Soft Propargylic Deprotonation: Designed Ligand Enables Au-Catalyzed Isomerization of Alkynes to 1,3-Dienes

Zhixun Wang,[†] Yanzhao Wang,[†] and Liming Zhang,*

Department of Chemistry & Biochemistry, University of California, Santa Barbara, CA 93106

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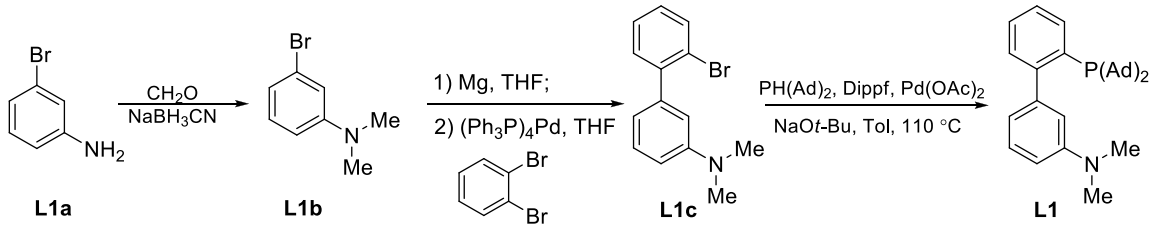
General. Ethyl acetate (ACS grade), hexanes (ACS grade) and diethyl ether (ACS grade) and α, α, α-Trifluorotolutene were purchased from Fisher Scientific and used without further purificationAnhydrous dichloromethane (HPLC grade), 1,2-dichloroethane (HPLC grade) was purified by distillation over calcium hydride. Tetrahydrofuran was distilled over sodium/benzophenone. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Flash column chromatography was performed over Silicycle silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz, 500 MHz and 600 MHz spectrometers using residue solvent peaks as internal standards (CHCl3, ^{1}H: 7.26 ppm; ^{13}C: 77.00 ppm). ^{31}P NMR spectra were recorded on Varian 400MHz spectrometer calibrated by phosphoric acid peak (H_3PO_4, ^{31}P: 0.00 ppm). ^{19}F NMR spectra were recorded on Varian 400MHz spectrometer calibrated by trifluoroacetic acid peak (CF_3COOH, ^{19}F: 76.55 ppm). Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm^{-1}). Mass spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization or Waters GCT Premier time-of-flight mass spectrometer with a field ionization (FI) ion source.

Synthesis of Ligands and Catalysts:

2'-(diadamantylphosphino)-*N*,*N*-dimethylbiphenyl-3-amine (L1)

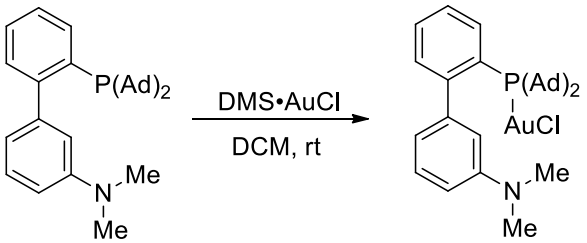


L1a **L1b** **L1c** **L1**

3-Bromo-*N*,*N*-dimethylaniline **L1b** was prepared according to the literature procedure[1] and biaryl compound **L1c** was obtained by using same literature procedure[2].Under nitrogen atmosphere 2 mmol **L1c** (1 equiv), 0.1 mmol $Pd(OAc)_2$ (5 mol%), 0.12 mmol DiPPF (1,1'-bis(diisopropylphosphino)ferrocene, 6 mol%), 2.4 mmol NaO*t*-Bu (1.2 equiv) and 5 mL dry toluene were added to a flamed dried Schlenk flask and the resulting

suspension was stirred until apparently homogeneous (around 15 min). Added 2.2 mmol di(1-adamantyl)phosphine (1.1 equiv), the flask was heated at 110 ^{o}C in oil bath overnight, which then was cooled to room temperature, and purified by column chromatography without work-up to yield the final ligand **L1** in 60% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.87 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.27 (m, 3H), 7.24 – 7.18 (m, 1H), 6.74 – 6.67 (m, 1H), 6.62 – 6.55 (m, 2H), 2.95 (s, 6H), 1.90 (q, *J* = 12.2 Hz, 18H), 1.65 (s, 12H).). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 152.63 (d, *J* = 32.5 Hz), 149.27, 144.77 (d, *J* = 7.5 Hz), 136.45 (*J* = 3.8 Hz), 133.10 (d, *J* = 26.3 Hz), 130.41 (d, *J* = 6.2 Hz), 127.96, 127.70, 125.08, 119.16 (d, *J* = 3.0 Hz), 115.72 (d, *J* = 3.6 Hz), 110.65, 42.00, 41.95 (d, *J* = 13.1 Hz), 37.18 (d, *J* = 26.0 Hz), 36.98, 28.87 (d, *J* = 8.5 Hz). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 22.88. **IR** (neat): 2901, 2847, 1602, 1584, 1498, 1449, 1343, 1301, 1047, 991, 955, 762, 743; **HRMS ESI** (*m/z*): $[MNa]^+$ calcd. for $C_{34}H_{44}NPNa$, 520.3109; found, 520.3088.

Gold Complex L1AuCl

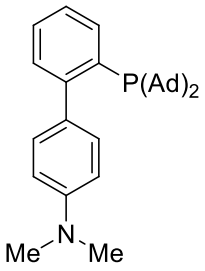


L1 **L1AuCl**

To a solution of 1 mmol ligand **L1** in 5 mL anhydrous DCM was added chloro(dimethylsulfide)gold(I) (294.5 mg, 1 mmol). The mixture was stirred for 30 min at room temperature and the solvent was evaporated off under reduced pressure to give the desired gold complex **L1AuCl** in quantitative yield. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.84 (t, *J* = 7.6 Hz, 1H), 7.48 (dt, *J* = 21.5, 7.4 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.28 (bs, 1H), 6.93 (bs, 1H), 6.60 – 6.30 (m, 2H), 3.01 (s, 6H), 2.27 – 2.05 (m, 12H), 1.98 (d, *J* = 21.1 Hz, 6H), 1.67 (d, *J* = 20.9 Hz, 12H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 151.42, 142.81, 134.24 (d, *J* = 2.3 Hz), 133.12 (d, *J* = 7.3 Hz), 130.17, 129.14, 125.95 (d, *J* = 6.2 Hz), 123.90, 123.55, 117.48, 113.95, 112.69, 42.31 (d, *J* = 45.5, 45 Hz), 42.14 (dd, *J* = 45.5, 2.7 Hz), 40.84, 36.28 (d, *J* = 8.2 Hz), 28.58 (dd, J_1 = J_2 = 9.9 Hz). **^{31}P NMR**

($CDCl_3$, 162 MHz) δ : 63.23. **IR** (neat): 2904, 2849, 2803, 1600, 1585, 1500, 1450, 1431, 1355, 1344, 1301, 1260, 1178, 1163, 1124, 1045, 990, 972, 842, 770, 733; **HRMS ESI** (*m/z*): $[MNa]^+$ calcd. for $C_{34}H_{44}AuClNPNa$, 754.2463; found, 754.2451.

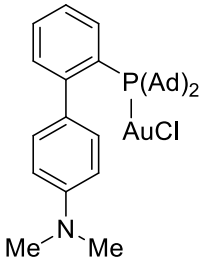
2'-(diadamantylphosphino)-*N*,*N*-dimethylbiphenyl-4-amine (L2)



L2

Starting with 4-Bromoaniline, ligand **L2** was synthesized the same way with **L1.** **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.88 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.75 – 6.70 (m, 2H), 3.00 (s, 6H), 1.90 (q, *J* = 12.2 Hz, 18H), 1.66 (s, 12H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 152.00 (d, *J* = 32.1 Hz), 148.83, 136.62 (d, *J* = 2.9 Hz), 133.19 (d, *J* = 26.3 Hz), 132.23 (d, *J* = 7.1 Hz), 131.29 (d, *J* = 3.9 Hz), 131.06 (d, *J* = 6.0 Hz), 128.08, 124.62, 111.21, 41.88 (d, *J* = 13.1 Hz), 40.52, 37.28 (d, *J* = 25.9 Hz), 36.97, 28.86 (d, *J* = 8.5 Hz). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 22.97. **IR** (neat): 3047, 2902, 2847, 1612, 1522, 1450, 1343, 1301, 1224, 1194, 1166, 1047, 970, 947, 814, 768, 743; **HRMS ESI** (*m/z*): $[MH]^+$ calcd. for $C_{34}H_{45}NP$, 498.3290; found, 498.3280.

Gold Complex L2AuCl

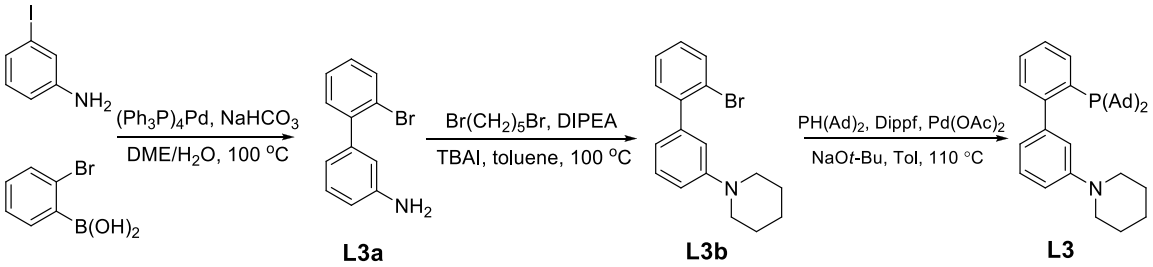


L2AuCl

Au complex **L2AuCl** was obtained in quantitative yield the same way as **L1AuCl**. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.83 (t, *J* = 7.5 Hz, 1H), 7.46 (dt, *J* = 23.5, 7.6 Hz, 2H), 7.36

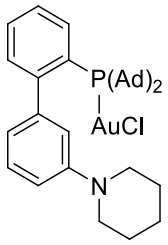
– 7.29 (m, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.87 (s, 2H), 3.05 (s, 6H), 2.24 – 2.05 (m, 12H), 1.98 (s, 6H), 1.67 (s, 12H). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 150 MHz) δ : 151.06, 134.35, 133.85 (d, *J* = 7.7 Hz), 130.27, 129.90, 129.66 (d, *J* = 7.8 Hz), 125.94 (d, *J* = 6.5 Hz), 124.12 (d, *J* = 45.1 Hz), 113.37 (d, *J* = 61.3 Hz), 42.45 (d, *J* = 23.5 Hz), 42.09 (d, *J* = 2.5 Hz), 36.25, 28.57 (d, *J* = 9.8 Hz). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 63.49. **IR** (neat): 2904, 2849, 2798, 1611, 1523, 1448, 1347, 1301, 1223, 1166, 1126, 1045, 972, 913, 815, 773, 744. **HRMS ESI** (*m/z*): $[MNa]^+$ calcd. for $C_{34}H_{45}AuClNPNa$, 752.2463; found, 752.2448.

***N*-(2'-(diadamantylphosphino)biphenyl-3-yl)piperidine (L3)**



2'-bromobiphenyl-3-amine **L3a** was prepared according to the literature procedure[3] and biaryl compound **L3b** was obtained by using the reported procedure[4]. **L3** was synthesized the same way as **L1** in the yield of 63%. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.87 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.31 (td, *J* = 7.5, 1.7 Hz, 1H), 7.28 (ddd, *J* = 7.4, 4.0, 1.6 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.79 (s, 1H), 6.70 (d, *J* = 7.4 Hz, 1H), 3.21 – 3.15 (m, 4H), 1.95 – 1.82 (m, 18H), 1.69 (q, *J* = 5.8 Hz, 4H), 1.65 (m, 12H), 1.60 – 1.54 (m, 2H). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 150 MHz) δ : 152.37 (d, *J* = 32.9 Hz), 150.71 , 144.60 (d, *J* = 7.3 Hz), 136.48 (d, *J* = 2.9 Hz), 133.16 (d, *J* = 27.8 Hz), 130.36 (d, *J* = 6.1 Hz), 128.00 (d, *J* = 1.2 Hz), 127.56 , 125.11 , 121.59 (d, *J* = 3.5 Hz), 119.69 (d, *J* = 3.7 Hz), 114.36 , 50.72 , 41.94 (d, *J* = 13.2 Hz), 37.19 (d, *J* = 26.3 Hz), 36.98 , 28.86 (d, *J* = 8.5 Hz), 25.85 , 24.43 . **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 22.00. **IR** (neat): 3049, 2901, 2847, 1599, 1451, 1383, 1343, 1301, 1239, 1218, 933, 763, 742. **MS ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{37}H_{49}NP$, 538.36; found, 538.33.

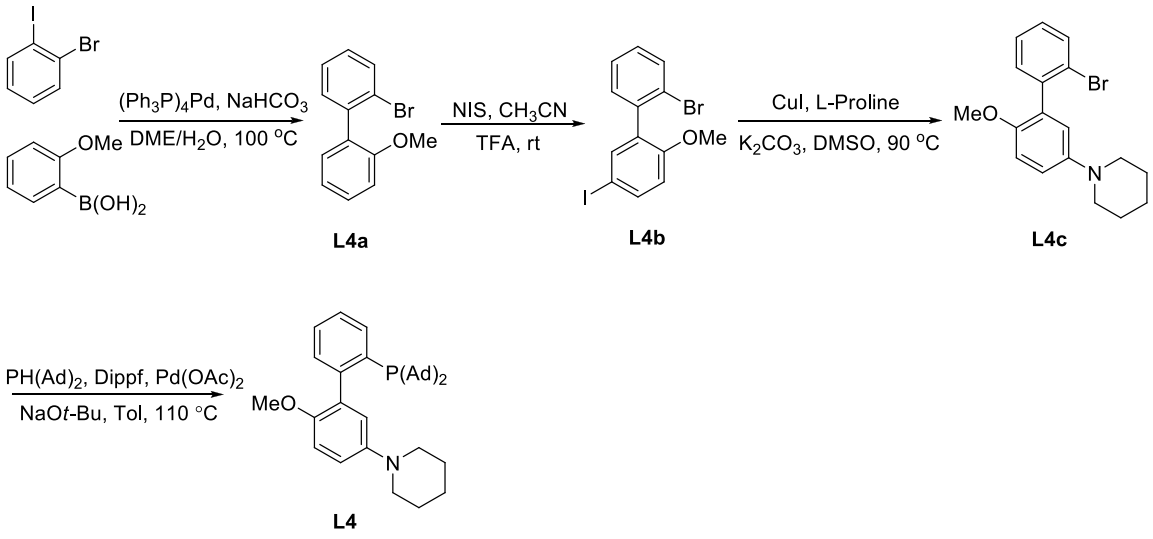
Gold Complex L3AuCl



L3AuCl

Au complex **L3AuCl** was obtained in quantitative yield the same way as **L1AuCl**. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.86 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 (td, *J* = 7.5, 1.7 Hz, 1H), 7.28-7.26 (m, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.88 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.79 (t, *J* = 1.9 Hz, 1H), 6.69 (d, *J* = 7.5 Hz, 1H), 3.21 – 3.15 (m, 4H), 1.96 – 1.79 (m, 18H), 1.72 – 1.62 (m, 18H), 1.60-1.55 (m, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 151.34 , 142.81 , 134.23 (d, *J* = 2.3 Hz), 133.20 (d, *J* = 7.3 Hz), 130.19 (d, *J* = 2.3 Hz), 129.26 , 126.03 , 125.99 , 123.72 (d, *J* = 43.9 Hz), 119.60 , 117.69 , 115.86 , 50.21 , 42.38 (d, *J* = 23.6 Hz), 42.15 (dd, *J* = 22.5, 2.7 Hz), 36.30 (dd, *J* = 7.4, 1.6 Hz), 28.60 (dd, *J* = 9.8, 5.3 Hz), 25.56 , 24.30 . **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 62.35. **IR** (neat): 3049, 2907, 2851, 1957, 1586, 1573, 1496, 1466, 1450, 1383, 1344, 1301, 1265, 1243, 1026, 973, 933, 772, 735. **MS ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{37}H_{49}AuClNP$, 770.30; found, 770.29.

***N*-(2'-(diadamantylphosphino)biphenyl-6-methoxy-3-yl)piperidine (L4)**



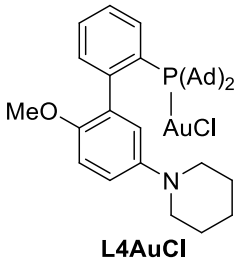
2’-bromo-2-methoxybiphenyl **L4a** was prepared the same way as **L3a**.

To a solution of 10 mmol **L4a** (1 equiv) in 20 mL of acetonitrile, 11 mmol N-iodosuccinimide (1.1 equiv) and 10 mmol trifluoroacetic acid (1 equiv) were added sequentially. The mixture was stirred under ambient condition for 5 h. After diluted with ethyl acetate, washed by aqueous Na_2SO_3 and water and concentrated under reduced pressure, the product 2’-bromo-5-iodo-2-methoxybiphenyl **L4b** was purified by flash chromatography (ethyl acetate/hexanes = 1/50) in 85% yield.

A solution of 5 mmol **L4b** (1 equiv), 10 mmol piperidine (2 equiv), 0.5 mmol CuI (0.1 equiv), 1 mmol L-proline (0.2 equiv) and 10 mmol K_2CO_3 (2 equiv) in 5 mL DMSO was heated at 90 ^oC for 20 h under N_2. After cooling to room temperature, the reaction mixture was diluted with water and extracted three times with ethyl ether. Dried over anhydrous Na_2SO_4, the ether was evaporated under reduced pressure. The crude product was purified flash chromatography (ethyl acetate/hexanes = 1/15), giving biaryl piperidine **L4c** in 71% yield.

L4 was synthesized the same way as L1 in the yield of 56%. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.82 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.21 (m, 1H), 6.93 – 6.88 (m, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.69 (d, *J* = 2.9 Hz, 1H), 3.67 (s, 3H), 3.09 – 2.93 (m, 4H), 2.01 – 1.76 (m, 20H), 1.76 – 1.57 (m, 18H), 1.53 (m, 2H). **^{13}C {^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 150.49 , 148.56 (d, *J* = 34.5 Hz), 145.21 , 136.21 (d, *J* = 2.9 Hz), 134.22 (d, *J* = 26.2 Hz), 132.92 (d, *J* = 7.5 Hz), 130.47 (d, *J* = 6.8 Hz), 128.22 , 125.27 , 123.14 (d, *J* = 2.2 Hz), 116.70 , 110.07 , 55.02 , 52.31 , 41.86 (dd, *J* = 48.1, 13.1 Hz), 37.05 (d, *J* = 10.4 Hz), 36.96 (dd, *J* = 91.8, 24.9 Hz), 28.92 (dd, *J* = 24.5, 8.6 Hz), 26.10 , 24.26 . **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 25.71. **IR** (neat): 3049, 2901, 2848, 1501, 1463, 1301, 1235, 1048, 1028, 935, 801, 736. **MS ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{38}H_{51}NOP$, 568.37; found, 568.36.

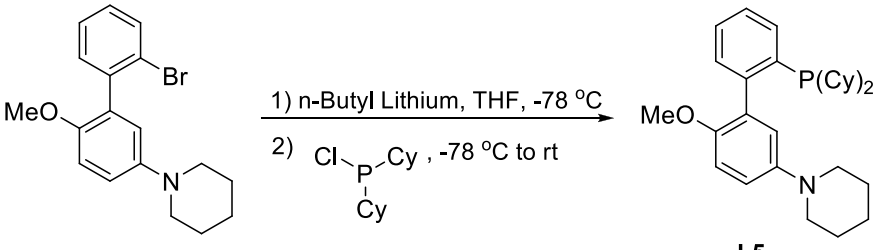
Gold complex L4AuCl



L4AuCl

Au complex **L4AuCl** was obtained in quantitative yield the same way as **L1AuCl**. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.83 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.29 – 7.23 (m, 1H), 7.12 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 1H), 6.56 (s, 1H), 3.65 (s, 3H), 3.10 (t, *J* = 5.5 Hz, 4H), 2.21 – 2.07 (m, 12H), 2.01 – 1.93 (m, 6H), 1.66 (m, 16H), 1.56 – 1.48 (m, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 150.17 , 147.73 , 145.81 , 134.18 (d, *J* = 2.3 Hz), 133.26 (d, *J* = 7.3 Hz), 130.90 (d, *J* = 6.9 Hz), 130.42 (d, *J* = 2.3 Hz), 125.93 (d, *J* = 6.6 Hz), 124.71 (d, *J* = 45.1 Hz), 121.06 , 118.29 , 112.31 , 55.31 , 51.92 , 42.42 (dd, *J* = 31.4, 23.9 Hz), 42.09 (dd, *J* = 30.4, 2.7 Hz), 36.29 (d, *J* = 4.4 Hz), 28.58 (dd, *J* = 23.0, 9.8 Hz), 25.79 , 24.17 . **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 62.96. **IR** (neat): 3048, 2905, 2850, 1505, 1466, 1459, 1451, 1302, 1271, 1254, 1234, 1046, 735. **MS ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{38}H_{51}AuClNOP$, 800.31; found, 800.31 $[M+H]^+$.

***N*-(2'-(dicyclohexylphosphino)biphenyl-6-methoxy-3-yl)piperidine (L5)**

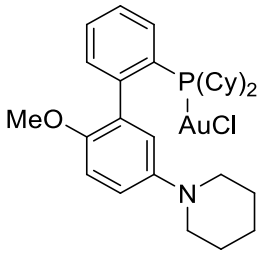


L4c **L5**

Under nitrogen atmosphere 0.5 mmol **L4c** (1 equiv) was dissolved in 2 ml dry THF in a flame dried flask. The resulting solution was cooled to -78 ^{o}C and 0.6 mmol *n*-butyl lithium (1.6M in THF) (1.2 equiv) was added dropwise. After the reaction mixture was stirred under -78 ^{o}C for 40 min, 0.65 mmol chlorodicyclohexylphosphine (1.3 equiv) was added by syringe and the reaction temperature was slowly raised up to room temperature

for *ca.* 2 h. After quenching the reaction with a few drops of saturated NH_4Cl, the reaction mixture was extracted with DCM 3 times. After removing the solvent under reduced pressure, pure ligand **L5** was obtained by flash chromatography in 35% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.57 – 7.53 (m, 1H), 7.39 – 7.34 (m, 1H), 7.35 – 7.31 (m, 1H), 7.26 – 7.22 (m, 1H), 6.92 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.80 (d, *J* = 8.9 Hz, 1H), 6.75 (d, *J* = 3.0 Hz, 1H), 3.67 (s, 3H), 3.12 – 2.95 (m, 4H), 1.99 (ddd, *J* = 11.7, 7.9, 4.2 Hz, 1H), 1.82 – 1.49 (m, 18H), 1.37 – 0.82 (m, 10H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 150.47 , 147.42 (d, *J* = 31.5 Hz), 145.64 , 135.26 (d, *J* = 19.4 Hz), 132.28 (d, *J* = 3.7 Hz), 132.24 , 130.01 (d, *J* = 6.0 Hz), 128.31 , 126.27 , 122.35 (d, *J* = 1.8 Hz), 117.01 , 110.39 , 55.35 , 52.27 , 35.20 (d, *J* = 15.4 Hz), 33.27 (d, *J* = 13.5 Hz), 31.01 (d, *J* = 16.4 Hz), 29.84 (dd, *J* = 27.3, 15.3 Hz), 28.48 (d, *J* = 4.7 Hz), 27.61 – 27.10 (m), 26.54 (d, *J* = 20.1 Hz), 26.12 , 24.28 (observed complexity due to P-C coupling, which haven't been assigned definitively). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : -9.66. **IR** (neat): 3050, 2926, 2850, 2791, 1731, 1586, 1501, 1465, 1457, 1448, 1340, 1295, 1272, 1238, 1157, 1049, 1028, 936, 748, 744, 737. **MS ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{30}H_{43}NOP$, 464.31; found, 464.34.

Gold Complex L5AuCl

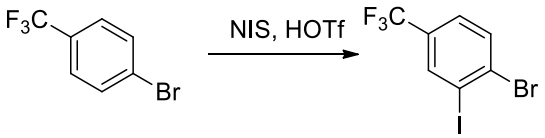


L5AuCl

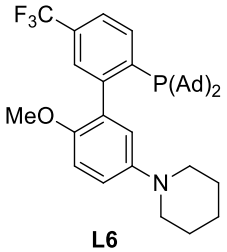
Au complex **L5AuCl** was obtained in quantitative yield the same way as **L1AuCl**. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.60 (t, *J* = 8.4 Hz, 1H), 7.54 – 7.46 (m, 1H), 7.47 – 7.42 (m, 1H), 7.29 – 7.26 (m, 1H), 7.10 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.62 (d, *J* = 3.0 Hz, 1H), 3.68 (s, 3H), 3.09 (t, *J* = 5.4 Hz, 4H), 2.27 – 2.16 (m, 1H), 2.11 – 2.01 (m, 1H), 2.01 – 1.91 (m, 2H), 1.86 – 1.61 (m, 12H), 1.54 (q, *J* = 5.9 Hz, 2H), 1.39 – 1.09 (m, 10H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 150.17 , 146.34 , 146.26 , 132.66 (d, *J* = 7.8 Hz), 132.59 (d, *J* = 5.5 Hz), 130.70 (d, *J* = 2.3 Hz), 130.12 (d, *J* = 6.0 Hz), 127.10 (d, *J* = 8.0 Hz), 125.72 (d, *J* = 53.0 Hz), 120.64 , 118.34 , 112.30 , 55.45 , 51.90 , 36.26 (dd,

J = 79.5, 33.9 Hz), 30.79 (d, *J* = 3.7 Hz), 30.36 (d, *J* = 3.8 Hz), 29.82 (d, *J* = 1.6 Hz), 28.99 , 26.76 – 26.25 (m), 25.98 , 25.65 (dd, *J* = 5.8, 1.7 Hz), 24.15 28 (observed complexity due to P-C coupling, which haven't been assigned definitively). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 41.13. **IR** (neat): 3051, 2852, 1505, 1465, 1449, 1271, 1237, 1180, 1125, 1047, 1026, 935, 817, 734. **MS ESI** (*m/z*): $[M+H]^+$ calcd. for $C_{30}H_{43}AuClNOP$, 696.24; found, 696.25.

1-(2'-(di(adamantan-1-yl)phosphino)-6-methoxy-5'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)piperidine (L6)



NIS (*N*-iodosuccinimide, 11 mmol) was added in small portions to a well-stirred solution of 1-bromo-4-(trifluoromethyl)benzene (10 mmol) in Triflic acid (50 mmol) which was cooled by an ice bath. The reaction mixture was stirred for 2 h at room temperature and then quenched by ice-water. After extraction with Et_2O, the combined organic extracts were washed with aqueous sodium bisulfite solution, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was used directly for the next step without further purification.

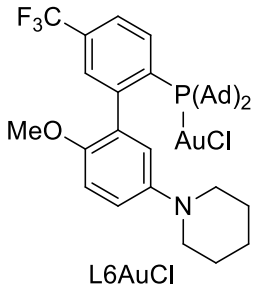


L6

Starting from above product, L6 was prepared following the same route as L4. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.50 (t, *J* = 2.5 Hz, 1H), 6.93 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.67 (d, *J* = 2.9 Hz, 1H), 3.67 (s, 3H), 3.10 – 2.91 (m, 4H). 2.00 – 1.87 (m, 9H), 1.87 -1.75 (m, 9H), 1.75 – 1.57 (m, 16H), 1.56 – 1.50 (m, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 150.23, 149.08 (d, *J* = 35.1 Hz), 145.42, 139.49 (d, *J* = 30.6 Hz), 136.42 (d, *J* = 2.9 Hz), 131.52 (d, *J* =7.2 Hz), 130.00 (q, *J* = 32.2 Hz), 127.30 – 127.10 (m), 124.25 (q, *J* = 272.3 Hz), 123.00

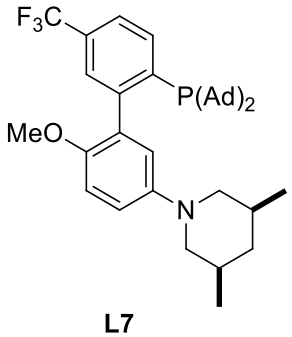
(d, *J* = 2.1 Hz), 121.68 (d, *J* = 3.8 Hz), 117.26, 54.93, 52.30, 41.81 (dd, *J* = 66.9 Hz, 13.1 Hz), 37.12 (dd, *J* = 126 Hz, 26 Hz), 36.95 (d, *J* = 15.4 Hz), 28.85 (dd, *J* = 30 Hz, 8.6 Hz), 26.10, 24.23. **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 19.89. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ : -66.69. **MS ESI** (*m/z*): $[MH]^+$ calcd. for $C_{39}H_{50}F_3NOP$, 636.36; found, 636.33.

Gold Complex L6AuCl



Au complex **L6AuCl** was obtained in quantitative yield the same way as **L1AuCl**. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.96 (t, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.53 (t, *J* = 2.6 Hz, 1H), 7.15 (bs, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 6.54 (bs, 1H), 3.65 (s, 3H), 3.10 (s, 2H), 2.21 – 2.08 (m, 12H), 2.00 (s, 6H), 1.71 – 1.61 (m, 18H), 1.53 (t, *J* = 6.3 Hz, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 149.98, 148.66, 146.04, 134.59 (d, *J* = 2.6 Hz), 132.16 (q, *J* = 32.8 Hz), 130.30 - 130.00 (m), 129.61, 129.34, 123.47 (d, *J* = 273.1 Hz), 122.46, 120.85, 118.91, 112.50, 55.23, 51.94, 42.61 (dd, *J* = 28.1, 22.9 Hz), 42.15 (dd, *J* = 32.1, 2.8 Hz), 36.24 (dd, *J* = 5.5, 1.6 Hz), 28.59 (dd, *J* = 23.9, 9.9 Hz), 25.82, 24.16. **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 57.59. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ : -67.23. **MS ESI** (*m/z*): $[MH]^+$ calcd. for $C_{39}H_{50}AuClF_3NOP$, 868.29; found, 868.30.

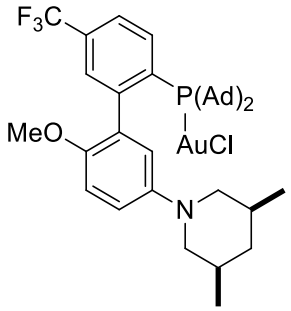
1-(2'-(di(adamantan-1-yl)phosphino)-6-methoxy-5'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)-3,5-dimethylpiperidine (L7)



L7

L7 was prepared in the same manner as L6. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.93 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.49 (s, 1H), 6.93 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 6.68 (d, *J* = 3.0 Hz, 1H), 3.66 (s, 3H), 3.48 – 3.32 (m, 2H), 2.11 (dt, *J* = 36.3, 11.2 Hz, 2H), 1.97 – 1.74 (m, 21H), 1.72 – 1.55 (m, 13H), 0.89 (dd, *J* = 34.2, 6.4 Hz, 6H), 0.62 (q, *J* = 12.2 Hz, 1H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 150.28, 149.05 (d, *J* = 34.5 Hz), 144.91, 139.41 (d, *J* = 29.7 Hz), 136.43 (d, *J* = 3.0 Hz), 131.61 (d, *J* = 7.1 Hz), 129.98 (q, *J* = 32.0 Hz), 127.35 – 127.15 (m), 125.34, 123.14 (d, *J* = 2.5 Hz), 121.71 (d, *J* = 3.6 Hz), 117.30, 110.31. **^{31}P NMR** ($CDCl_3$, 162 MHz) δ : 24.80. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ : -61.40. **MS ESI** (*m/z*): $[MH]^+$ calcd. for $C_{41}H_{54}F_3NOP$, 664.39; found, 664.37.

Gold Complex L7AuCl

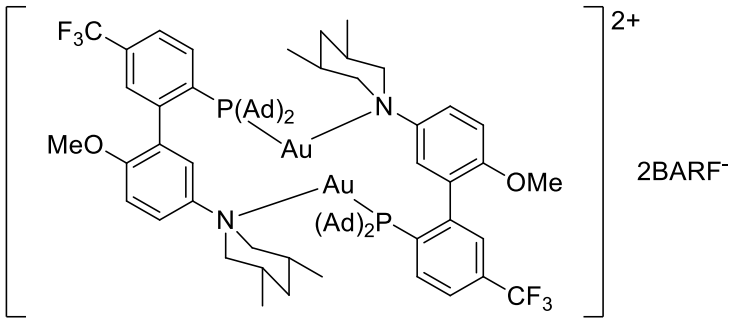


L7AuCl

Au complex **L7AuCl** was obtained in quantitative yield the same way as **L1AuCl**. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.97 (t, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.54 (s, 1H), 7.26 (s, 0H), 7.13 (dd, *J* = 9.1, 2.9 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.54 (d, *J* = 2.9 Hz, 1H), 3.66 (s, 3H), 3.42 (s, 1H), 2.27 (q, *J* = 11.2 Hz, 2H), 2.22 – 2.08 (m, 10H), 2.02 – 1.96 (m, 6H), 1.90 – 1.76 (m, 2H), 1.72 – 1.62 (m, 13H), 0.87 (dd, *J* = 32.7, 6.6 Hz, 6H), 0.66 (q, *J* = 12.1 Hz, 1H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 149.78, 148.75 (d, *J* = 13.7 Hz), 145.49, 134.57 (d, *J* = 2.6 Hz), 132.14 (q, *J* = 31.8 Hz), 130.25 – 130.00 (m), 129.69 (d, *J* = 6.6 Hz), 129.46 (d, *J* = 41.8 Hz), 123.48 (d, *J* = 273.0 Hz), 122.55 – 122.30 (m), 120.84, 118.33, 112.53, 59.44, 57.35, 55.27, 42.63 (dd, *J* = 29.0, 22.8 Hz), 42.14 (dd, *J* = 42.2, 2.8 Hz), 41.92, 36.24 (dd, *J* = 8.5, 1.6 Hz), 30.85 (d, *J* = 5.9 Hz), 28.60 (dd, *J* = 23.0, 9.9 Hz), 19.45 (d, *J* = 22.8 Hz). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ :

62.85. . **^{19}F NMR** ($CDCl_3$, 376 MHz) δ : -61.95. **MS ESI** (*m/z*): $[MH]^+$ calcd. for $C_{41}H_{54}AuClF_3NOP$, 896.32; found, 896.33.

Dimerized gold complex [(L7Au)$_2$]BARF$_2$



[L7Au)$_2$]BARF$_2$

In a vial, 0.16 mmol NaBARF(1 equiv) was added to a solution of 0.16 mmol L7AuCl(1 equiv) in 5 mL dichloromethane. After stirring for 10 min, the reaction mixture was left to stand for 1 h. The resulting suspension was filtered through a short silica pad. The filtrate was collected in a sealed clean vial wrapped with aluminum foil and left to stand for 1 d, giving 72 mg desired product as colorless crystals. **^{1}H NMR** (CD_2Cl_2, 500 MHz) δ : 8.16 (t, *J* = 7.8 Hz, 1H), 8.01 (dd, *J* = 8.9, 3.1 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.70 (d, *J* = 2.8 Hz, 8H), 7.54 (s, 4H), 7.39 (s, 1H), 7.03 – 6.98 (m, 2H), 3.76 (d, *J* = 8.9 Hz, 4H), 3.43 – 3.36 (m, 1H), 2.88 – 2.73 (m, 3H), 2.46 (td, *J* = 12.0, 4.3 Hz, 1H), 2.40 – 1.21 (m, 30H), 1.05 (d, *J* = 6.3 Hz, 3H), 0.92 – 0.84 (m, 4H), 0.75 (q, *J* = 12.2 Hz, 1H). **^{31}P NMR** (CD_2Cl_2, 162 MHz) δ : 58.18. **^{19}F NMR** (CD_2Cl_2, 376 MHz) δ : -61.62, -62.58.

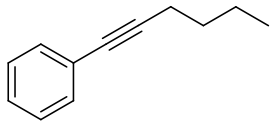
Preparation of Alkynes or Enynes:

General Procedure A: Preparation of aryl internal alkynes via Sonogashira reaction

A dry round bottle was charged with 10.0 mmol aryl iodide or vinyl iodide (1 equiv), $Pd(Ph_3P)_2Cl_2$ (5 mol%) , CuI (10 mol%). The mixture was vacuumed and flushed with N_2 for three times. 20 mL Et_3N and 12 mmol corresponding alkyne substrate (1.2 equiv) was

then added. The mixture was stirred at room temperature until all the aryl iodide or vinyl iodide was consumed. The reaction mixture was diluted with diethyl ether, washed with water and brine, dried with anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under *vacuum*. The residue was purified through silica gel flash chromatography, giving the desired product in 80-95% yield.

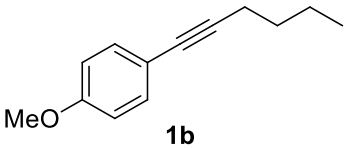
Hex-1-ynylbenzene (1a)



1a

The known compound was prepared according to the general procedure A (eluents: hexanes) and its spectroscopic data were in accordance with the literature data[5].

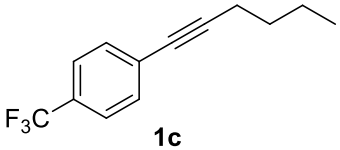
1-(hex-1-ynyl)-4-methoxybenzene (1b)



1b

The known compound was prepared according to the general procedure A (eluents: hexanes) and its spectroscopic data were in accordance with the literature data[5].

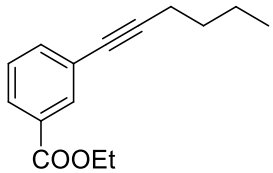
1-(hex-1-ynyl)-4-(trifluoromethyl)benzene (1c)



1c

The known compound was prepared according to the general procedure A (eluents: hexanes) and its spectroscopic data were in accordance with the literature data[6].

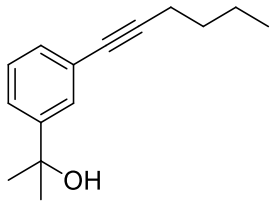
ethyl 3-(hex-1-yn-1-yl)benzoate (1d)



1d

The known compound was prepared according to the general procedure A (eluents: hexanes/ethyl acetate = 10/1) and its spectroscopic data were in accordance with the literature data[7].

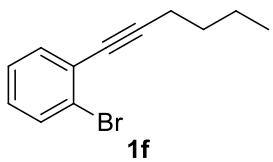
2-(3-(hex-1-yn-1-yl)phenyl)propan-2-ol (1e)



1e

To a solution of ethyl 3-(hex-1-yn-1yl)benzoate (254mg, 1.1 mmol) in dry diethyl ether (5 mL) was added dropwise to excess of methylmagnesium iodide solution (2.5 M, 3.3 mmol). The reaction was monitored by TLC. Upon completion, NH_4Cl (aq) was added and the aqueous phase was extracted with dichloromethane (20 mL × 3). The combined extract was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by flash chromatography, giving 192 mg desired product in 81% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.52 (t, *J* = 1.8 Hz, 1H), 7.40 (dt, *J* = 7.1, 1.9 Hz, 1H), 7.30 – 7.23 (m, 2H), 2.41 (t, *J* = 7.1 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.57 (s, 6H), 1.49 (dp, *J* = 9.4, 7.2 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 149.14, 129.83, 128.12, 127.64, 123.89, 123.67, 90.20, 80.69, 72.37, 31.67, 30.87, 22.03, 19.09, 13.64. **IR** (neat): 3369, 3064, 2961, 2933, 2873, 2226, 1599, 1482, 1460, 1417, 1364, 1174, 954, 891, 796. **GCMS** (m/z): 216 (M^+).

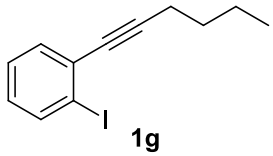
1-bromo-2-(hex-1-ynyl)benzene (1f)



1f

The known compound was prepared according to the general procedure A (eluents: hexanes) and its spectroscopic data were in accordance with the literature data[8].

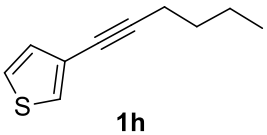
1-iodo-2-(hex-1-ynyl)benzene (1g)



1g

The known compound was prepared according to the general procedure A. In this case, 1 equiv. 1-hexyne and 1.2 equiv. *o*-diiodobenzene were used. Its spectroscopic data were in accordance with the literature data[9].

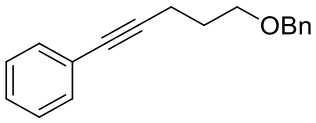
3-(hex-1-yn-1-yl)thiophene (1h)



1h

The known compound was prepared according to the general procedure A. Its spectroscopic data were in accordance with the literature data[10].

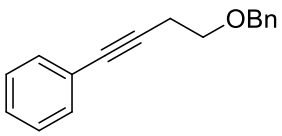
(5-(benzyloxy)pent-1-ynyl)benzene (1i)



1i

The known compound was prepared according to the general procedure A. Its spectroscopic data were in accordance with the literature data[11].

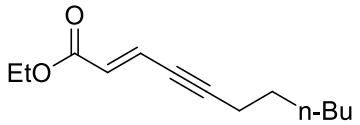
(4-(benzyloxy)but-1-ynyl)benzene (1j)



1j

The known compound was prepared according to the general procedure A. Its spectroscopic data were in accordance with the literature data[11].

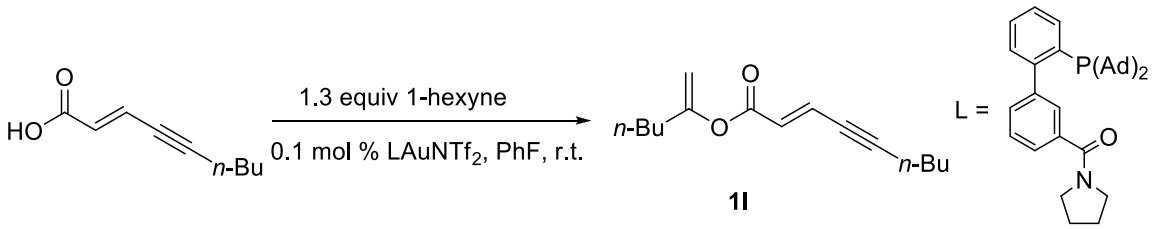
(*E*)-ethyl undec-2-en-4-ynoate (1k)



1k

This known compound was prepared according to the literature. Its spectroscopic data were in accordance with the literature data[12].

