Supporting Information

Tempering the Reactivities of α-Oxo Gold Carbenes by Bidentate Ligands: Implication of Tricoordinated Gold Intermediates and the Development of an Expedient [3+2] Assembly of 2,4-Disubstituted Oxazoles

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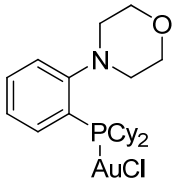
General. Ethyl acetate (ACS grade), hexanes (ACS grade), diethyl ether (ACS grade) and anhydrous 1, 2-dichloroethane (HPLC grade) were purchased from Fisher Scientific and used without further purification. Chlorobenzene (HPLC grade) was purchased from Acros without further purification. Methylene chloride and tetrahydrofuran were purified using MBraun Solvent Purifier. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using Sorbent Technologies' pre-coated silica gel plates. Flash column chromatography was performed over Sorbent Technologies' 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. 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.

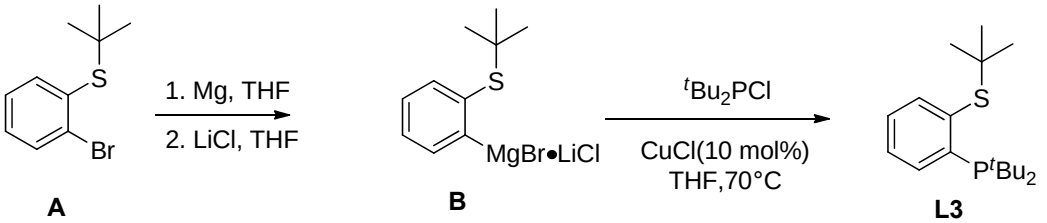
L1 is known compound and was prepared according to the literature procedure.[1]

L1AuCl



This complex was prepared quantitatively by stirring the ligand with an equivalent of Me_2SAuCl followed by simple concentration under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 7.2, 4.2 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 4.11-4.09 (m, 2H), 3.92-3.90 (m, 2H), 3.05-3.03 (m, 2H), 2.80 – 2.65 (m, 2H), 2.39 (q, *J* = 12.0 Hz, 2H), 2.08 (d, *J* = 12.0 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.73 (d, *J* = 8.0 Hz, 2H), 1.66 (d, *J* = 8.7 Hz, 2H), 1.57-1.48 (m, 4H), 1.34-1.27 (m, 4H), 1.25 – 1.10 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.11 , 136.27 , 133.05 (d, J_{PC} = 2.0 Hz), 126.42 (d, J_{PC} = 10.2 Hz), 125.76 (d, J_{PC} = 5.7 Hz), 124.60 (d, J_{PC} = 55.0 Hz), 66.80 , 54.72 , 36.20 (d, J_{PC} = 34.0 Hz), 30.86 (d, J_{PC} = 3.1 Hz), 30.09 , 26.57, (d, J_{PC} = 18.0 Hz), 26.52 (d, J_{PC} = 16.2 Hz), 25.58 .IR(cm^{-1}): 2929, 2852, 1569, 1449, 1180, 1114, 1002, 731. ESI $[M+Na]^{+}$: 614.16

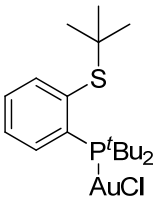
Di-*tert*-butyl-(2-tert-butylsulfanylphenyl)phosphine (L3):



A **B** **L3**

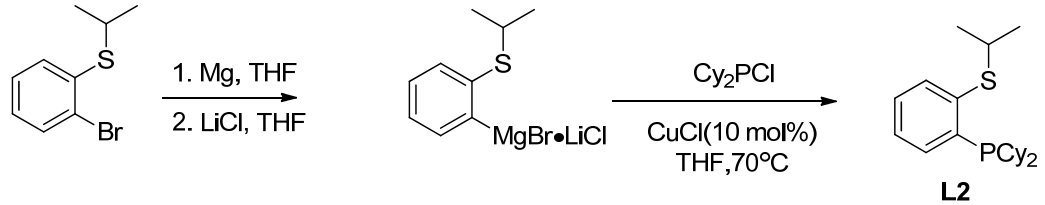
Under argon atmosphere a 10 mL Schlenk tube equipped with a magnetic stir bar was charged with Mg (2.2 mmol) and THF(0.5 mL). To this vigorously stirred mixture was added the aryl bromide **A** in THF (0.2 mL out of a 1.5 mL THF solution with 2 mmol of **A** dissolved). The Grignard reaction was initiated upon heating the reaction mixture to reflux, and the remaining aryl bromide **A** was added slowly while maintaining refluxing. Upon the completion of the addition, the reaction mixture was further stirred for 1 h at ambient temperature before the introduction of LiCl (2 mmol) under argon. The resulting mixture was stirred for 30 min at room temperature before the addition of $^{t}Bu_2PCl$ (1.8 mmol, 0.9 equiv) and CuCl (0.2 mmol, 0.1 equiv). The reaction was then stirred at 70 °C for 8 h. The reaction was quenched by the addition of aqueous NH_4OH, and the resulting mixture was extracted with diethyl ether. The combined organic layers were dried with Na_2SO_4 and concentrated under vacuum. The residue thus obtained was purified by silica gel flash column chromatography using a mixture of diethyl ether/pentane as the eluent to afford the the desired ligand in 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 1H), 7.66 (ddd, J = 6.2, 4.0, 2.2 Hz, 1H), 7.26 (q, J = 3.2 Hz, 2H), 1.39 (s, 9H), 1.21 (s, 9H), 1.18 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.11(d, J_{PC} = 23.8 Hz), 142.89 (d, J_{PC} = 32.5 Hz), 136.82 (d, J_{PC} = 3.3 Hz), 135.78 (d, J_{PC} = 2.7 Hz), 128.02 , 126.02 , 47.82 , 33.04 (d, J_{PC} = 26.2 Hz), 31.62 (d, J_{PC} = 1.1 Hz), 30.66 (d, J_{PC} = 15.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.42. IR(cm^{-1}):3393, 2961, 2894, 1643,1474, 1363, 1171, 1042, 808, 756. Found ESI $[M+H]^+$:311.15

L3AuCl



This complex was prepared quantitatively by stirring the ligand with an equivalent of Me_2SAuCl followed by simple concentration under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (td, J = 7.1, 2.0 Hz, 2H), 7.47 (t, J = 7.1 Hz, 2H), 1.50 (s, 9H), 1.42 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.87 (d, J_{PC} = 8.4 Hz), 139.87 (d, J_{PC} = 4.7 Hz), 134.54 (d, J_{PC} = 3.0 Hz), 132.09 (d, J_{PC} = 49.4 Hz), 130.38 , 127.40 , 51.93 , 37.75 (d, J_{PC} = 24.1 Hz), 31.48 , 30.75 (d, J_{PC} = 7.0 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ 61.40. IR(cm^{-1}): 2960, 2900, 2865, 1474, 1459, 1367, 1164, 916, 768, 730. ESI $[M+Na]^+$:565.13

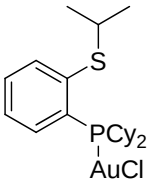
Dicyclohexyl-(2-isopropylsulfanylphenyl)phosphine (L2)



L2

This Ligand **L2** was prepared in 73% yield following the same procedure as that for **L3** except that Cy_2PCl was used instead of $^tBu_2PCl$. ^1H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.27 – 7.23 (m, 1H), 7.14 (t, J = 7.4 Hz, 1H), 3.49 (p, J = 6.6 Hz, 1H), 1.90 (q, J = 14.0, 10.5 Hz, 4H), 1.76 (d, J = 12.5 Hz, 2H), 1.64 (t, J = 14.9 Hz, 4H), 1.55 (d, J = 13.0 Hz, 2H), 1.32 (d, J = 6.7 Hz, 6H), 1.29 – 1.01 (m, 10H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.03 (d, J_{PC} = 28.7 Hz), 136.14 (d, J_{PC} = 16.2 Hz), 132.96 , 129.26 (d, J_{PC} = 4.8 Hz), 128.75 , 124.74 , 37.72 (d, J_{PC}= 9.3 Hz), 33.95 (d, J_{PC} = 13.9 Hz), 30.17 (d, J_{PC} = 16.2 Hz), 28.99 (d, J_{PC} = 9.0 Hz), 27.21(d, J_{PC} = 18.0 Hz), 27.14 (d, J_{PC} = 16.2 Hz), 26.37 , 22.81 .^{31}P NMR (162 MHz, $CDCl_3$) δ -12.43. . IR(cm^{-1}): 2924, 2850, 1639, 1446, 1365, 1236, 915, 745. Found ESI $[M+H]^+$: 349.19

