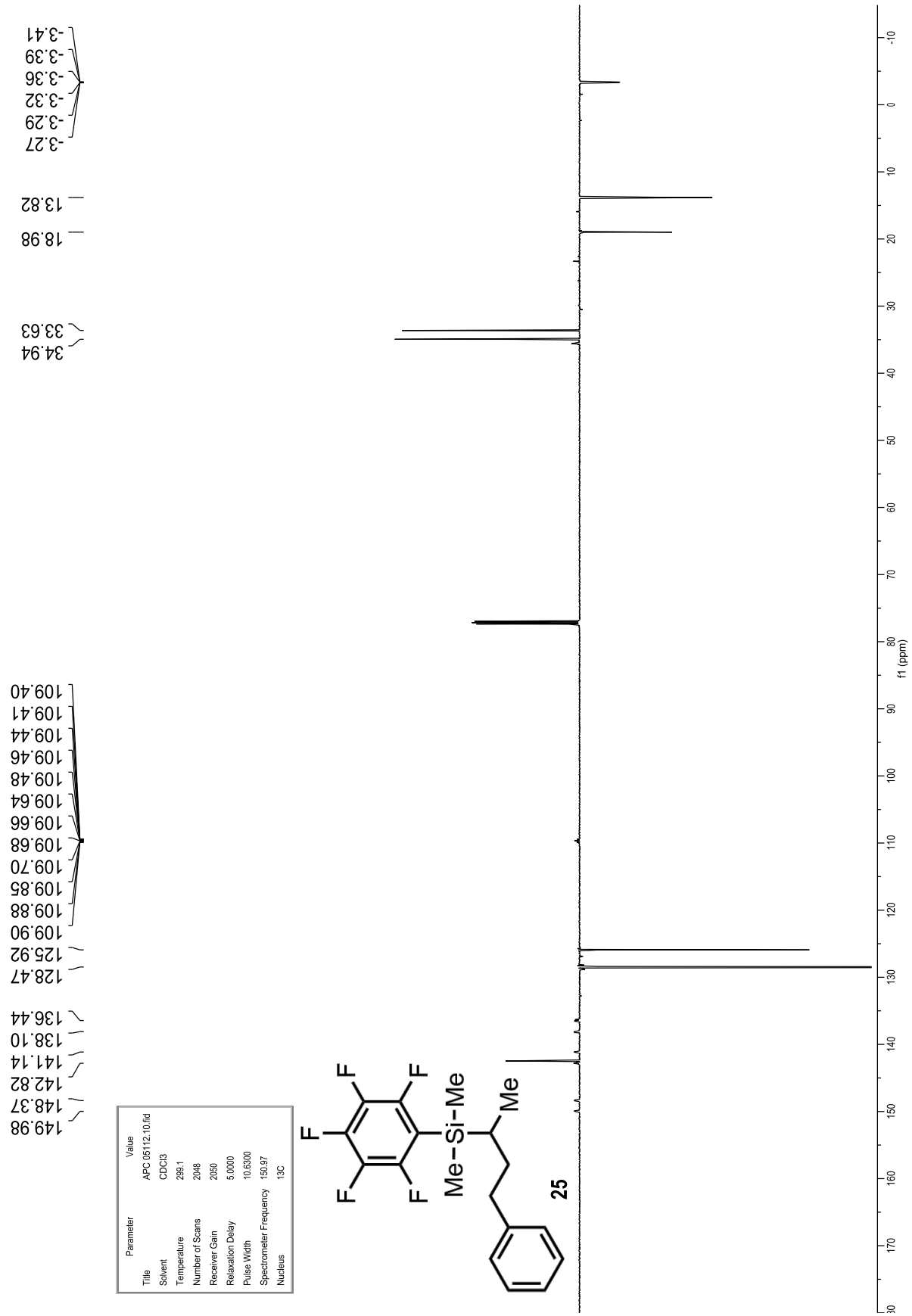

Parameter Value
Title APC 05134-3.fid
Solvent CDCl3
Temperature 297.0
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
5.42
Me
Me
Si
Me
Br
23
Me3Si
O
SiMe3
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

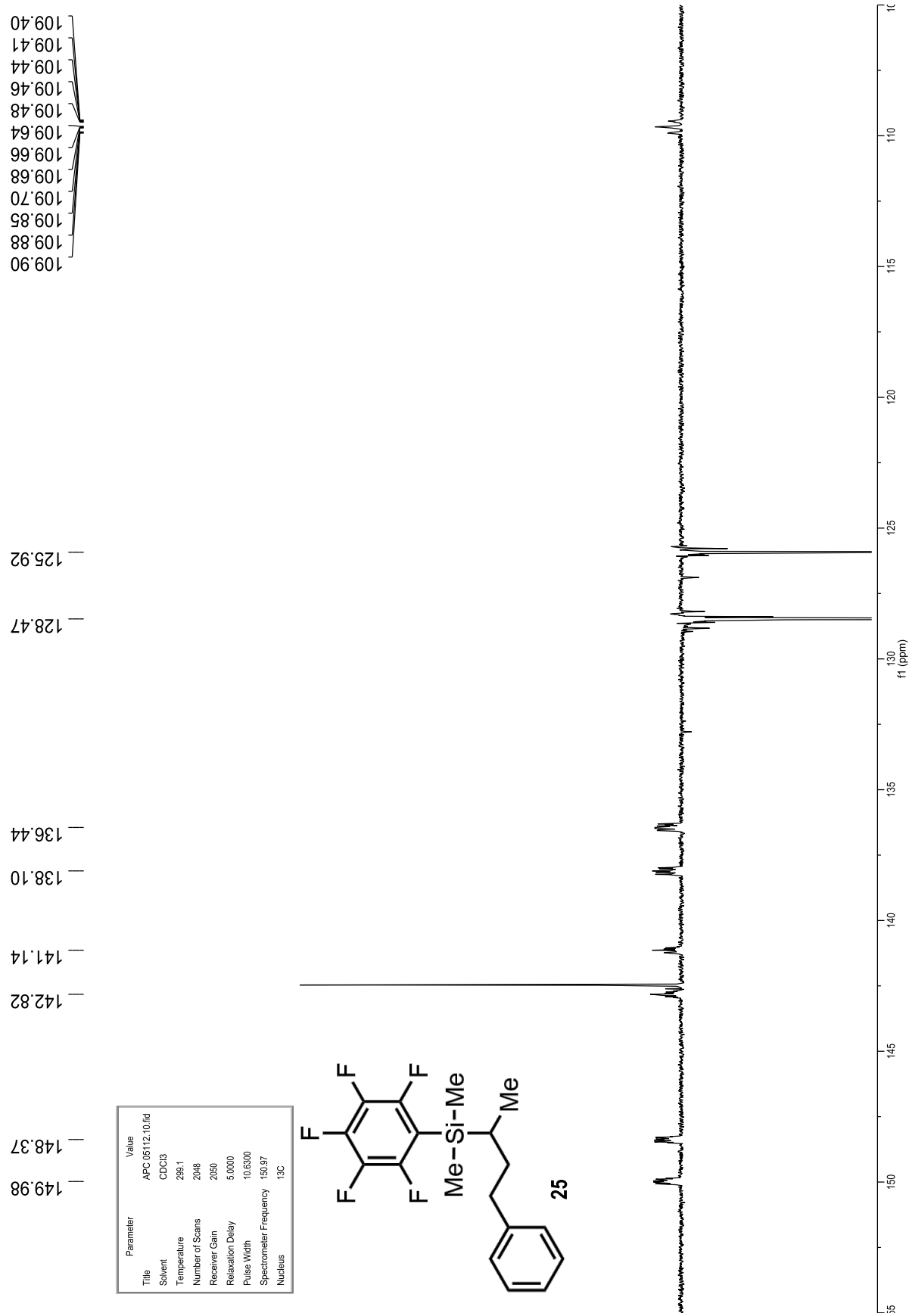

Parameter Value
Title APC 05086.4.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me
Si
Me
24
2.00
2.94
0.83
0.87
0.86
1.00
1.00
1.89
1.00
2.86
1.94
3.01
0.99
1.97
3.01
3.13
f1 (ppm)

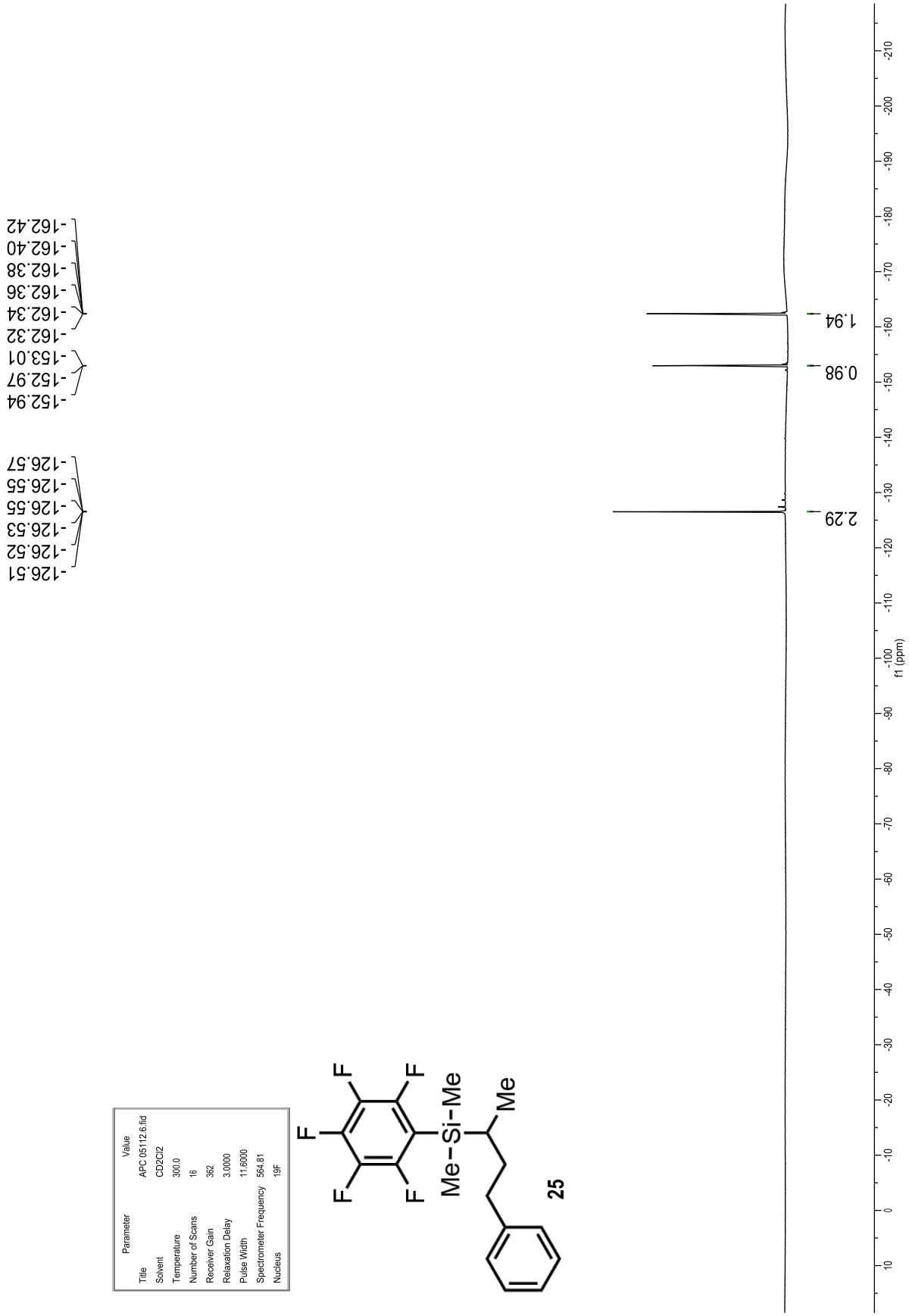

-4.94
13.72
14.05
18.60
23.55
33.10
33.64
34.13
35.18
114.27
125.71
128.41
128.56
139.29
143.23
Parameter Value
Title APC 05086.5.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
Me
Me
Si
Me
24
f1 (ppm)

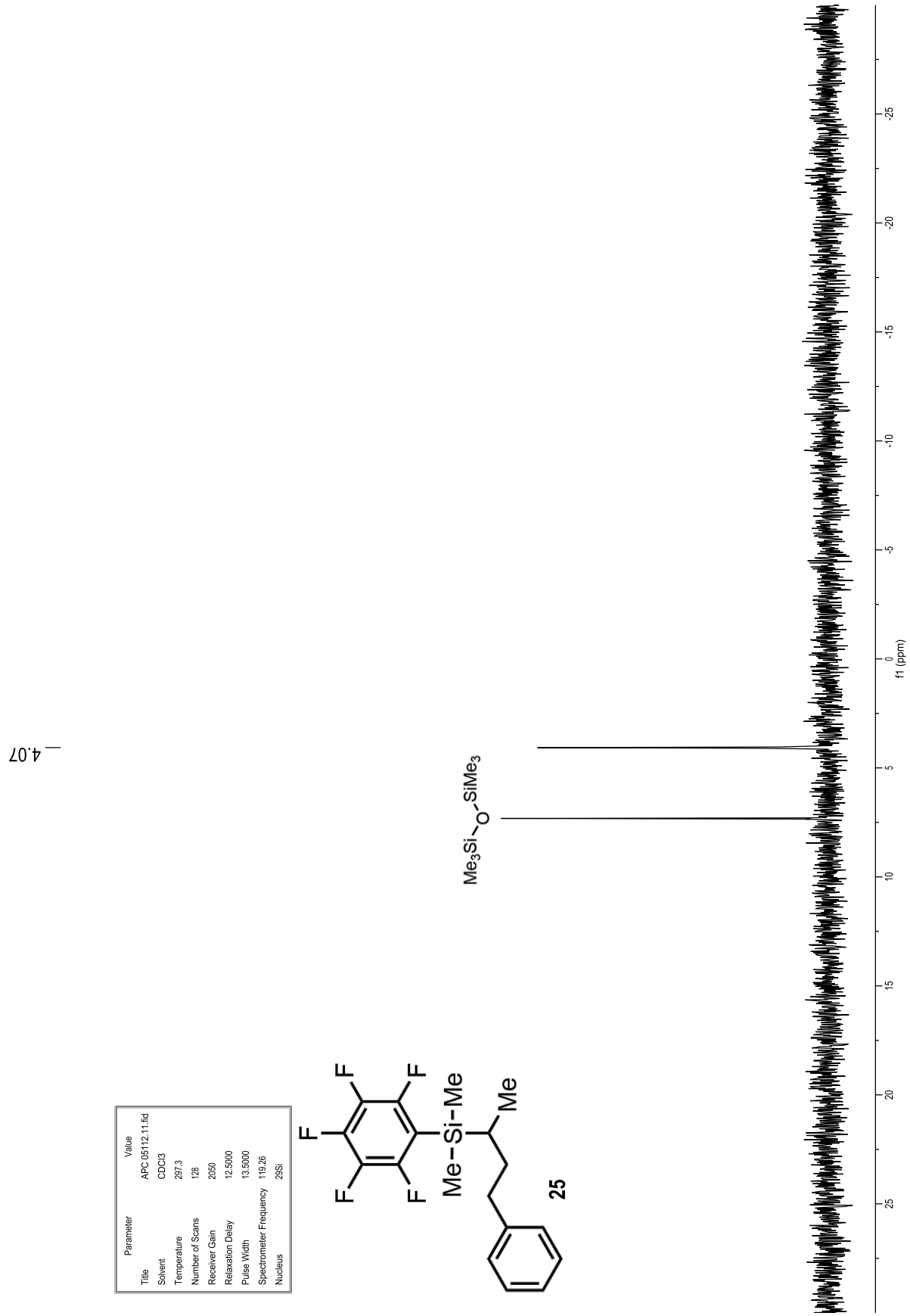

5.31
Parameter Value
Title APC 05086.6.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
Me
Me
Si
Me
24
Me3Si
O
SiMe3
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