(*E*)-hex-1-en-2-yl non-2-en-4-ynoate (1l)

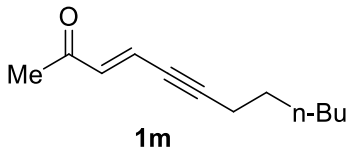


1l

(*E*)-Non-2-en-4-ynoic acid was prepared according to the literature [13].

In a sealed 1 dr reaction vial equipped with a magnetic stirring bar, 3 mmol (*E*)-Non-2-en-4-ynoic acid (1 equiv), 3.9 mmol 1-hexyne (1.3 equiv) and 3.1 mg **L**AuNTf$_2$ (0.003 mmol) were added to 2 mL fluorobenzene and then the reaction mixture stireed at room temperature for 12 h. Once the reaction finished by TLC, it was concentrated and then further purified through silica gel flash chromatography to give the desired product in 92% yield. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 6.81 (dt, *J* = 15.8, 2.3 Hz, 1H), 6.18 (d, *J* = 15.8 Hz, 1H), 4.75 (dt, *J* = 3.8, 1.4 Hz, 2H), 2.39 (td, *J* = 7.1, 2.3 Hz, 3H), 2.27 – 2.17 (m, 2H), 1.59 – 1.50 (m, 2H), 1.48 – 1.38 (m, 4H), 1.38 – 1.30 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 4H), 0.90 (t, *J* = 7.6 Hz, 4H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 164.02, 156.21, 128.48, 127.22, 101.65, 100.90, 77.67, 32.83, 30.12, 28.35, 21.86, 21.74, 19.28, 13.61, 13.33. **MS ESI** (*m/z*): $[MNa]^+$ calcd. for $C_{15}H_{22}NaO_2$, 257.15; found, 257.15.

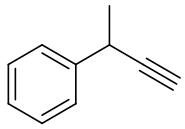
(*E*)-dodec-3-en-5-yn-2-one (1m)



1m

This known compound was prepared according to the literature. Its spectroscopic data were in accordance with the literature data[14].

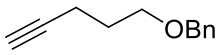
but-3-yn-2-ylbenzene (1o)



1o

This known compound was prepared according to the literature. Its spectroscopic data were in accordance with the literature data[15].

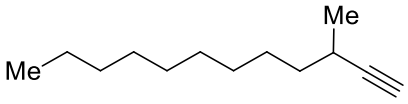
((pent-4-yn-1-yloxy)methyl)benzene (1p)



1p

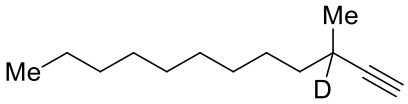
This known compound was prepared according to the literature. Its spectroscopic data were in accordance with the literature data[16].

3-methyldodec-1-yne (1q)



1q

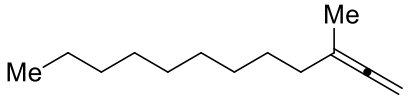
This compound was prepared according to the literature [15]. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 2.46 – 2.34 (m, 1H), 2.02 (d, *J* = 2.3 Hz, 1H), 1.50 - 1.34 (m, 4H), 1.33 – 1.21 (m, 12H), 1.17 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 89.31, 67.97, 36.77, 31.91, 29.60, 29.58, 29.45, 29.33, 27.26, 25.67, 22.69, 20.97, 14.10. **GCMS** (m/z): 179.20 $(M-1)^+$.



1q-D

^{1}H NMR ($CDCl_3$, 600 MHz) δ : ^{1}H NMR (600 MHz) δ 2.46 – 2.34 (m, 0.06H), 2.02 (s, 1H), 1.50 - 1.34 (m, 4H), 1.33 – 1.21 (m, 12H), 1.17 (s, 3H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 89.29, 67.97, 36.66, 31.91, 29.60, 29.58, 29.45, 29.33, 27.23, 25.31 (t, *J* = 20 Hz), 22.69, 20.85, 14.10.

3-methyldodeca-1,2-diene (7)

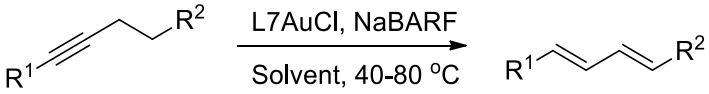


7

This known compound was prepared according to the literature [17].

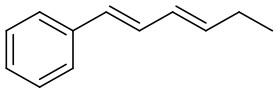
Alkynes or Enynes isomerization:

General Procedure B: Alkynes or Enynes Isomerization into Dienes or Trienes.



To a 3 dram vial were added sequentially 0.3 mmol alkyne or enyne, 0.006 mmol or 0.015 mmol **L7AuCl** (2 mol% or 5 mol%), 0.03 mmol NaBARF (10 mol%) and 3 mL α,α,α-trifluorotoluene as solvent. The reaction was then heated at the indicated temperature monitored by TLC using p-anisaldehyde staining reagent (anisaldehyde/perchloric acid/acetone/water = 1/10/20/80, v/v) or GCMS. Upon completion, the reaction was concentrated under reduced pressure. The residue was purified through silica gel flash chromatography to obtain pure product.

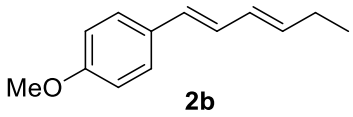
(*1E,3E*)-hexa-1,3-dienylbenzene (2a)



2a

The desired product was obtained in 92% yield ((1E, 3E) / (1E, 3Z) = 49/1) by added 2 mol% catalyst and heated at 60 ^{o}C for 12 h according to general procedure B. The spectra match the reported data[18]. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ : 7.38 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.76 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.21 (dd, *J* = 15.0, 10.6 Hz, 1H), 5.88 (dt, *J* = 15.1, 6.6 Hz, 1H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 137.66, 137.36, 129.95, 129.53, 129.45, 128.50, 127.02, 126.09, 25.86, 13.52.

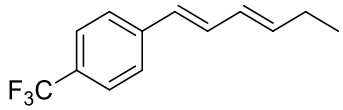
1-((*1E,3E*)-hexa-1,3-dienyl)-4-methoxybenzene (2b)



2b

The product was obtained in 68% yield ((1E, 3E) / (1E, 3Z) = 49/1) by added 2 mol% catalyst and heated at 60 ^{o}C for 17 h according to general procedure B. The spectra match the reported data[19]. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ : 7.31 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.63 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.19 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.82 (dt, *J* = 15.1, 6.6 Hz, 1H), 3.81 (s, 3H), 2.16 (p, *J* = 6.3 Hz, 1H), 1.04 (d, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz) δ : 158.86, 136.20, 130.52, 129.67, 129.50, 127.50, 127.25, 114.00, 55.28, 25.85, 13.62.

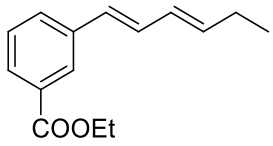
1-((*1E,3E*)-hexa-1,3-dienyl)-4-(trifluoromethyl)benzene (2c)



2c

The product was obtained in 87% yield ((1E, 3E) / (1E, 3Z) >50:1) by added 2 mol% catalyst and heated at 60 ^{o}C for 41 h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ : 7.54 (d, *J* = 8.2 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 6.83 (dd, *J* = 15.7, 10.4 Hz, 0H), 6.47 (s, 0H), 6.22 (ddtd, *J* = 15.2, 10.4, 1.6, 0.7 Hz, 0H), 5.96 (dt, *J* = 15.2, 6.6 Hz, 0H), 2.24 – 2.15 (m, 1H), 1.06 (t, *J* = 7.5 Hz, 1H). **^{13}C {^{1}H} NMR** ($CDCl_3$, 125 MHz) δ : 141.18 , 139.35 , 131.91 , 129.13 , 128.34 , 126.11 , 125.47 (q, *J* = 3.8 Hz), 25.91 , 13.39. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ : -61.33. **IR** (neat): 3015, 2975, 1614, 1415, 1325, 1172, 1120, 1109, 994, 954, 879, 843, 811. **GCMS** (m/z): 226 (M^{+}).

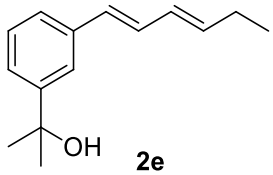
Ethyl 3-((*1E,3E*)-hexa-1,3-dien-1-yl)benzoate (2d)



2d

The product was obtained in 92% yield ((1E, 3E) / (1E, 3Z) = 20/1) by added 2 mol% catalyst and heated at 60 ^{o}C for 24 h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ : 7.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.50 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.89 (td, *J* = 7.6, 1.6 Hz, 1H), 6.66 – 6.62 (m, 2H), 6.32 – 6.25 (m, 1H), 5.93 (dt, *J* = 15.1, 6.6 Hz, 1H), 2.19 (pd, *J* = 7.4, 1.5 Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz) δ : 140.48, 139.58, 138.71, 133.35, 132.32, 129.35, 128.46, 128.24, 125.82, 100.02, 25.89, 13.41. **IR** (neat): 2966, 2935, 1720, 1599, 1581, 1443, 1368, 1284, 1201, 1106, 988, 751. **GCMS** (m/z): 230 (M^+).

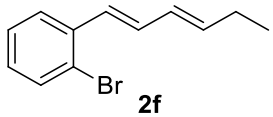
2-(3-((*1E,3E*)-hexa-1,3-dien-1-yl)phenyl)propan-2-ol (2e)



2e

The product was obtained in 88% yield ((1E, 3E) / (1E, 3Z) = 33/1) by added 2 mol% catalyst and heated at 60 ^{o}C for 24 h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.52 (s, 1H), 7.33 – 7.25 (m, 3H), 6.79 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.21 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.89 (dt, *J* = 15.0, 6.6 Hz, 1H), 2.22 – 2.14 (m, 2H), 1.59 (s, 6H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 149.35, 137.62, 137.45, 130.03, 129.60, 129.51, 128.43, 124.46, 123.21, 122.19, 72.54, 31.70, 25.87, 13.53. **IR** (neat): 3377, 3018, 2970, 2932, 2873, 1599, 1460, 1364, 1168, 987, 789. **GCMS** (m/z): 216 (M^+).

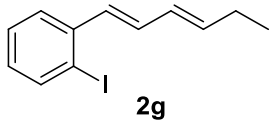
1-bromo-2-((*1E,3E*)-hexa-1,3-dienyl)benzene (2f)



2f

The product was obtained in 96% yield ((1E, 3E) / (1E, 3Z) = 16:1) by using 2 mol% catalyst and heated at 60 ^{o}C for 12 h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.59 – 7.48 (m, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.04 (td, *J* = 7.6, 1.4 Hz, 1H), 6.80 (d, *J* = 15.6 Hz, 0H), 6.70 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.31 – 6.23 (m, 1H), 5.93 (dt, *J* = 14.9, 6.6 Hz, 1H), 2.18 (h, *J* = 6.8, 6.1 Hz, 1H), 1.06 (td, *J* = 7.4, 1.3 Hz, 2H).**^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 138.68, 137.28, 132.97, 132.11, 129.46, 128.38, 128.21, 127.34, 126.26, 123.63, 25.88, 13.40. **GCMS** (m/z): 236.3 (M^+).

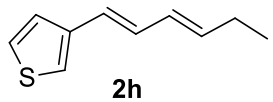
Ethyl 3-((*1E,3E*)-hexa-1,3-dien-1-yl)benzoate (2g)



2g

The product was obtained in 92% yield ((1E, 3E) / (1E, 3Z) = 8.3/1) by added 2 mol% catalyst and heated at 60 ^{o}C for 24 h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ : 8.05 (t, *J* = 1.8 Hz, 1H), 7.86 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.54 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 6.83 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.25 – 6.18 (m, 1H), 5.92 (dt, *J* = 15.2, 6.6 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.23 – 2.14 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz) δ : 166.59, 138.33, 137.98, 130.81, 130.61, 130.23, 129.27, 128.84, 128.51, 127.94, 127.09, 60.98, 25.88, 14.34, 13.46. **IR** (neat): 3019, 2964, 2930, 2871, 1642, 1580, 1460, 1432, 1278, 1009, 985, 943, 747. **GCMS** (m/z): 284 (M^+).

3-((*1E,3E*)-hexa-1,3-dien-1-yl)thiophene (2h)

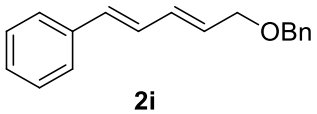


2h

The product was obtained in 77% yield ((1E, 3E) / (1E, 3Z) = 24/1) by added 5 mol% catalyst and heated at 80 ^{o}C for 12 h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.25 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.21 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.10 (dd, *J* =

3.0, 1.2 Hz, 1H), 6.60 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.16 (ddt, *J* = 15.1, 10.4, 1.6 Hz, 1H), 5.83 (dt, *J* = 15.2, 6.6 Hz, 1H), 2.16 (pd, *J* = 7.4, 1.5 Hz, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 140.37, 136.84, 129.52, 129.40, 125.84, 124.86, 124.14, 121.14, 25.85, 13.55. **IR** (neat): 3103, 2966, 2931, 2877, 1675, 1462, 1379, 1247, 1121, 966, 866, 775. **GCMS** (m/z): 164 (M^+).

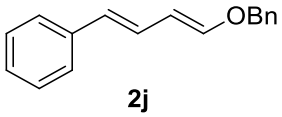
((*1E,3E*)-5-(benzyloxy)penta-1,3-dienyl)benzene (2i)



2i

The product was obtained in 88% yield ((1E, 3E) / (1E, 3Z) > 99/1) by added 2 mol% catalyst and heated at 60 ^{o}C for 12 h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ : 7.44 – 7.28 (m, 9H), 7.24 (td, *J* = 7.3, 1.3 Hz, 1H), 6.86 – 6.78 (m, 1H), 6.57 (d, *J* = 15.7 Hz, 1H), 6.50 – 6.42 (m, 1H), 5.94 (dt, *J* = 15.2, 6.1 Hz, 1H), 4.57 (d, *J* = 1.1 Hz, 2H), 4.14 (d, *J* = 6.1 Hz, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz) δ : 138.26, 137.14, 132.95, 132.69, 130.08, 128.58, 128.38, 128.24, 127.76, 127.61, 127.57, 126.37, 72.13, 70.41. **IR** (neat): 3061, 3026, 2925, 2852, 1496, 1450, 1362, 1111, 1071, 1028, 745. **GCMS** (m/z): 250 (M^+).

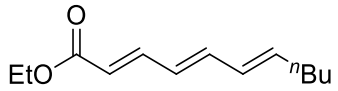
((*1E,3E*)-4-(benzyloxy)buta-1,3-dienyl)benzene (2j)



2j

The product was obtained in 53% yield by adding 2 mol% catalyst and heating at 60 ^{o}C for 22 h according to general procedure B. The spectra match the reported data[20]. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.48 – 7.06 (m, 10H), 6.78 (d, *J* = 12.4 Hz, 1H), 6.67 (dd, *J* = 15.6, 10.7 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 5.85 (dd, *J* = 12.4, 10.8 Hz, 1H), 4.86 (s, 2H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 150.88, 138.02, 136.55, 128.59, 128.51, 128.13, 127.56, 127.38, 126.52, 125.62, 125.59, 108.09, 72.02.

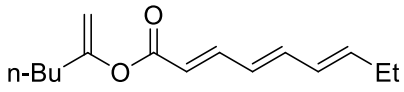
(2*E*,4*E*,6*E*)-ethyl undeca-2,4,6-trienoate (2k)



2k

The product was obtained in 73% yield ((2E, 4E, 6E) / (2E, 4E, 6Z) = 12/1) with 10 % starting material recovered by adding 3 mol% catalyst plus 8 mol % NaBARF and heated at 60 ^{o}C for 24 h and another 2 mol% catalyst plus 8 mol % NaBARF for another 24 h according to general procedure B. This compound is known and its spectroscopic data were in accordance with the literature data [13].

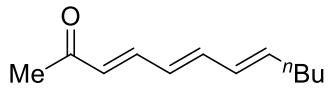
(2*E*,4*E*,6*E*)-hex-1-en-2-yl nona-2,4,6-trienoate (2l)



2l

The product was obtained in 82% yield ((2E, 4E, 6E) / (2E, 4E, 6Z) = 9.6/1) by adding 2 mol % catalyst and 8 mol % NaBARF and heated at 60 ^{o}C for 1 day, another 2 mol % catalyst plus 8 mol % NaBARF for one more day, then another 2 mol % catalyst plus 4 mol % NaBARF for 1 day according to general procedure B. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.35 (dd, *J* = 15.2, 11.3 Hz, 1H), 6.57 (dd, *J* = 14.9, 10.6 Hz, 1H), 6.24 (dd, *J* = 14.9, 11.3 Hz, 1H), 6.15 (dd, *J* = 15.2, 10.7 Hz, 1H), 6.00 (dt, *J* = 15.1, 6.6 Hz, 1H), 5.88 (d, *J* = 15.2 Hz, 1H), 4.78 – 4.69 (m, 2H), 2.24 (t, *J* = 7.6 Hz, 2H), 2.18 (t, *J* = 7.8 Hz, 2H), 1.51 – 1.42 (m, 2H), 1.40 - 1.31 (m, 2H), 1.04 (t, *J* = 7.5 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 165.29, 156.65, 146.07, 142.50, 141.93, 128.83, 127.60, 119.28, 100.87, 33.15, 28.62, 26.01, 22.11, 13.83, 13.12. **MS ESI** (*m/z*): $[MNa]^+$ calcd. for $C_{15}H_{22}NaO_2$, 257.15; found, 257.15.

(*3E*,*5E*,*7E*)-dodeca-3,5,7-trien-2-one (2m)

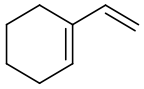


2m

The product was obtained in 46% yield ((2E, 4E, 6E) / (2E, 4E, 6Z) > 8/1) with 21% starting material recovered by adding 3 mol% catalyst plus 8 mol % NaBARF and heated at 70 ^{o}C for 24 h and then another 2 mol% catalyst plus 8 mol % NaBARF for another 24

h according to general procedure B. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ : 7.14 (dd, *J* = 15.5, 11.1 Hz, 1H), 6.58 (dd, *J* = 14.9, 10.7 Hz, 1H), 6.22 (dd, *J* = 14.9, 11.1 Hz, 1H), 6.15 (dd, *J* = 15.3, 10.7 Hz, 1H), 6.11 (d, *J* = 15.5 Hz, 1H), 5.96 (dt, *J* = 14.7, 7.1 Hz, 1H), 2.26 (s, 3H), 2.15 (q, *J* = 7.3 Hz, 2H), 1.44 – 1.26 (m, 4H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 150 MHz) δ : 198.43, 143.77, 142.16, 141.17, 129.84, 129.36, 128.10, 32.66, 31.04, 27.24, 22.22, 13.86. **GCMS** (m/z): 178 (M^+).

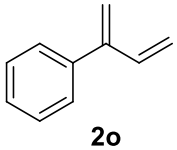
1-vinylcyclohex-1-ene (2n)



2n

The volatile product was obtained in 80% yield by using 2 mol% catalyst in DCM at 40 ^{o}C for 12 h according to general procedure B. This compound is known and its spectroscopic data were in accordance with the literature data [21].

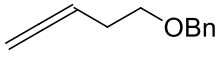
buta-1,3-dien-2-ylbenzene (2o)



2o

The product was obtained in 84% yield by using 2 mol% catalyst and heated at 40 ^{o}C for 12 h according to general procedure B. This compound is known and its spectroscopic data were in accordance with the literature data [22].

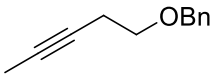
((penta-3,4-dien-1-yloxy)methyl)benzene (2p')



2p'

The product was obtained in 30% yield (NMR yield determined by using diethyl phthalate as internal references) using 2 mol% catalyst and heated at 60 ^{o}C for 8 h according to general procedure B. This compound is known and its spectroscopic data were in accordance with the literature data [23].

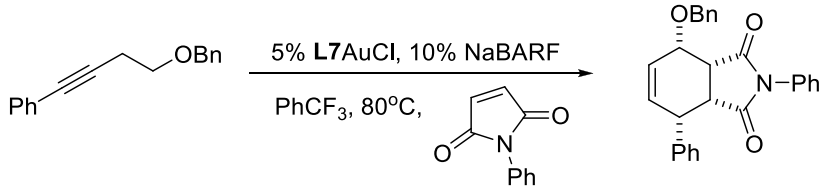
((pent-3-yn-1-yloxy)methyl)benzene (4)



4

The product was obtained in 52% yield (NMR yield determined by using diethyl phthalate as internal references) using 2 mol% catalyst and heated at 60 ^{o}C for 8 h according to general procedure B. This compound is known and its spectroscopic data were in accordance with the literature data[24].

One-pot synthesis (3aR,4S,7R,7aR)-4-(benzyloxy)-2,7-diphenyl-3a,4,7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione (3)

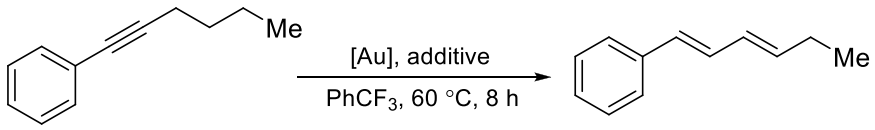


3

To a 3 dram vial were added sequentially 0.3 mmol (4-(benzyloxy)but-1-ynyl)benzene, 0.33 mmol N-phenylmaleimide (1.1 equiv), 0.015 mmol **L7**AuCl (5 mol%), 0.03 mmol $NaBAr^{F}_{4}$ (10 mol%) and 3 mL α,α,α-trifluorotoluene as solvent. The reaction was then heated at the indicated temperature monitored by TLC using p-anisaldehyde staining reagent (anisaldehyde/perchloric acid/acetone/water = 1/10/20/80, v/v). Upon completion, the reaction was concentrated under reduced pressure. The residue was purified through silica gel flash chromatography to obtain pure product in 62% yield. **^{1}H NMR** ($CDCl_3$, 500 MHz) δ : 7.48 – 7.42 (m, 2H), 7.42 – 7.26 (m, 11H), 7.13 – 7.08 (m, 2H), 6.34 (ddd, *J* = 9.8, 4.3, 1.6 Hz, 1H), 6.27 (ddd, *J* = 9.8, 3.7, 2.3 Hz, 1H), 4.89 (d, *J* = 11.3 Hz, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 4.52 (ddt, *J* = 6.8, 3.3, 1.5 Hz, 1H), 3.84 – 3.80 (m, 1H), 3.65 (dd, *J* = 9.1, 6.9 Hz, 1H), 3.57 (dd, *J* = 9.1, 7.6 Hz, 1H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 125 MHz) δ : 175.00, 174.18, 138.91, 137.55, 132.19, 131.82, 129.03, 128.98, 128.87, 128.44, 128.31, 128.16, 128.05, 127.85, 127.05, 126.54, 71.45, 71.10, 43.83, 43.39, 40.57. **IR** (neat): 3063, 3032, 2864, 1778, 1714, 1598, 1499, 1455, 1382, 1034, 1176, 1128, 1073, 1038, 913, 752. **MS ESI**: 432.11 $[M + Na]^{+}$.

Mechanistic Study

Silver salt and Conteranion effects: To rule out the possibility that AgCl generated in situ is detrimental to this reaction an experiment was conducted in which AgCl was filtered off with Celite (Entry 3), giving a poor yield (~1%) as the reaction without filtration (Entry 2). On the other hand, the reaction wasn't hampered totally (43% yield) by adding commercial available AgCl (Entry 5), comparing 54% yield without AgCl (Entry 4). A loss of yield was observed possibly due to inevitable Cl^- residue in AgCl. Moreover, the reactivity can be restored by adding NaBARF (Entry 6), giving a reasonable 74% yield, which can be ascribed to the reaction: $L7AuNTf_2$ + NaBARF → [L7AuBARF] + $NaNTf_2$ (s).



1a **2a**

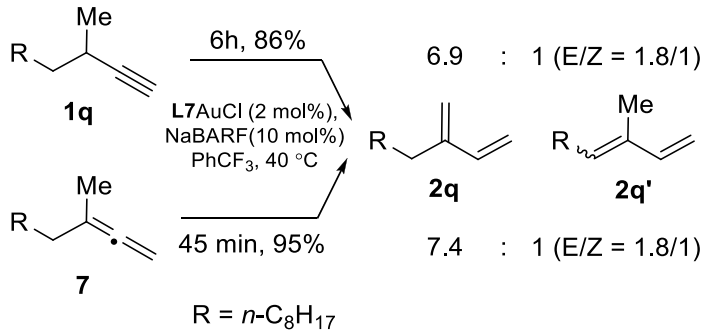
Entry	Method	Yield (Conv.)[a]
1	L7AuCl (5 mol%), NaBARF (10%) (In Table 1, Entry 7)	90% (96%)
2	L7AuCl (6 mol%), $AgNTf_2$ (5 mol%), no fitration (In Table 1, Entry 9)	~1% (<4%)
3	L7AuCl (6 mol%), $AgNTf_2$ (5 mol%), filter through Celite	~1% (<4%)
4	$[(L7Au)_2]^{2+}$ $2BARF^-$ (2.5 mol%) (In Table 1, Entry 8)	54% (55%)
5	$[(L7Au)_2]^{2+}$ $2BARF^-$ (2.5 mol%), AgCl (5 mol%)	43% (44%)
6	L7AuCl (6 mol%), $AgNTf_2$ (5 mol%), filter through Celite, NaBARF (10%)	74% (77%)
7	L7AuPh (4 mol%), HA (3.3 mol%, A = NTf_2, OTf, OMs)	(<3%)[b]
8	L7AuPh (4 mol%), $HNTf_2$ (3.3 mol%), NaBARF (10%)	(>99%)[b]

[a] Yield using diethyl phthalate as internal reference. [b] Conversion determined by terminal methyl group.

To further investigate the effect of counter anion, we synthesized gold complex L7AuPh by mixing L7AuCl with PhMgCl (ACIE, 2012, 51, 2452). $L7AuNTf_2$ can be generated *in*

situ by reaction: L7AuPh + HA → L7AuA + PhH (A: Counter anion), which would remove any possible effect of silver salts. As we proposed, poor reactivity (<3% conversion) was observed for counter anions OTf, NTf_2, OMs (Entry 7), while the catalyst was rejuvenated, again, by adding NaBARF, giving a clean reaction with high yield (Entry 8).In summary , it was confirmed that the lack of reactivity was resulted from the counter anions.

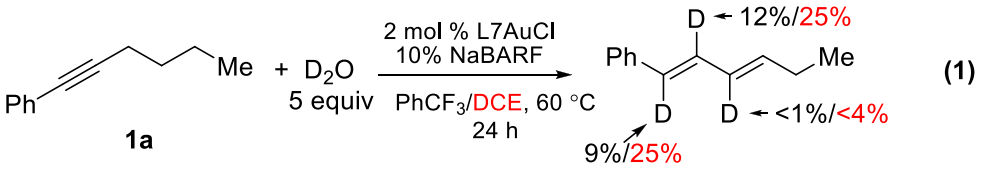
Intermediate study: 3-Methyl-1-dodecane **1q** was subjected to general procedure B by adding 2 mol% catalyst plus 10 mol % NaBARF and heating at 40 ^{o}C for 6 h to give 86% yield of 3-methylenedodec-1-ene, (E)-3-methyldodeca-1,3-diene and (Z)-3-methyldodeca-1,3-diene (19.3/1.8/1).



3-methyldodeca-1,2-diene **7** was subjected to general procedure B by adding 2 mol% catalyst plus 10 mol % NaBARF and heating at 40 ^{o}C for 45 min to give 95% yield of 3-methylenedodec-1-ene, (E)-3-methyldodeca-1,3-diene and (Z)-3-methyldodeca-1,3-diene (20.8/1.8/1).

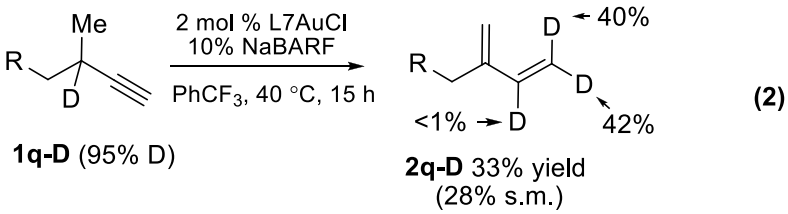
Deuterium labeling study: To provide further support for the mechanism, we performed deuterium labeling studies. As shown in Eq. 1, with **1q-D**, in which its propargylic position was 94% deuterated, the major diene product **2q** possessed significant amount of deuterium labeling at the vinyl methylene while little at the vinyl methine. Importantly, little product with the methylene moiety fully deuterated was detected, and there were deuterium loss in the process. The latter observation is consistent with that in this gold catalysis the hydrogens migrate in the form of protons instead of metal hydrides as deuteron/proton exchange with residual water in the reaction mixture could readily explain the outcome (Eq. 2). With **1a** as the substrate, the addition of D_2O (5 equiv) to the reaction run in $PhCF_3$ resulted in observable deuterium incorporation at the C-C double

bond proximal to the benzene ring. When the reaction was run in DCE, a solvent of higher polarity (normalized parameter: 0.327 vs. 0.241 of $PhCF_3$)[25] and hence likely of being more capable of dissolving water (0.15%w/w at 25 ˚C) than $PhCF_3$, the amount of deuterium labeling at the same C-C double bond of the product more than doubled. These results confirmed proton migration in the reaction and supported the proposed mechanism.



(1)

To a Schlenk tube were added 0.004 mmol **L7AuCl** (2 mol%), 0.02 mmol $NaBAr^F_4$ (10 mol %), 0.2 mmol 1-phenyl-1-hexyne and 2 mL anhydrous solvent. The mixture was stirred at room temperature for 10 min and then 1 mmol D_2O was added. The reaction was then heated at 60 ^oC for 24 h and then the reaction was concentrated under reduced pressure. The ratio of deuterium was determined by crude NMR.



1q-D (95% D)

2q-D 33% yield
(28% s.m.)

(2)

To a 1 dr vial were added 0.004 mmol **L7AuCl** (2 mol%), 0.02 mmol $NaBAr^F_4$ (10 mol %), 0.2 mmol **1q-D** and 2 mL $PhCF_3$. The mixture was stirred at 40 ^oC for 15 h and then the reaction was concentrated under reduced pressure. The yield and ratio of deuterium were determined by crude NMR.

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Parameter	Value
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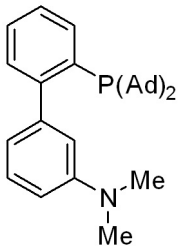
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



L1

Parameter	Value
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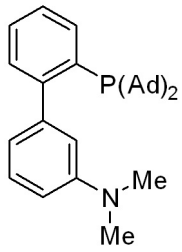
Spectrometer Frequency	125.70
Nucleus	13C



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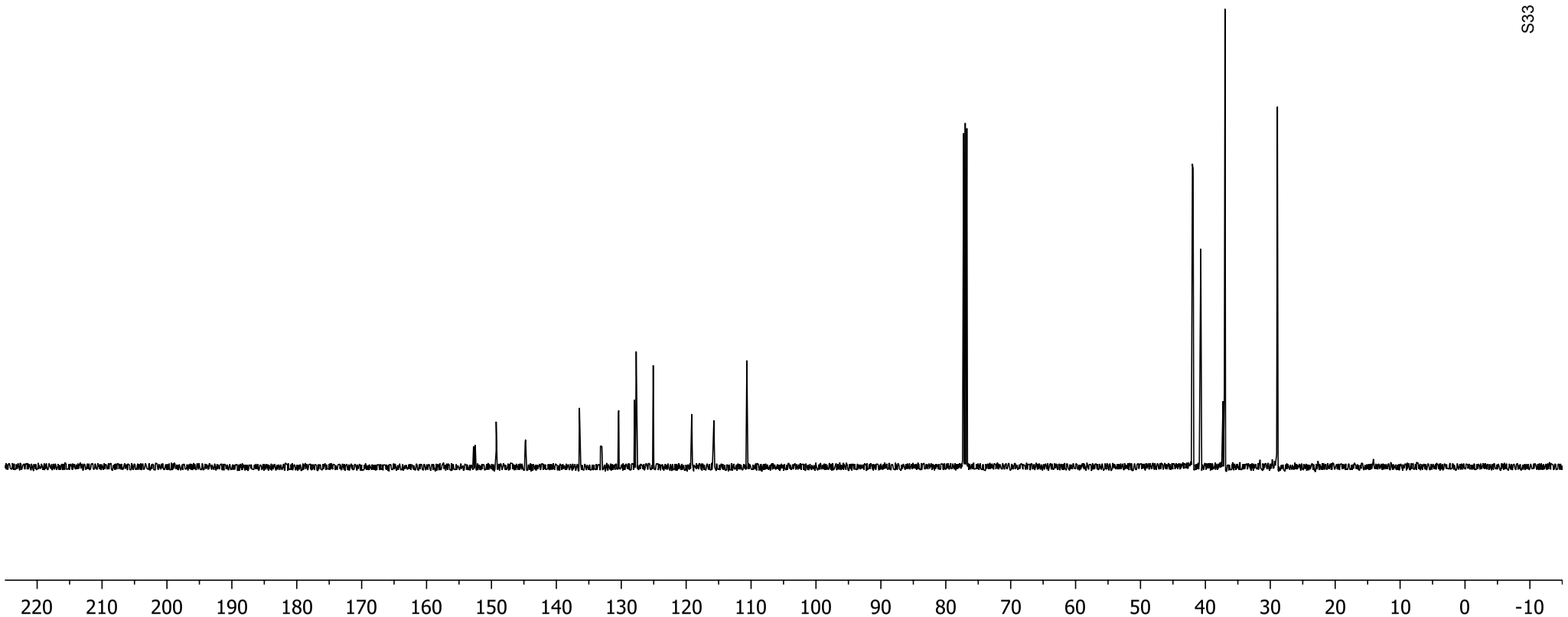

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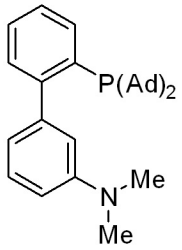
Nucleus	31P



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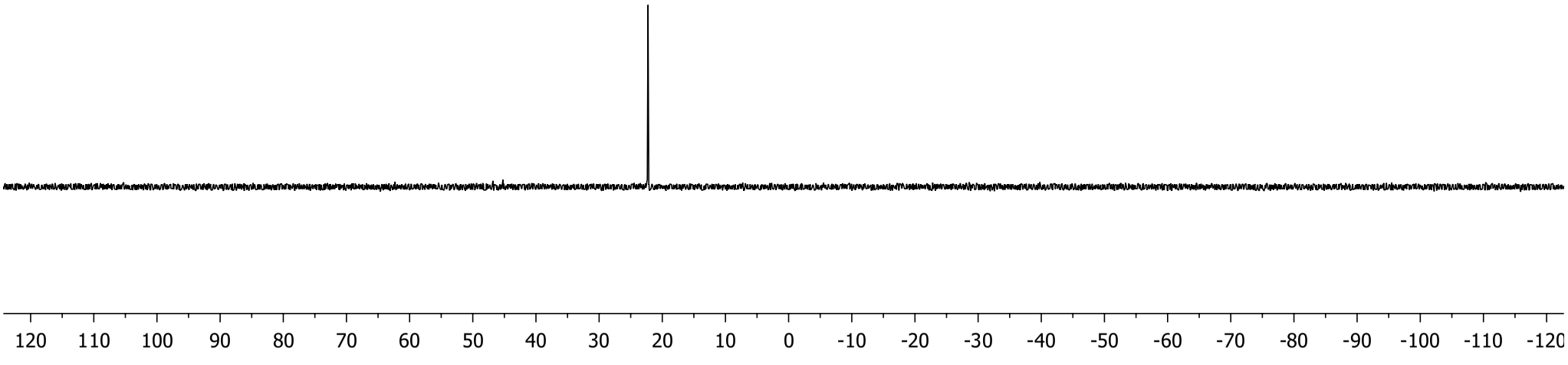

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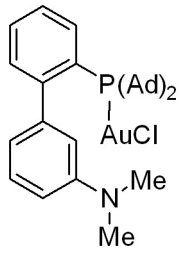

L1AuCl

Parameter	Value
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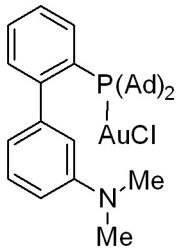
Spectrometer Frequency	125.70
Nucleus	13C



L1AuCl

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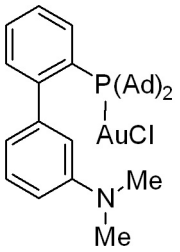
Spectrometer Frequency	161.90
Nucleus	31P



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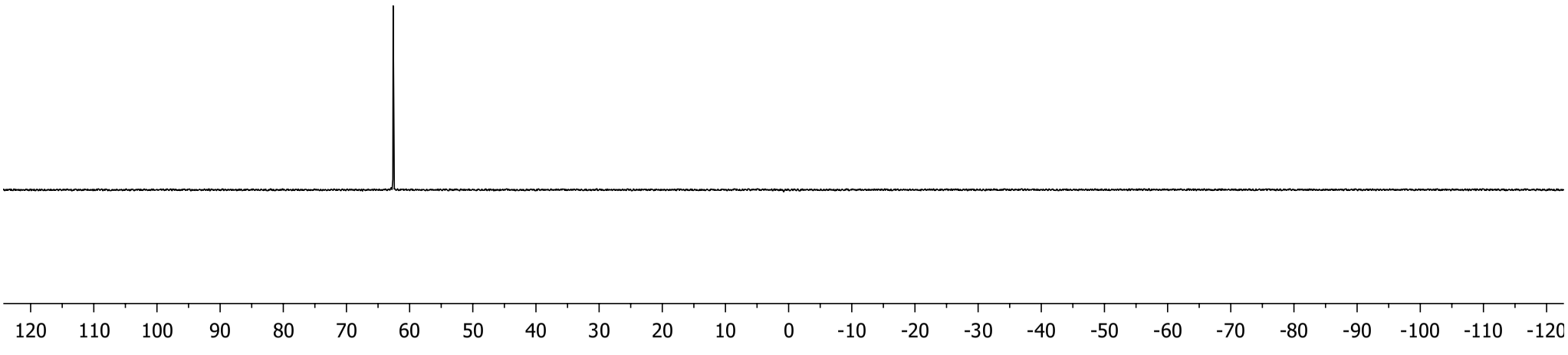

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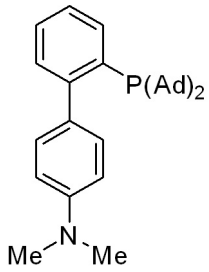
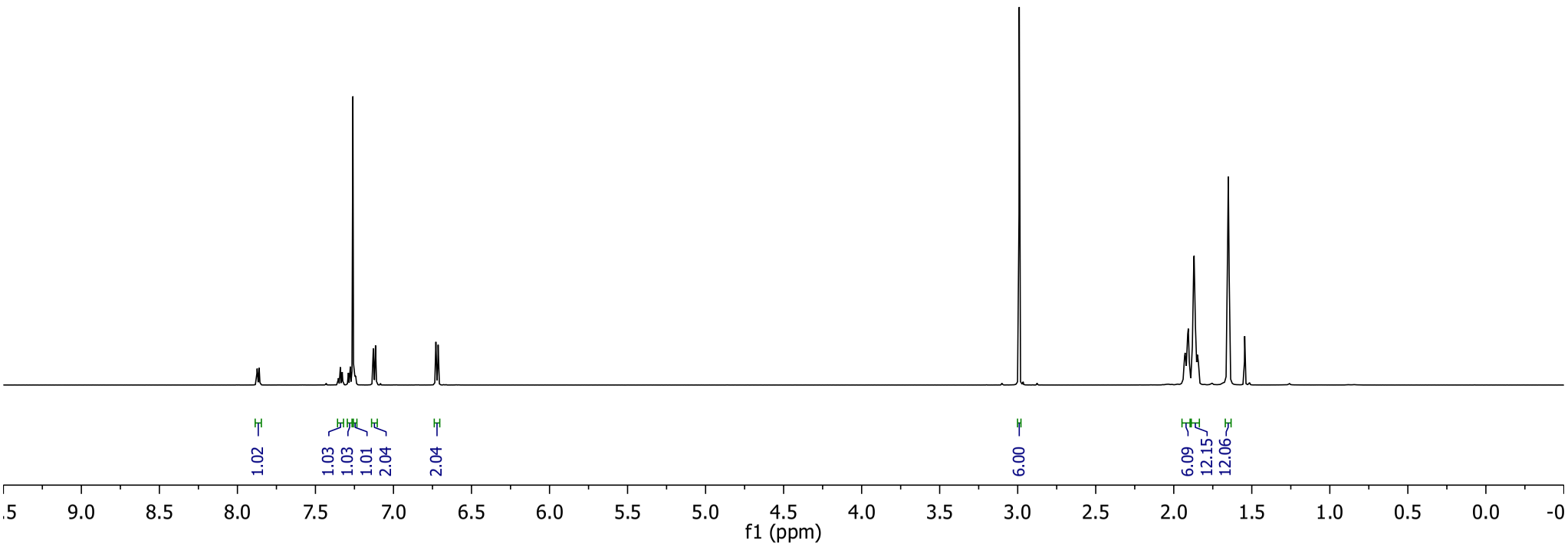


L2



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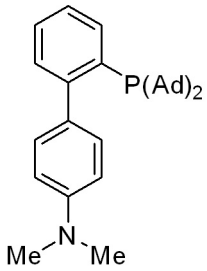
Nucleus	13C