L2AuCl



This complex was prepared quantitatively by stirring the ligand with an equivalent of Me_2SAuCl followed by simple concentration under vacuum. ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.56 (s, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.30 (s, 1H), 3.75 – 3.63 (m, 1H), 2.70 (s, 2H), 2.51 (s, 2H), 2.08 (d, J = 11.7 Hz, 2H), 1.86 (d, J = 10.9 Hz, 2H), 1.79 – 1.63 (m, 4H), 1.53 (s, 2H), 1.41 (d, J = 6.6 Hz, 6H), 1.37 – 1.11 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.20(br), 136.37(br), 133.07 (br), 131.42 , 127.20 (d, J_{PC} = 54.4 Hz), 126.18 , 41.01(br) , 35.18 (d, J_{PC} = 33.1 Hz), 30.93 , 29.26 , 26.48 (d, J_{PC} = 3.9 Hz), 26.39 (d, J_{PC} = 5.9 Hz), 25.55 , 22.67 . ^{31}P NMR (162 MHz, $CDCl_3$) δ (br, 54.16-36.62). IR(cm^{-1}):2929, 2853, 1448, 1239, 1202, 916, 731.ESI $[M+Na]^+$: 603.14

Gold-catalyzed synthesis of oxazole

General procedure A:

To a 3 dram vial containing 2 mL of chlorobenzene were added sequentially a carboxamide (0.2 mmol), an alkyne (0.3 mmol), Mor-DalPhosAuCl (0.01 mmol) and $NaBAr^F_4$ (0.02 mmol). The resulting mixture was stirred and heated to 60 ℃. To this vial a solution of 8-methylquinoline *N*-oxide (64 mg, 0.4 mmol) in 4 mL of chlorobenzene was then added via a syringe pump in 16 h. Upon completion, the reaction mixture was further stirred for 6 h before concentration under vacuum. The resulting residue was purified by silica gel flash chromatography.

General procedure B:

A solution of 8-methylquinoline *N*-oxide (96 mg, 0.6 mmol) in 4 ml of chlorobenzene was added by syringe pump within 16 h to a 60 ℃ solution of amide (0.2 mmol), alkyne (0.4 mmol), Mor-DalPhosAuCl (0.01 mmol) and $NaBAr^F_4$ (0.02 mmol) in 2

ml chlorobenzene. Upon completion, the reaction mixture was further stirred for 6 h before concentration under vacuum. The resulting residue was purified by silica gel flash chromatography.

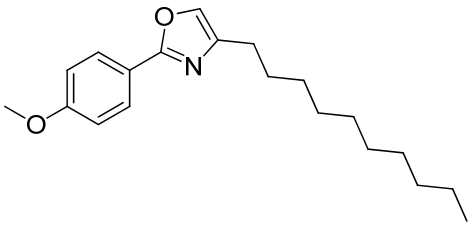
General procedure C:

A solution of 8-methylquinoline *N*-oxide (64 mg, 0.4 mmol) and an alkyne (0.3 mmol) in 4 ml of chlorobenzene was added by syringe pump within 16 h to a 60 ℃ solution of amide (0.2 mmol), Mor-DalPhosAuCl (0.01 mmol) and $NaBAr^F_4$ (0.02 mmol) in 2 ml chlorobenzene. Upon completion, the reaction mixture was further stirred for 6 h before concentration under vacuum. The resulting residue was purified by silica gel flash chromatography.

General procedure D:

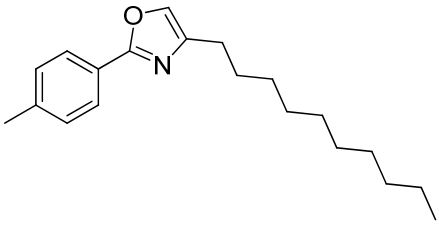
A solution of 8-methylquinoline *N*-oxide (64 mg, 0.4 mmol) in 4 ml of chlorobenzene was added via a syringe pump within 16 h to a 100 ℃ solution of amide (0.2 mmol), alkyne (0.3 mmol), Mor-DalPhosAuCl (0.01 mmol) and $NaBAr^F_4$ (0.02 mmol) in 2 ml chlorobenzene. Upon completion, the reaction mixture was further stirred for 6 h before concentration under vacuum. The resulting residue was purified by silica gel flash chromatography..

4-decyl-2-(4-methoxyphenyl)oxazole (3a)



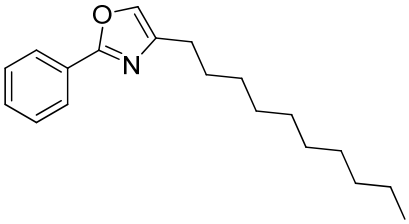
This compound was prepared in 81 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.9 Hz, 2H), 7.36 (s, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.42 – 1.22 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.38, 161.10, 142.34, 133.23, 127.89, 120.65, 114.07, 55.34, 31.90, 29.60, 29.58, 29.41, 29.32, 28.40, 26.53, 22.68, 14.11.; IR(neat): 3131, 3045, 2922, 2851, 1657, 1616, 1561, 1468, 1406, 1257, 1109, 1033.; MS(ES^+) Calculated for $[C_{20}H_{30}NO_2]^+$: 316.23; Found: 316.24.

4-decyl-2-(p-tolyl)oxazole (3b)



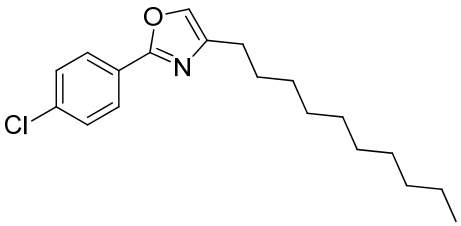
This compound was prepared in 79 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.38 (s, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.39 (s, 3H), 1.72 – 1.63 (m, 2H), 1.43 – 1.19 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.53, 142.41, 140.30, 133.49, 129.38, 126.24, 125.04, 31.90, 29.60, 29.57, 29.40, 29.32, 29.31, 28.40, 26.51, 22.68, 21.48, 14.11.; IR(neat): 3044, 2921, 2851, 1648, 1468, 1104, 1074, 913, 747, 726. MS(ES^+) Calculated for $[C_{20}H_{29}NNaO]^+$: 322.21; Found: 322.23.

4-decyl-2-phenyloxazole (3c)



This compound was prepared in 72 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.01 (m, 2H), 7.47 – 7.40 (m, 4H), 2.60 – 2.56 (m, 2H), 1.68 (m, 2H), 1.42 – 1.22 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.31, 142.62, 133.82, 130.04, 128.66, 127.76, 126.26, 31.90, 29.60, 29.58, 29.40, 29.32, 29.30, 28.40, 26.51, 22.68, 14.11.; IR(neat): 2926, 2854, 1642, 1590, 1553, 1487, 1449, 1345, 1102, 1062, 1025, 933, 777, 712.; MS(ES^+) Calculated for $[C_{19}H_{28}NO]^+$: 286.22; Found: 286.23.

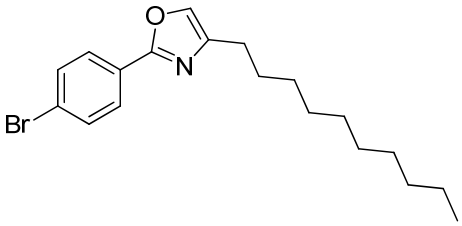
2-(4-chlorophenyl)-4-decyloxazole (3d)



This compound was prepared in 79 % yield according to the general procedure B. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.44 – 7.39 (m, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.42 – 1.19 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).; ^{13}C

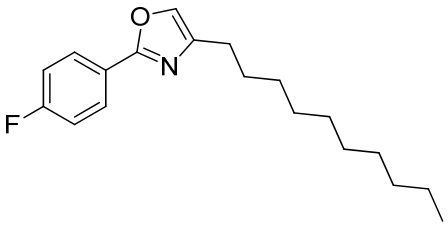
NMR (125 MHz, $CDCl_3$) δ 160.39, 142.82, 136.12, 134.06, 128.98, 127.53, 126.25, 31.89, 29.59, 29.56, 29.38, 29.31, 29.28, 28.37, 26.46, 22.67, 14.10.; IR(neat): 2922, 2851, 1468, 1405, 1092, 1065, 839, 736.; MS(ES^+) Calculated for $[C_{19}H_{27}ClNO]^+$: 320.18; Found: 320.19.