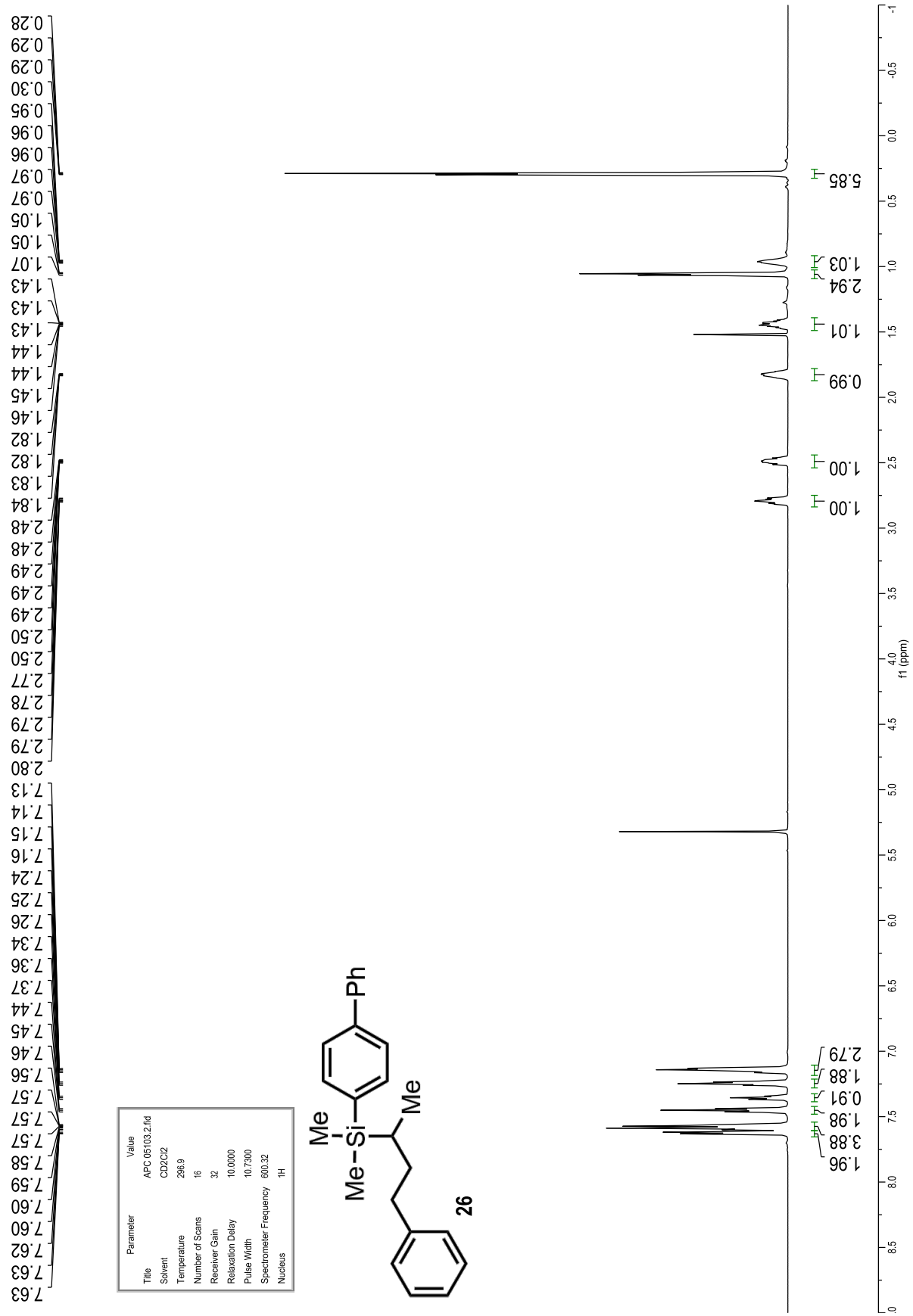

Parameter Value
Title APC 05112-9.fid
Solvent CD2Cl2
Temperature 297.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
F
F
F
F
Me–Si–Me
Me
25
1.95
1.05
1.89
1.00
1.00
1.08
1.00
1.13
2.98
3.10
2.99
f1 (ppm)

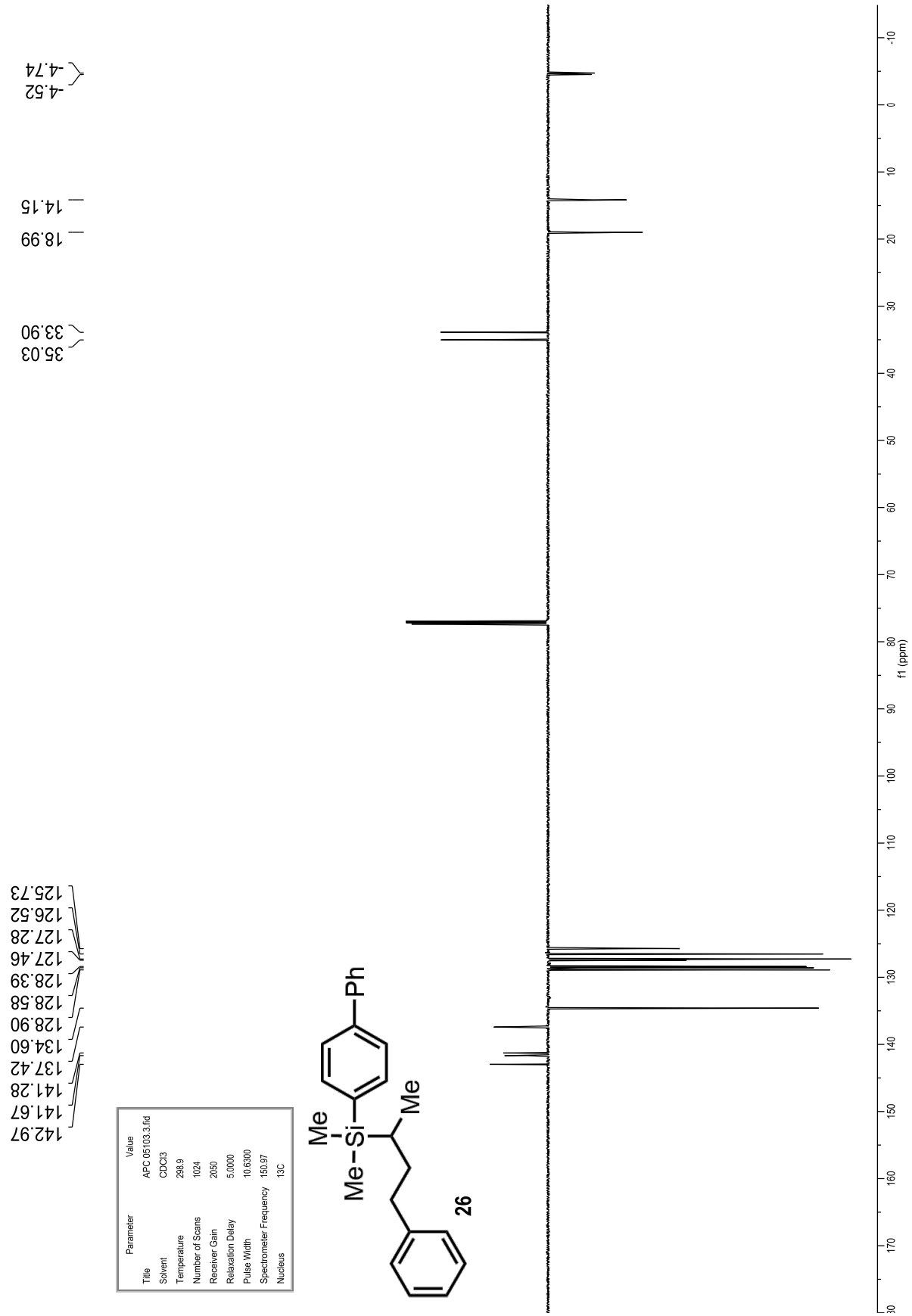

-3.41
-3.39
-3.36
-3.32
-3.29
-3.27
13.82
18.98
33.63
34.94
109.40
109.41
109.44
109.46
109.48
109.64
109.66
109.68
109.70
109.85
109.88
109.90
125.92
128.47
136.44
138.10
141.14
142.82
148.37
149.98
Parameter Value
Title APC 05112.10.fid
Solvent CDCl3
Temperature 299.1
Number of Scans 2048
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
F
F
F
F
Me–Si–Me
Me
25
f1 (ppm)

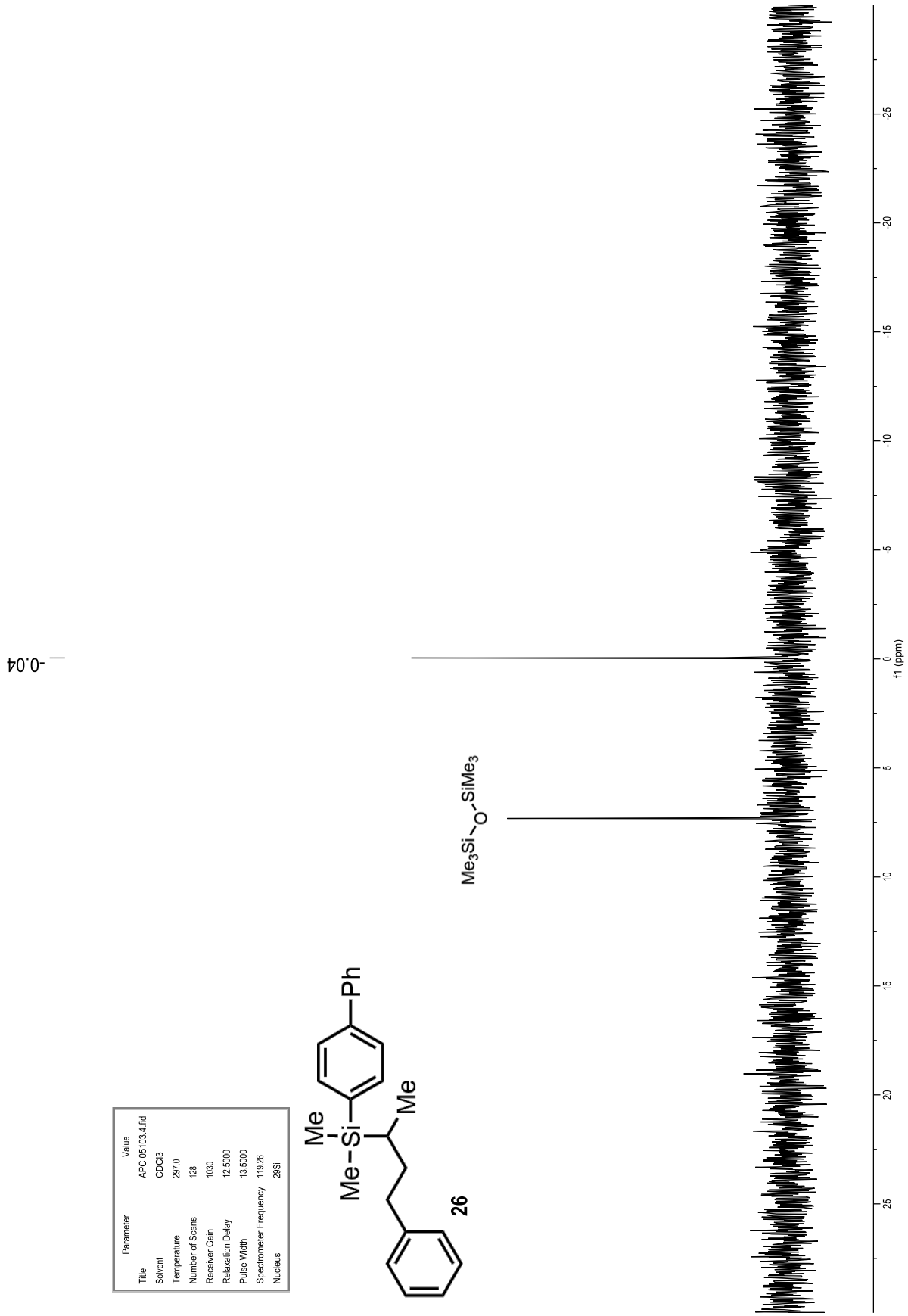

109.90
109.88
109.85
109.70
109.68
109.66
109.64
109.48
109.46
109.44
109.41
109.40
125.92
128.47
136.44
138.10
141.14
142.82
148.37
149.98
Parameter Value
Title APC 05112.10.fid
Solvent CDCl3
Temperature 299.1
Number of Scans 2048
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
F
F
F
F
Me–Si–Me
Me
25
f1 (ppm)

