Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Synthesis of tri- and tetraynes using a butadiynyl synthon

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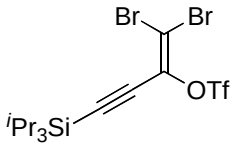
General Experimental. Reagents were purchased reagent grade from commercial suppliers and used without further purification. DMF was dried over 4Å molecular sieves. Diisopropylamine was distilled from CaH_2. Anh. $MgSO_4$ was used as the drying agent after aqueous work-up. Evaporation and concentration in vacuo was performed at H_2O-aspirator pressure.

All reactions were performed in standard, dry glassware under an inert N_2 atmosphere. Column chromatography: *silica gel-60* (230-400 mesh) from *General Intermediates of Canada*. Thin layer chromatography (TLC): Plastic sheets covered with *silica gel-60 F254* from *Macherey-Nagel*; visualization by UV light or $KMnO_4$ stain. IR spectra (cm^{-1}): *Nicolet Magna-IR 750* (neat) or Nic-plan. ^1H- and ^{13}C-NMR: Varian Gemini-300 or 400 instruments, at room temperature in $CDCl_3$; Solvent peaks (7.24 for ^1H and 77.0 for ^{13}C) as reference. Coupling constants are reported as observed (±0.5 Hz). For simplicity, the coupling constants of the aryl protons for *para*-substituted aryl groups have been reported as pseudo first-order (i.e., doublets), even though they are second-order (AA'XX') spin systems.

EI MS (*m/z*): Kratos MS50 instrument. For mass spectrometrical analyses, low-resolution data are provided in cases when M^+ is not the base peak; otherwise, only high-resolution data are provided.

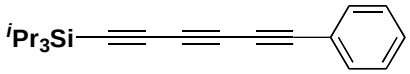


1,1-Dibromo-2-trifluoromethanesulfoxy-4-triisopropylsilyl-but-1-en-3-yne (1).

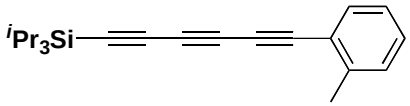
Procedure 1. To a mixture of **4** (200 mg, 0.526 mmol) and HMPA (141 mg, 0.789 mmol) in THF (5 mL) at –78 °C was added LiHMDS (0.684 mmol) in THF (5 mL). The mixture was stirred at –78 °C for 30 min and *N*-phenyltriflamide (226 mg, 0.631 mmol) in THF (4 mL) was added. The solution was allowed to warm to rt over 3 h. Sat. NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 x 30 mL), the organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexanes) to give **1** (191 mg, 0.372 mmol, 70%) as a colorless oil.

Procedure 2. To a solution of **4** (4.80 g, 12.56 mmol) in dry ether (50 ml) at –78 °C was added LiHMDS (15.07 mmol) in ether (30 mL). The mixture was stirred at –78 °C for 30 min and triflic anhydride (5.14 g, 18.24 mmol) was added slowly via a syringe. The reaction was stirred for 40 min at –78°C and then allowed to reach rt over 2 h. The solution was washed twice with sat. NH_4Cl (50 mL) and once with brine (50 mL). The organic layer was dried ($MgSO_4$), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexanes) to

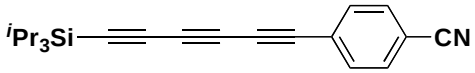
give **1** (5.30 g, 10.31 mmol, 82%) as a colorless oil. R_f = 0.7 (hexane/Et_2O 30:1). IR (neat) 2946, 2893, 2867, 1571, 1463, 1433, 1385, 1368 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.02-1.10 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.6, 118.2 (q, *J* = 319 Hz, *C*F_3), 108.7, 100.5, 94.8, 18.4, 11.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.54. EIMS *m/z* 513 (M^+, 22); HRMS calcd. for $C_{14}H_{21}O_3SiF_3S^{79}Br^{81}Br$ 513.9279, found 513.9273.



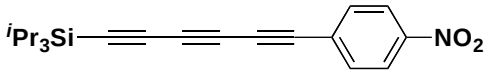
General procedure for tri– or tetrayne formation. Triyne 3a. To a degassed solution of dibromovinyltriflate **1** (0.150 g, 0.291 mmol) and phenylacetylene (0.09 g, 0.58 mmol) in DMF (5 mL) and *i*-Pr_2NH (0.12 g, 0.16 mL, 1.2 mmol) was added P(*t*-Bu)$_3$ (0.25 M in toluene, 0.23 mL, 0.058 mmol), CuI (0.011 g, 0.058 mmol) and $Pd(OAc)_2$ (0.006 g, 0.029 mmol). TLC analysis was used to monitor the reaction, indicating that the dibromovinyltriflate was completely consumed after 30 min of stirring at room temperature. The mixture was then filtered through a plug of silica. Ethyl acetate (20 mL) and satd. aq. NH_4Cl (5 mL) were added. The organic phase separated, washed with water (5 mL) and brine (5 mL), dried over $MgSO_4$, filtered, and the solvent reduced in vacuo. The crude of the reaction was purified by column chromatography (silica gel, hexanes) and afforded **3a** (0.055 g, 62%) as a yellow oil. R_f = 0.6 (hexanes); IR (CH_2Cl_2, cast) 3063, 2944, 2866, 2176, 2074; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.51 (m, 2H), 7.28-7.39 (m, 3H), 1.05-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 129.7, 128.5, 120.9, 89.7, 86.7, 76.5, 74.3, 67.2, 60.6, 18.5, 11.3. EIMS *m/z* 306.2 (M^+, 21), 263.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{21}H_{26}Si$ (M^+) 306.1804, found 306.1805.



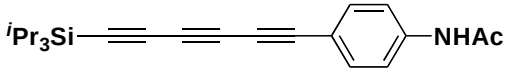
Triyne 3b. Dibromovinyltriflate **1** (0.140 g, 0.272 mmol) and 2-methylphenylacetylene (0.09 g, 0.54 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.027 mmol), P(*t*-Bu)$_3$ (0.22 mL, 0.25 M in toluene, 0.054 mmol), CuI (0.010, 0.054 mmol) and *i*-Pr_2NH (0.11 g, 0.15 mL, 1.1 mmol) in DMF (5 mL) to afford **3b** (0.054 g, 62%) as a yellow oil. R_f = 0.6 (hexanes); IR (CH_2Cl_2, cast) 2945, 2867, 2178, 2072; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.0 Hz, *J* = 1.2 Hz, 1H), 7.28 (td, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.20-7.23 (m, 1H), 7.13-7.17 (m, 1H), 2.46 (s, 3H), 1.05-1.12 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 133.4, 129.6, 125.7, 120.7, 89.8, 86.9, 77.9, 75.6, 67.9, 60.6, 20.6, 18.5, 11.3 (one coincident signal not observed). EIMS *m/z* 320.2 (M^+, 45), 277.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{22}H_{28}Si$ (M^+) 320.1960, found 320.1965.



Triyne 3c. Dibromovinyltriflate **1** (0.135 g, 0.262 mmol) and 4-cyanophenylacetylene (0.067 g, 0.520 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.026 mmol), P(*t*-Bu)$_3$ (0.21 mL, 0.25 M in toluene, 0.05 mmol), CuI (0.010, 0.052 mmol) and *i*-Pr_2NH (0.11 g, 0.14 mL, 1.0 mmol) in DMF (5 mL) to afford **3c** (0.053 g, 61%) as a brown solid. Mp = 95-97 °C. R_f = 0.59 (hexanes/ether 4:1); IR (CH_2Cl_2, cast); 2944, 2866, 2175, 2074; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.62 (m, 4H), 1.02-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4, 132.1, 125.9, 118.0, 112.9, 89.2, 88.7, 78.3, 74.1, 69.4, 59.6, 18.5, 11.2. EIMS *m/z* 331.2 (M^+, 24), 288.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{22}H_{25}NSi$ (M^+) 331.1756, found 331.1752. Data are consistent with those reported in ref. 1.



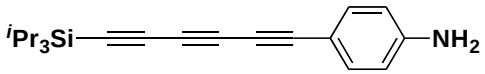
Triyne 3d. Dibromovinyltriflate **1** (0.150 g, 0.290 mmol) and 4-nitro-phenylacetylene (0.085 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.029 mmol), P(*t*-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol), CuI (0.011, 0.058 mmol) and *i*-Pr_2NH (0.11 g, 0.14 mL, 1.0 mmol) in DMF (5 mL) to afford **3d** (0.069 g, 68%) as a yellow solid. Mp = 105-108 °C. R_f = 0.6 (hexanes/ether 95:5); IR (CH_2Cl_2, cast) 3102, 2953, 2867, 2071, 1523, 1343; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 9.2 Hz, 2H), 7.63 (d, *J* = 9.2 Hz, 2H), 1.05-1.11 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 133.7, 127.8, 123.6, 89.1, 88.9, 79.0, 73.7, 69.7, 59.5, 18.5, 11.1. EIMS *m/z* 351.2 (M^+, 22), 308.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{21}H_{25}NO_2Si$ (M^+) 351.1655, found 351.1662.



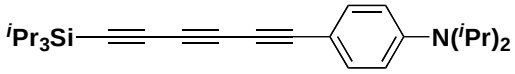
Triyne 3e. Dibromovinyltriflate **1** (0.135 g, 0.262 mmol) and 4-(acetylamino)-phenylacetylene (0.067 g, 0.520 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.026 mmol), P(*t*-Bu)$_3$ (0.21 mL, 0.250 M in toluene, 0.052 mmol) CuI (0.010, 0.052 mmol) and *i*-Pr_2NH (0.11 g, 0.14 mL, 1.0 mmol) in DMF (5 mL) to afford **3e** (0.050 g, 53%) as a brown solid. Mp = 182-185 °C. R_f = 0.6 (hexanes/ether 95:5); IR (CH_2Cl_2, cast) 3305, 3257, 3106, 3054, 2944, 2867, 2167, 2070, 1671; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (br s, 1H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 2.15 (s, 3H), 1.03-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) d 168.5, 139.2, 134.0, 119.3, 116.1, 89.8, 86.8, 76.4, 74.1, 67.3,

1 Luu, T.; Morisaki, Y.; Cunningham, N.; Tykwinski, R. R. *J. Org. Chem.* **2007**, *72*, 9622-9629.

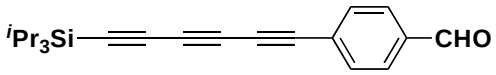
60.7, 24.7, 18.5, 11.3. EIMS *m/z* 363.2 (M^+, 68), 320.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{23}H_{29}NOSi$ (M^+) 363.2018, found 363.2013.



Triyne 3f. Dibromovinyltriflate **1** (0.200 g, 0.390 mmol) and 4-amino-phenylacetylene (0.09 g, 0.78 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.009 g, 0.078 mmol), P(*t*-Bu)$_3$ (0.31 mL, 0.25 M in toluene, 0.078 mmol) CuI (0.015, 0.078 mmol) and *i*-Pr_2NH (0.16 g, 0.22 mL, 1.6 mmol) in DMF (8 mL) to afford **3f** (0.041 g, 33%) as a red oil. R_f = 0.46 (hexanes/ethyl acetate 2:3); IR (CH_2Cl_2, cast) 3470, 3375, 3286, 3226, 2925, 2865, 2185, 2099, 1622, 1595, 1511; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 3.86 (b s, NH_2), 1.03-1.06 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 134.7, 114.5, 109.3, 90.0, 85.9, 77.9, 72.6, 66.8, 61.2, 18.4, 11.2. HRMS calcd. for $C_{21}H_{27}NSi$ (M^+) 321.1913, found 321.1917.

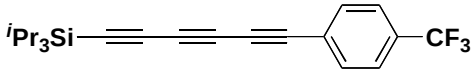


Triyne 3g. Dibromovinyltriflate **1** (0.120 g, 0.234 mmol) and 4-(diisopropylamino)-phenylacetylene (0.093 g, 0.460 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.005 g, 0.023 mmol), P(Cy)$_3$ (0.013 g, 0.046 mmol), CuI (0.009, 0.046 mmol) and *i*-Pr_2NH (0.093 g, 0.13 mL, 0.92 mmol) in DMF (5 mL) to afford **3g** (0.046 g, 48%) as a yellow oil. R_f = 0.64 (hexanes/ether 9:1); IR (CH_2Cl_2, cast) 3470, 2943, 2866, 2166, 2068, 1601, 1517; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 3.87 (sept, *J* = 6.8 Hz, 2H), 1.26 (d, *J* = 6.8 Hz, 12H), 1.07-1.11 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 134.0, 115.0, 106.1, 90.2, 85.8, 78.8, 72.8, 66.9, 61.7, 47.3, 21.0, 18.4, 11.2. EIMS *m/z* 405.3 (M^+, 87), 390.3 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{27}H_{39}NSi$ (M^+) 405.2852, found 405.2852.

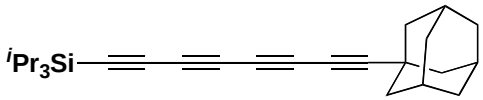


Triyne 3h. Dibromovinyltriflate **1** (0.140 g, 0.272 mmol) and *para*-ethynylbenzaldehyde (0.07 g, 0.54 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.027 mmol), P(*t*-Bu)$_3$ (0.22 mL, 0.25 M in toluene, 0.054 mmol), CuI (0.010, 0.054 mmol) and *i*-Pr_2NH (0.11 g, 0.15 mL, 1.1 mmol) in DMF (5 mL) to afford **3h** (0.036 g, 40%) as a yellow solid. Mp = 66-68 °C. R_f = 0.6 (hexanes/ether 99:1); IR (CH_2Cl_2, cast) 2945, 2866, 2074, 1705, 1601; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 1.05-1.10 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 136.3, 133.5, 129.5, 127.1,

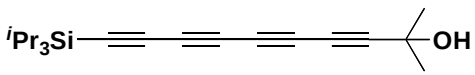
89.4, 88.4, 78.0, 75.0, 69.1, 59.9, 18.6, 11.3. EIMS *m/z* 334.2 (M^+, 21), 291.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{22}H_{26}OSi$ (M^+) 334.1753, found 334.1751.



Triyne 3i. Dibromovinyltriflate **1** (0.100 g, 0.194 mmol) and 4-(trifluoromethyl)phenylacetylene (0.06 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.004 g, 0.019 mmol), P(*t*-Bu)$_3$ (0.15 mL, 0.25 M in toluene, 0.038 mmol), CuI (0.007, 0.038 mmol) and *i*-Pr_2NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford **3i** (0.029 g, 40%) as a yellow oil. R_f = 0.6 (hexanes/ether 99:1); IR (CH_2Cl_2, cast) 2946, 2868, 2076, 1322; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.55 (m, 4H), 1.06-1.11 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.1, 131.1 (q, J_{CF} = 32.8 Hz), 125.3 (q, J_{CF} = 3.7 Hz), 124.7, 123.4 (q, J_{CF} = 270.3 Hz), 89.3, 87.8, 76.5, 74.5, 68.3, 59.8, 18.5, 11.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.43. EIMS *m/z* 374.2 (M^+, 11), 331.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{22}H_{25}F_3Si$ (M^+) 374.1678, found 374.1677.

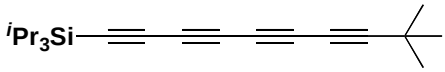


Tetrayne 3k. Dibromovinyltriflate **1** (0.100 g, 0.194 mmol) and 1-butadiynyladamantane (0.07 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.004 g, 0.019 mmol), P(*t*-Bu)$_3$ (0.15 mL, 0.25 M in toluene, 0.038 mmol), CuI (0.007, 0.038 mmol) and *i*-Pr_2NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford **3k** (0.020 g, 26%) as a white solid. Mp = 130-132 °C. R_f = 0.6 (hexanes); IR (CH_2Cl_2, cast) 2930, 2867, 2206, 2138, 2057; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (br s, 3H), 1.84-1.95 (m, 6H), 1.64-1.71 (m, 6H), 1.05-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.7, 87.5, 84.7, 64.6, 62.2, 61.6, 61.5, 61.4, 41.8, 41.7, 35.9, 30.2, 27.4, 18.4, 11.2. EIMS *m/z* 388.3 (M^+, 13), 345.2 ([M – ^{i}Pr]$^+$, 66); HRMS calcd. for $C_{27}H_{36}Si$ (M^+) 388.2587, found 388.2583.

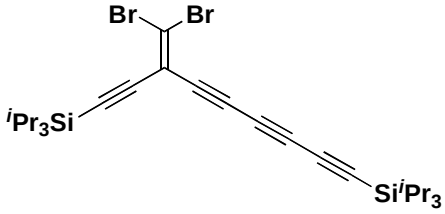


Tetrayne 3l. Dibromovinyltriflate **1** (0.100 g, 0.194 mmol) and 2-methylhexa-3,5-diyn-2-ol (0.04 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.004 g, 0.019 mmol), P(*t*-Bu)$_3$ (0.15 mL, 0.25 M in toluene, 0.038 mmol), CuI (0.007, 0.038 mmol) and *i*-Pr_2NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford **3l** (0.027 g, 45%) as a red oil. R_f = 0.6 (hexanes/ether 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (br s, 1H), 1.54 (s, 6H), 1.08-1.03 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.4, 85.9, 82.1, 67.3, 65.5, 64.2, 62.8,

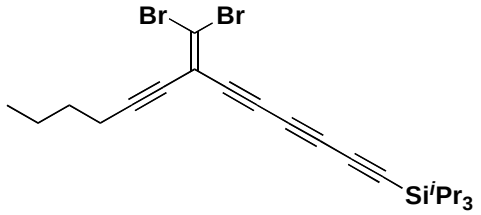
61.0, 60.8, 30.8, 18.4, 11.2. EIMS *m/z* 312.2 (M^+, 6), 269.1 ([M – ^{i}Pr]$^+$, 78); HRMS calcd. for $C_{20}H_{28}OSi$ (M^+) 312.1910, found 312.1909.



Tetrayne 3m. Dibromovinyltriflate **1** (0.100 g, 0.194 mmol) and 5,5-dimethylhexa-1,3-diyne (0.04 g, 0.38 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.004 g, 0.019 mmol), P(*t*-Bu)$_3$ (0.15 mL, 0.25 M in toluene, 0.038 mmol), CuI (0.007, 0.038 mmol) and *i*-Pr_2NH (0.077 g, 0.11 mL, 0.76 mmol) in DMF (3 mL) to afford **3m** (0.009 g, 15%) as a yellow oil. R_f = 0.63 (hexanes); IR (CH_2Cl_2, cast) 2945, 2867, 2210, 2149, 2058, 1239; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.05-1.08 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.7, 88.0, 84.7, 64.3, 62.0, 61.5, 61.4, 30.1, 28.1, 18.4, 11.2 (one coincident signal not observed). EIMS *m/z* 310.2 (M^+, 28), 267.1 ([M – ^{i}Pr]$^+$, 100); HRMS calcd. for $C_{21}H_{30}Si$ (M^+) 310.2117, found 310.2116.

