

Identifying a Cobalt Catalyst for Highly Selective Hydrosilylation of Allenenes

Zheng Yang,^{a,b†} Dongjie Peng,^{a,b†} Xiaoyong Du,^{a,b} Zheng Huang,^{*a,b} and Shengming Ma^{*a,b,c}

^a State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China

^b University of Chinese Academy of Sciences, Beijing 100049, P. R. China

^c Department of Chemistry, Fudan University, 220 Handan Lu, Shanghai 200433, P. R. China

Email: masm@sioc.ac.cn,

Fax: 86-21-64167510

Email: huangzh@sioc.ac.cn,

Fax: 86-21-54925533

[†] These authors contributed equally.

Supporting Information

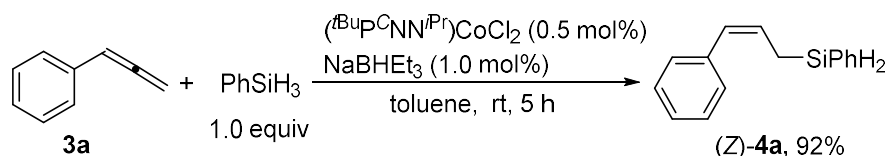
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General Information: NMR spectra were recorded on Agilent 400 MHz, 600 MHz, or Varian Mercury 400 MHz. ^{19}F NMR chemical shifts were referenced to an internal CFCl_3 standard. Toluene was dried over sodium wire and distilled freshly before use. PhSiH_3 was purchased from Aladdin Industrial Corporation or Adamas Reagent, Ltd. NaBHET_3 (1.0 M in THF) was purchased from Acros Organics. Room temperature in laboratory was in the range of 20 to 26 °C. The iron and cobalt complexes of phosphinite-iminopyridine ($\text{P}^{\text{O}}\text{NN}$) ligand **1**¹ and phosphine-iminopyridine ($\text{P}^{\text{C}}\text{NN}$) ligands **2a-2d**,² allenes **3a-3h**,³ **3i**,⁴ **3j**,⁵ **3k-m**,⁴ **3n**,⁶ **3o**,⁷ and **3p**⁸ were prepared according to literatures.

Hydrosilylation of allenes **3** with PhSiH_3 .

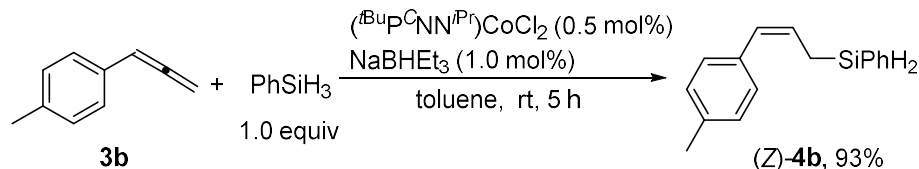
(1) Preparation of (Z)-(3-phenyl-2-propenyl)(phenyl)silane ((Z)-**4a**) (yz-4-132)



Typical Procedure: In a nitrogen filled glove box, $(t\text{BuP}^{\text{C}}\text{NN}^i\text{Pr})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3a** (116.2 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88 \text{ g/mL}$, 108.2 mg, 1.0 mmol), and NaBHET_3 (1.0 M in THF, 10 μL , 0.01 mmol) were sequentially added to a 25 mL flame-dried Schlenk tube equipped with a magnetic stir bar. After being stirred at room temperature for 5 h, the solvent was then removed in vacuo. (Z)-**4a** (206.3 mg, 92%) was obtained via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 6.8 \text{ Hz}$, 2 H, ArH), 7.43-7.27 (m, 5 H, ArH), 7.27-7.17 (m, 3 H, ArH), 6.40 (d, $J = 11.6 \text{ Hz}$, 1 H, =CH), 5.81-5.71 (m, 1 H, =CH), 4.40 (t, $J = 3.4 \text{ Hz}$, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si}-\text{H}} = 198.0 \text{ Hz}$, $J = 3.6 \text{ Hz}$, 0.10 H, $^{29}\text{SiH}_2$), 2.22-2.16 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 135.2, 131.5, 129.8, 128.5, 128.3, 128.2, 128.0, 127.3, 126.4, 13.1; MS (EI, 70 eV) m/z (%) 224 (M^+ , 14.90), 196 (100); IR (neat, cm^{-1}) 3011, 2133, 1491, 1427, 1153, 1115; HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{16}\text{Si}$ [M^+]: 224.1021, found: 224.1014.

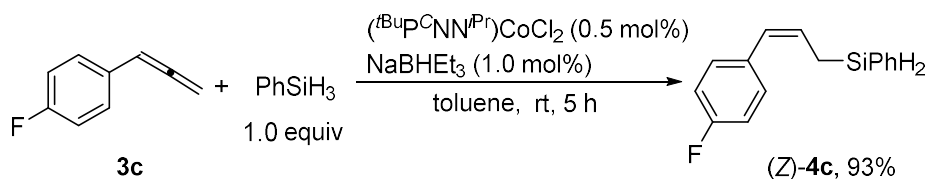
The following compounds were prepared according to **Typical Procedure**.

(2) Preparation of (Z)-(3-(*p*-tolyl)-2-propenyl)(phenyl)silane ((Z)-**4b**) (yz-4-133)



The reaction of (*t*BuP^CNNⁱPr)CoCl₂ (**2b**) (2.8 mg, 0.005 mmol), **3b** (130.1 mg, 1.0 mmol), toluene (1.0 mL), PhSiH₃ (123 μL, d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHET₃ (1.0 M in THF, 10 μL, 0.01 mmol) afforded (Z)-**4b** (220.6 mg, 93%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.55 (m, 2 H, ArH), 7.43-7.32 (m, 3 H, ArH), 7.16-7.09 (m, 4 H, ArH), 6.36 (d, *J* = 11.6 Hz, 1 H, =CH), 5.75-5.67 (m, 1 H, =CH), 4.39 (t, *J* = 3.6 Hz, 1.90 H, ²⁸SiH₂; dt, ¹*J*_{Si-H} = 197.6 Hz, *J* = 3.5 Hz, 0.10 H, ²⁹SiH₂), 2.33 (s, 3 H, CH₃), 2.22-2.15 (m, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 136.0, 135.2, 134.6, 131.6, 129.8, 128.9, 128.4, 128.2, 128.0, 126.6, 21.1, 13.1; MS (EI, 70 eV) *m/z* (%) 238 (M⁺, 20.05), 210 (100); IR (neat, cm⁻¹) 3010, 2133, 1510, 1426, 1115; HRMS (EI) *m/z* calcd. for C₁₆H₁₈Si [M⁺]: 238.1178, found: 238.1182.

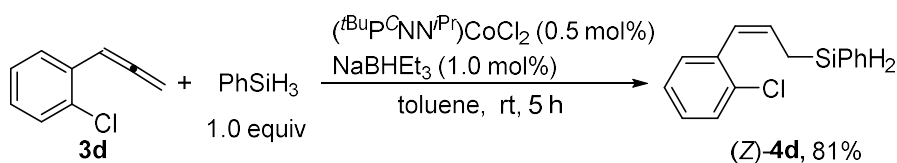
(3) Preparation of (Z)-(3-(4-fluorophenyl)-2-propenyl)(phenyl)silane ((Z)-**4c**) (yz-4-152)



The reaction of (*t*BuP^CNNⁱPr)CoCl₂ (**2b**) (2.9 mg, 0.005 mmol), **3c** (134.3 mg, 1.0 mmol), toluene (1.0 mL), PhSiH₃ (123 μL, d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHET₃ (1.0 M in THF, 10 μL, 0.01 mmol) afforded (Z)-**4c** (224.8 mg, 93%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.54 (m, 2 H, ArH), 7.44-7.32 (m, 3 H, ArH), 7.19-7.13 (m, 2 H, ArH), 7.01-6.94 (m, 2 H, ArH), 6.34 (d, *J* = 11.6 Hz, 1 H, =CH),

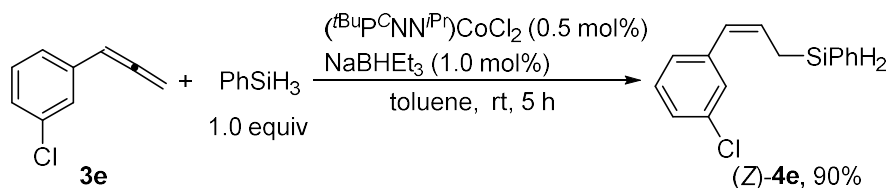
5.74 (dt, $J = 11.6$ Hz, 8.8 Hz, 1 H, =CH), 4.38 (t, $J = 3.6$ Hz, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}} = 198.1$ Hz, $J = 3.7$ Hz, 0.10 H, $^{29}\text{SiH}_2$), 2.17-2.10 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 161.3 (d, $J = 243.9$ Hz), 135.2, 133.5 (d, $J = 3.8$ Hz), 131.4, 130.0 (d, $J = 7.8$ Hz), 129.9, 128.1, 127.3, 127.2, 115.0 (d, $J = 21.0$ Hz), 13.0; ^{19}F NMR (376 MHz, CDCl_3) δ -116.4; MS (EI, 70 eV) m/z (%) 242 (M^+ , 11.03), 107 (100); IR (neat, cm^{-1}) 3012, 2135, 1601, 1505, 1428, 1221, 1156, 1116; HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{15}\text{FSi}$ [M^+]: 242.0927, found: 242.0934.

(4) Preparation of (Z)-(3-(2-chlorophenyl)-2-propenyl)(phenyl)silane ((Z)-**4d**) (yz-4-155)



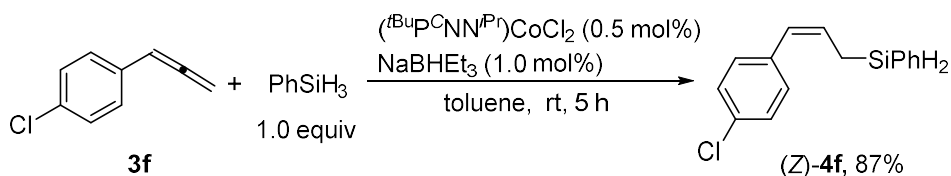
The reaction of $(^t\text{BuPCNNi}^i\text{Pr})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3d** (150.6 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88$ g/mL, 108.2 mg, 1.0 mmol), and NaBHEt_3 (1.0 M in THF, 10 μL , 0.01 mmol) afforded (Z)-**4d** (208.6 mg, 81%) via column chromatography on silica gel (eluent: petroleum ether (60-90 $^\circ\text{C}$)) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.52 (m, 2 H, ArH), 7.43-7.32 (m, 4 H, ArH), 7.26-7.20 (m, 1 H, ArH), 7.19-7.12 (m, 2 H, ArH), 6.46 (d, $J = 11.6$ Hz, 1 H, =CH), 5.89 (dt, $J = 11.6$ Hz, 8.8 Hz, 1 H, =CH), 4.36 (t, $J = 3.6$ Hz, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}} = 198.7$ Hz, $J = 3.7$ Hz, 0.10 H, $^{29}\text{SiH}_2$), 2.10-2.03 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 135.6, 135.2, 133.6, 131.3, 130.2, 129.9, 129.4, 128.9, 128.1, 127.9, 126.2, 125.7, 13.0; MS (EI, 70 eV) m/z (%) 260 (M^+ (^{37}Cl), 1.34), 258 (M^+ (^{35}Cl), 3.30), 115 (100); IR (neat, cm^{-1}) 2134, 1469, 1430, 1116, 1034; HRMS (EI) m/z calcd. for $\text{C}_{15}\text{H}_{15}^{35}\text{ClSi}$ [M^+]: 258.0632, found: 258.0621.

(5) Preparation of (Z)-(3-(3-chlorophenyl)-2-propenyl)(phenyl)silane ((Z)-**4e**) (yz-4-169)



The reaction of (*t*BuP^CNNⁱPr)CoCl₂ (**2b**) (2.8 mg, 0.005 mmol), **3e** (150.7 mg, 1.0 mmol), toluene (1.0 mL), PhSiH₃ (123 μL, d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHET₃ (1.0 M in THF, 10 μL, 0.01 mmol) afforded (*Z*)-**4e** (232.2 mg, 90%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 6.4 Hz, 2 H, ArH), 7.44-7.32 (m, 3 H, ArH), 7.24-7.13 (m, 3 H, ArH), 7.08 (d, *J* = 7.2 Hz, 1 H, ArH), 6.31 (d, *J* = 11.6 Hz, 1 H, =CH), 5.80 (dt, *J* = 11.6 Hz, 9.0 Hz, 1 H, =CH), 4.39 (t, *J* = 3.4 Hz, 1.90 H, ²⁸SiH₂; dt, ¹*J*_{Si-H} = 198.5 Hz, *J* = 3.5 Hz, 0.10 H, ²⁹SiH₂), 2.19-2.11 (m, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 139.3, 135.2, 134.0, 131.1, 129.9, 129.3, 128.8, 128.5, 128.1, 127.0, 126.6, 126.4, 13.3; MS (EI, 70 eV) *m/z* (%) 260 (M⁺ (³⁷Cl), 3.90), 258 (M⁺ (³⁵Cl), 11.35), 115 (100); IR (neat, cm⁻¹) 3012, 2135, 1591, 1562, 1475, 1426, 1191, 1115; HRMS (EI) *m/z* calcd. for C₁₅H₁₅³⁵ClSi [M⁺]: 258.0632, found: 258.0640.

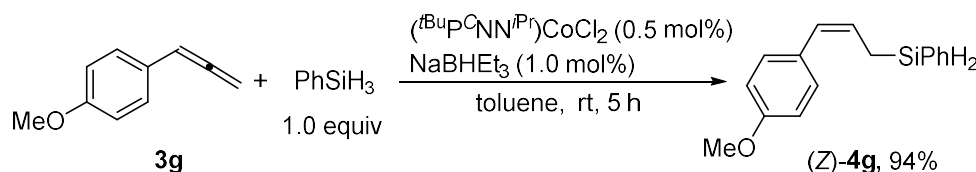
(6) Preparation of (*Z*)-(3-(4-chlorophenyl)-2-propenyl)(phenyl)silane ((*Z*)-**4f**) (yz-4-134)



The reaction of (*t*BuP^CNNⁱPr)CoCl₂ (**2b**) (2.8 mg, 0.005 mmol), **3f** (150.7 mg, 1.0 mmol), toluene (1.0 mL), PhSiH₃ (123 μL, d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHET₃ (1.0 M in THF, 10 μL, 0.01 mmol) afforded (*Z*)-**4f** (225.5 mg, 87%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.53 (m, 2 H, ArH), 7.45-7.32 (m, 3 H, ArH), 7.28-7.23 (m, 2 H, ArH), 7.13 (d, *J* = 8.4 Hz, 2 H, ArH), 6.33 (d, *J* = 11.6 Hz, 1 H, =CH), 5.78 (dt, *J* = 11.6 Hz, 9.2 Hz, 1 H, =CH), 4.38 (t, *J* = 3.6 Hz, 1.90 H, ²⁸SiH₂; dt, ¹*J*_{Si-H} = 198.4 Hz, *J* = 3.6 Hz, 0.10 H, ²⁹SiH₂), 2.18-2.11 (m, 2 H, CH₂); ¹³C NMR

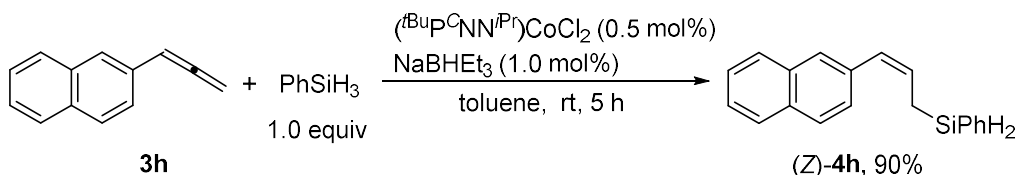
(100 MHz, CDCl₃) δ 135.9, 135.2, 132.0, 131.2, 129.9, 129.8, 128.3, 128.13, 128.07, 127.1, 13.2; MS (EI, 70 eV) m/z (%) 260 (M^+ (³⁷Cl), 3.68), 258 (M^+ (³⁵Cl), 9.06), 115 (100); IR (neat, cm⁻¹) 3012, 2135, 1488, 1426, 1115, 1089, 1012; HRMS (EI) m/z calcd. for C₁₅H₁₅³⁵ClSi [M^+]: 258.0632, found: 258.0623.

(7) Preparation of (Z)-(3-(4-methoxyphenyl)-2-propenyl)(phenyl)silane ((Z)-**4g**) (yz-4-142)



The reaction of (^tBuP^CNNⁱPr)CoCl₂ (**2b**) (2.8 mg, 0.005 mmol), **3g** (146.1 mg, 1.0 mmol), toluene (1.0 mL), PhSiH₃ (123 μ L, d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHET₃ (1.0 M in THF, 10 μ L, 0.01 mmol) afforded (Z)-**4g** (238.1 mg, 94%) via column chromatography on silica gel (petroleum ether (60-90 °C)/ ethyl acetate = 10/1) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.56 (m, 2 H, ArH), 7.44-7.33 (m, 3 H, ArH), 7.23-7.16 (m, 2 H, ArH), 6.87-6.82 (m, 2 H, ArH), 6.33 (d, J = 11.6 Hz, 1 H, =CH), 5.67 (dt, J = 11.6 Hz, 8.8 Hz, 1 H, =CH), 4.39 (t, J = 3.6 Hz, 1.90 H, ²⁸SiH₂; dt, ¹ J_{Si-H} = 197.9 Hz, J = 3.7 Hz, 0.10 H, ²⁹SiH₂), 3.81 (s, 3 H, CH₃), 2.21-2.13 (m, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 158.0, 135.2, 131.5, 130.1, 129.8, 129.7, 128.0, 127.7, 125.7, 113.5, 55.1, 13.0; MS (EI, 70 eV) m/z (%) 254 (M^+ , 25.14), 147 (100); IR (neat, cm⁻¹) 3005, 2132, 1605, 1508, 1427, 1300, 1243, 1174, 1114, 1034; HRMS (EI) m/z calcd. for C₁₆H₁₈OSi [M^+]: 254.1127, found: 254.1122.

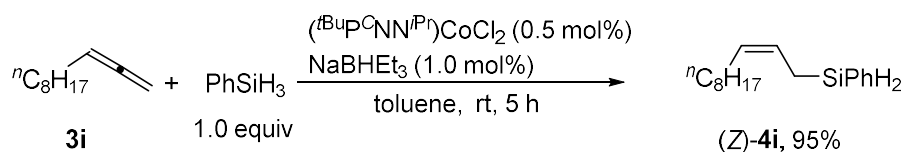
(8) Preparation of (Z)-(3-(naphthalen-2-yl)-2-propenyl)(phenyl)silane ((Z)-**4h**) (yz-4-147)



The reaction of (^tBuP^CNNⁱPr)CoCl₂ (**2b**) (2.8 mg, 0.005 mmol), **3h** (166.3 mg, 1.0

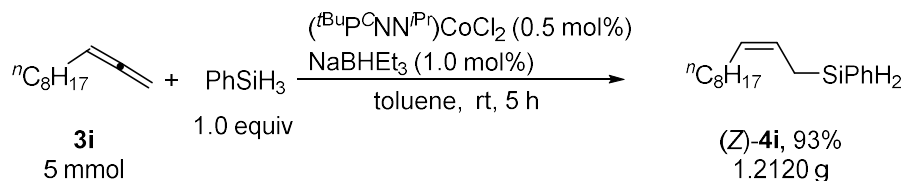
mmol), toluene (1.0 mL), PhSiH₃ (123 μL, d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHET₃ (1.0 M in THF, 10 μL, 0.01 mmol) afforded (Z)-**4h** (246.6 mg, 90%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.79-7.68 (m, 3 H, ArH), 7.62 (s, 1 H, ArH), 7.60-7.55 (m, 2 H, ArH), 7.45-7.30 (m, 6 H, ArH), 6.53 (d, *J* = 11.2 Hz, 1 H, =CH), 5.84 (dt, *J* = 11.2 Hz, 9.2 Hz, 1 H, =CH), 4.44 (t, *J* = 3.8 Hz, 1.90 H, ²⁸SiH₂; dt, ¹*J*_{Si-H} = 198.1 Hz, *J* = 3.7 Hz, 0.10 H, ²⁹SiH₂), 2.27-2.22 (m, 2 H, CH₂); ¹³C NMR (100 MHz, CDCl₃) δ 135.3, 135.0, 133.3, 132.0, 131.5, 129.9, 128.3, 128.1, 127.87, 127.86, 127.6, 127.5, 127.1, 127.0, 126.0, 125.6, 13.4; MS (EI, 70 eV) *m/z* (%) 274 (M⁺, 37.44), 167 (100); IR (neat, cm⁻¹) 3050, 3008, 2132, 1594, 1503, 1426, 1268, 1151, 1115; HRMS (EI) *m/z* calcd. for C₁₉H₁₈Si [M⁺]: 274.1178, found: 274.1174.

(9) Preparation of (Z)-(2-undecen-1-yl)(phenyl)silane ((Z)-**4i**) (yz-4-175)



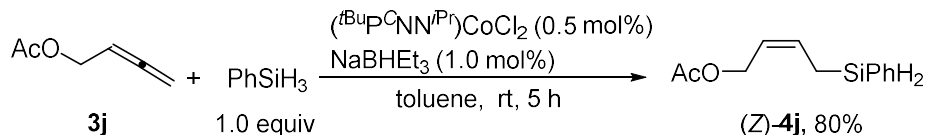
The reaction of (tBuP^CNN^{tPr})CoCl₂ (**2b**) (2.8 mg, 0.005 mmol), **3i** (152.2 mg, 1.0 mmol), toluene (1.0 mL), PhSiH₃ (123 μL, d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHET₃ (1.0 M in THF, 10 μL, 0.01 mmol) afforded (Z)-**4i** (246.3 mg, 95%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 6.8 Hz, 2 H, ArH), 7.43-7.31 (m, 3 H, ArH), 5.48-5.40 (m, 1 H, =CH), 5.38-5.28 (m, 1 H, =CH), 4.29 (t, *J* = 3.4 Hz, 1.90 H, ²⁸SiH₂; dt, ¹*J*_{Si-H} = 196.5 Hz, *J* = 3.8 Hz, 0.10 H, ²⁹SiH₂), 1.98-1.90 (m, 2 H, CH₂), 1.90-1.84 (m, 2 H, CH₂), 1.35-1.20 (m, 12 H, 6 × CH₂), 0.88 (t, *J* = 6.6 Hz, 3 H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 135.2, 132.2, 129.69, 129.65, 127.9, 123.8, 31.9, 29.6, 29.5, 29.4, 29.3, 27.0, 22.7, 14.1, 11.7; MS (EI, 70 eV) *m/z* (%) 260 (M⁺, 3.04), 107 (100); IR (neat, cm⁻¹) 2923, 2853, 2135, 1461, 1429, 1152, 1116; HRMS (EI) *m/z* calcd. for C₁₇H₂₈Si [M⁺]: 260.1960, found: 260.1956.