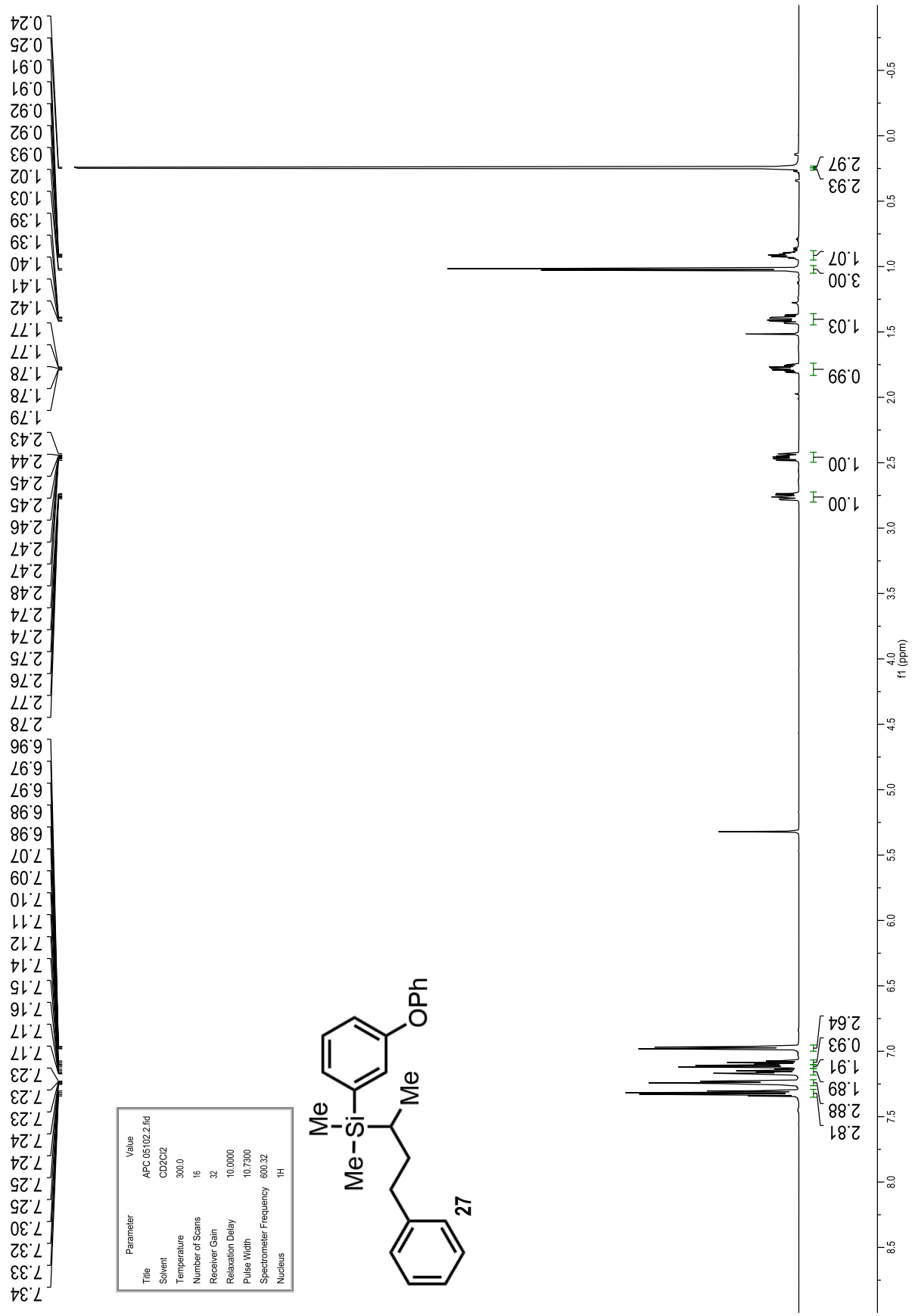

-126.51
-126.52
-126.53
-126.55
-126.55
-126.57
-152.94
-152.97
-153.01
-162.32
-162.34
-162.36
-162.38
-162.40
-162.42
2.29
0.98
1.94
f1 (ppm)
Parameter Value
Title APC 05112.6.fid
Solvent CD2Cl2
Temperature 300.0
Number of Scans 16
Receiver Gain 362
Relaxation Delay 3.0000
Pulse Width 11.8000
Spectrometer Frequency 564.81
Nucleus 19F
F
F
F
F
Me–Si–Me
Me
25

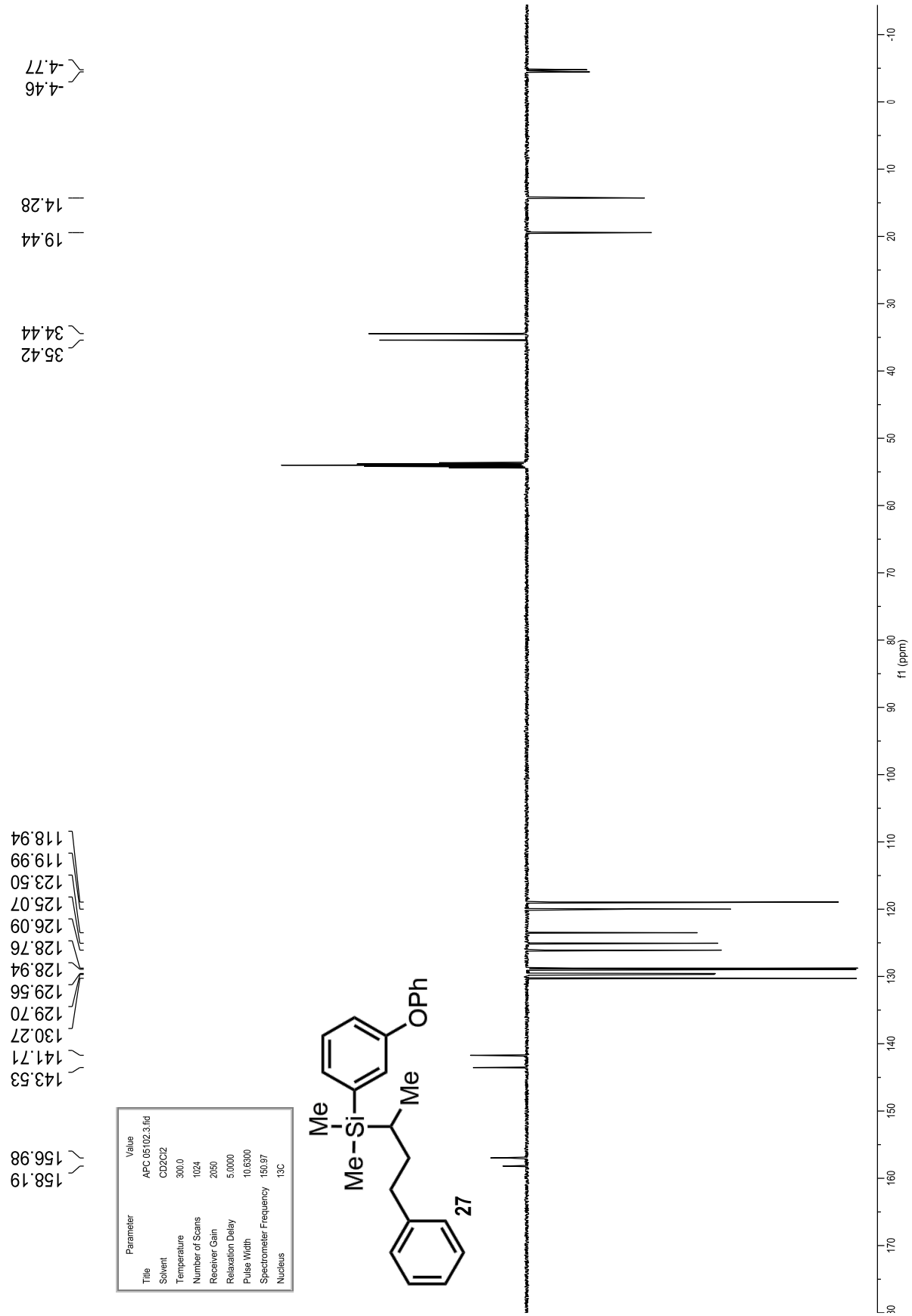

Parameter Value
Title APC 05112.11.fid
Solvent CDCl3
Temperature 297.3
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
F
F
F
F
Me–Si–Me
Me
25
Me3Si
O
SiMe3
4.07
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

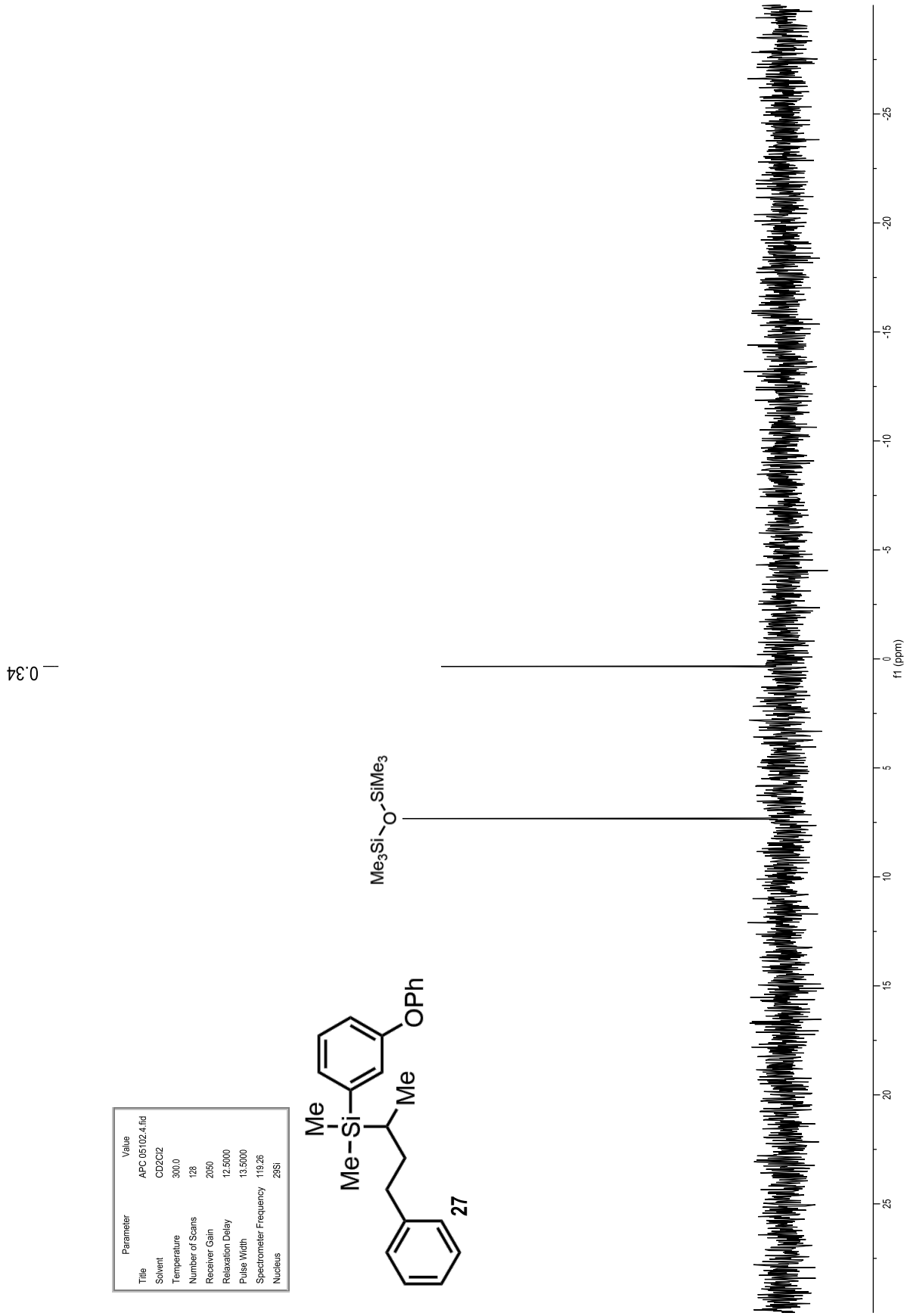

Parameter Value
Title APC 05103.2.fid
Solvent CD2Cl2
Temperature 296.9
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me-Si-Ph
Me
26
5.85
1.03
2.94
1.01
0.99
1.00
1.00
1.96
3.88
1.98
0.91
1.88
2.79
f1 (ppm)

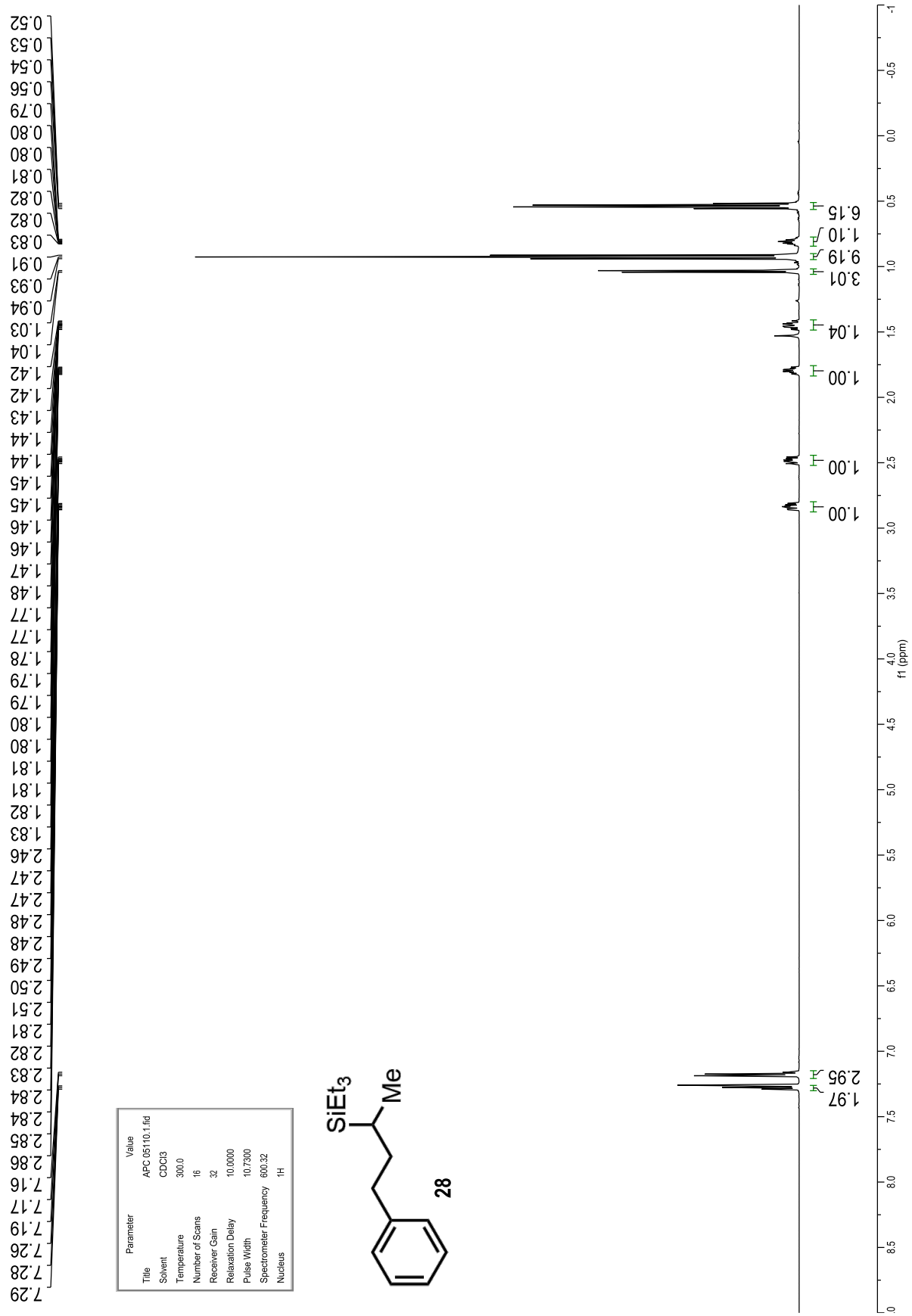

-4.74
-4.52
14.15
18.99
33.90
35.03
142.97
141.67
141.28
137.42
134.60
128.90
128.58
128.39
127.46
127.28
126.52
125.73
Parameter Value
Title APC 05103.3.fid
Solvent CDCl3
Temperature 298.9
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
Me
Me-Si
Ph
Me
26
f1 (ppm)