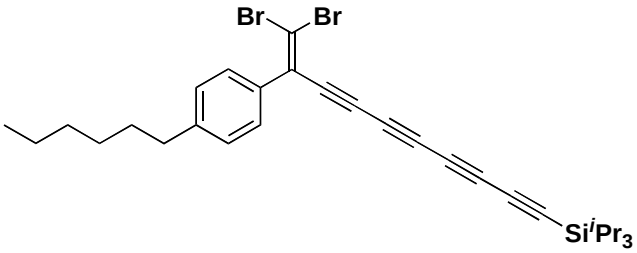


Triyne 6a. Dibromovinytriflate **1** (0.150 g, 0.291 mmol) and **5a** (0.23 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.029 mmol), P(*t*-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol), CuI (0.011, 0.058 mmol), and *i*-Pr_2NH (0.12 g, 0.16 mL, 1.2 mmol) in DMF (5 mL) to afford **6a** (0.086 g, 50%) as a yellow oil. R_f = 0.6 (hexanes); IR (CH_2Cl_2, cast) 2944, 2891, 2866, 2181, 2071, 2043; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05-1.10 (m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.3, 113.2, 101.2, 100.7, 89.5, 89.2, 80.2, 72.0, 70.7, 60.0, 18.6, 18.5, 11.2, 11.1. EIMS *m/z* 594.1 (M^+, 2), 367.2 ([M – $C_5H_7Br_2$]$^+$, 100); HRMS calcd. for $C_{28}H_{42}{}^{79}Br^{81}BrSi$ (M^+) 594.1171, found 594.1178.

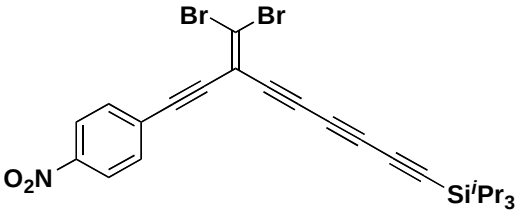


Triyne 6b. Dibromovinyltriflate **1** (0.150 g, 0.291 mmol) and **5b** (0.17 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.029 mmol), P(*t*-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol), CuI (0.011, 0.058 mmol), and *i*-Pr_2NH (0.12 g, 0.16 mL, 1.2 mmol) in DMF (5 mL) to afford **6b** (0.044 g, 31%) as a yellow oil.

R_f = 0.68 (hexanes/ether 95:5); IR (CH_2Cl_2, cast) 2944, 2866, 2237, 2180, 2072; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (t, *J* = 7.2 Hz, 2H), 1.55 (sext, *J* = 7.2 Hz, 2H), 1.42 (quint, *J* = 7.2 Hz, 2H), 1.05-1.08 (m, 21H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.3, 111.0, 99.6, 89.5, 89.0, 79.8, 72.5, 70.5, 59.9, 30.0, 21.9, 19.4, 18.5, 13.5, 11.2 (one coincident signal not observed). EIMS *m/z* 494.0 (M^+, 67), 57 (Bu^+, 100); HRMS calcd. for $C_{23}H_{30}{}^{79}Br^{81}BrSi$ (M^+) 494.0463, found 494.0460.



Tetrayne 6c. Dibromovinyltriflate **1** (0.150 g, 0.291 mmol) and **5c** (0.24 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.029 mmol), P(*t*-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol), CuI (0.011, 0.058 mmol) and *i*-Pr_2NH (0.12 g, 0.16 mL, 1.2 mmol) in DMF (5 mL) to afford **6c** (0.088 g, 49%) as a yellow oil. R_f = 0.64 (hexanes/ether 95:5); IR (CH_2Cl_2, cast) 2943, 2929, 2866, 2186, 2122, 2054; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 1.62 (quint, *J* = 7.2 Hz, 2H), 1.30-1.28 (m, 6H), 1.04-108 (m, 21H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 133.9, 129.5, 128.6, 128.3, 104.4, 89.5, 88.0, 81.9, 74.6, 71.2, 66.3, 61.0, 60.8, 35.8, 31.7, 31.2, 29.0, 22.6, 18.5, 14.0, 11.2. EIMS *m/z* 598.2 (M^+, 2), 555.1 ([M – ^{i}Pr]$^+$, 7); HRMS calcd. for $C_{33}H_{38}{}^{79}Br^{81}BrSi$ (M^+) 598.1089, found 598.1072.



Triyne 6d. Dibromovinyltriflate **1** (0.150 g, 0.291 mmol) and **5d** (0.205 g, 0.58 mmol) were subjected to the conditions outlined in the general procedure using $Pd(OAc)_2$ (0.006 g, 0.029 mmol), P(*t*-Bu)$_3$ (0.23 mL, 0.25 M in toluene, 0.058 mmol) CuI (0.011, 0.058 mmol) and *i*-Pr_2NH (0.12 g, 0.16 mL, 1.2 mmol in DMF (5 mL) to afford **6d** (0.057 g, 35%) as a yellow oil. R_f = 0.64 (hexanes/ether 95:5); IR (CH_2Cl_2, cast) 2943, 2866, 2179, 2073, 1523, 1343; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 1.06-1.08 (s, 21H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 132.4, 128.4, 123.7, 114.4, 112.6, 94.1, 89.9, 89.32, 89.30, 81.1, 71.30,

71.26, 59.7, 18.5, 11.2. EIMS *m/z* 559.0 (M^+, 5), 516.0 ([M – ^{i}Pr]$^+$, 100); HRMS analysis was not successful due to the apparent instability of the compound to the analysis conditions.