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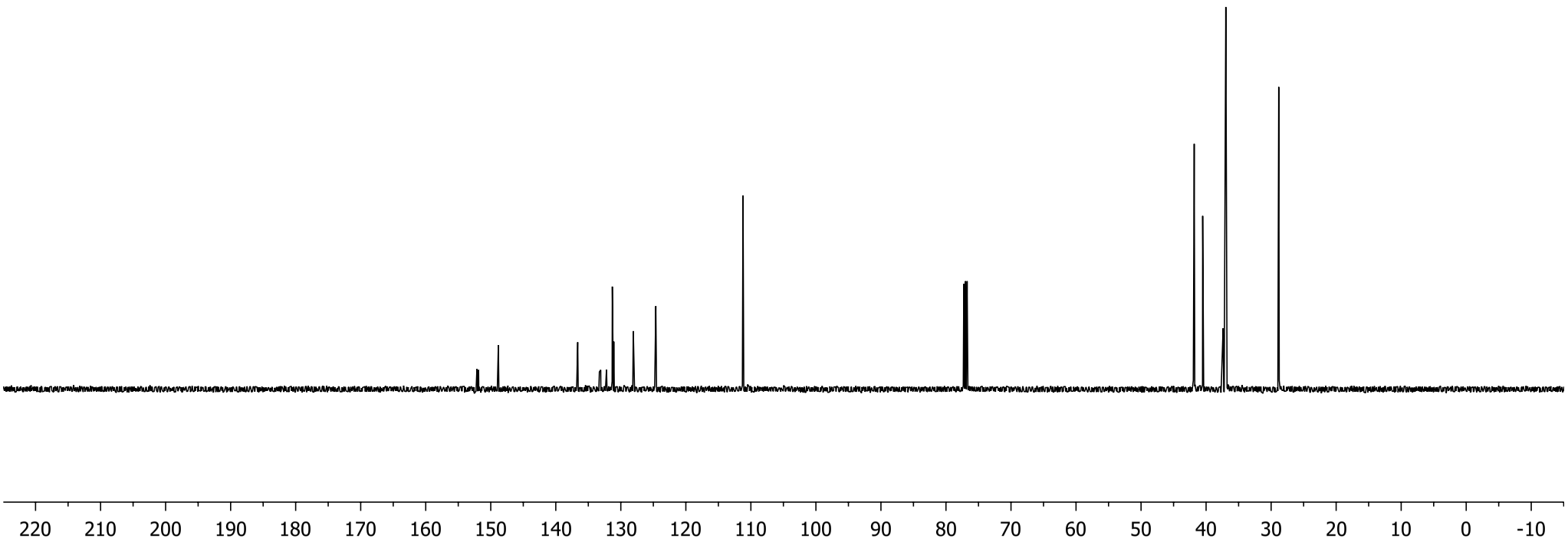

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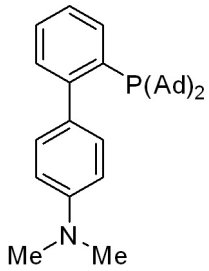

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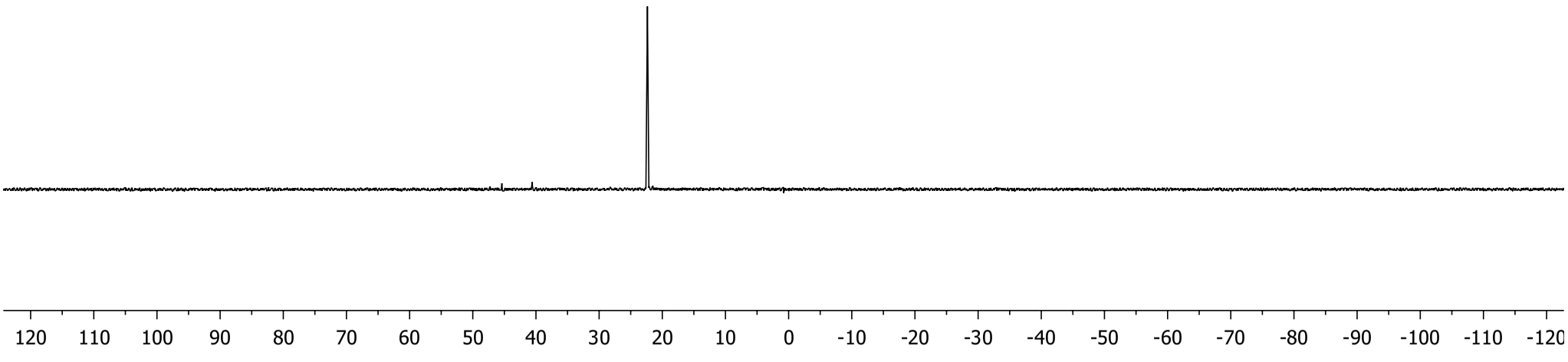

Parameter	Value
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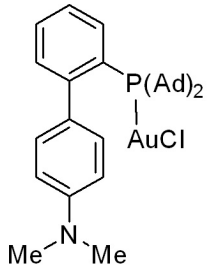

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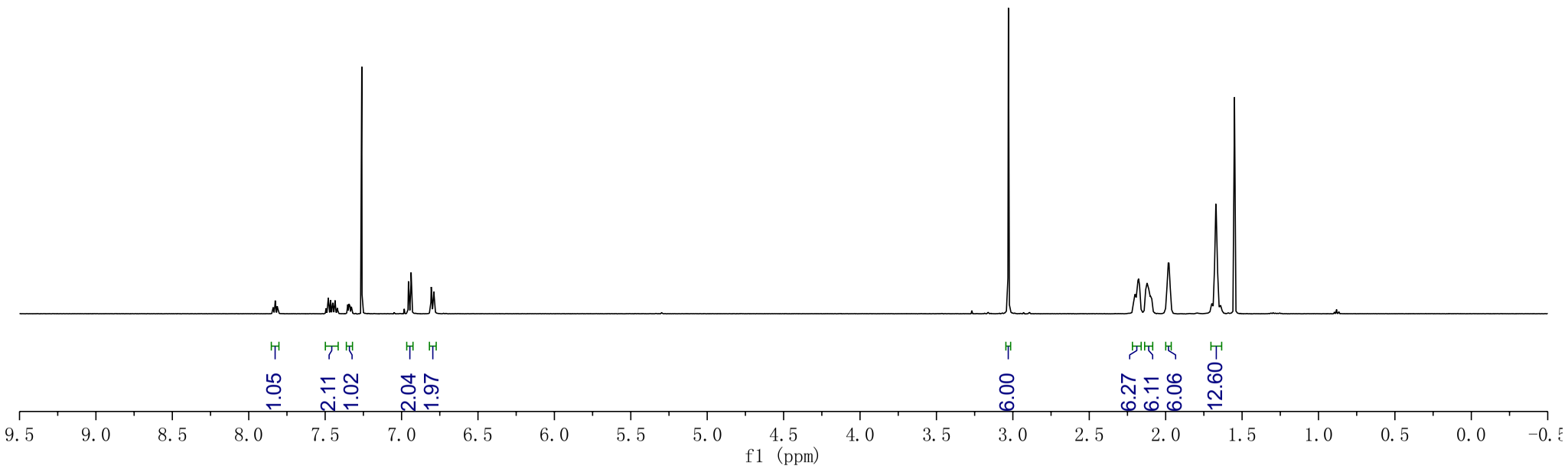

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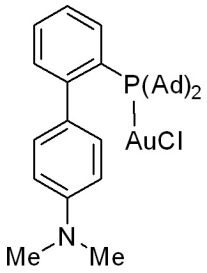

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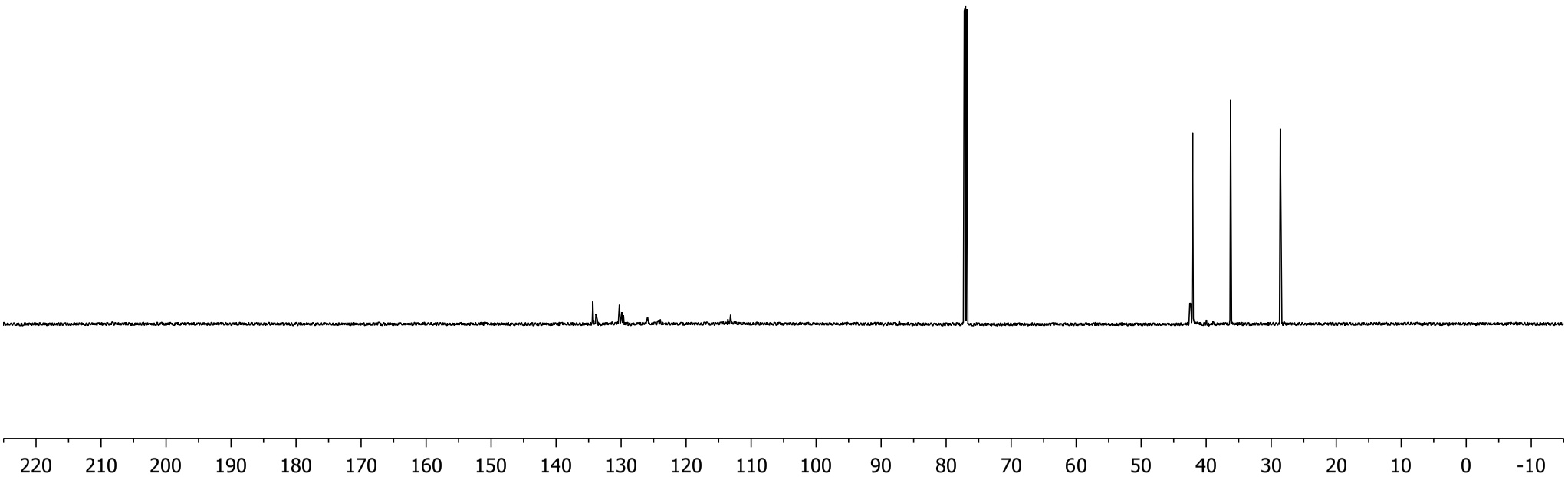

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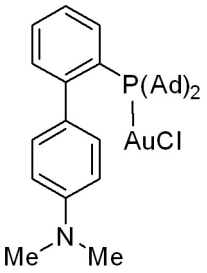

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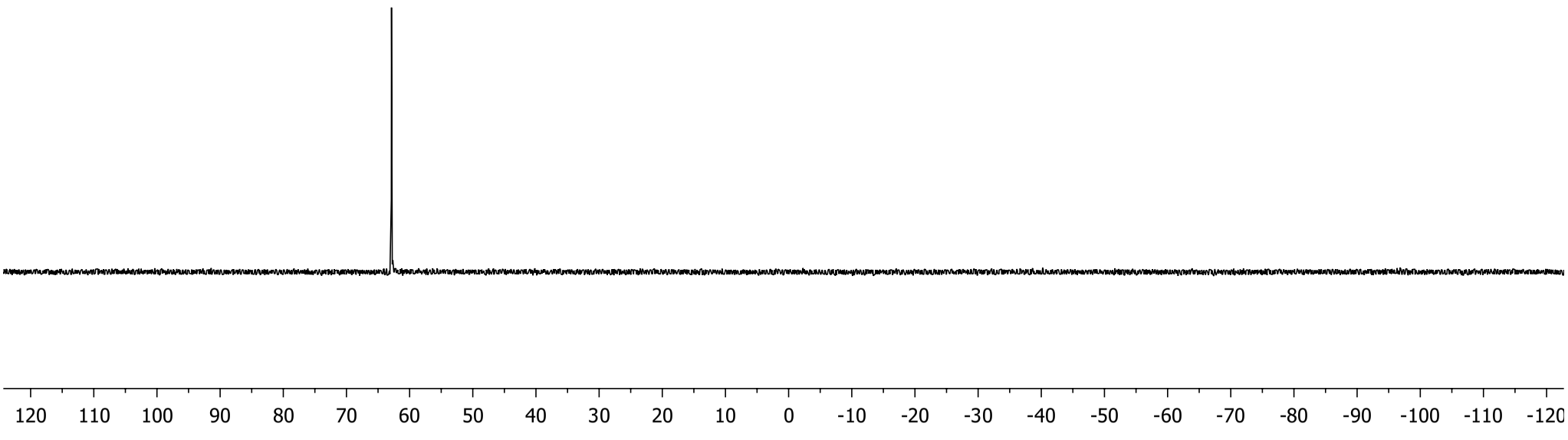

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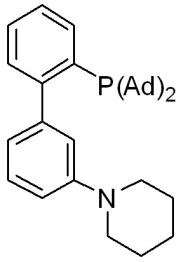
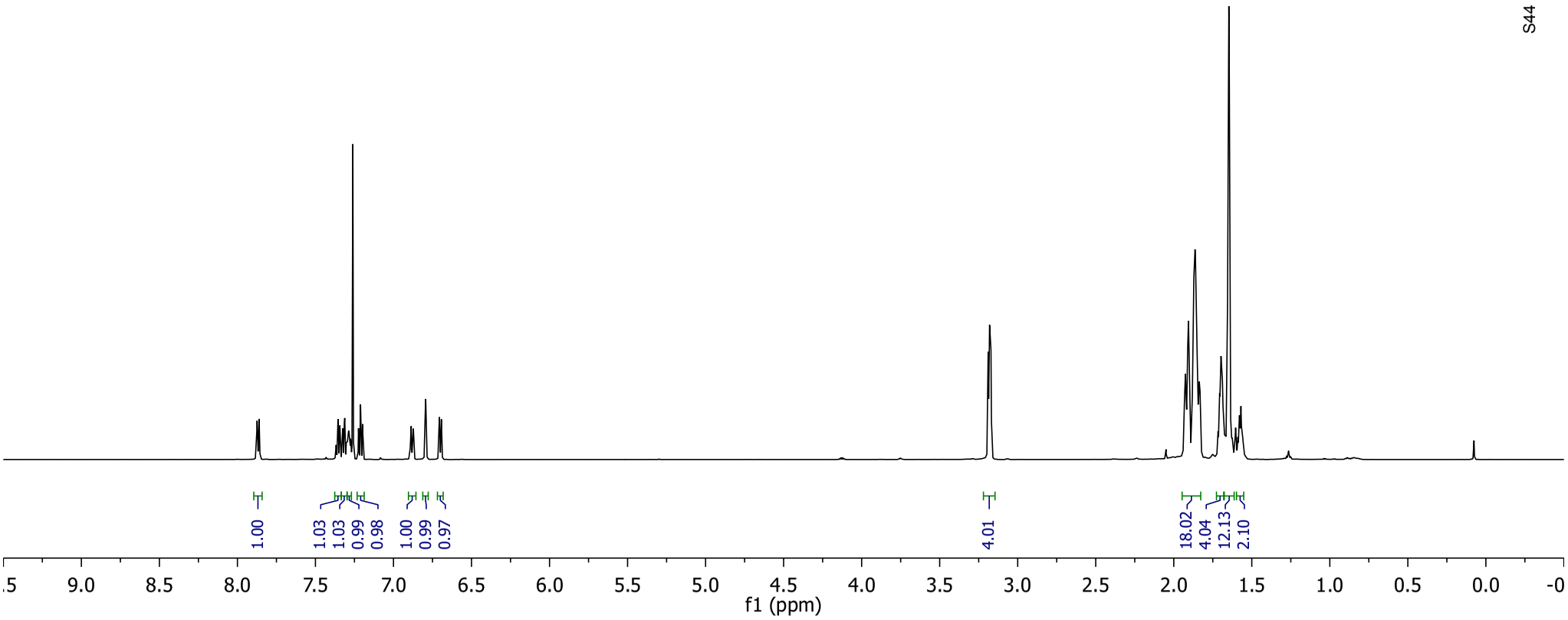
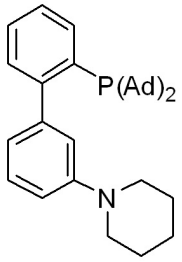
Solvent	cdcl3
Spectrometer Frequency	599.64



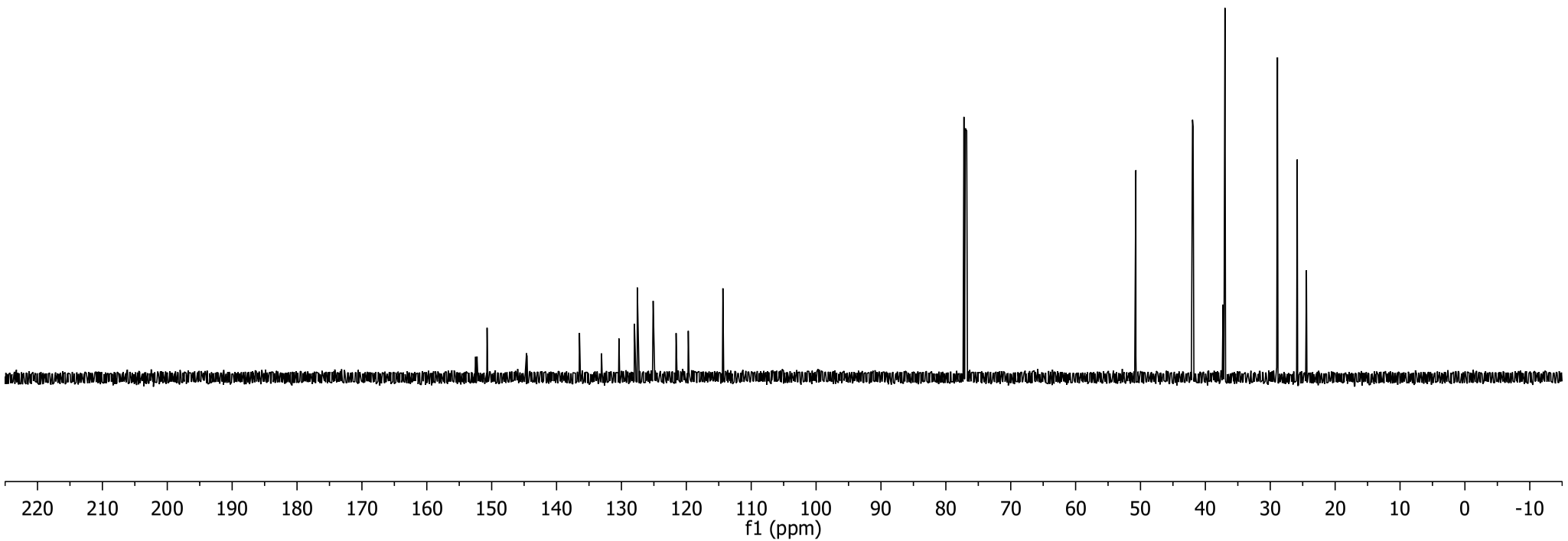
L3



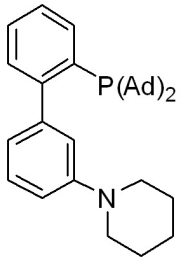
Parameter	Value
Title	jeremy-1-010-pure-C13
Solvent	cdcl3
Spectrometer Frequency	150.79



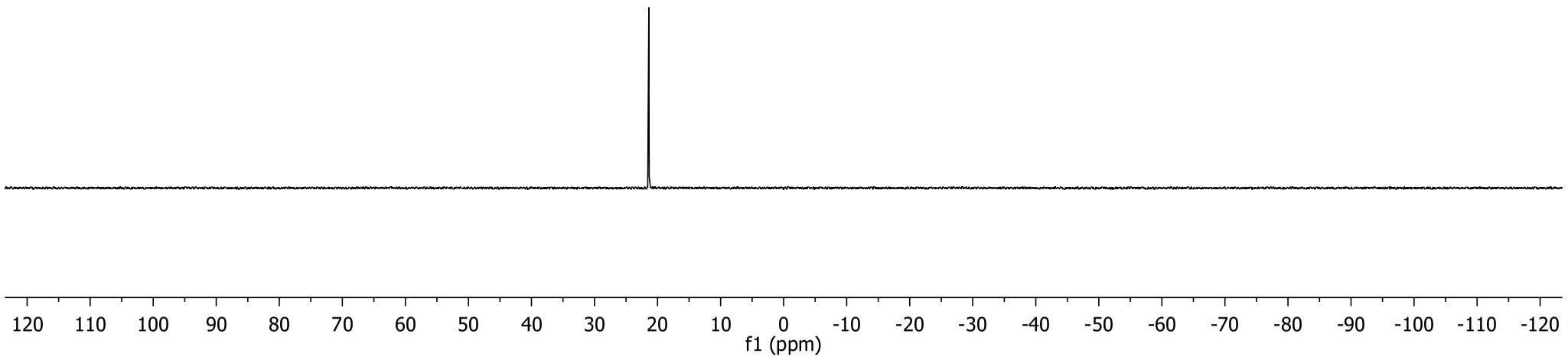
L3



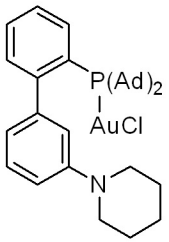
Parameter	Value
Title	jeremy-1-010-pure-p31
Solvent	cdcl3
Spectrometer Frequency	161.90



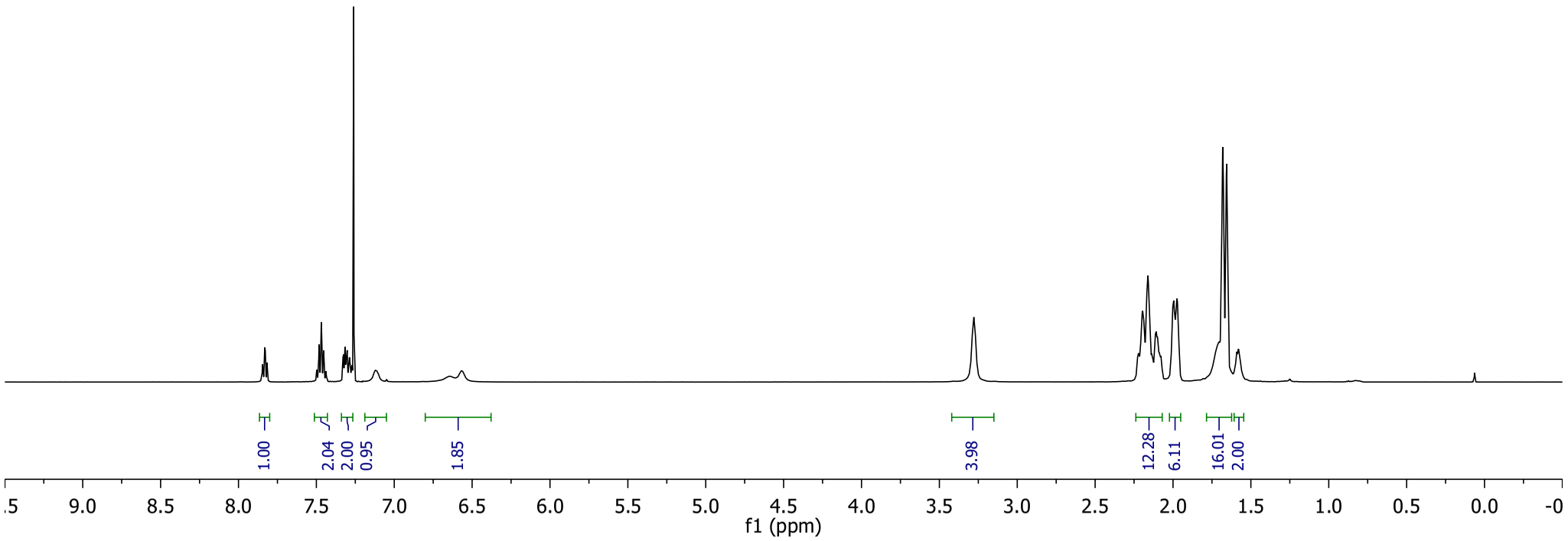
L3



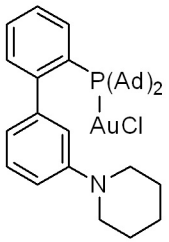
Parameter	Value
Title	zhixun-3-project2-L3AuCl
Solvent	CDCl3
Spectrometer Frequency	499.86



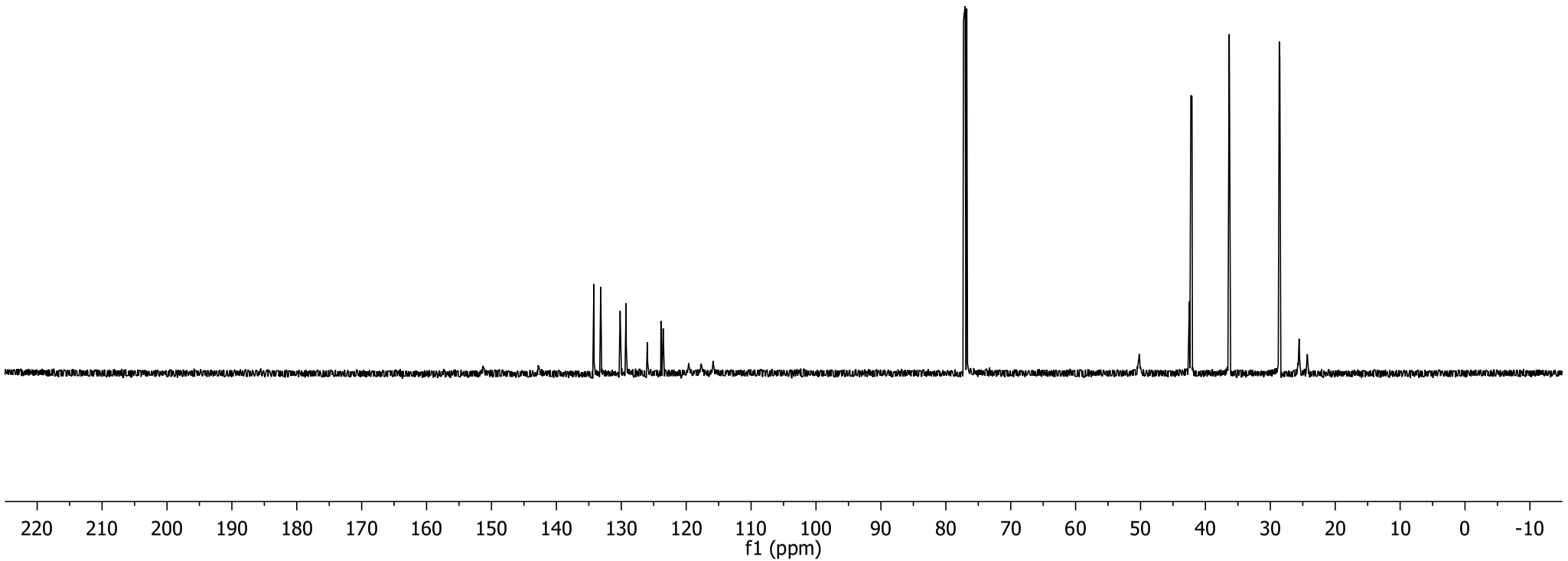
L3AuCl



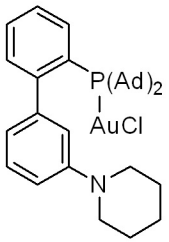
Parameter	Value
Title	zhixun-3-project2-L3AuCl-C13
Solvent	CDCl3
Spectrometer Frequency	125.70



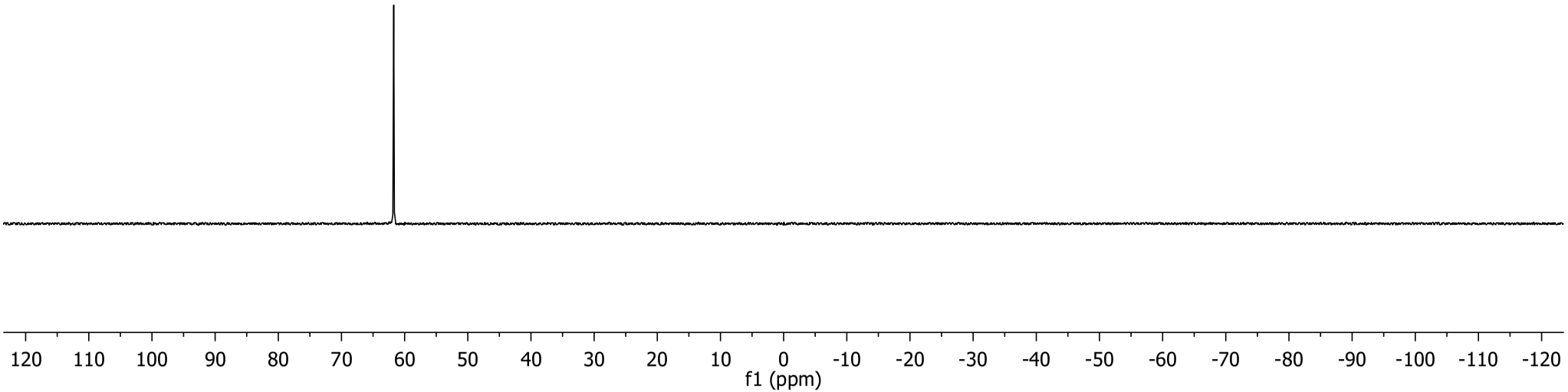
L3AuCl



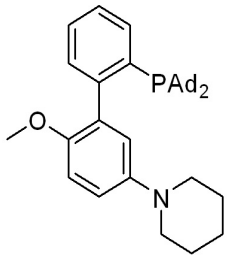
Parameter	Value
Title	zhixun-3-project2-L3AuCl-P31
Solvent	cdcl3
Spectrometer Frequency	161.90



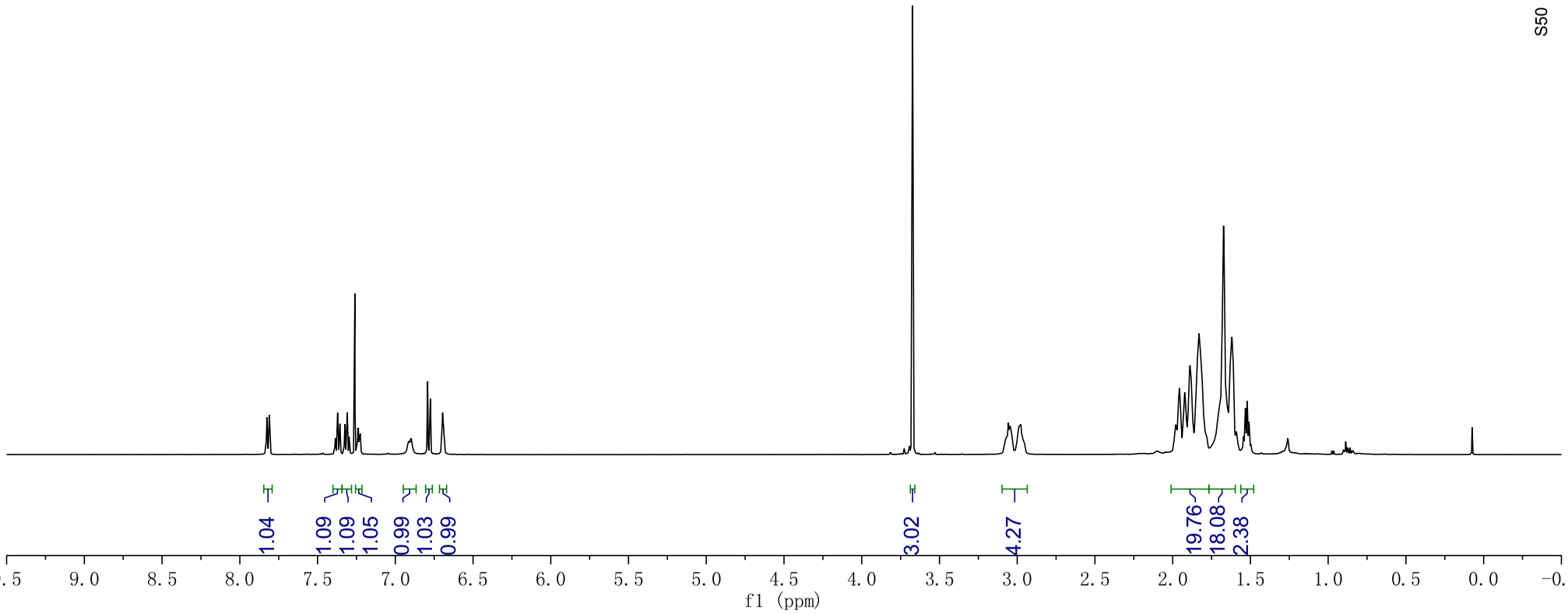
L3AuCl



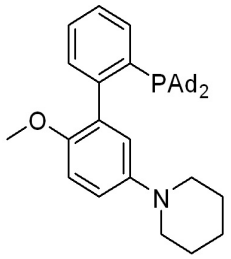
Parameter	Value
Title	zhixun-2-L4-H1
Solvent	CDCl3
Spectrometer Frequency	499.86



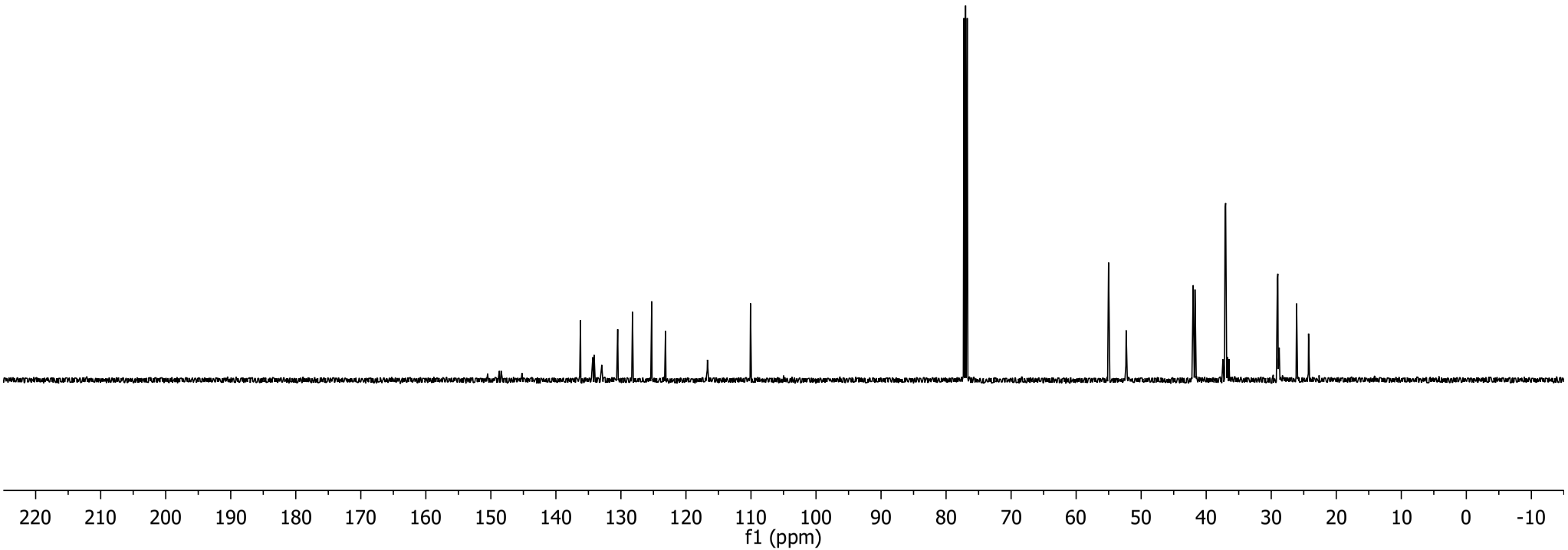
L4



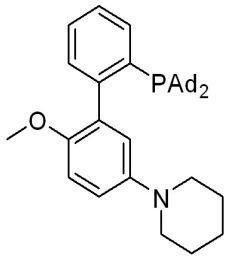
Parameter	Value
1 Title	zhixun-2-L4-C13
2 Solvent	CDCl3
3 Spectrometer Frequency	125.70



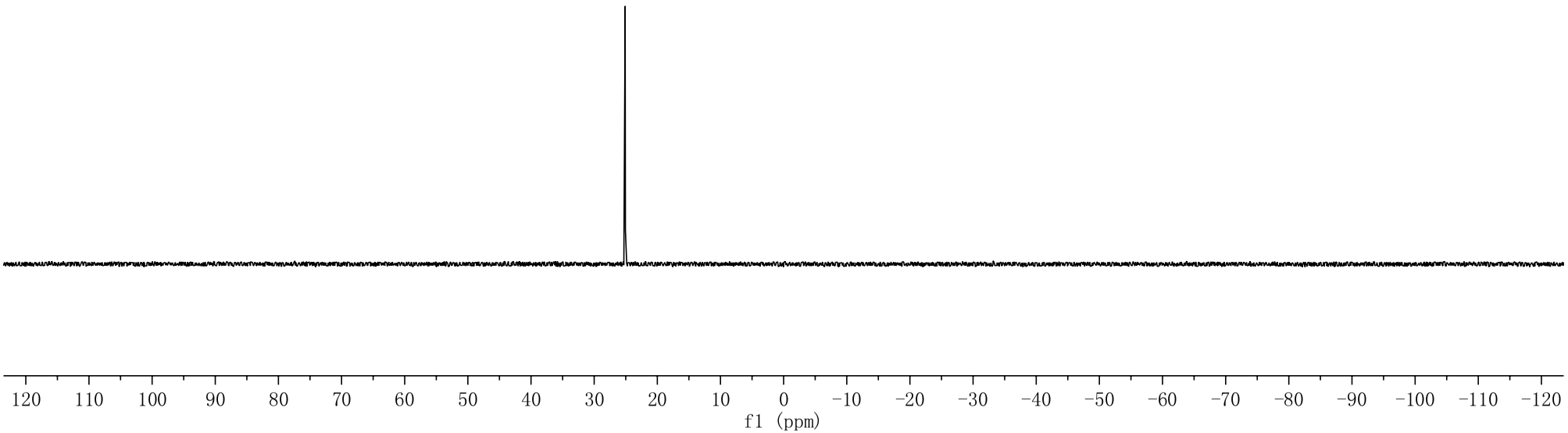
L4



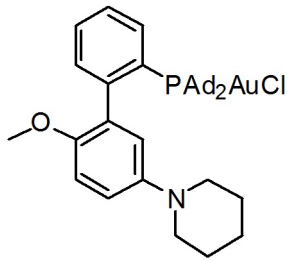
Parameter	Value
Title	zhixun-2-L4-P31
Solvent	cdcl3
Spectrometer Frequency	161.90



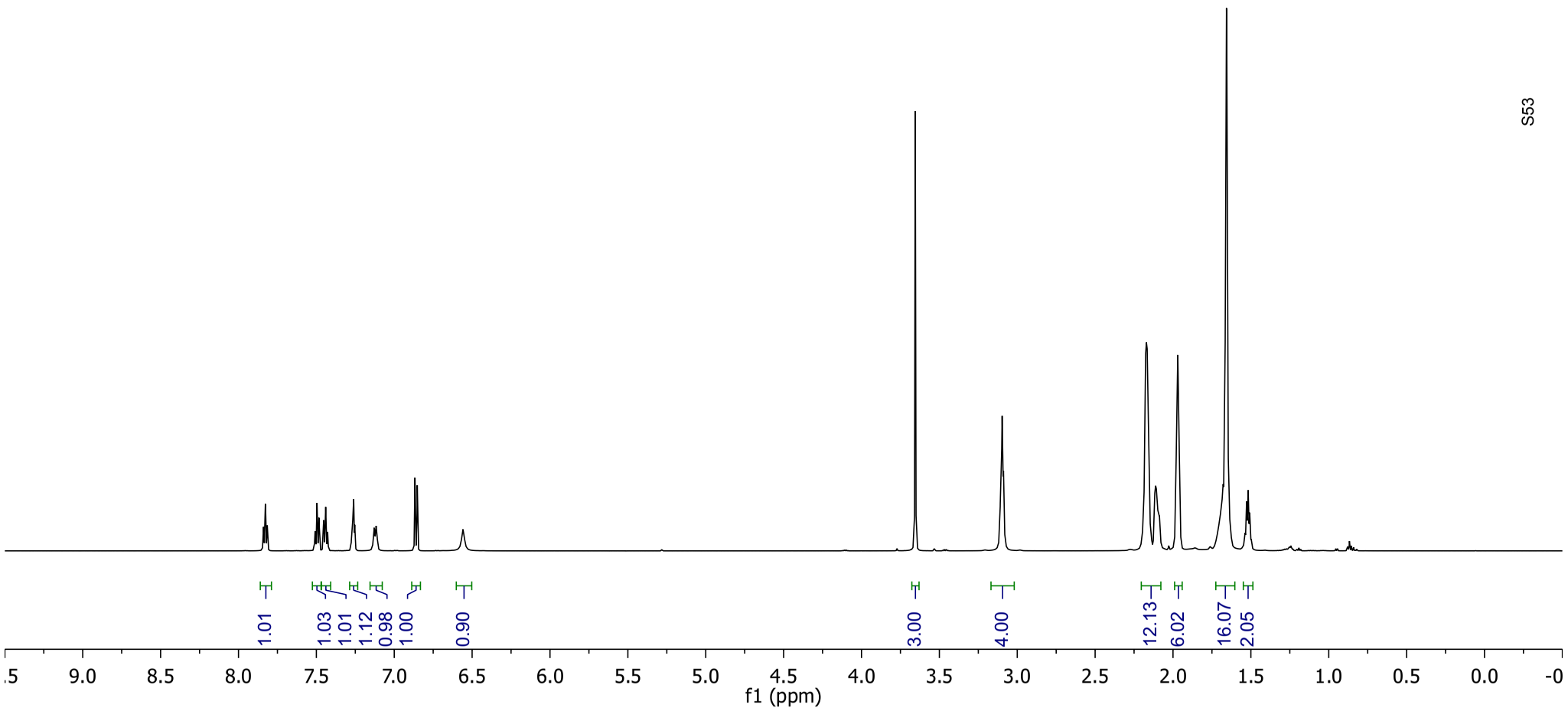
L4



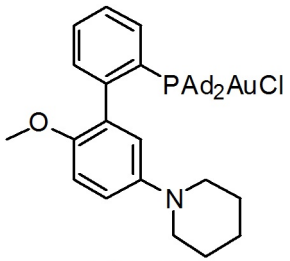
Parameter	Value
1 Title	zhixun-2-L4AuCl-H1
2 Solvent	cdcl3
3 Spectrometer Frequency	599.64