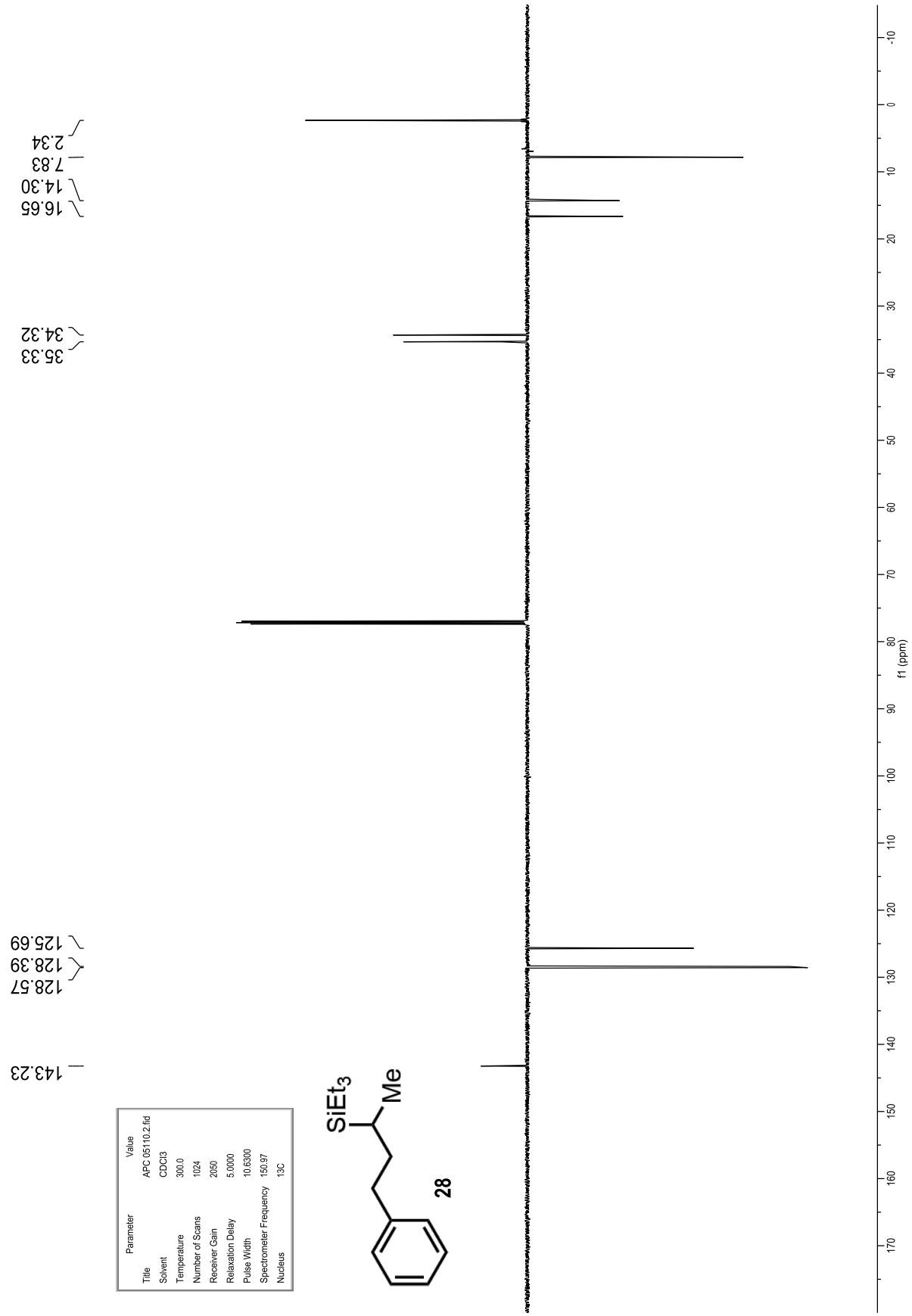

Parameter Value
Title APC 05103.4.fid
Solvent CDCl3
Temperature 297.0
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
Me
Me-Si
Ph
Me
26
Me3Si
O
SiMe3
-0.04
f1 (ppm)


Parameter Value
Title APC 05102.2.fid
Solvent CD2Cl2
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
Me
Me-Si
Me
OPh
27
f1 (ppm)

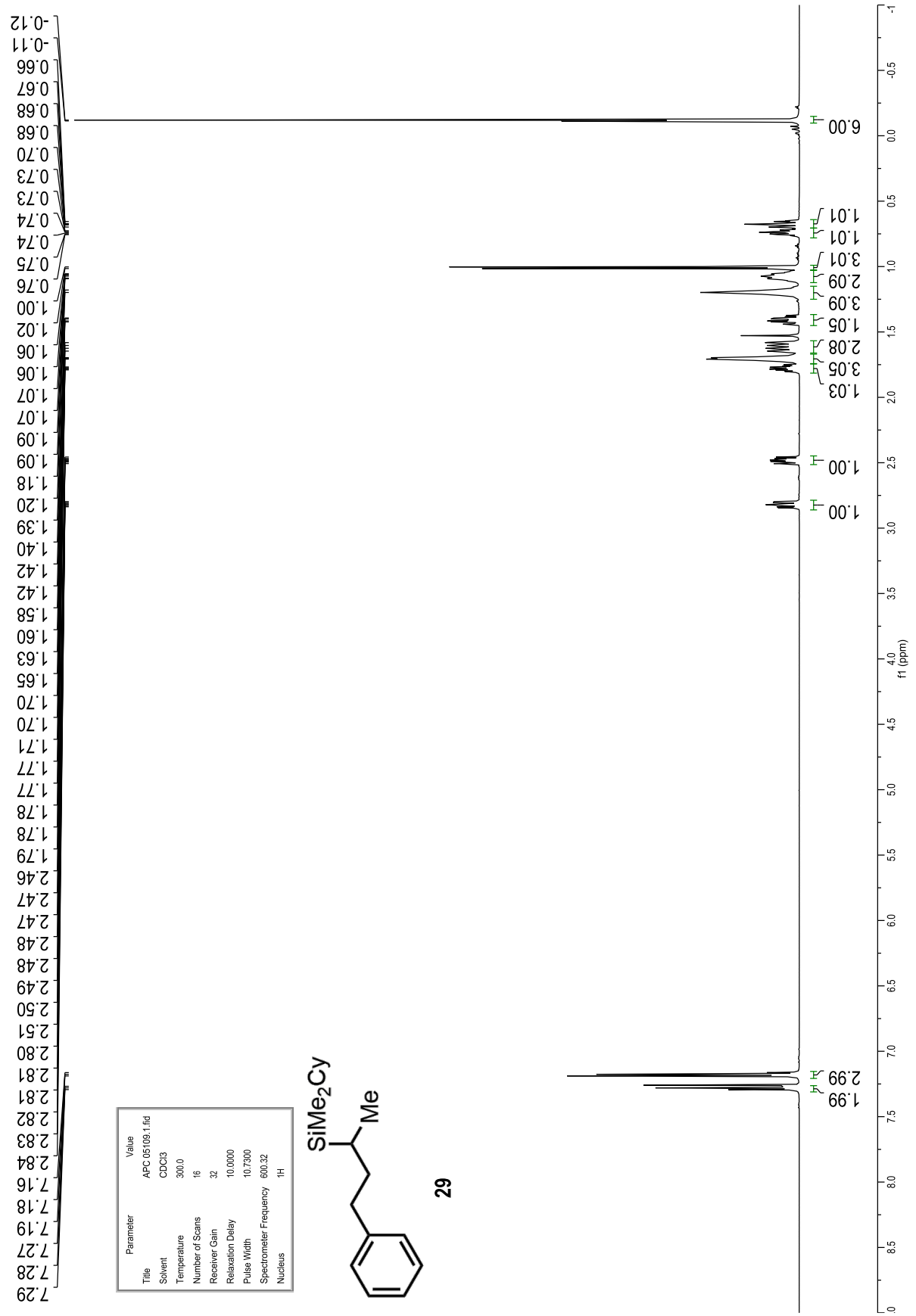

158.19
156.98
143.53
141.71
130.27
129.70
129.56
128.94
128.76
126.09
125.07
123.50
119.99
118.94
35.42
34.44
19.44
14.28
-4.46
-4.77
Me
Me-Si
Me
OPh
27
Parameter Value
Title APC 05102_3.fid
Solvent CD2Cl2
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

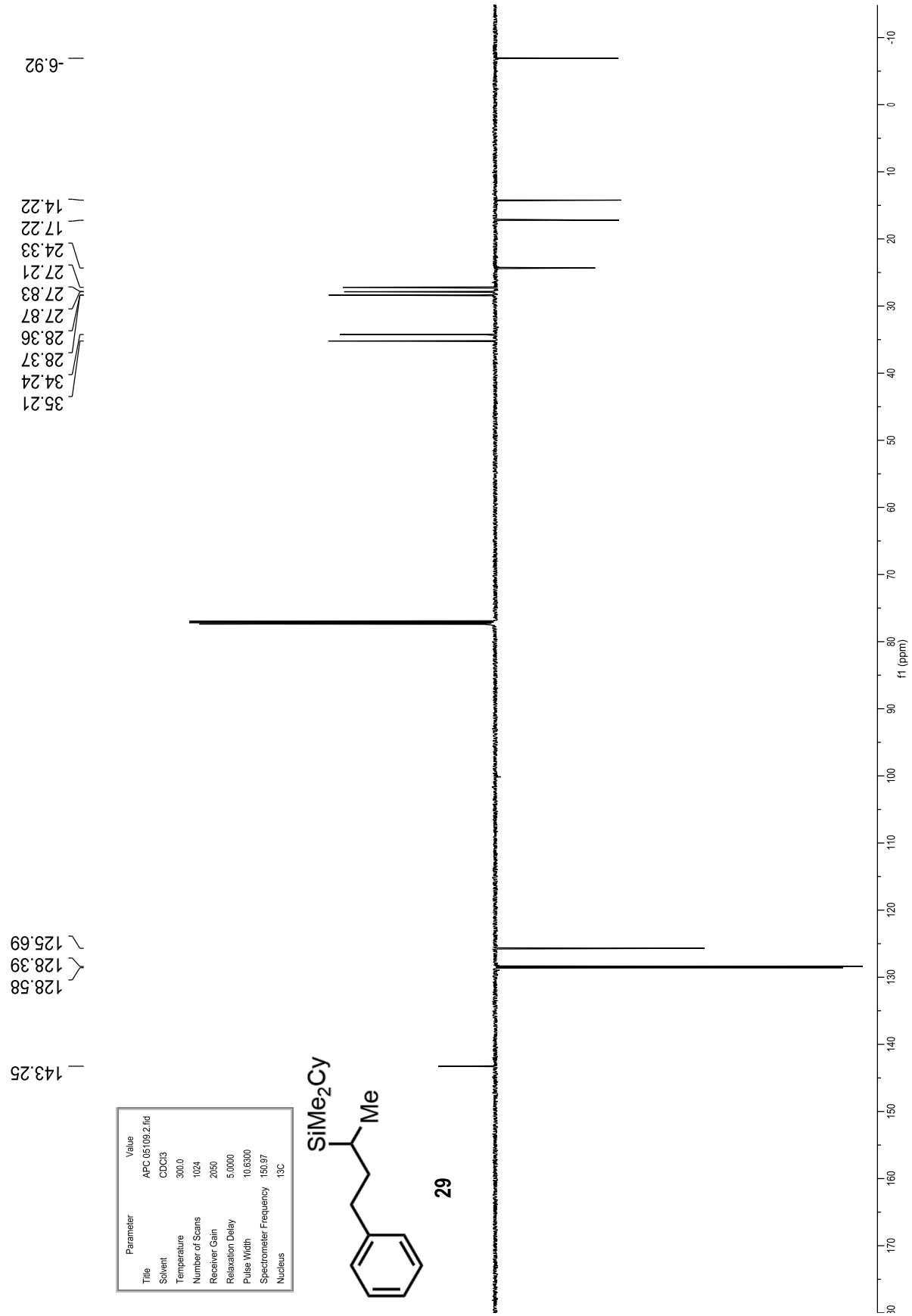

Parameter Value
Title APC 05102_4.fid
Solvent CD2Cl2
Temperature 300.0
Number of Scans 128
Receiver Gain 2050
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
Me
Me-Si
Me
OPh
27
Me3Si
O
SiMe3
0.34
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)


0.52
0.53
0.54
0.56
0.79
0.80
0.80
0.81
0.82
0.82
0.83
0.91
0.93
0.94
1.03
1.04
1.42
1.42
1.43
1.44
1.44
1.45
1.45
1.46
1.46
1.47
1.48
1.77
1.77
1.78
1.79
1.79
1.80
1.80
1.81
1.81
1.82
1.83
2.46
2.47
2.47
2.48
2.48
2.49
2.50
2.51
2.81
2.82
2.83
2.84
2.84
2.85
2.86
7.16
7.17
7.19
7.26
7.28
7.29
Parameter Value
Title APC 05110.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiEt3
Me
28
1.97
2.95
1.00
1.00
1.00
1.04
3.01
9.19
1.10
6.15
f1 (ppm)