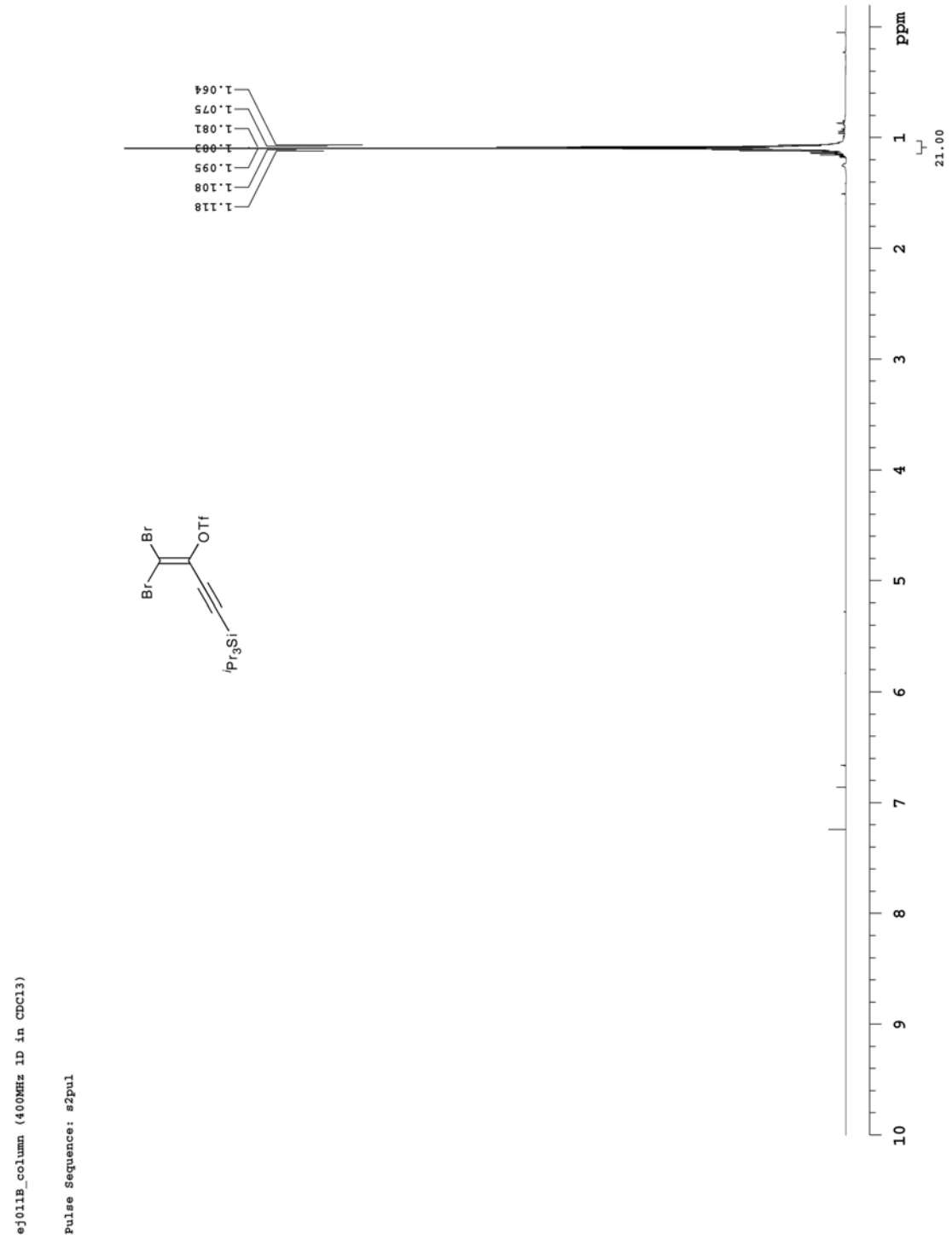


Figure S1. ^{1}H NMR Spectrum of **1**

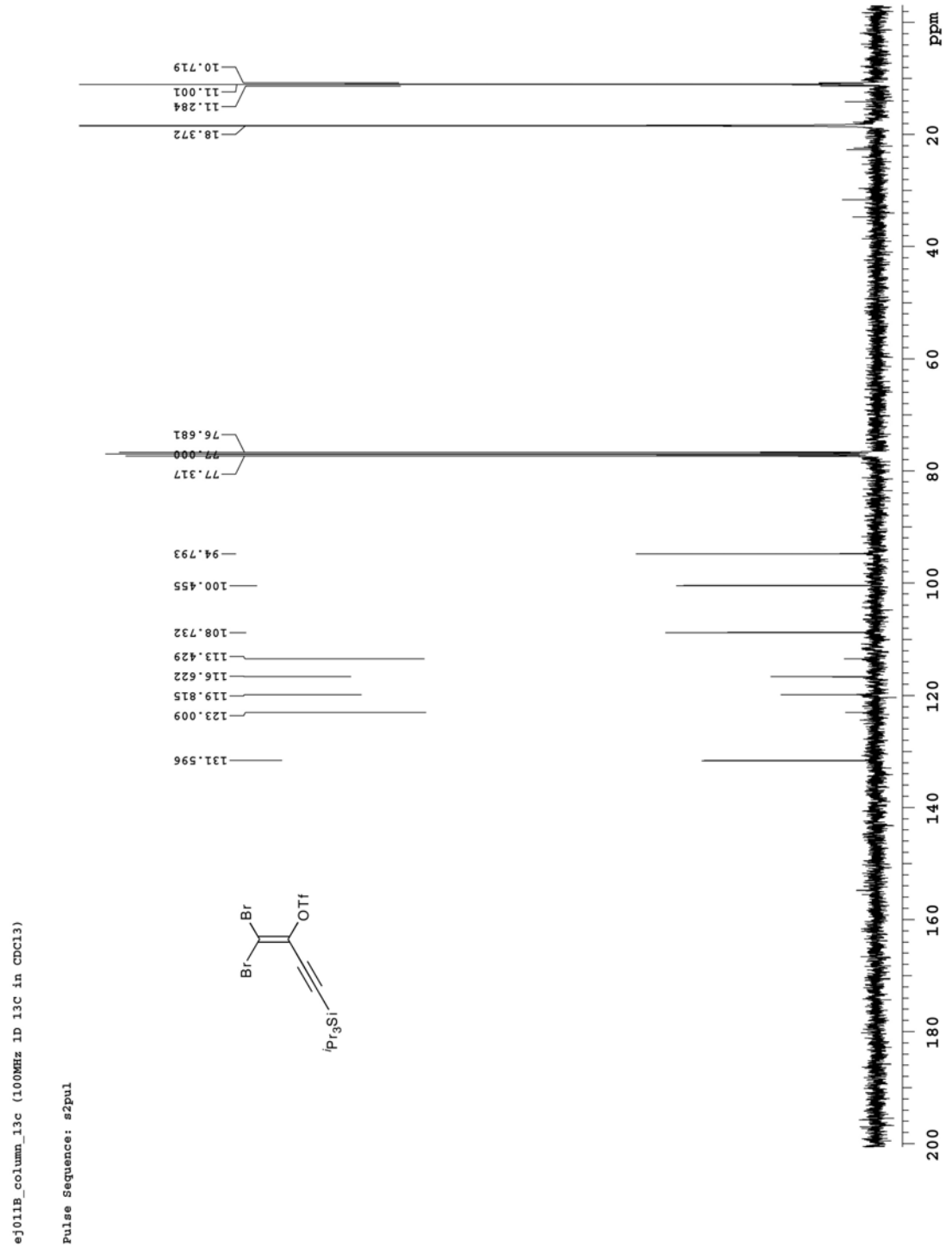


Figure S2. ^{13}C NMR Spectrum of **1**

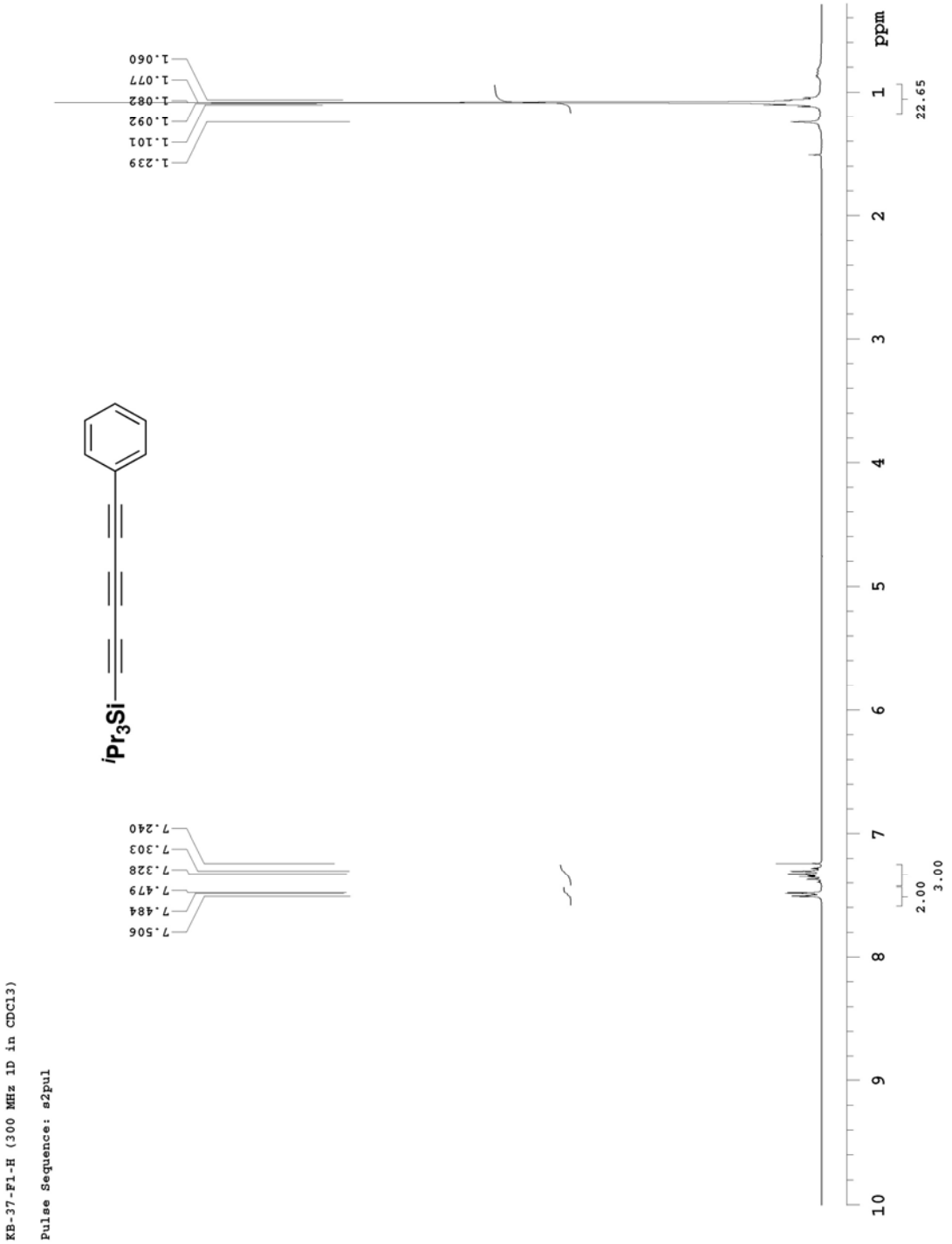


Figure S1. ^{1}H NMR Spectrum of **3a**

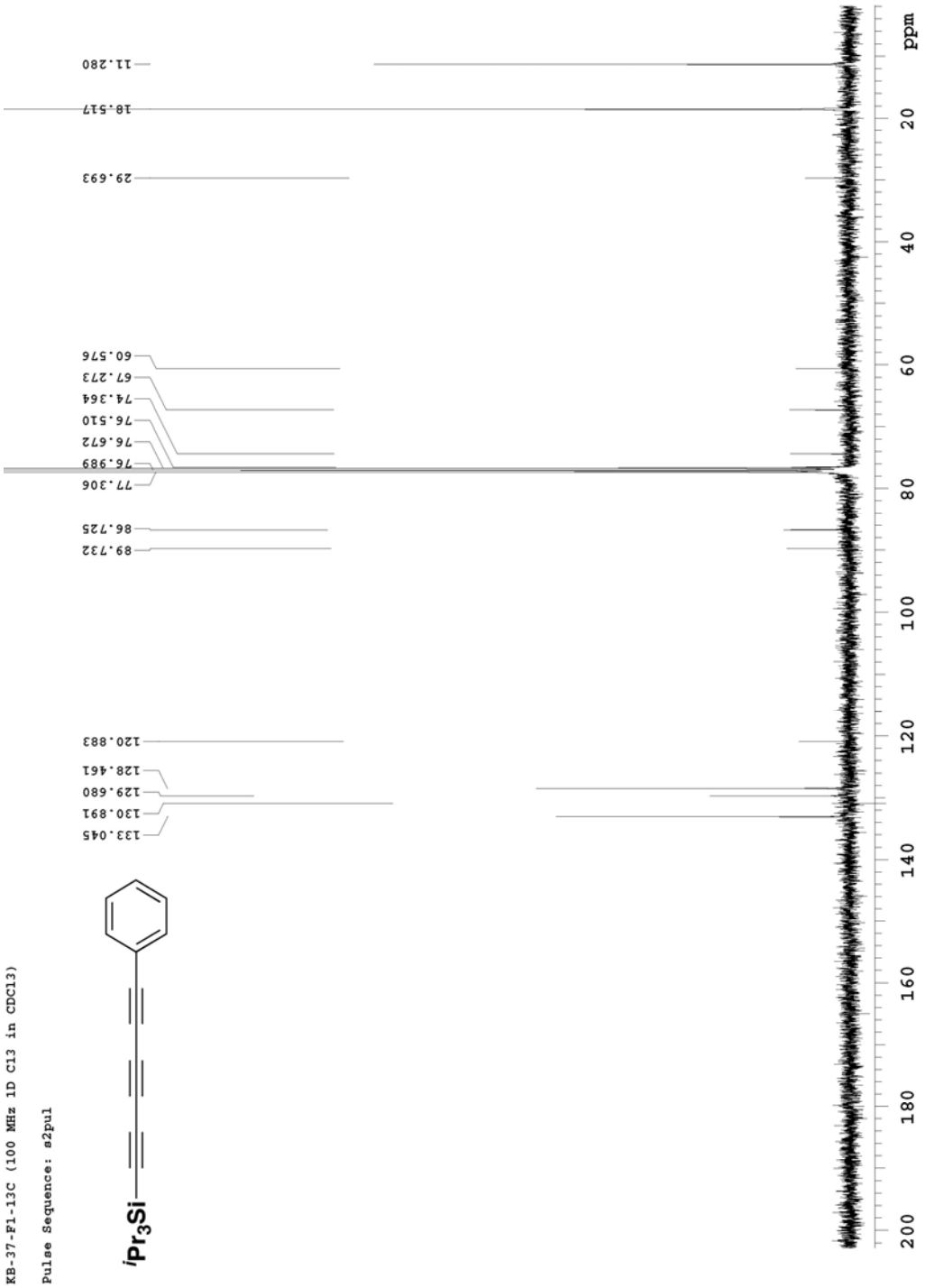


Figure S2. ^{13}C NMR Spectrum of **3a**

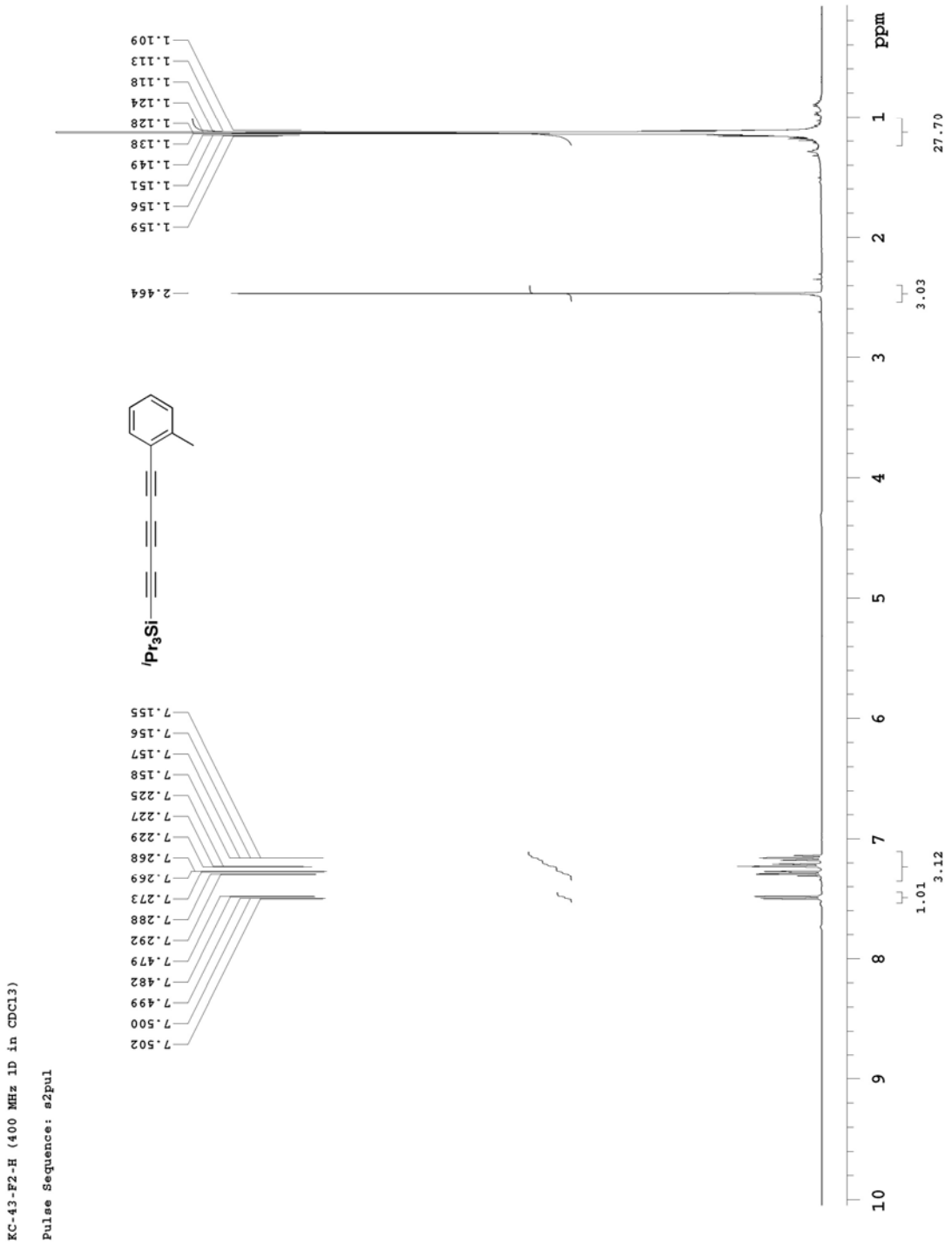


Figure S3. ^{1}H NMR Spectrum of **3b**

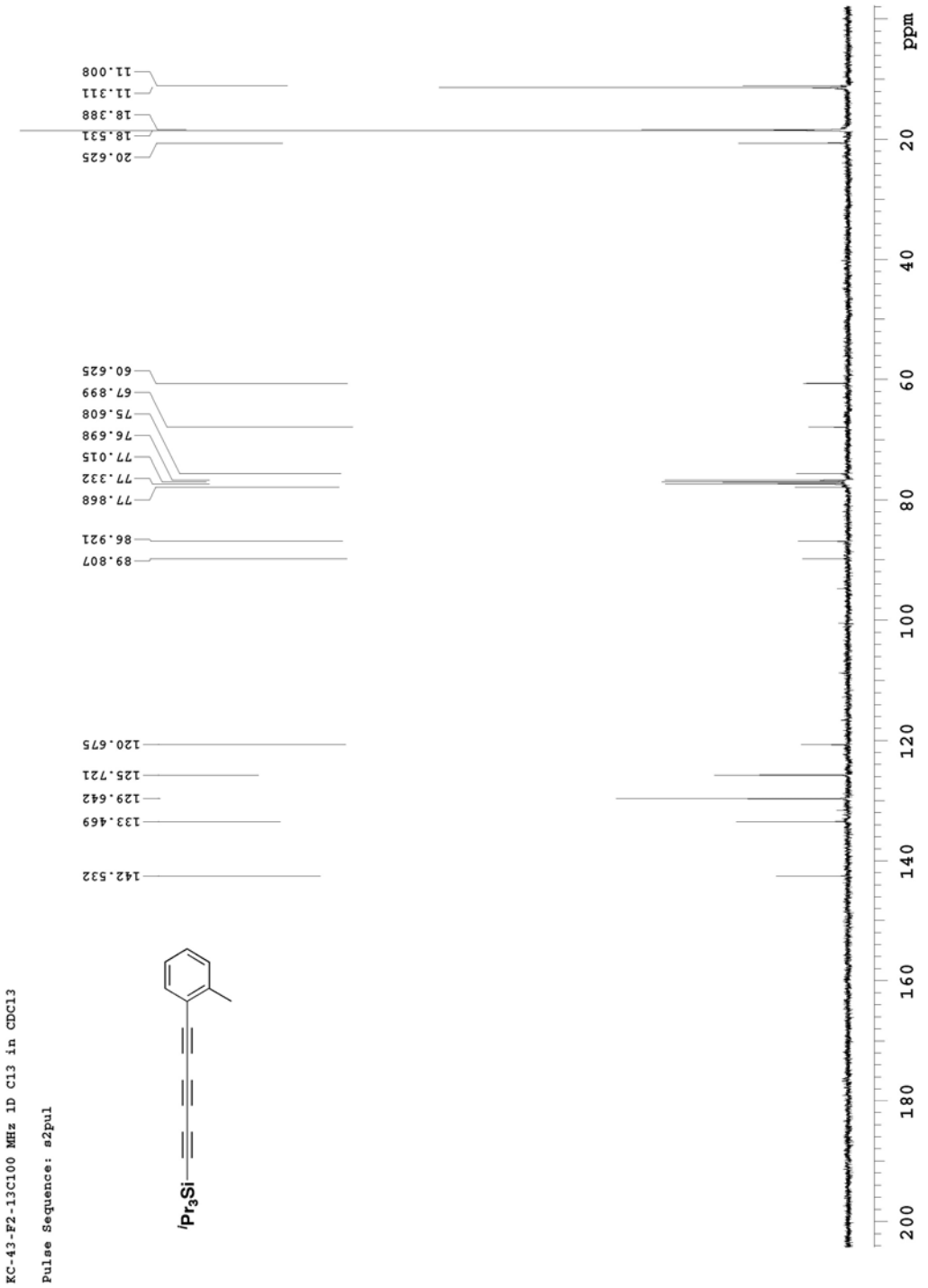