2-(4-bromophenyl)-4-decyloxazole (3e)



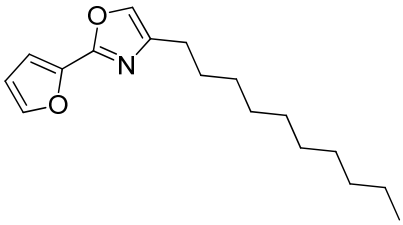
This compound was prepared in 73 % yield according to the general procedure B. ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.61 – 7.55 (m, 2H), 7.41 (s, 1H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.70 – 1.63 (m, 2H), 1.41 – 1.20 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.44, 142.85, 134.10, 131.93, 127.74, 126.66, 124.48, 31.89, 29.59, 29.56, 29.38, 29.31, 29.28, 28.37, 26.45, 22.67, 14.10.; IR(neat): 3135, 3046, 2921, 2850, 1666, 1467, 1401, 1107, 1077, 836, 758.; MS(ES^+) Calculated for $[C_{17}H_{27}BrNO]^+$: 364.13; Found: 364.14.

4-decyl-2-(4-fluorophenyl)oxazole (3f)



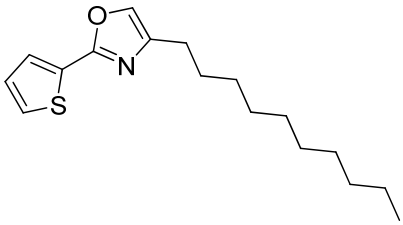
This compound was prepared in 60 % yield according to the general procedure A. ^1H NMR (500 MHz, $CDCl_3$) δ 8.03 – 7.98 (m, 2H), 7.39 (t, *J* = 1.0 Hz, 1H), 7.15 – 7.09 (m, 2H), 2.58 – 2.53 (m, 2H), 1.71 – 1.63 (m, 2H), 1.42 – 1.21 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.86, 162.87, 160.50, 142.64, 133.86, 133.85, 128.37, 128.30, 124.15, 124.12, 115.91, 115.74, 31.90, 29.60, 29.57, 29.39, 29.32, 29.29, 28.38, 26.47, 22.68, 14.11.; IR(neat): 3232, 2955, 2920, 2850, 1910, 1601, 1560, 1499, 1469, 1415, 1232, 1064, 935, 844, 738.; MS(ES^+) Calculated for $[C_{19}H_{26}FNNaO]^+$: 326.19; Found: 326.20.

4-decyl-2-(furan-2-yl)oxazole (3g)



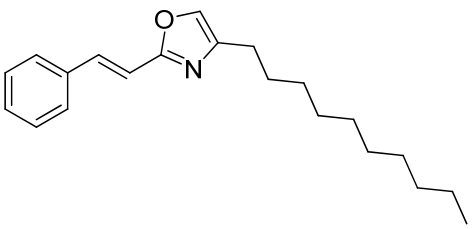
This compound was prepared in 73 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.36 (t, *J* = 1.0 Hz, 1H), 6.97 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.8 Hz, 1H), 2.58 – 2.53 (m, 2H), 1.70 – 1.63 (m, 2H), 1.40 – 1.22 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.16, 144.11, 143.18, 142.44, 133.31, 111.71, 110.92, 31.89, 29.59, 29.56, 29.37, 29.32, 29.26, 28.31, 26.35, 22.68, 14.11.; IR(neat): 3042, 3039, 2926, 2855, 1636, 1589, 1539, 1450, 1405, 1107, 1010, 895, 741.; MS(ES^+) Calculated for $[C_{17}H_{25}NNaO_2]^+$: 298.18; Found: 298.18.

4-decyl-2-(thiophen-2-yl)oxazole (3h)



This compound was prepared in 73 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.39 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.34 (s, 1H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 2.55 (t, *J* = 7.5 Hz, 2H), 1.74 – 1.60 (m, 2H), 1.42 – 1.19 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.49, 142.61, 133.25, 130.32, 127.85, 127.82, 127.36, 31.89, 29.59, 29.56, 29.38, 29.31, 29.28, 28.35, 26.43, 22.67, 14.10.; IR(neat): 2926, 2854, 1593, 1466, 1425, 1371, 1093, 1004, 853, 703.; MS(ES^+) Calculated for $[C_{17}H_{25}NNaOS]^+$: 314.16; Found: 314.17.

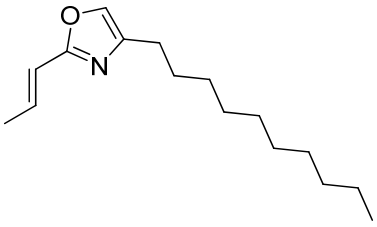
(E)-4-decyl-2-styryloxazole (3i)



This compound was prepared in 79 % yield according to the general procedure A. ^{1}H

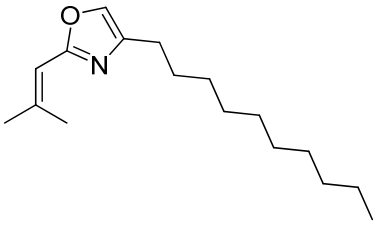
NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.4 Hz, 2H), 7.47 (d, *J* = 16.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.30 (m, 2H), 6.92 (d, *J* = 16.4 Hz, 1H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.70 – 1.62 (m, 2H), 1.42 – 1.20 (m, 13H), 0.88 (t, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.16, 142.65, 135.63, 135.53, 133.52, 129.00, 128.83, 127.08, 114.11, 31.91, 29.60, 29.57, 29.40, 29.33, 29.29, 28.39, 26.41, 22.69, 14.12.; IR(neat): 3106, 2948, 2922, 2866, 2851, 1590, 1526, 1466, 1447, 967, 752.; MS(ES^+) Calculated for $[C_{21}H_{295}NNaO]^+$: 334.21; Found: 334.23.

(E)-4-decyl-2-(prop-1-en-1-yl)oxazole (3j)



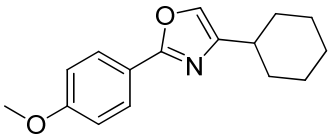
This compound was prepared in 55 % yield according to the general procedure A. ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (s, 1H), 6.67 (dq, *J* = 15.8, 6.9 Hz, 1H), 6.27 (dd, *J* = 15.9, 1.7 Hz, 1H), 2.48 (t, *J* = 7.6 Hz, 2H), 1.91 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.65 – 1.57 (m, 2H), 1.37 – 1.19 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.89, 141.84, 134.50, 132.86, 118.06, 31.89, 29.58, 29.55, 29.38, 29.31, 29.26, 28.35, 26.34, 22.67, 18.38, 14.10.; IR(neat): 3098, 2959, 2923, 2852, 1718, 1531, 1464, 1405, 1240, 926.; MS(ES^+) Calculated for $[C_{16}H_{17}NNaO]^+$: 272.20; Found: 272.21.

4-decyl-2-(2-methylprop-1-en-1-yl)oxazole (3k)



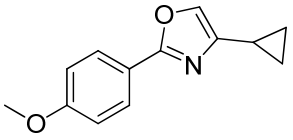
This compound was prepared in 95 % yield according to the general procedure A. ^1H NMR (400 MHz, cdcl$_3$) δ 7.24 (s, 1H), 6.07 (s, 1H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.17 (s, 3H), 1.93 (s, 3H), 1.68 – 1.54 (m, 2H), 1.39 – 1.16 (m, 14H), 0.87 (t, *J* = 6.8 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.30, 144.97, 141.58, 132.14, 112.01, 31.89, 29.59, 29.56, 29.39, 29.31, 29.28, 28.35, 27.11, 26.40, 22.67, 20.31, 14.08.; IR(neat): 2926, 2855, 1721, 1660, 1592, 1546, 1523, 1455, 1377, 1358, 1260, 1104, 983, 837, 800, 738.; MS(ES^+) Calculated for $[C_{17}H_{29}NNaO]^+$: 286.21; Found: 286.23.