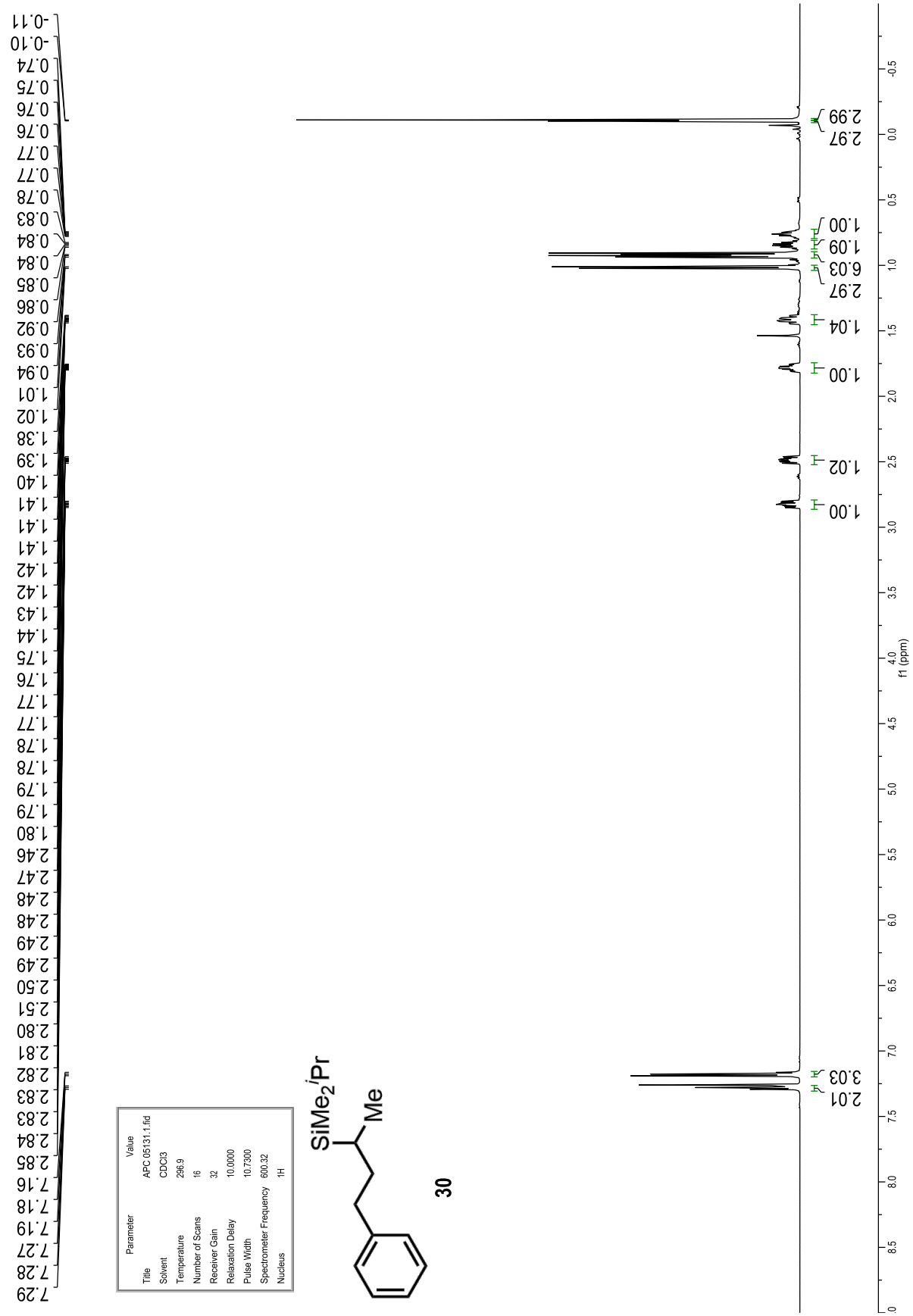

143.23
128.57
128.39
125.69
35.33
34.32
16.65
14.30
7.83
2.34
SiEt3
Me
28
f1 (ppm)
Parameter Value
Title APC 05110.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C

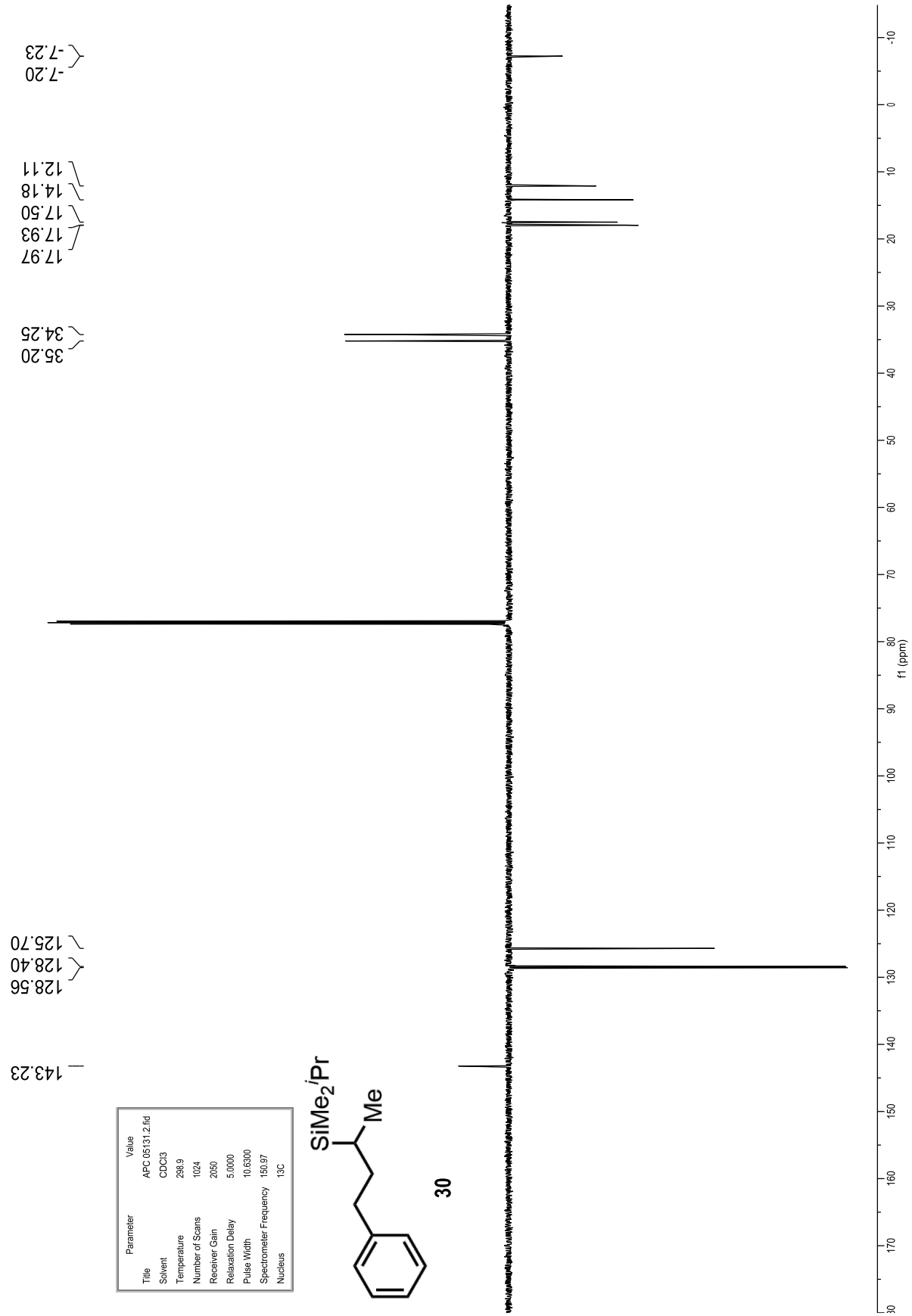
Parameter	Value
Title	APC 05110.3.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	128
Receiver Gain	1030
Relaxation Delay	12.5000
Pulse Width	13.5000
Spectrometer Frequency	119.26
Nucleus	29Si

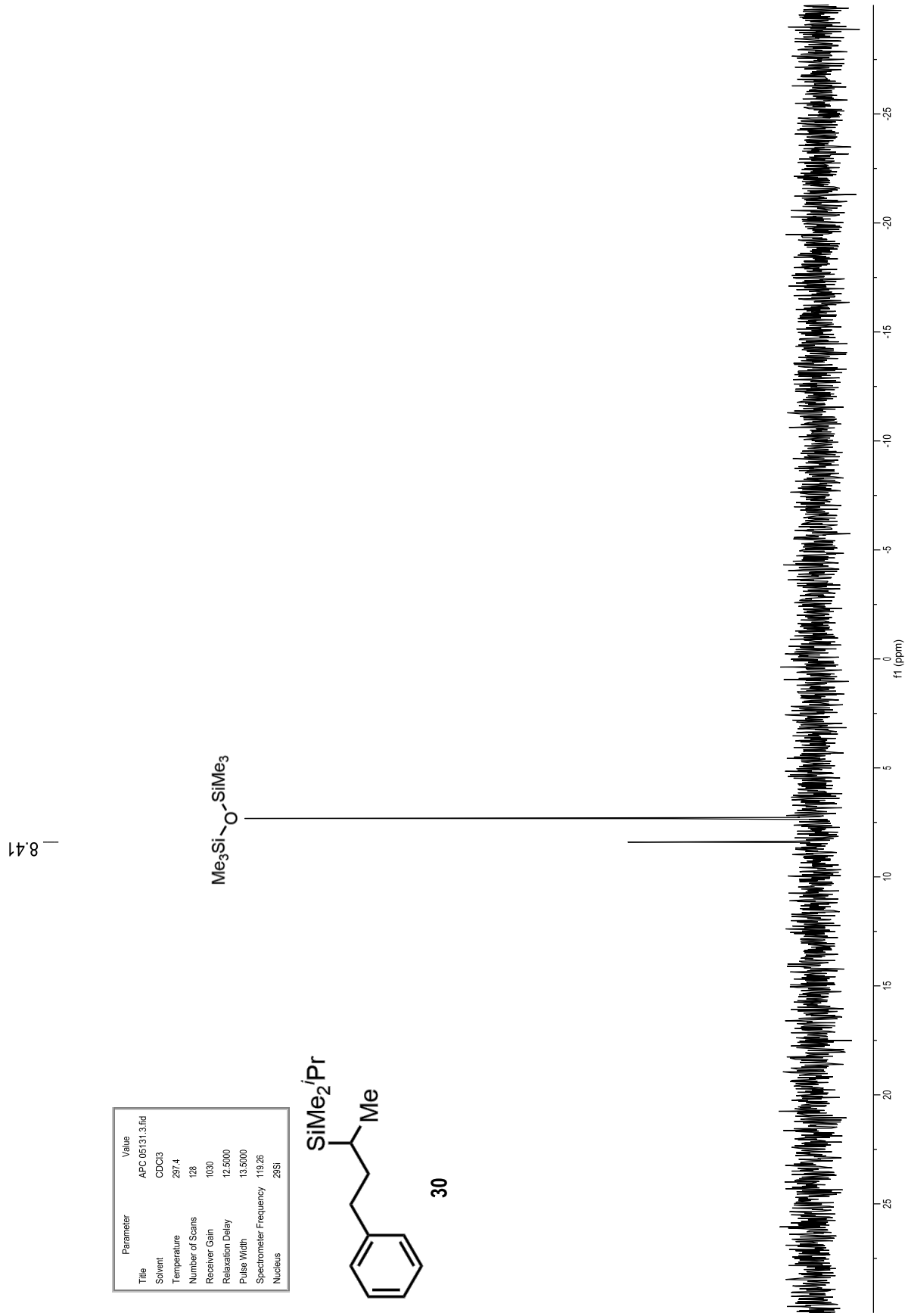

Parameter Value
Title APC 05109.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2Cy
Me
29
6.00
1.01
1.01
3.01
2.09
3.09
1.05
2.08
3.05
1.03
1.00
1.00
2.99
1.99
f1 (ppm)

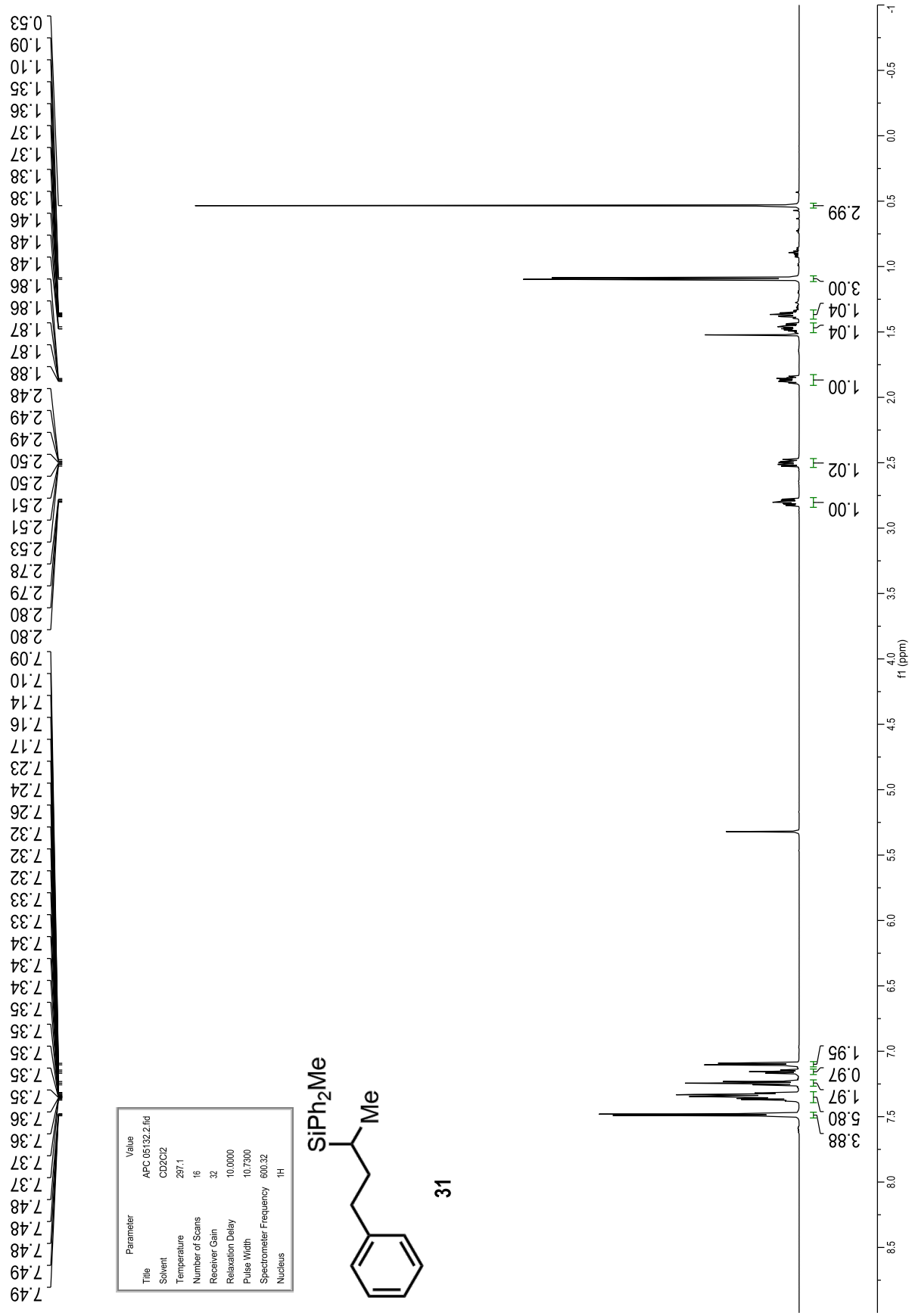

-6.92
14.22
17.22
24.33
27.21
27.83
27.87
28.36
28.37
34.24
35.21
128.58
128.39
125.69
143.25
SiMe2Cy
Me
29
Parameter Value
Title APC 05109.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