Figure S4. ^{13}C NMR Spectrum of **3b**

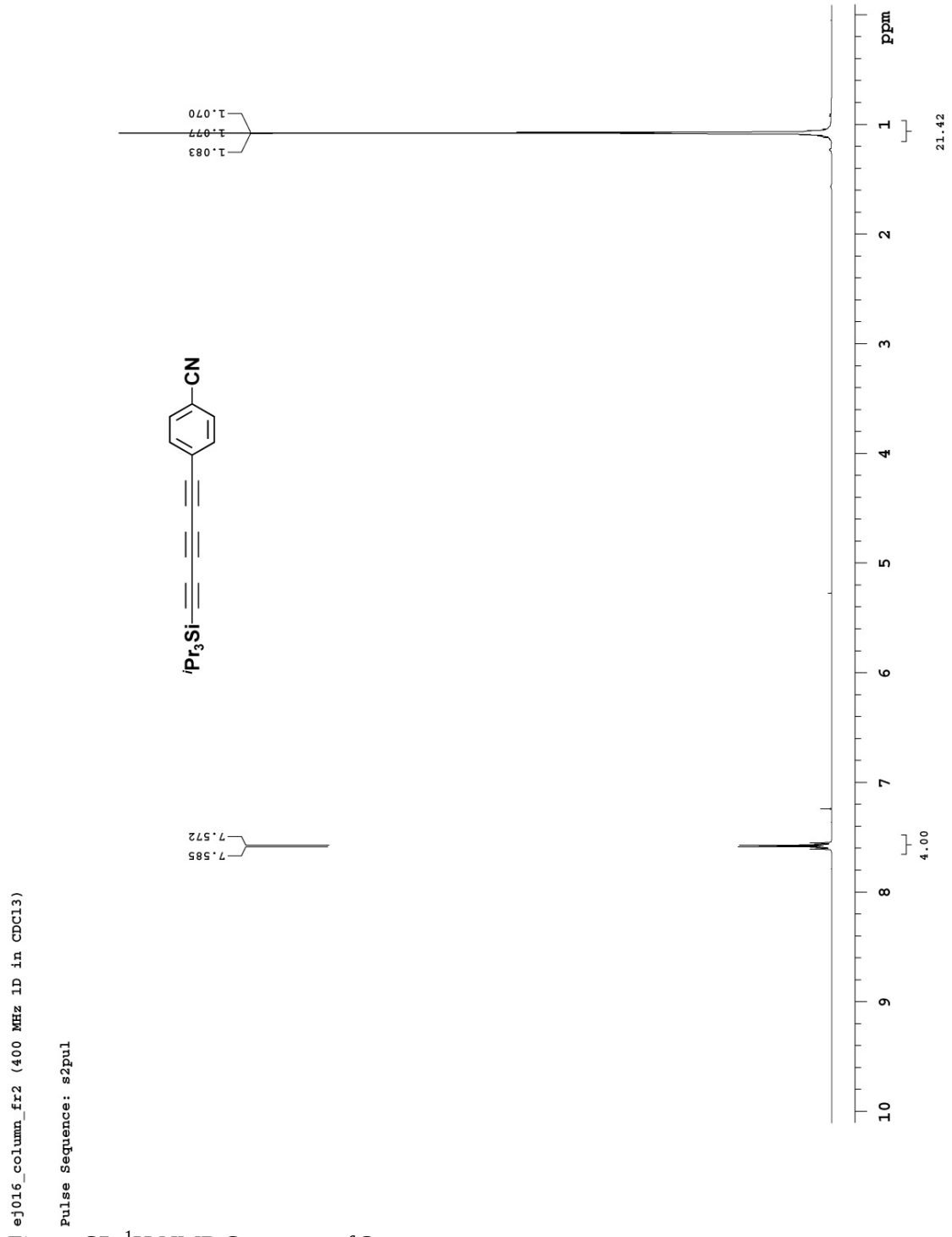


Figure S5. ^{1}H NMR Spectrum of **3c**

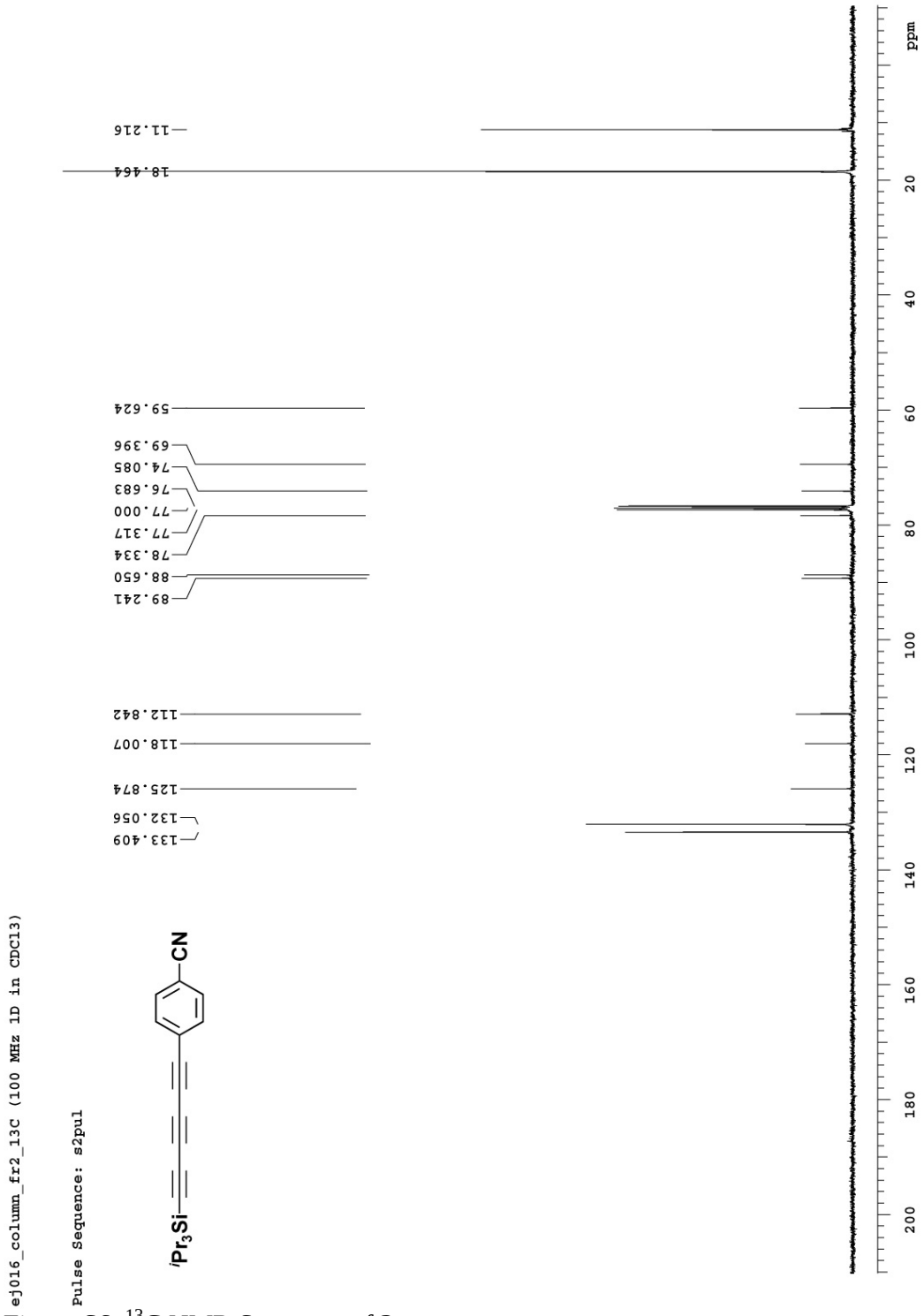


Figure S6. ^{13}C NMR Spectrum of **3c**

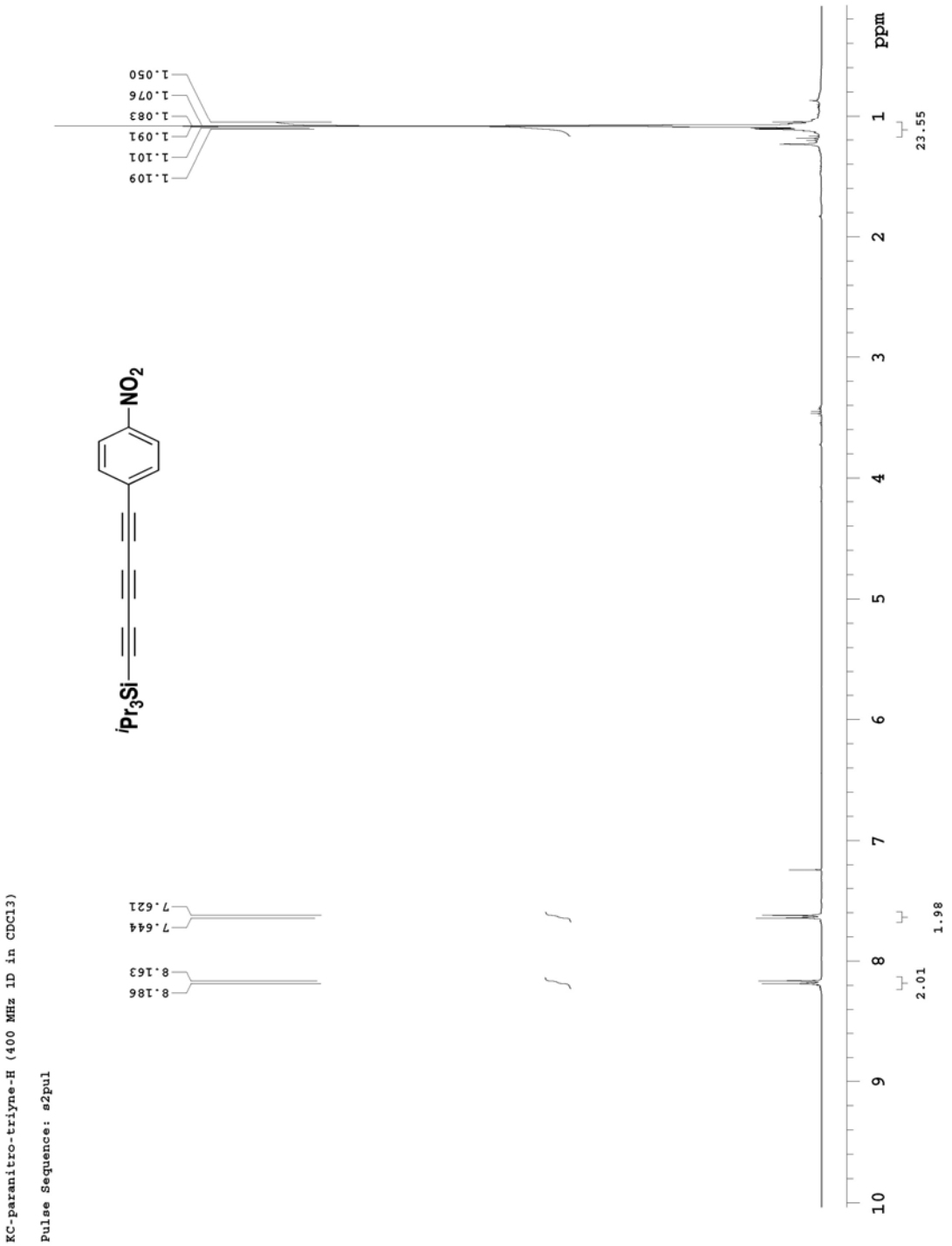


Figure S7. ^{1}H NMR Spectrum of **3d**

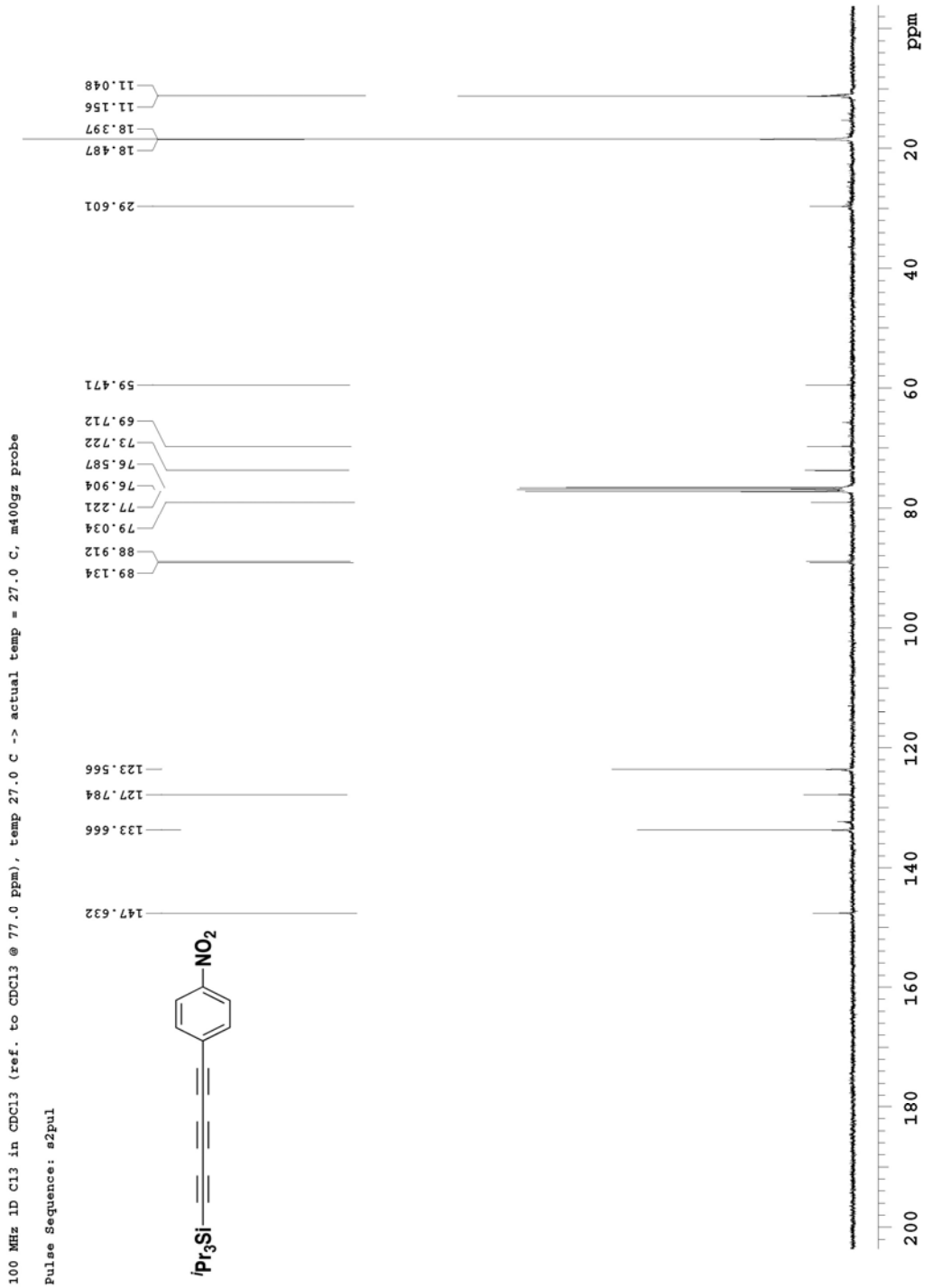


Figure S8. ^{13}C NMR Spectrum of **3d**

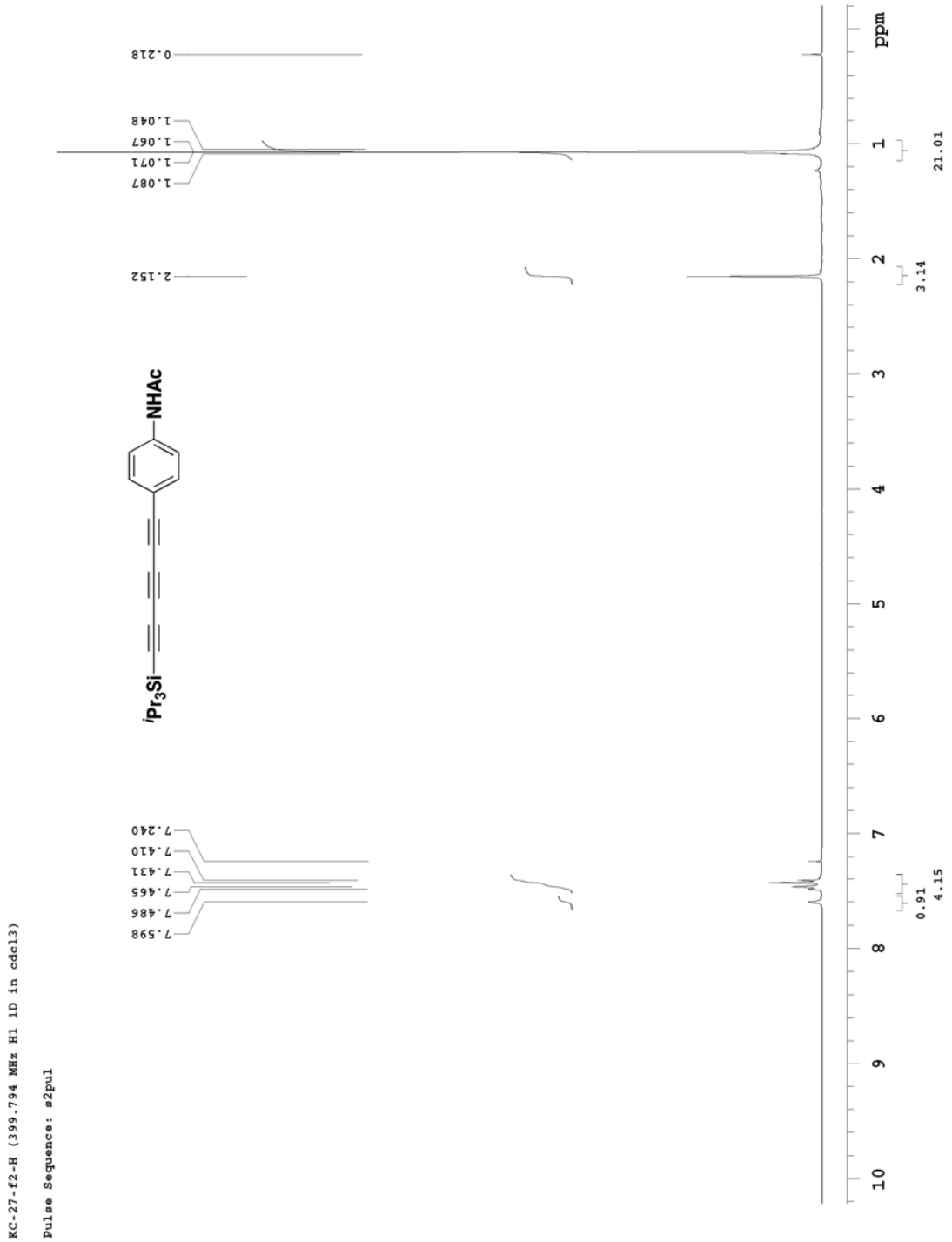


Figure S9. ^{1}H NMR Spectrum of **3e**

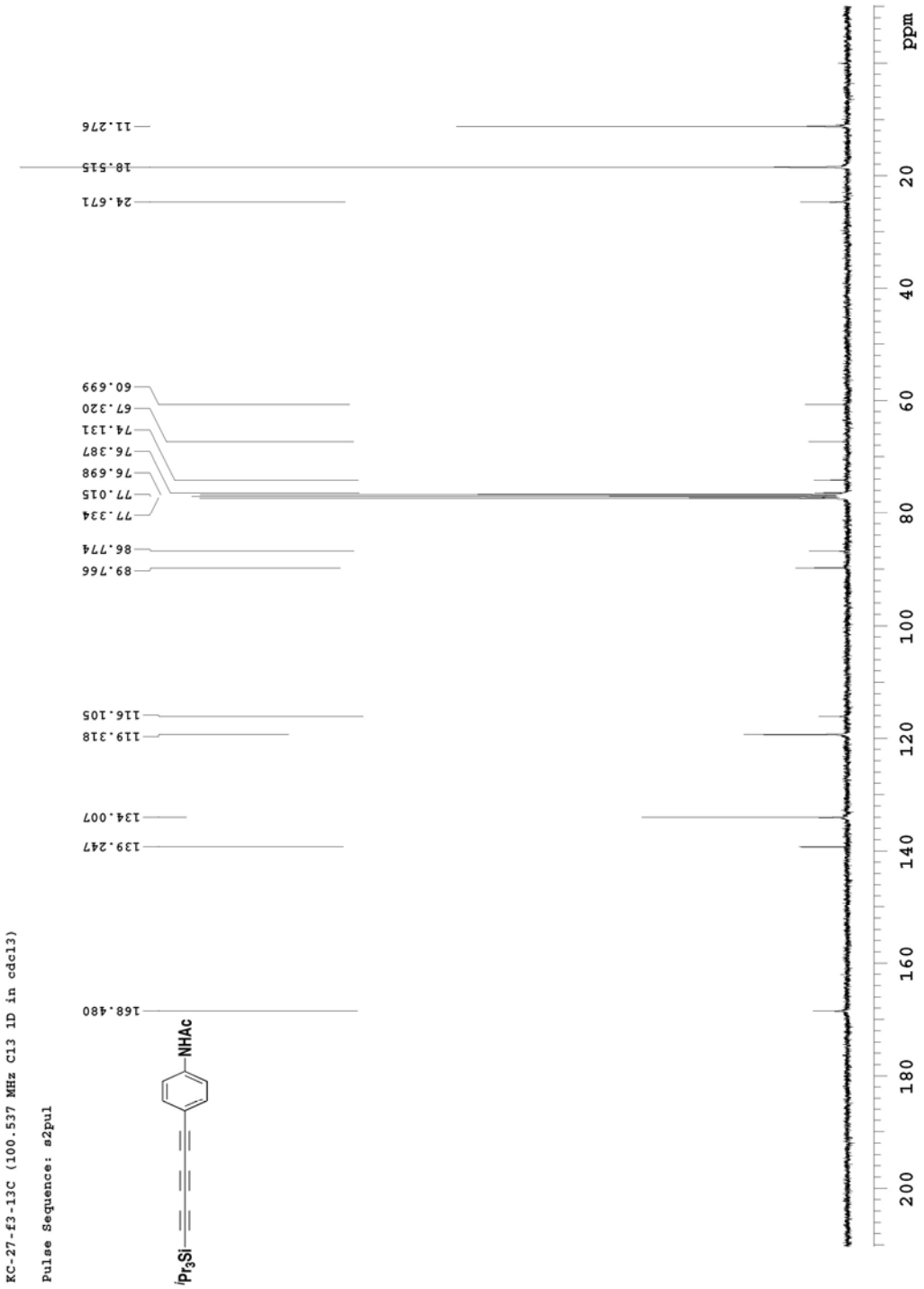