Gram scale reaction of **3i** (yz-5-004)



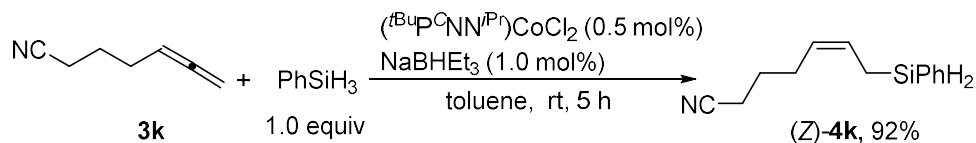
The reaction of $(t\text{BuP}^{\text{C}}\text{NN}^{i\text{Pr}})\text{CoCl}_2$ (**2b**) (14.2 mg, 0.025 mmol), **3i** (761.0 mg, 5.0 mmol), toluene (5.0 mL), PhSiH_3 (615 μL , $d = 0.88 \text{ g/mL}$, 541.2 mg, 5.0 mmol), and NaBHET_3 (1.0 M in THF, 50 μL , 0.05 mmol) afforded (Z)-**4i** (1.2120 g, 93%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.54 (m, 2 H, ArH), 7.44-7.32 (m, 3 H, ArH), 5.48-5.39 (m, 1 H, =CH), 5.38-5.29 (m, 1 H, =CH), 4.29 (t, $J = 3.6 \text{ Hz}$, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}} = 196.5 \text{ Hz}$, $J = 3.5 \text{ Hz}$, 0.10 H, $^{29}\text{SiH}_2$), 1.98-1.91 (m, 2 H, CH_2), 1.90-1.83 (m, 2 H, CH_2), 1.35-1.20 (m, 12 H, $6 \times \text{CH}_2$), 0.88 (t, $J = 6.8 \text{ Hz}$, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 135.2, 132.2, 129.69, 129.66, 127.9, 123.8, 31.9, 29.6, 29.5, 29.4, 29.3, 27.0, 22.7, 14.1, 11.7.

(10) Preparation of (Z)-(4-acetoxy-2-butenyl)(phenyl)silane ((Z)-**4j**) (yz-4-165)



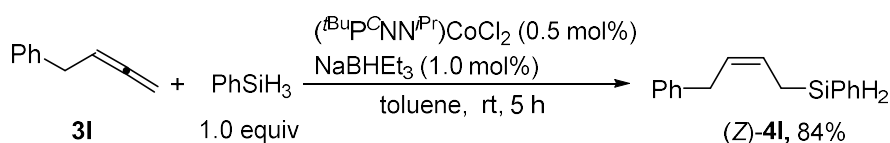
The reaction of $(t\text{BuP}^{\text{C}}\text{NN}^{i\text{Pr}})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3j** (112.3 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88 \text{ g/mL}$, 108.2 mg, 1.0 mmol), and NaBHET_3 (1.0 M in THF, 10 μL , 0.01 mmol) afforded (Z)-**4j** (175.6 mg, 80%) via column chromatography on silica gel (petroleum ether (60-90 °C)/ ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.54 (m, 2 H, ArH), 7.44-7.33 (m, 3 H, ArH), 5.80-5.72 (m, 1 H, =CH), 5.54-5.46 (m, 1 H, =CH), 4.50 (d, $J = 6.8 \text{ Hz}$, 2 H, OCH_2), 4.31 (t, $J = 3.8 \text{ Hz}$, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}} = 198.8 \text{ Hz}$, $J = 3.6 \text{ Hz}$, 0.10 H, $^{29}\text{SiH}_2$), 2.03 (s, 3 H, CH_3), 2.00-1.94 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 135.2, 131.2, 130.3, 129.9, 128.0, 122.5, 59.9, 20.9, 12.6; MS (ESI) m/z 243 ($[\text{M}+\text{Na}]^+$), 238 ($[\text{M}+\text{NH}_4]^+$); IR (neat, cm^{-1}) 2136, 1735, 1427, 1370, 1226, 1152, 1116, 1023; HRMS (ESI) m/z calcd. for $\text{C}_{12}\text{H}_{20}\text{NO}_2\text{Si}$ ($[\text{M}+\text{NH}_4]^+$): 238.1258, found: 238.1256

(11) Preparation of (Z)-(6-cyano-2-hexenyl)(phenyl)silane ((Z)-**4k**) (yz-4-176)



The reaction of $(t\text{Bu}^{\text{C}}\text{P}^{\text{C}}\text{NN}^{\text{iPr}})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3k** (107.4 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88 \text{ g/mL}$, 108.2 mg, 1.0 mmol), and NaBHET_3 (1.0 M in THF, 10 μL , 0.01 mmol) afforded (Z)-**4k** (197.5 mg, 92%) via column chromatography on silica gel (petroleum ether (60-90 °C)/ ethyl acetate = 20/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 6.4 \text{ Hz}$, 2 H, ArH), 7.45-7.33 (m, 3 H, ArH), 5.62-5.53 (m, 1 H, =CH), 5.28-5.20 (m, 1 H, =CH), 4.30 (t, $J = 3.2 \text{ Hz}$, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{\text{Si-H}} = 197.6 \text{ Hz}$, $J = 3.2 \text{ Hz}$, 0.10 H, $^{29}\text{SiH}_2$), 2.23 (t, $J = 7.4 \text{ Hz}$, 2 H, CH_2CN), 2.08 (q, $J = 7.3 \text{ Hz}$, 2 H, CH_2), 1.92-1.86 (m, 2 H, CH_2), 1.59 (quint, $J = 7.3 \text{ Hz}$, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 135.3, 131.7, 129.8, 128.0, 126.6, 126.3, 119.7, 25.8, 25.2, 16.4, 12.1; MS (EI, 70 eV) m/z (%) 215 (M^+ , 2.24), 107 (100); IR (neat, cm^{-1}) 3010, 2936, 2246, 2133, 1426, 1153, 1115; HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{NSi}$ [M^+]: 215.1130, found: 215.1122.

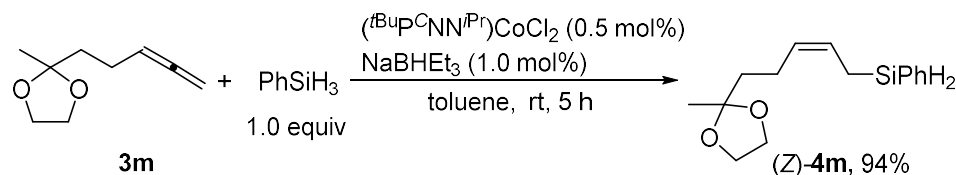
(12) Preparation of (Z)-(4-phenyl-2-butenyl)(phenyl)silane ((Z)-**4l**) (yz-4-180)



The reaction of $(t\text{Bu}^{\text{C}}\text{P}^{\text{C}}\text{NN}^{\text{iPr}})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3l** (130.2 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88 \text{ g/mL}$, 108.2 mg, 1.0 mmol), and NaBHET_3 (1.0 M in THF, 10 μL , 0.01 mmol) afforded (Z)-**4l** (199.2 mg, 84%) via column chromatography on silica gel (eluent: petroleum ether (60-90 °C)) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.56 (m, 2 H, ArH), 7.43-7.32 (m, 3 H, ArH), 7.28-7.21 (m, 2 H, ArH), 7.20-7.10 (m, 3 H, ArH), 5.65-5.58 (m, 2 H, $2 \times =\text{CH}$), 4.34 (t, $J = 3.8 \text{ Hz}$, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{\text{Si-H}} = 197.5 \text{ Hz}$, $J = 3.7 \text{ Hz}$, 0.10 H, $^{29}\text{SiH}_2$), 3.31 (d, $J = 6.8 \text{ Hz}$, 2 H, CH_2), 2.01-1.95 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ

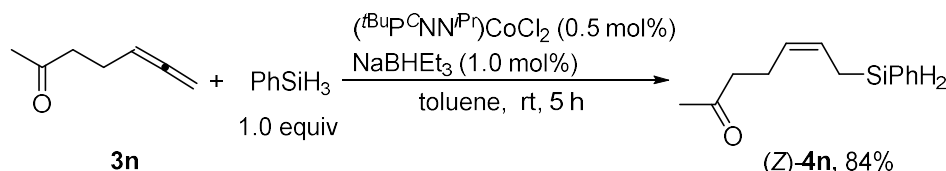
141.0, 135.3, 131.9, 129.8, 128.4, 128.0, 127.7, 125.8, 125.2, 33.2, 11.9; MS (EI, 70 eV) m/z (%) 238 (M^+ , 2.35), 160 (100); IR (neat, cm^{-1}) 2133, 1492, 1427, 1152, 1115; HRMS (EI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{Si}$ [M^+]: 238.1178, found: 238.1183.

(13) Preparation of (Z)-(5-(2-methyl-1,3-dioxolan-2-yl)-2-pentenyl)(phenyl)silane ((Z)-**4m**) (yz-4-198)



The reaction of $(t\text{BuPCNNiPr})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3m** (154.4 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88 \text{ g/mL}$, 108.2 mg, 1.0 mmol), and NaBHET_3 (1.0 M in THF, 10 μL , 0.01 mmol) afforded (Z)-**4m** (247.0 mg, 94%) via column chromatography on silica gel (petroleum ether (60-90 $^\circ\text{C}$)/ ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.55 (m, 2 H, ArH), 7.42-7.32 (m, 3 H, ArH), 5.50-5.42 (m, 1 H, =CH), 5.37-5.29 (m, 1 H, =CH), 4.29 (t, $J = 3.6 \text{ Hz}$, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}} = 196.8 \text{ Hz}$, $J = 3.8 \text{ Hz}$, 0.10 H, $^{29}\text{SiH}_2$), 3.92-3.86 (m, 4 H, $2 \times \text{OCH}_2$), 2.09-2.01 (m, 2 H, CH_2), 1.91-1.86 (m, 2 H, CH_2), 1.64-1.56 (m, 2 H, CH_2), 1.29 (s, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 135.2, 132.1, 129.7, 128.8, 127.9, 124.3, 109.8, 64.6, 38.8, 23.8, 21.8, 11.7; MS (ESI) m/z 263 ($[\text{M}+\text{H}]^+$); IR (neat, cm^{-1}) 2982, 2877, 2133, 1428, 1375, 1215, 1116, 1057; HRMS (ESI) m/z calcd. for $\text{C}_{15}\text{H}_{23}\text{O}_2\text{Si}$ ($[\text{M}+\text{H}]^+$): 263.1462, found: 263.1459.

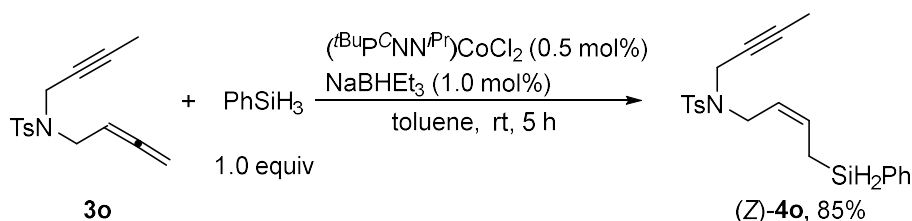
(14) Preparation of (Z)-(6-oxo-2-heptenyl)(phenyl)silane ((Z)-**4n**) (yz-5-001)



The reaction of $(t\text{BuPCNNiPr})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3n** (110.3 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88 \text{ g/mL}$, 108.2 mg, 1.0 mmol), and NaBHET_3 (1.0 M in THF, 10 μL , 0.01 mmol) afforded (Z)-**4n** (183.2 mg, 84%) via

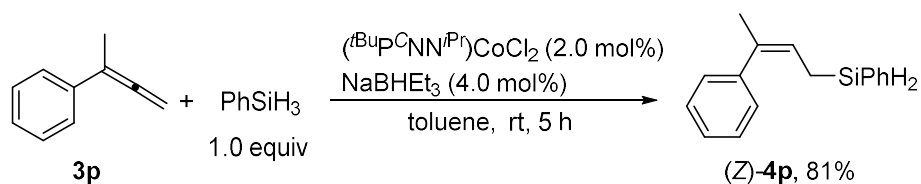
column chromatography on silica gel (petroleum ether (60-90 °C)/ ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.54 (m, 2 H, ArH), 7.43-7.32 (m, 3 H, ArH), 5.54-5.44 (m, 1 H, =CH), 5.32-5.24 (m, 1 H, =CH), 4.29 (t, J = 3.6 Hz, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}}$ = 197.2 Hz, J = 3.6 Hz, 0.10 H, $^{29}\text{SiH}_2$), 2.32 (t, J = 7.4 Hz, 2 H, CH_2), 2.24-2.16 (m, 2 H, CH_2), 2.08 (s, 3 H, CH_3), 1.92-1.85 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 208.4, 135.3, 131.9, 129.7, 128.0, 127.2, 125.4, 43.3, 29.9, 21.3, 11.9; MS (EI, 70 eV) m/z (%) 218 (M^+ , 55.02), 123 (100); IR (neat, cm^{-1}) 3009, 2132, 1713, 1427, 1359, 1157, 1115; HRMS (EI) m/z calcd. for $\text{C}_{13}\text{H}_{18}\text{OSi}$ [M^+]: 218.1127, found: 218.1137.

(15) Preparation of (*Z*)-*N*-tosyl-5-azanon-2-en-7-yn-1-yl(phenyl)silane ((*Z*)-**4o**) (yz-4-184)



The reaction of $(t\text{BuPCNN}^i\text{Pr})\text{CoCl}_2$ (**2b**) (2.8 mg, 0.005 mmol), **3o** (275.5 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , d = 0.88 g/mL, 108.2 mg, 1.0 mmol), and NaBHEt_3 (1.0 M in THF, 10 μL , 0.01 mmol) afforded (*Z*)-**4o** (324.6 mg, 85%) via column chromatography on silica gel (petroleum ether (60-90 °C)/ ethyl acetate = 10/1) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 8.0 Hz, 2 H, ArH), 7.57-7.52 (m, 2 H, ArH), 7.45-7.33 (m, 3 H, ArH), 7.28 (d, J = 8.4 Hz, 2 H, ArH), 5.78-5.69 (m, 1 H, =CH), 5.32-5.25 (m, 1 H, =CH), 4.29 (t, J = 3.6 Hz, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}}$ = 198.8 Hz, J = 3.6 Hz, 0.10 H, $^{29}\text{SiH}_2$), 3.97-3.93 (m, 2 H, CH_2), 3.68 (d, J = 7.2 Hz, 2 H, CH_2), 2.42 (s, 3 H, CH_3), 1.98-1.91 (m, 2 H, CH_2), 1.50 (t, J = 2.2 Hz, 3 H, CH_3); ^{13}C NMR (100 MHz, CDCl_3) δ 143.1, 136.0, 135.2, 131.4, 130.8, 129.9, 129.1, 128.0, 127.9, 122.4, 81.4, 72.0, 42.5, 36.1, 21.5, 12.3, 3.2; MS (EI, 70 eV) m/z (%) 383 (M^+ , 1.23), 87 (100); IR (neat, cm^{-1}) 2134, 1596, 1429, 1344, 1157, 1114, 1092; HRMS (EI) m/z calcd. for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{SSi}$ [M^+]: 383.1375, found: 383.1376.

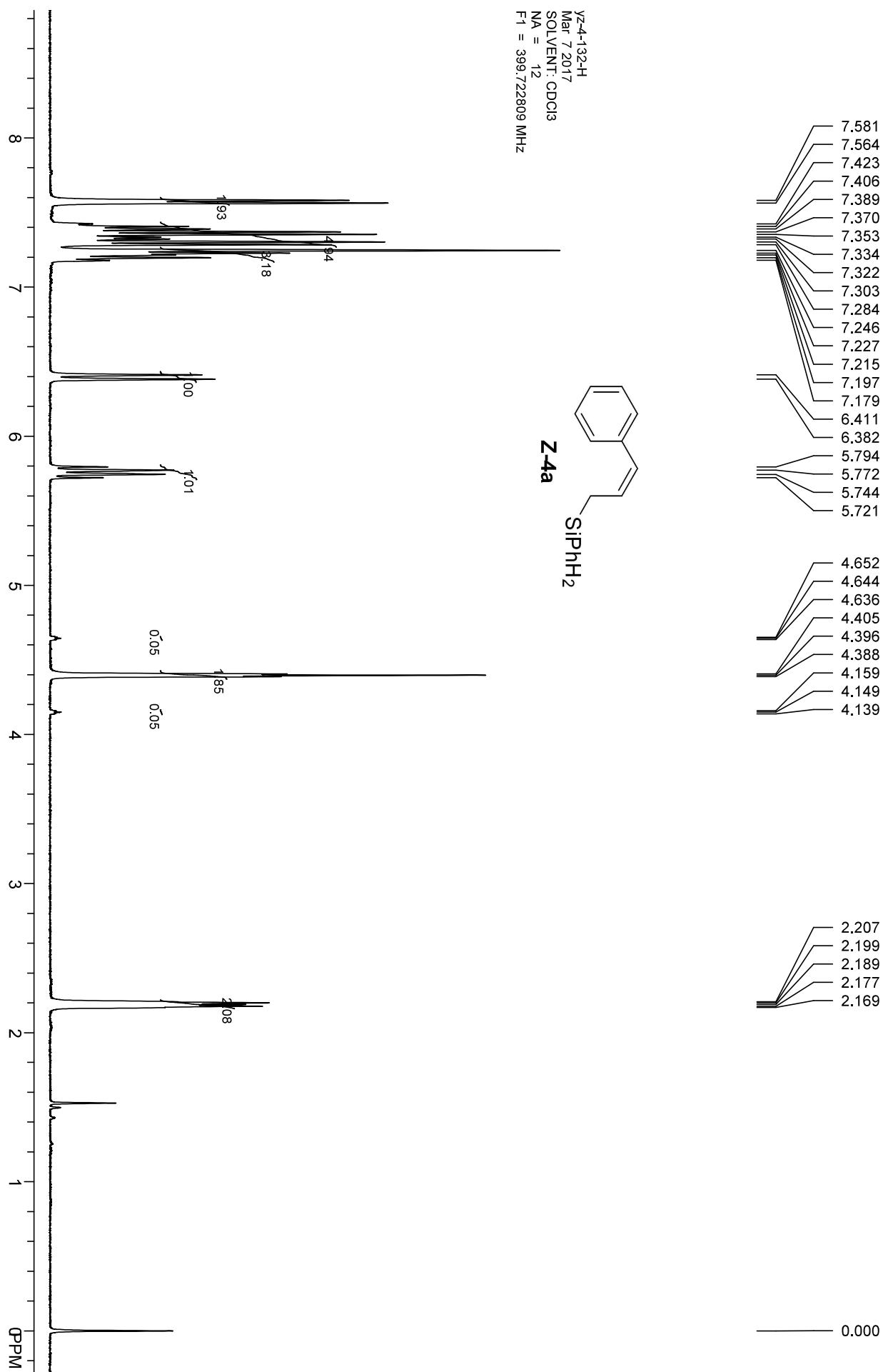
(16) Preparation of (Z)-phenyl(3-phenyl-2-butenyl)silane ((Z)-**4p**) (yz-4-148)



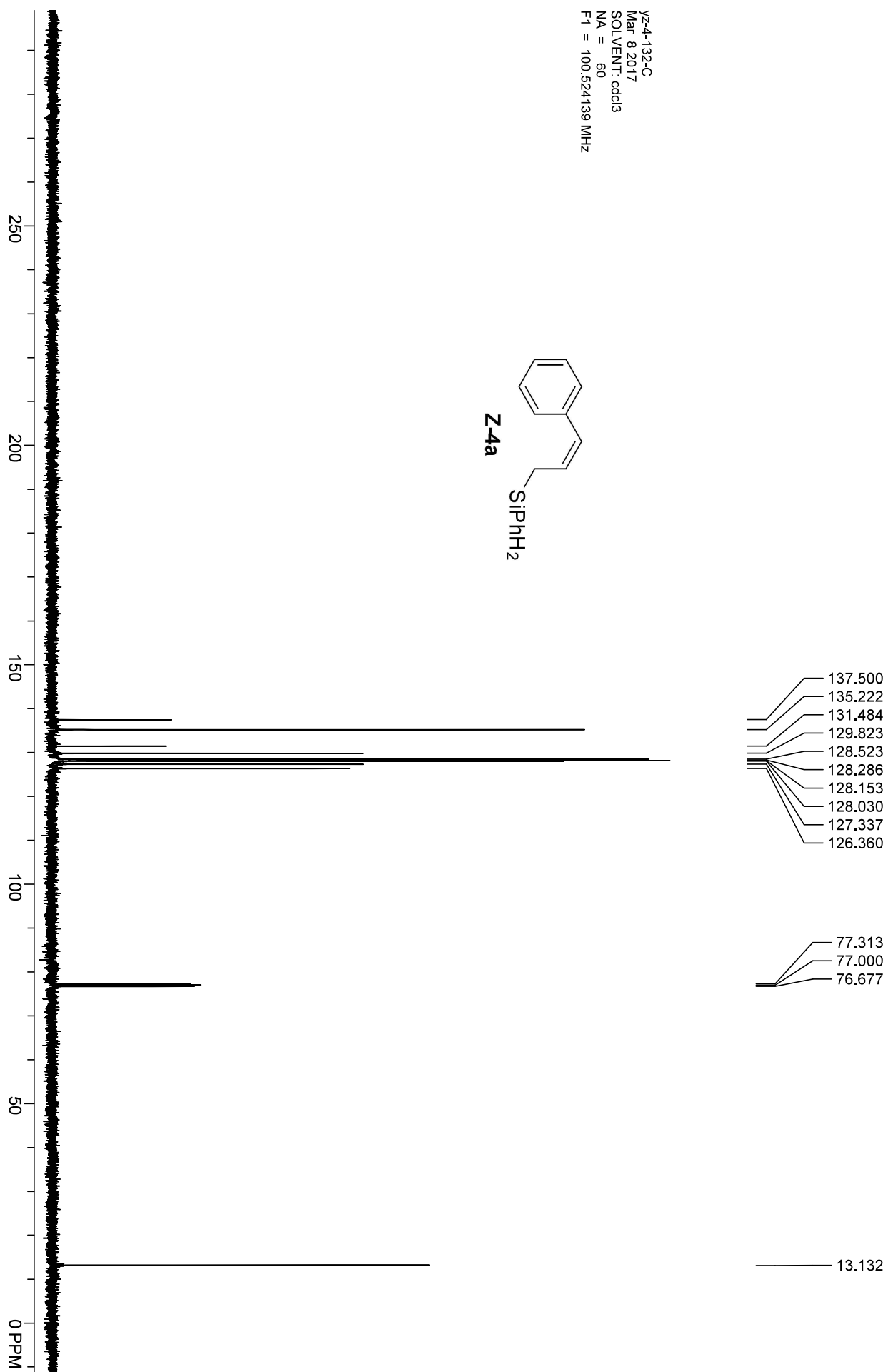
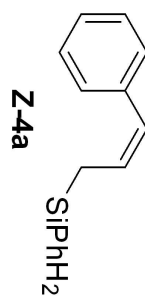
The reaction of $(t\text{BuPCNN}^{i\text{Pr}})\text{CoCl}_2$ (**2b**) (11.4 mg, 0.02 mmol), **3p** (130.2 mg, 1.0 mmol), toluene (1.0 mL), PhSiH_3 (123 μL , $d = 0.88 \text{ g/mL}$, 108.2 mg, 1.0 mmol), and NaBHEt_3 (1.0 M in THF, 40 μL , 0.04 mmol) afforded (Z)-**4p** (192.2 mg, 81%) via column chromatography on silica gel (petroleum ether (60-90 °C)) as an oil: ^1H NMR (400 MHz, CDCl_3) δ 7.51-7.47 (m, 2 H, ArH), 7.40-7.26 (m, 5 H, ArH), 7.23-7.18 (m, 1 H, ArH), 7.12-7.08 (m, 2 H, ArH), 5.53 (td, $J = 8.4 \text{ Hz}$, 1.3 Hz , 1 H, =CH), 4.28 (t, $J = 3.8 \text{ Hz}$, 1.90 H, $^{28}\text{SiH}_2$; dt, $^1J_{^{29}\text{Si-H}} = 196.5 \text{ Hz}$, $J = 3.7 \text{ Hz}$, 0.10 H, $^{29}\text{SiH}_2$), 2.00 (d, $J = 1.2 \text{ Hz}$, 3 H, CH_3), 1.84-1.78 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, CDCl_3) δ 141.9, 136.0, 135.2, 132.0, 129.6, 128.1, 128.0, 127.9, 126.4, 121.6, 25.7, 12.9; MS (EI, 70 eV) m/z (%) 238 (M^+ , 39.83), 131 (100); IR (neat, cm^{-1}) 2131, 1491, 1429, 1364, 1157, 1115, 1069, 1028. HRMS (EI) m/z calcd. for $\text{C}_{16}\text{H}_{18}\text{Si}$ [M^+]: 238.1178, found: 238.1172.