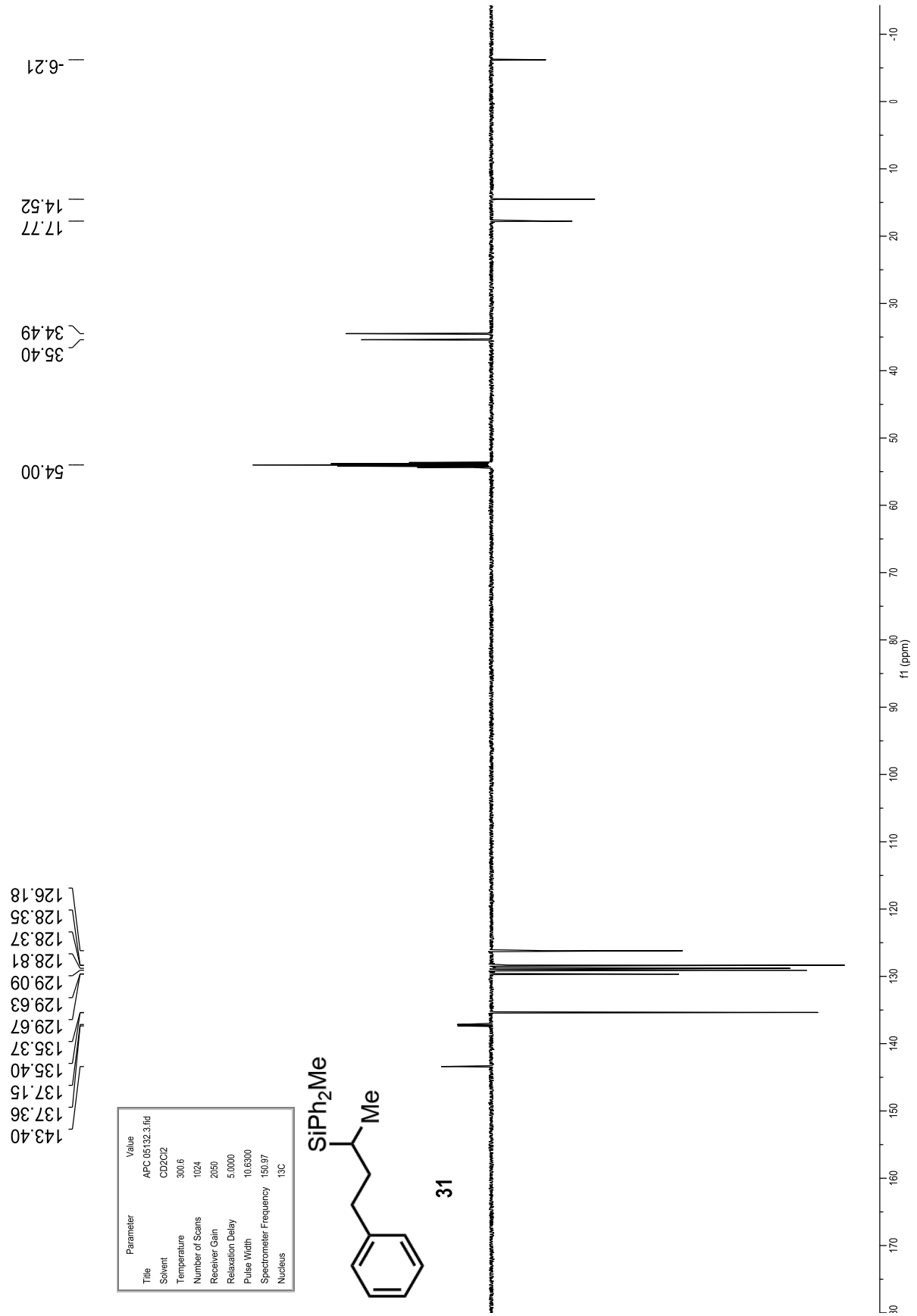
Parameter Value
Title APC 05109.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
5.66
Me3Si O SiMe3
SiMe2Cy
Me
29
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

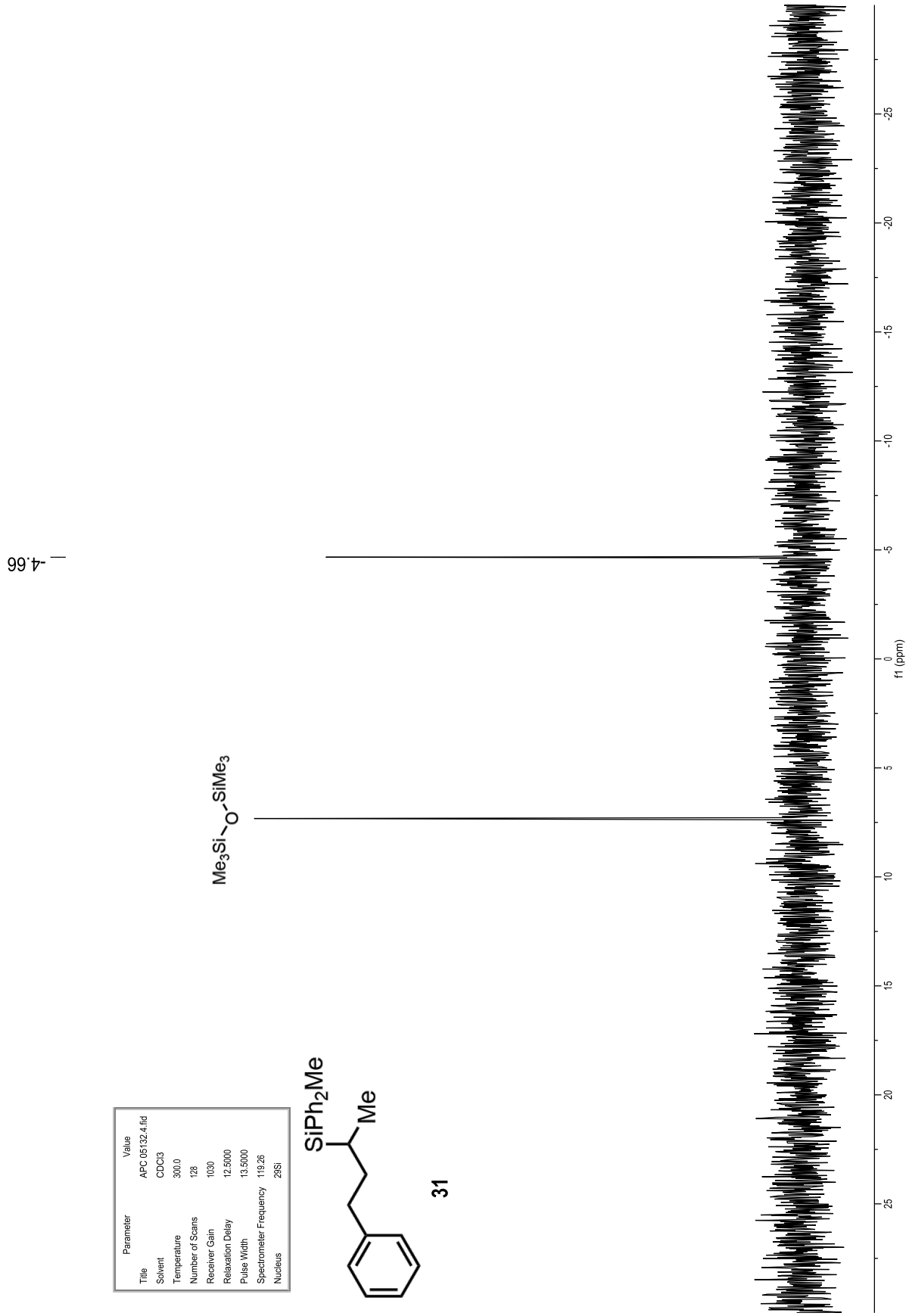

Parameter Value
Title APC 05131.1.fid
Solvent CDCl3
Temperature 296.9
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2iPr
Me
30
2.01
3.03
1.00
1.02
1.00
1.04
2.97
6.03
1.09
1.00
2.97
2.99
f1 (ppm)

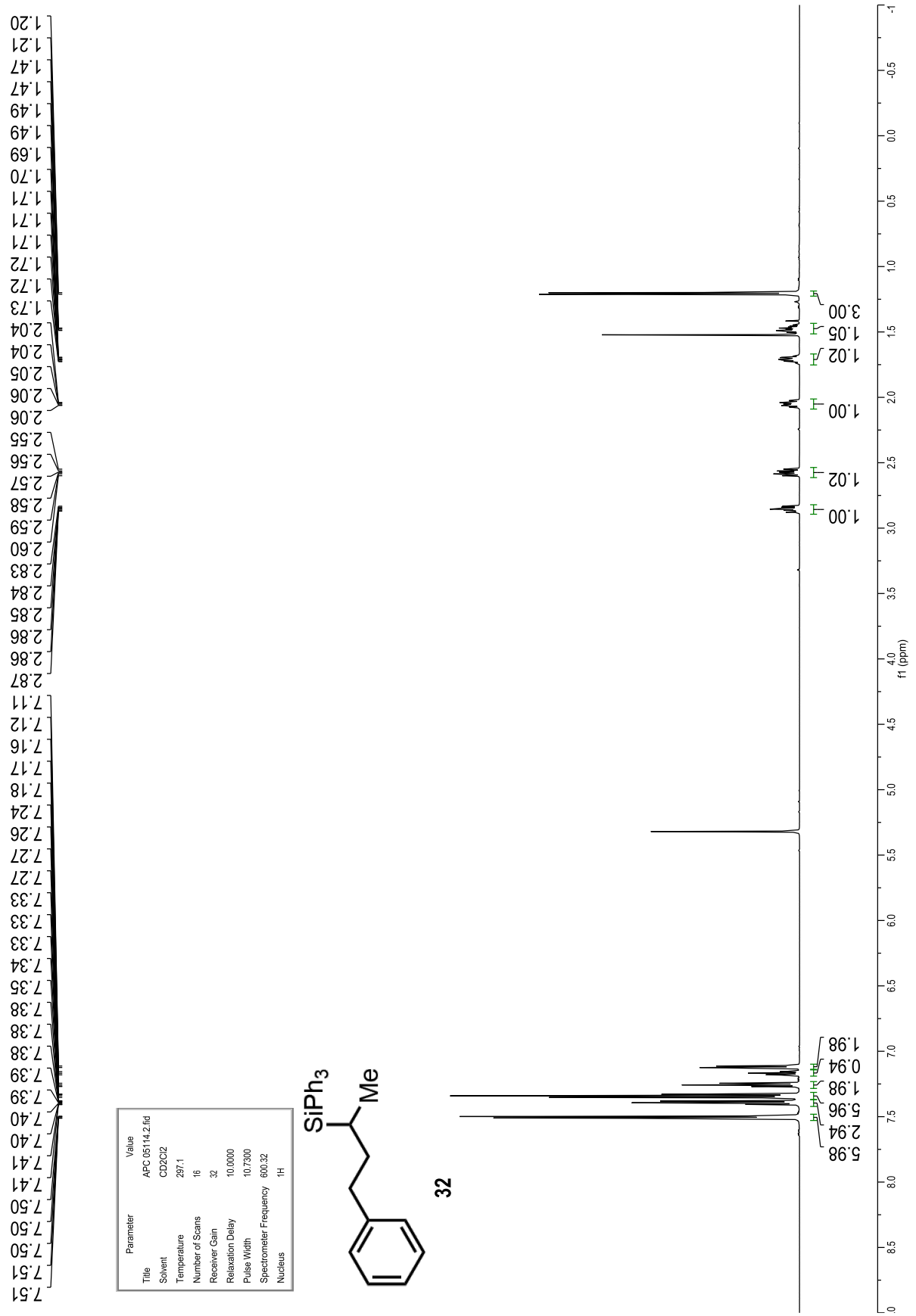

143.23
128.56
128.40
125.70
35.20
34.25
17.97
17.93
17.50
14.18
12.11
-7.20
-7.23
SiMe2iPr
Me
30
Parameter Value
Title APC 05131.2.fid
Solvent CDCl3
Temperature 298.9
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