Figure S10. ^{13}C NMR Spectrum of **3e**

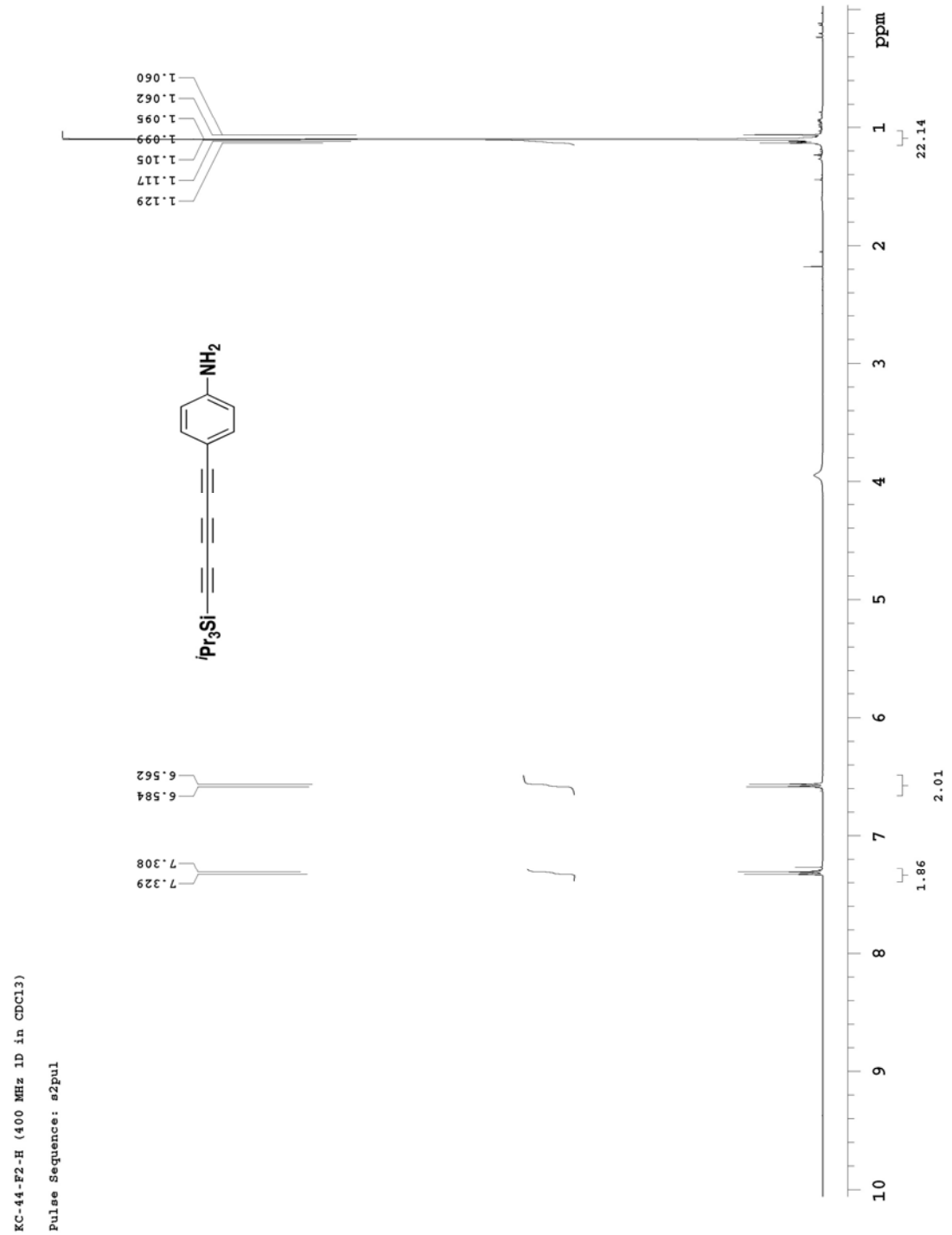


Figure S11. ^{1}H NMR Spectrum of **3f**

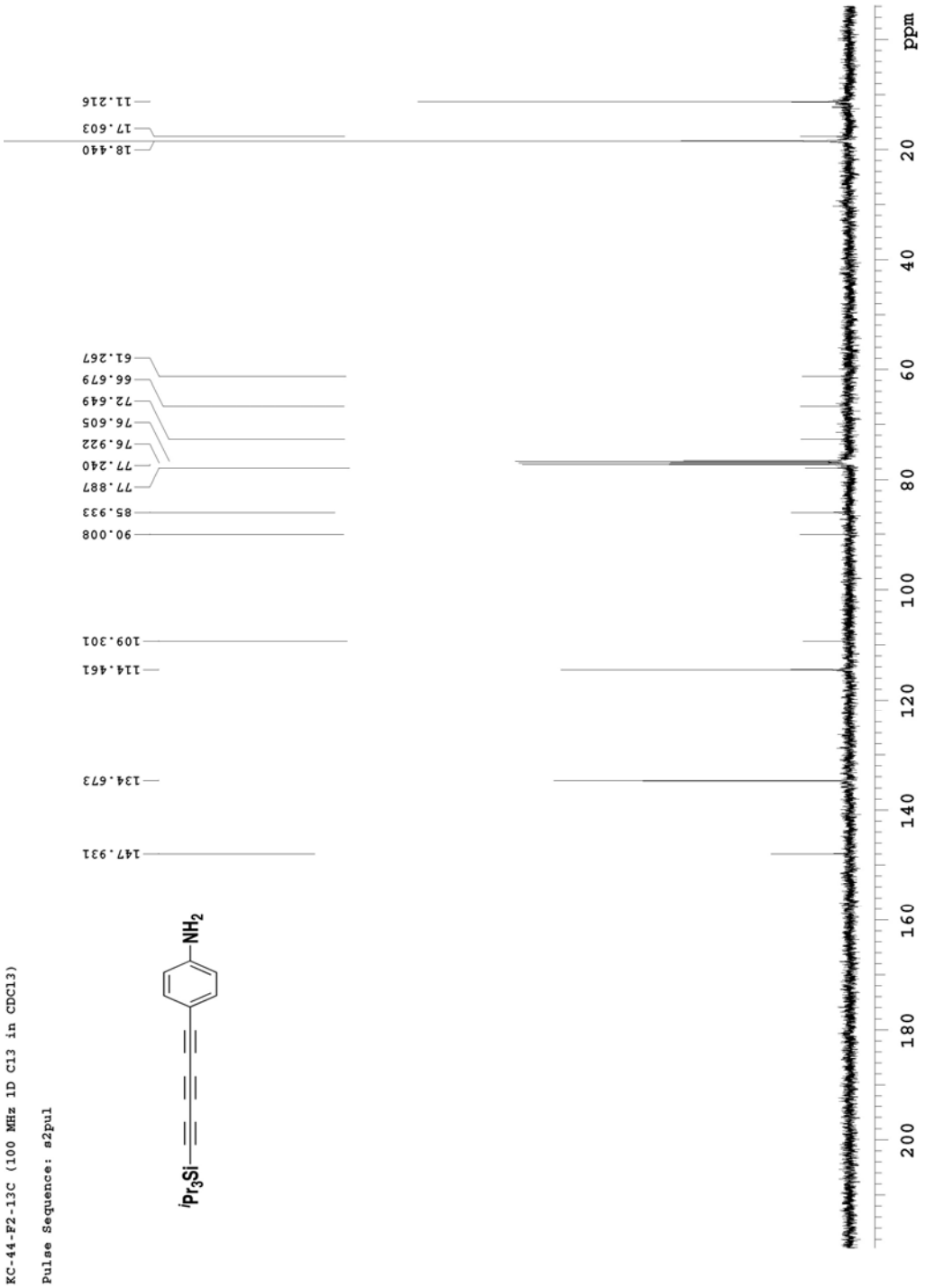


Figure S12. ^{13}C NMR Spectrum of **3f**

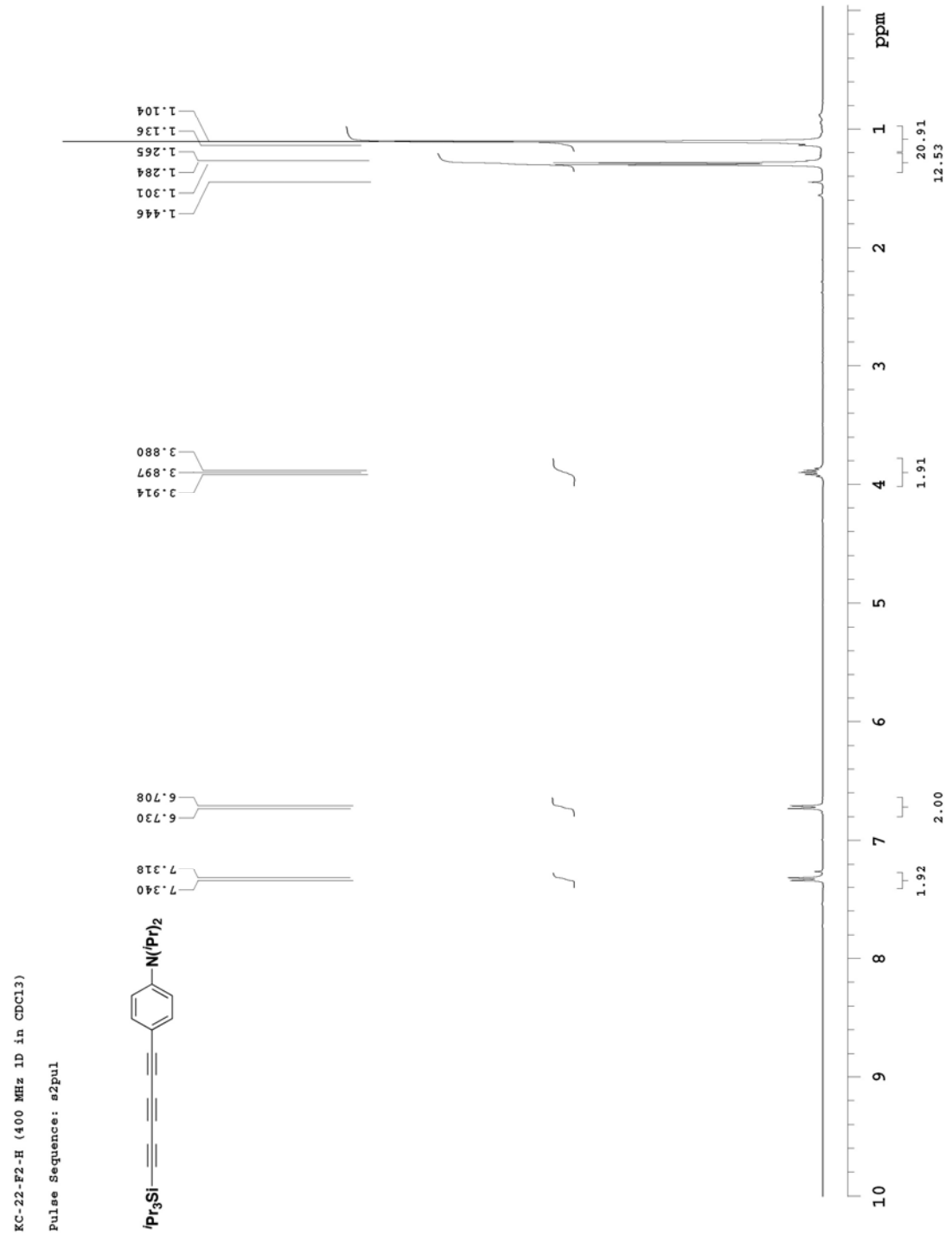


Figure S13. ^{1}H NMR Spectrum of **3g**

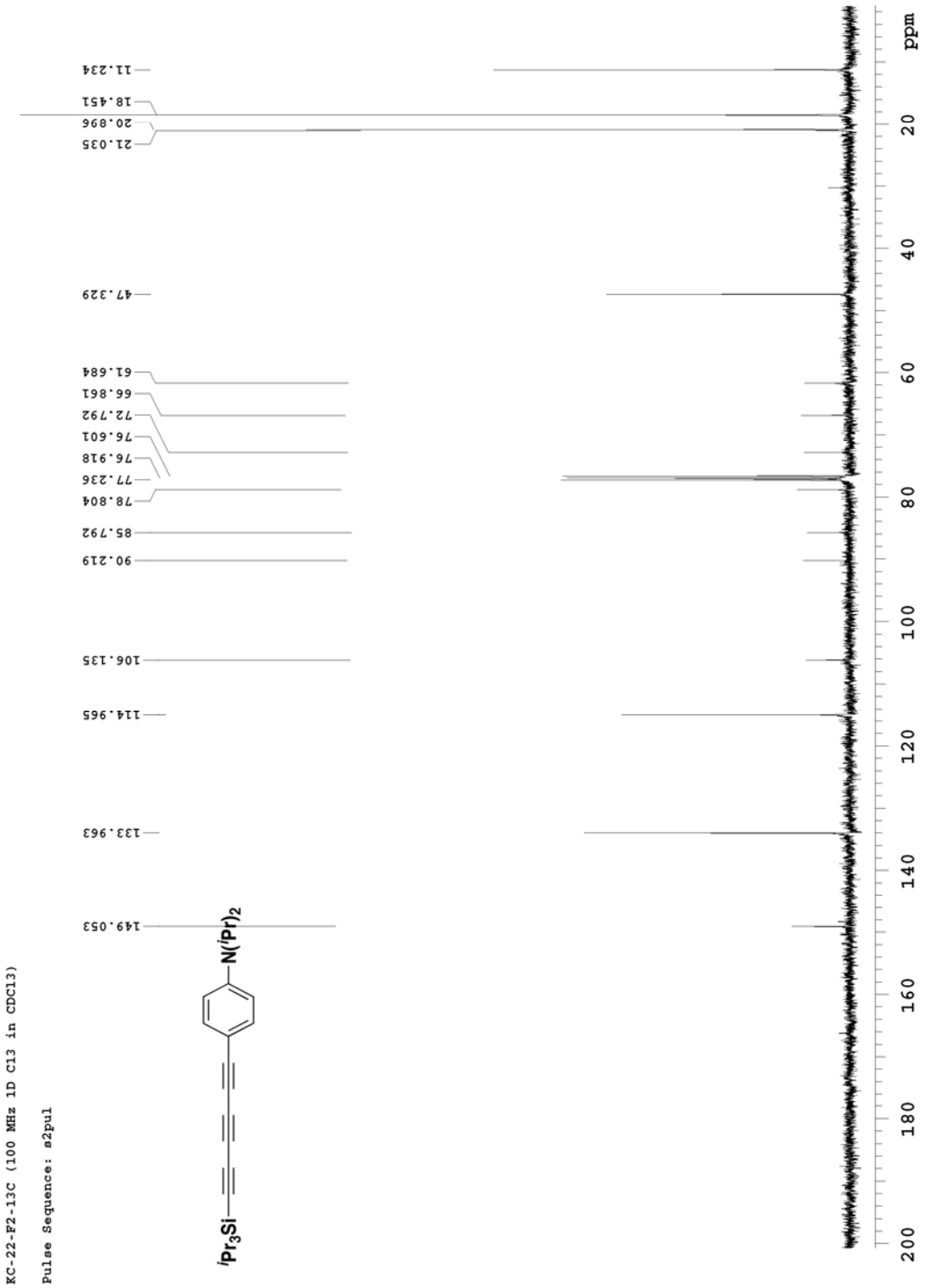


Figure S14. ^{13}C NMR Spectrum of **3g**

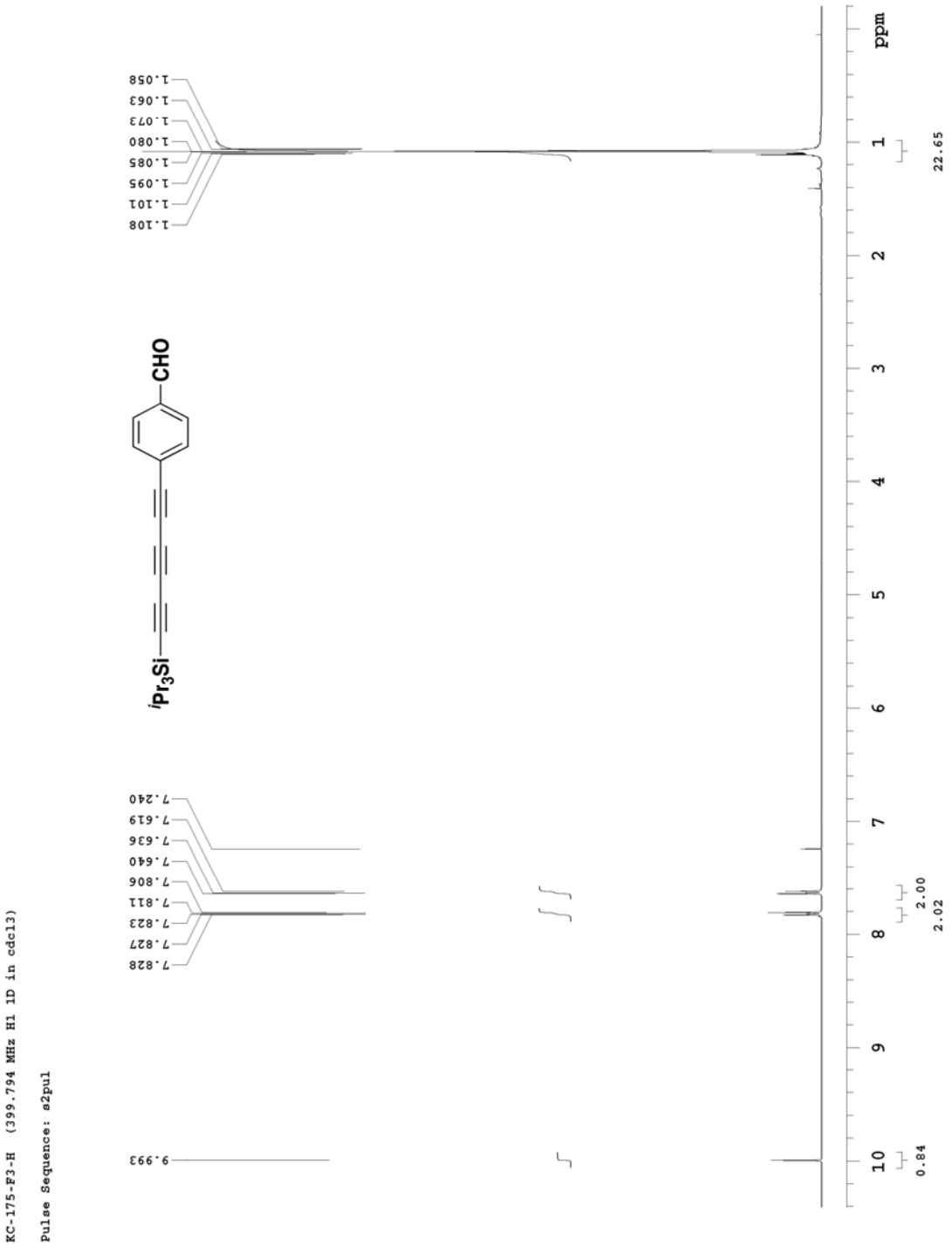


Figure S15. ^{1}H NMR Spectrum of **3g**