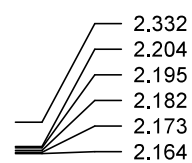
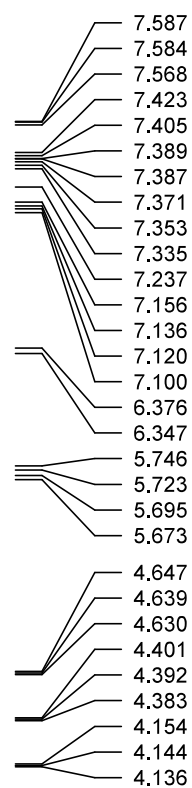
References:

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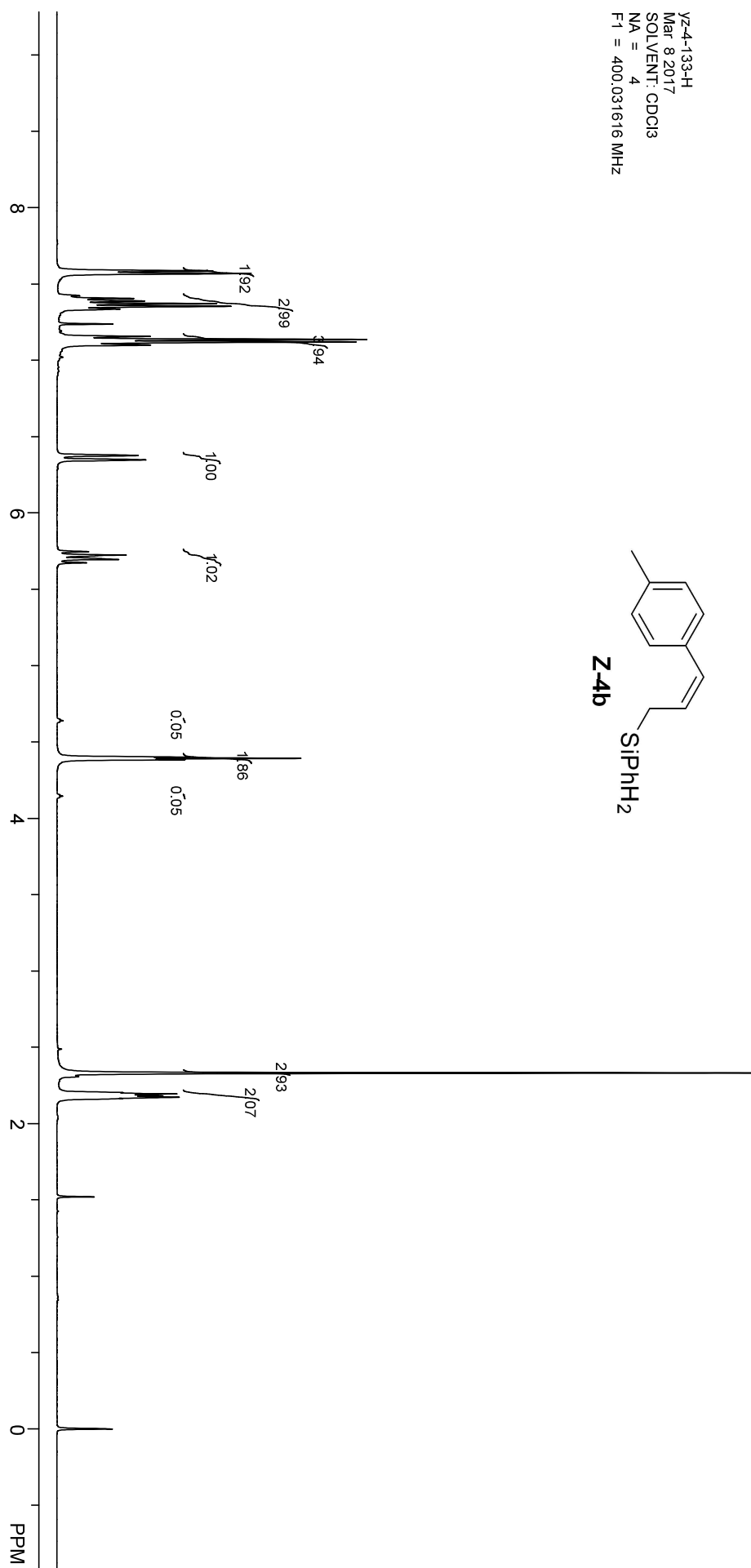
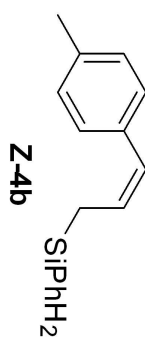
yz-4-132-C
Mar 8 2017
SOLVENT: cdcl3
NA = 60
F1 = 100.524139 MHz



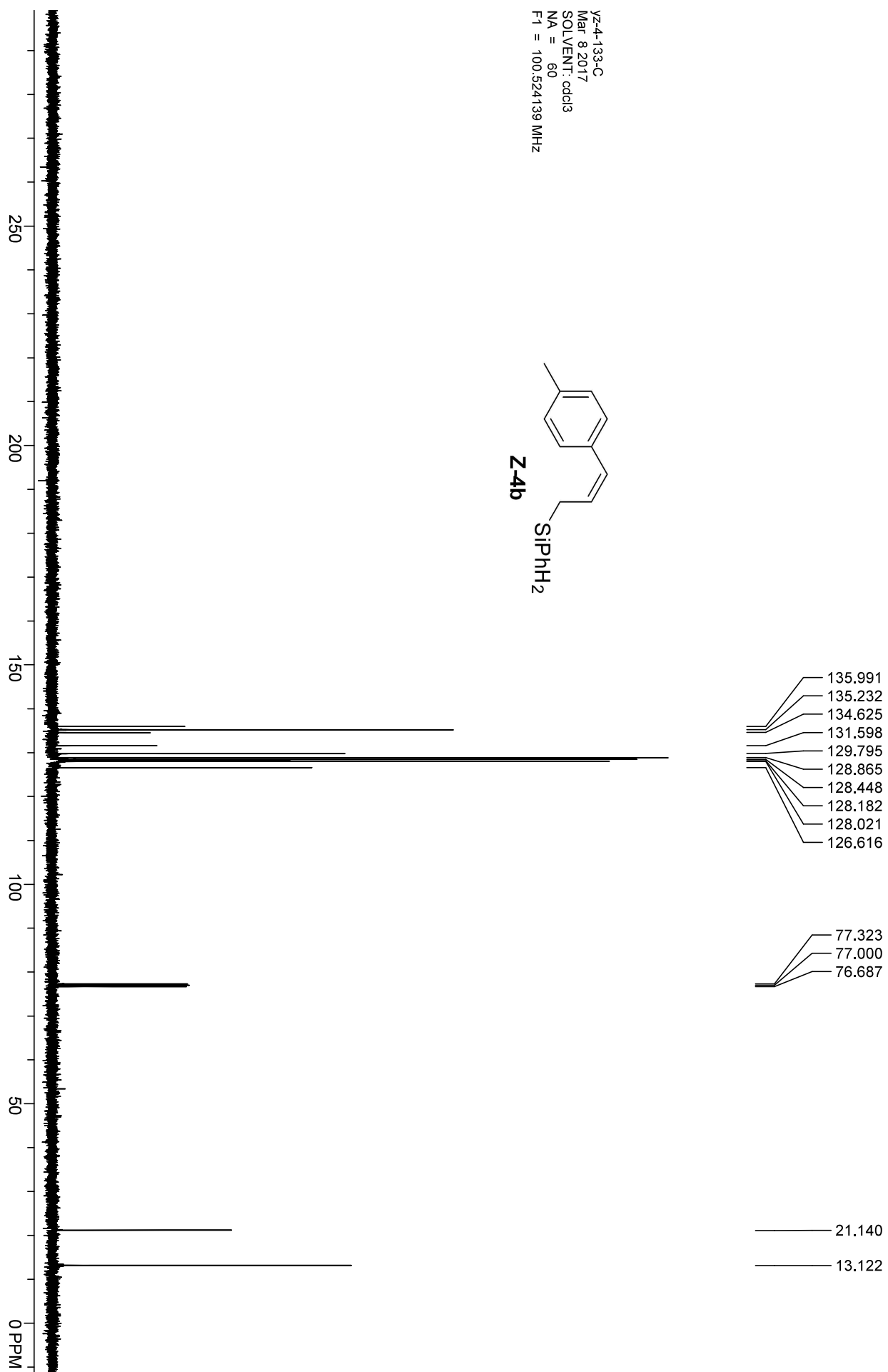
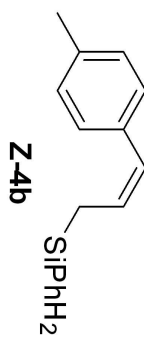


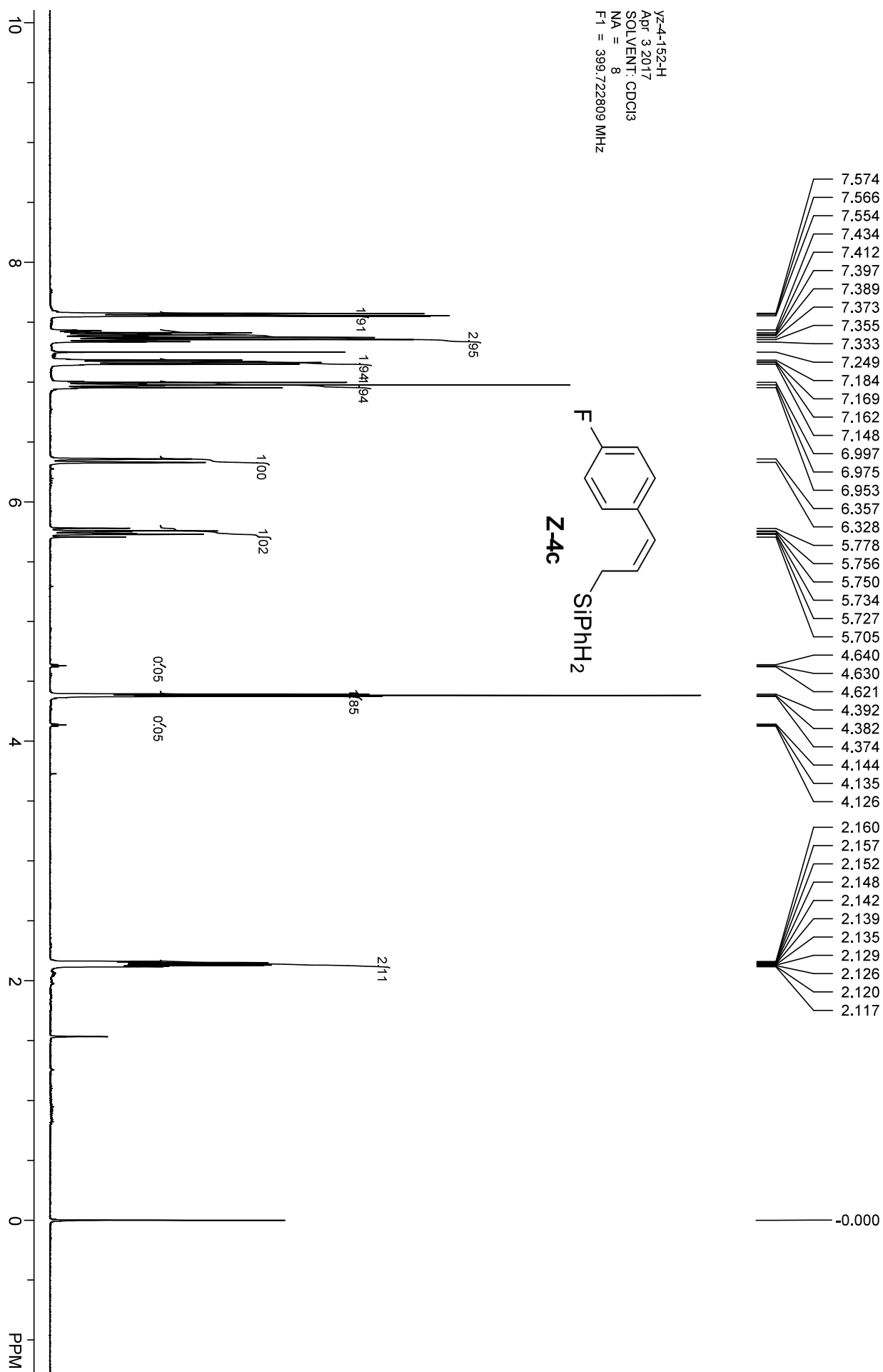
-0.000

YZ-4-133-H
Mar 8 2017
SOLVENT: CDCl3
NA = 4
F1 = 400.031616 MHz

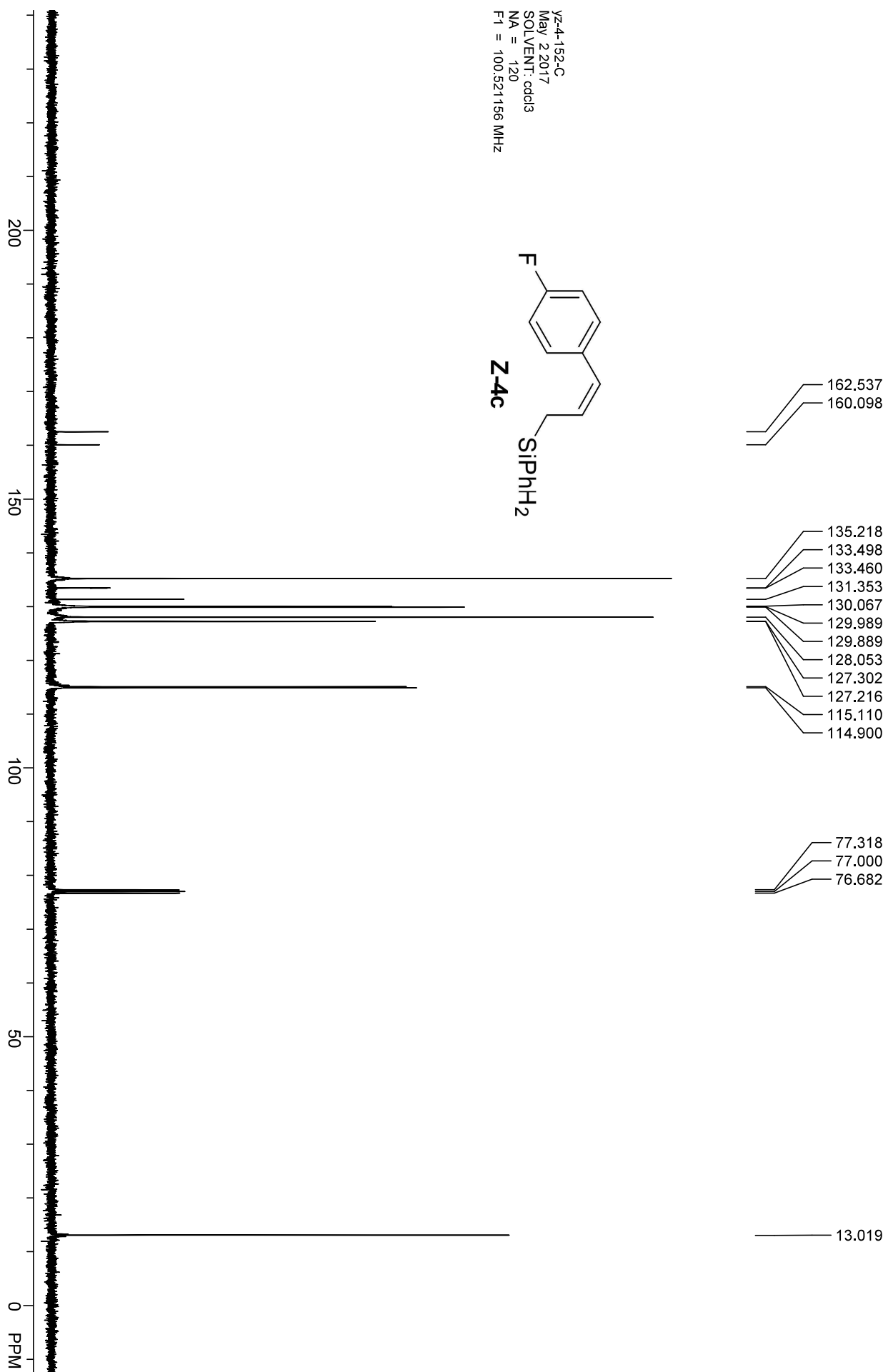
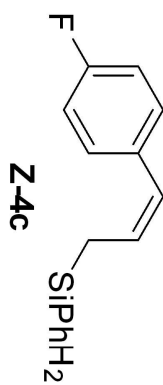


yz-4-133-C
Mar 8 2017
SOLVENT: cdcl3
NA = 60
F1 = 100.524139 MHz

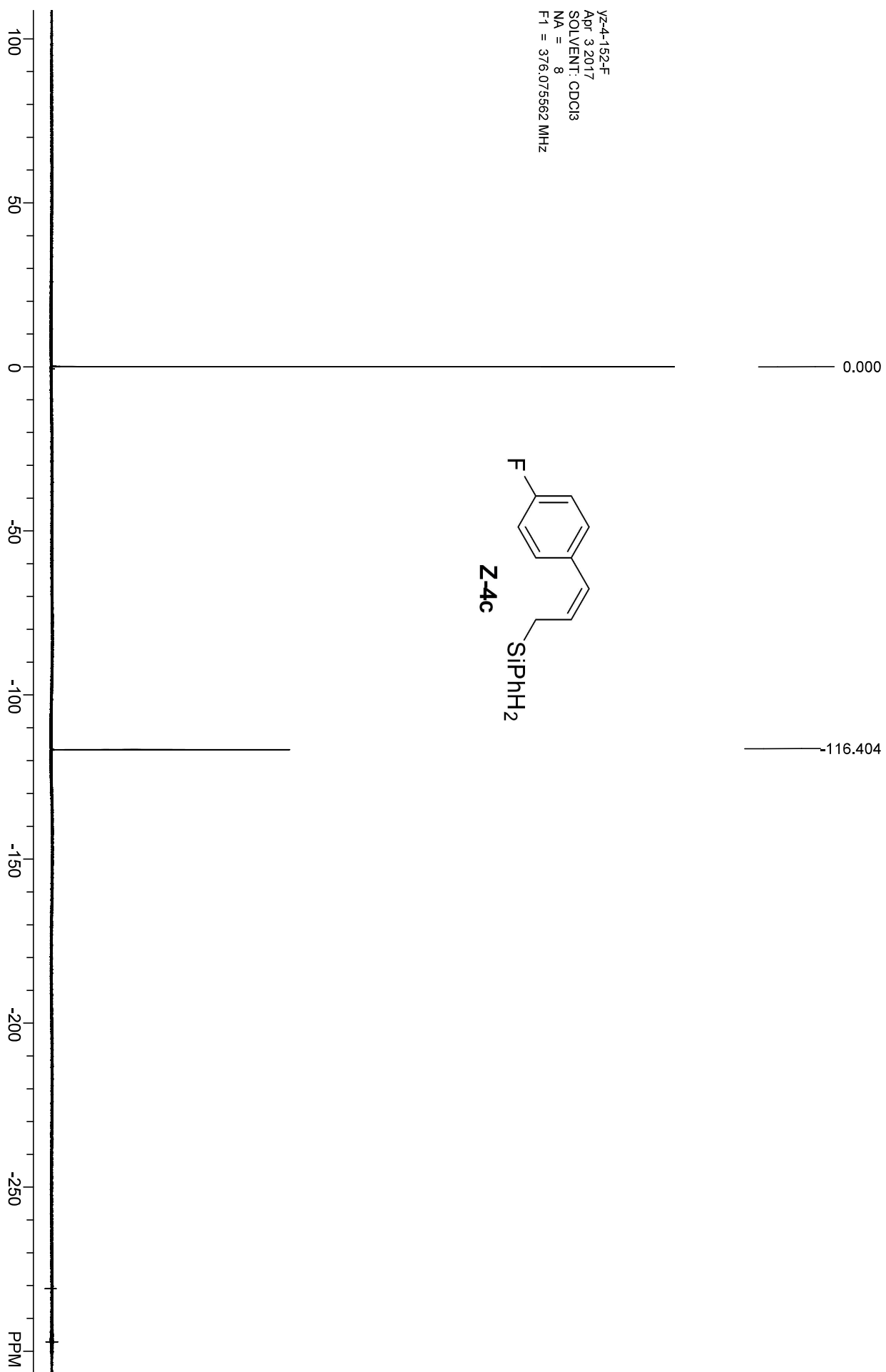
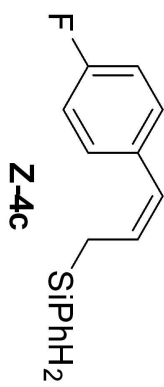


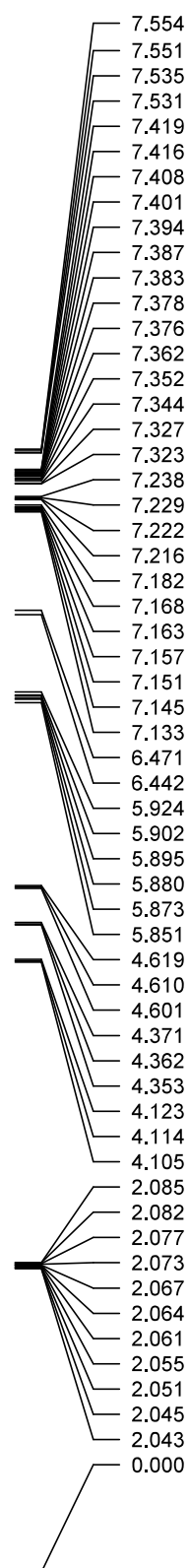


YZ-4-152-C
May 2 2017
SOLVENT: cdcl3
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F1 = 100.521156 MHz