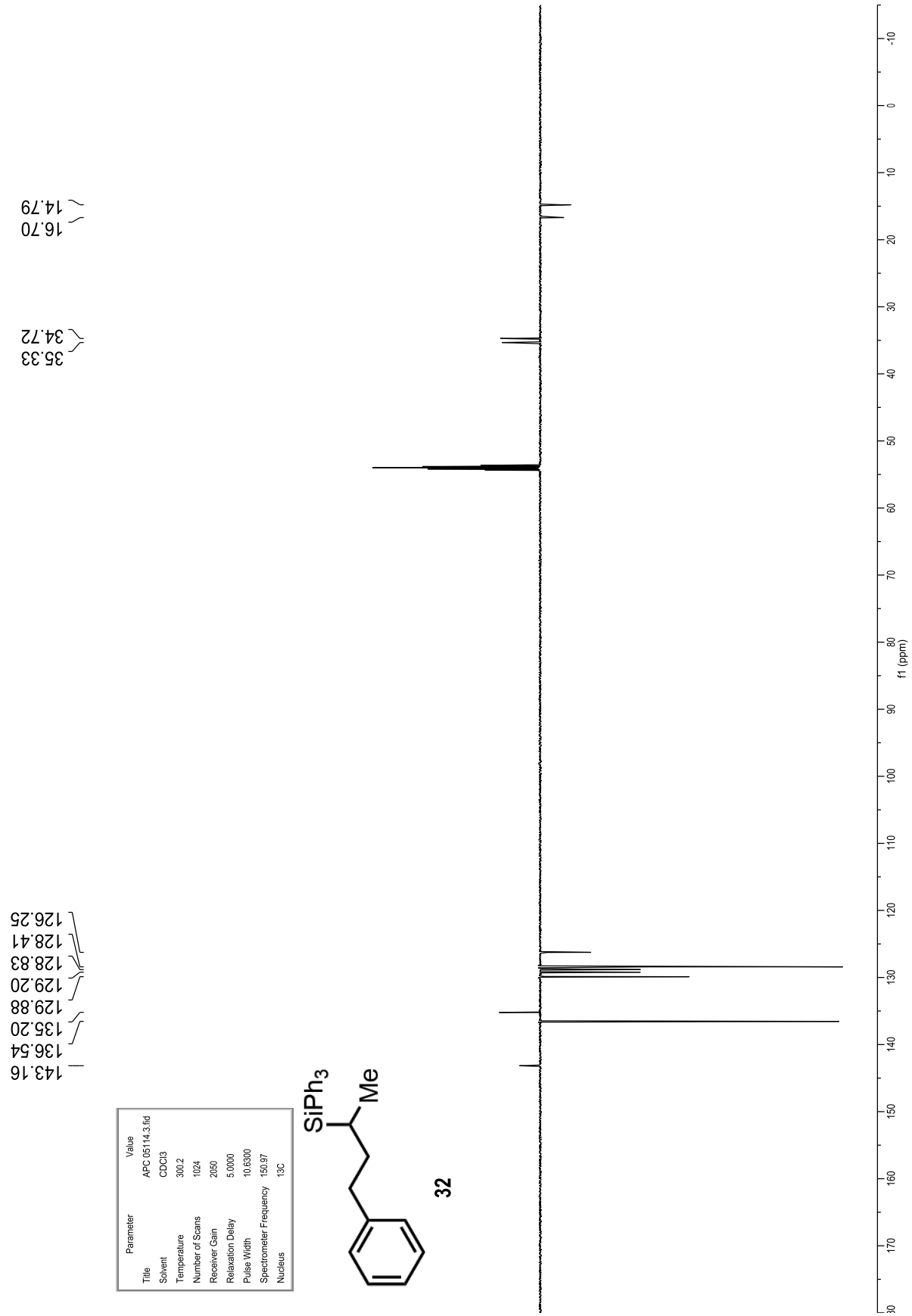

8.41
Me3Si
O
SiMe3
SiMe2iPr
Me
30
Parameter Value
Title APC 05131.3.fid
Solvent CDCl3
Temperature 297.4
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

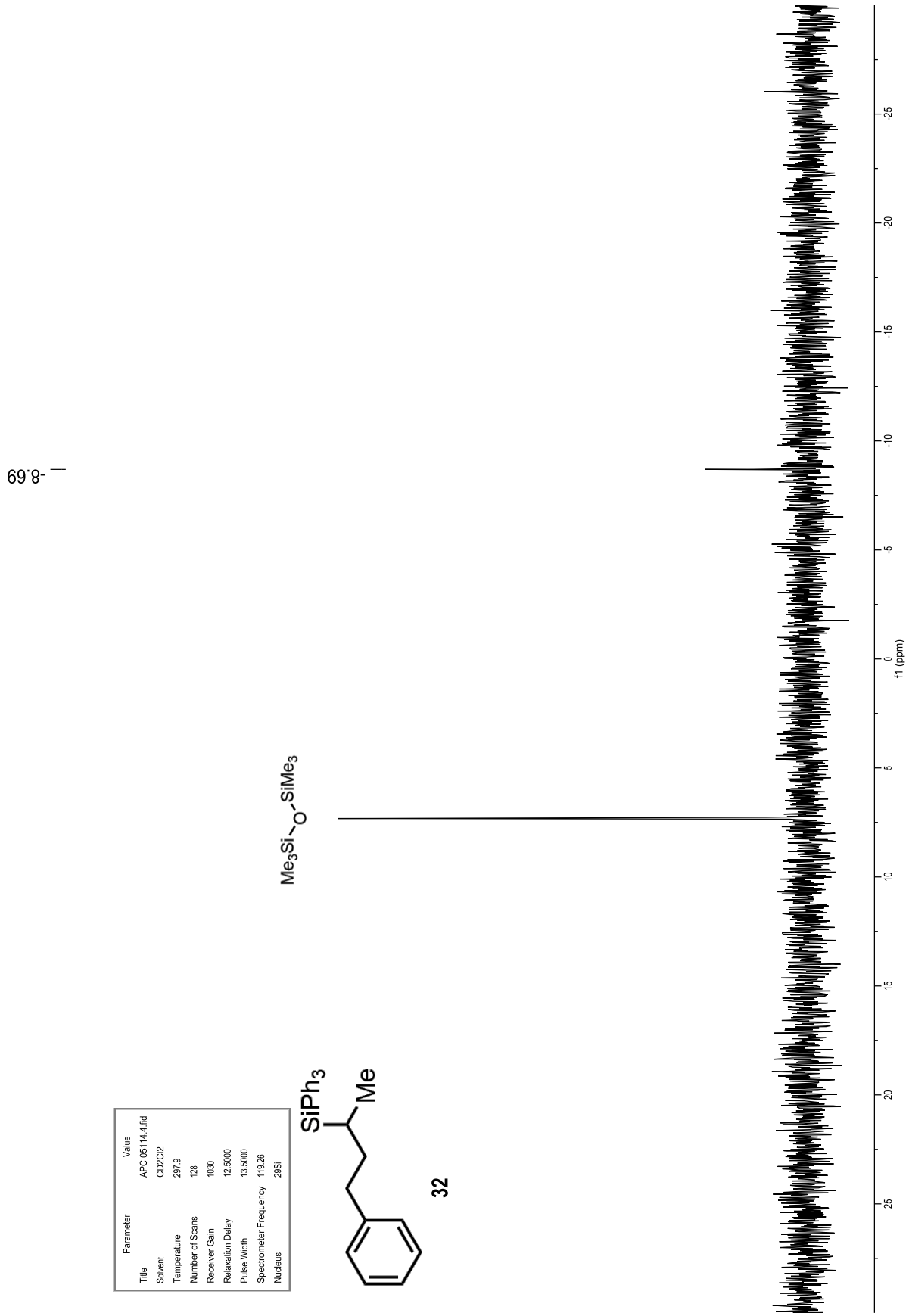

Parameter Value
Title APC 05132.2.fid
Solvent CD2Cl2
Temperature 297.1
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiPh2Me
Me
31
3.88
5.80
1.97
0.97
1.95
2.99
3.00
1.04
1.04
1.00
1.02
1.00
f1 (ppm)

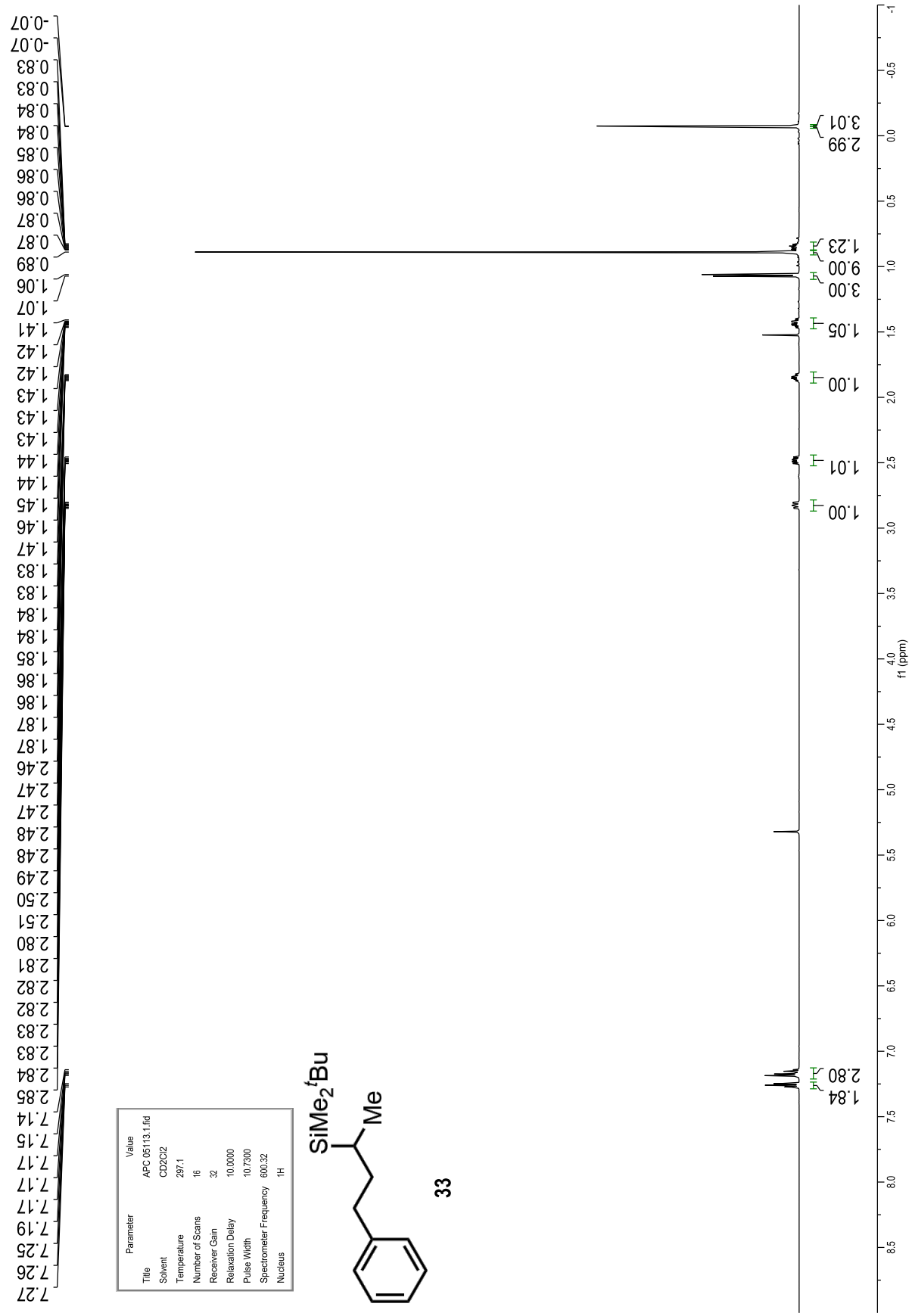

-6.21
14.52
17.77
34.49
35.40
54.00
126.18
128.35
128.37
128.81
129.09
129.63
129.67
135.37
135.40
137.15
137.36
143.40
Parameter Value
Title APC 05132_3.fid
Solvent CD2Cl2
Temperature 300.6
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
SiPh2Me
Me
31
f1 (ppm)

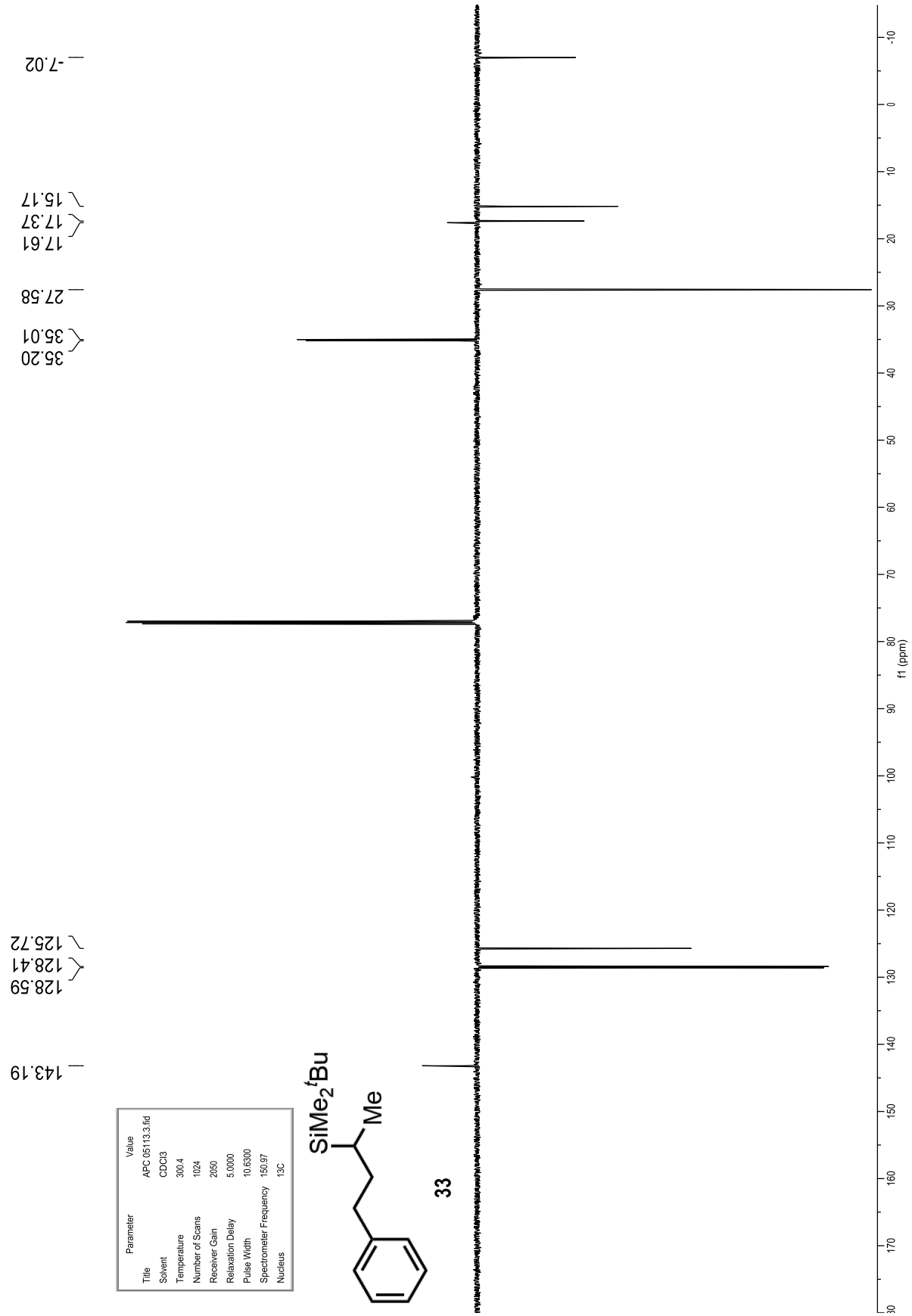

Parameter Value
Title APC 05132_4.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
SiPh2Me
Me
31
Me3Si
O
SiMe3
-4.66
25
20
15
10
5
0
-5
-10
-15
-20
-25
f1 (ppm)