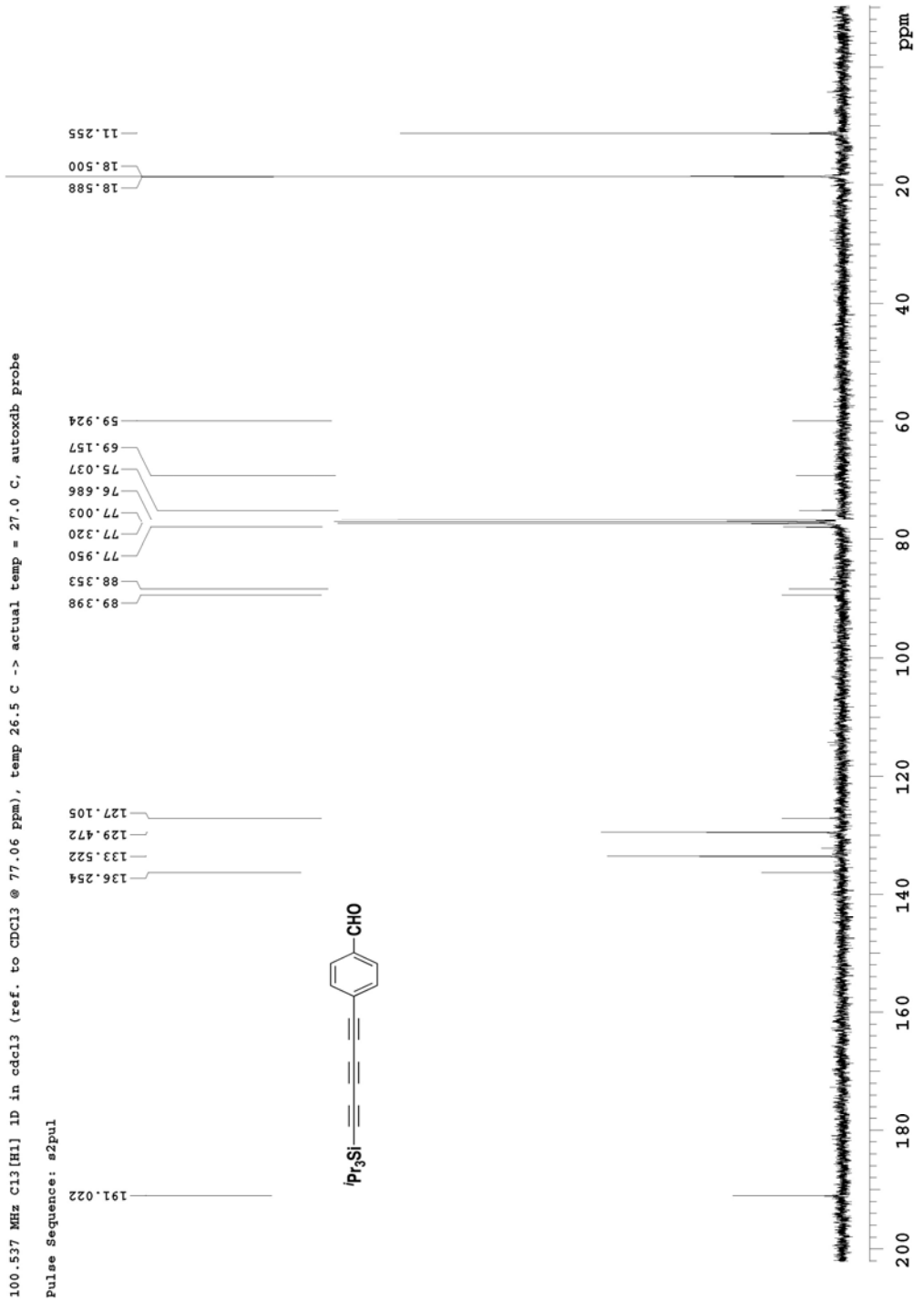


Figure S16. ^{13}C NMR Spectrum of **3g**

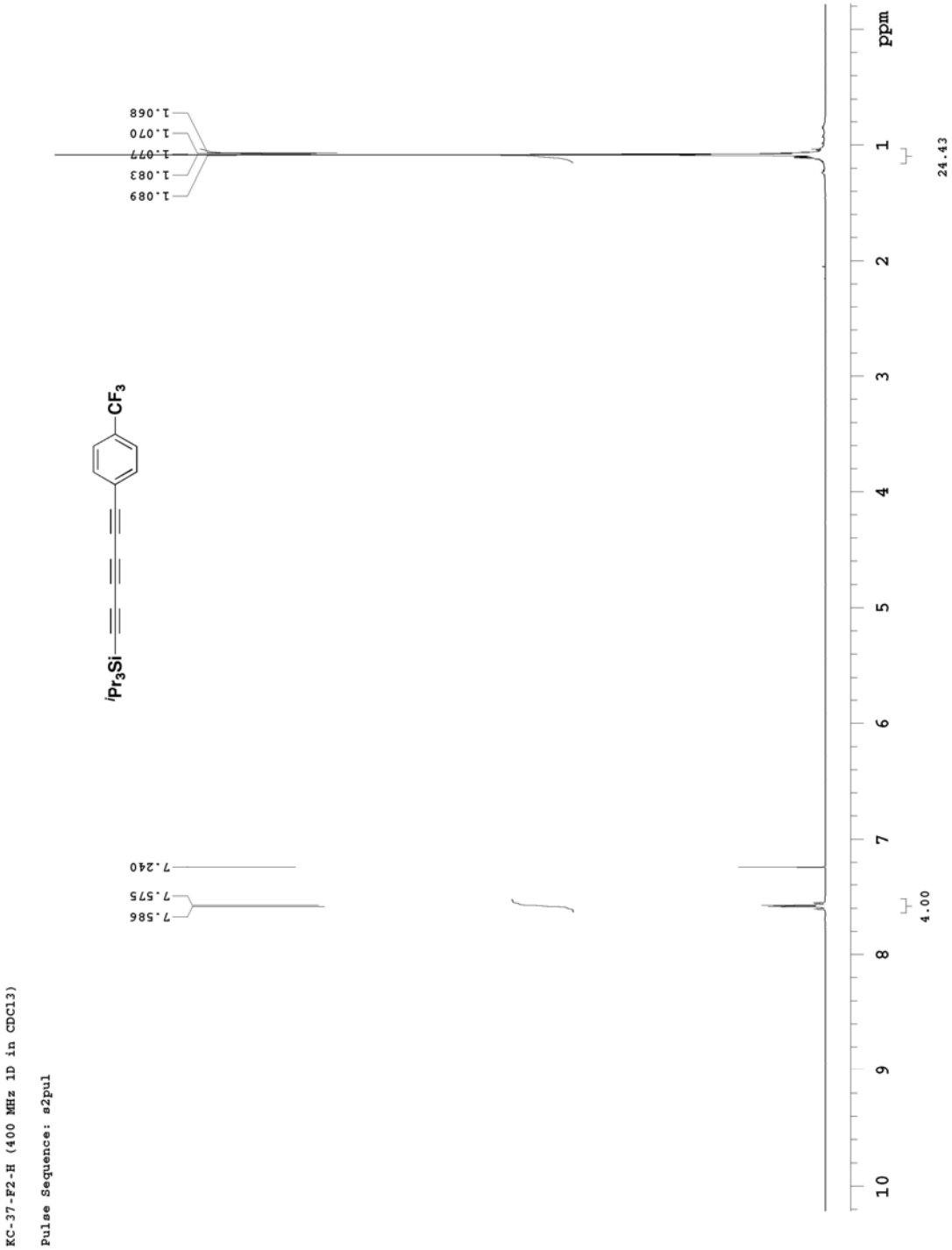


Figure S17. ^{1}H NMR Spectrum of **3i**

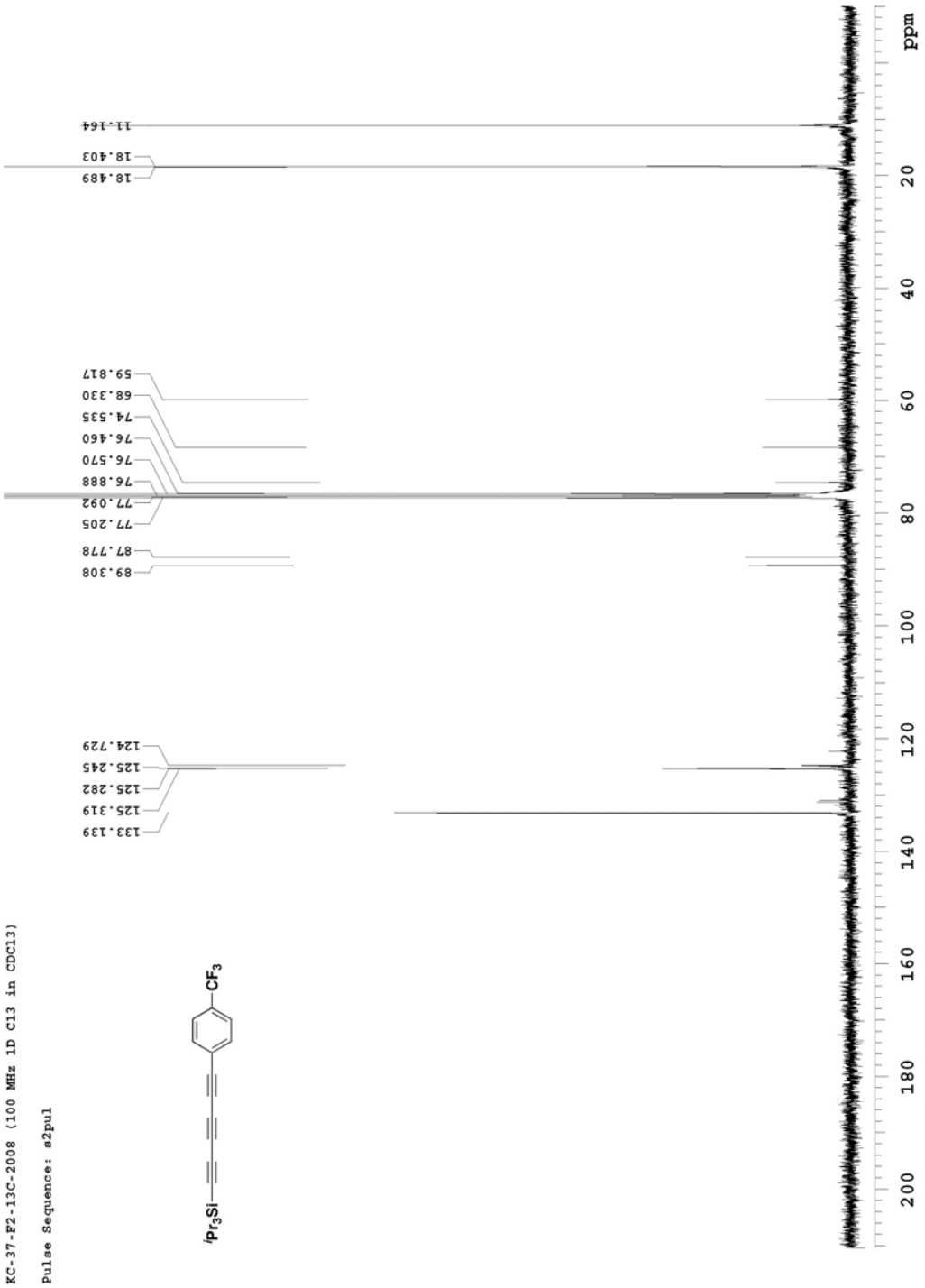


Figure S18. ^{13}C NMR Spectrum of **3i**

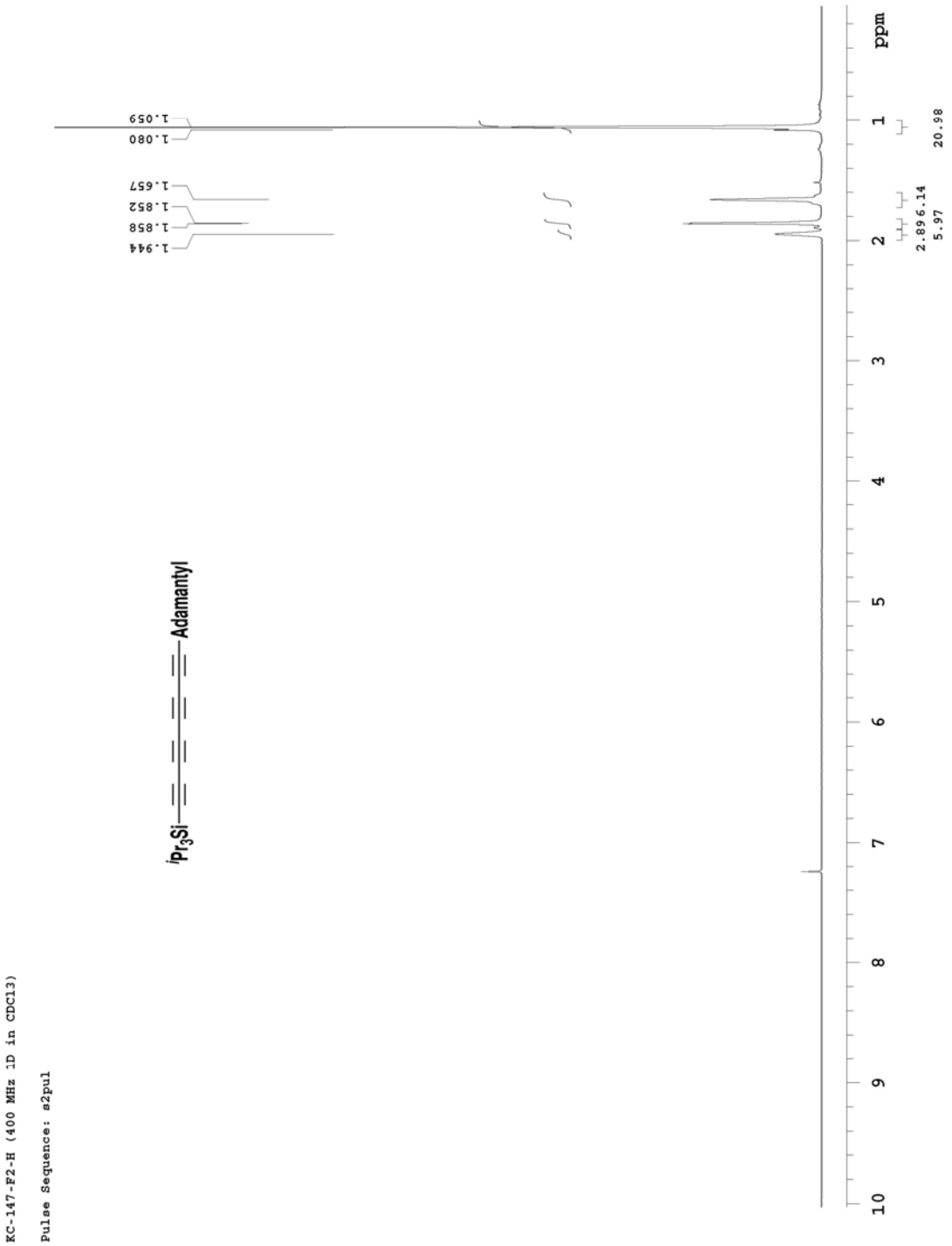


Figure S19. ^{1}H NMR Spectrum of **3k**

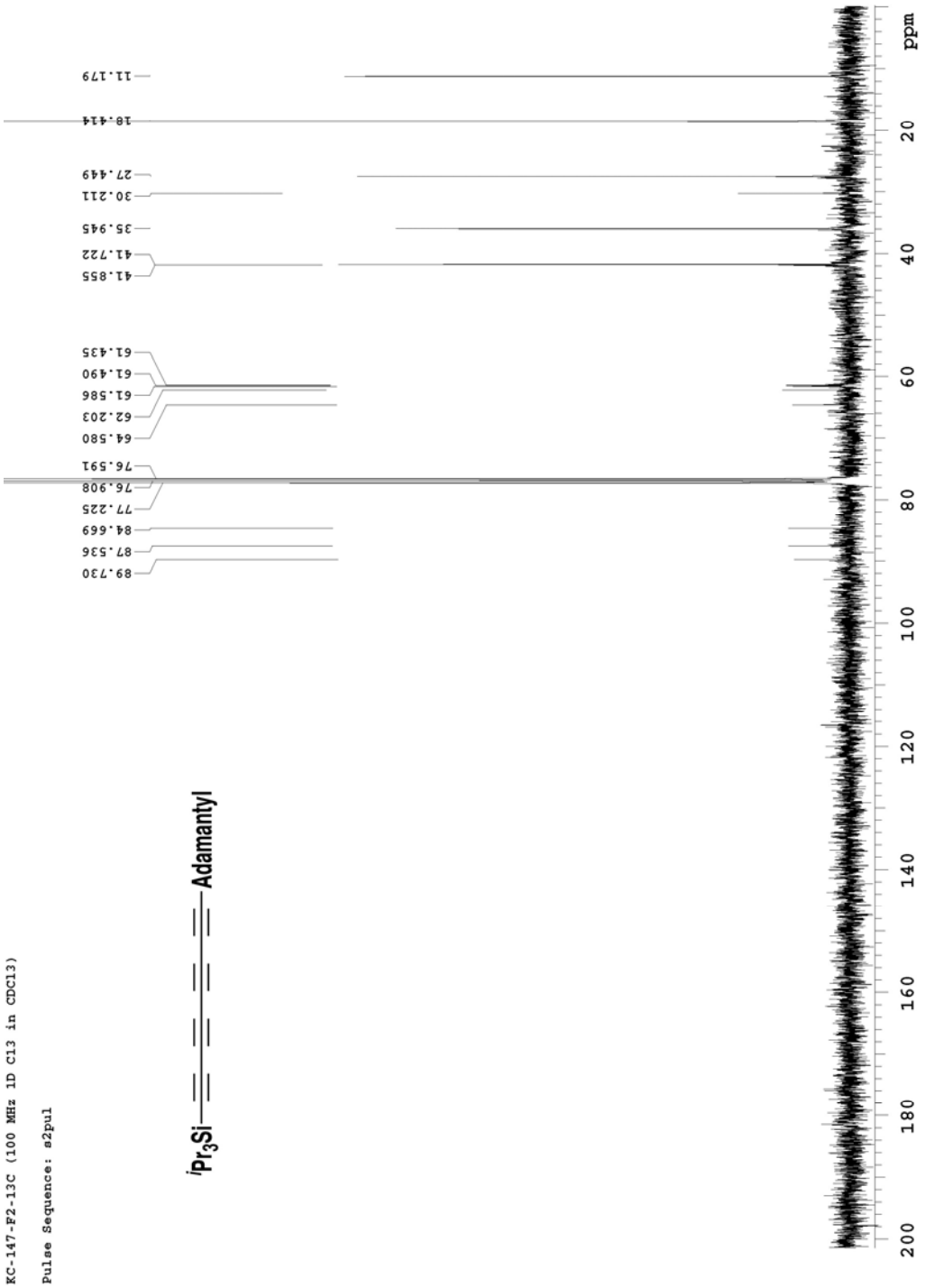


Figure S20. ^{13}C NMR Spectrum of **3k**

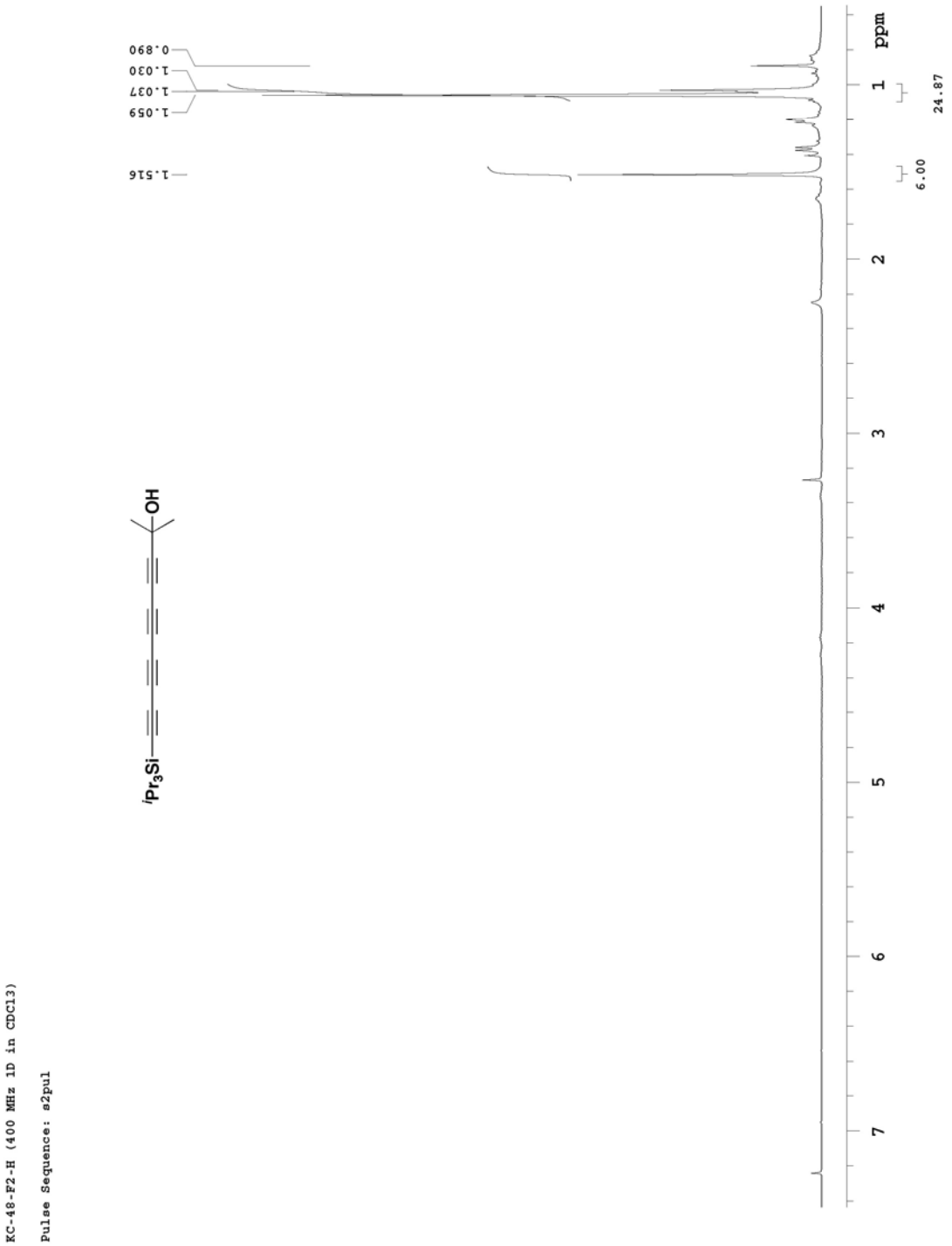