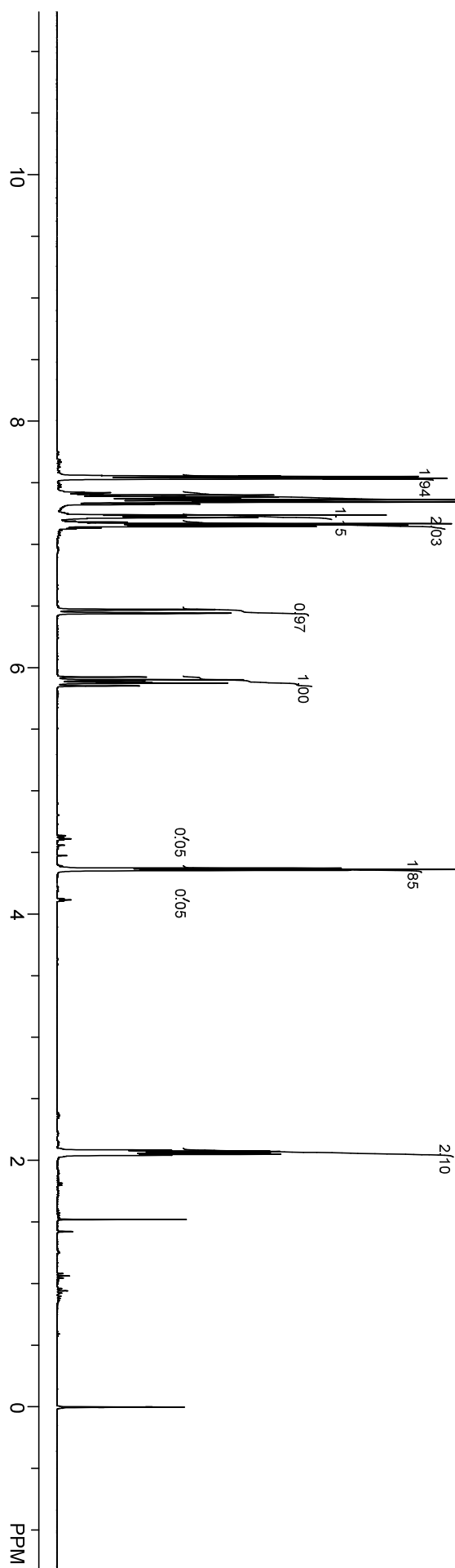
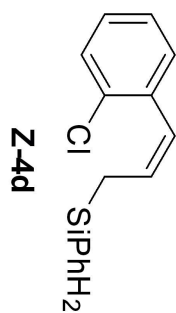


VZ-4-152-F
Apr 3 2017
SOLVENT: CDCl3
NA = 8
F1 = 376.075562 MHz

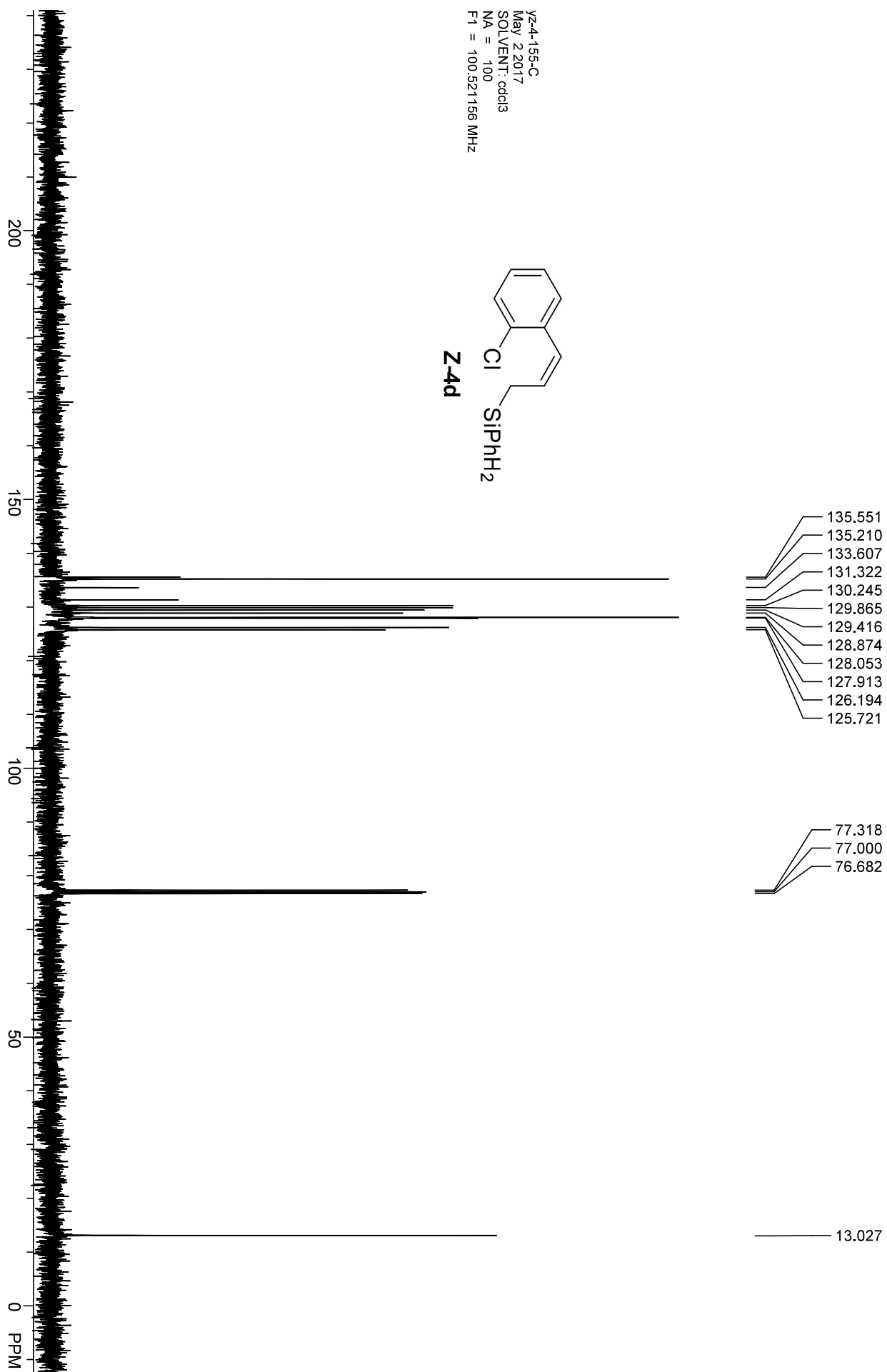
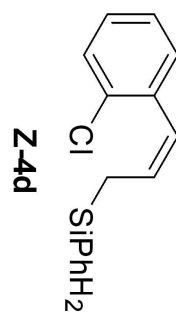


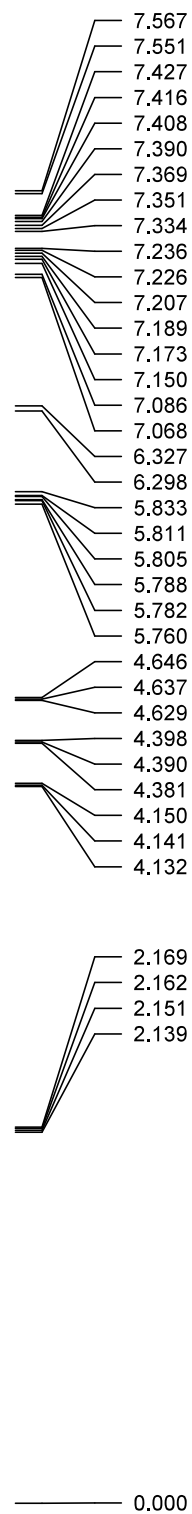


yz4-155-H
 Apr 5 2017
 SOLVENT: CDCl3
 NA = 8
 F1 = 399.722809 MHz

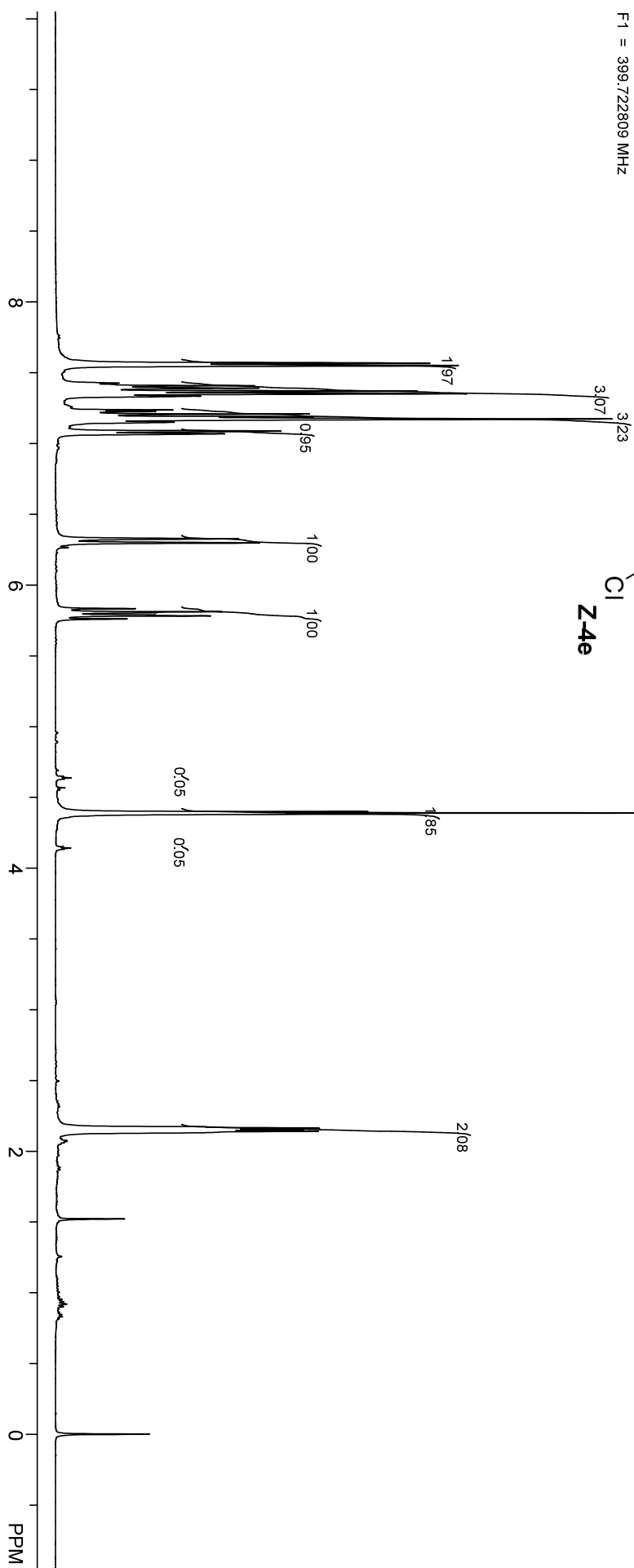
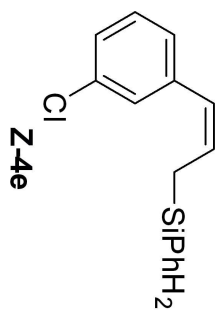


yz4-155-C
May 2 2017
SOLVENT: cdcl3
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F1 = 100.521156 MHz

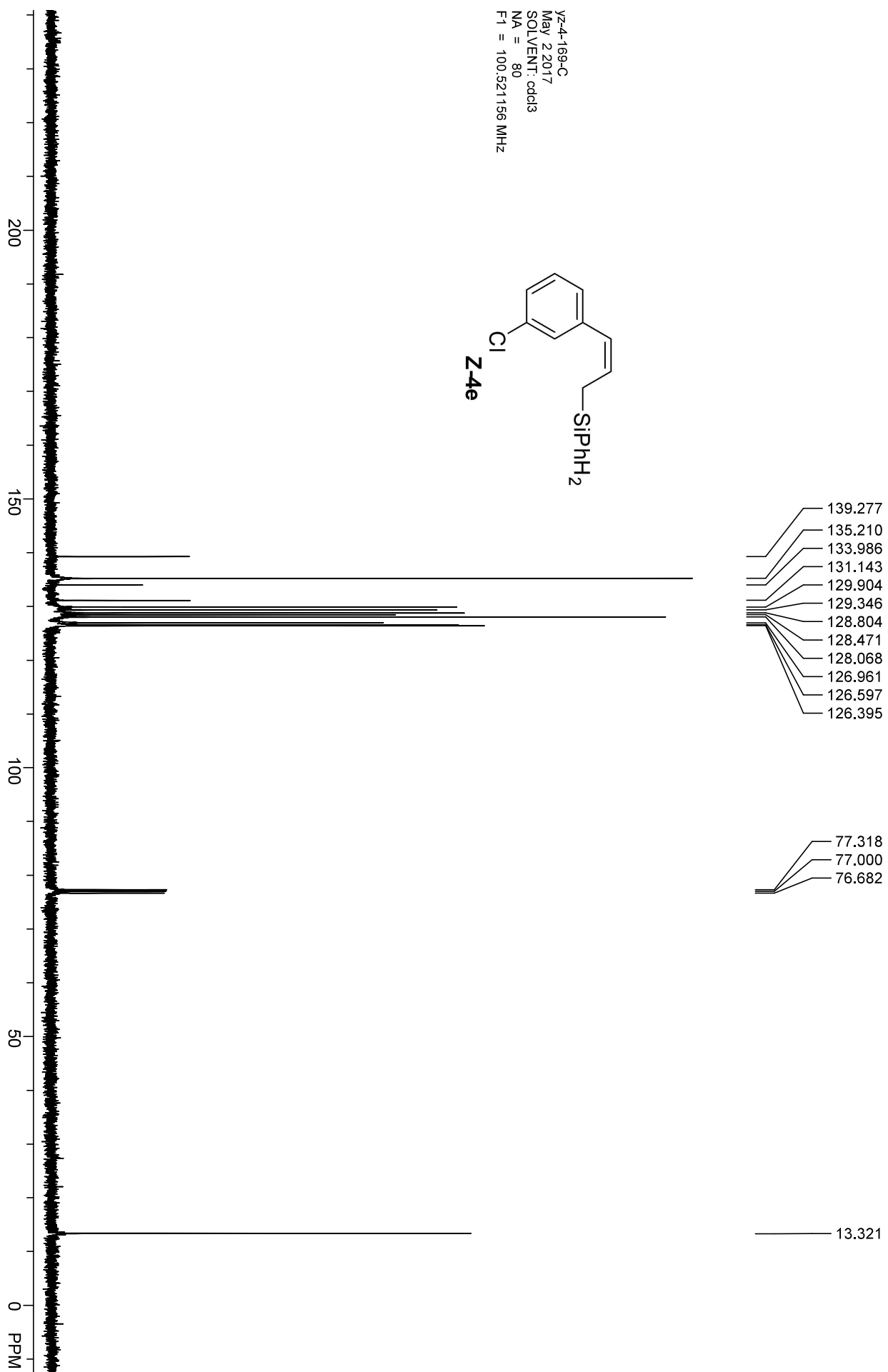
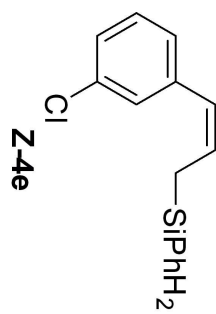


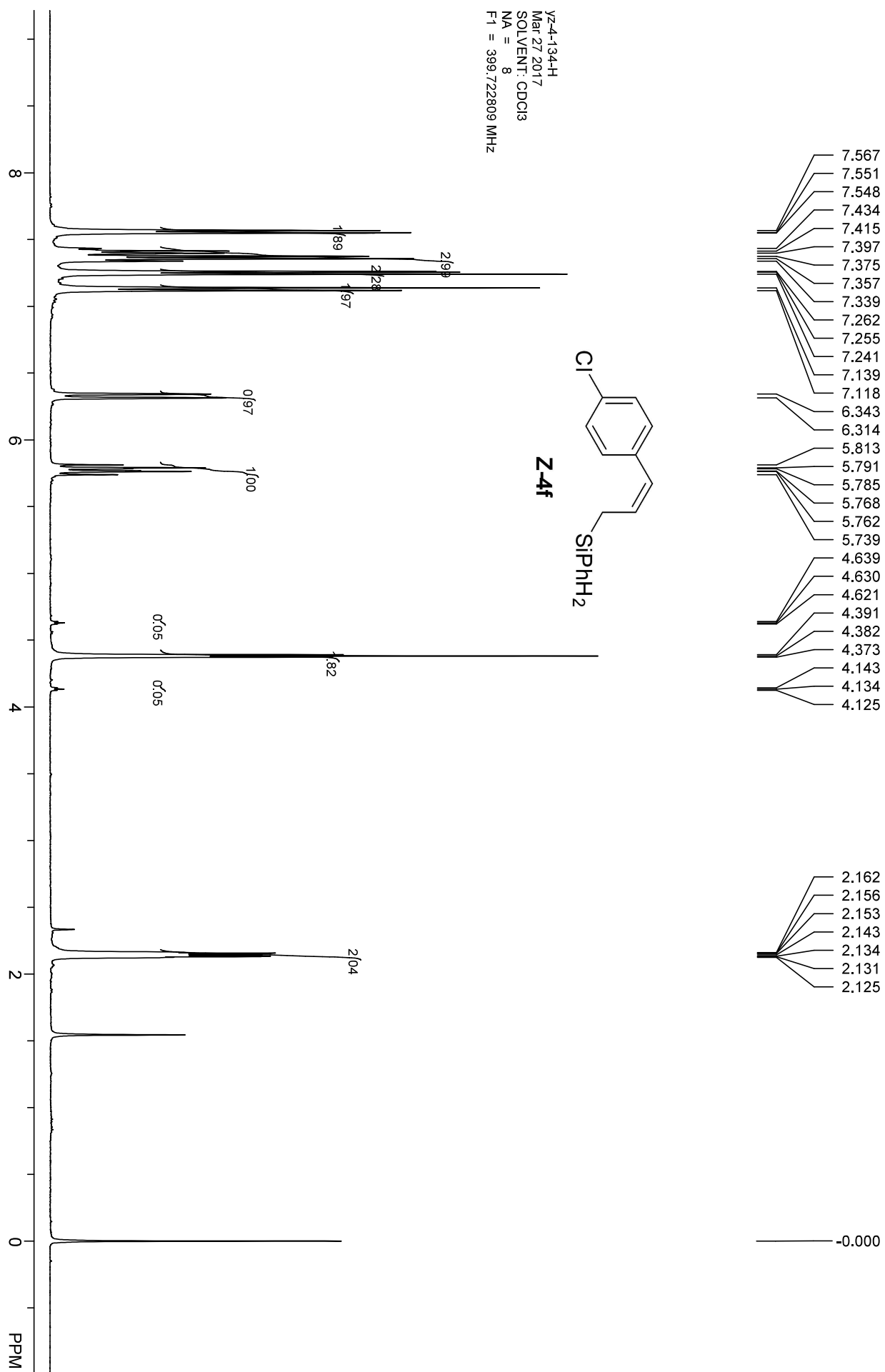


yz-4-169-H
Apr 24 2017
SOLVENT: CDCl3
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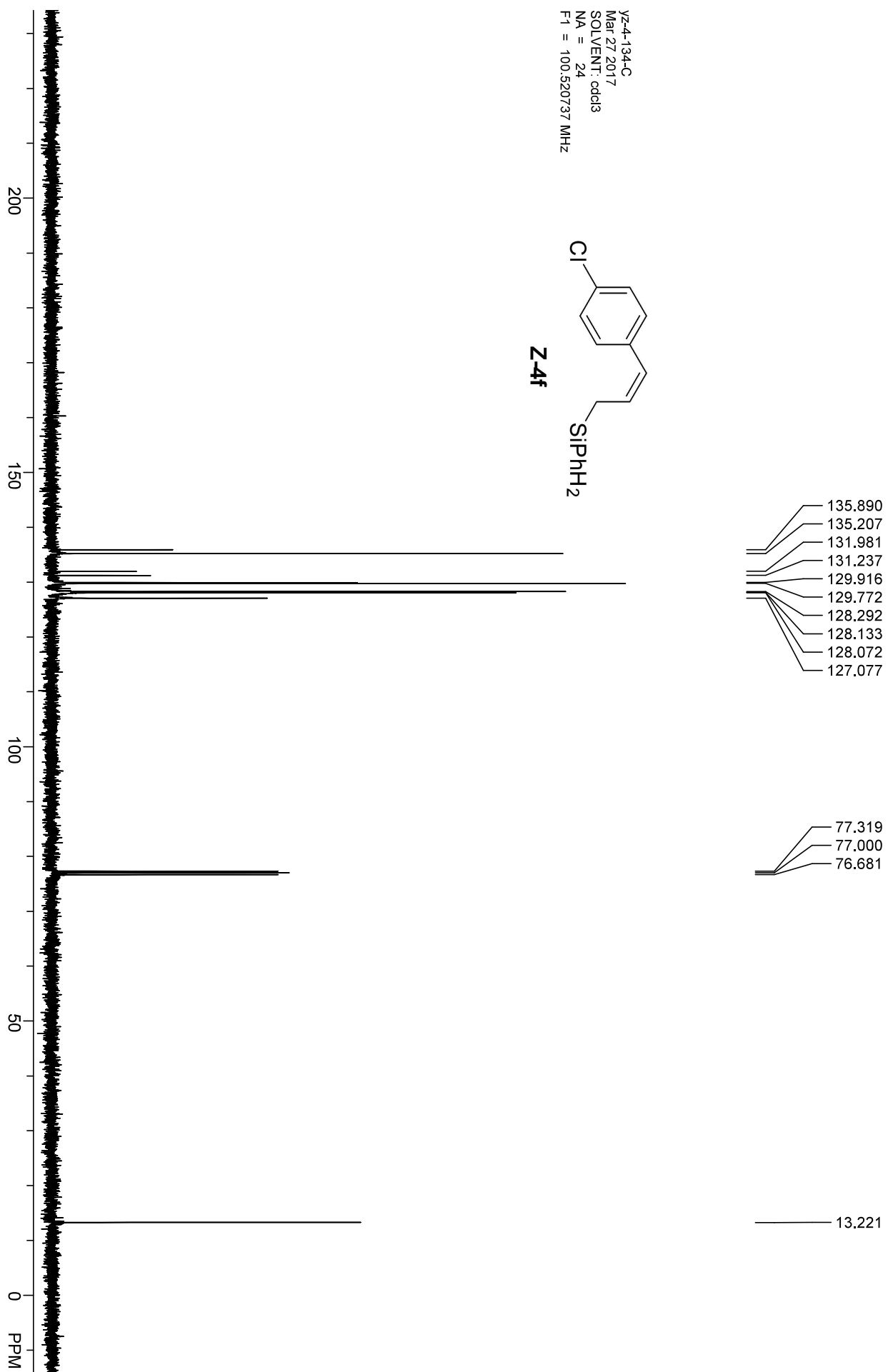
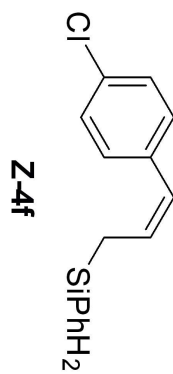


yz-4-169-C
May 2 2017
SOLVENT: cdcl3
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F1 = 100.521156 MHz