4-cyclohexyl-2-(4-methoxyphenyl)oxazole (3l)



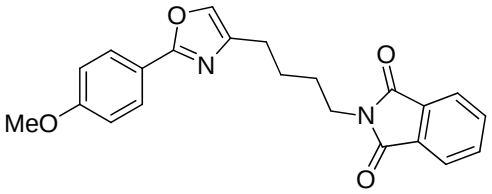
This compound was prepared in 83 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 1H), 7.31 (s, 1H), 6.97 – 6.91 (m, 1H), 3.84 (s, 1H), 2.62 – 2.50 (m, 1H), 2.09 (t, *J* = 11.7 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.77 – 1.68 (m, 1H), 1.46 – 1.32 (m, 4H), 1.32 – 1.20 (m, 1H).; ^{13}C NMR (125MHz, $CDCl_3$) δ 161.22, 161.04, 147.61, 132.02, 127.90, 120.77, 114.03, 55.32, 36.09, 32.09, 26.16, 26.10.; IR(neat): 2927, 2853, 1614, 1588, 1500, 1464, 1449, 1422, 1344, 1305, 1254, 1172, 1031, 837.; MS(ES^+) Calculated for $[C_{16}H_{20}NO_2]^+$: 258.15; Found: 258.14.

4-cyclopropyl-2-(4-methoxyphenyl)oxazole (3m)



This compound was prepared in 63 % yield according to the general procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.91 (m, 2H), 7.36 (s, 1H), 6.97 – 6.91 (m, 2H), 1.87 – 1.79 (m, 1H), 0.93 – 0.86 (m, 2H), 0.83 – 0.76 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.39, 161.09, 144.00, 132.64, 127.91, 120.62, 114.04, 55.34, 7.14, 6.42.; IR(neat): 3007, 2961, 1615, 1501, 1253, 1172, 1028, 746.; MS(ES^+) Calculated for $[C_{13}H_{14}NO_2]^+$: 216.10; Found: 216.11.

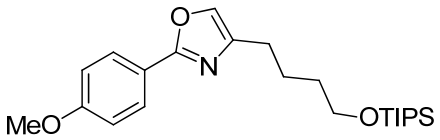
2-(4-(2-(4-methoxyphenyl)oxazol-4-yl)butyl)isoindoline-1,3-dione (3n)



This compound was prepared in 82 % yield according to the general procedure C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.90 (m, 2H), 7.83 (td, *J* = 5.3, 2.1 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.38 (d, *J* = 0.9 Hz, 1H), 6.96 – 6.91 (m, 2H), 3.85 (s, 3H), 3.73 (t, *J* = 6.5 Hz, 2H), 2.61 (t, *J* = 7.1 Hz, 2H), 1.82 – 1.70 (m, 4H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.42, 161.51, 161.13, 141.46, 133.85, 133.49, 132.13, 127.92, 123.17, 120.55, 114.07, 55.35, 37.70, 28.12, 25.92, 25.68.; IR(neat): 2940, 2862, 1770, 1710,

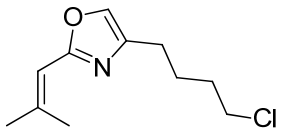
1614, 1500, 1397, 1172, 1032, 838, 720.; MS(ES^+) Calculated for $[C_{22}H_{20}N2NaO_4]^+$: 399.13; Found: 399.14.

2-(4-methoxyphenyl)-4-(4-((triisopropylsilyl)oxy)butyl)oxazole (3o)



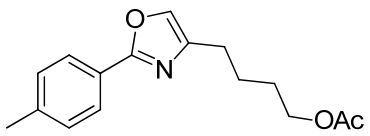
This compound was prepared in 71 % yield according to the general procedure C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.37 (s, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.77 – 3.68 (m, 2H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.68 – 1.60 (m, 2H), 1.08 – 1.03 (m, 21H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.40, 161.11, 142.15, 133.32, 127.89, 120.62, 114.06, 63.14, 55.32, 32.57, 26.32, 24.66, 18.03, 12.00.; IR(neat): 2943, 2893, 2866, 1615, 1589, 1501, 1463, 1442, 1304, 1254, 1172, 1069, 1032, 883.; MS(ES^+) Calculated for $[C_{23}H_{37}NNaO_3Si]^+$: 426.24; Found: 426.26.

4-(4-chlorobutyl)-2-(2-methylprop-1-en-1-yl)oxazole (3p)



This compound was prepared in 71 % yield according to the general procedure C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.07 (dt, *J* = 2.5, 1.2 Hz, 1H), 3.56 (t, *J* = 6.4 Hz, 2H), 2.57 – 2.53 (m, 2H), 2.18 (s, 3H), 1.94 (s, 3H), 1.88 – 1.75 (m, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.49, 145.39, 140.72, 132.36, 111.88, 44.79, 32.06, 27.15, 25.66, 25.56, 20.35.; IR(neat): 2937, 1723, 1659, 1592, 1545, 1522, 1447, 1377, 1278, 1103, 840, 799, 744.; MS(ES^+) Calculated for $[C_{11}H_{17}ClNO]^+$: 214.10; Found: 214.10.

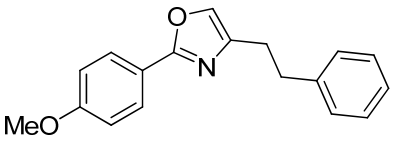
4-(2-(p-tolyl)oxazol-4-yl)butyl acetate (3q)



This compound was prepared in 73 % yield according to the general procedure D. ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 0.9 Hz, 1H), 7.26 – 7.23 (m, 2H), 4.10 (t, *J* = 6.2 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.05 (s,

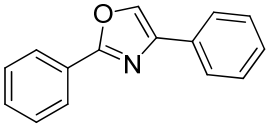
3H), 1.83 – 1.68 (m, 4H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.17, 161.72, 141.69, 140.40, 133.66, 129.40, 126.24, 124.95, 64.25, 28.21, 26.04, 24.90, 21.48, 21.00.; IR(neat): 2966, 2929, 1722, 1473, 1431, 1409, 1118, 1071, 1050, 935, 827, 729.; MS(ES^+) Calculated for $[C_{16}H_{19}NNaO_3]^+$: 296.13; Found: 296.14.

2-(4-methoxyphenyl)-4-phenethyloxazole (3r)



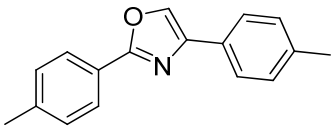
This compound was prepared in 67 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 2H), 7.34 – 7.17 (m, 6H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.06 – 2.97 (m, 2H), 2.94 – 2.86 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.49, 161.19, 141.37, 141.28, 133.65, 128.43, 128.36, 127.94, 126.00, 120.55, 114.12, 55.36, 34.64, 28.30.; IR(neat): 3027, 2933, 2838, 1614, 1500, 1254, 1172, 1029, 837, 746.; MS(ES^+) Calculated for $[C_{18}H_{17}NNaO_2]^+$: 302.12; Found: 302.13.

2,4-diphenyloxazole (3s)



This compound was prepared in 70 % yield according to the general procedure A. ^{1}H NMR (600 MHz, $cdcl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.97 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.46 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 10.8, 3.9 Hz, 1H).; ^{13}C NMR (151 MHz, $cdcl_3$) δ 161.91, 141.99, 133.40, 131.11, 130.37, 128.73, 128.72, 128.09, 127.49, 126.49, 125.62.; IR(neat): 3156, 3066, 3043, 2925, 1727, 1657, 1554, 1488, 1448, 1340, 1124, 1070, 930, 783.; MS(ES^+) Calculated for $[C_{1521}NO]^+$: 222.09; Found: 222.10.

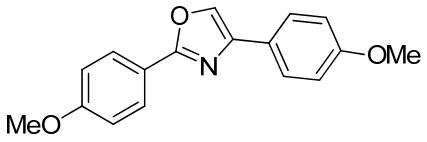
2,4-di-p-tolyloxazole (3t)



This compound was prepared in 63 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.28 (d,

J = 7.9 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.94, 141.88, 140.58, 137.85, 132.69, 129.43, 129.39, 128.37, 126.45, 125.51, 124.88, 21.54, 21.32.; IR(neat): 3135, 3029, 2919, 1649, 1505, 1444, 1413, 1108, 1076, 932, 735.; MS(ES$^+$) Calculated for $[C_{17}H_{16}NO]^+$: 250.12; Found: 250.14.

2,4-bis(4-methoxyphenyl)oxazole (3u)



This compound was prepared in 53 % yield according to the general procedure A. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.9 Hz, 2H), 7.83 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 2H), 6.97 (dd, *J* = 12.0, 8.8 Hz, 5H), 3.87 (s, 3H), 3.85 (s, 3H).; ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.85, 161.30, 159.48, 141.55, 131.86, 128.12, 126.90, 124.00, 120.44, 114.13, 114.07, 55.37, 55.32.; IR(neat): 3042, 2964, 2841, 1648, 1611, 1505, 1254, 1171, 1109, 1027, 836, 746.; MS(ES$^+$) Calculated for $[C_{17}H_{16}NO_3]^+$: 282.11; Found: 282.13.