Figure S21. ^{1}H NMR Spectrum of **3l**

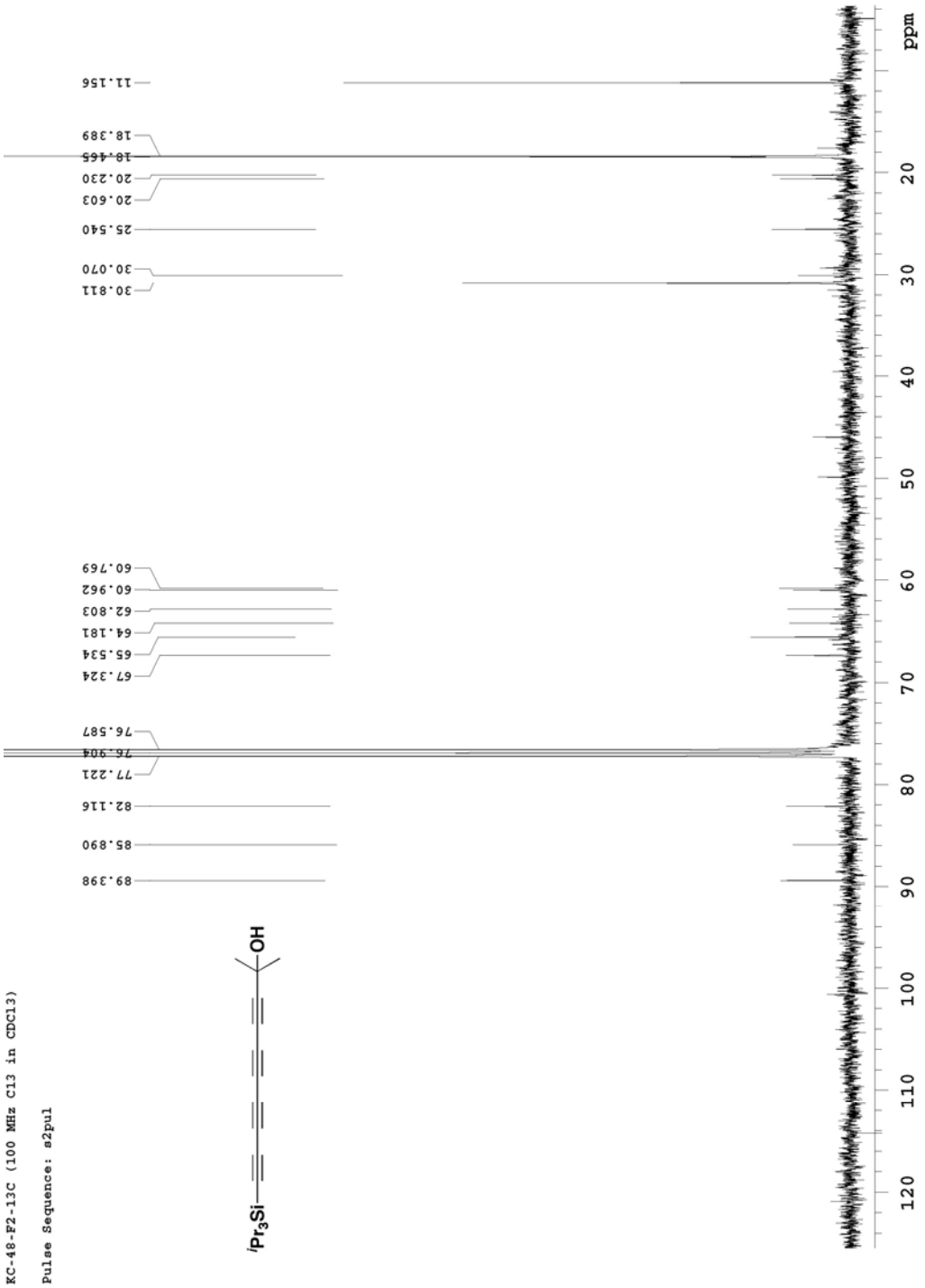


Figure S22. ^{13}C NMR Spectrum of **3l**

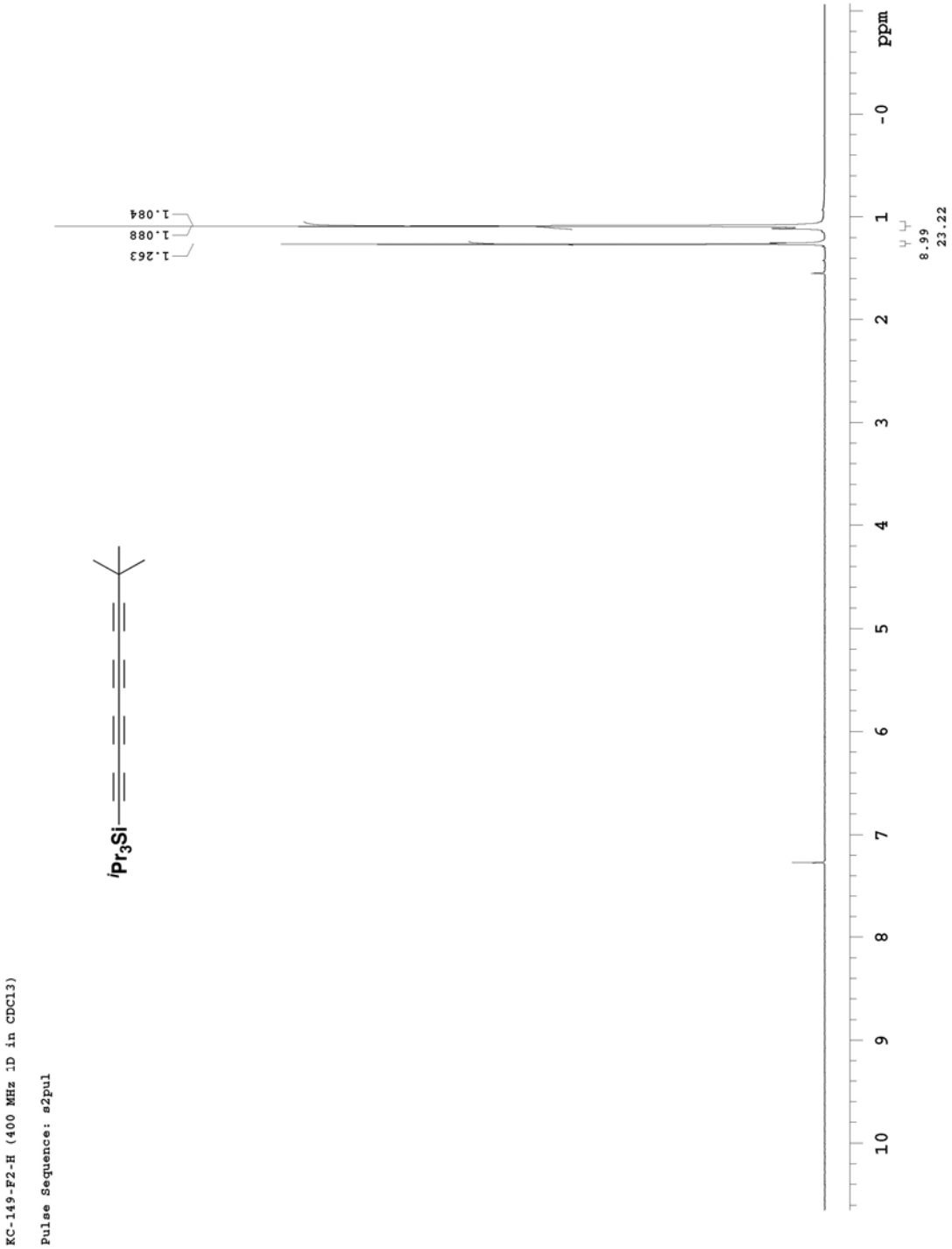


Figure S23. ^{1}H NMR Spectrum of **3m**

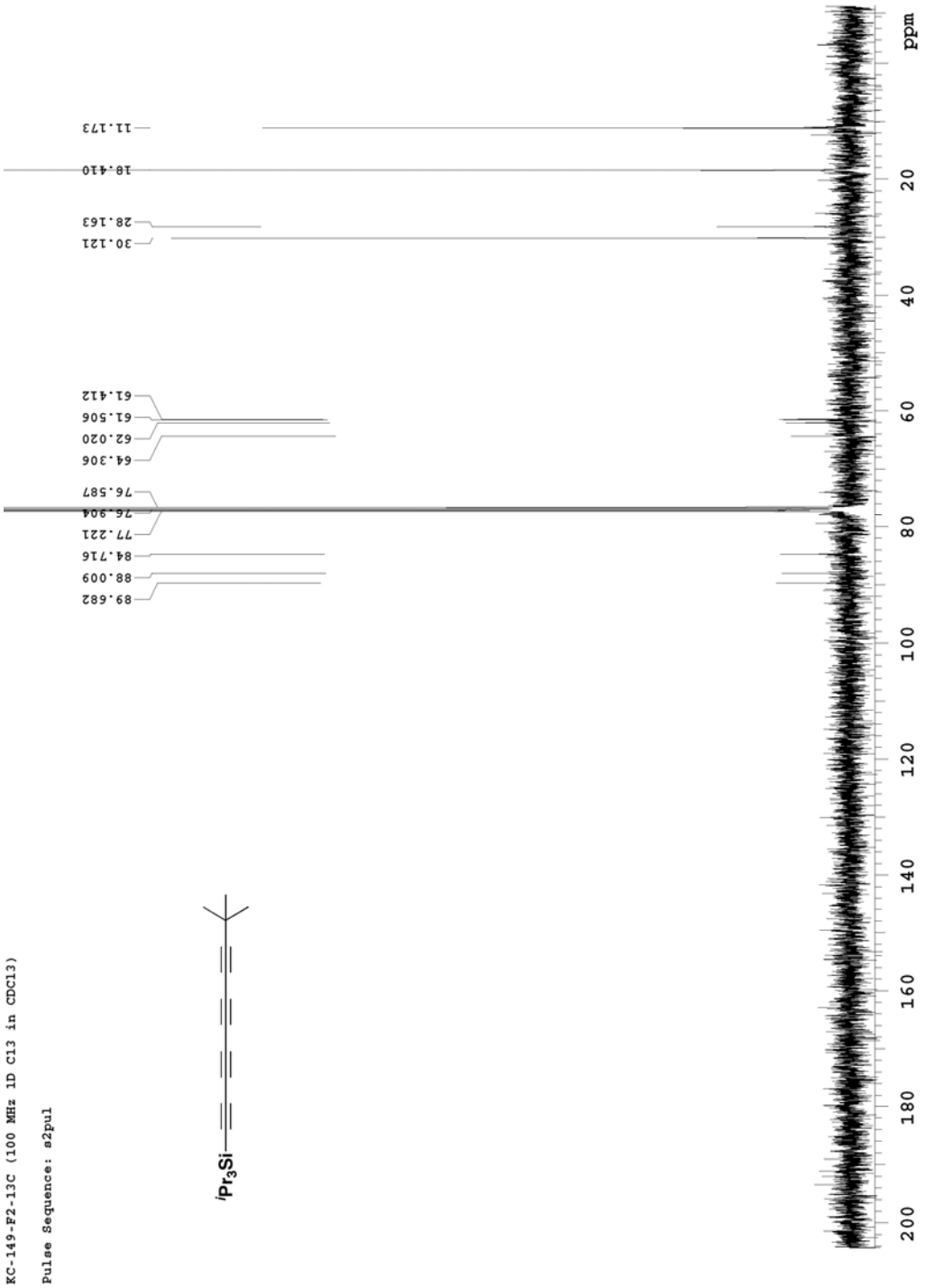


Figure S24. ^{13}C NMR Spectrum of **3m**

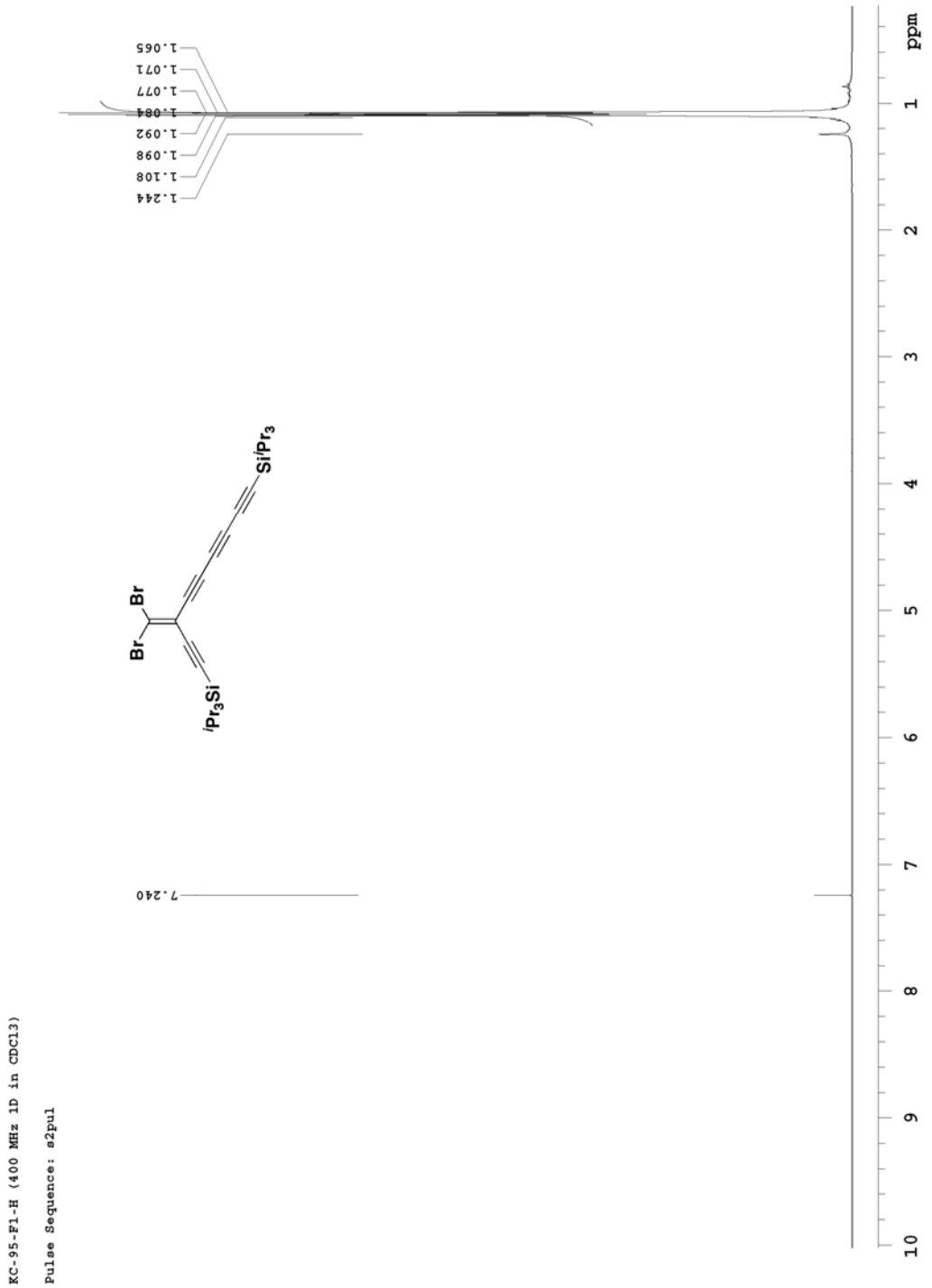


Figure S25. ^{1}H NMR Spectrum of **6a**

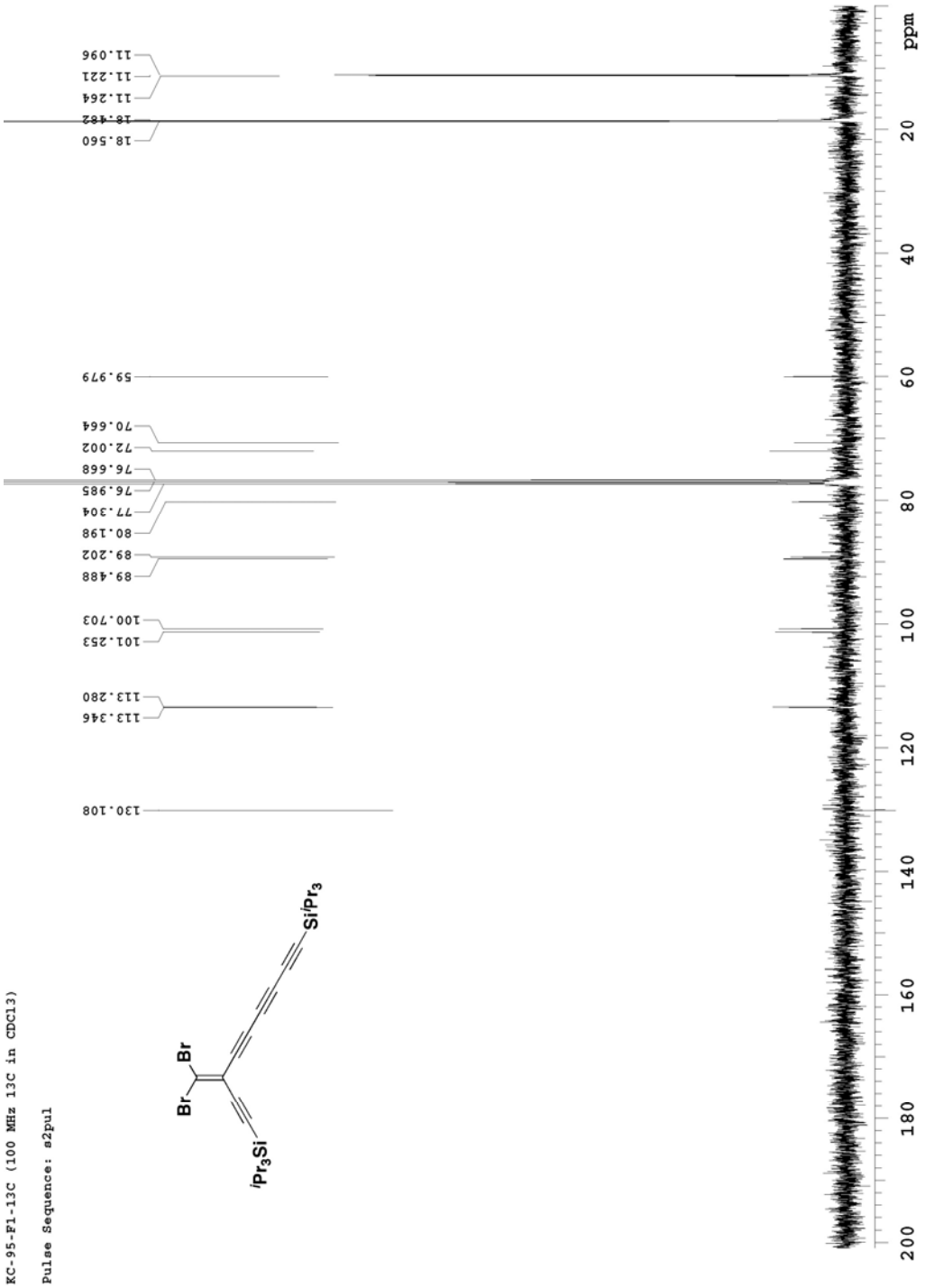


Figure S26. ^{13}C NMR Spectrum of **6a**

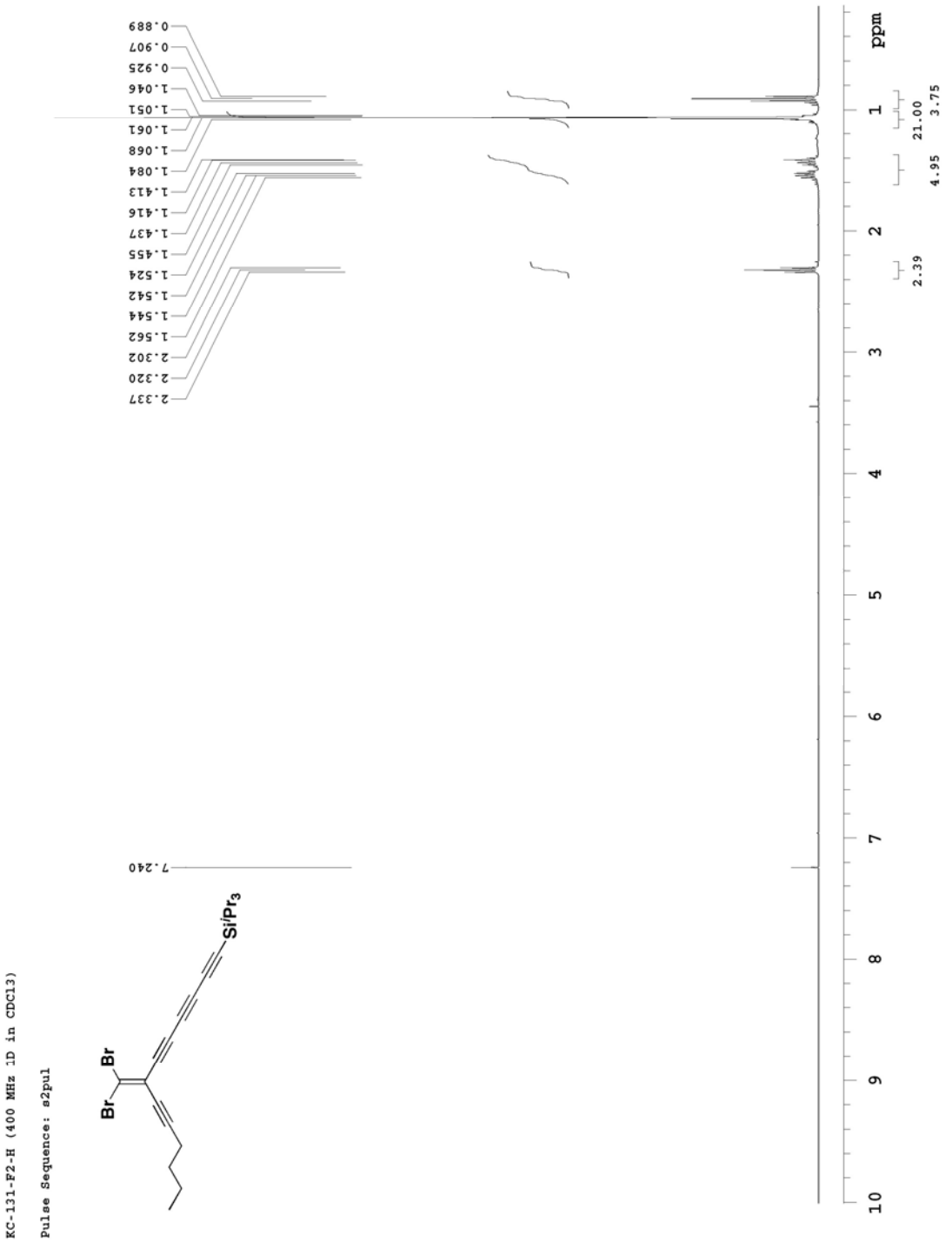