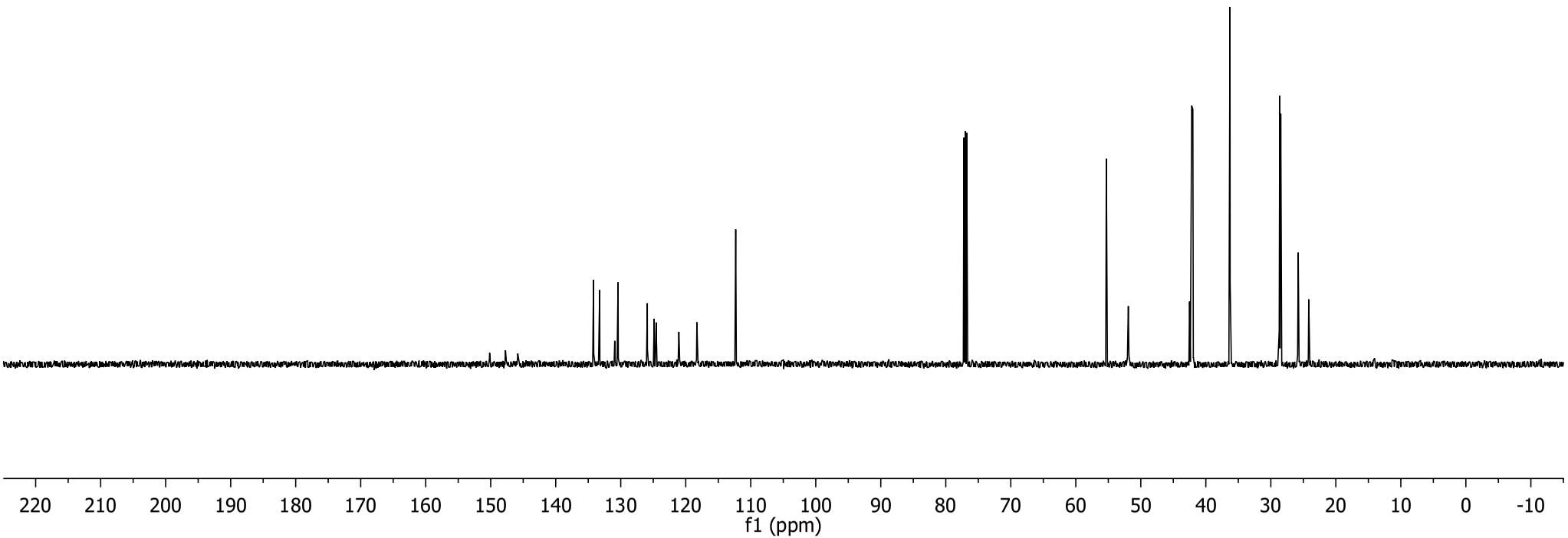
L4AuCl



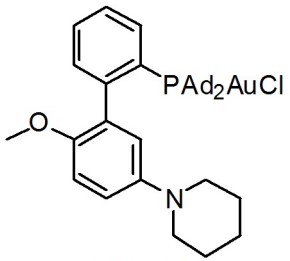
Parameter	Value
1 Title	zhixun-2-L4AuCl-C13
2 Solvent	cdcl3
3 Spectrometer Frequency	150.79



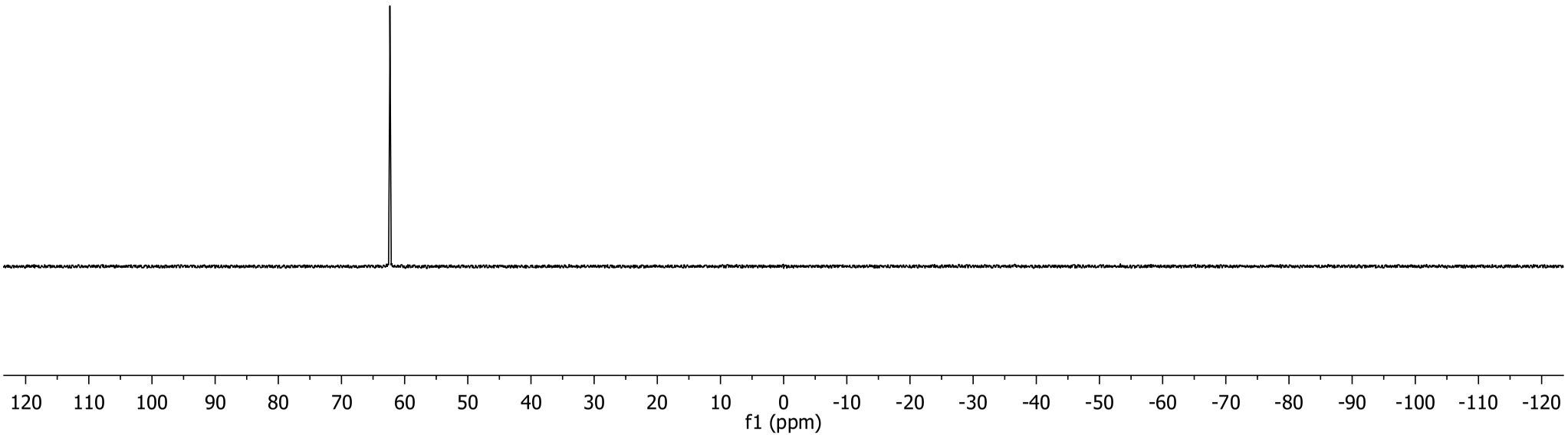
L4AuCl



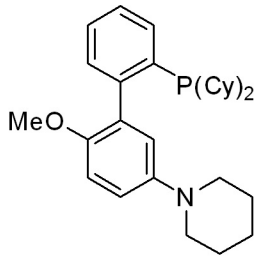
Parameter	Value
1 Title	zhixun-2-L4AuCl-P31
2 Solvent	cdcl3
3 Spectrometer Frequency	161.90



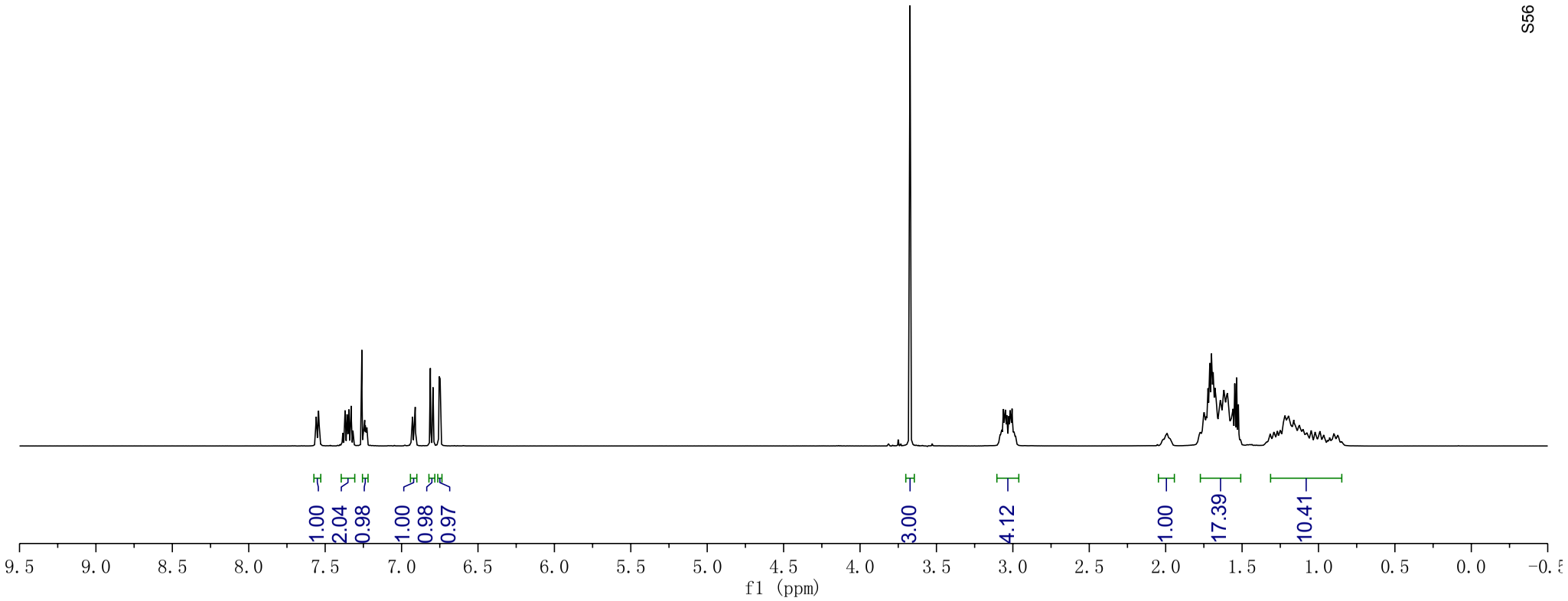
L4AuCl



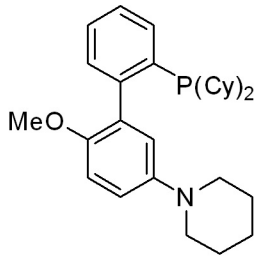
Parameter	Value
1 Title	zhixun-3-078B
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



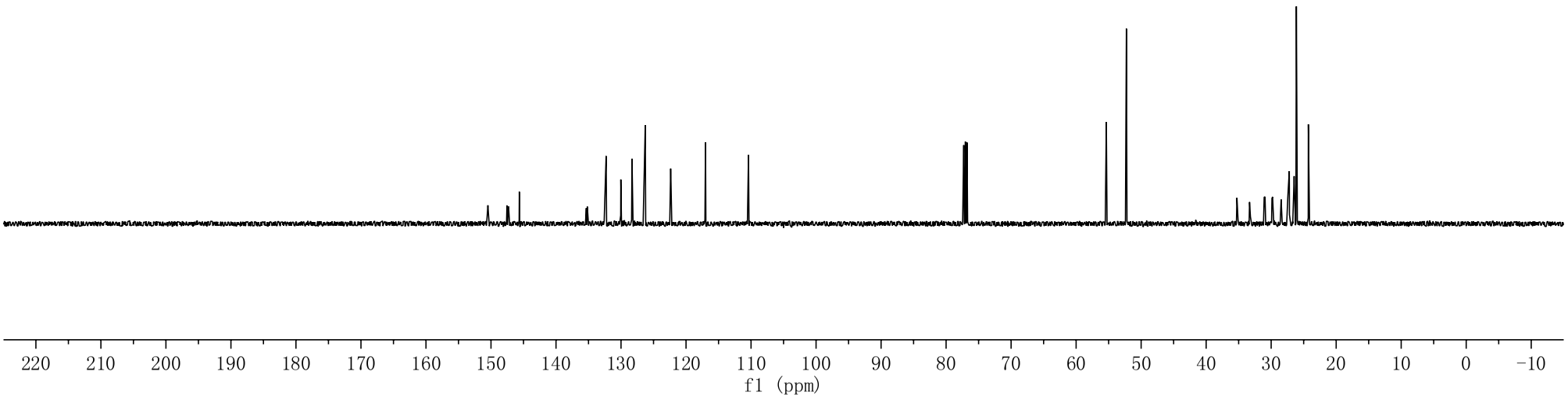
L5



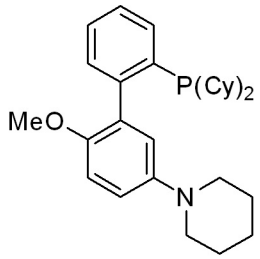
Parameter	Value
Title	zhixun-3-078B-C13
Solvent	CDCl3
Spectrometer Frequency	125.70



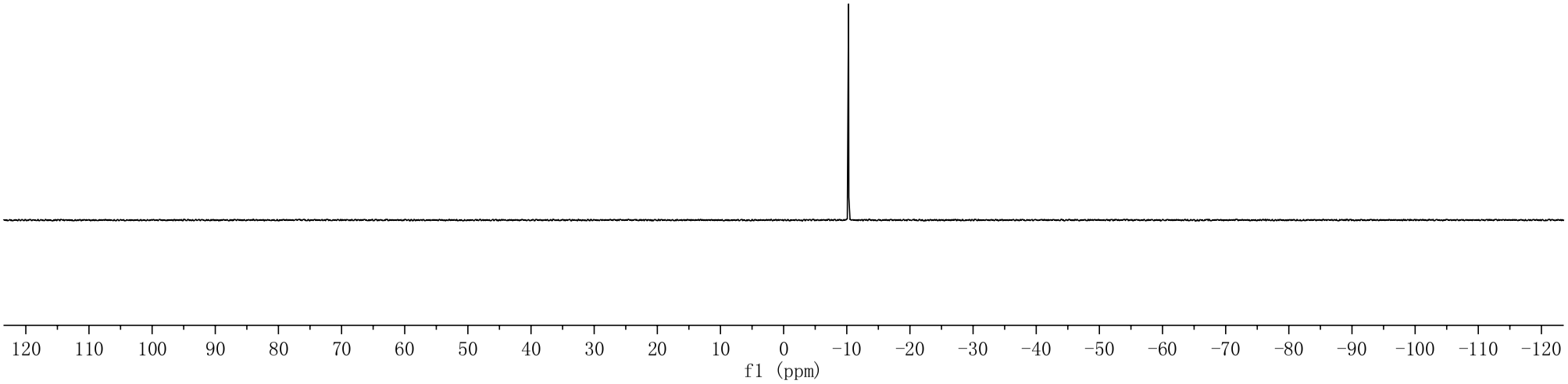
L5



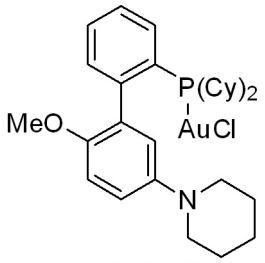
Parameter	Value
1 Title	zhixun-3-078B-P31
2 Solvent	cdcl3
3 Spectrometer Frequency	161.90



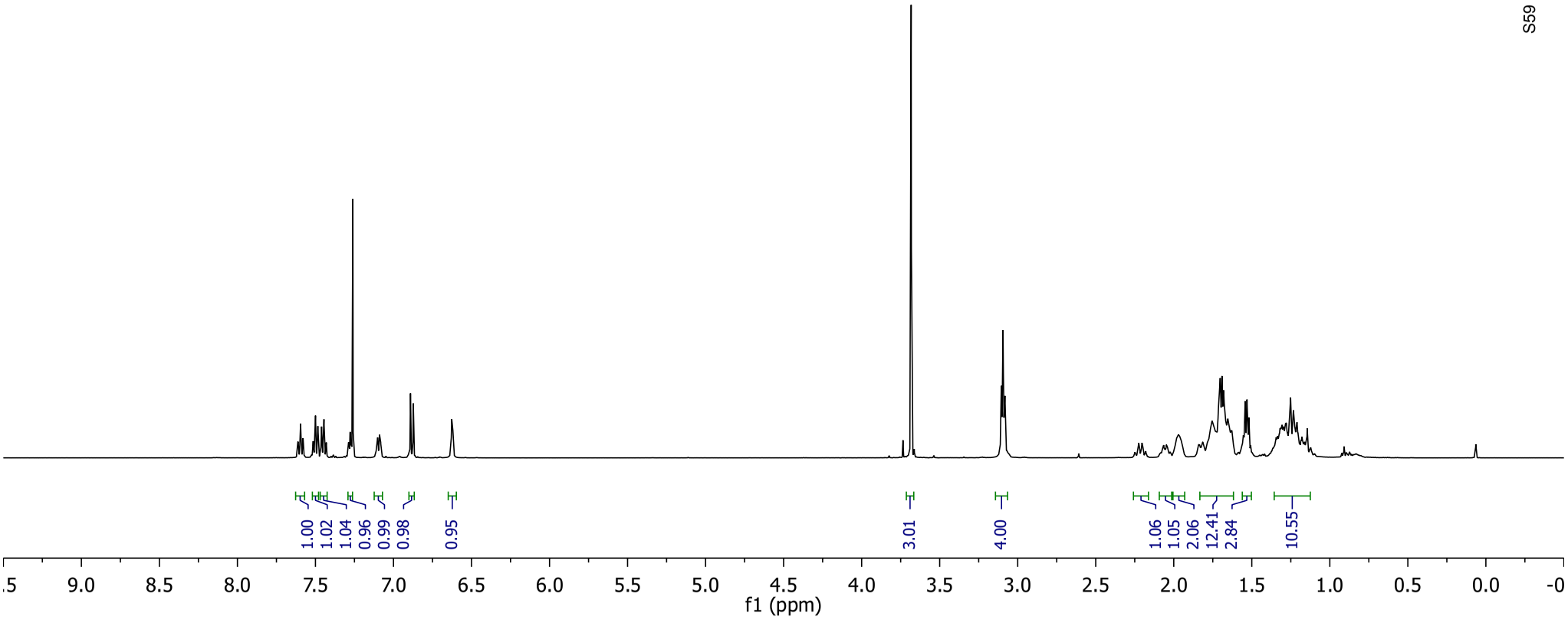
L5



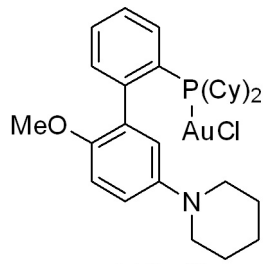
Parameter	Value
Title	zhixun-3-L5AuCl-alkyne-2
Solvent	CDCl3
Spectrometer Frequency	499.86



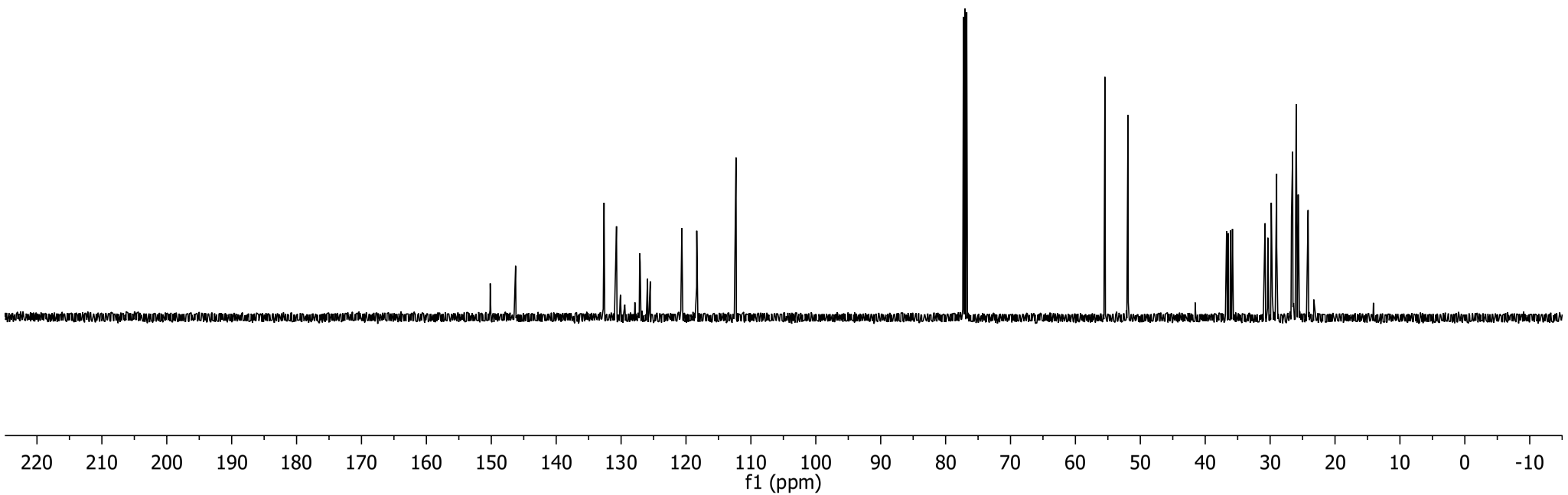
L5AuCl



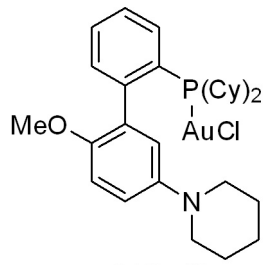
Parameter	Value
Title	zhixun-3-L5AuCl-alkyne-2-C13
Solvent	CDCl3
Spectrometer Frequency	125.70



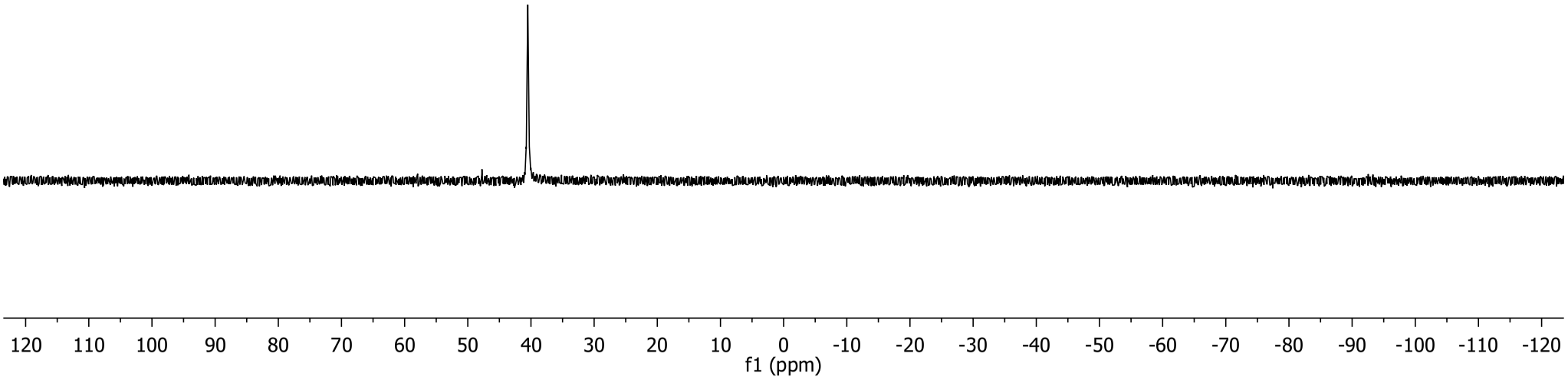
L5AuCl



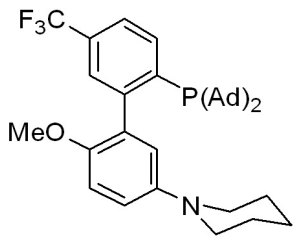
Parameter	Value
Title	zhixun-3-L5AuCl-alkyne-2-P31
Solvent	cdcl3
Spectrometer Frequency	161.90



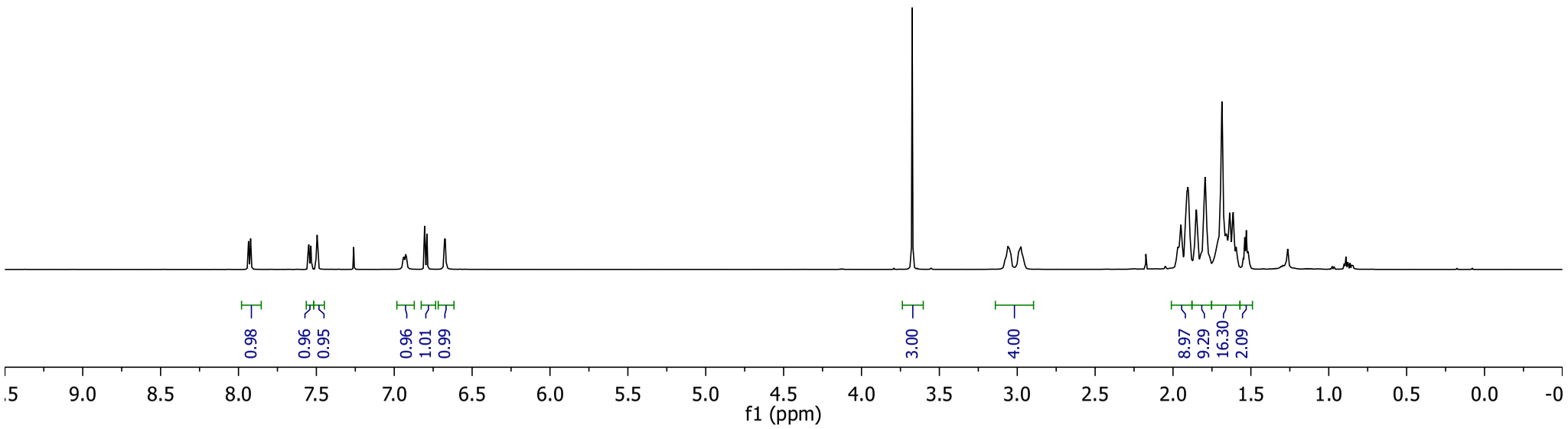
L5AuCl



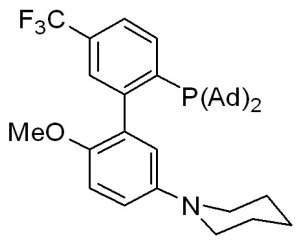
Parameter	Value
Title	wyz8-135-H1
Solvent	cdcl3
Spectrometer Frequency	599.64



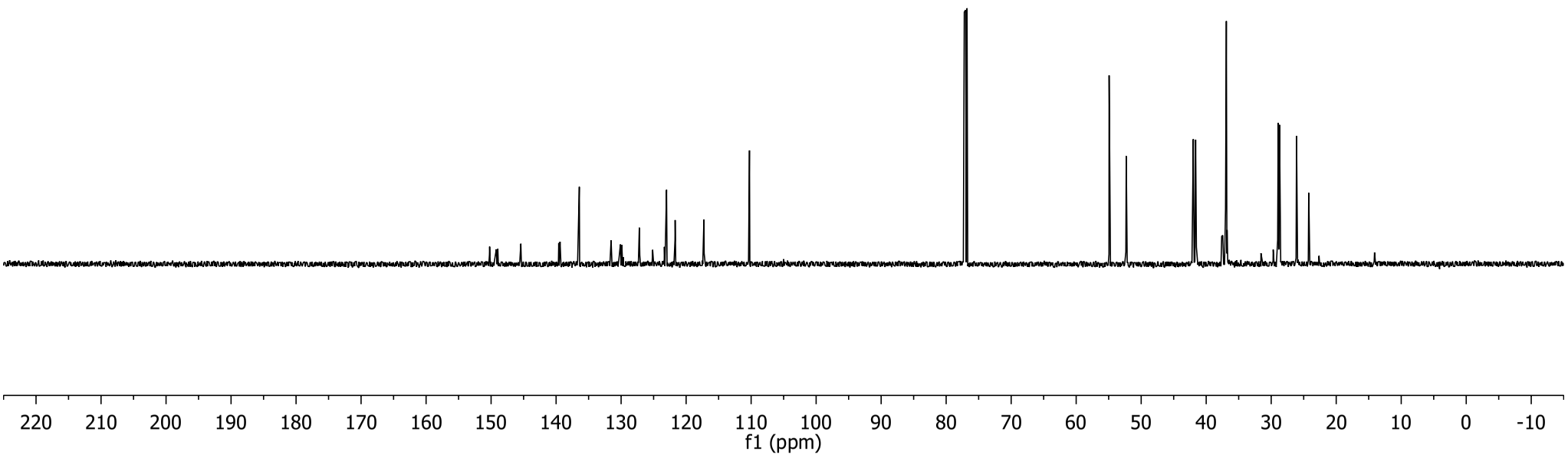
L6



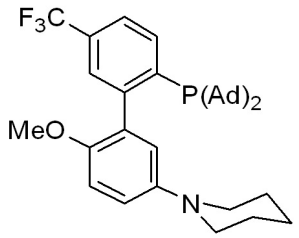
Parameter	Value
Title	wyz8-135-C13
Solvent	cdcl3
Spectrometer Frequency	150.79



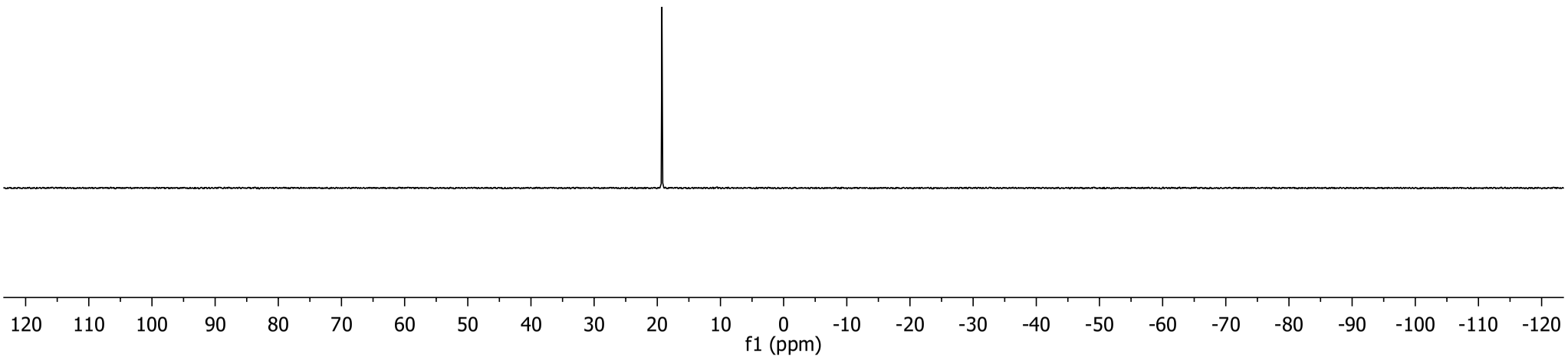
L6



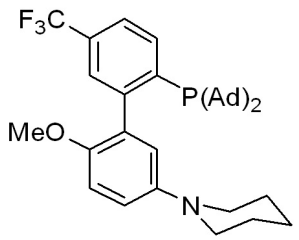
Parameter	Value
Title	wyz8-135-P31
Solvent	cd3cn
Spectrometer Frequency	161.90



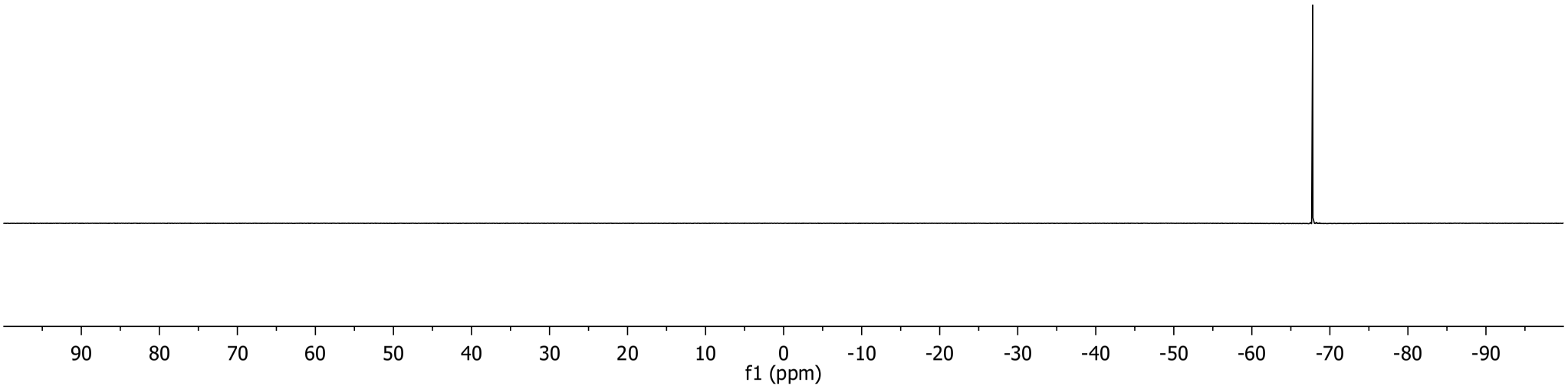
L6



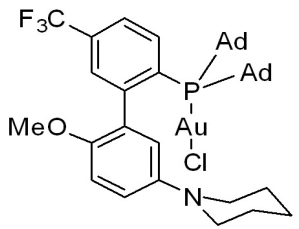
Parameter	Value
Title	wyz8-135-F19
Solvent	cd3cn
Spectrometer Frequency	376.33



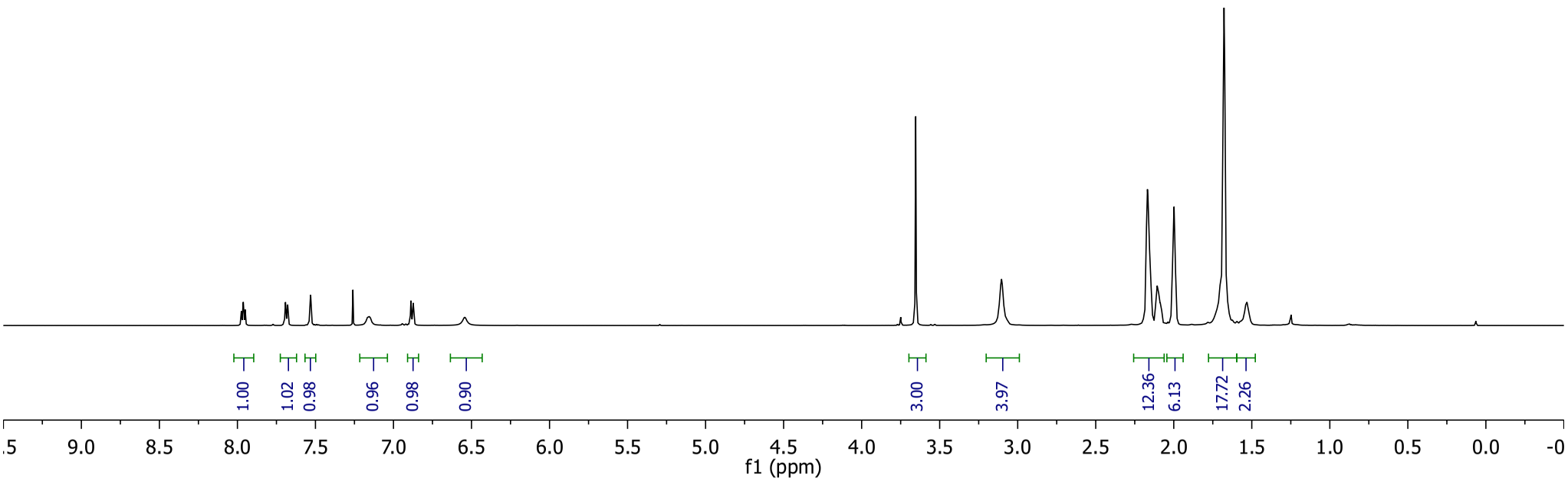
L6



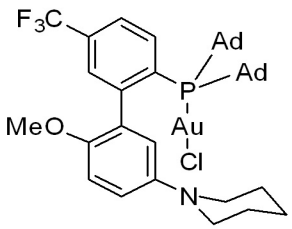
Parameter	Value
Title	wyz8-138-H1
Solvent	cdcl3
Spectrometer Frequency	599.64



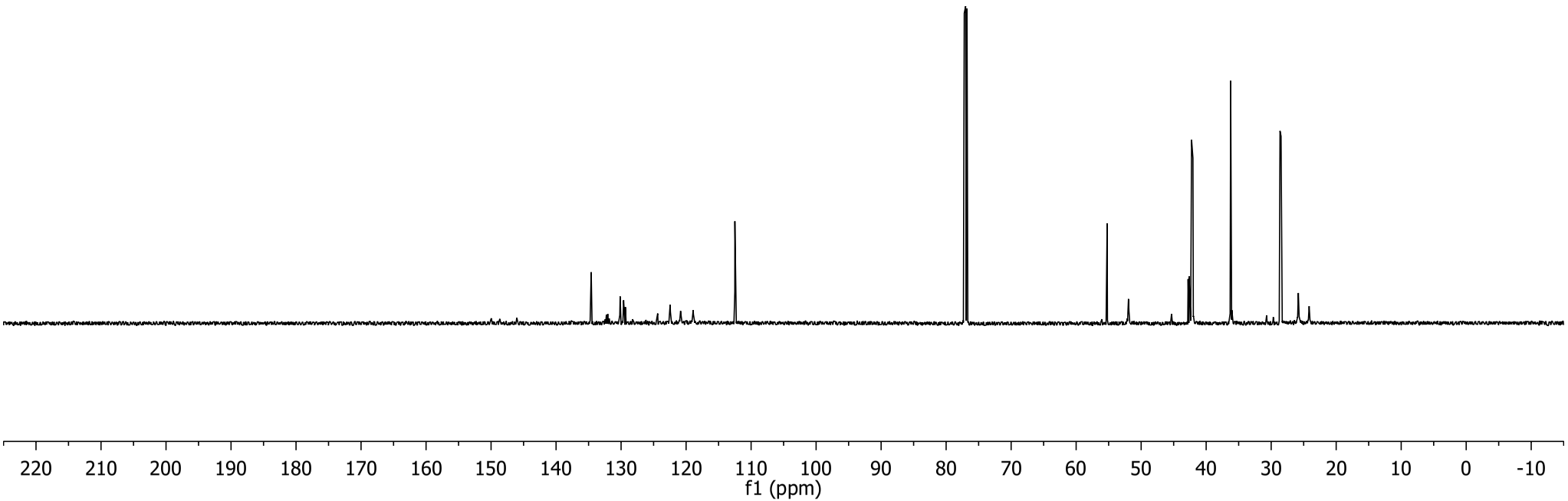
L6AuCl



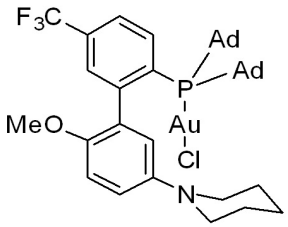
Parameter	Value
Title	wyz8-138-C13
Solvent	cdcl3
Spectrometer Frequency	150.79



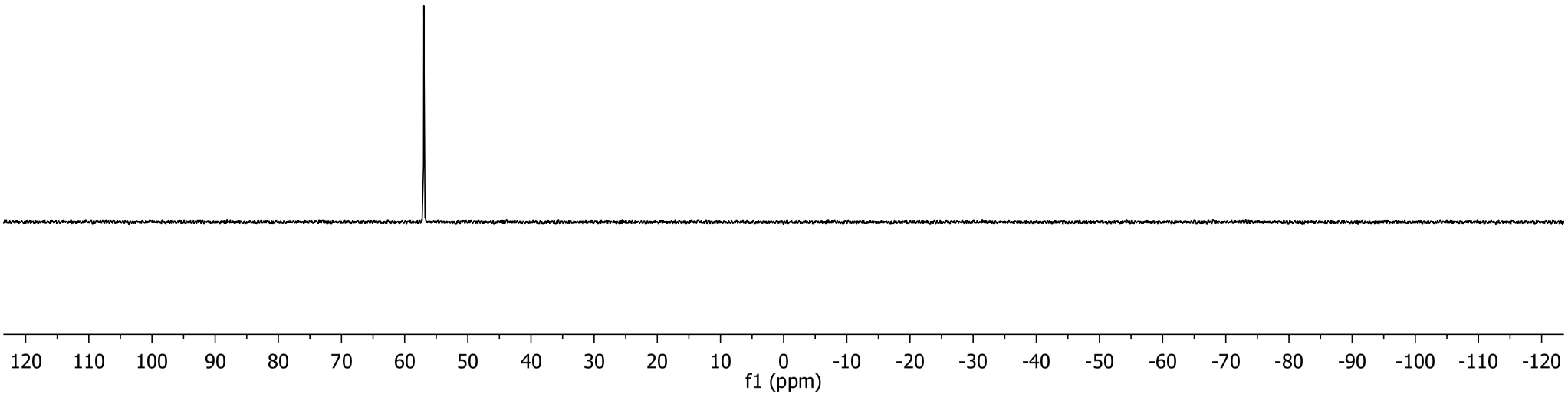
L6AuCl



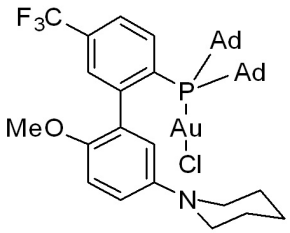
Parameter	Value
Title	wyz8-138-P31
Solvent	cd3cn
Spectrometer Frequency	161.90



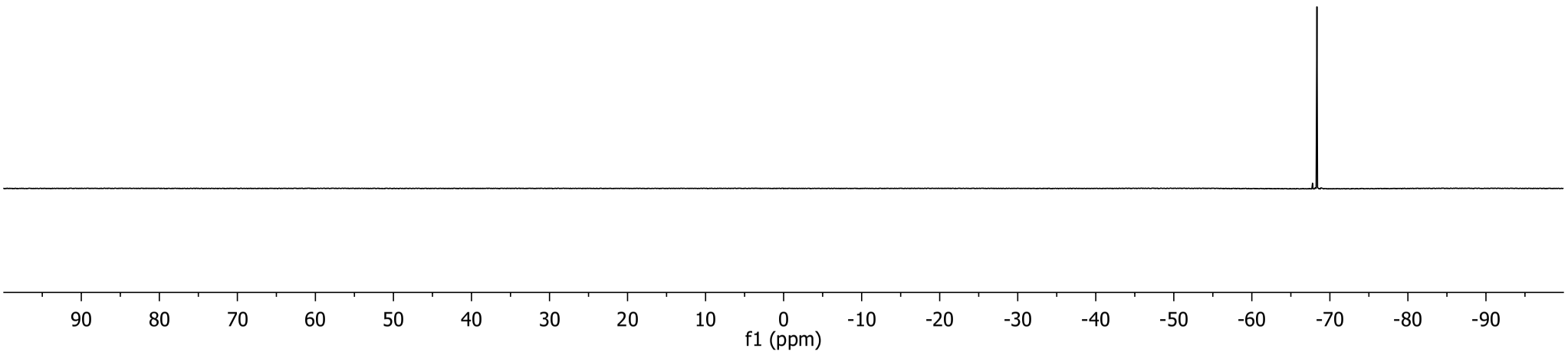
L6AuCl



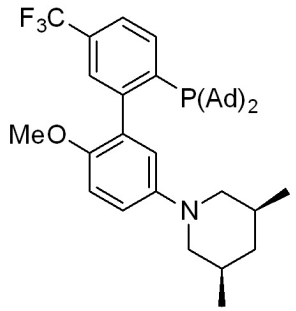
Parameter	Value
Title	wyz8-138-F19
Solvent	cd3cn
Spectrometer Frequency	376.33



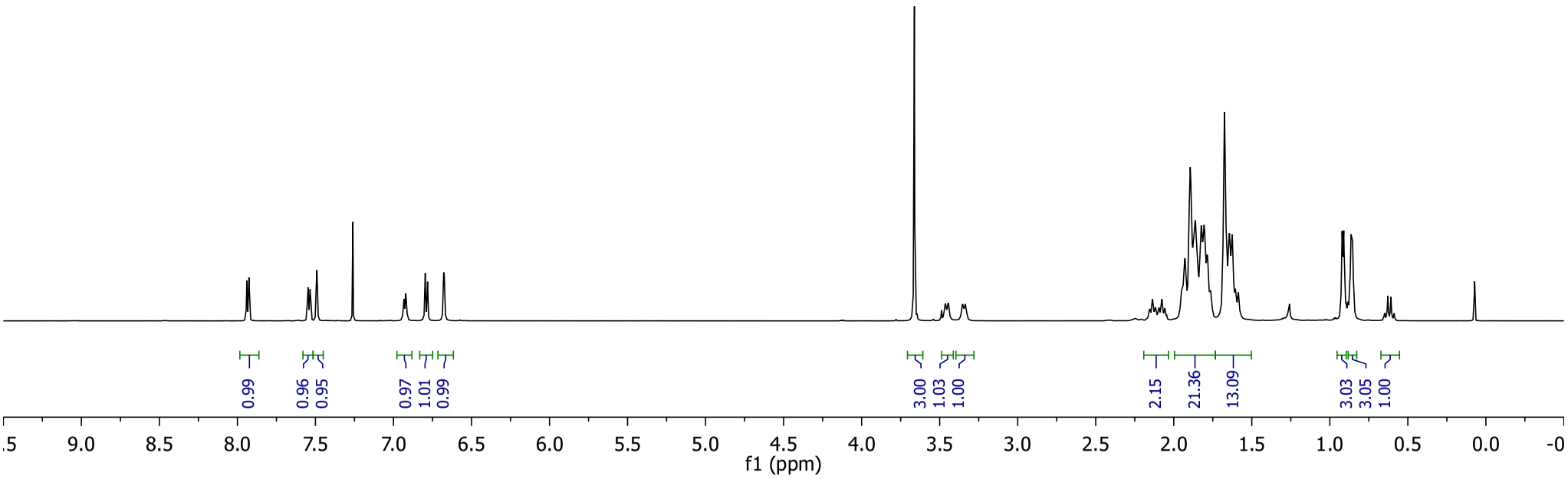
L6AuCl



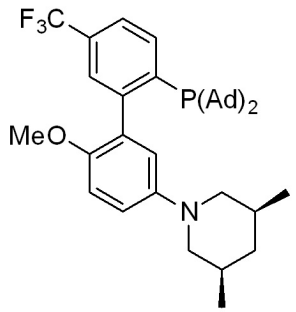
Parameter	Value
Title	wyz8-142-H1
Solvent	cdcl3
Relaxation Delay	4.8000
Spectrometer Frequency	599.64