DFT studies.

Calculation details. To get more information about the possible tricoordinated gold complex, density functional theory (DFT)[2] studies have been performed with GAUSSIAN09[3] program at PBE1PBE[4]/6-311+G**/SDD[5] level. Our test calculation shows that this method can reproduce the structure of Mor-DalPhosAuCl in good quality compared with the X-ray data.

1. The tricoordinated gold complex.

To understand the influence of the coordination of the N atom to the gold center, model **D** is used as a benchmark to compare with, it is a "non-coordinated model" in which the N-Au distance is fixed to 2.930Å, the same as that in the Mor-DalPhosAuCl crystal. The tricoordinated gold complex **E** is fully optimized.

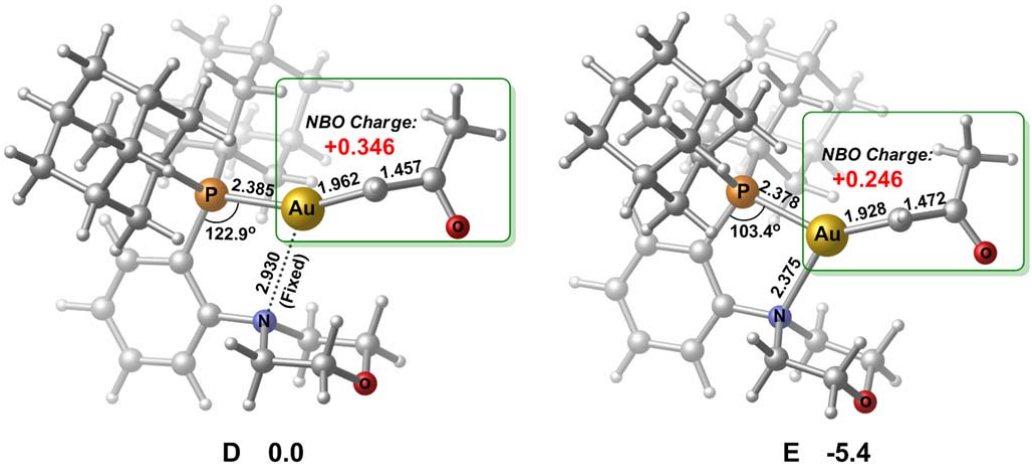


Figure S1. The partially optimized structure **D** with fixed Au-N distance of 2.930Å and the fully optimized structure **E**. The selected bond lengths are in angstroms, bond angles are in degrees. The relative energies ΔE are in kcal/mol. Calculated at PBE1PBE/6-311+G** level.

The results in Figure S1 show that **E** is 5.4 kcal/mol stable than **D**, indicating the coordination of the N atom is favorable in energy. The NBO charge of the metal carbene moiety in **D** is +0.346, whereas in **E** the charge decreased to +0.246. Apparently, the coordination of the N atom donates more electrons to the metal carbene moiety. Consequently, the Au-C bond becomes stronger, its bond length decrease from 1.962 to 1.928 Å. The P-Au bond length in **E** is slightly shorter than in **D**, this may results from a better coordination angle of the lone pair of the P atom.

2. The test calculation.

The optimized structure (Figure S2) shows that PBE1PBE method can produce reliable results. The difference between the calculated and experimental (from X-ray data) bond length of C-P, P-Au, and Au-Cl are 0.011, 0.035 and 0.009 Å, respectively. For the N-Au distance, the difference is 0.090 Å, this result is not bad for a long distance weak interaction. The calculated and experimental C-P-Au angle are also quite close.

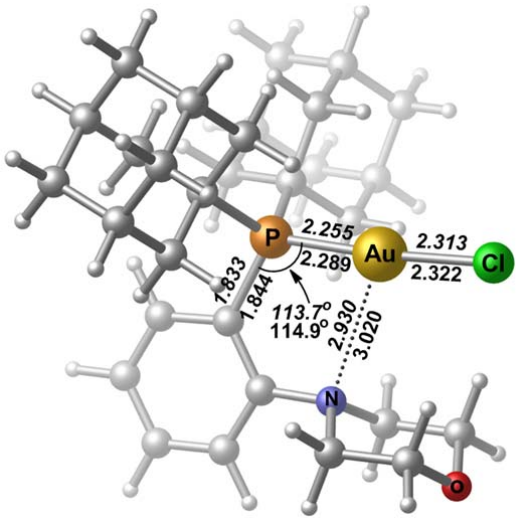


Figure S2. The optimized structure of Mor-DalPhosAuCl. The bond lengths (in angstroms) and bond angle (in degrees) in italic are taken from the X-ray data. Calculated at PBE1PBE/6-311+G** level.

3. Calculated total energies and geometry coordinates.

D

SCF Done: E(RPBE1PBE) = -1965.79170067 A.U.

Au,-0.18715482 93,-1.4649363403,-0.4209405787
P,0.7296738659,0.6694921066,0.117550828 4
O,2.5816728697,-4.6779721531,-0.1971512543
N,2.6501657999,-1.8651976 757,0.1908619413
C,2.5303750643,0.6028591718,0.4789290481
C,3.26027058 61,-0.5977118363,0.4851174586
C,4.6270502956,-0.5653642547,0.773131903
C,5.2838142804,0.6241701494,1.0416780269
C,4.5726386117,1.8165033166, 1.0243914677
C,3.2148992619,1.7977731469,0.7487012736
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H,2.1054967469,-4.827605 9783,1.7569402498
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H,-1.6867883138,1.774698374 1,-1.3125934059
H,-2.0535346516,2.087756464,-3.7195781756
H,-0.1087207 641,2.4231654039,-5.2563497011
H,-0.0868435426,0.8102432785,-4.5488865 412
H,-1.7183809345,4.1222842676,-2.328290813
H,-1.0727715164,4.375377 3011,-3.9471856397
C,-1.5241505135,-2.7978959742,-0.9540694367
C,-2.25 94518893,-3.700921199,-0.0785749251
H,-1.7492740349,-2.9800479222,-2.0 10847871
O,-1.6268949873,-4.7415745207,-0.1403212621
C,-3.4627476962,- 3.4276238986,0.735187909
H,-3.268194235,-2.588128135,1.409679729
H,-4. 288154711,-3.1303265225,0.0794802117
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E

SCF Done: E(RPBE1PBE) = -1965.80027834 A.U.

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C,4.5283000952,-0.6830575636,0.7761200773
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C,2.4856352944,-2.7747933032,1.3549834305
C,1.921242653,-4.1403376837,1.0074598692
C,2.4586920582,-3.8994697599,-1.2266966276
C,3.0493251035,-2.5207197616,-0.9987401078
C,-0.0940671258,1.303995464,1.7286462705
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C,0.4796653881,1.8149005269,-1.3782626118
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C,1.380921263,2.220999225,-3.6981786551
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C,-1.0811028987,2.279508869,-3.3052697479
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Mor-DalPhosAuCl

SCF Done: E(RPBE1PBE) = -2234.39856016 A.U.

Au,0.133879 2682,-1.4131533081,-0.4207077787
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P,0.4718010946,0.7952463059,0.0791343319
O,3.9173046664,-3.734 6397448,-0.2326011066
N,3.1018606553,-1.0264144074,-0.0161674506
C,2.2 401748472,1.2927530986,0.2379775458
C,3.3082003669,0.3762057736,0.1695 571768
C,4.618641751,0.8527958293,0.2937494838
C,4.898366071,2.1967248 067,0.4717488244
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References:

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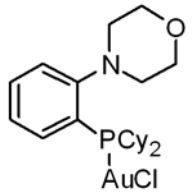
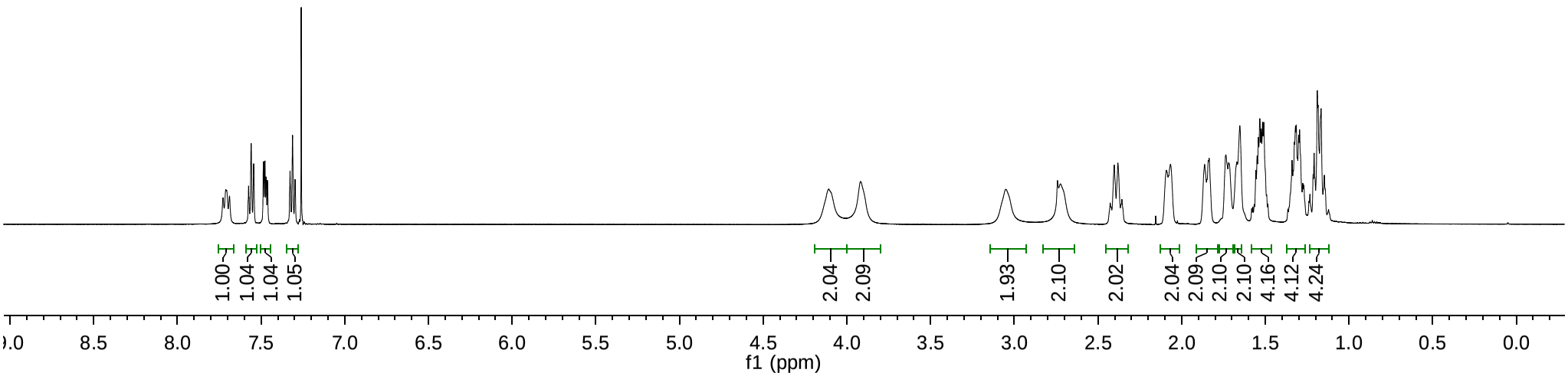
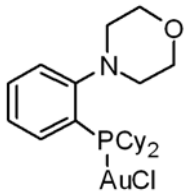
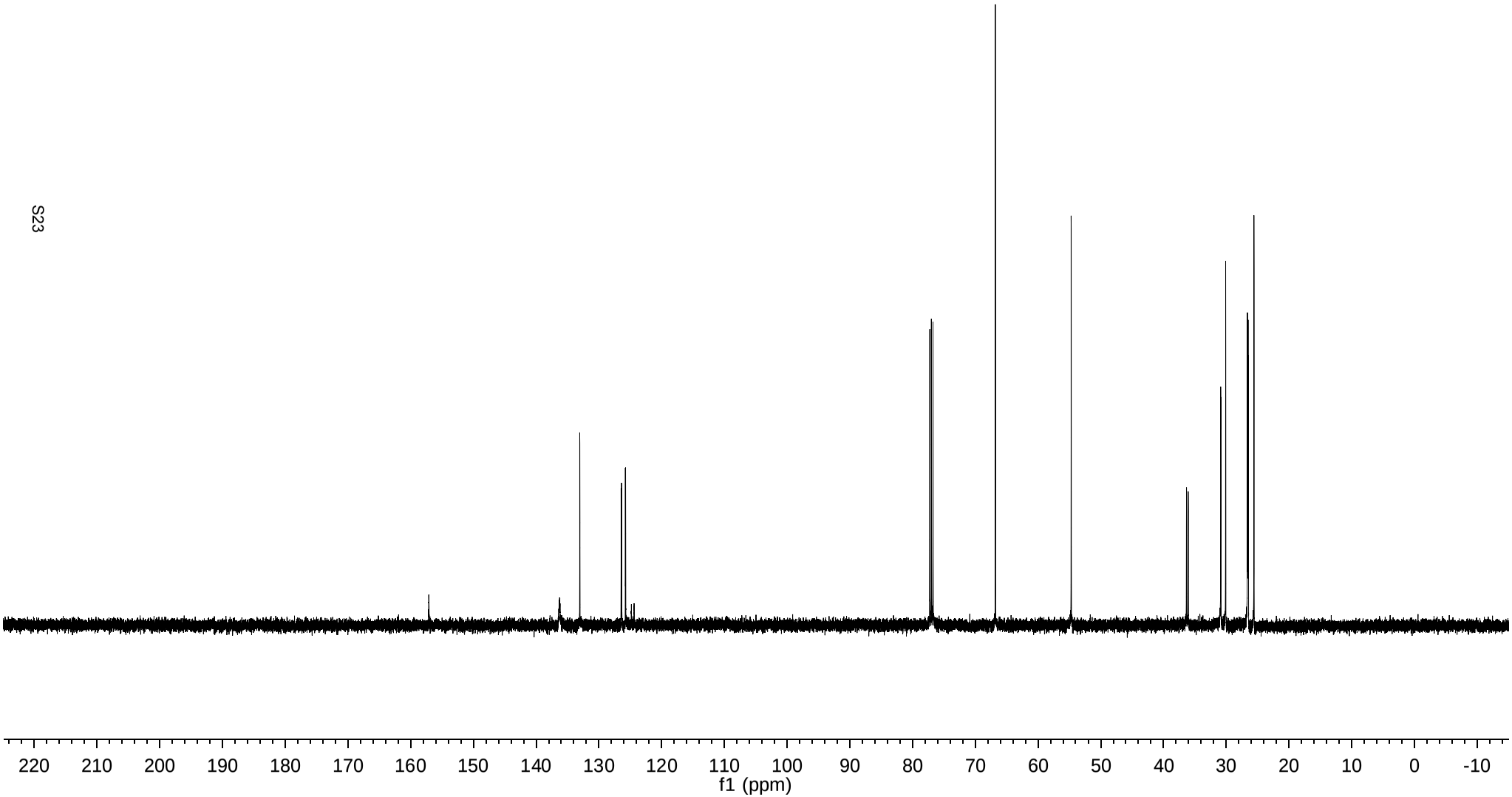
Title jkg-III-166C-1-H
Solvent CDCl3
Spectrometer Frequency 499.86



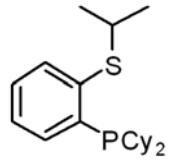


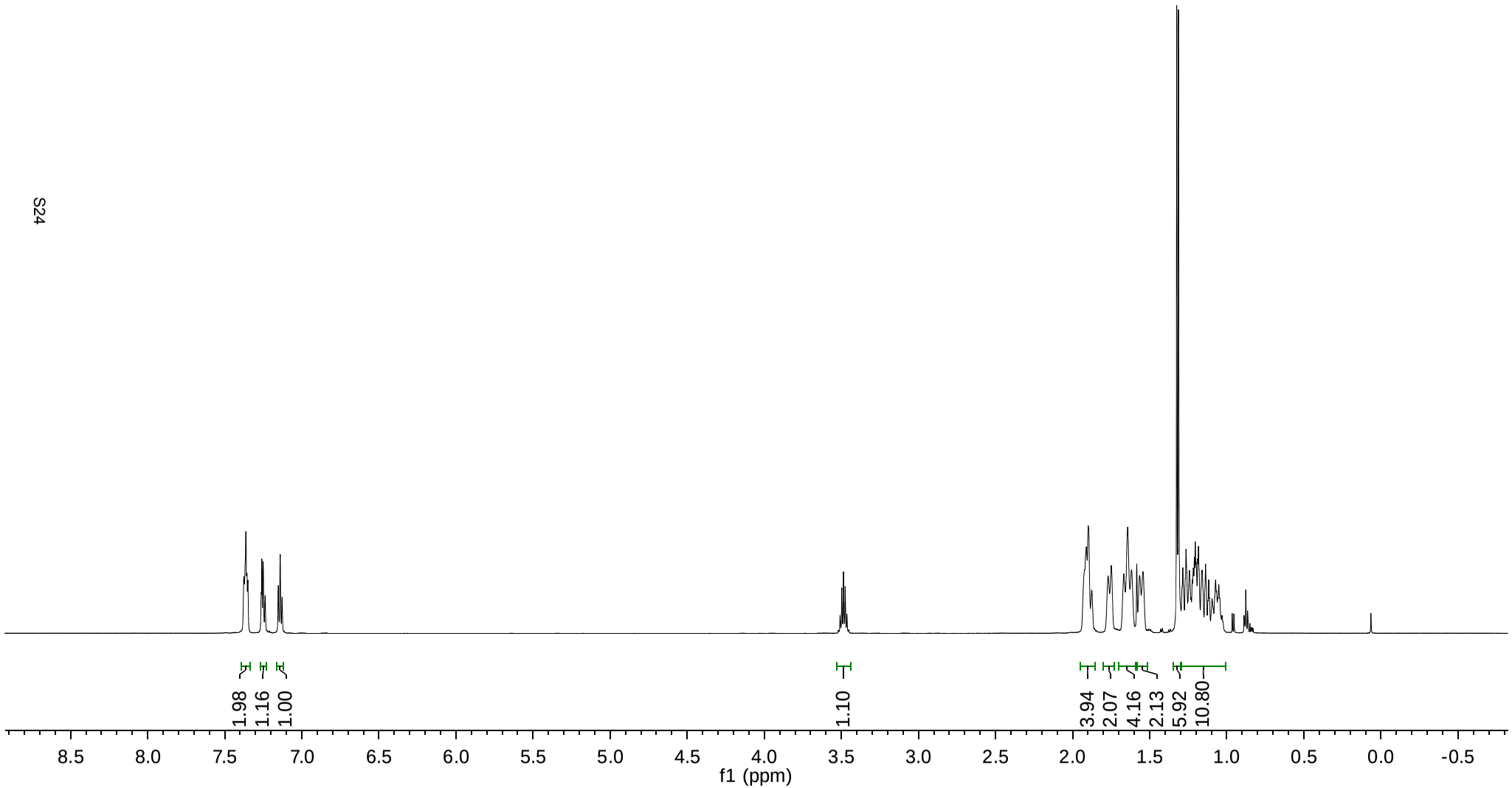
Title jkg-III-166C-1-C
Solvent CDCl3
Spectrometer Frequency 125.70