Figure S27. ^{13}C NMR Spectrum of **6b**

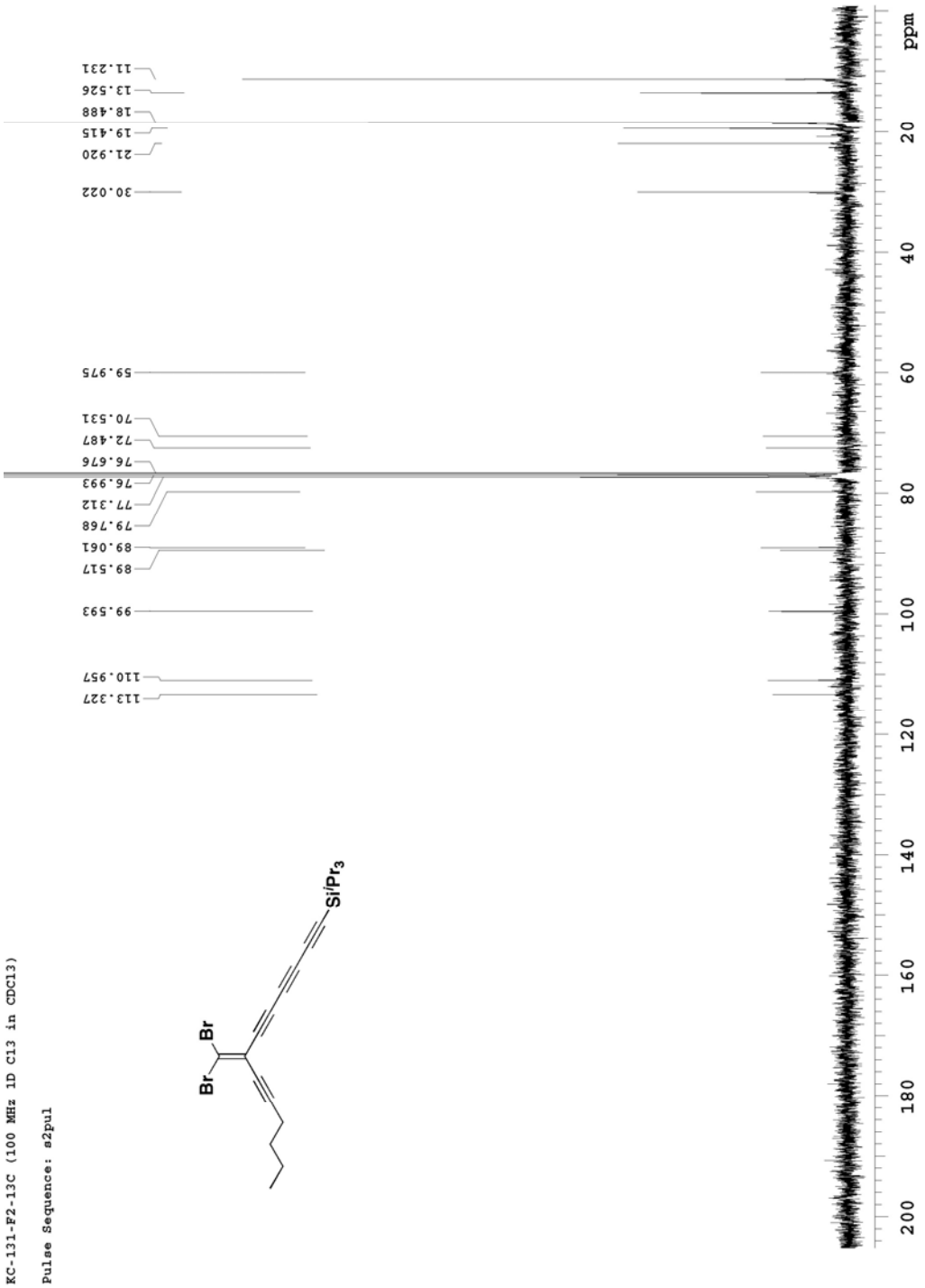


Figure S28. ^{13}C NMR Spectrum of **6b**

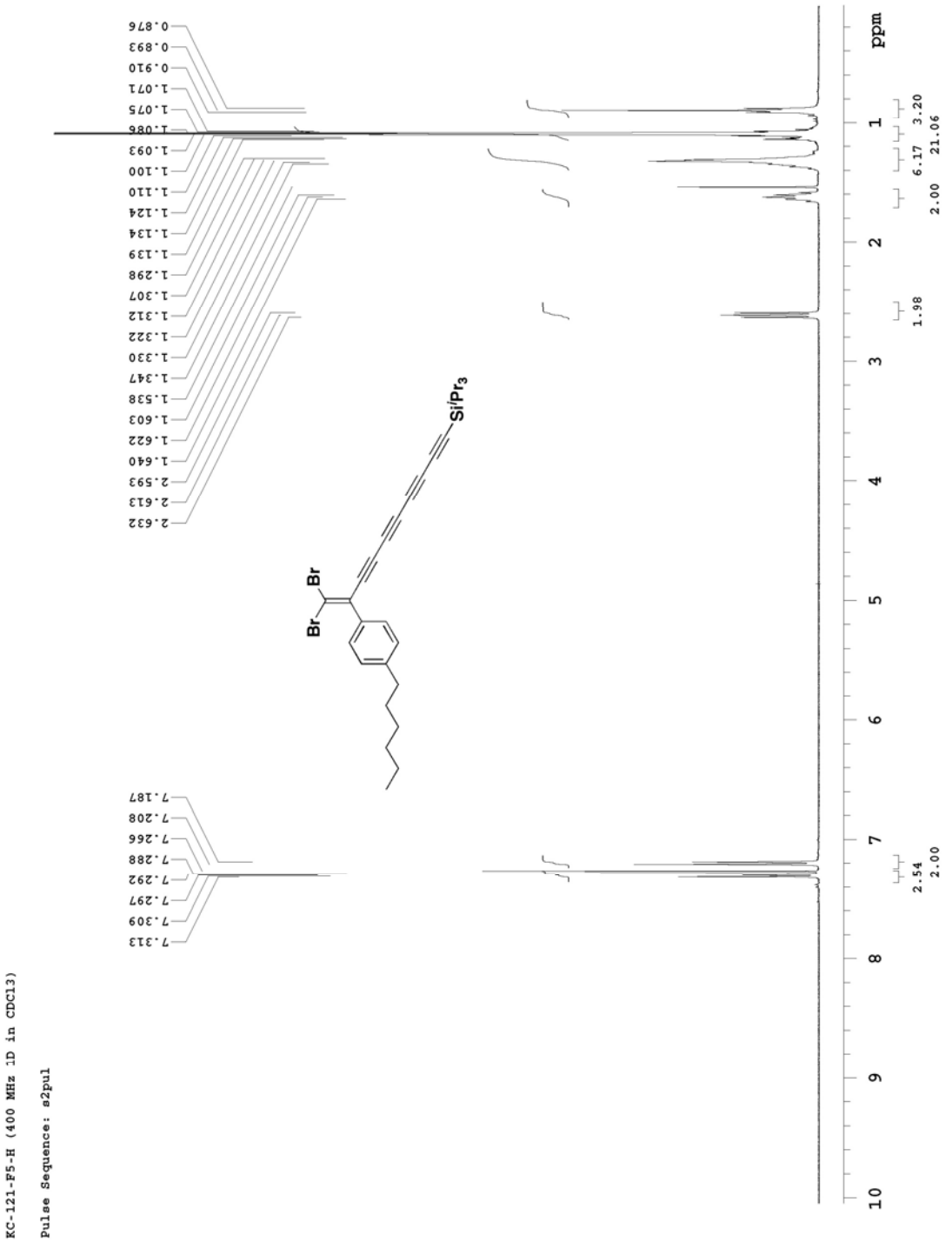


Figure S29. ^{1}H NMR Spectrum of **6c**

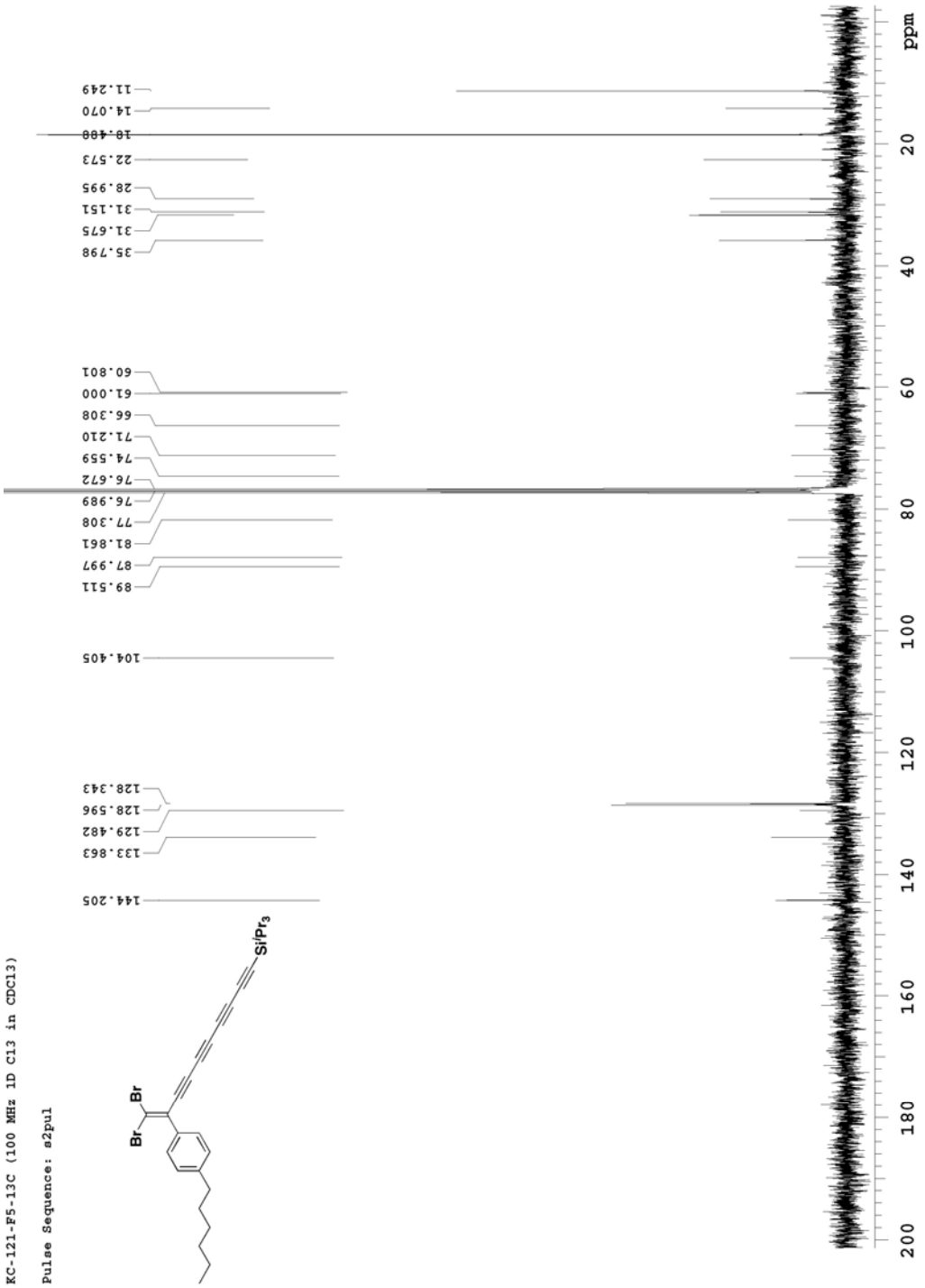


Figure S30. ^{13}C NMR Spectrum of **6c**

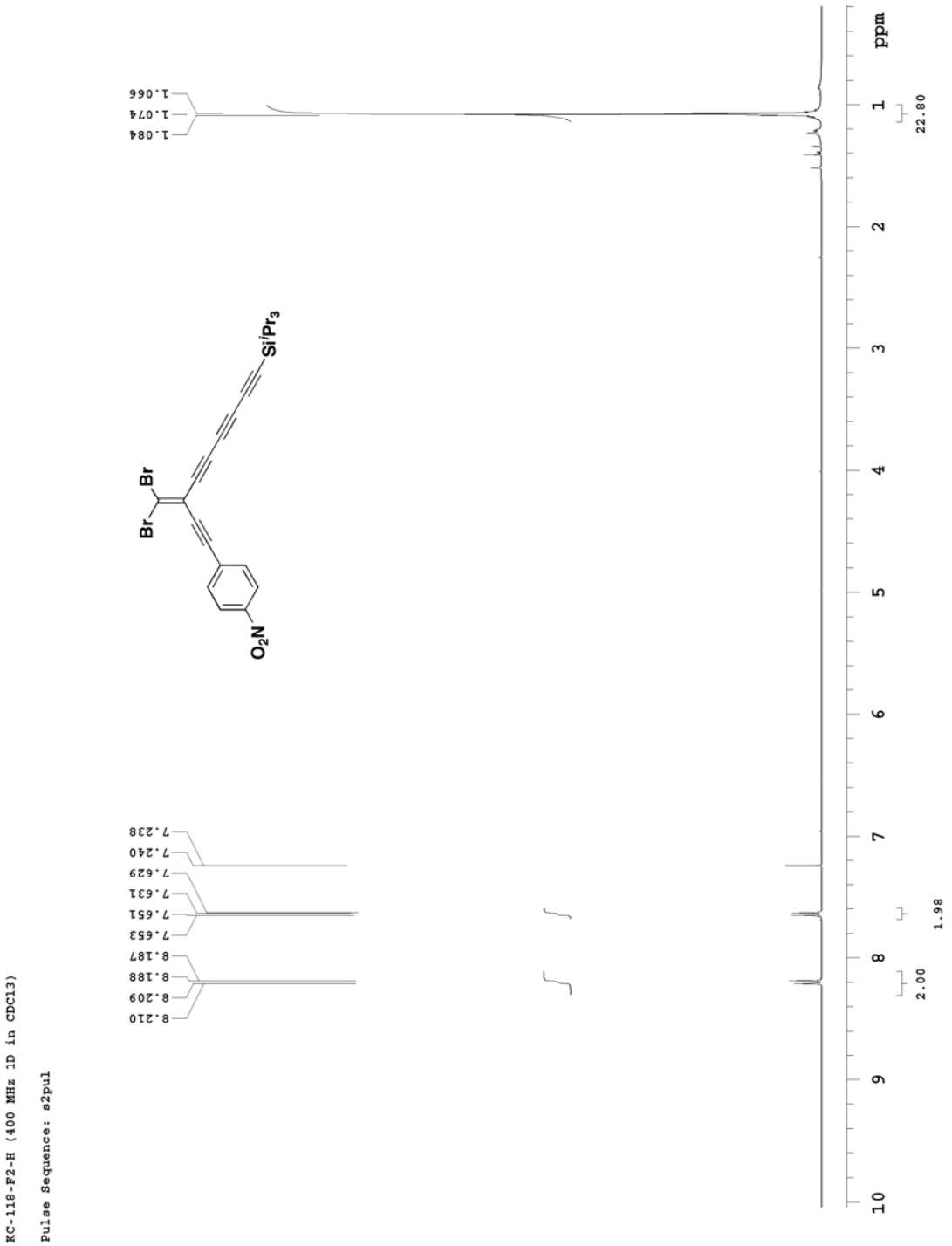


Figure S31. ^{1}H NMR Spectrum of **6d**

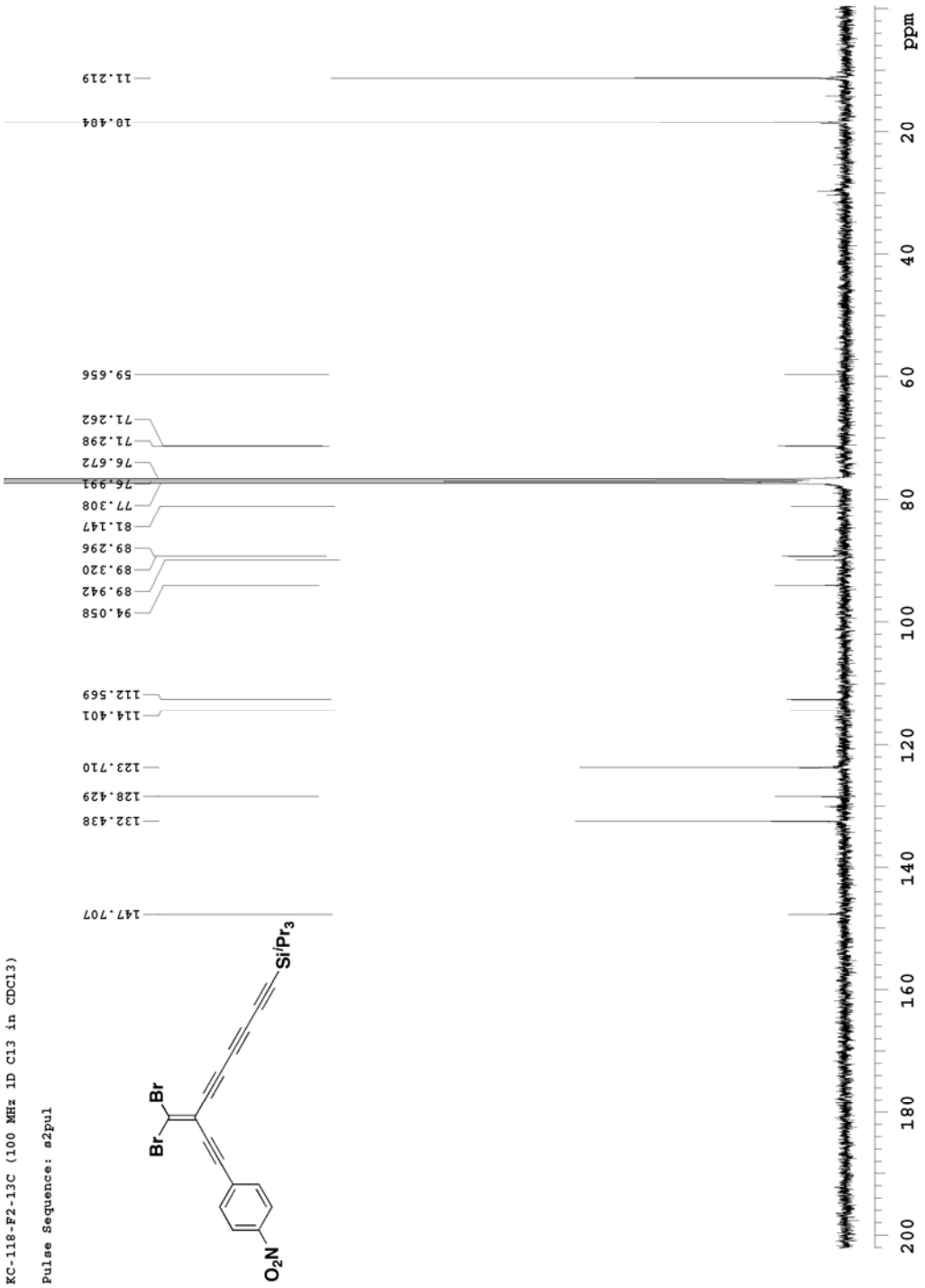


Figure S32. ^{13}C NMR Spectrum of **6d**