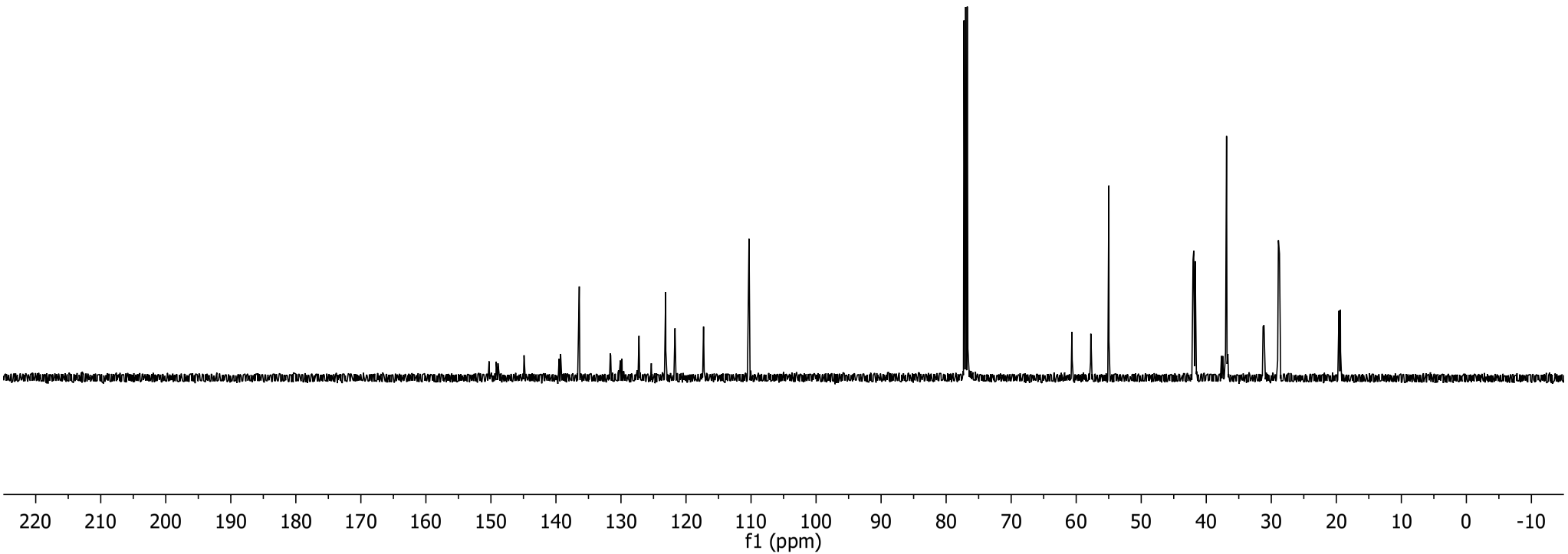
L7



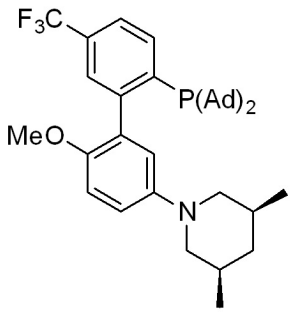
Parameter	Value
Title	wyz8-142-C13
Solvent	CDCl3
Relaxation Delay	1.0000
Spectrometer Frequency	125.70



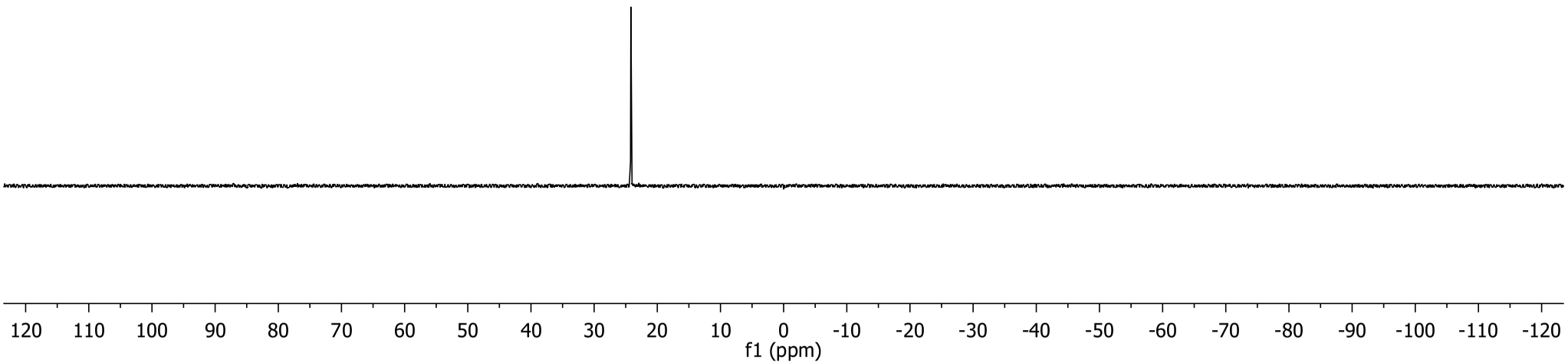
L7



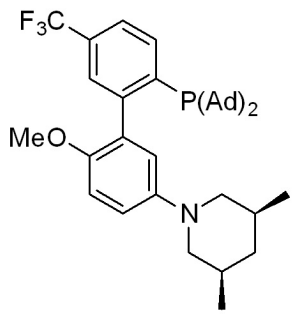
Parameter	Value
Title	wyz8-142-P31
Solvent	cdcl3
Spectrometer Frequency	161.90



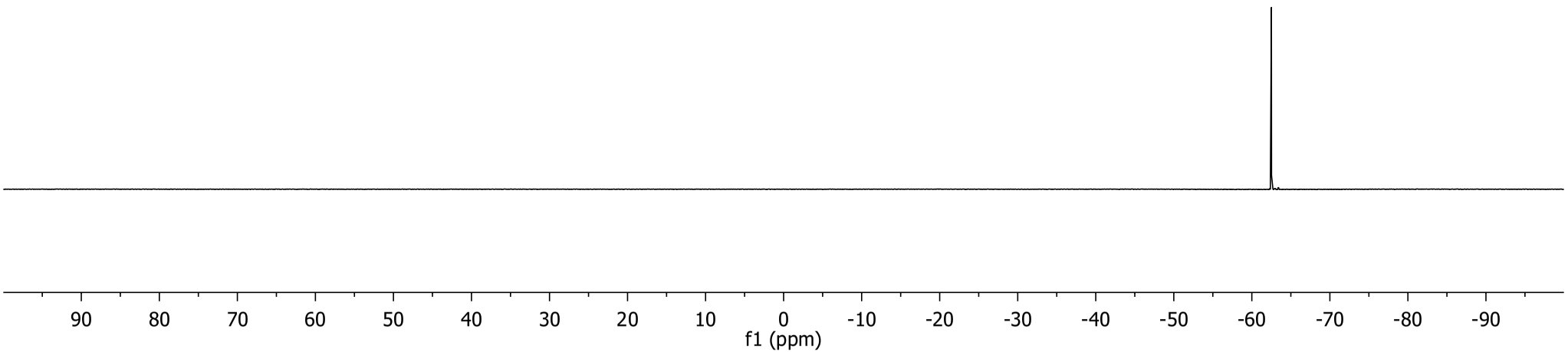
L7



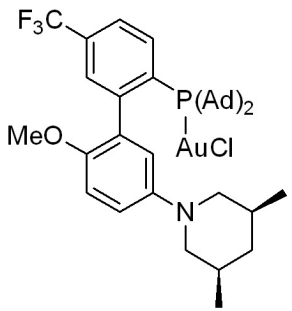
Parameter	Value
Title	wyz8-142-F19
Solvent	cdcl3
Spectrometer Frequency	376.33



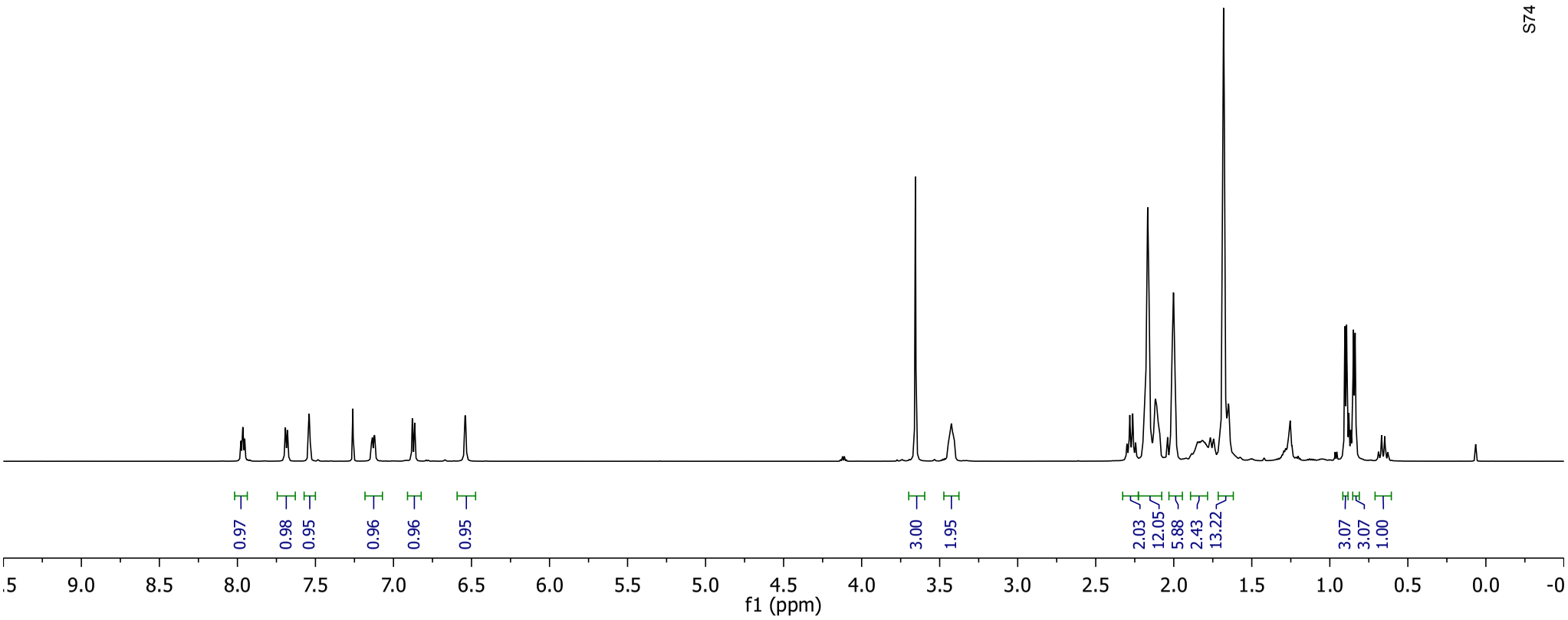
L7



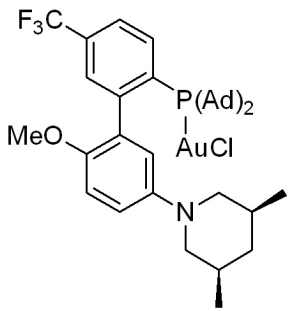
Parameter	Value
Title	wyz8-143-pro-H1
Solvent	cdcl3
Spectrometer Frequency	599.63



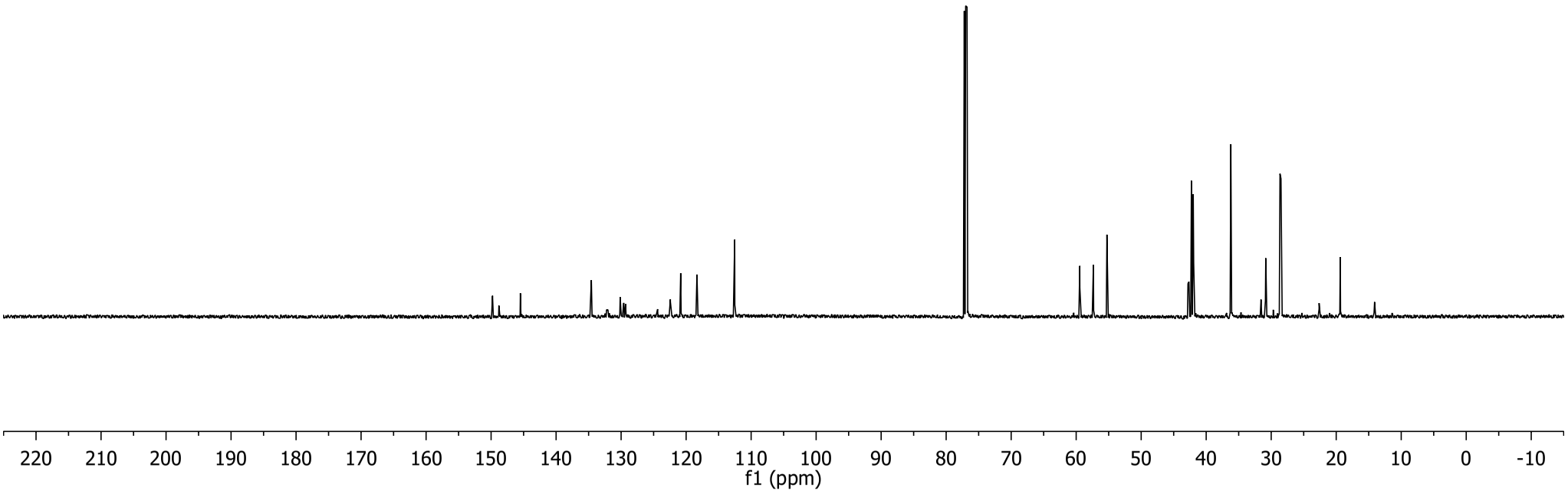
L7AuCl



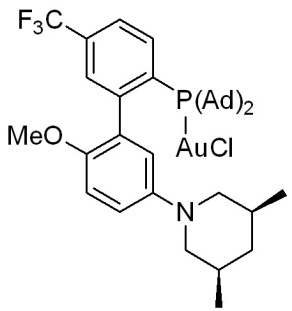
Parameter	Value
Title	wyz8-143-pro-C13
Solvent	cdcl3
Spectrometer Frequency	150.79



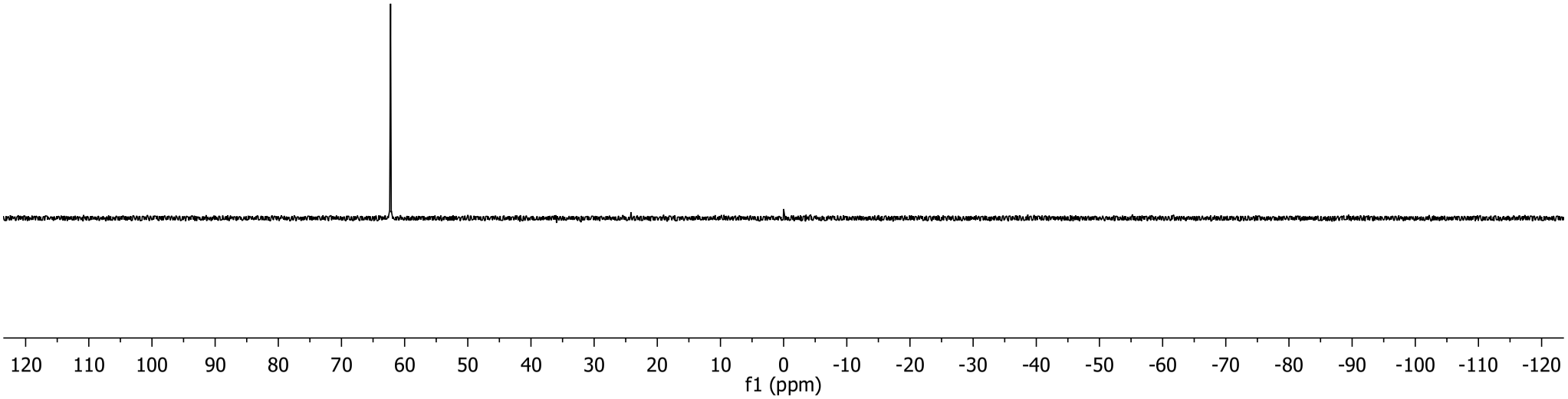
L7AuCl



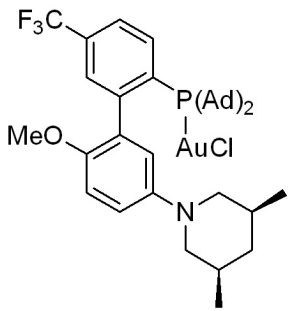
Parameter	Value
Title	wyz8-143-P31
Solvent	cdcl3
Spectrometer Frequency	161.90



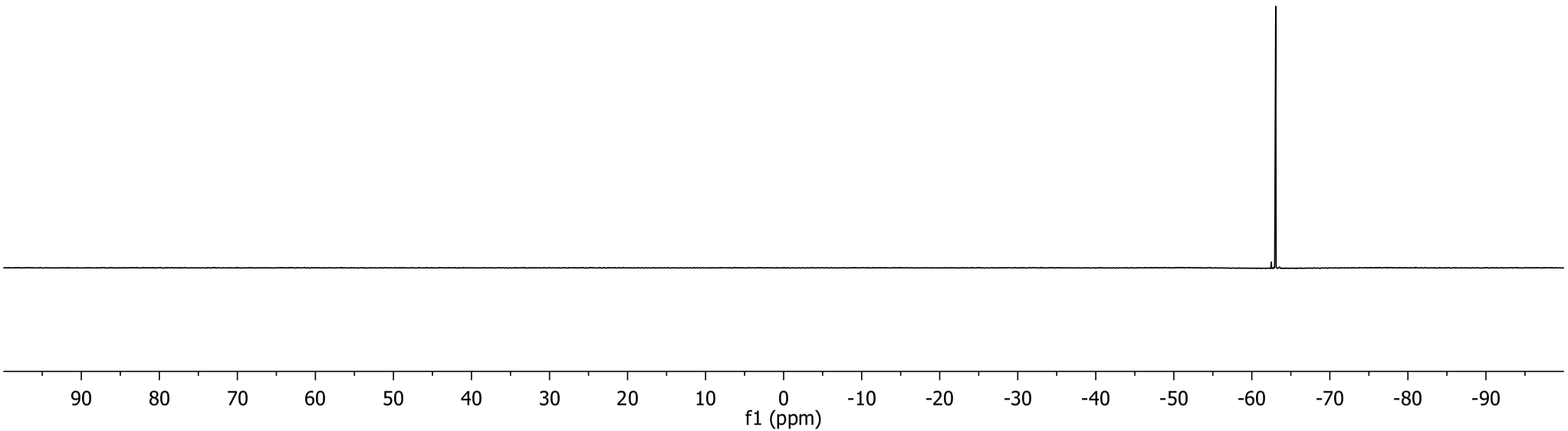
L7AuCl



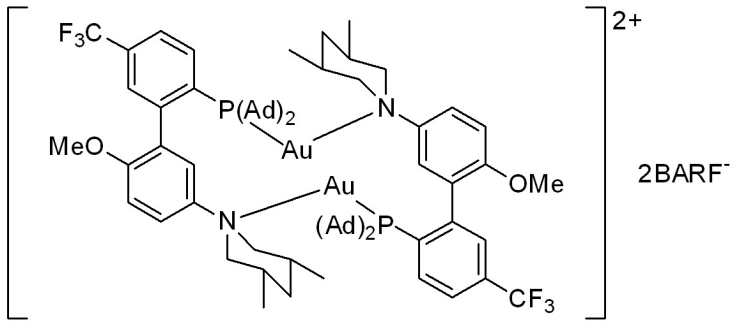
Parameter	Value
Title	wyz8-143-F19
Solvent	cdcl3
Spectrometer Frequency	376.33



L7AuCl

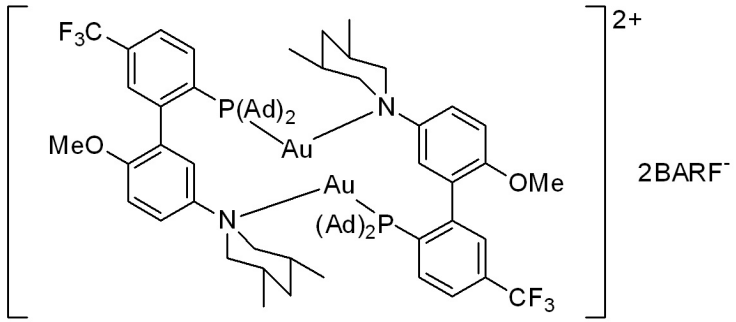


Parameter	Value
Title	zhixun-3-088A-1-D2-DCM
Solvent	"cd2cl2"
Relaxation Delay	4.8000
Spectrometer Frequency	499.86

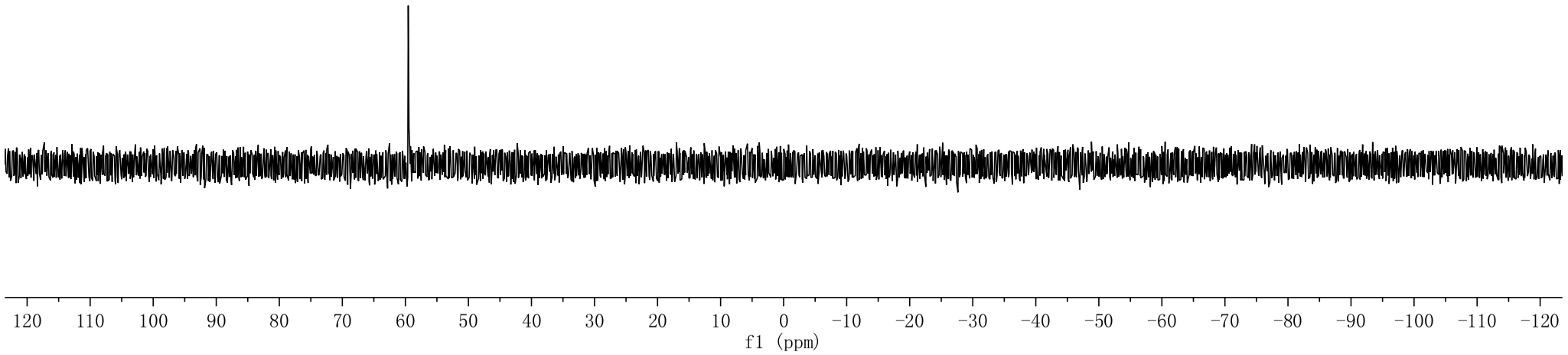


$[L7Au)_2]BARF_2$

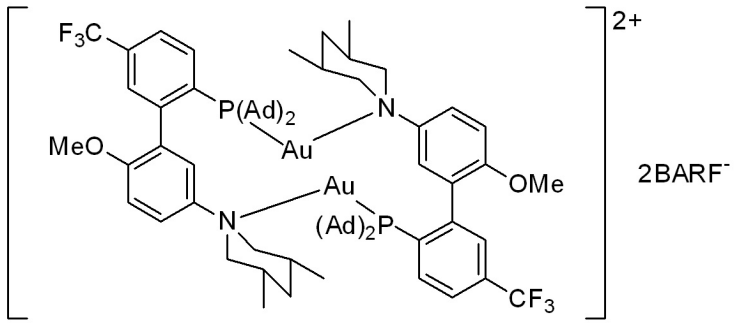
Parameter	Value
Title	zhixun-3-088A-P31-1
Solvent	"cd2cl2"
Relaxation Delay	4.0000
Spectrometer Frequency	161.90



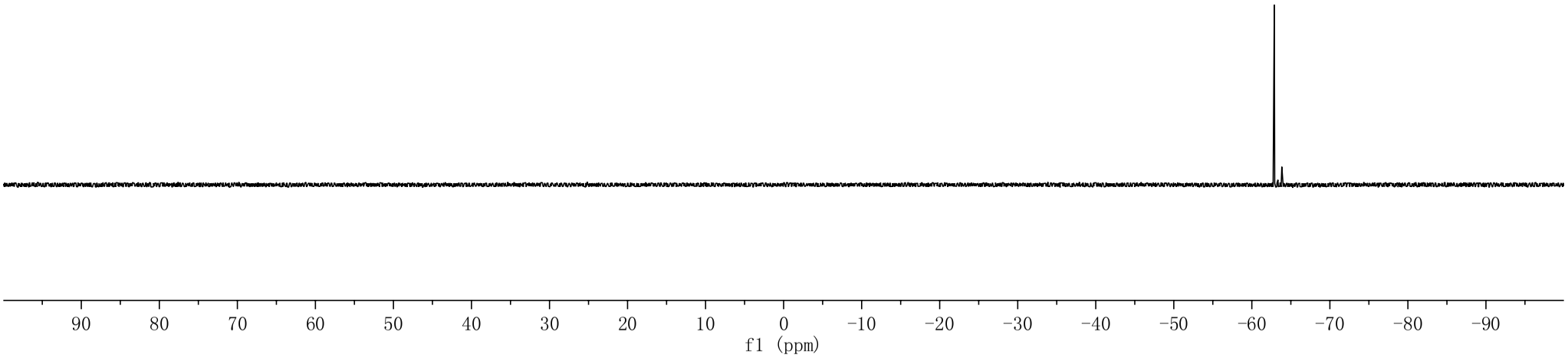
$[L7Au)_2]BARF_2$



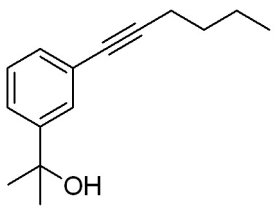
Parameter	Value
Title	zhixun-3-088A-F19-1
Solvent	"cd2cl2"
Relaxation Delay	3.0000
Spectrometer Frequency	376.33



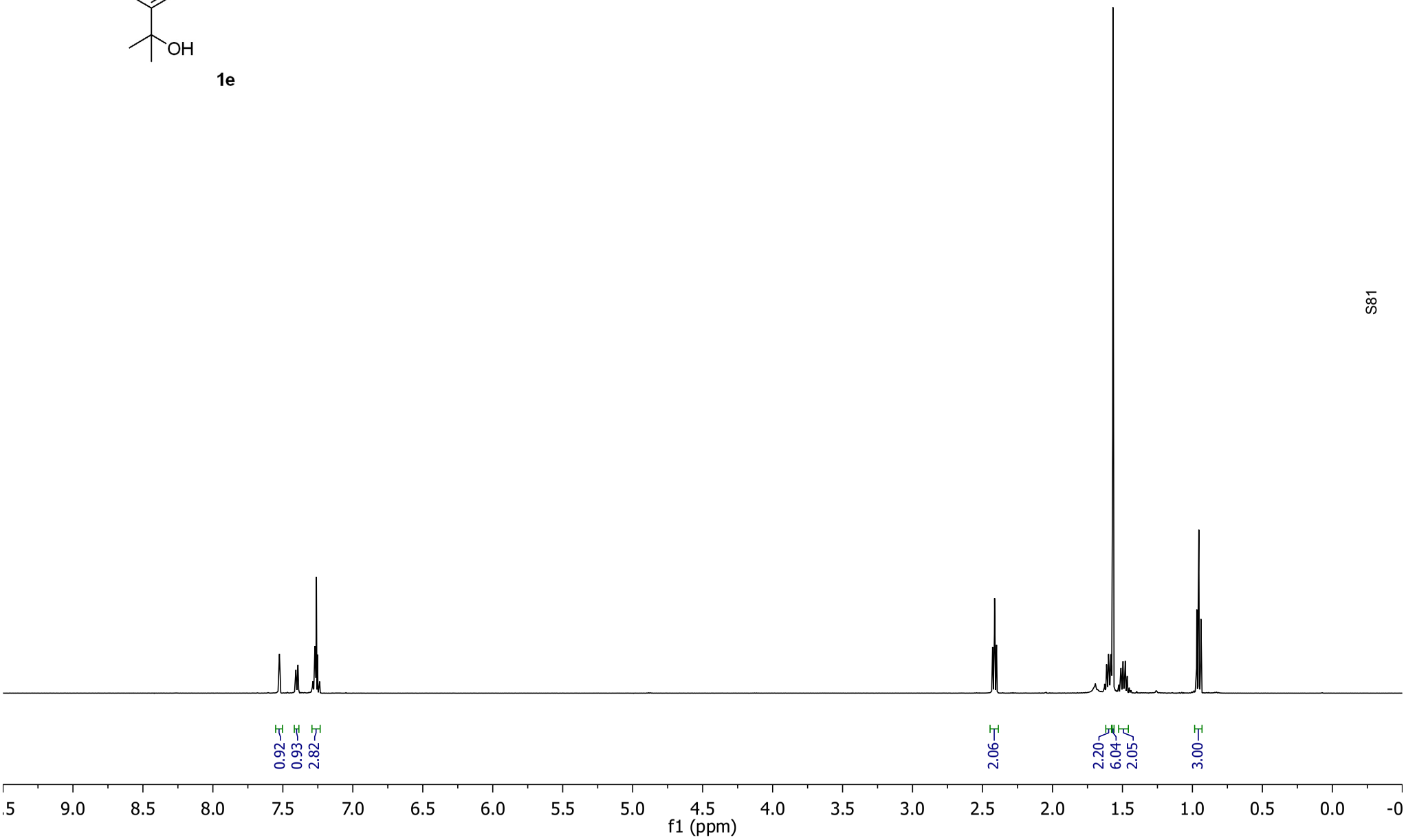
[L7Au)$_2$]BARF$_2$



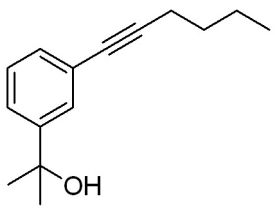
Parameter	Value
Title	zhixun-3-083B-check
Solvent	"CDCl3"
Spectrometer Frequency	499.86



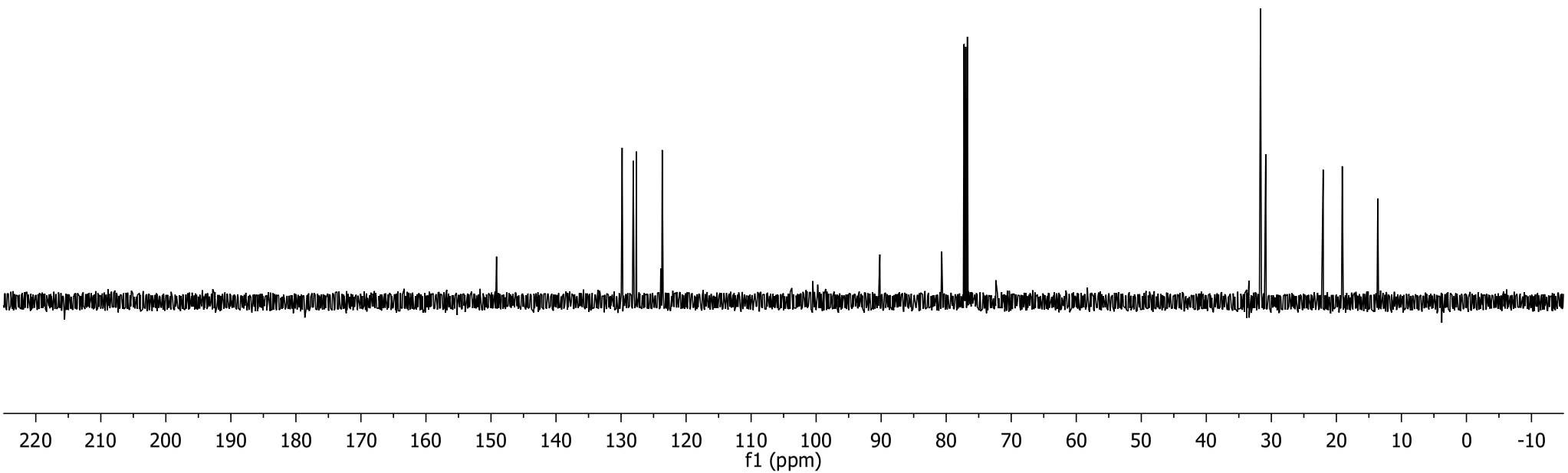
1e



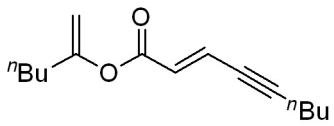
Parameter	Value
Title	zhixun-3-083B-C13check
Solvent	"CDCl3"
Spectrometer Frequency	125.70



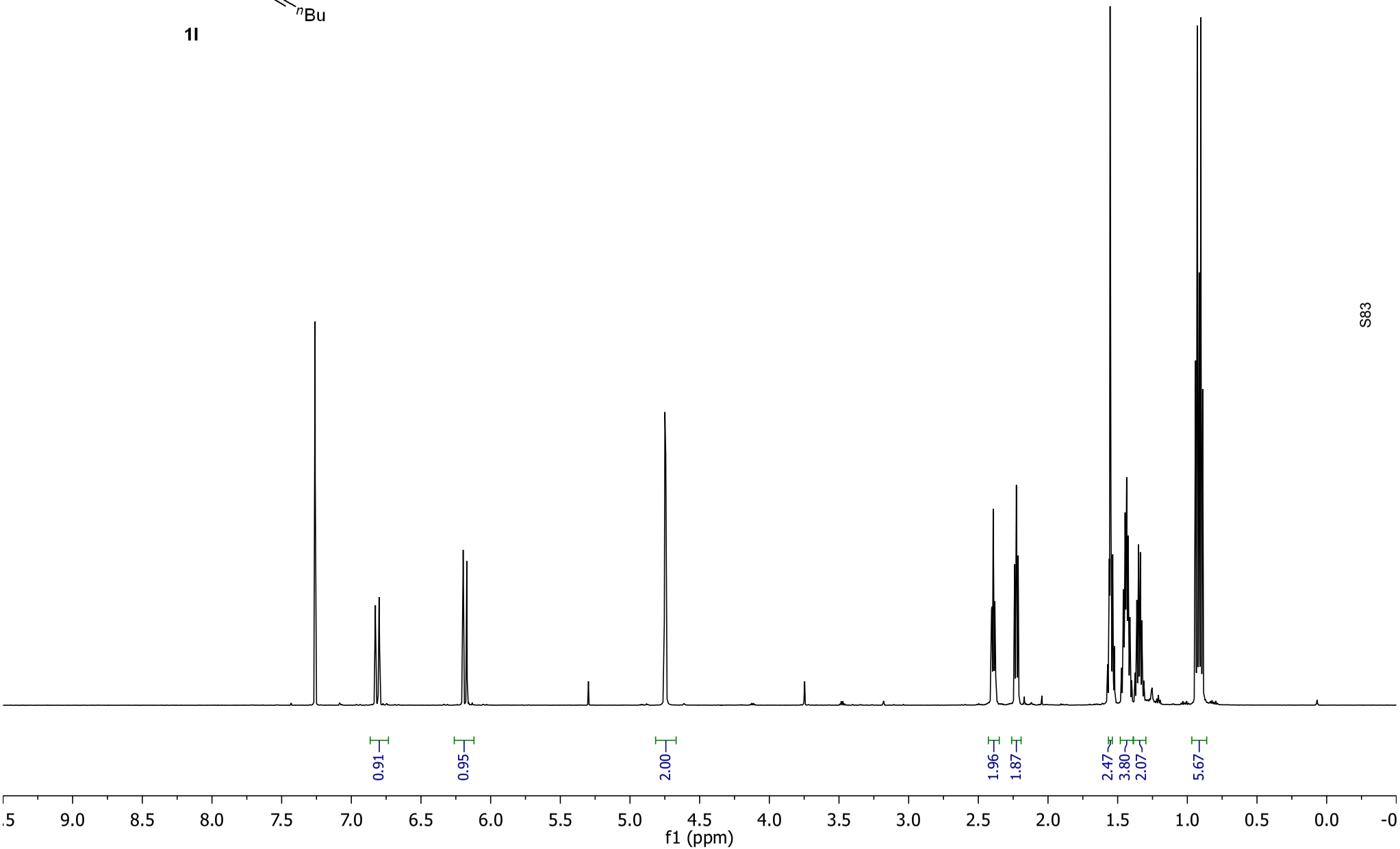
1e



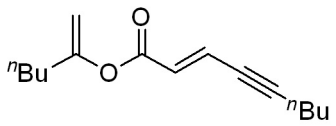
Parameter	Value
Title	wyz8-249-2-H1
Solvent	"cdcl3"
Spectrometer Frequency	599.63



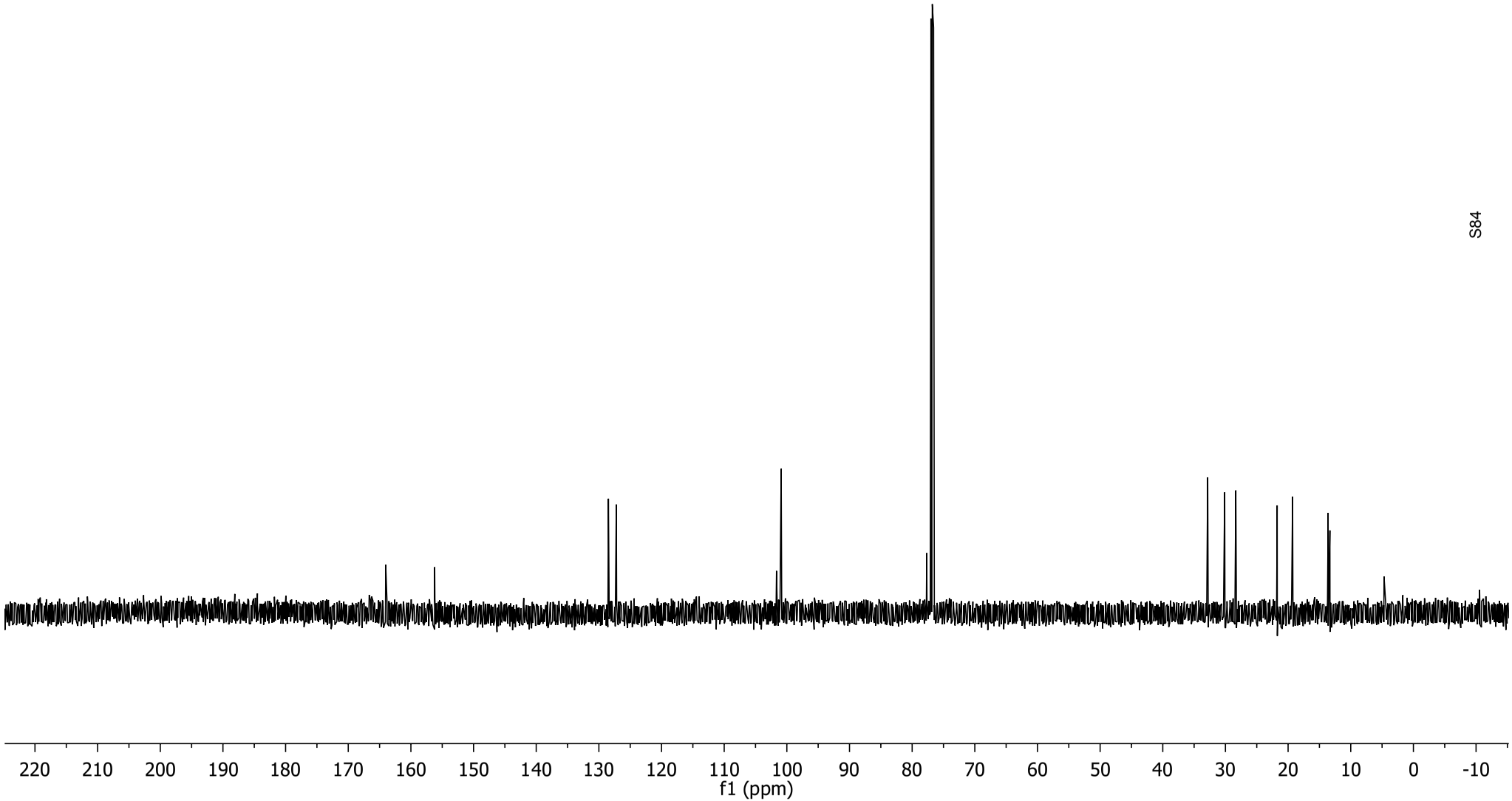
1l



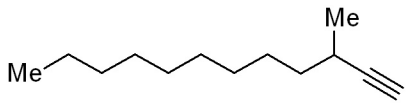
Parameter	Value
Title	wyz8-249-2-pro-c13
Solvent	"cdcl3"
Spectrometer Frequency	150.79