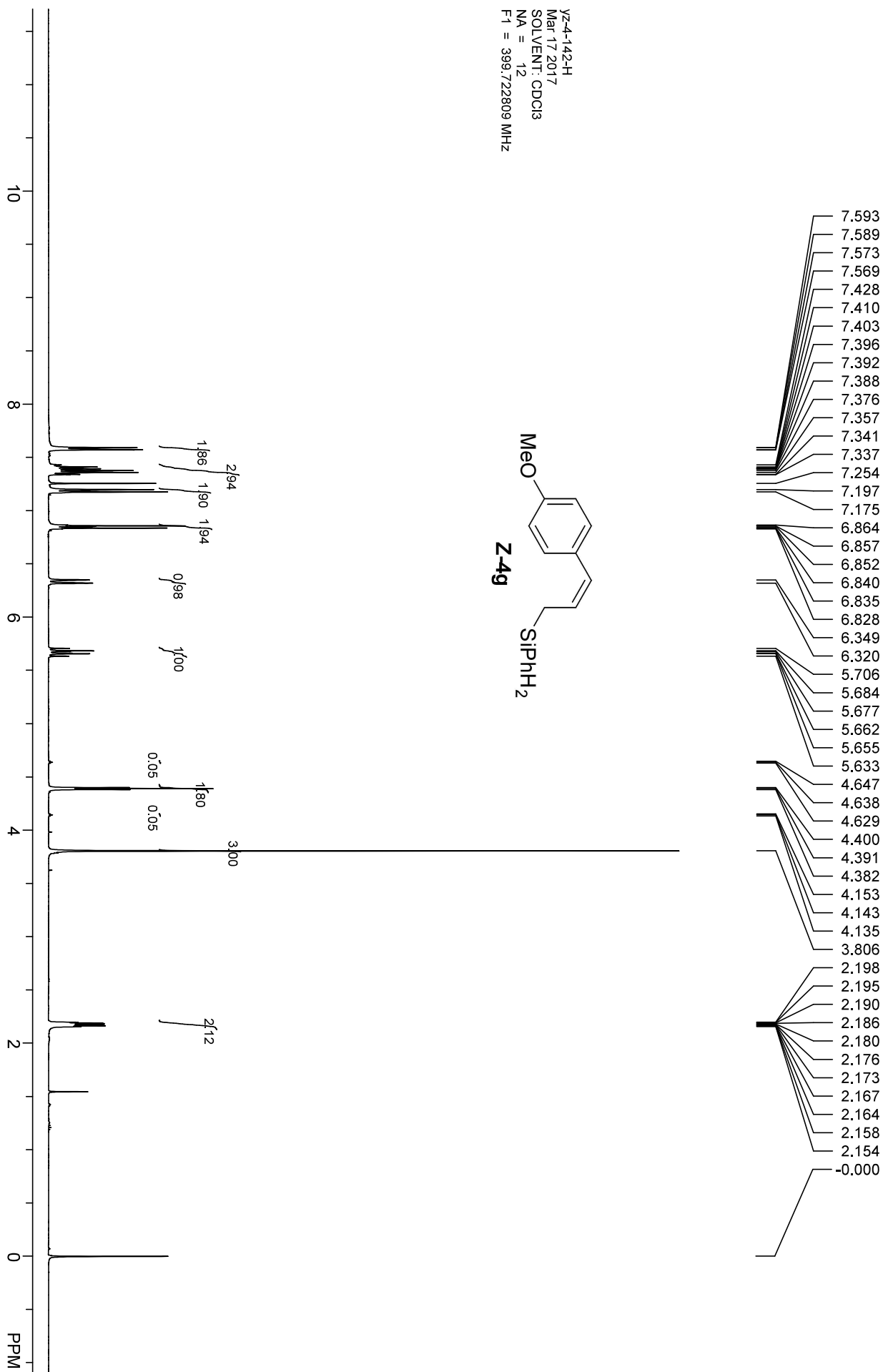
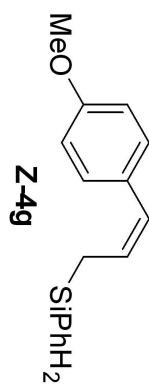




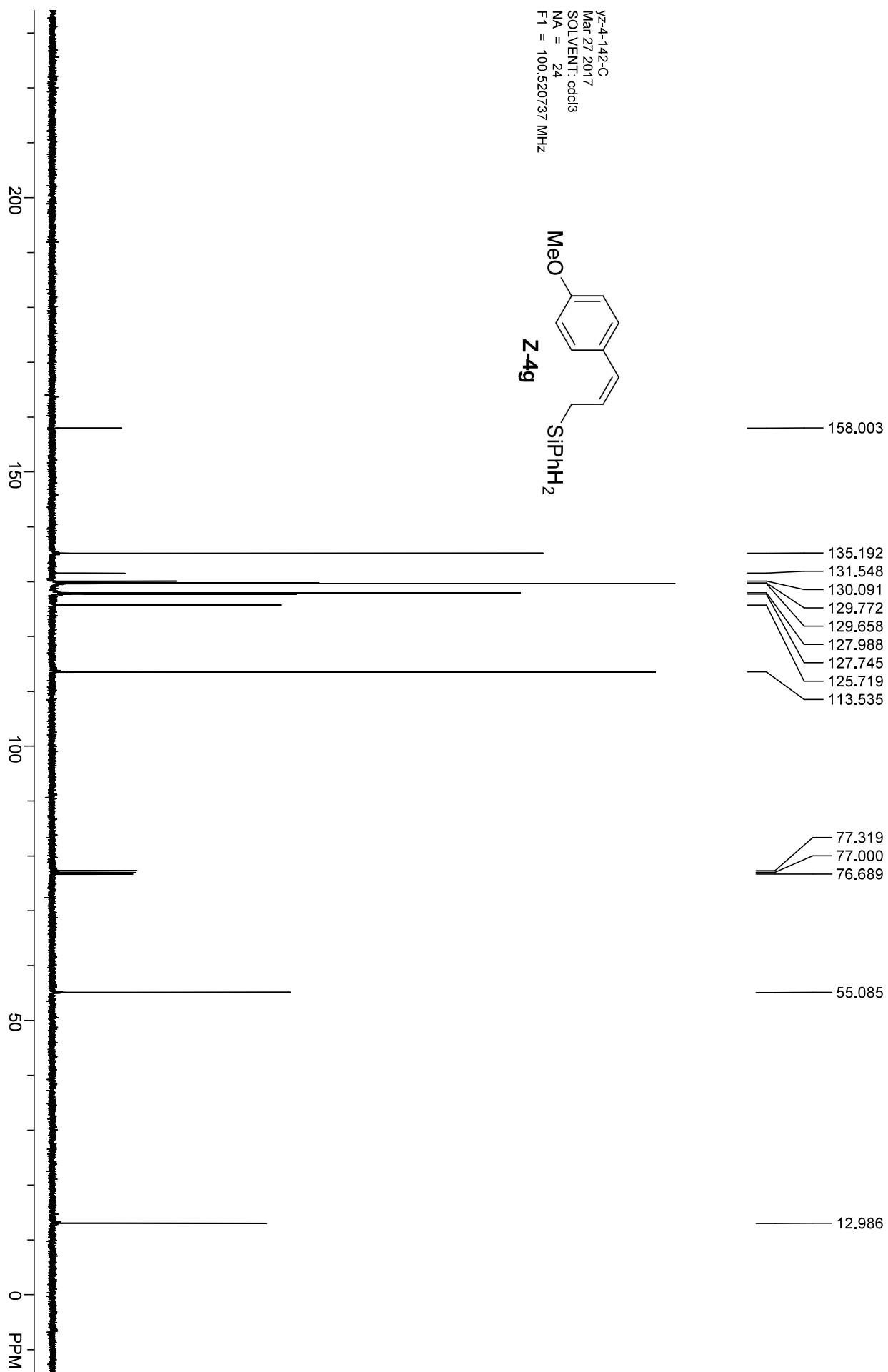
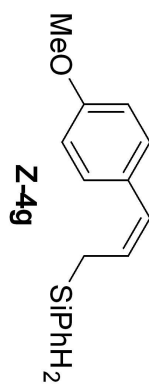
YZ-4-134-C
Mar 27 2017
SOLVENT: cdcl3
NA = 24
F1 = 100.520737 MHz

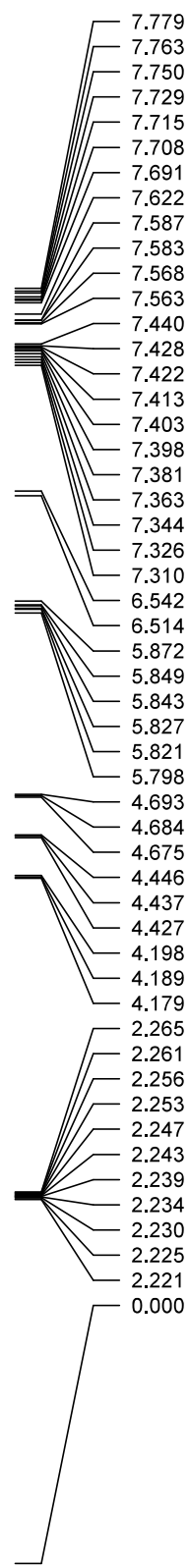


YZ-4-142-H
 Mar 17 2017
 SOLVENT: CDCl3
 NA = 12
 F1 = 399.722809 MHz

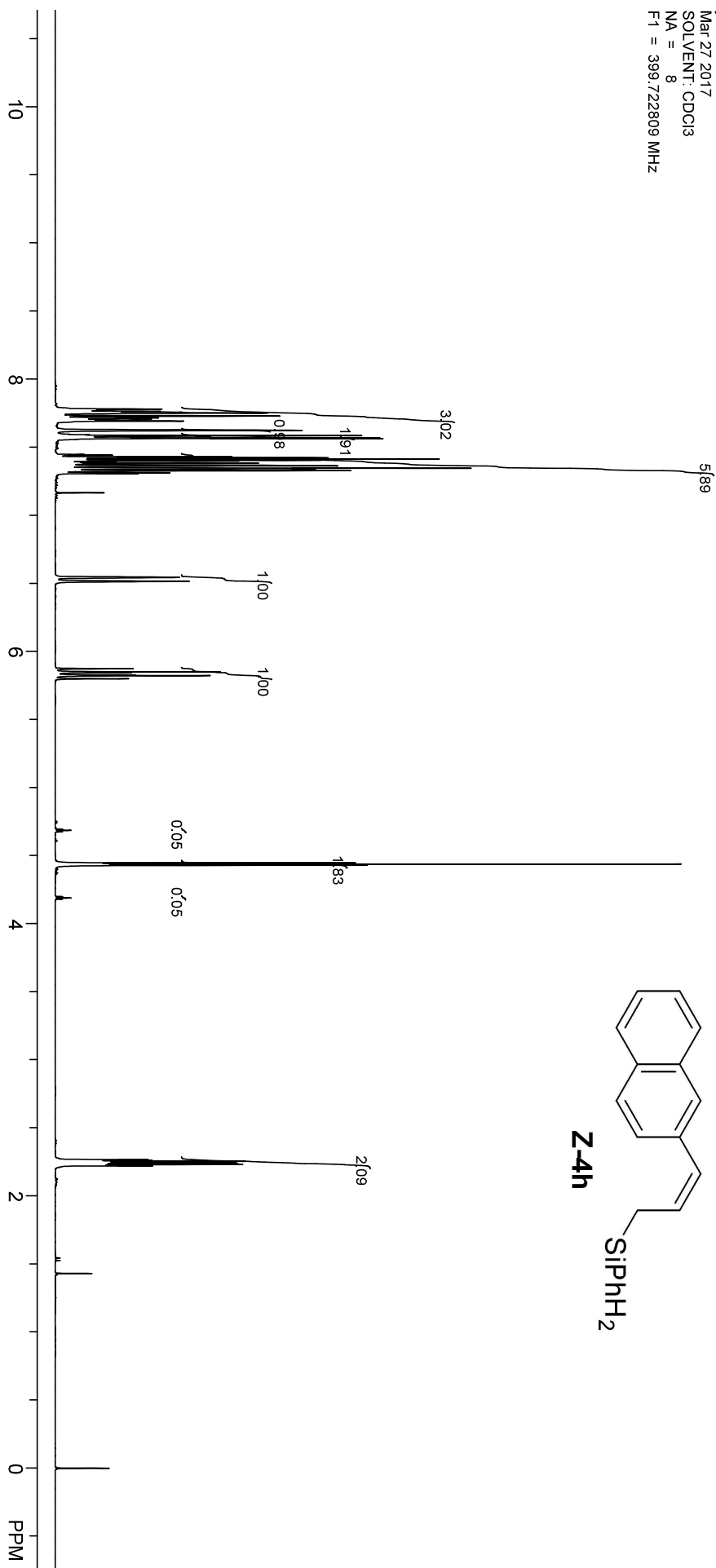
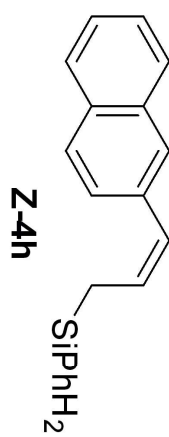


YZ-4-142-C
Mar 27 2017
SOLVENT: cdcl3
NA = 24
F1 = 100.520737 MHz

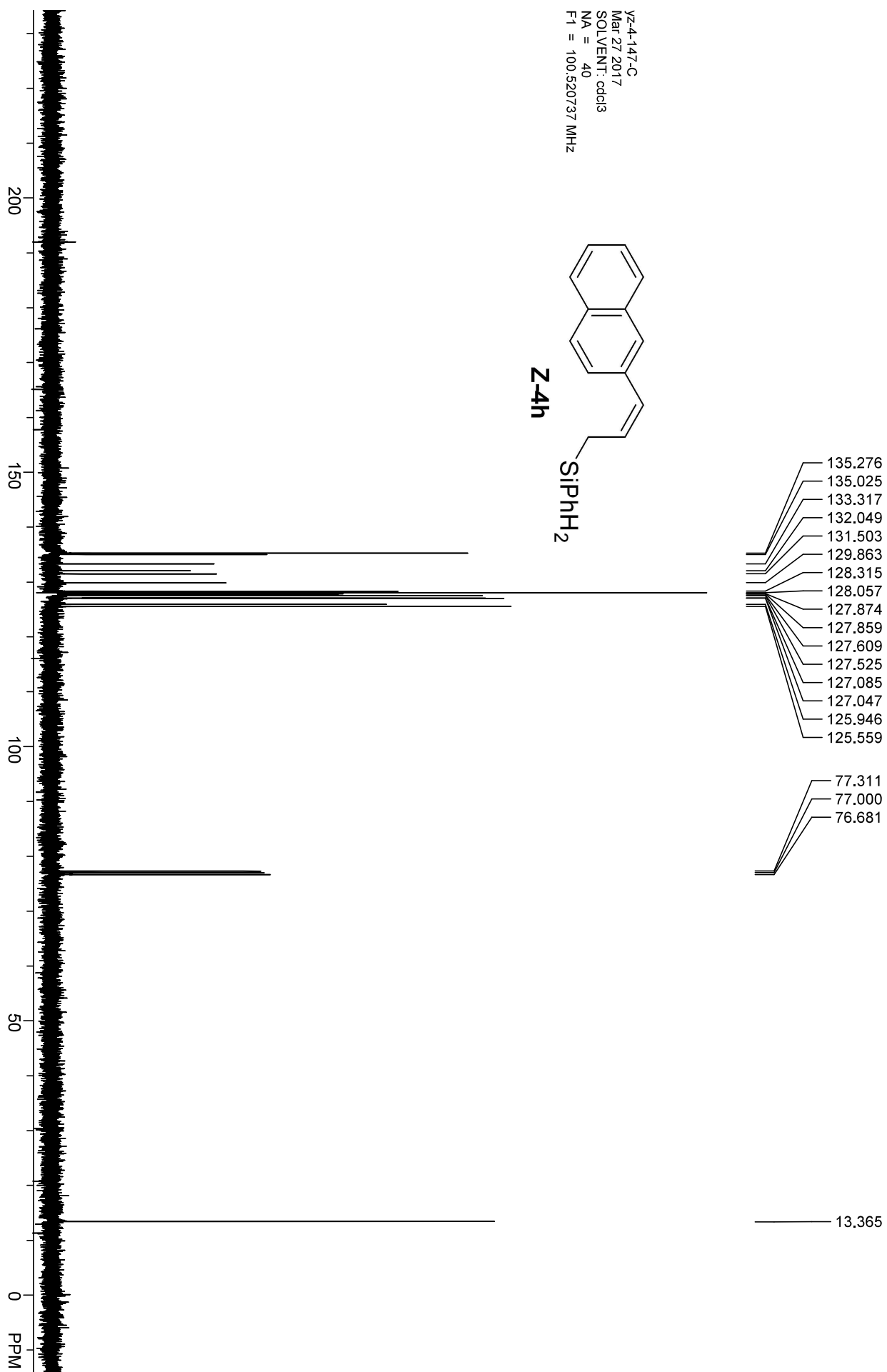
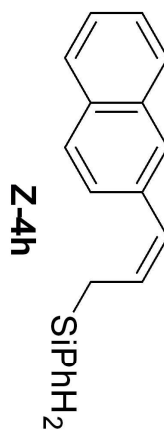




YZ-4-147-H
Mar 27 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz



yz-4-147-C
Mar 27 2017
SOLVENT: cdcl3
NA = 40
F1 = 100.520737 MHz



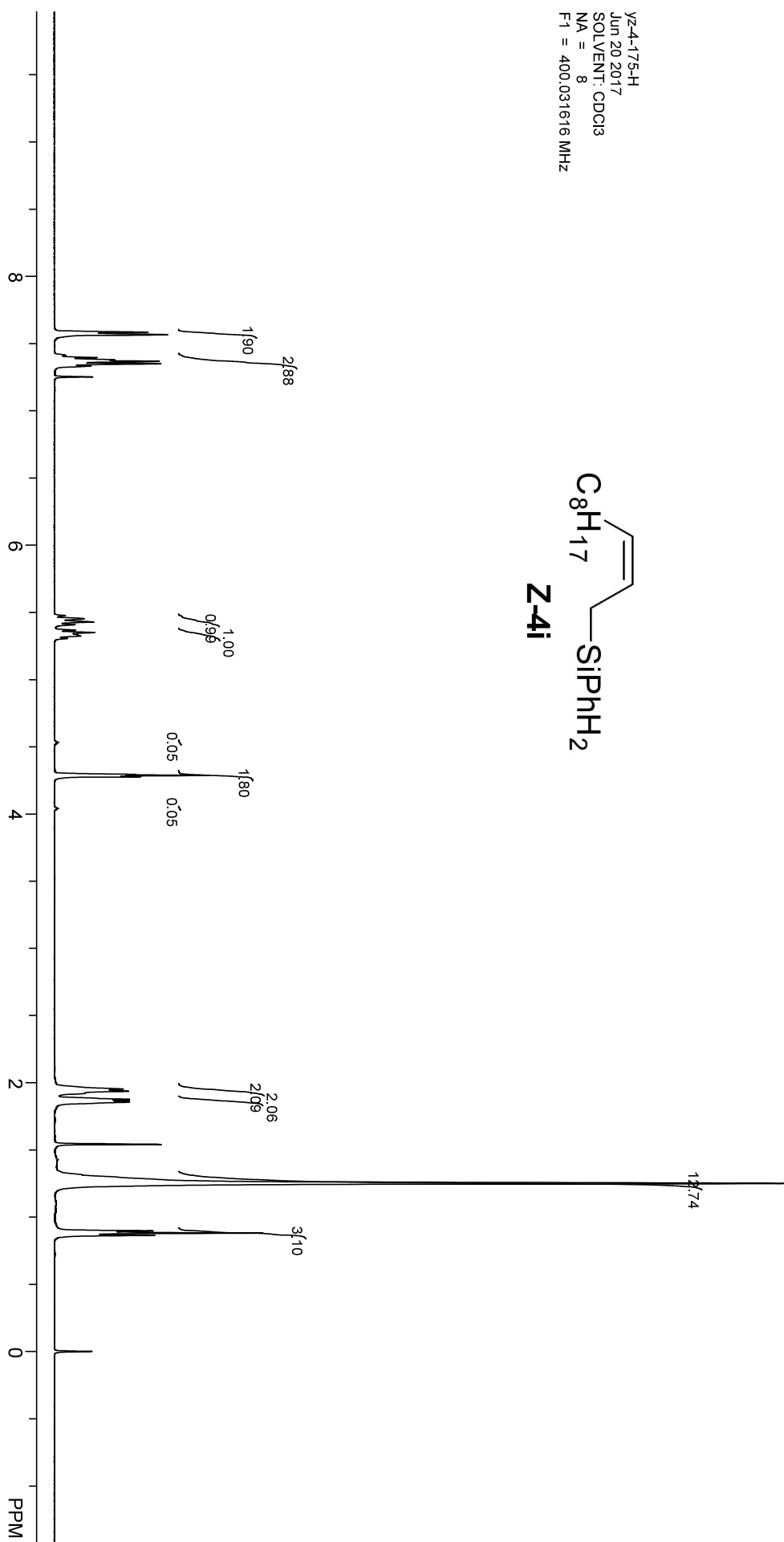
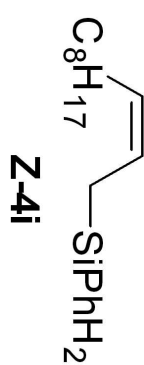
7.584
7.567
7.412
7.396
7.379
7.367
7.350
7.333
7.251

5.475
5.453
5.429
5.408
5.367
5.350
5.332
5.329
5.323
5.305
4.541
4.531
4.521
4.294
4.286
4.277
4.049
4.039
4.031