Title jkg-III-164-B-H
Solvent cdcl3
Spectrometer Frequency 599.63





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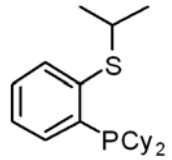
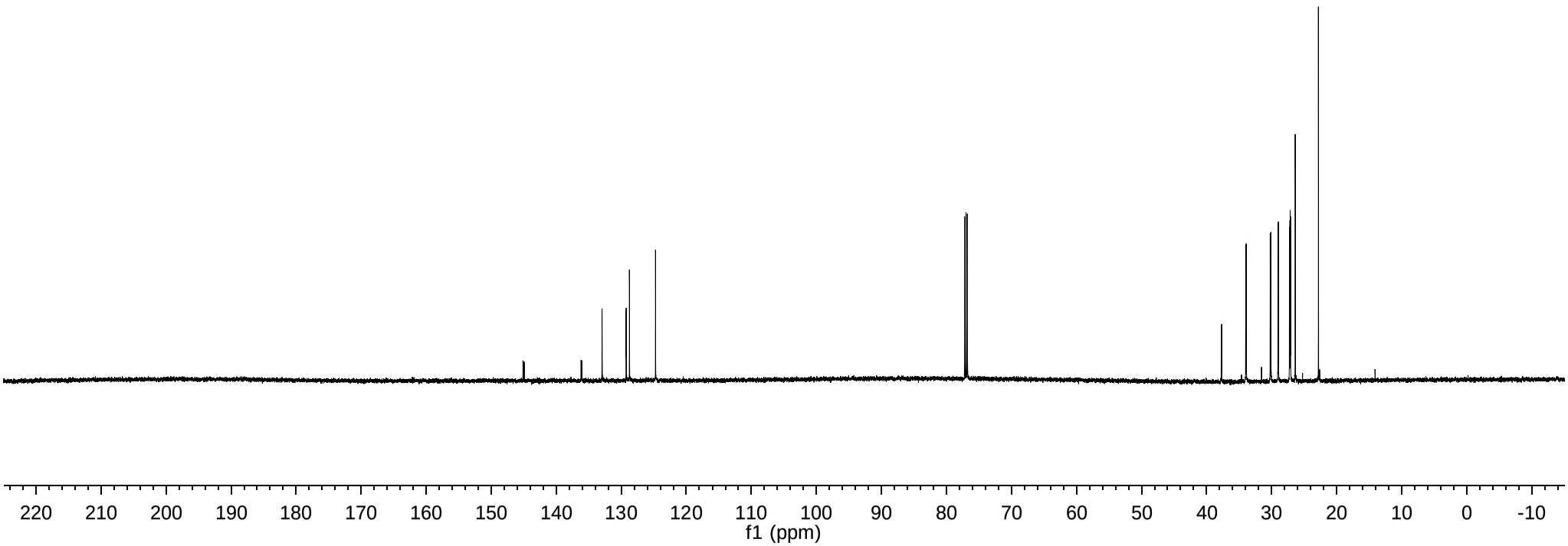
Solvent	cdcl3
Spectrometer Frequency	150.79





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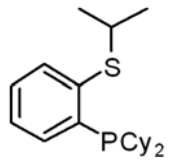
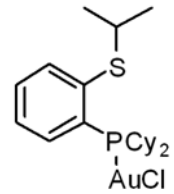
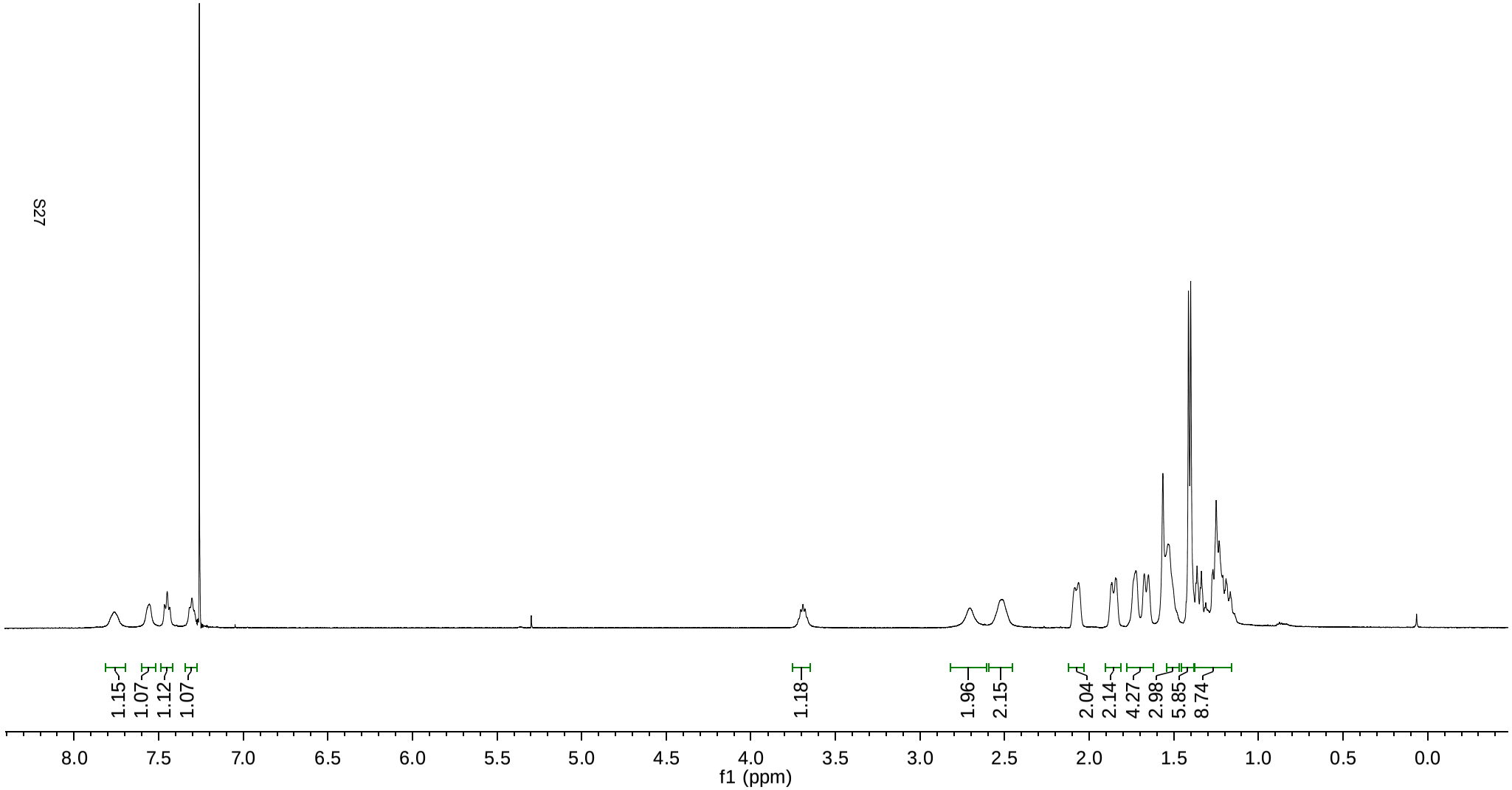
Solvent cdcl3
Spectrometer Frequency 161.90



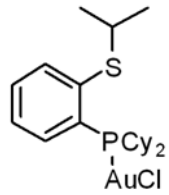
Title jkg-III-166-B-H
Solvent CDCl3
Spectrometer Frequency 499.86



S27



Title jkg-III-166B-C
Solvent cdcl3
Spectrometer Frequency 150.79



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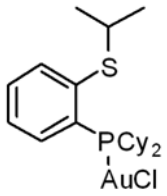
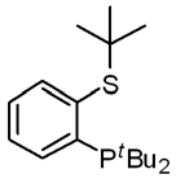
f1 (ppm)