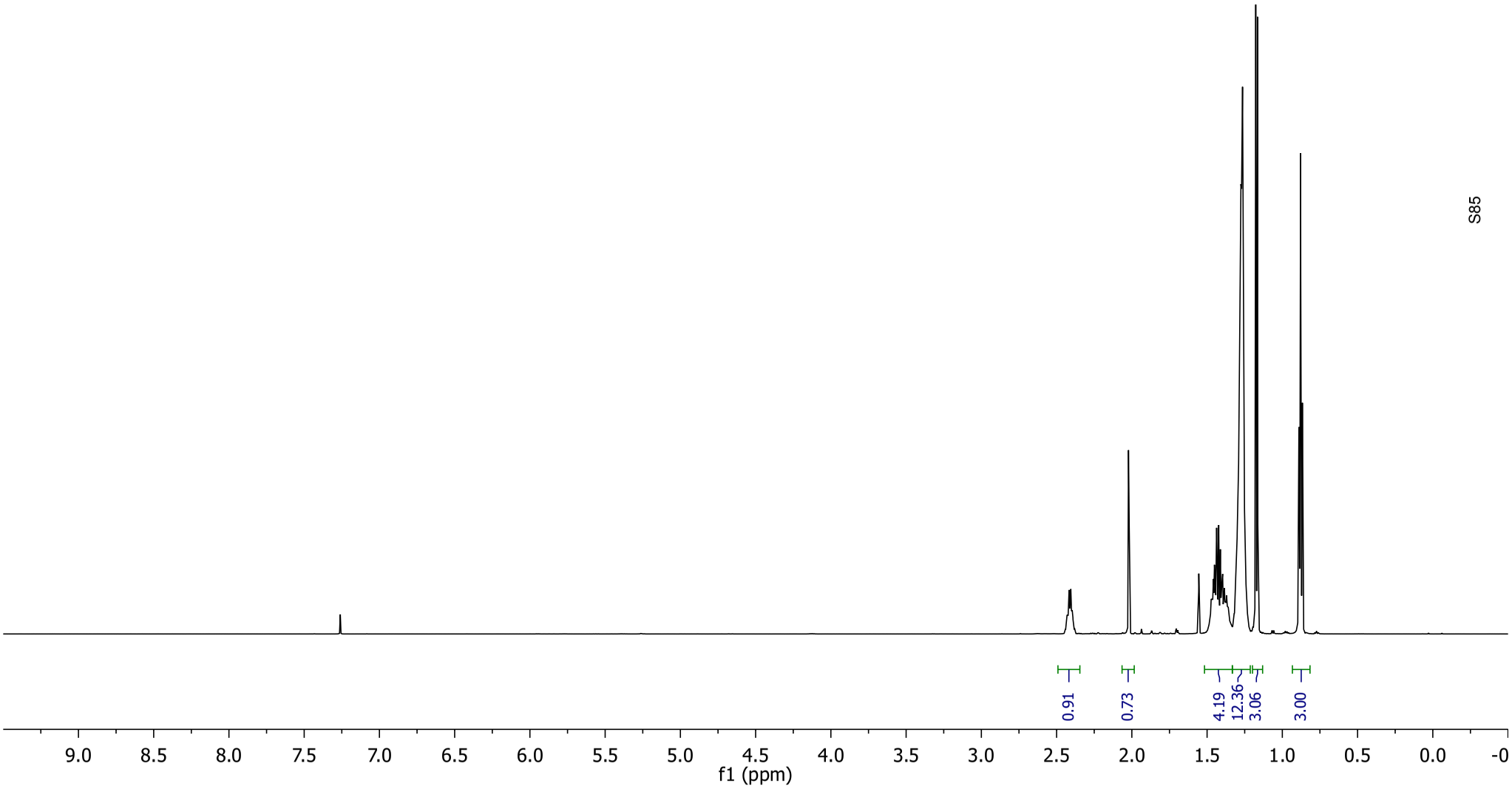
1l



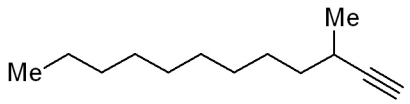
Parameter	Value
Title	wyz8-209-2-H1
Solvent	"cdcl3"
Relaxation Delay	4.8000
Spectrometer Frequency	599.64



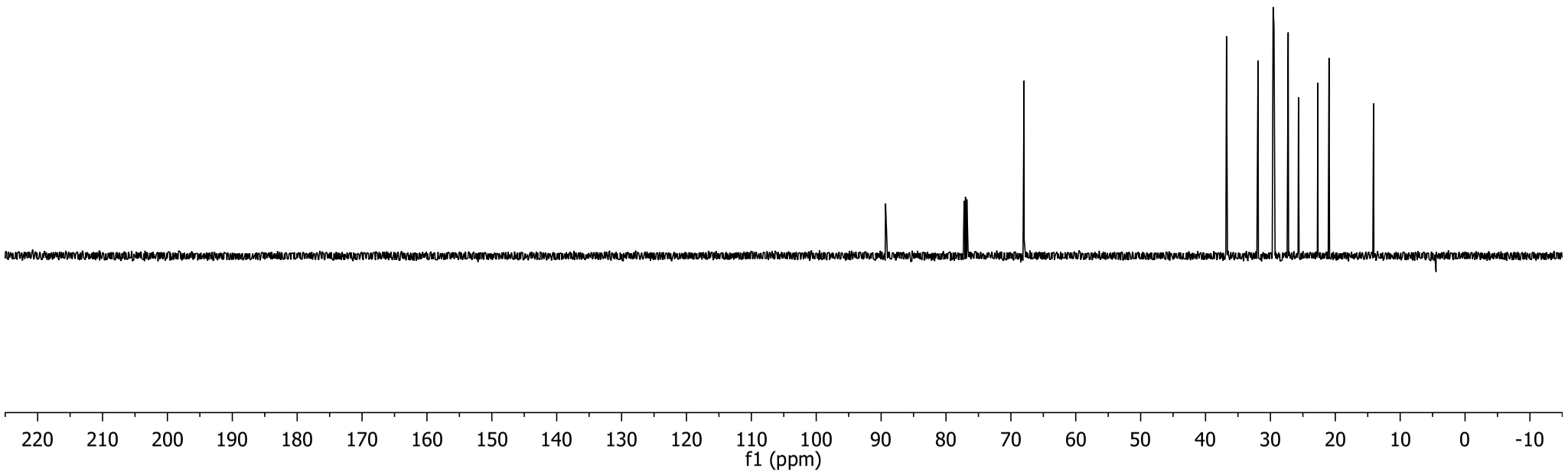
1q



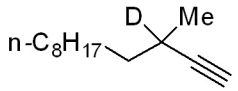
Parameter	Value
Title	wyz8-209-2-C13
Solvent	"cdcl3"
Spectrometer Frequency	150.79



1q

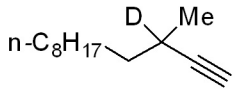


Parameter	Value
Title	wyz9-diene-1q-D-60s
Solvent	"cdcl3"
Relaxation Delay	60.0000
Spectrometer Frequency	599.64

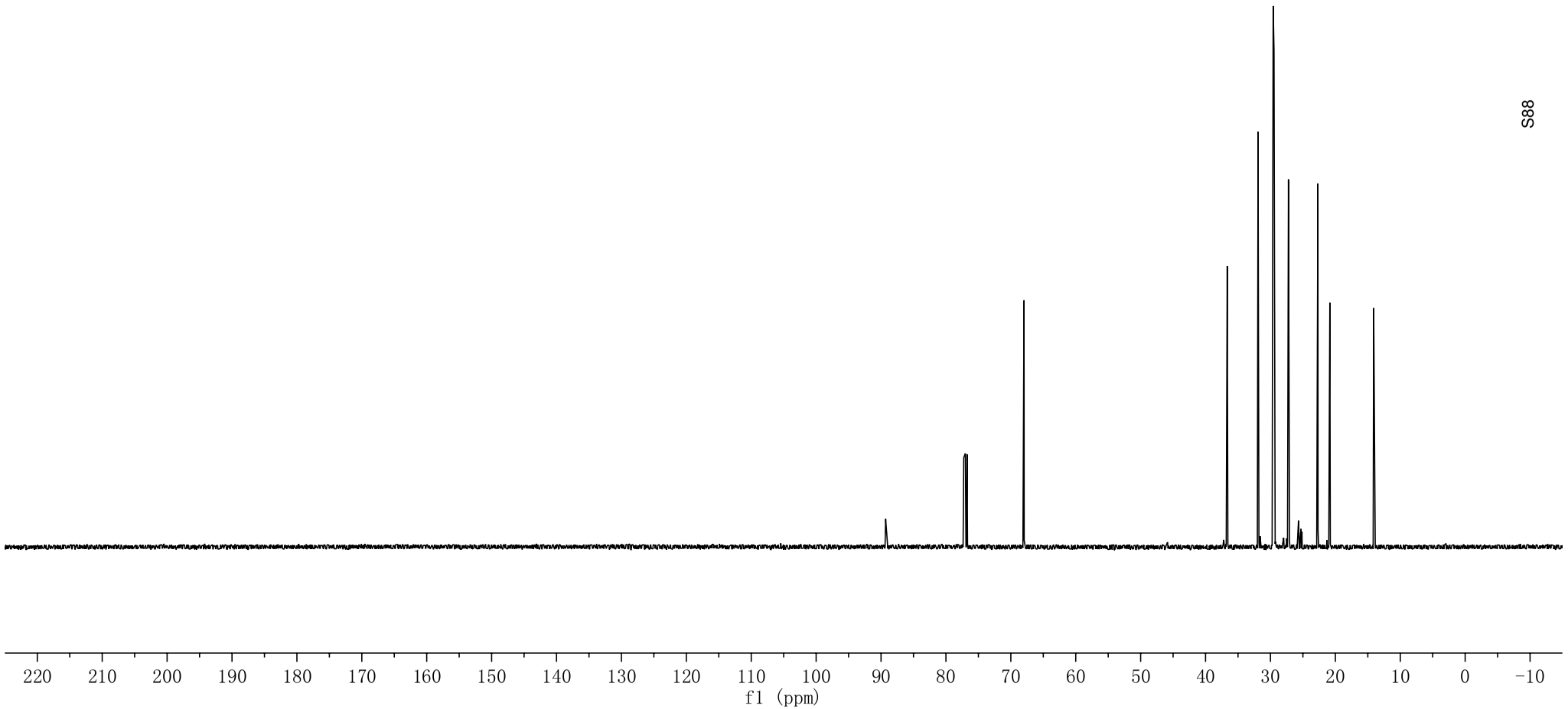


1q-D

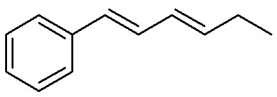
Parameter	Value
Title	wyz8-217-pro-c13-75
Solvent	"CDCl3"
Relaxation Delay	1.0000
Spectrometer Frequency	125.70



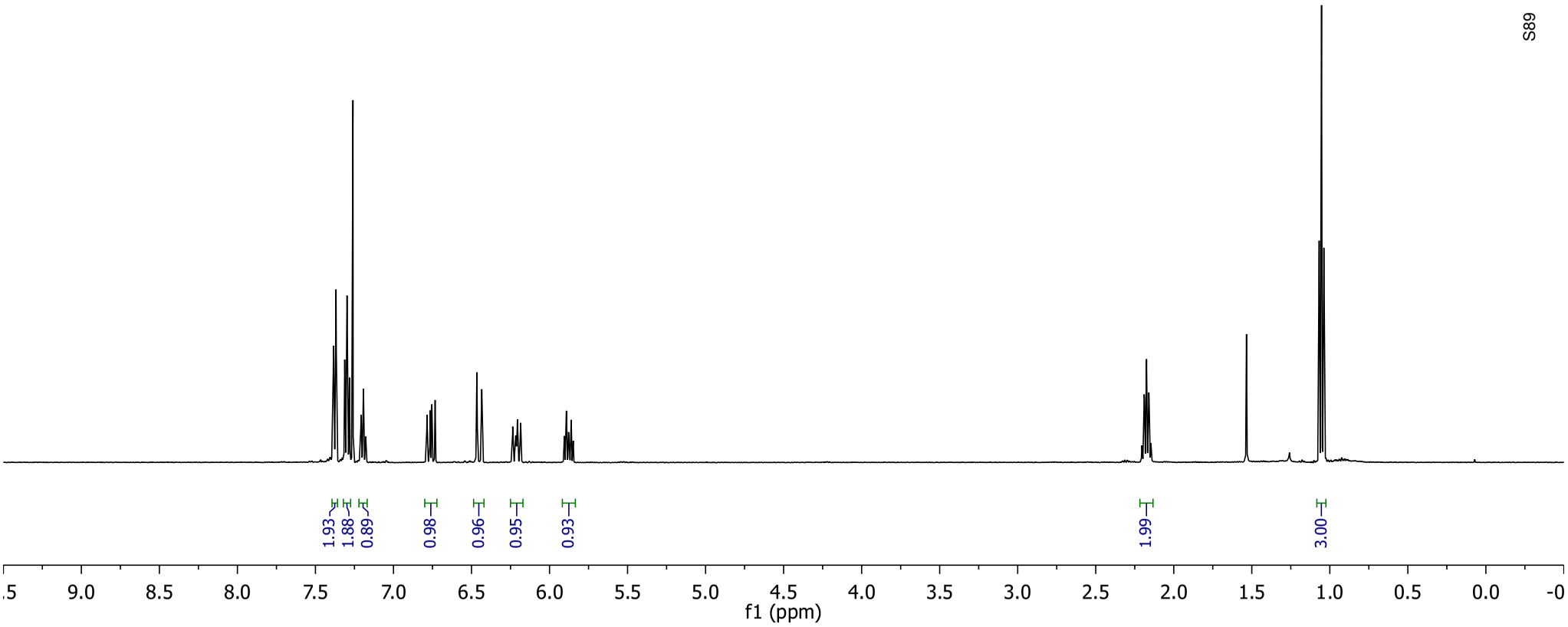
1q-D



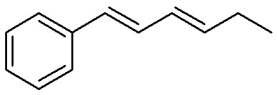
Parameter	Value
Title	zhixun-2-277B
Solvent	CDCl3
Spectrometer Frequency	499.86



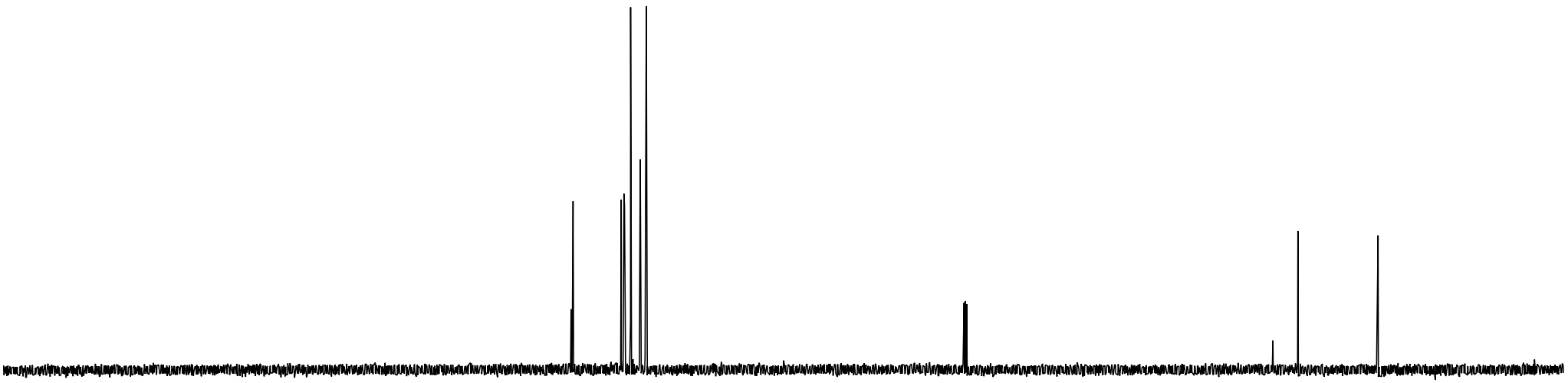
2a

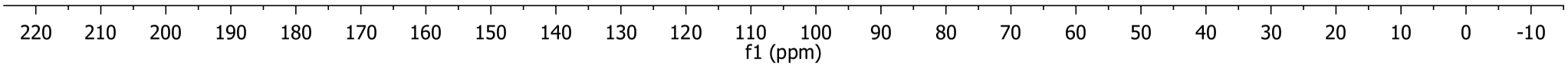


Parameter	Value
Title	zhixun-2-267-Prod-C13
Solvent	cdcl3
Spectrometer Frequency	150.79

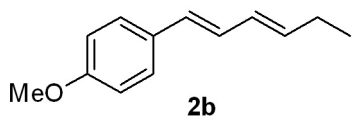


2a

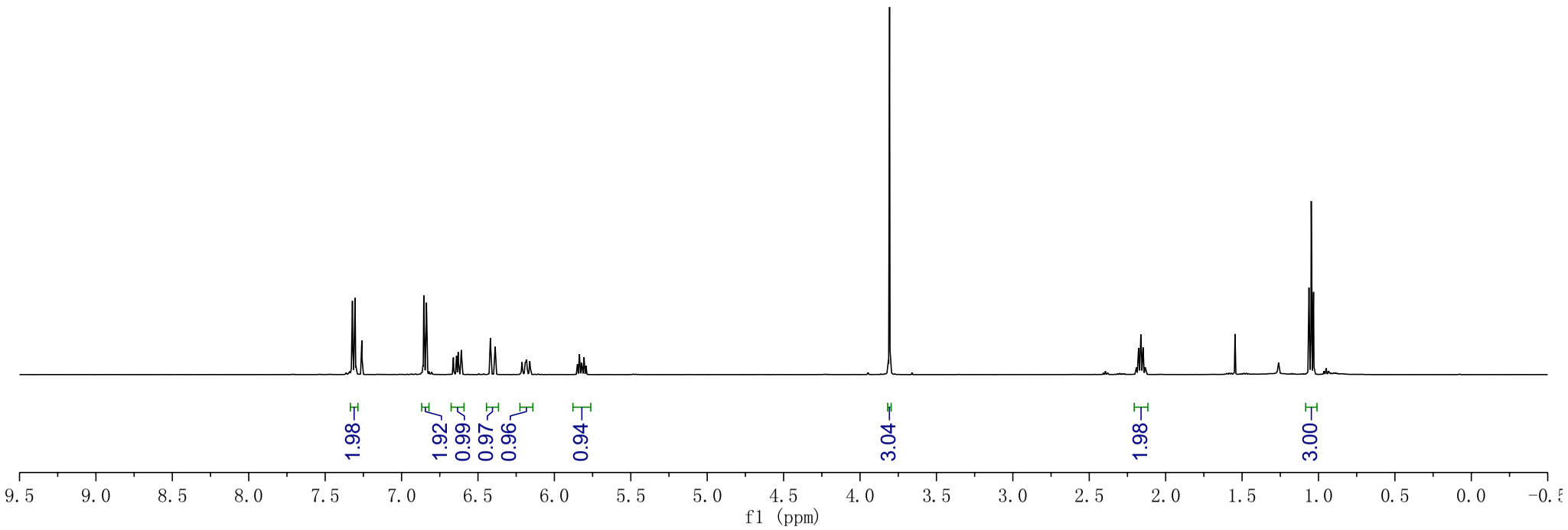




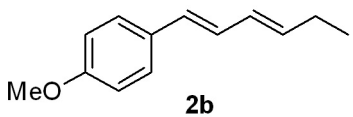
Parameter	Value
Title	zhixun-2-281E-H1
Solvent	CDCl3
Spectrometer Frequency	499.86



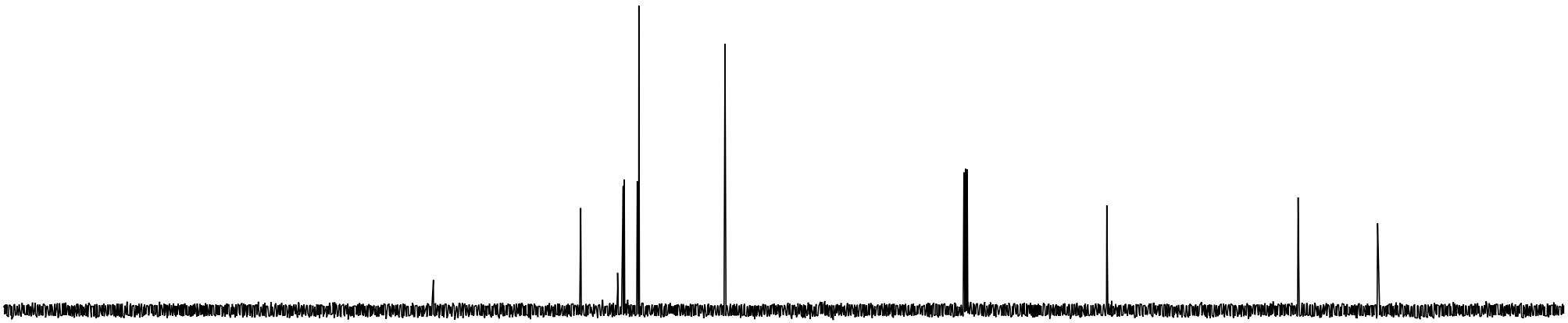
2b

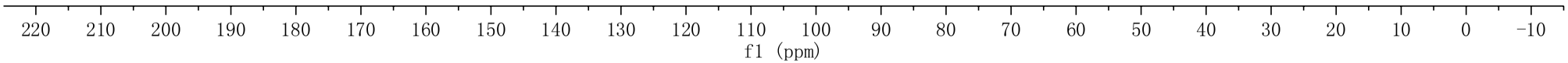


Parameter	Value
Title	zhixun-2-281E-C13
Solvent	CDCl3
Spectrometer Frequency	125.70

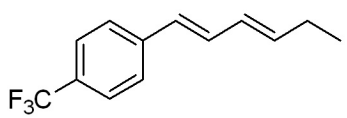


2b

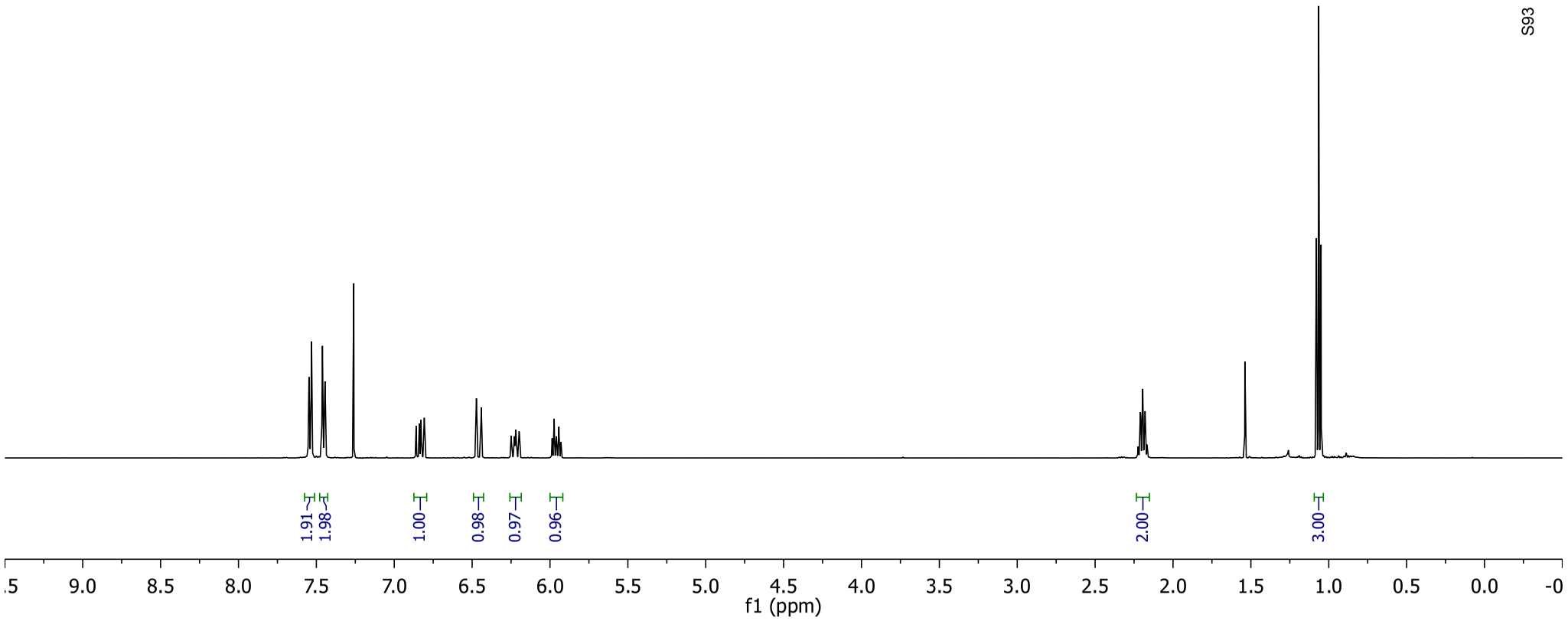




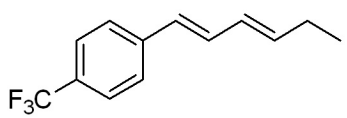
Parameter	Value
Title	zhixun-3-091B
Solvent	"CDCl3"
Spectrometer Frequency	499.86



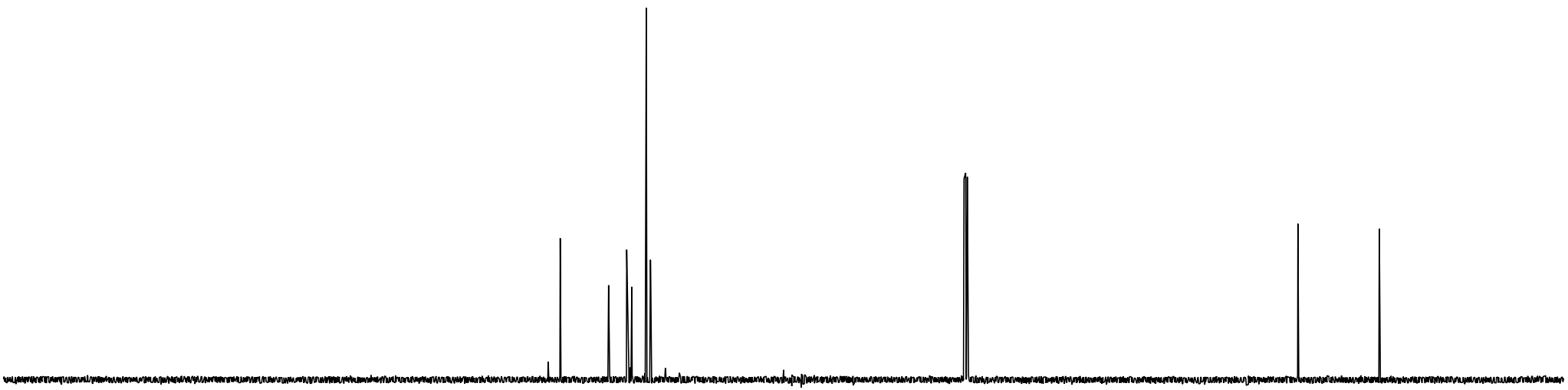
2c

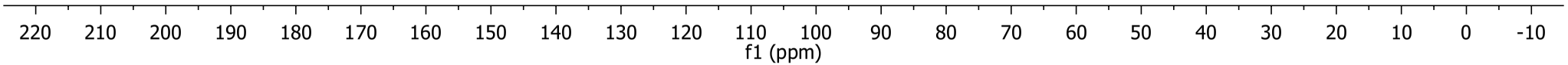


Parameter	Value
Title	zhixun-3-091B-C13
Solvent	"CDCl3"
Spectrometer Frequency	125.70

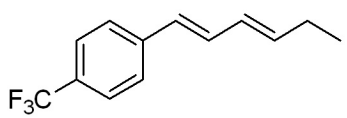


2c

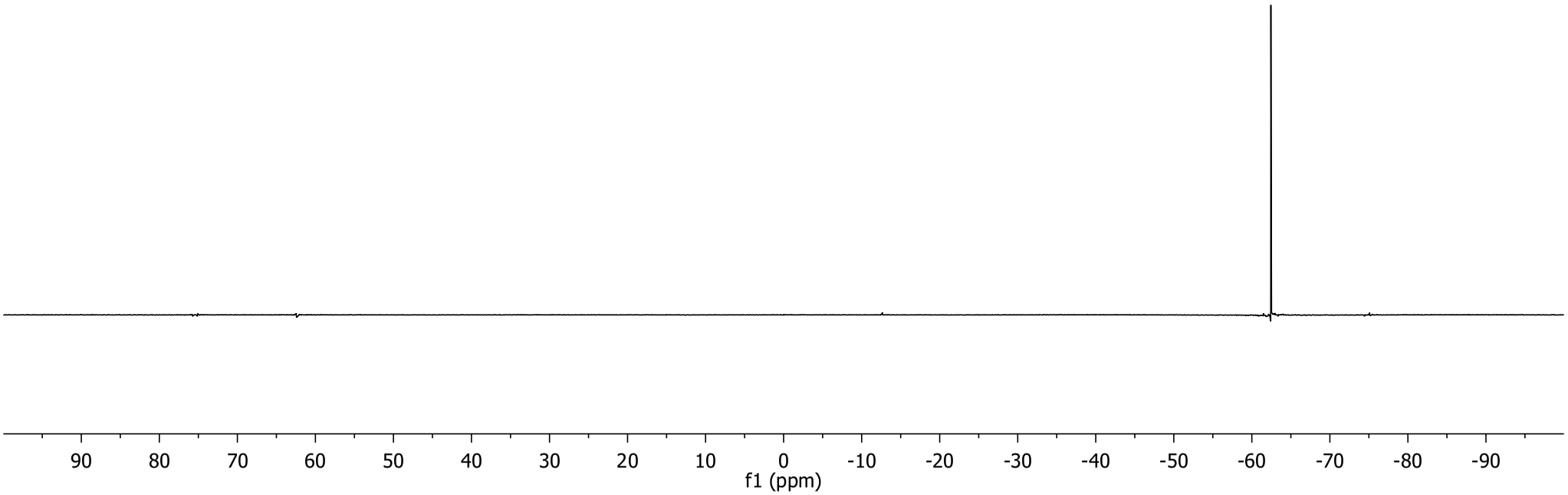




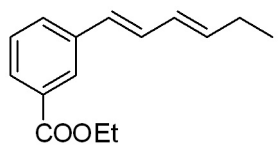
Parameter	Value
Title	zhixun-3-091B-F19
Solvent	"cdcl3"
Spectrometer Frequency	376.33



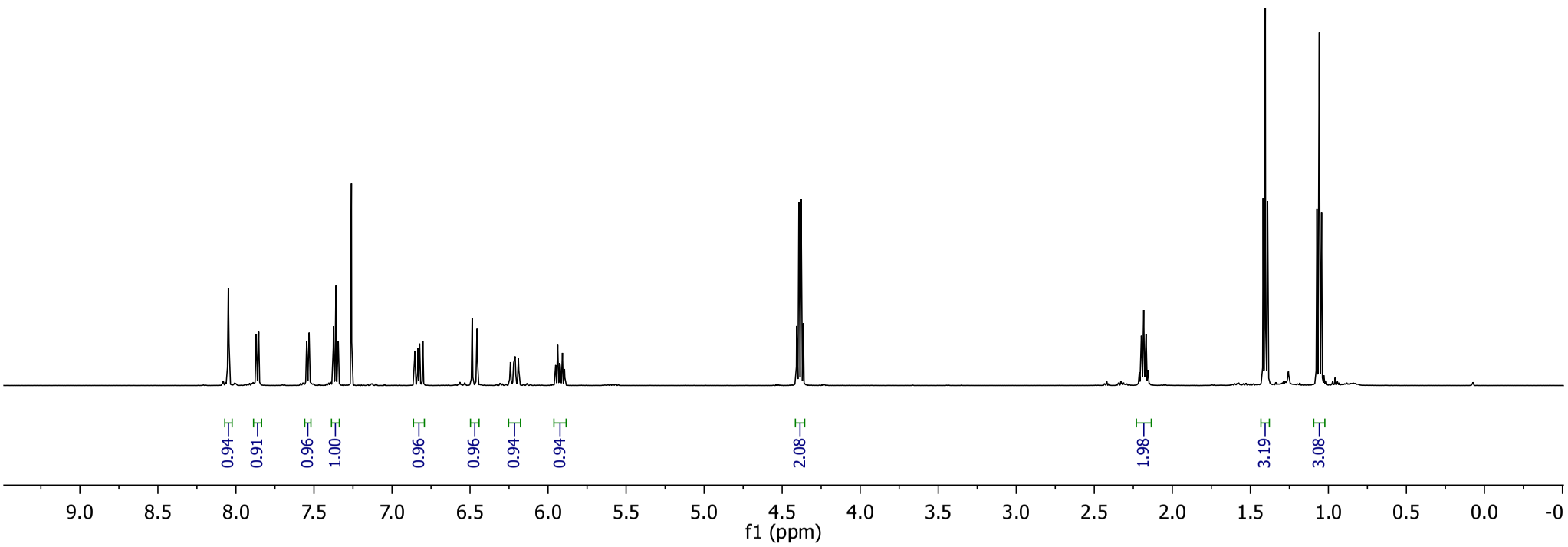
2c



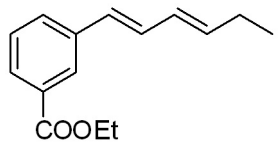
Parameter	Value
Title	zhixun-3-082A
Solvent	CDCl3
Spectrometer Frequency	499.86



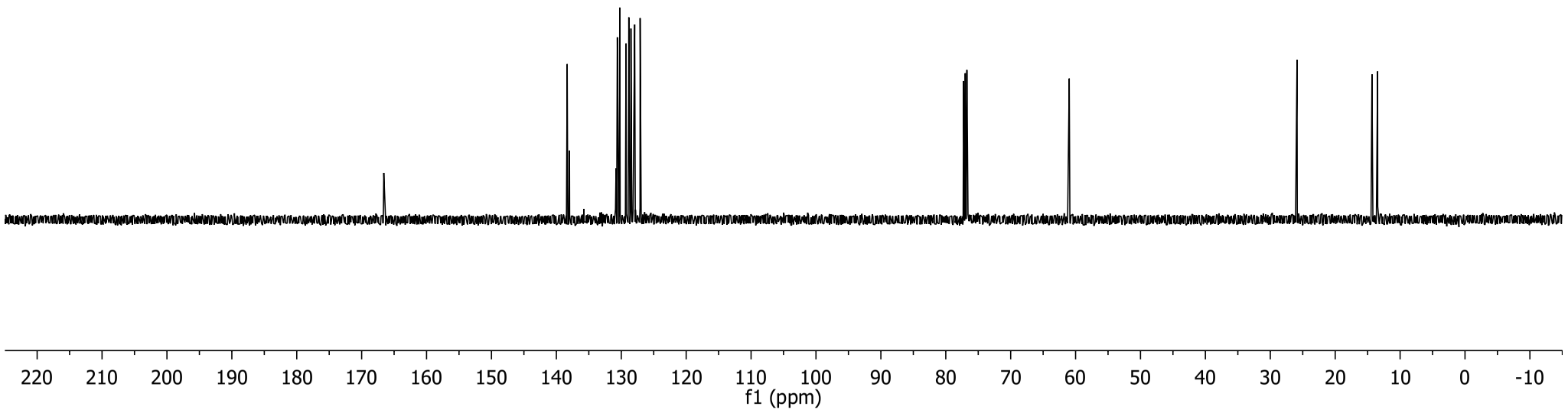
2d



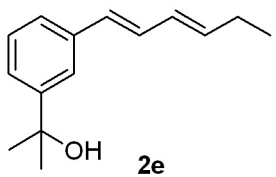
Parameter	Value
Title	zhixun-3-082A-C13
Solvent	CDCl3
Spectrometer Frequency	125.70



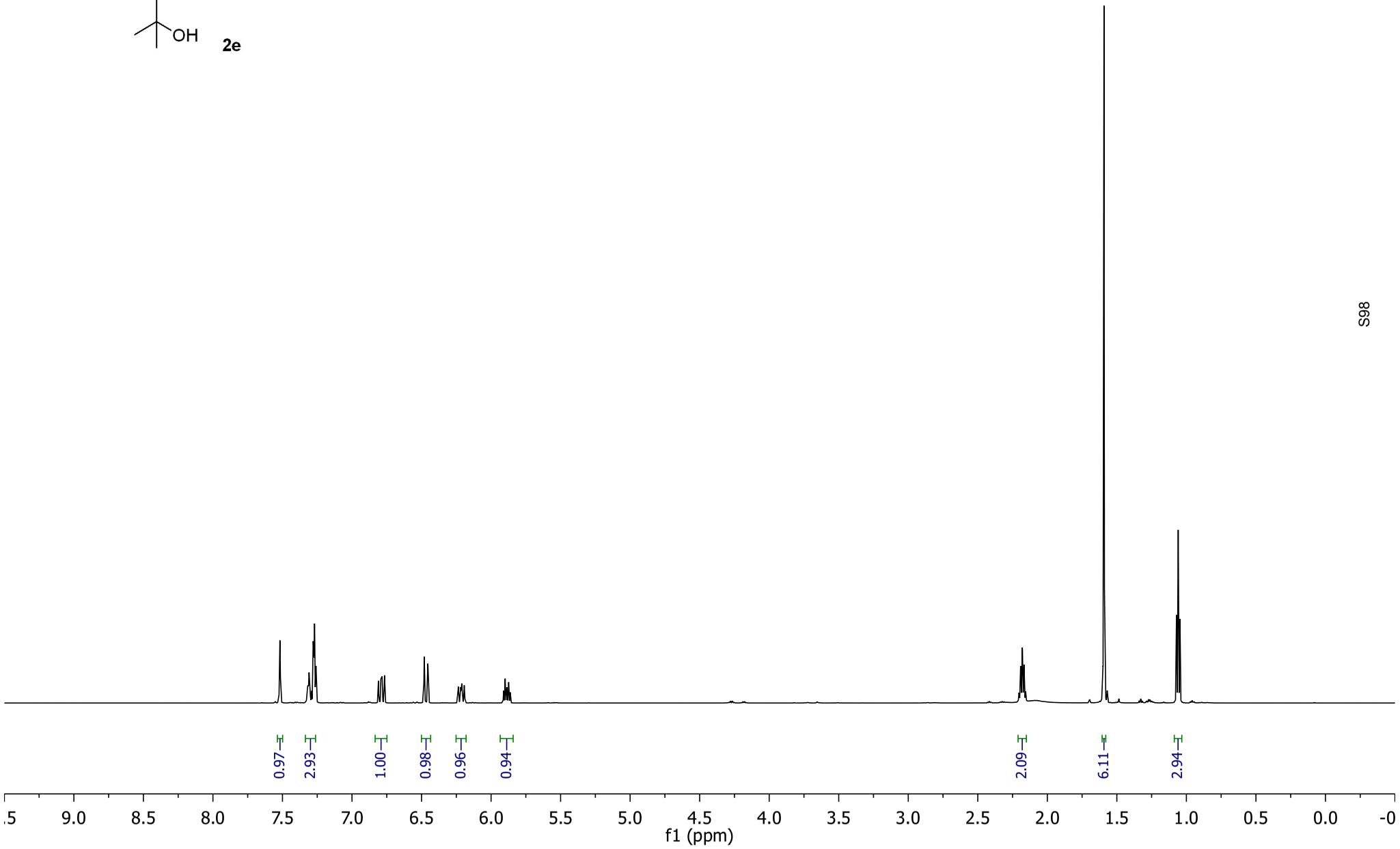
2d



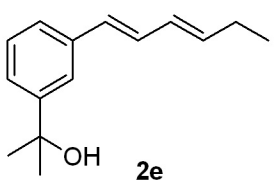
Parameter	Value
Title	zhixun-3-085B
Solvent	cdcl3
Spectrometer Frequency	599.63



2e



Parameter	Value
Title	zhixun-3-085B-C13
Solvent	cdcl3
Spectrometer Frequency	150.79



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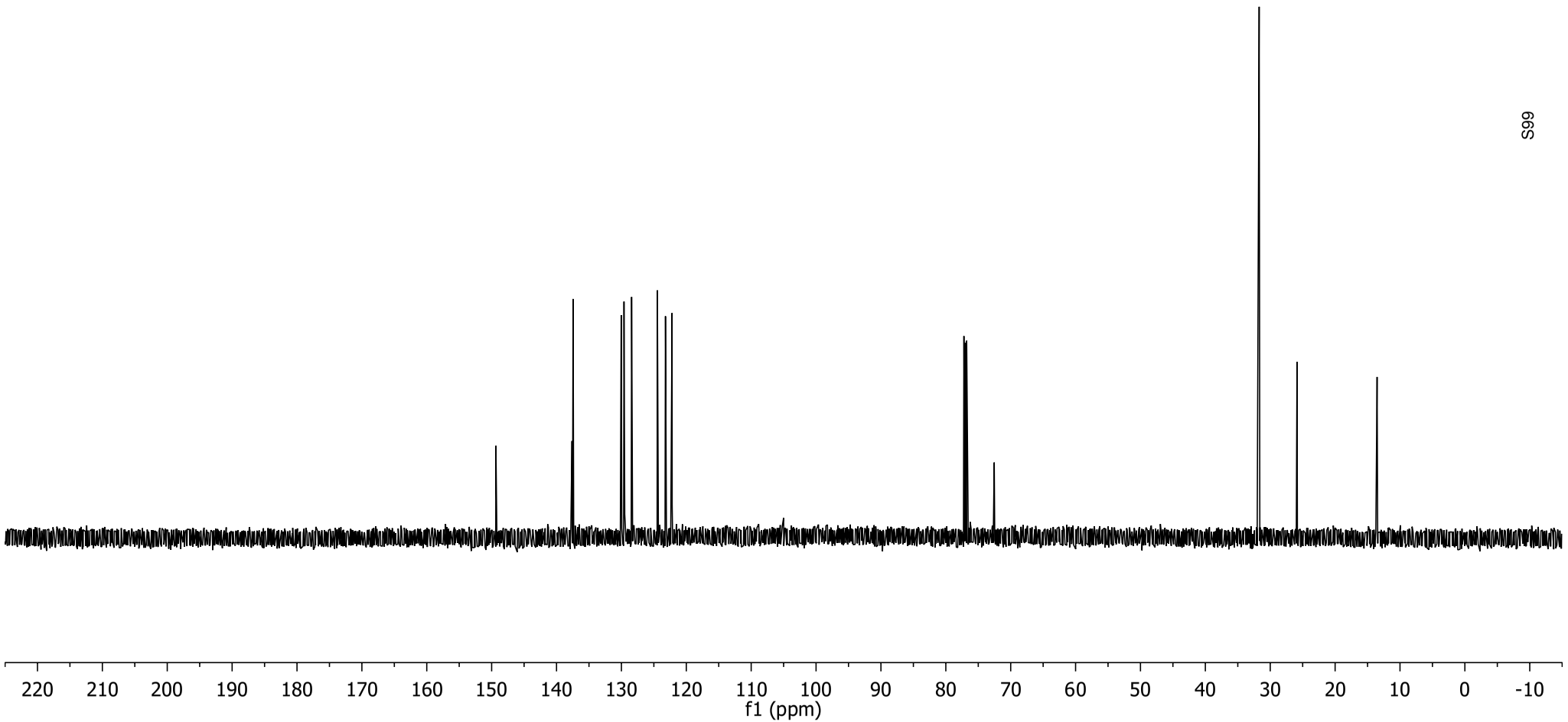
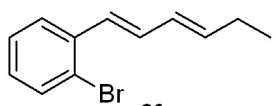