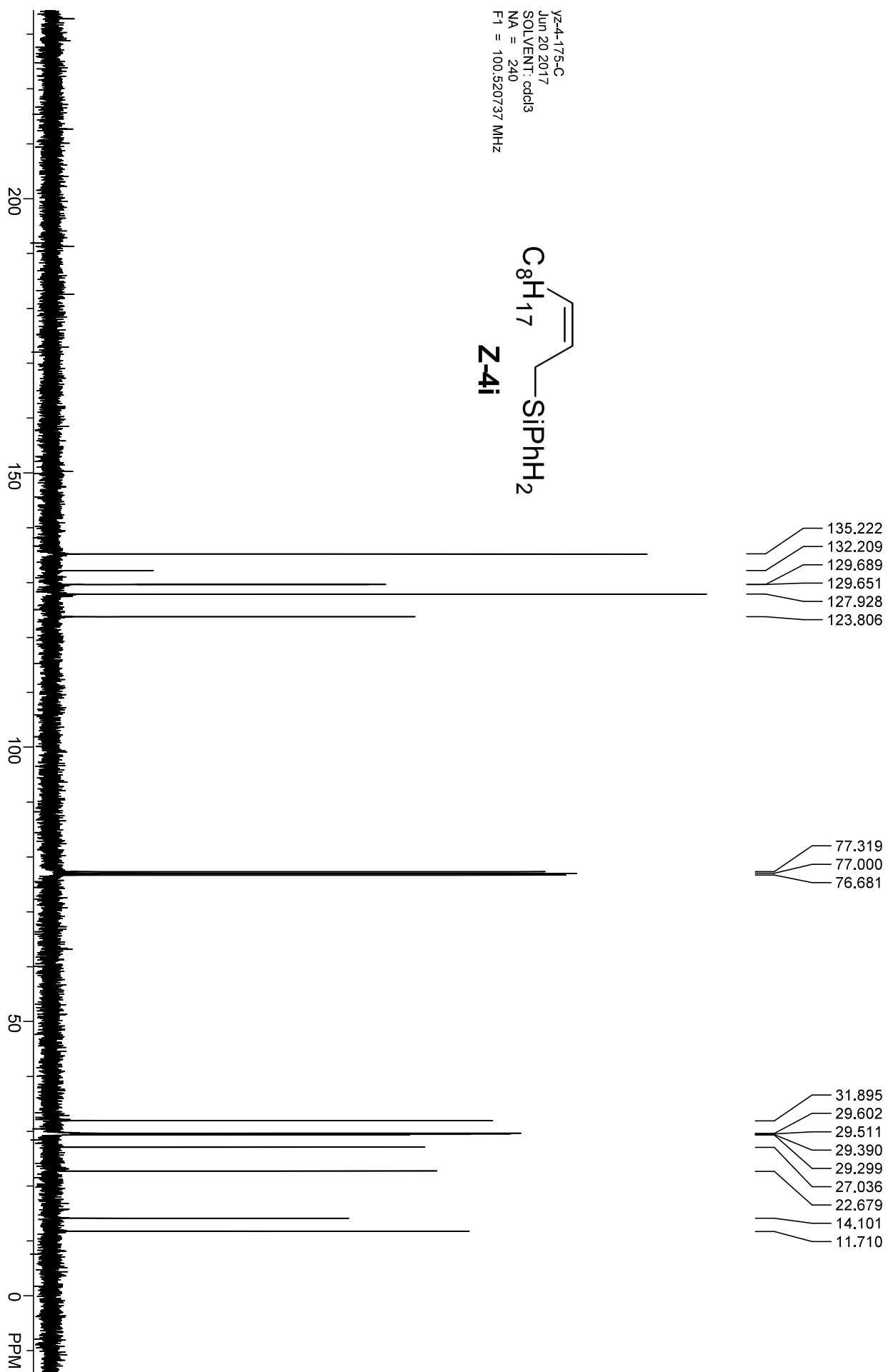
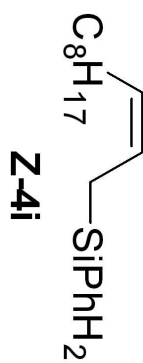
1.952
1.938
1.921
1.875
1.866
1.855
1.541
1.250
0.897
0.881
0.864

-0.000

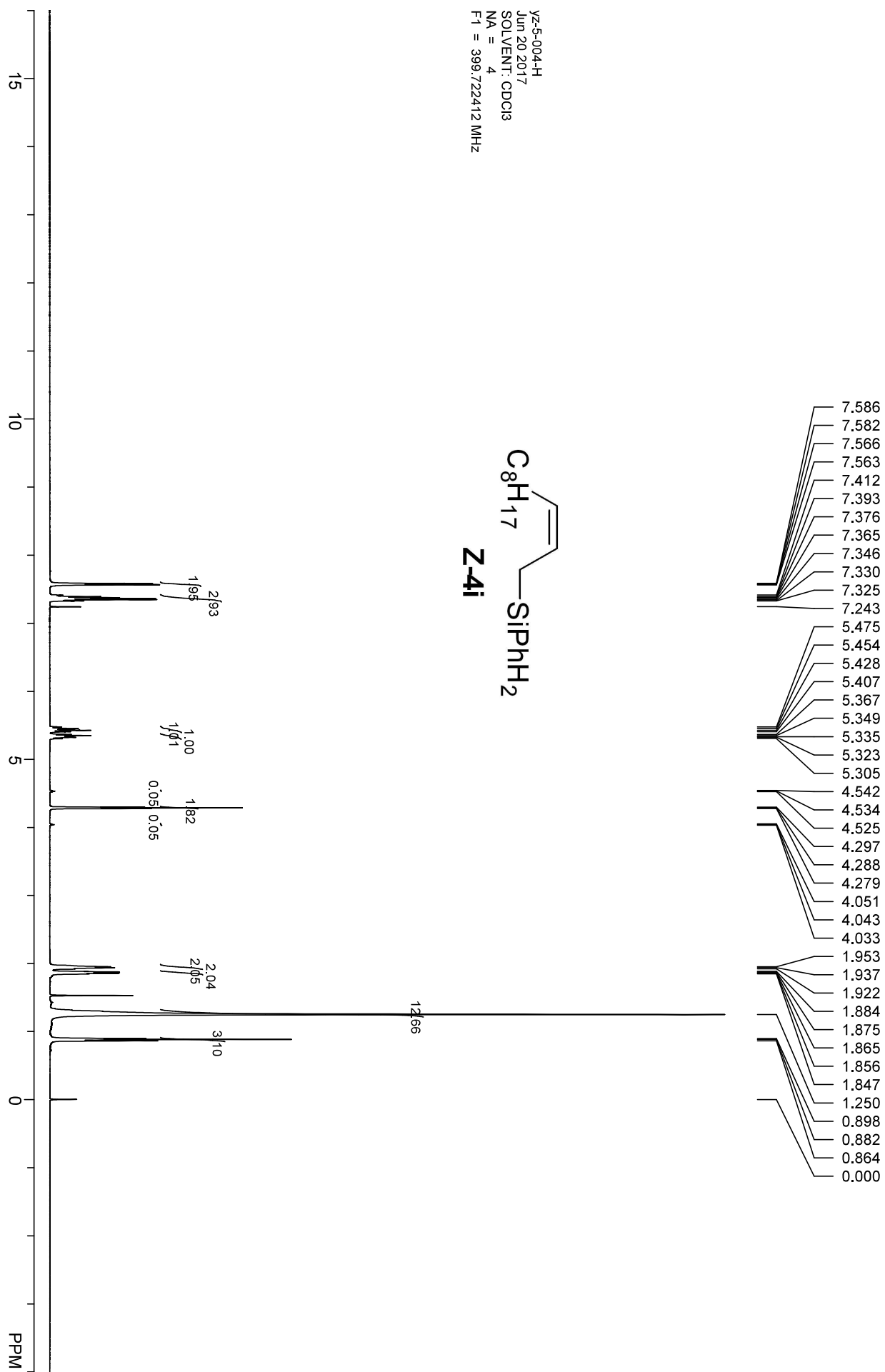
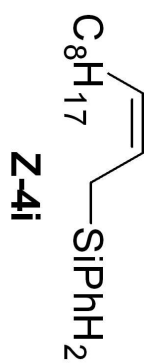
yz4-175-H
Jun 20 2017
SOLVENT: CDCl3
NA = 8
F1 = 400.031616 MHz



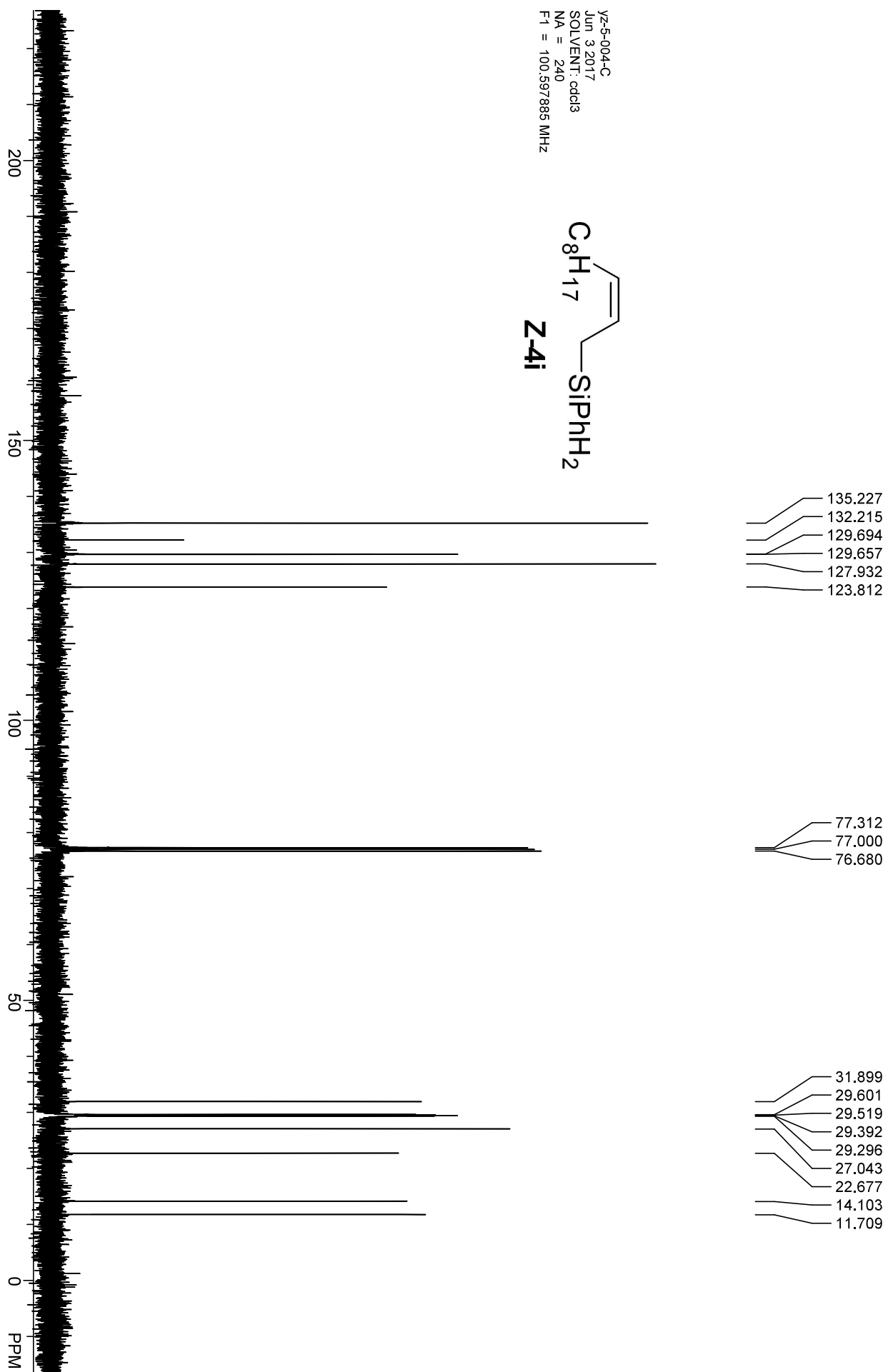
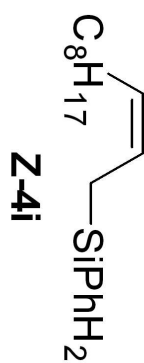
yz4-175-C
Jun 20 2017
SOLVENT: cdcl3
NA = 240
F1 = 100.520737 MHz



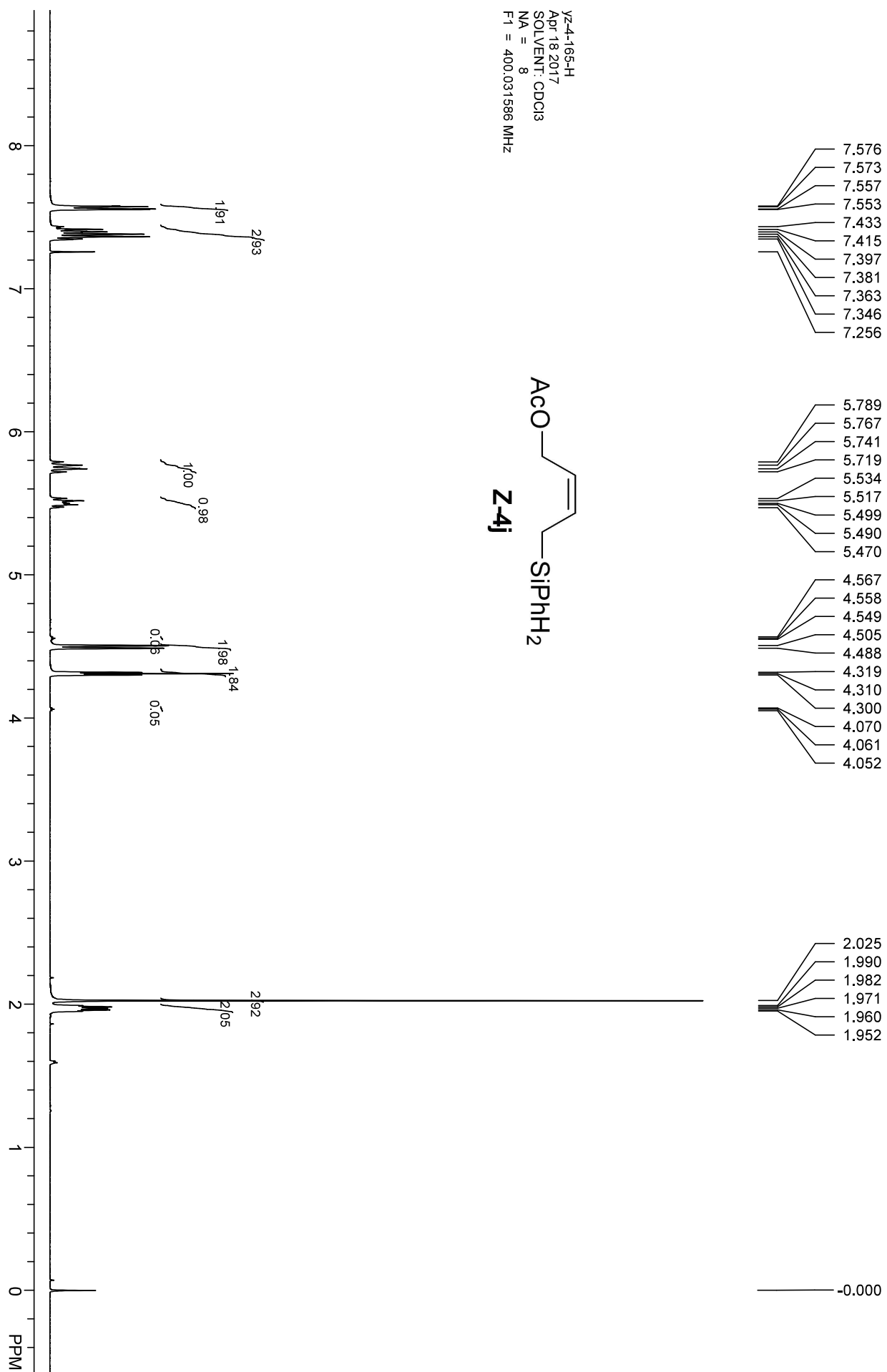
yz-5-004-H
 Jun 20 2017
 SOLVENT: CDCl3
 NA = 4
 F1 = 399.722412 MHz



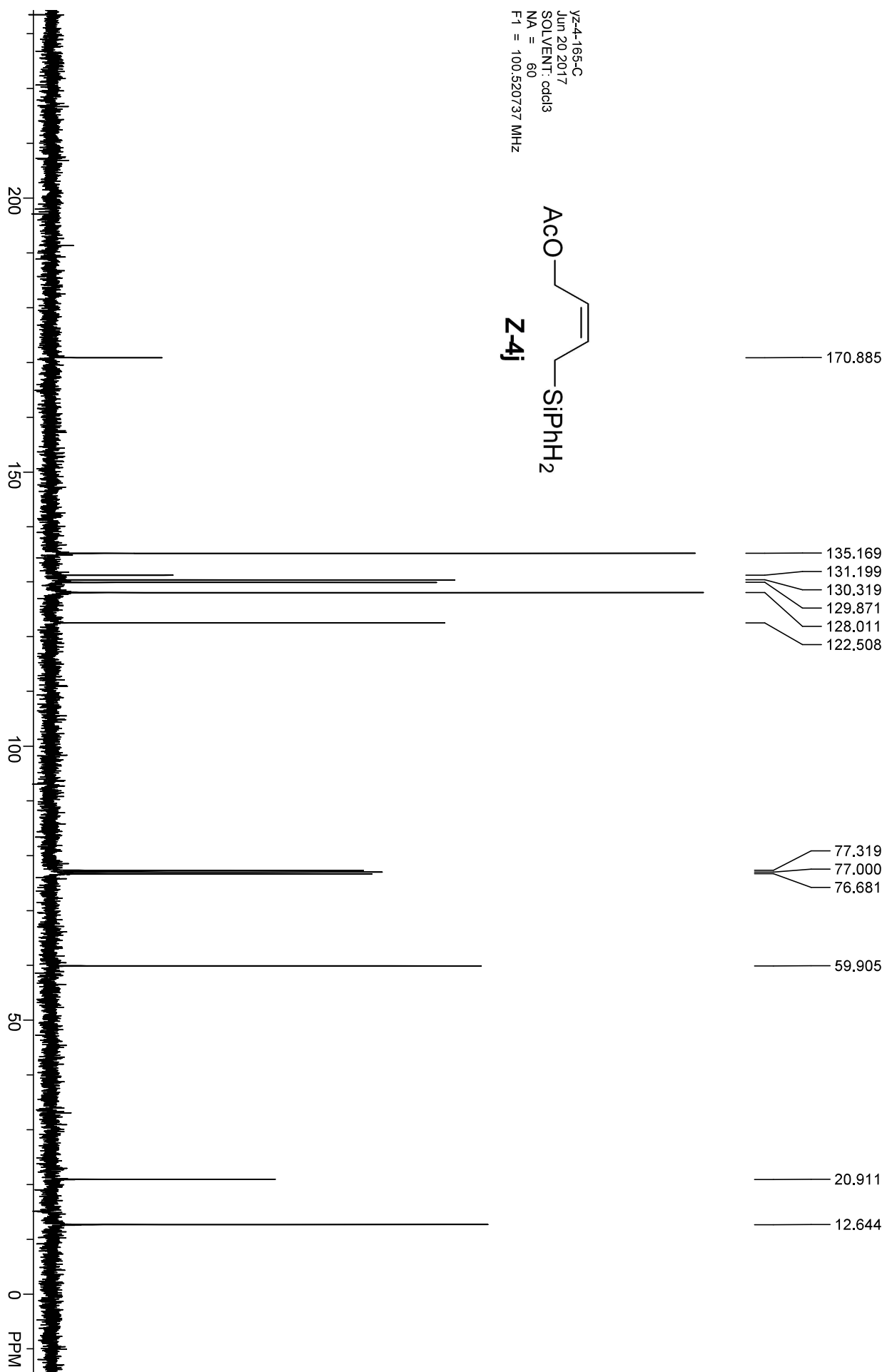
yz-5-004-C
 Jun 3 2017
 SOLVENT: cdcl3
 NA = 240
 F1 = 100.597885 MHz



YZ-4-165-H
 Apr 18 2017
 SOLVENT: CDCl₃
 NA = 8
 F1 = 400.031586 MHz



yz-4-165-C
Jun 20 2017
SOLVENT: cdcl3
NA = 60
F1 = 100.520737 MHz

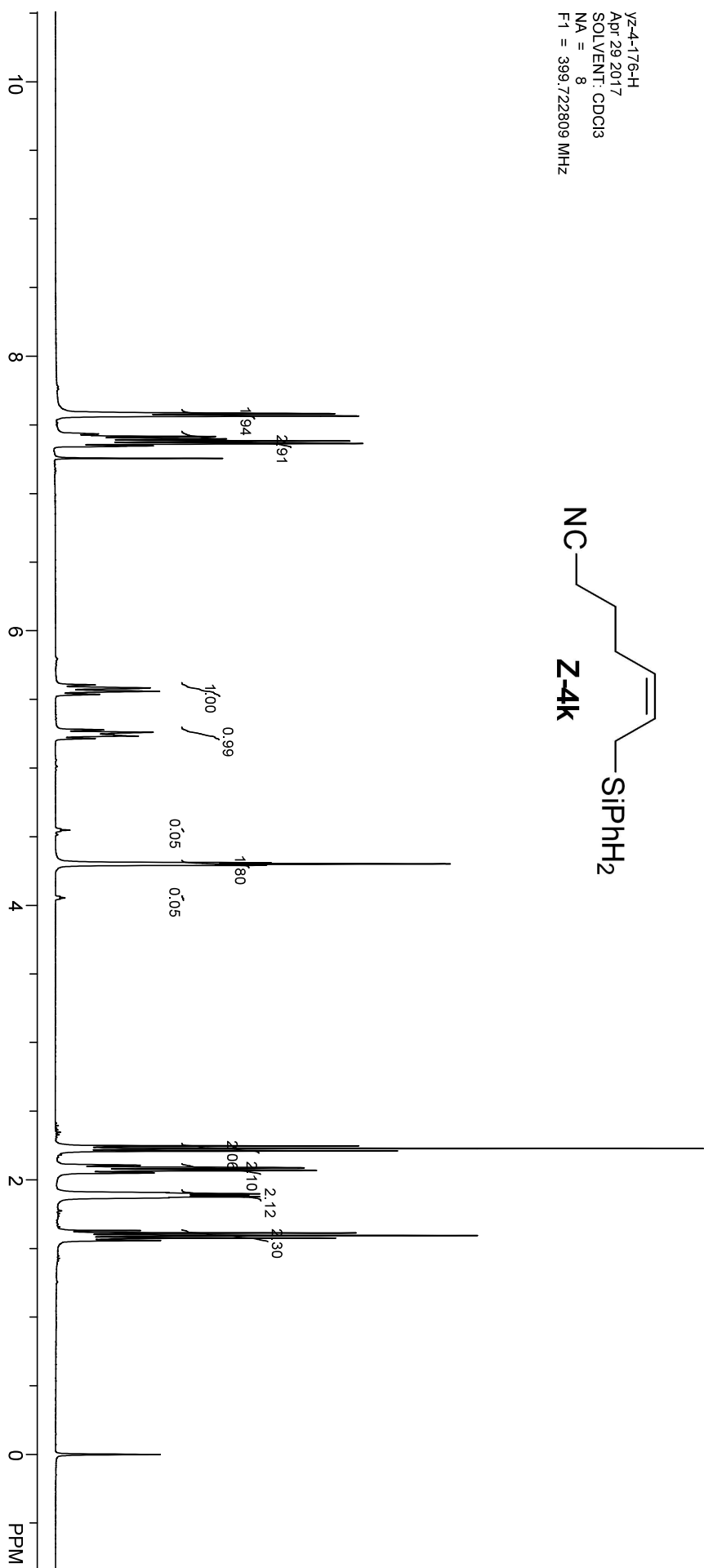
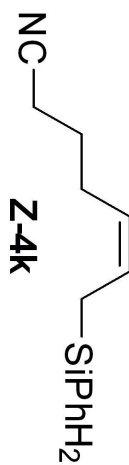