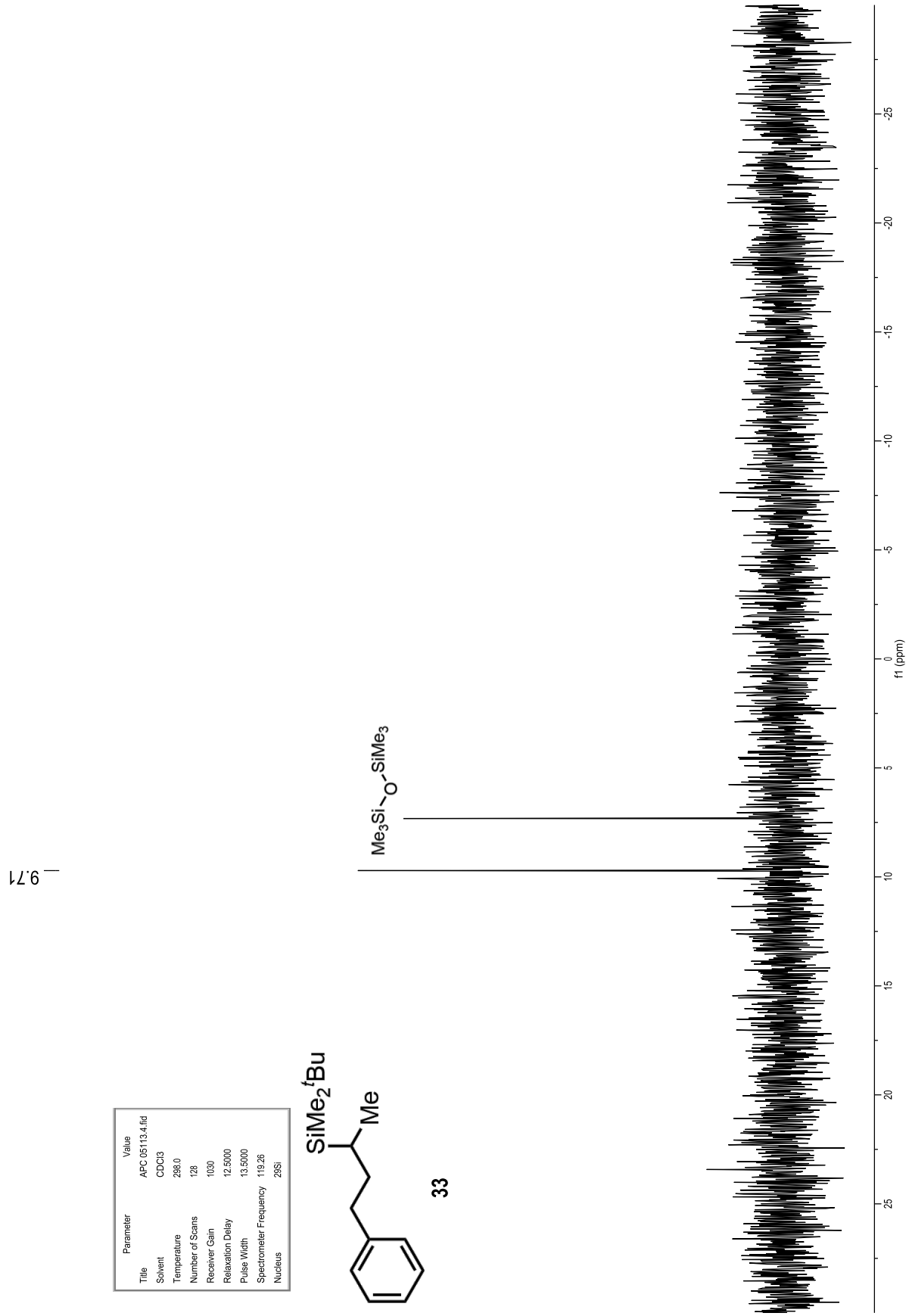

Parameter Value
Title APC 05114-2.fid
Solvent CD2Cl2
Temperature 297.1
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiPh3
Me
32
5.98
2.94
5.96
1.98
0.94
1.98
3.00
1.05
1.02
1.00
1.02
1.00
f1 (ppm)


143.16
136.54
135.20
129.88
129.20
128.83
128.41
126.25
35.33
34.72
16.70
14.79
SiPh3
Me
32
Parameter Value
Title APC 05114-3.fid
Solvent CDCl3
Temperature 300.2
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)

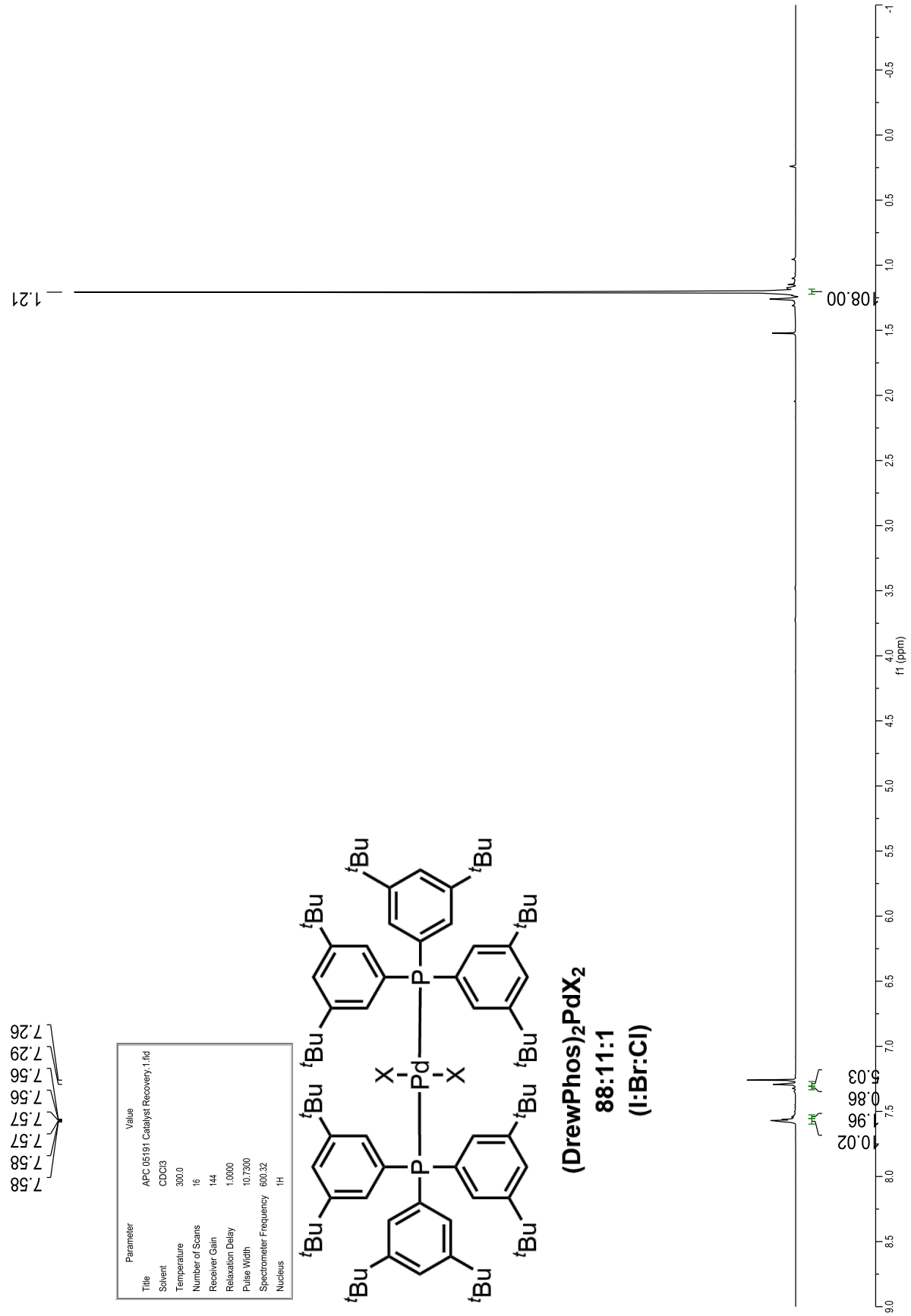

-8.69
Me3Si
O
SiMe3
SiPh3
Me
32
Parameter Value
Title APC 05114.4.fid
Solvent CD2Cl2
Temperature 297.9
Number of Scans 128
Receiver Gain 1030
Relaxation Delay 12.5000
Pulse Width 13.5000
Spectrometer Frequency 119.26
Nucleus 29Si
25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

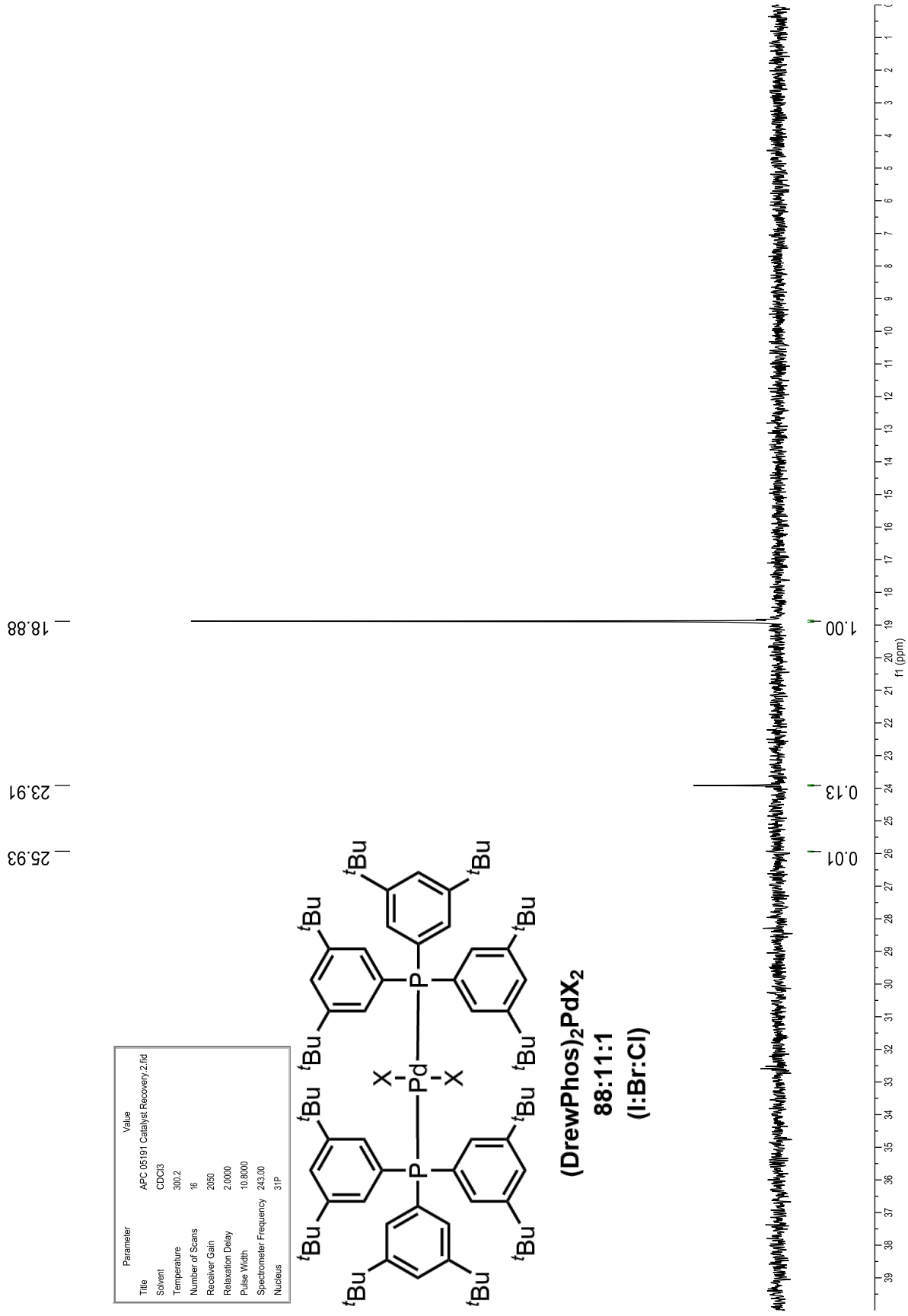

Parameter Value
Title APC 05113.1.fid
Solvent CD2Cl2
Temperature 297.1
Number of Scans 16
Receiver Gain 32
Relaxation Delay 10.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
SiMe2tBu
Me
33
3.01
2.99
1.23
9.00
3.00
1.05
1.00
1.01
1.00
2.80
1.84
f1 (ppm)


-7.02
15.17
17.37
17.61
27.58
35.01
35.20
128.41
128.59
125.72
143.19
SiMe2tBu
Me
33
Parameter Value
Title APC 05113.3.fid
Solvent CDCl3
Temperature 300.4
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Spectrometer Frequency 150.97
Nucleus 13C
f1 (ppm)



Parameter	Value
Title	APC 05113.4.fid
Solvent	CDCl3
Temperature	298.0
Number of Scans	128
Receiver Gain	1030
Relaxation Delay	12.5000
Pulse Width	13.5000
Spectrometer Frequency	119.26
Nucleus	29Si


7.58
7.58
7.57
7.57
7.56
7.56
7.29
7.26
Parameter Value
Title APC 05191 Catalyst Recovery 1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 144
Relaxation Delay 1.0000
Pulse Width 10.7300
Spectrometer Frequency 600.32
Nucleus 1H
tBu
P
Pd
X
(DrewPhos)2PdX2
88:11:1
(I:Br:Cl)
1.21
108.00
10.02
1.96
0.86
5.03
f1 (ppm)


Parameter Value
Title APC 05191 Catalyst Recovery 2.fid
Solvent CDCl3
Temperature 300.2
Number of Scans 16
Receiver Gain 2050
Relaxation Delay 2.0000
Pulse Width 10.8000
Spectrometer Frequency 243.00
Nucleus 31P
(DrewPhos)2PdX2
88:11:1
(I:Br:Cl)
18.88
23.91
25.93
1.00
0.13
0.01
f1 (ppm)