Parameter	Value
Title	wyz8-220-pro-h1
Solvent	cdcl3
Spectrometer Frequency	599.64



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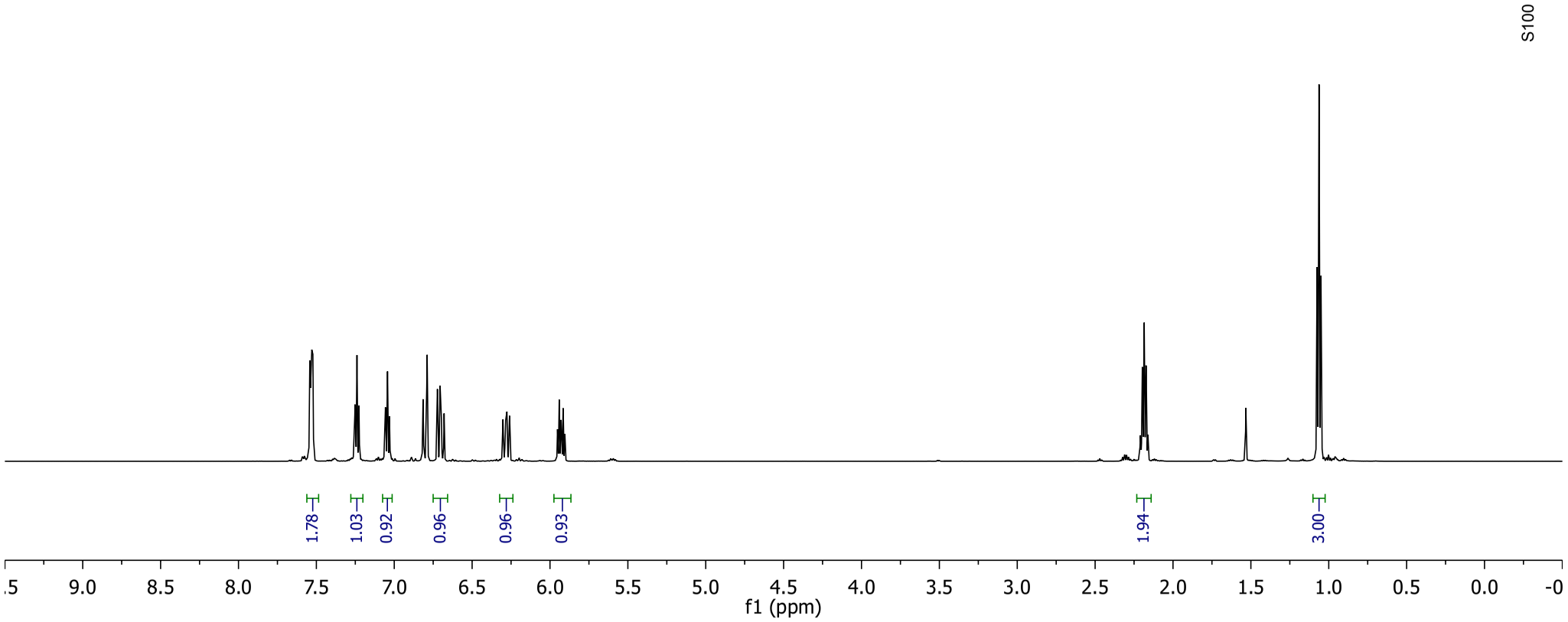
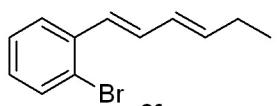


Parameter	Value
Title	wyz8-220-pro-c13-49
Solvent	cdcl3
Spectrometer Frequency	150.79



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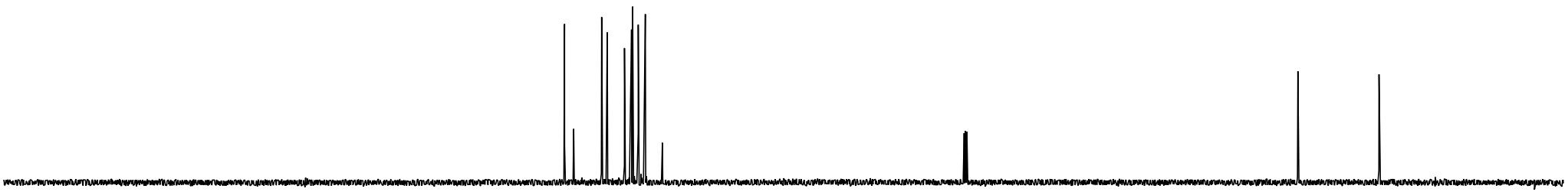
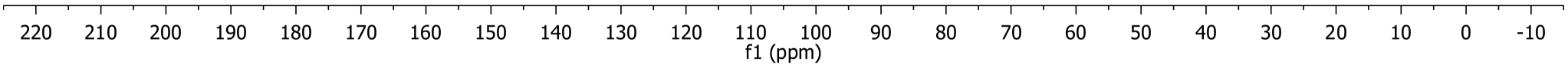
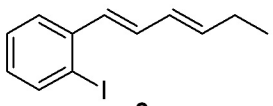
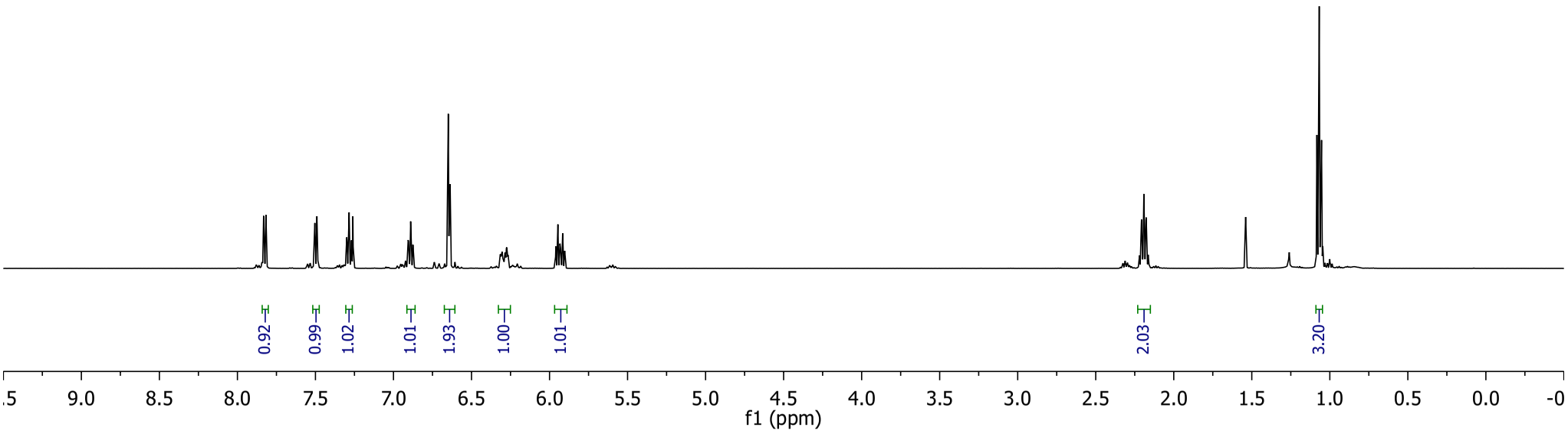




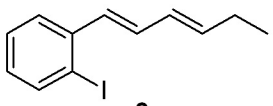
Parameter	Value
Title	zhixun-3-072A-1
Solvent	CDCl3
Spectrometer Frequency	499.86



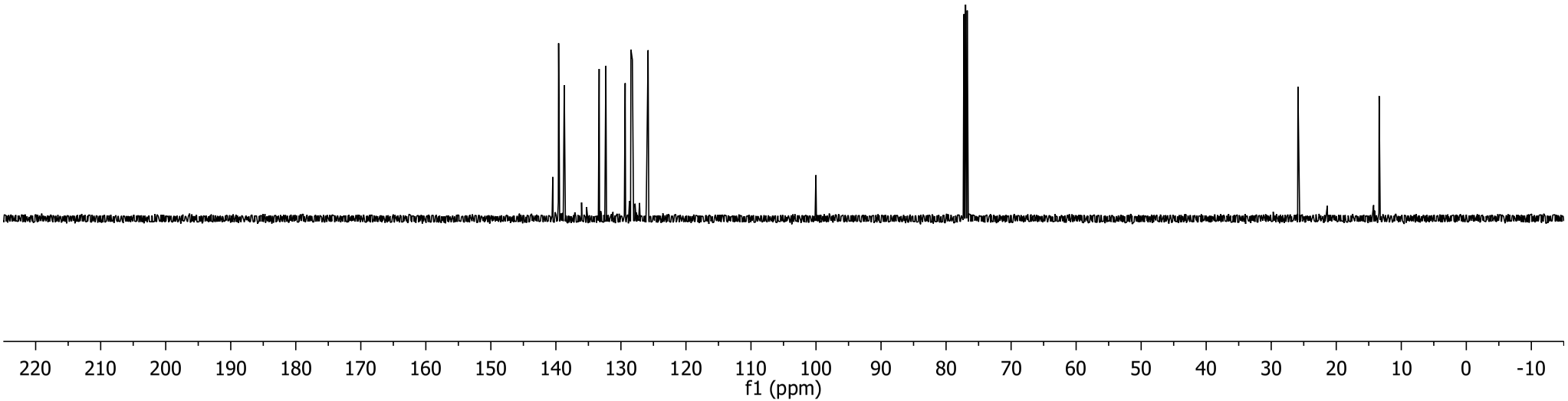
2g



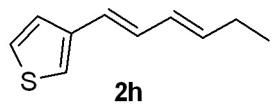
Parameter	Value
Title	zhixun-3-072A-1-C13
Solvent	CDCl3
Spectrometer Frequency	125.70



2g



Parameter	Value
Title	zhixun-3-057B
Solvent	cdcl3
Spectrometer Frequency	599.64



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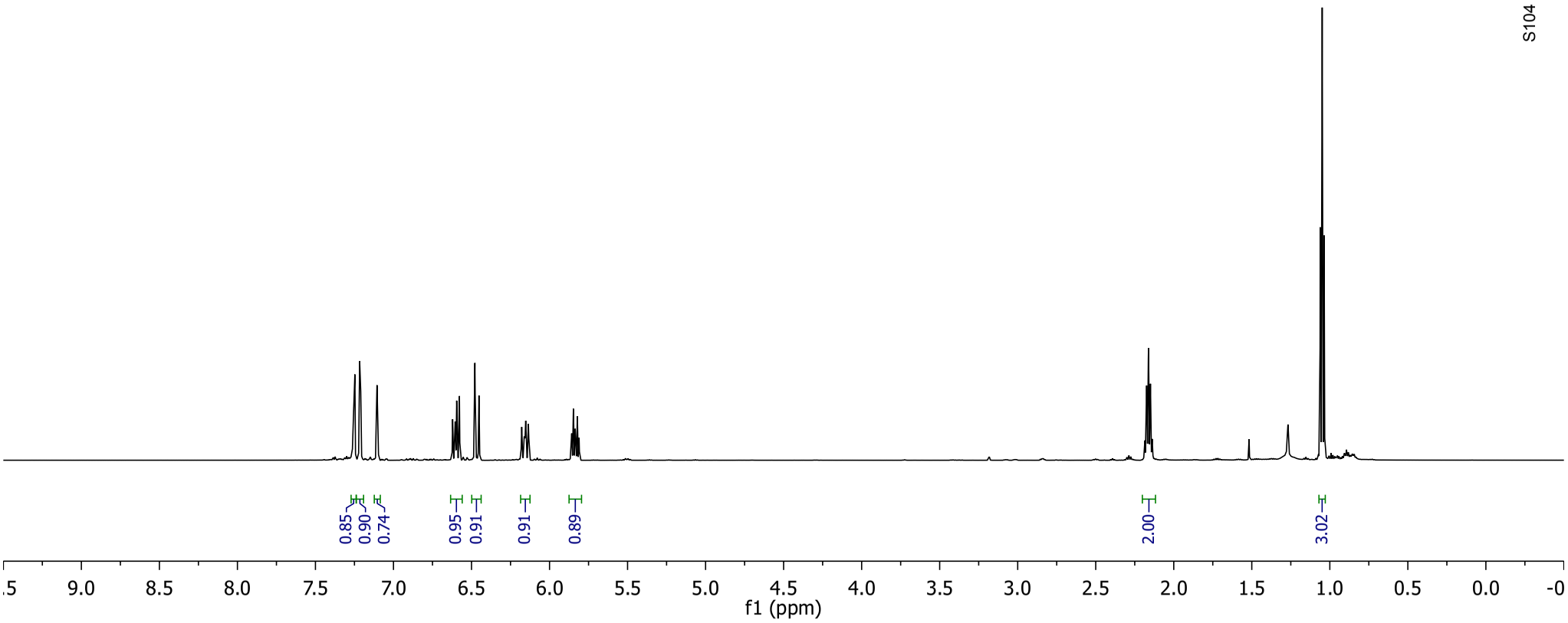
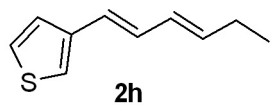
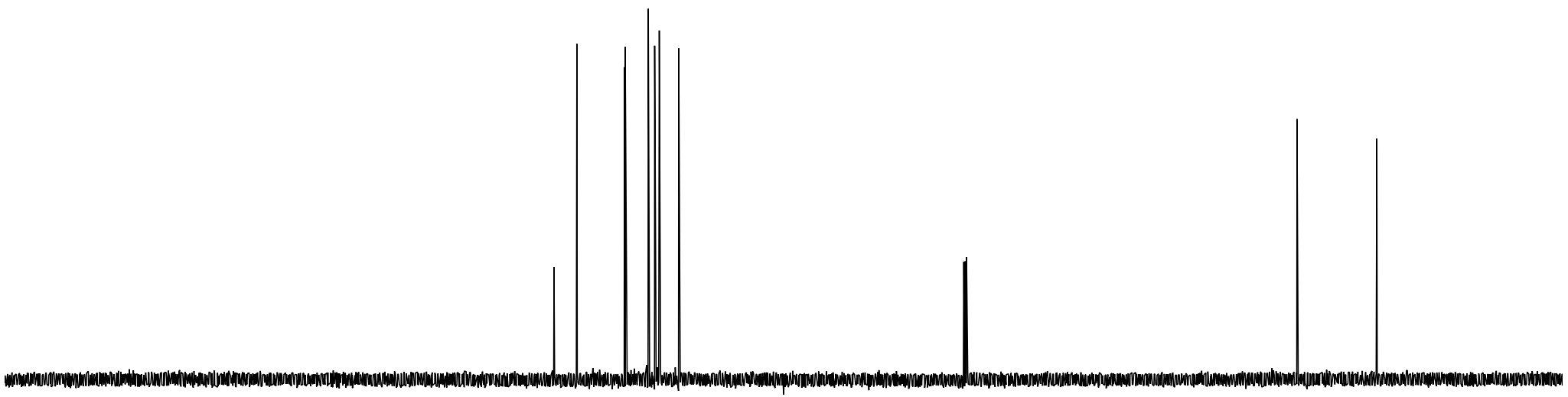
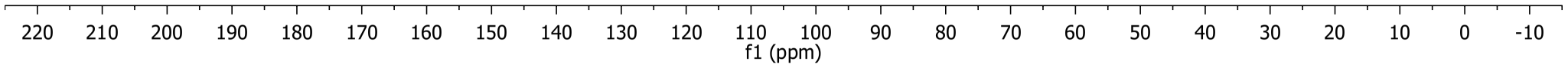


Parameter	Value
Title	zhixun-3-057B-C13
Solvent	cdcl3
Spectrometer Frequency	150.79

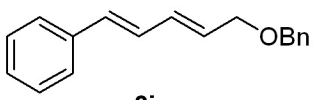


2h





Parameter	Value
Title	zhixun-2-303A-Product
Solvent	CDCl3
Spectrometer Frequency	499.86



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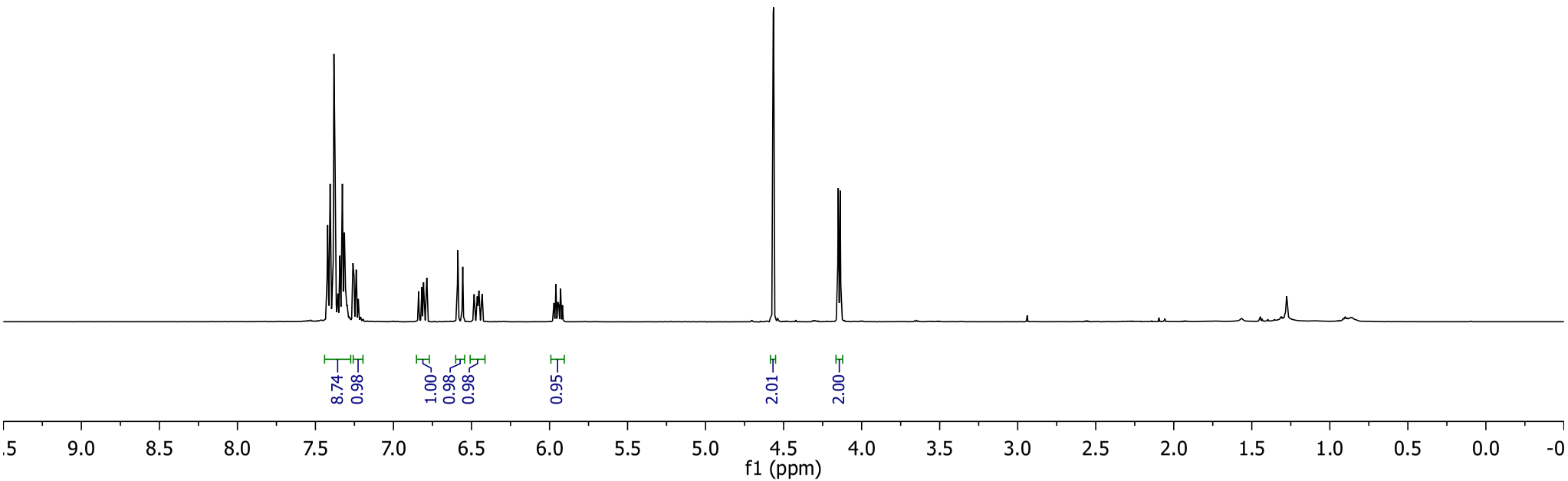
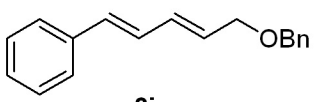
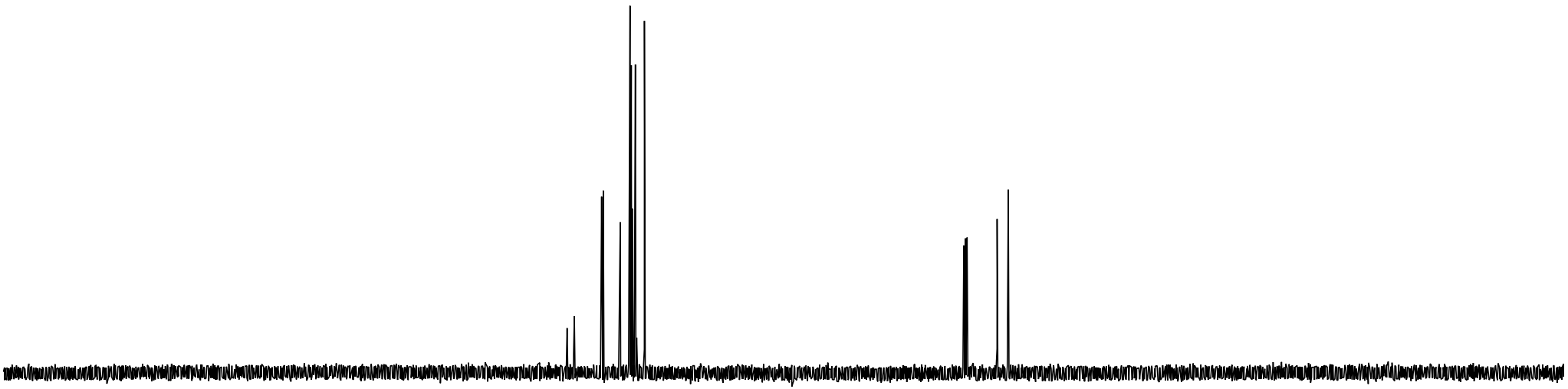
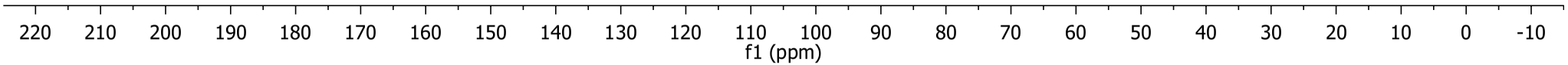


Parameter	Value
Title	zhixun-2-303A-Product-C13
Solvent	CDCl3
Spectrometer Frequency	125.70

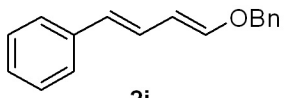


2i





Parameter	Value
Title	zhixun-3-054A-1
Solvent	"CDCl3"
Spectrometer Frequency	499.86



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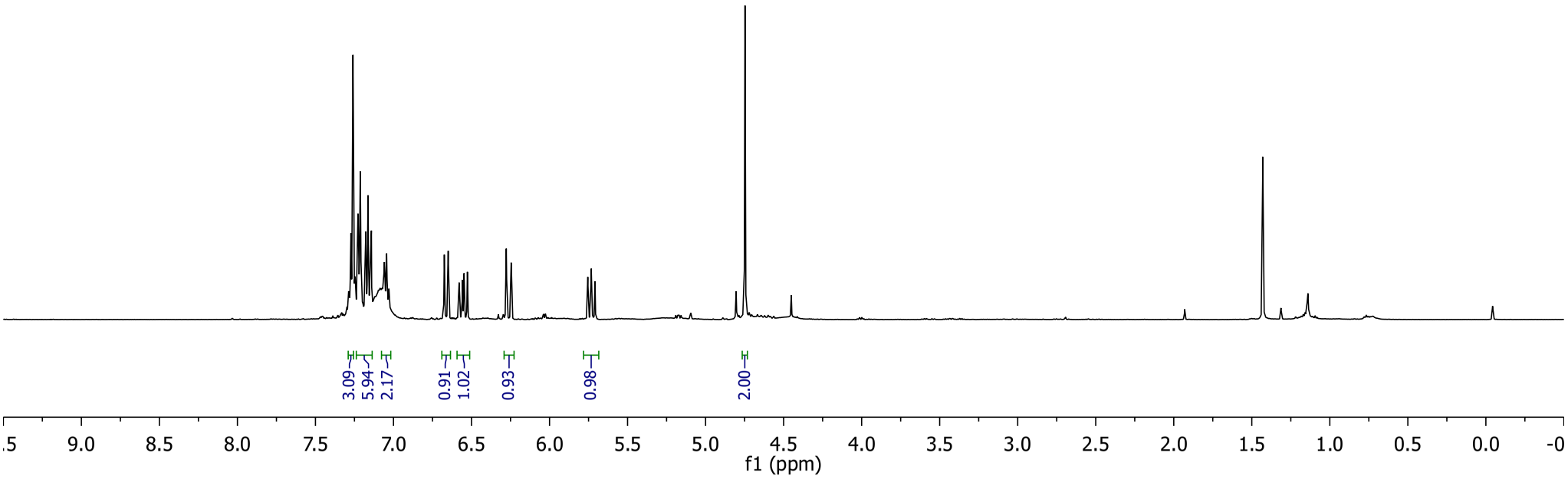
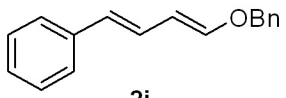


Parameter	Value
Title	zhixun-3-054A-C13
Solvent	cdcl3
Spectrometer Frequency	150.79



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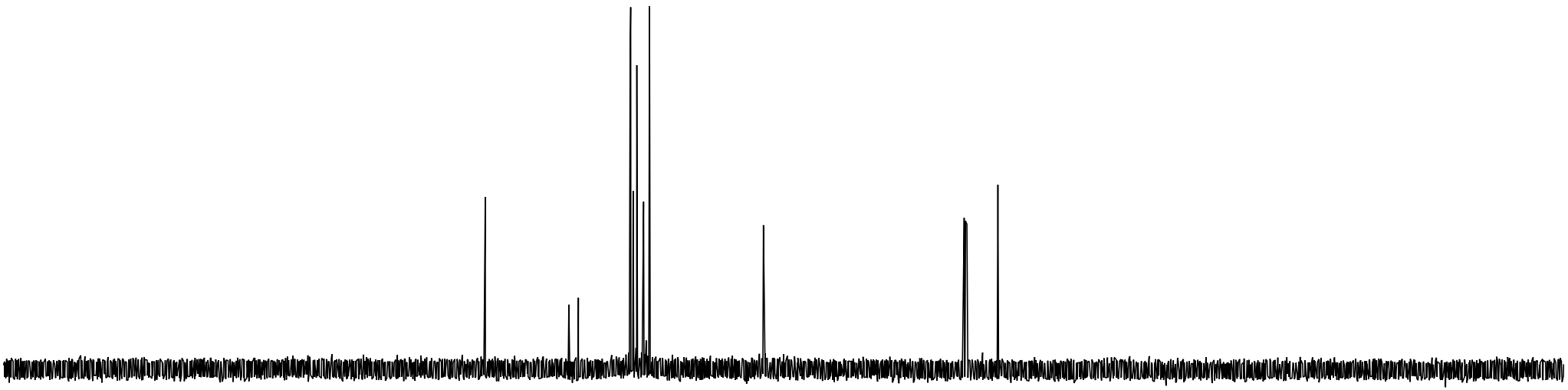
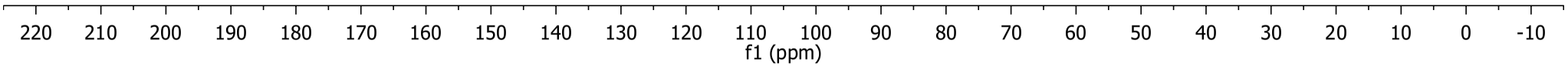
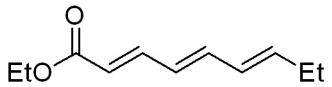




Parameter	Value
Title	wyz8-246-pro-h1-again
Solvent	cdcl3
Relaxation Delay	4.8000
Spectrometer Frequency	599.64



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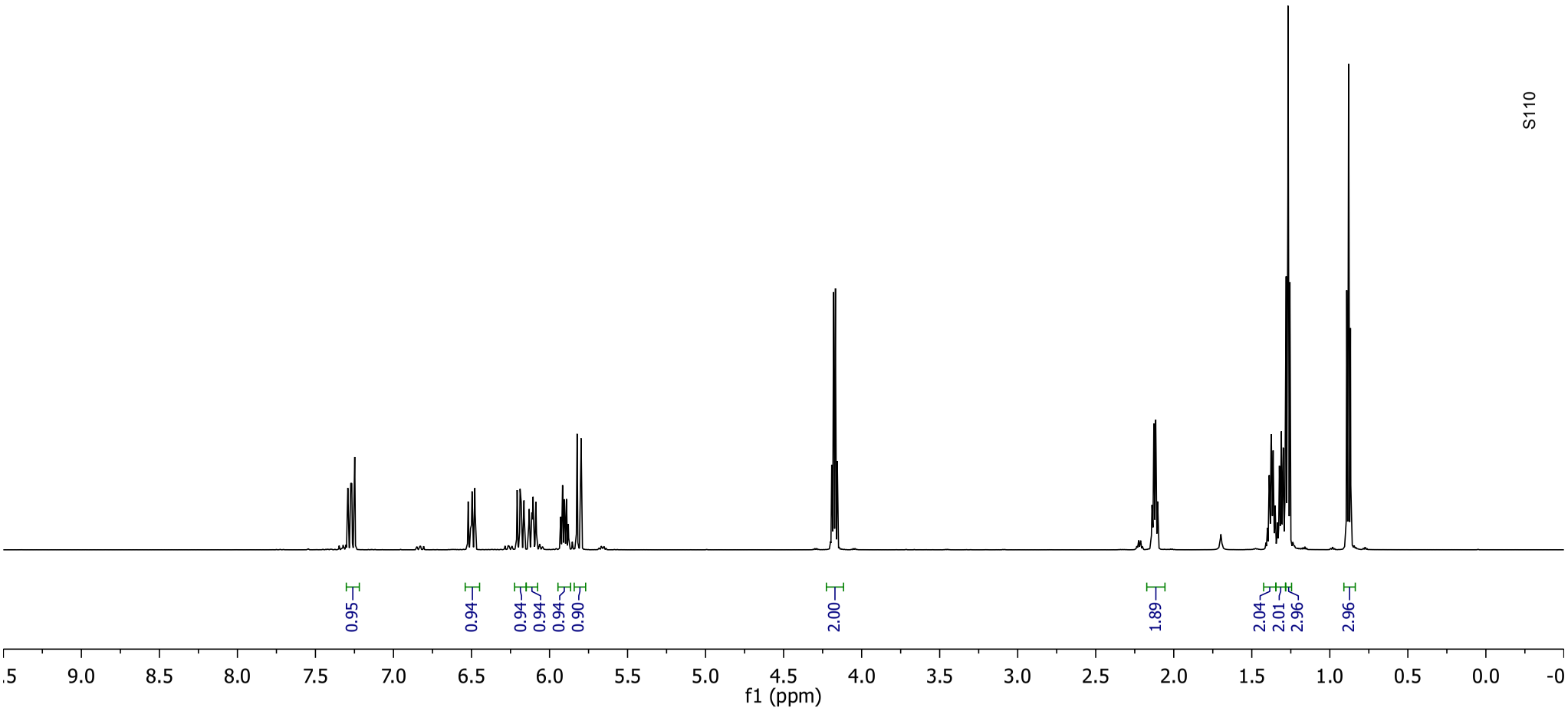
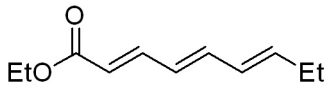
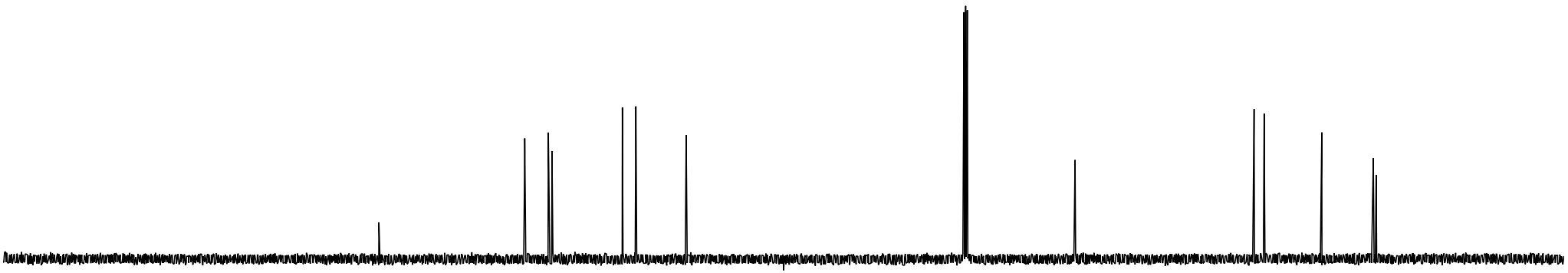
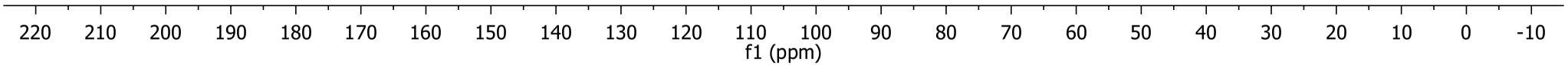


Parameter	Value
Title	wyz8-246-pro3-c13
Solvent	CDCl3
Relaxation Delay	1.0000
Spectrometer Frequency	125.70

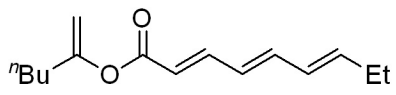


2k

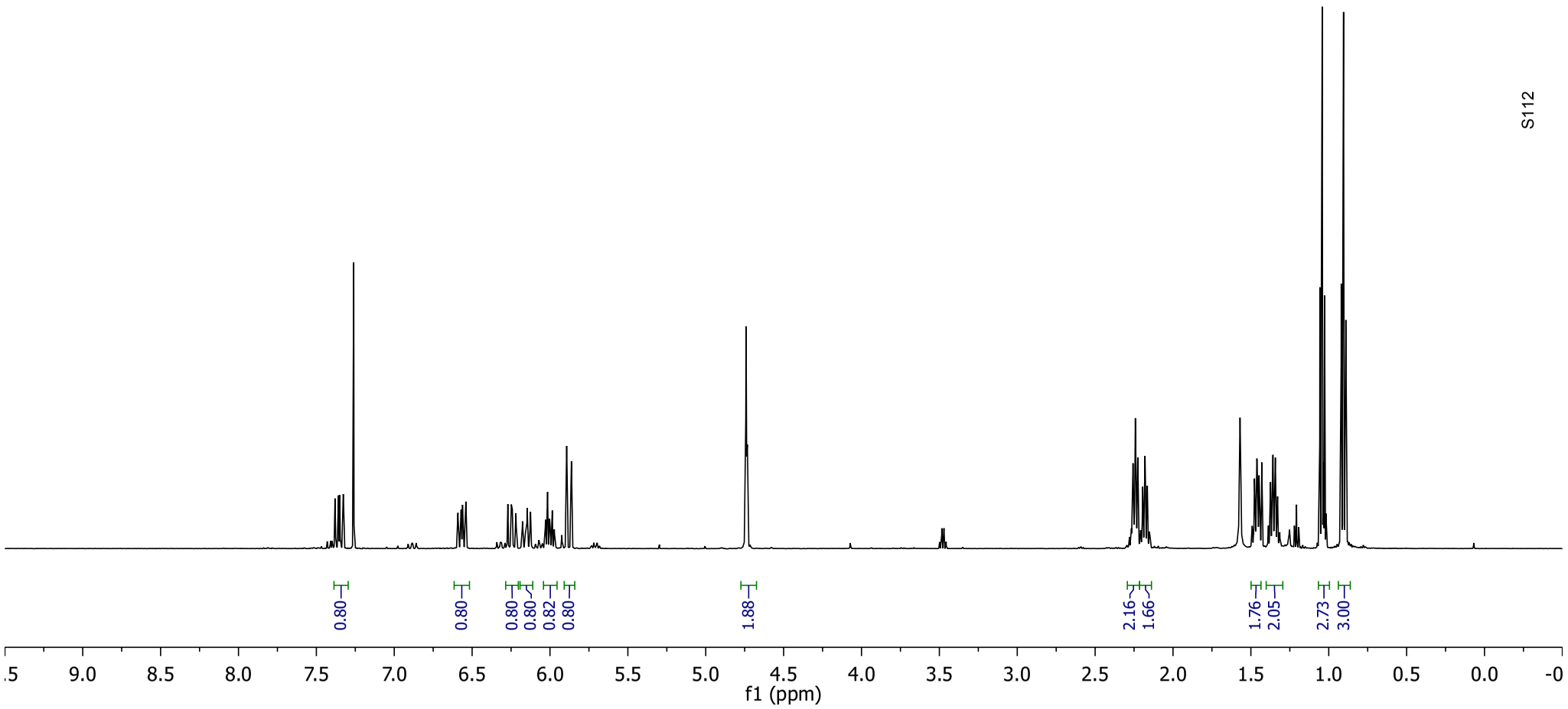




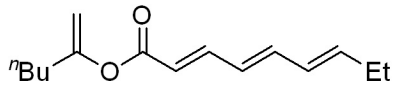
Parameter	Value
Title	wyz8-256-pro-h1
Solvent	CDCl3
Relaxation Delay	4.8000
Spectrometer Frequency	499.86



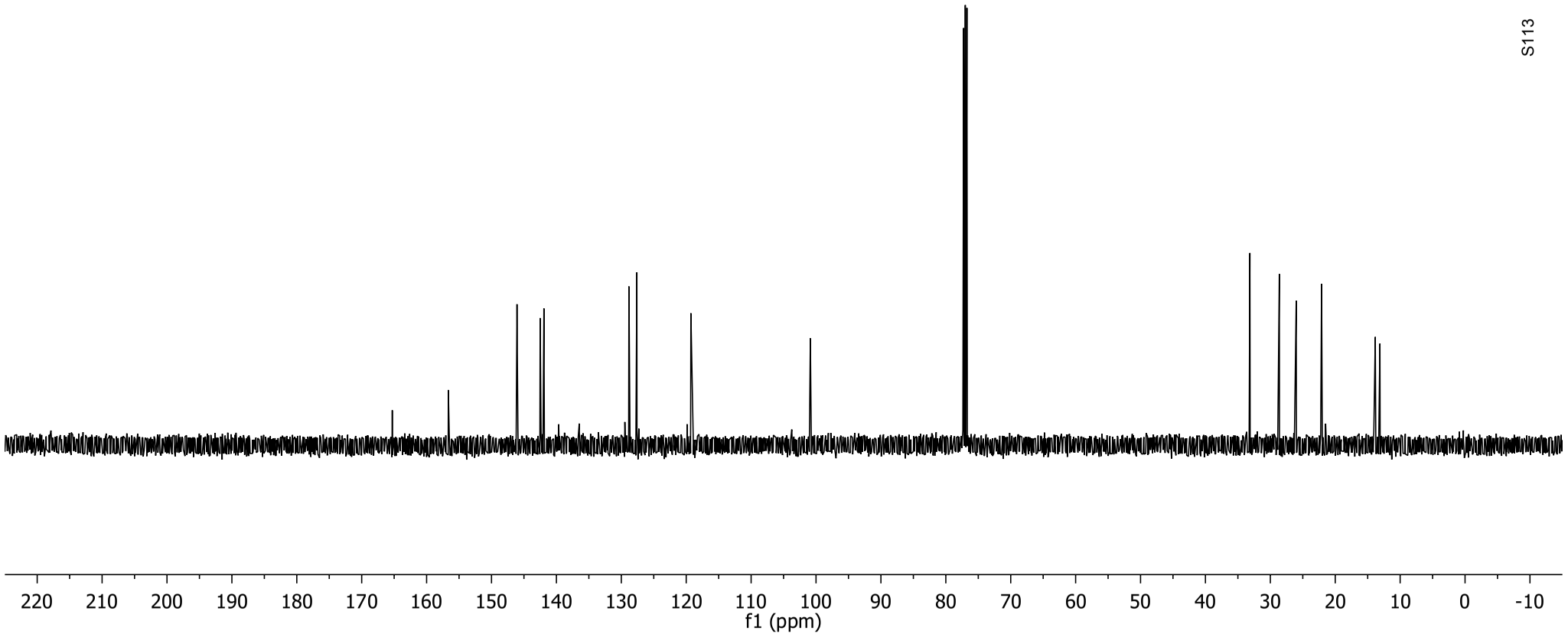
2l



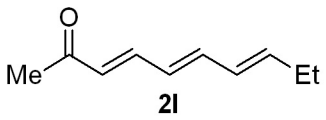
Parameter	Value
Title	wyz8-256-pro-c13
Solvent	CDCl3
Relaxation Delay	1.0000
Spectrometer Frequency	125.70



2l



Parameter	Value
Title	wyz8-247-pro-h1-again
Solvent	cdcl3
Relaxation Delay	4.8000
Spectrometer Frequency	599.64