7.582
7.566
7.434
7.416
7.399
7.383
7.364
7.348
7.257

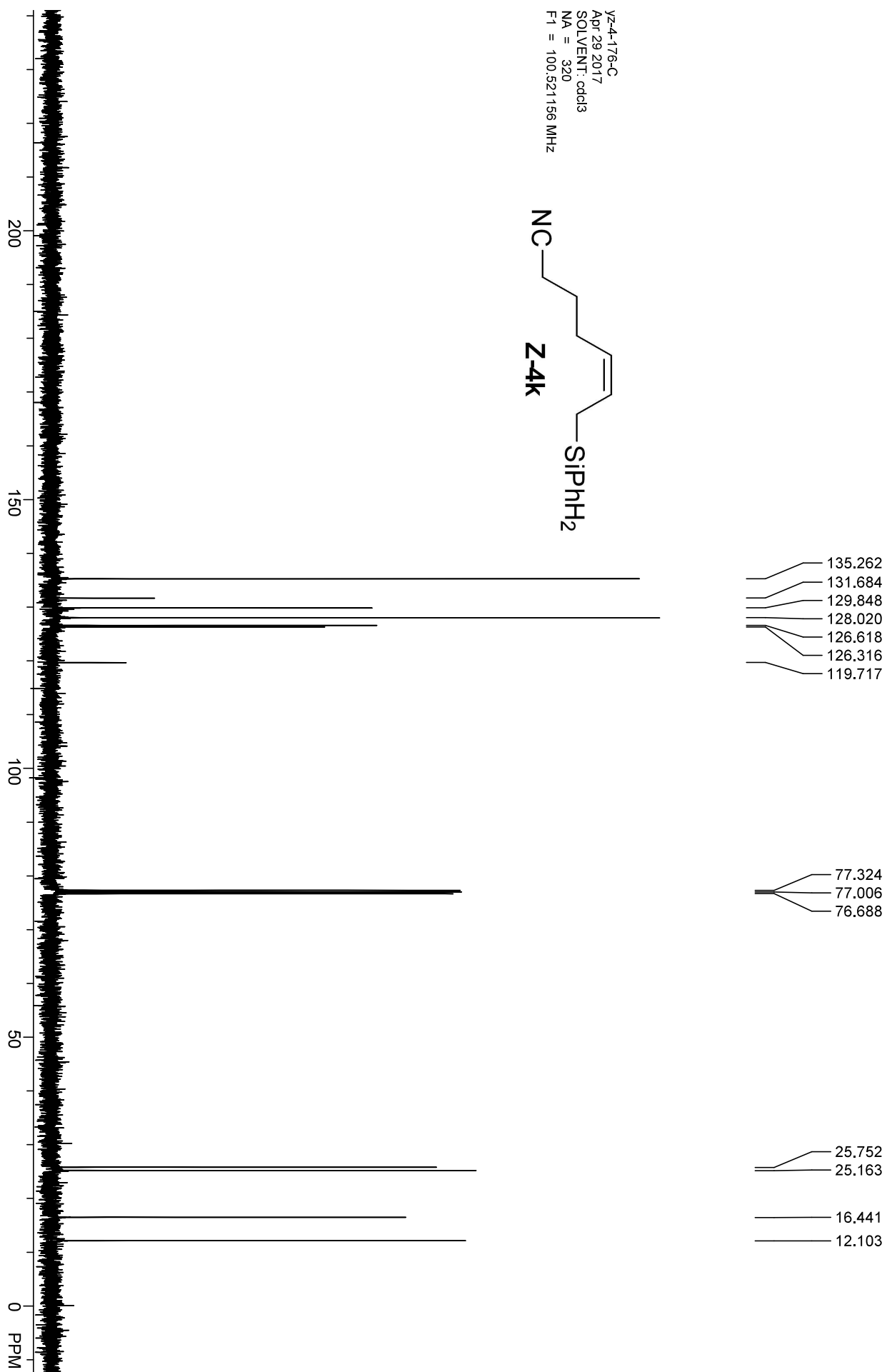
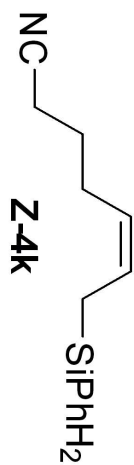
5.606
5.584
5.558
5.536
5.278
5.259
5.241
5.233
5.215
4.556
4.547
4.540
4.309
4.301
4.293
4.062
4.053
4.046

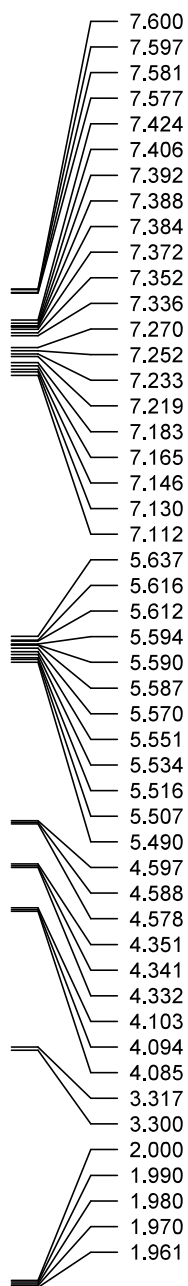
2.247
2.229
2.210
2.106
2.088
2.069
2.051
1.907
1.898
1.888
1.877
1.870
1.631
1.613
1.594
1.576
1.558
-0.000

vz-4-176-H
Apr 29 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz



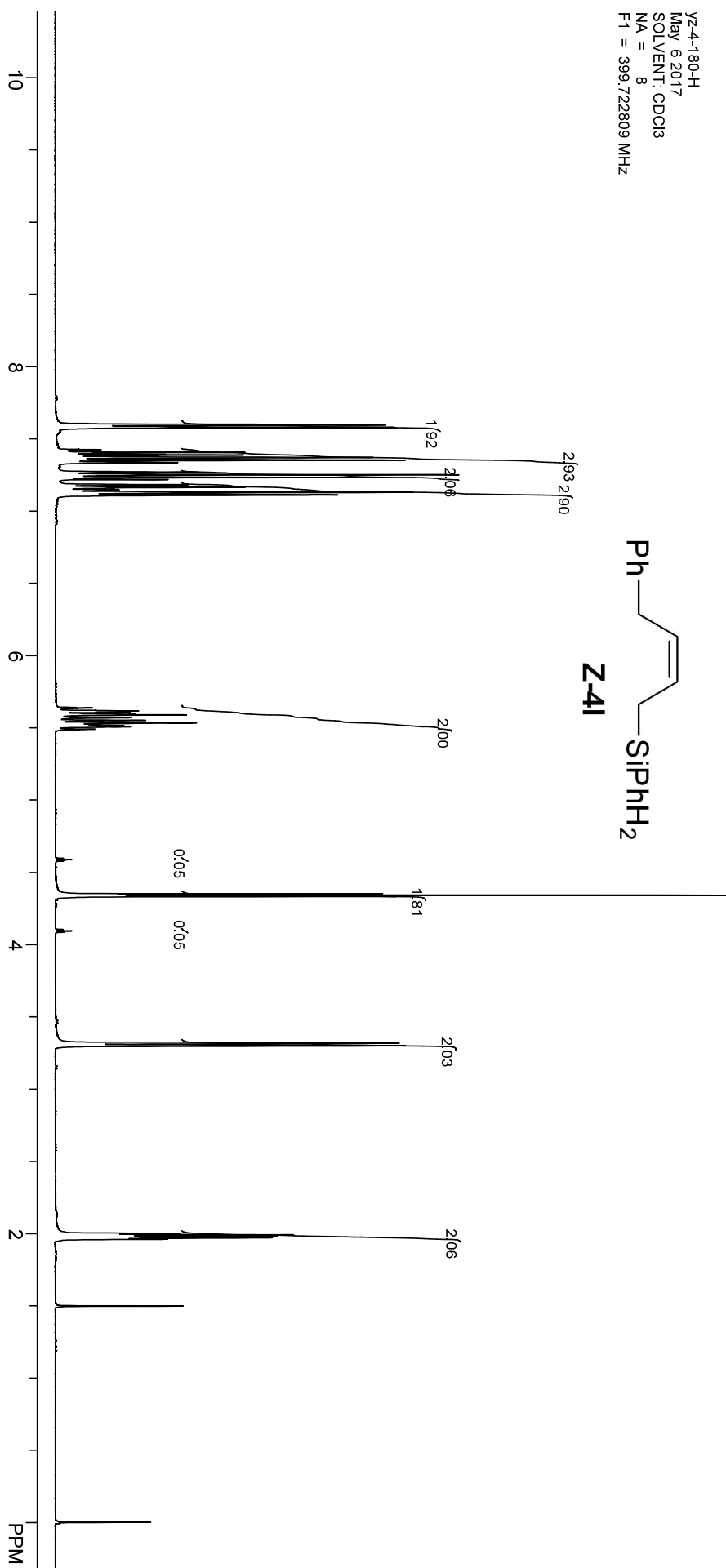
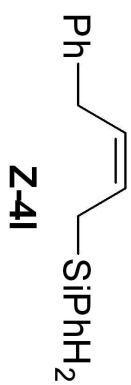
yz4-176-C
Apr 29 2017
SOLVENT: cdcl3
NA = 320
F1 = 100.521156 MHz



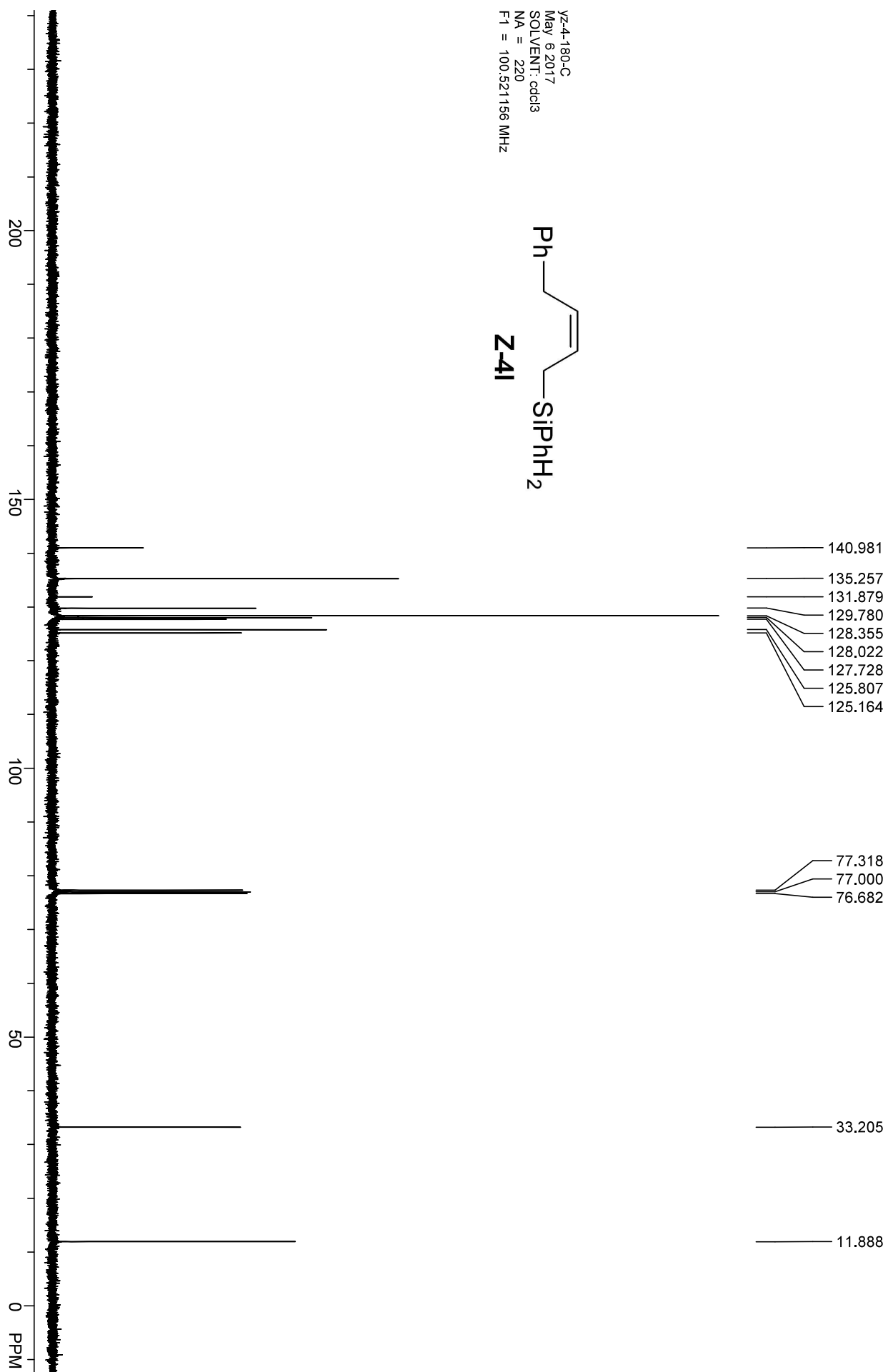
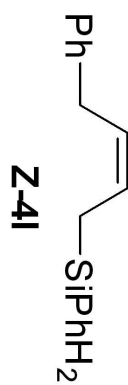


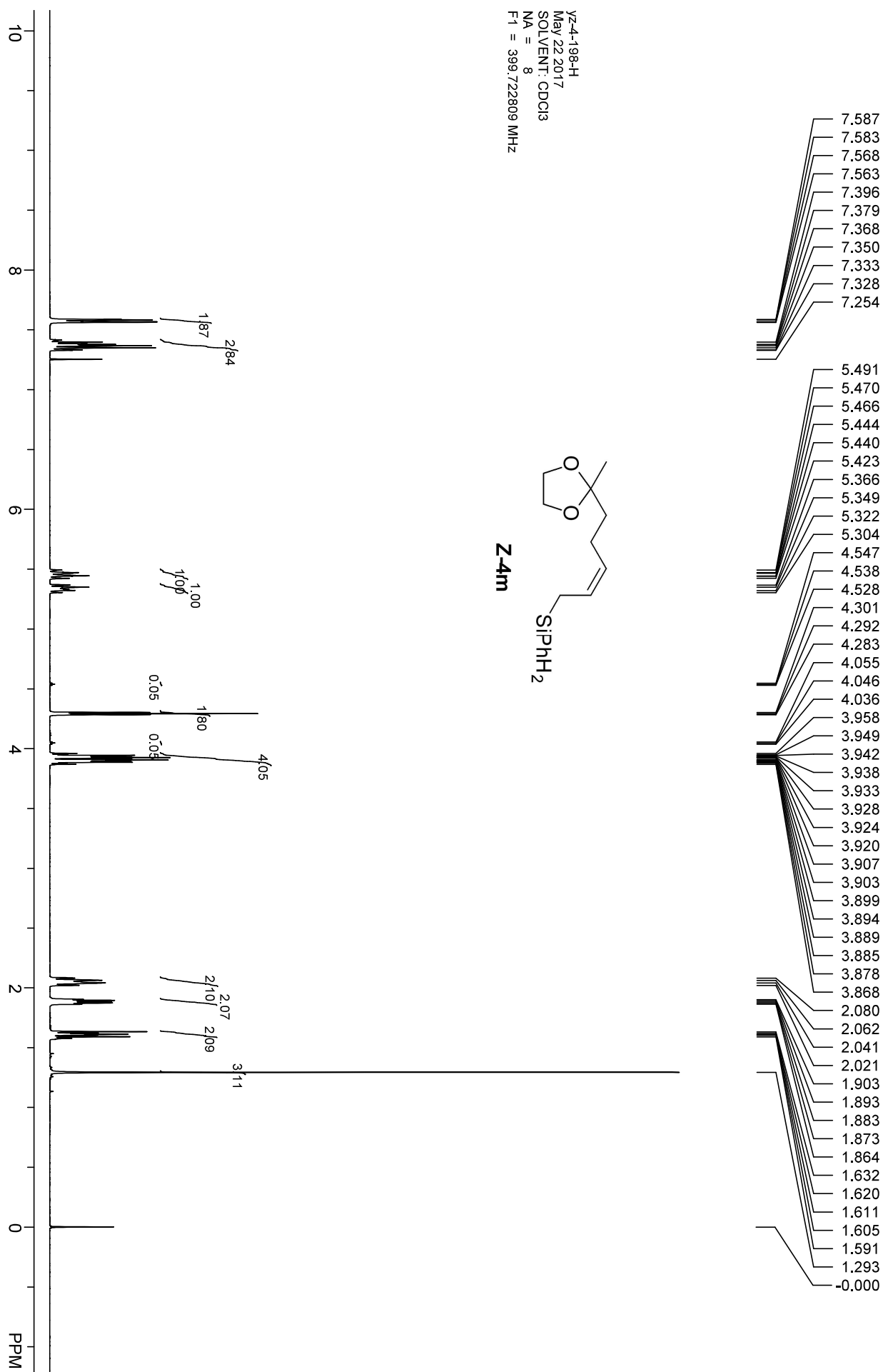
-0.000

yz-4-180-H
May 6 2017
SOLVENT: CDCl3
NA = 8
F1 = 399.722809 MHz

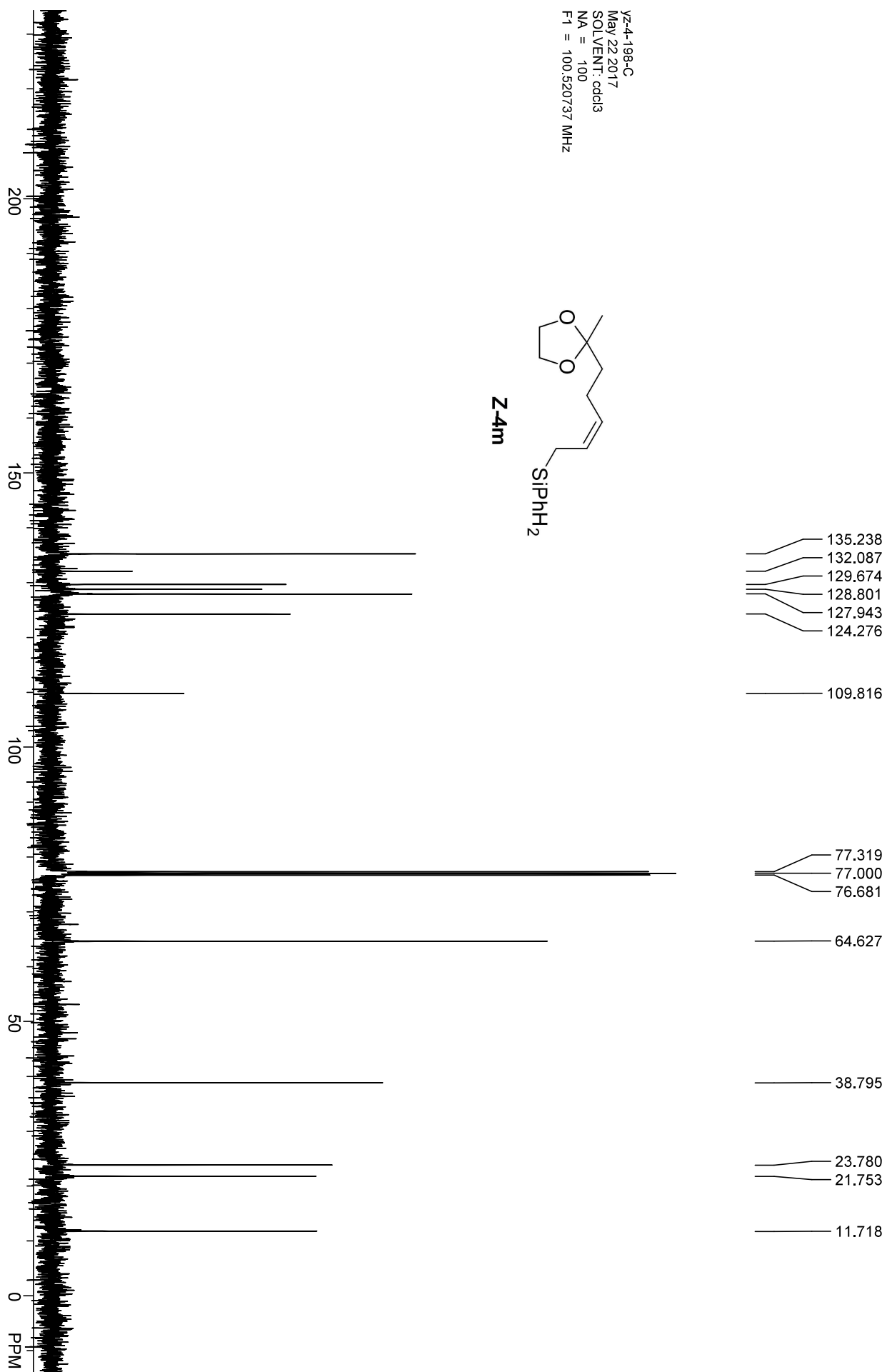
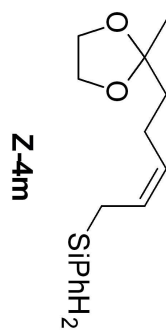


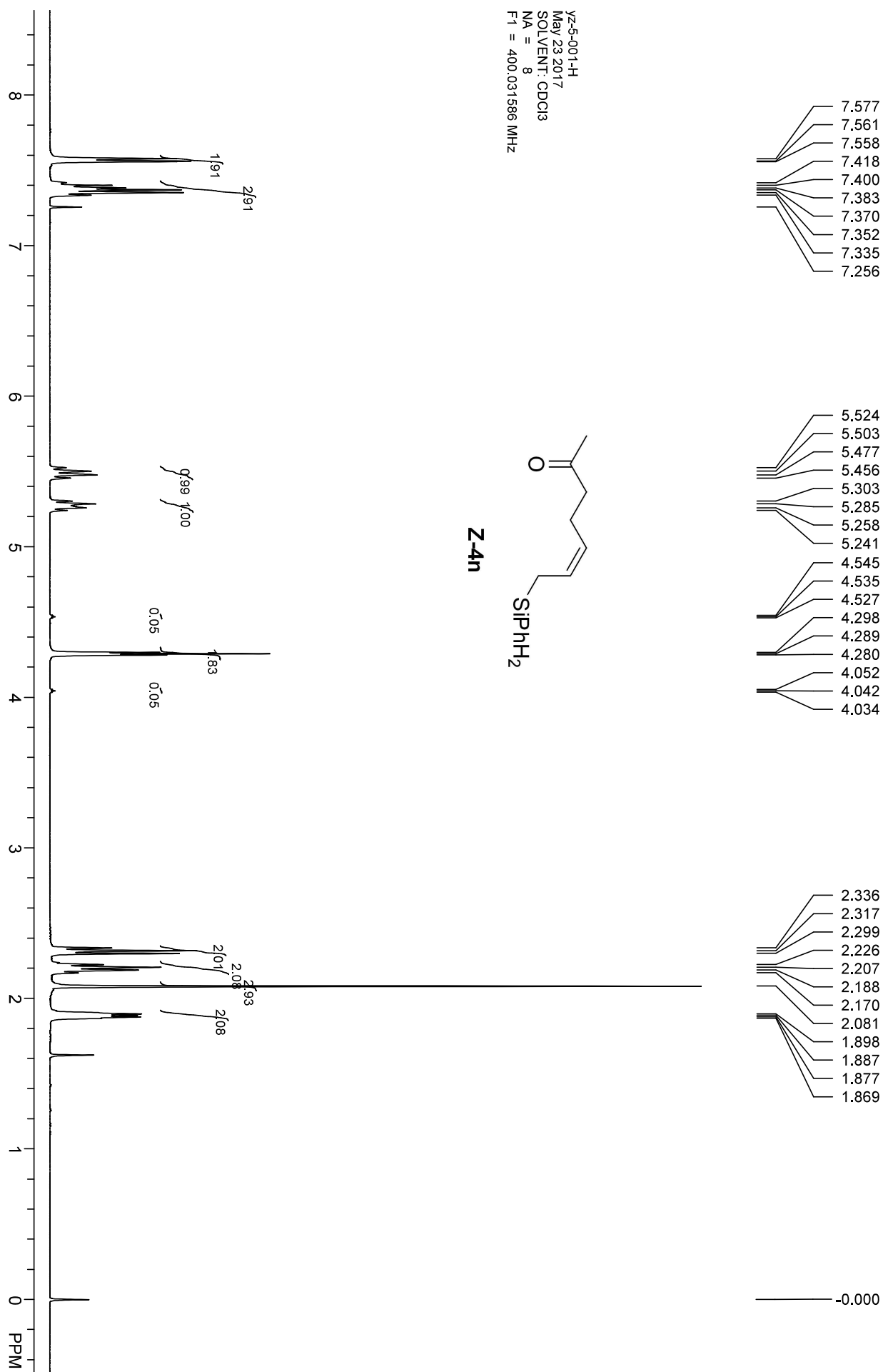
yz-4-180-C
May 6 2017
SOLVENT: cdcl3
NA = 220
F1 = 100.521156 MHz

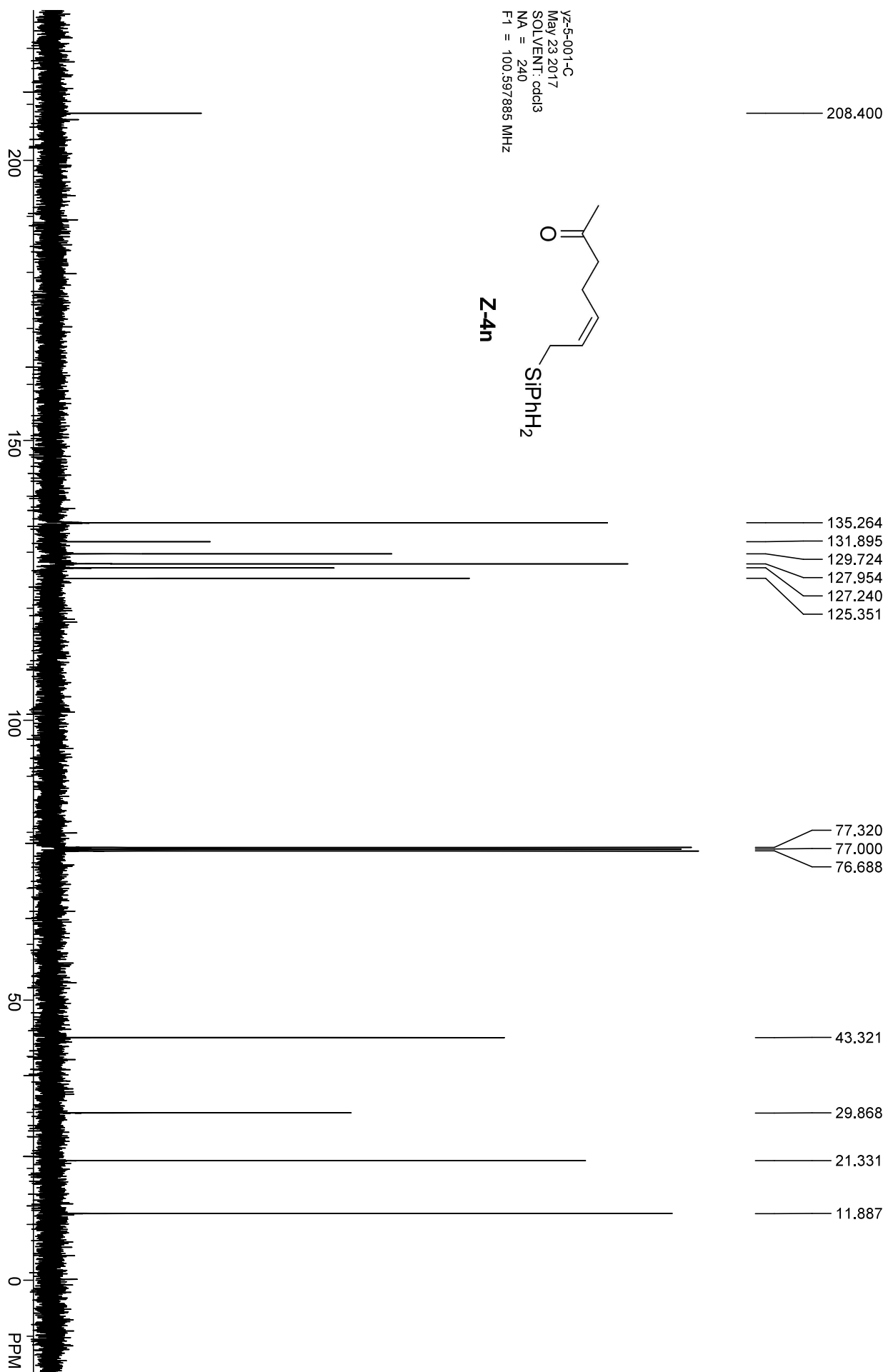


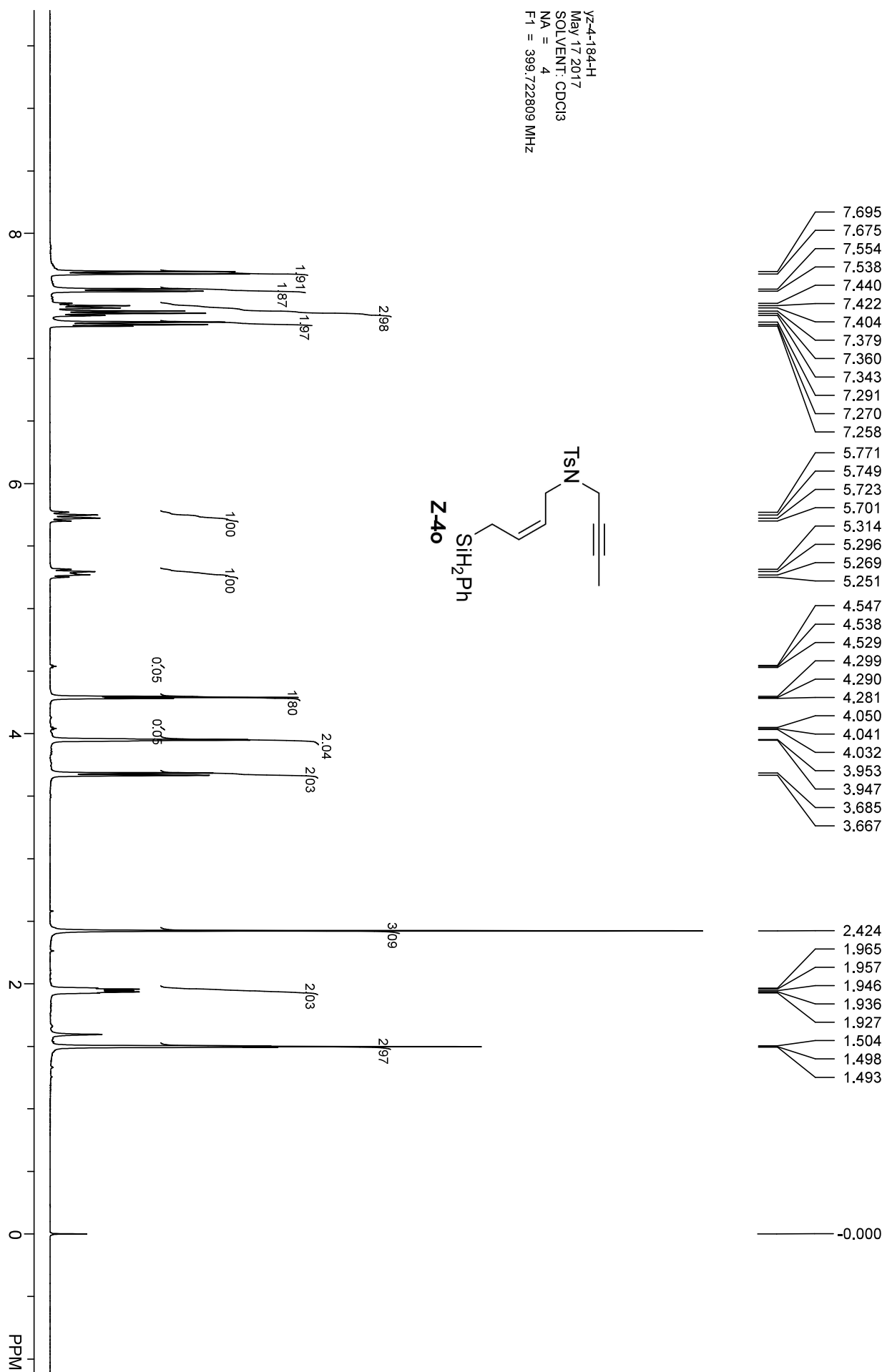


YZ-4-198-C
May 22 2017
SOLVENT: cdcl3
NA = 100
F1 = 100.520737 MHz

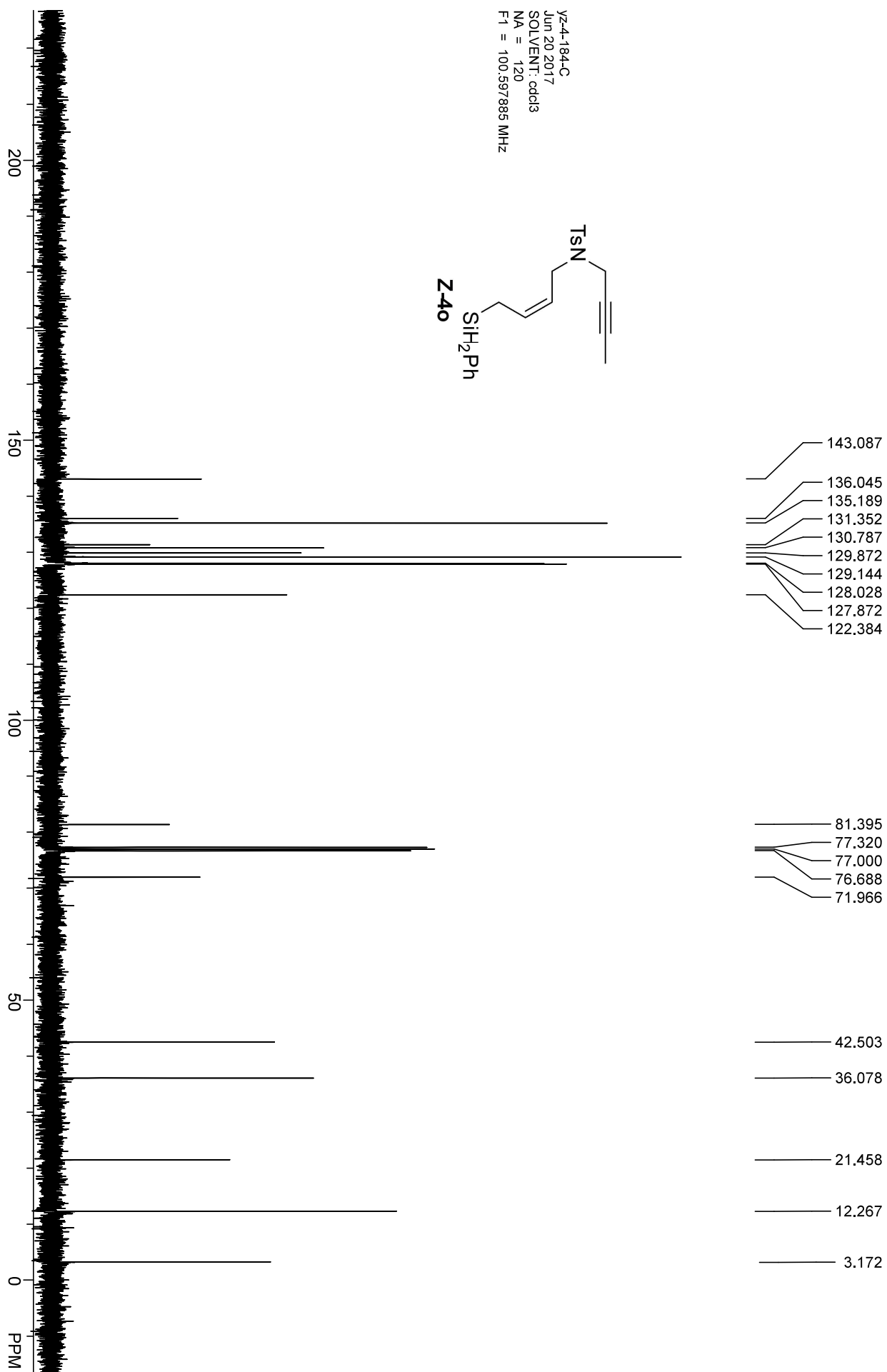
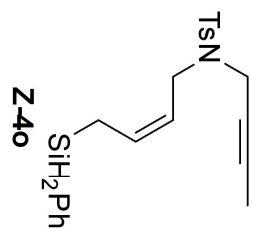


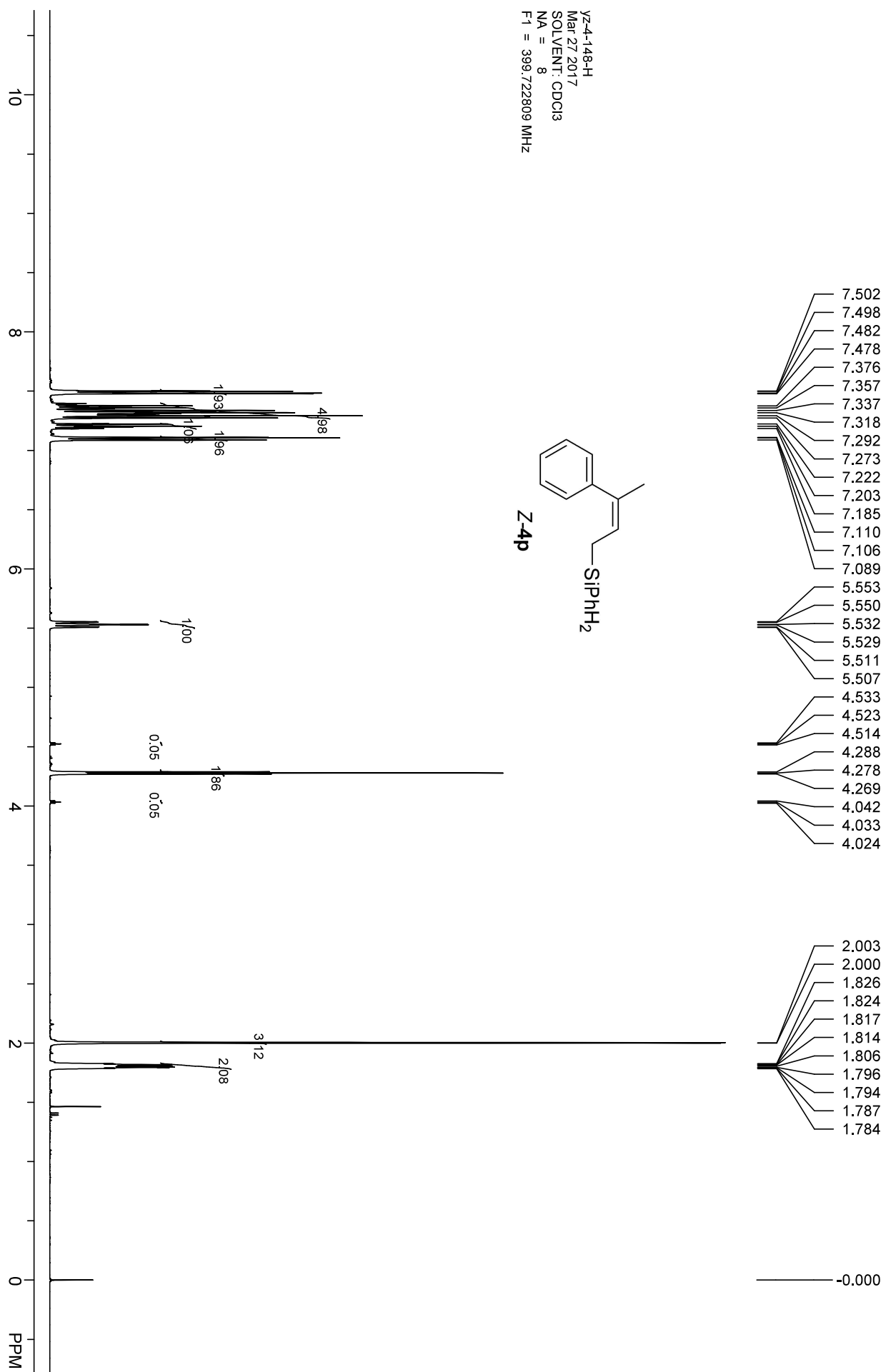






yz-4-184-C
Jun 20 2017
SOLVENT: cddcl3
NA = 120
F1 = 100.597885 MHz





yz-4-148-NOESY

Sample Name:

yz-4-148-NOESY

Data Collected on:

OMC-NMR600-vnmr600

Archive directory:

/home/omc/vnmr600/data

Sample directory:

yz-4-148-NOESY_20170518_01

FidFile: NOESY_01

Pulse Sequence: NOESY

Solvent: cdcl3

Data collected on: May 18 2017

Temp. 25.0 C / 298.1 K

Operator: omc

Relax. delay 1.500 sec

Acq. time 0.262 sec

Width 7716.0 Hz

2D Width 7716.0 Hz

8 repetitions

2 x 128 increments

OBSERVE H1, 599.7751422 MHz

DATA PROCESSING

Line broadening 5.0 Hz

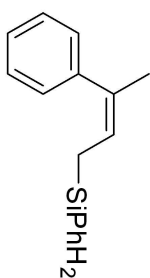
Gauss apodization 0.097 sec

F1 DATA PROCESSING

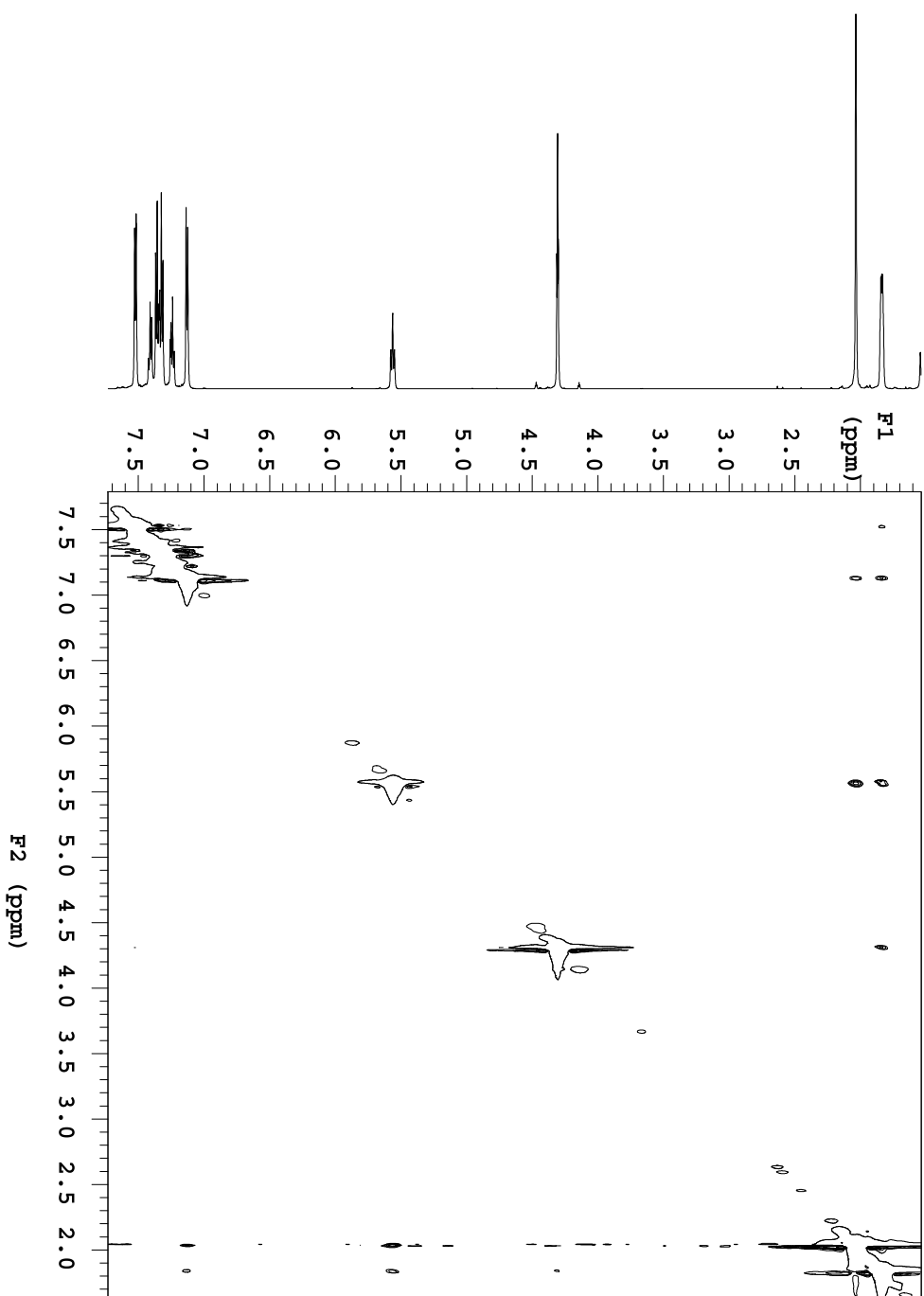
Gauss apodization 0.012 sec

FT size 4096 x 4096

Total time 1 hr, 19 min



Z-4p



Plotname: --Not assigned--

YZ-4-148-C
Mar 27 2017
SOLVENT: cdcl3
NA = 48
F1 = 100.520737 MHz