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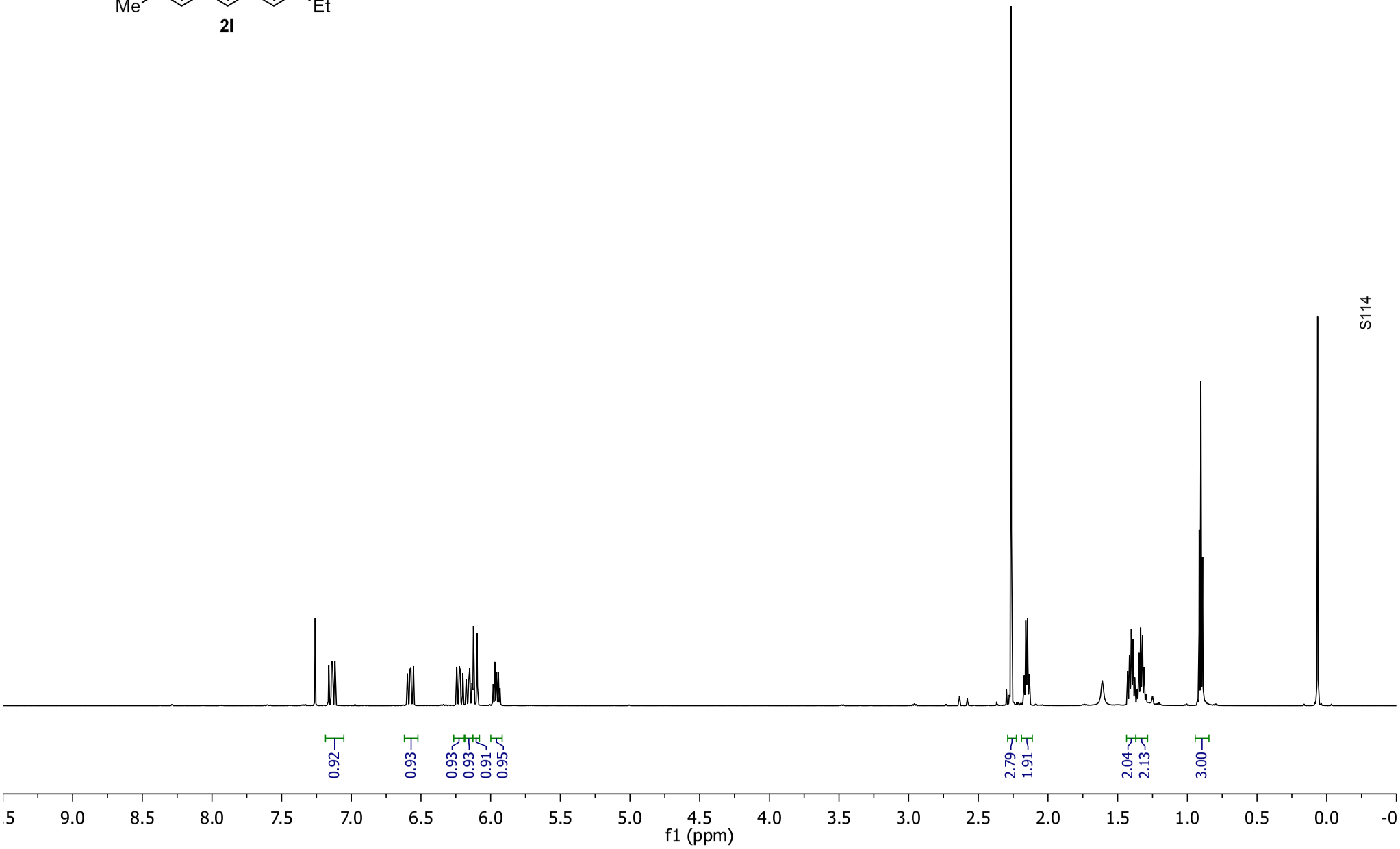
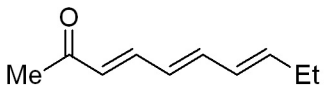
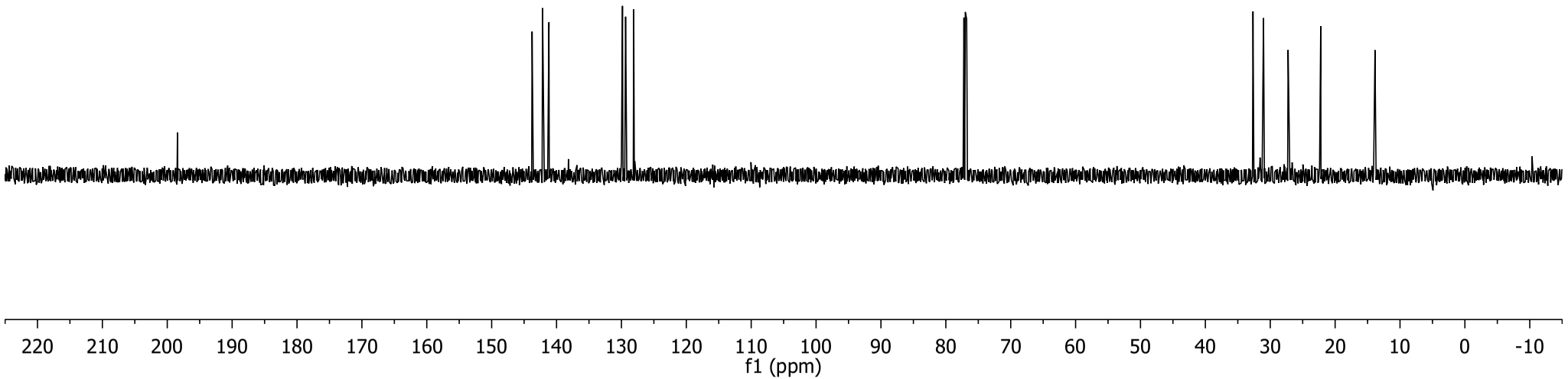


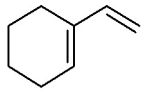
Parameter	Value
Title	wyz8-247-pro2-c13-32
Solvent	cdcl3
Relaxation Delay	1.0000
Spectrometer Frequency	150.79



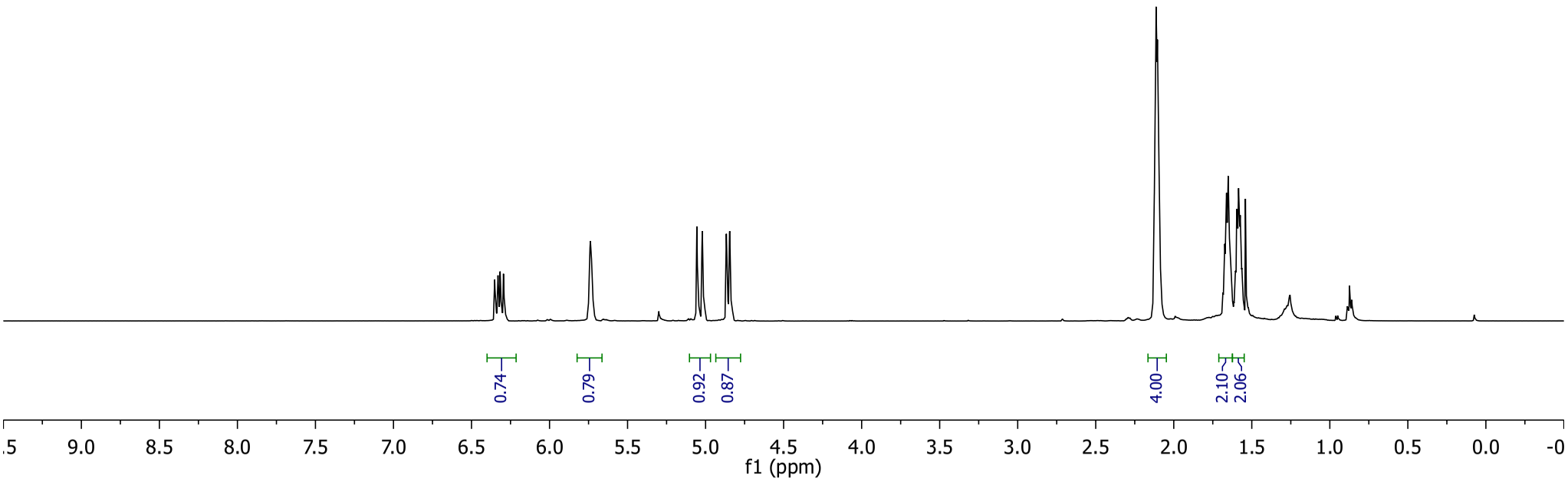
2l



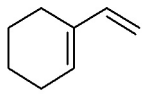
Parameter	Value
Title	wyz8-161-H1-pure
Solvent	cd2cl2
Relaxation Delay	4.8000
Spectrometer Frequency	499.86



2n



Parameter	Value
Title	wyz8-161-C13-pure
Solvent	cd2cl2
Relaxation Delay	1.0000
Spectrometer Frequency	125.70



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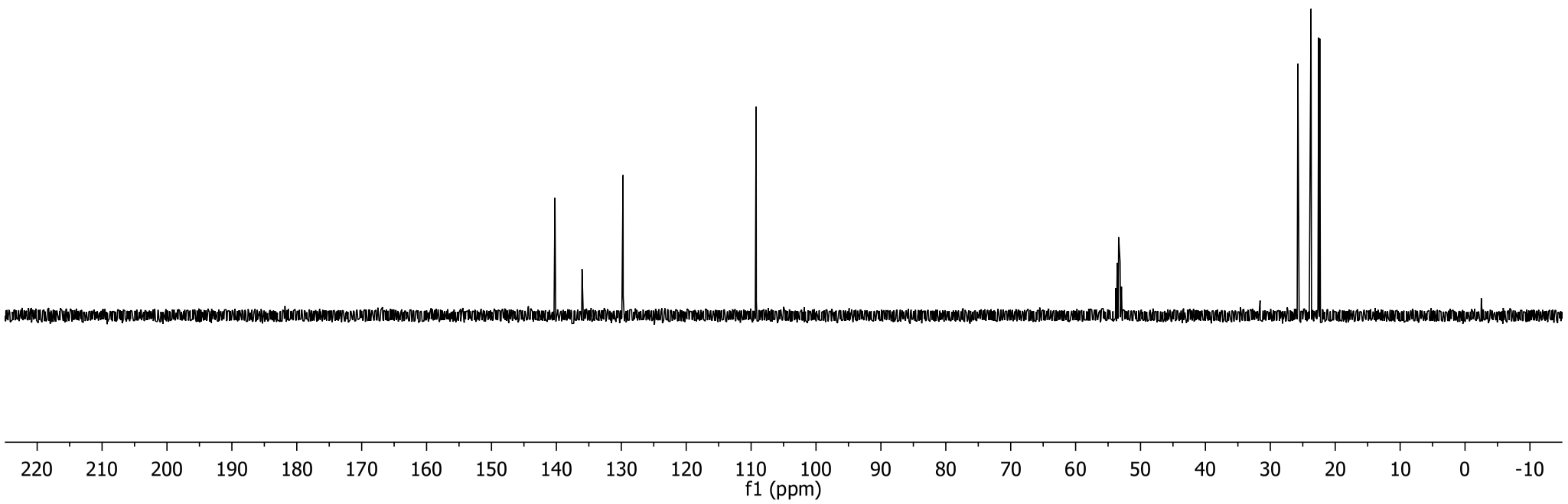
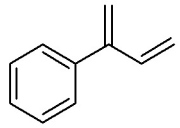
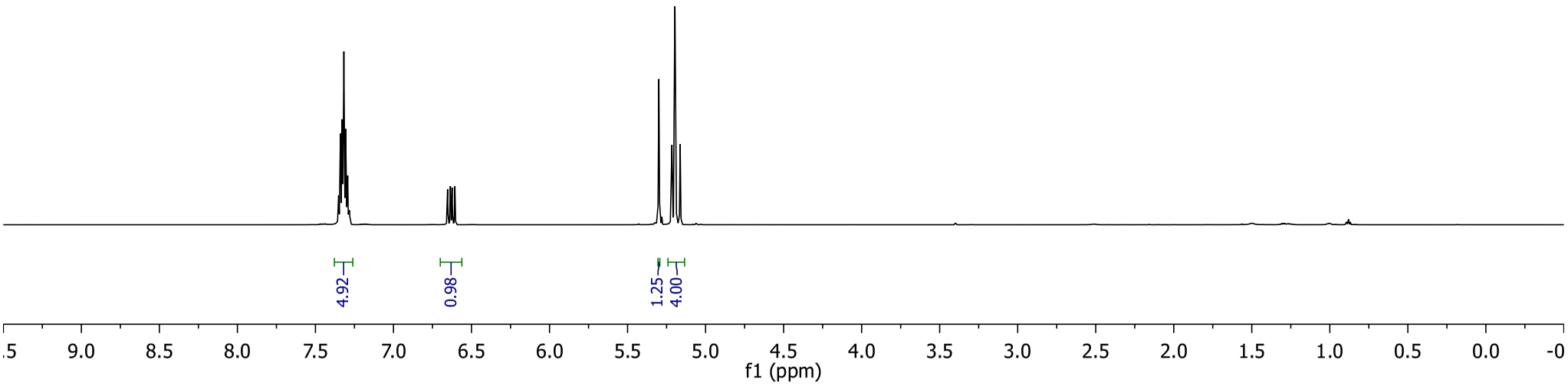


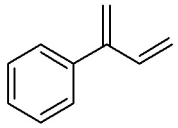
Parameter	Value
Title	wyz8-213-pro-h1
Solvent	cd2cl2
Spectrometer Frequency	599.64



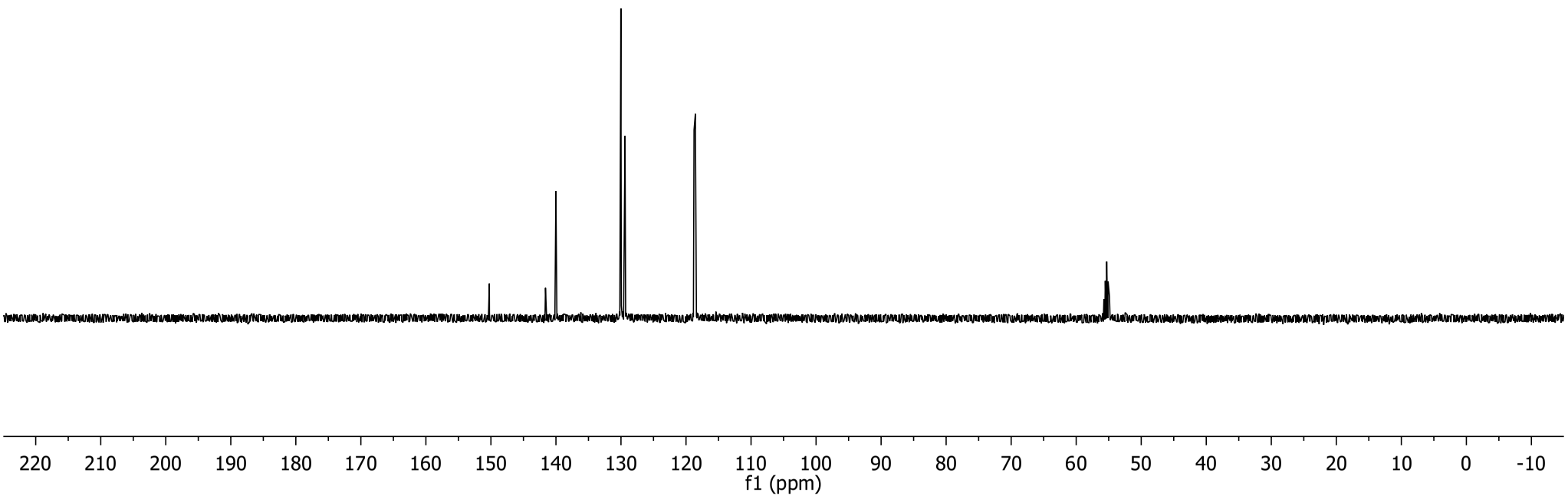
2o



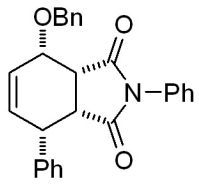
Parameter	Value
Title	wyz8-213-pro-c13
Solvent	CDCl3
Spectrometer Frequency	125.70



2o



Parameter	Value
Title	zhixun-3-061A
Solvent	CDCl3
Spectrometer Frequency	499.86



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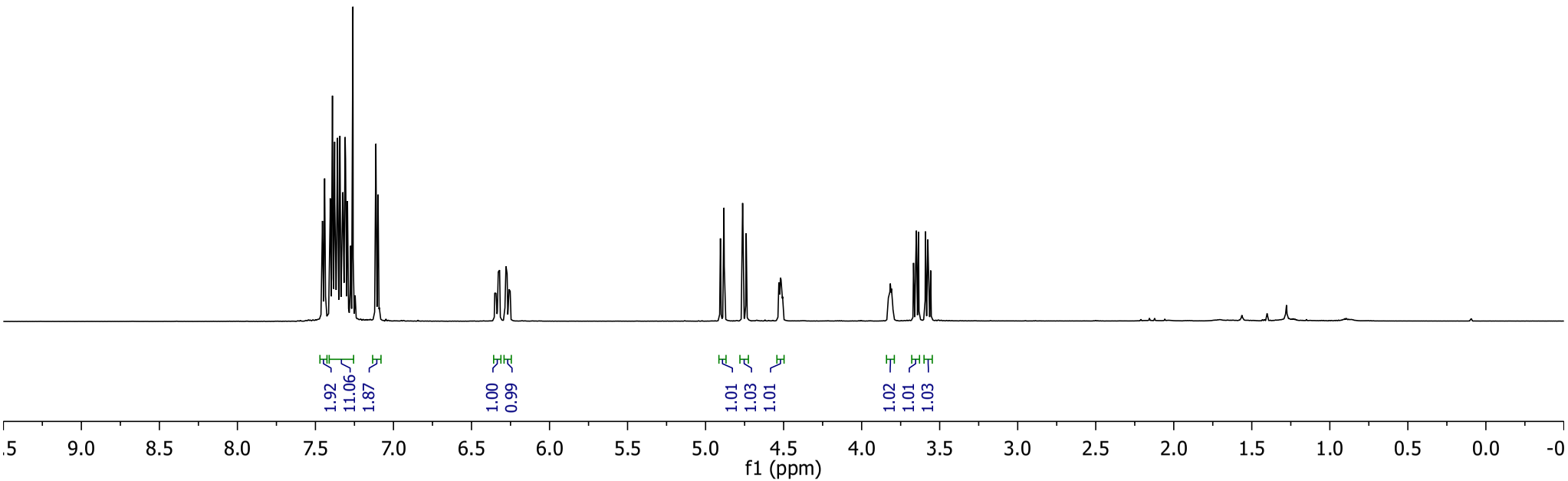
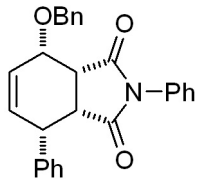
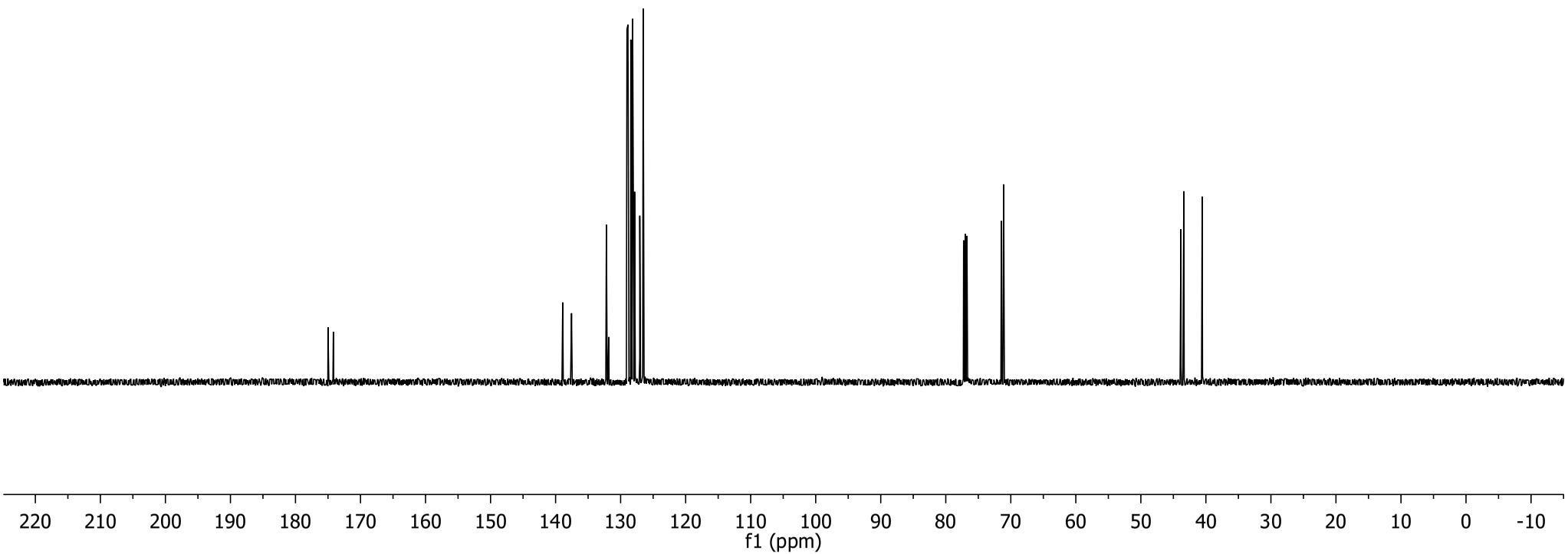


Parameter	Value
Title	zhixun-3-061A-C13
Solvent	CDCl3
Spectrometer Frequency	125.70

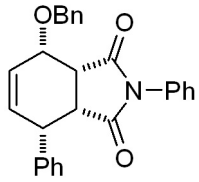


3



Parameters

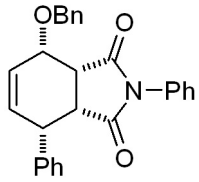
Parameter	Value (f2, f1)
Title	zhixun-3-061A-cosy
Solvent	cdcl3
Spectrometer Frequency	(599.63, 599.63)
Spectral Width	(4613.6, 4613.6)



3

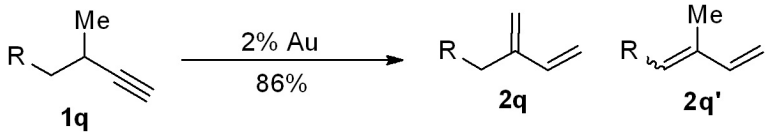
Parameters

Parameter	Value (f2, f1)
Title	zhixun-3-061A-noesy
Solvent	cdcl3
Spectrometer Frequency	(599.63, 599.63)
Spectral Width	(4613.6, 4613.6)



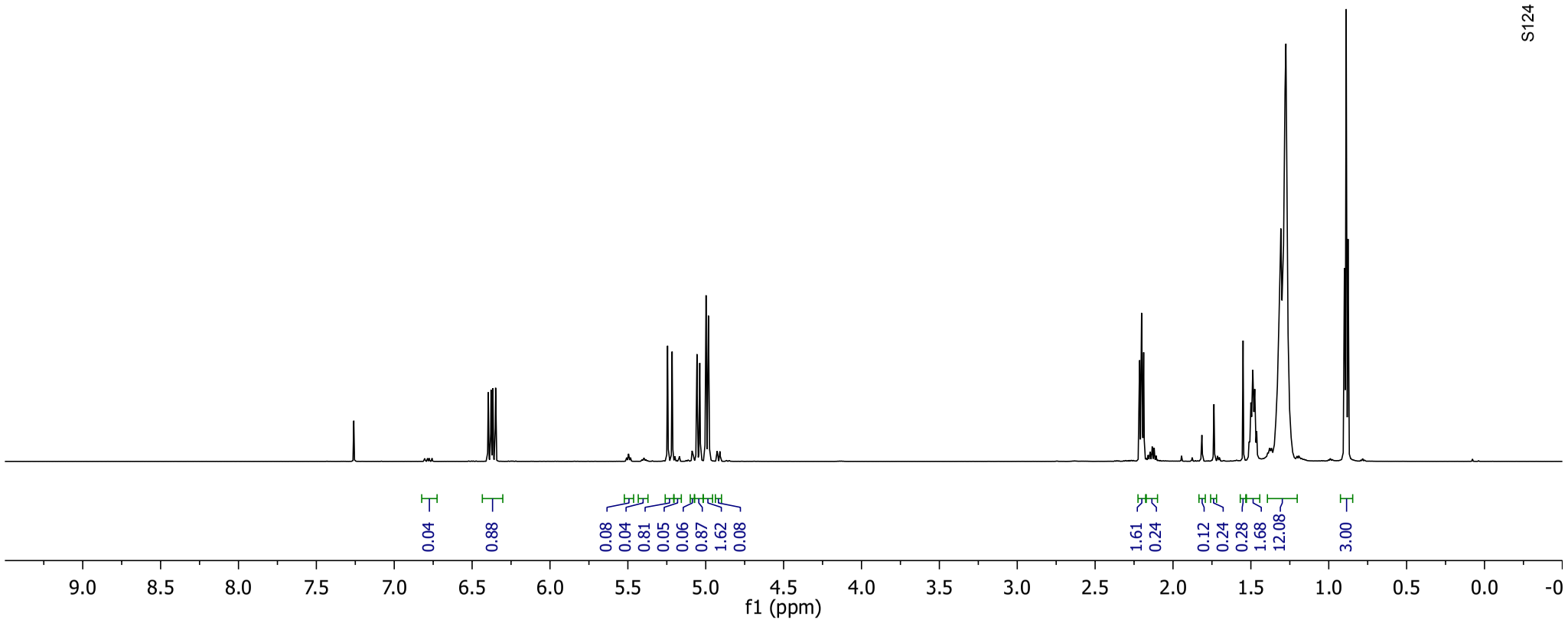
3

Parameter	Value
Title	wyz8-211-pro-h1
Solvent	cdcl3
Relaxation Delay	25.0000
Spectrometer Frequency	599.64

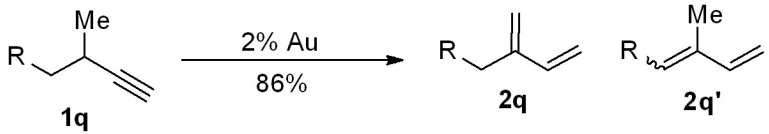


R = *n*-C_8H_{17}

6.9 : 1 (E/Z = 1.8/1)

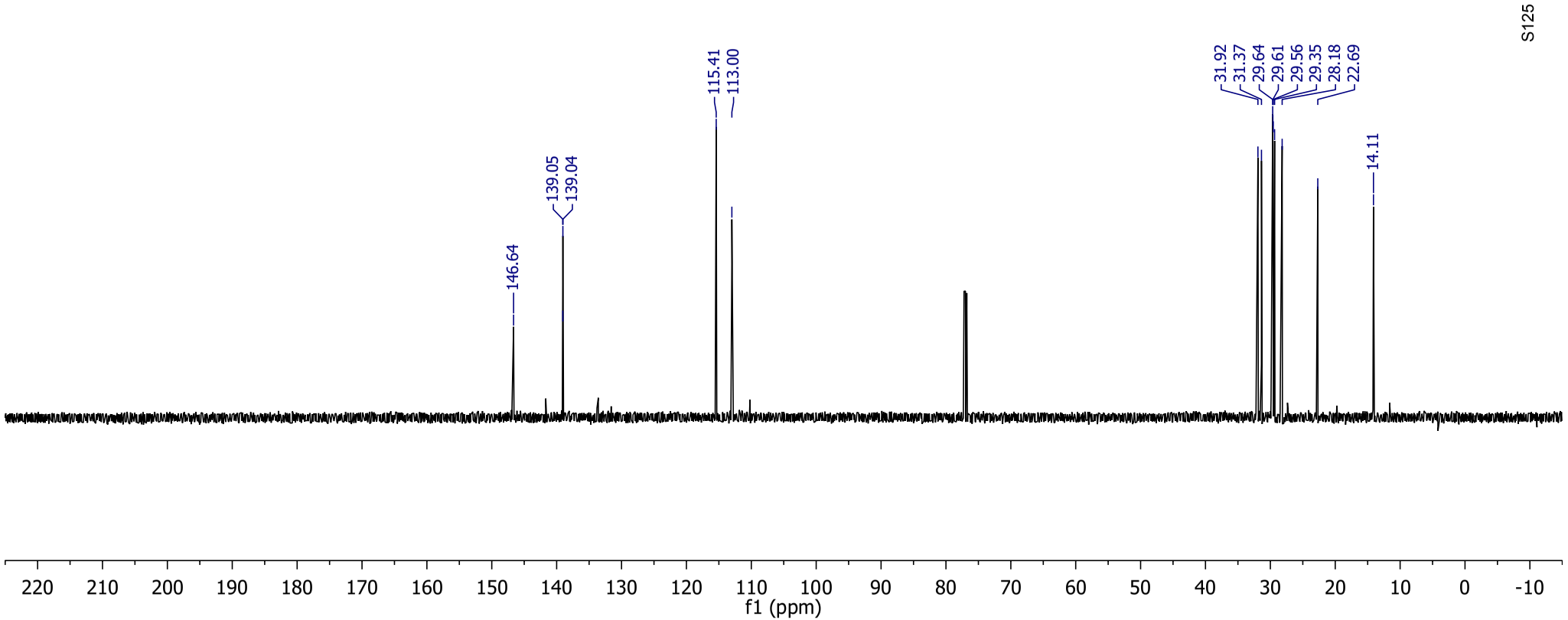


Parameter	Value
Title	wyz8-211-pro-C13-55
Solvent	cdcl3
Relaxation Delay	1.0000
Spectrometer Frequency	150.79

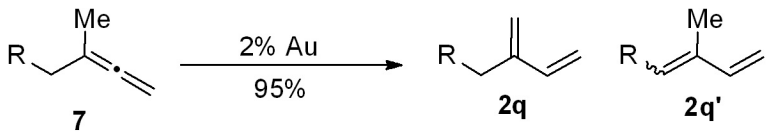


R = *n*-C_8H_{17}

6.9 : 1 (E/Z = 1.8/1)



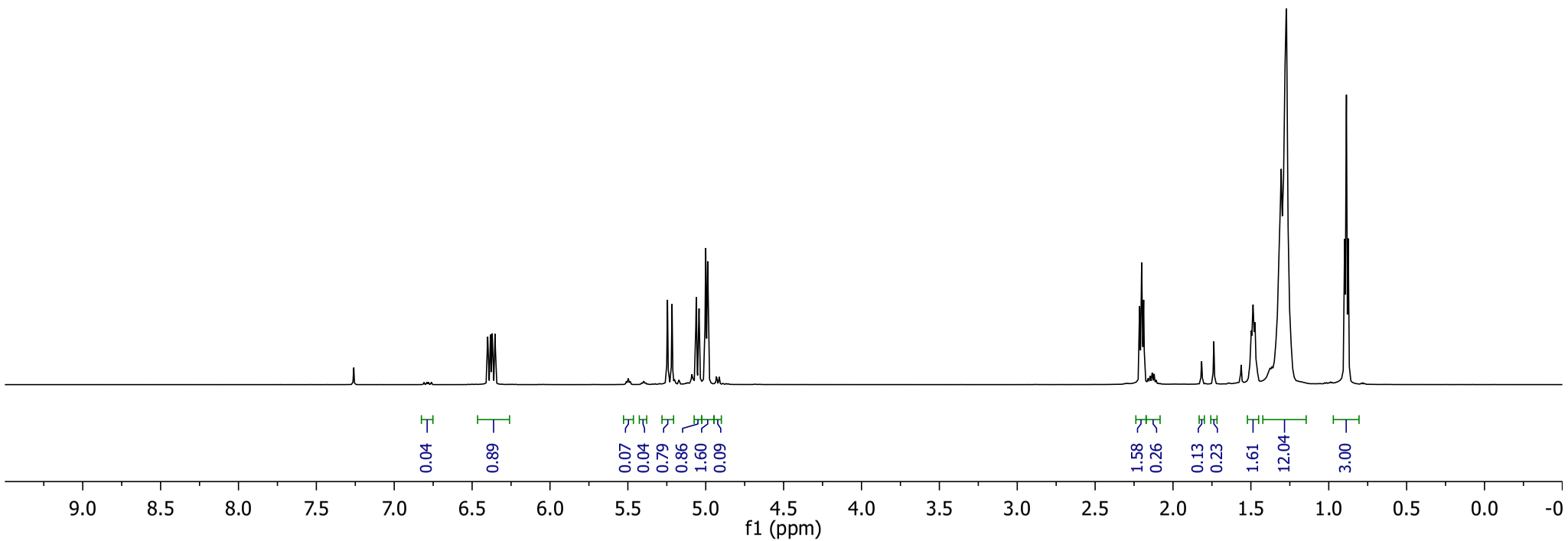
Parameter	Value
Title	wyz8-226-pro-h1
Solvent	cdcl3
Relaxation Delay	25.0000
Spectrometer Frequency	599.64



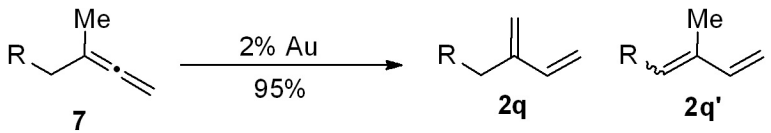
7 **2q** **2q'**

R = *n*-C_8H_{17}

7.4 : 1 (E/Z = 1.8/1)



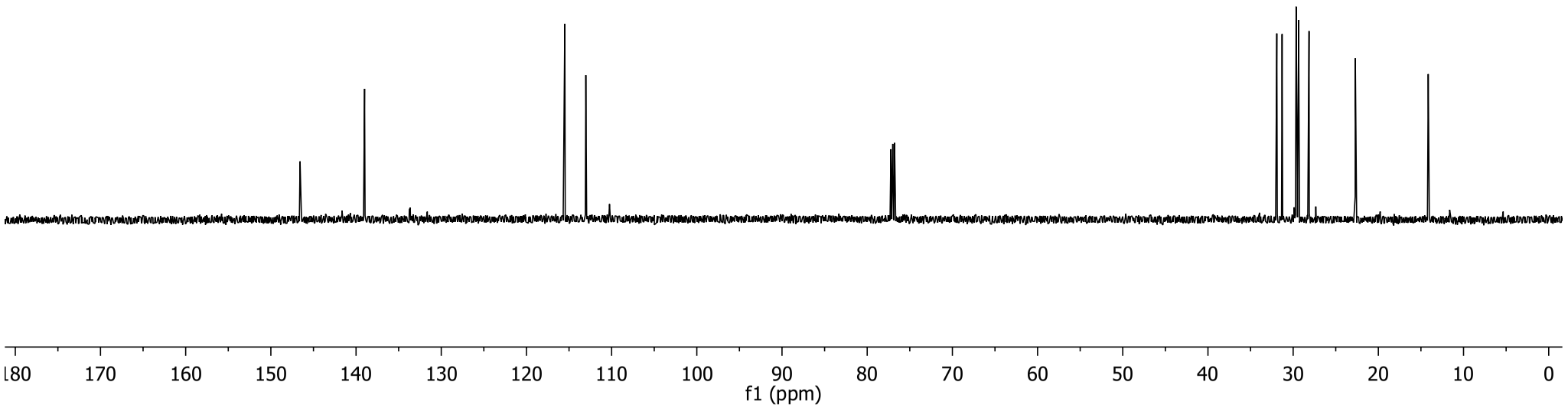
Parameter	Value
Title	wyz8-226-pro-c13-36
Solvent	cdcl3
Relaxation Delay	1.0000
Spectrometer Frequency	150.79

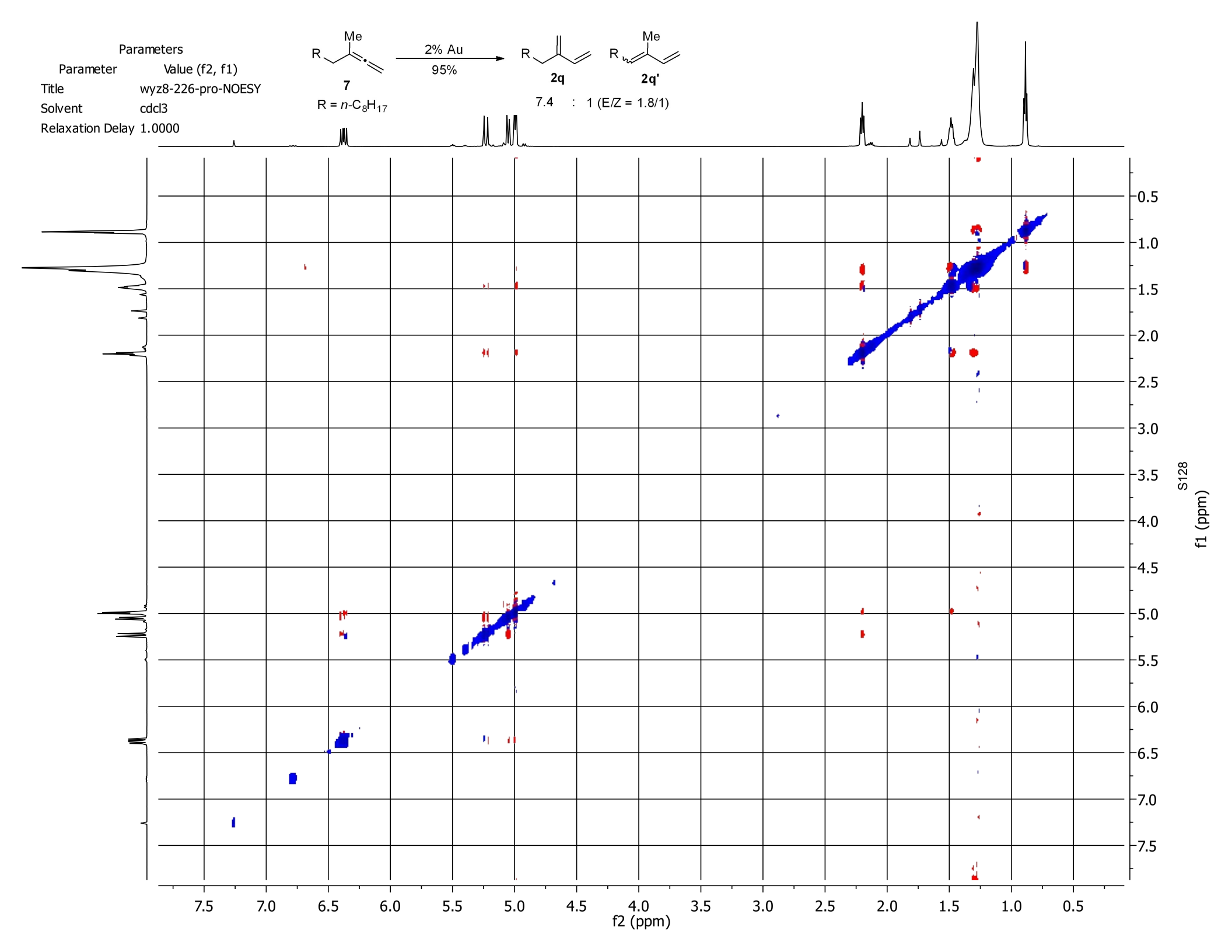


7 **2q** **2q'**

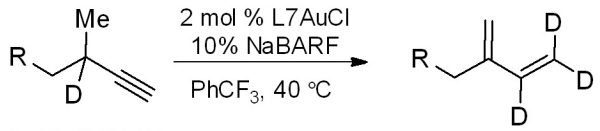
R = *n*-C_8H_{17}

7.4 : 1 (E/Z = 1.8/1)

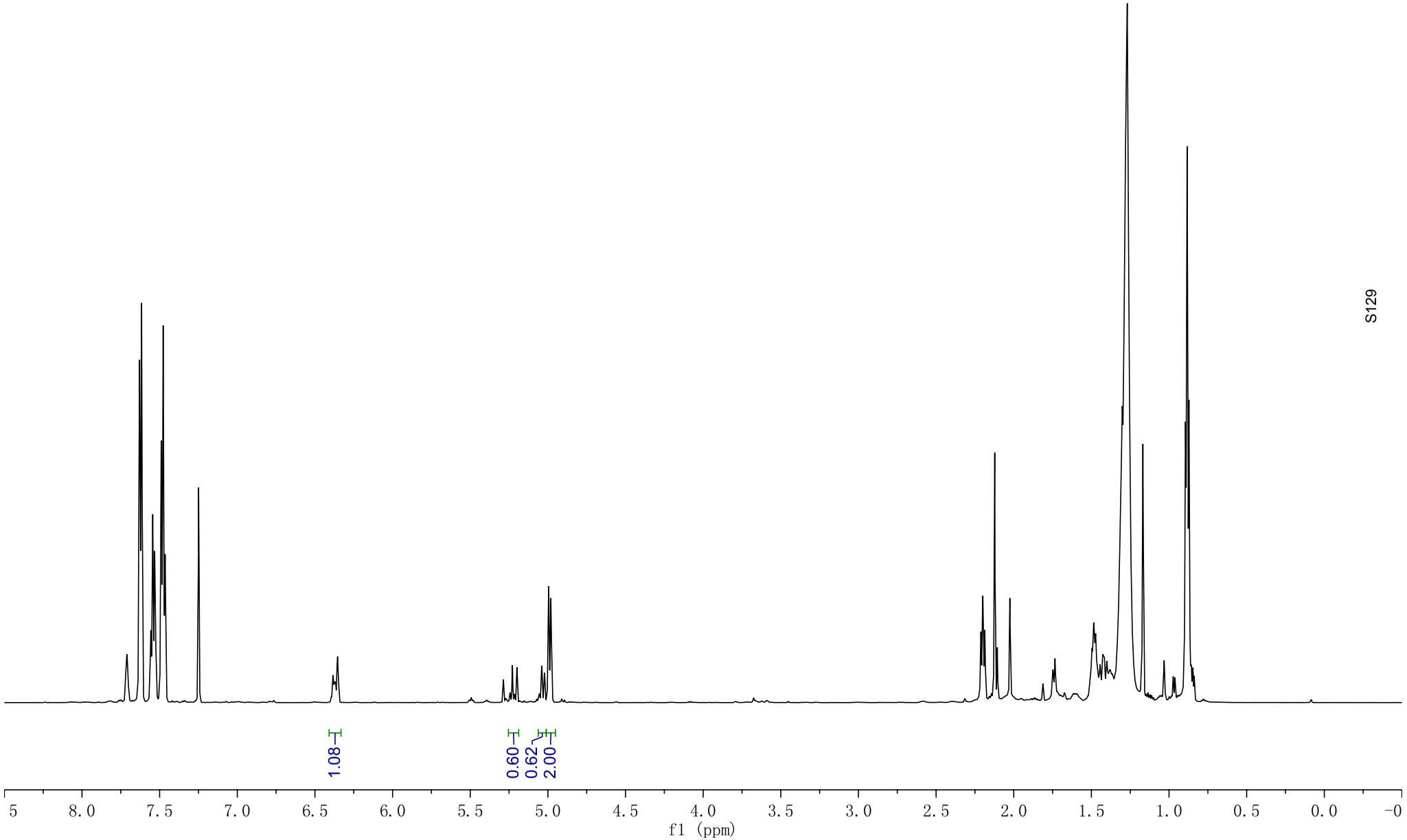



Parameters
Parameter Value (f2, f1)
Title wyz8-226-pro-NOESY
Solvent cdcl3
Relaxation Delay 1.0000
Me
R
7
R = n-C8H17
2% Au
95%
R
2q
Me
R
2q'
7.4 : 1 (E/Z = 1.8/1)
S128
f1 (ppm)
f2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

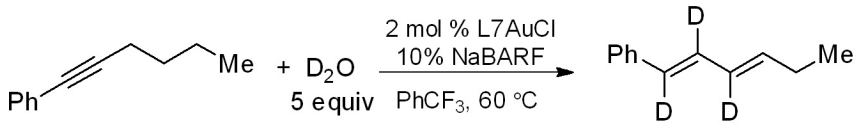
Parameter	Value
Title	wyz9-135-3-15h
Solvent	"cdcl3"
Relaxation Delay	25.0000
Spectrometer Frequency	599.64



1q-D (95% D)



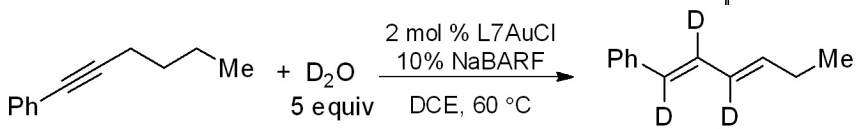
Parameter	Value
Title	wyz9-137-3
Solvent	"cdcl3"
Relaxation Delay	25.0000
Spectrometer Frequency	599.64



0.88 0.91 0.98 1.00

f1 (ppm)

Parameter	Value
Title	wyz9-137-4
Solvent	"cdcl3"
Relaxation Delay	25.0000
Spectrometer Frequency	599.64



S131

0.75 0.75 0.96 1.00 0.17 2.08

f1 (ppm)