Title jkg-III-166B-P-1
Solvent cdcl3
Spectrometer Frequency 161.90



Title jkg-III-118-H
Solvent CDCl3
Spectrometer Frequency 499.86



S30

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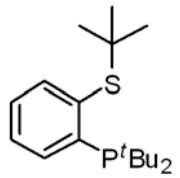
f1 (ppm)

Title jkg-III-118-C
Solvent CDCl3
Spectrometer Frequency 125.70



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Title jkg-III-118-P
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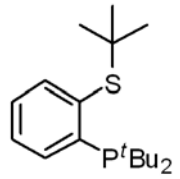

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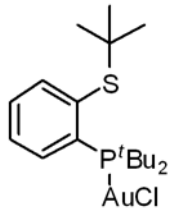
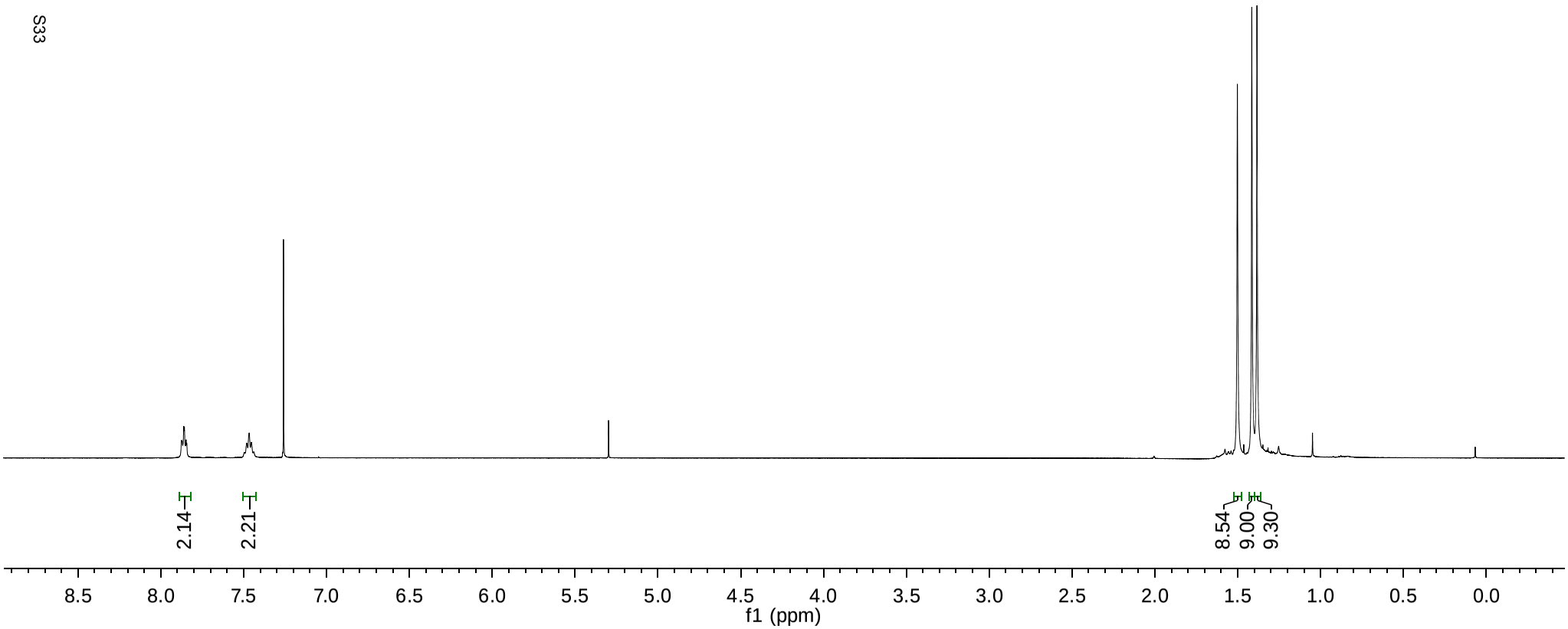
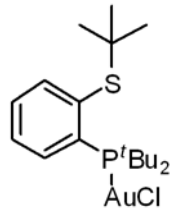


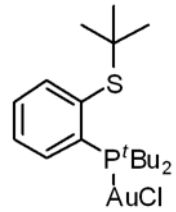
S33



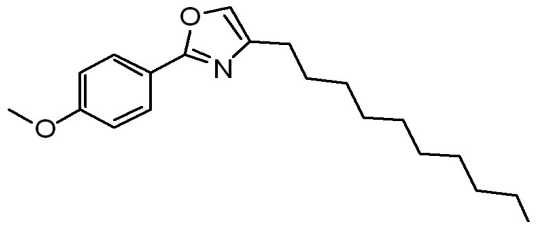
Title jkg-III-119-C
Solvent CDCl3
Spectrometer Frequency 125.70



Title jkg-III-119-P
Solvent cdcl3
Spectrometer Frequency 161.90



Title lyd-3-144-2proafterptlc
Solvent CDCl3
Spectrometer Frequency 499.86



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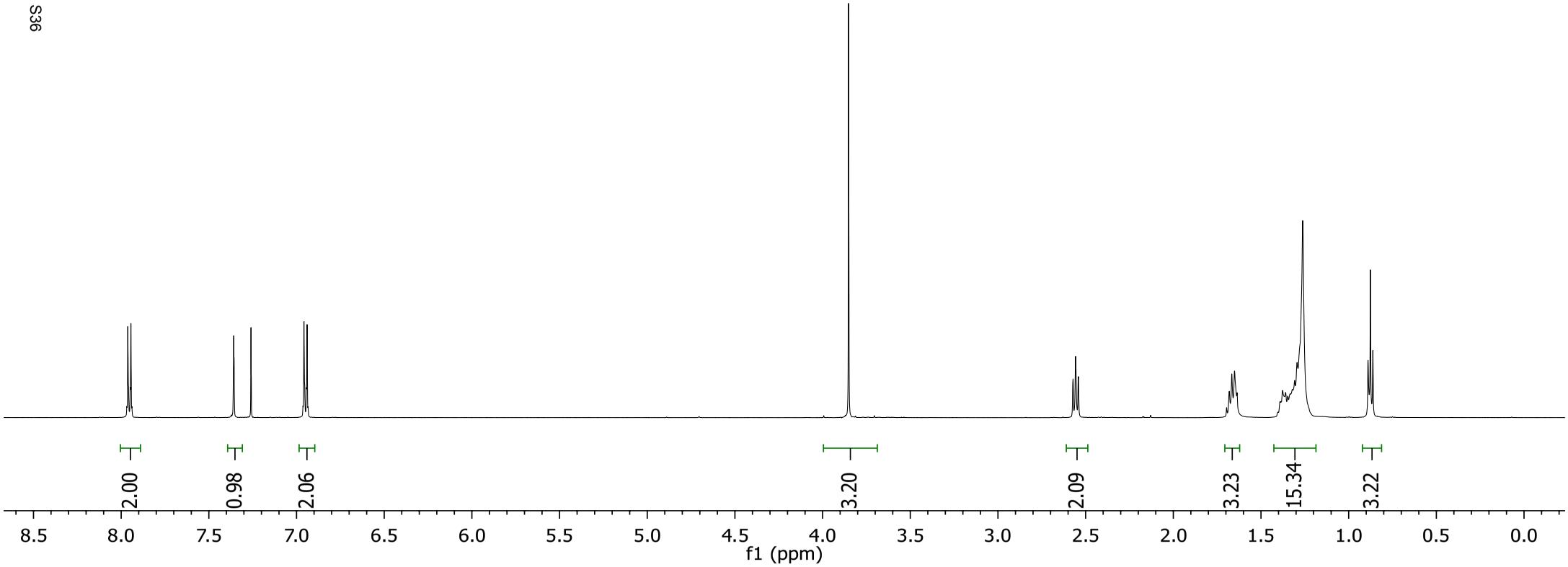
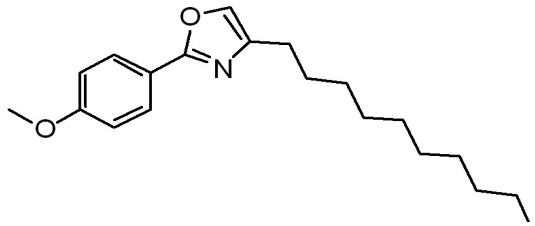


Title lyd-3-144-2proafterptlc-c
Solvent CDCl3
Spectrometer Frequency 125.70



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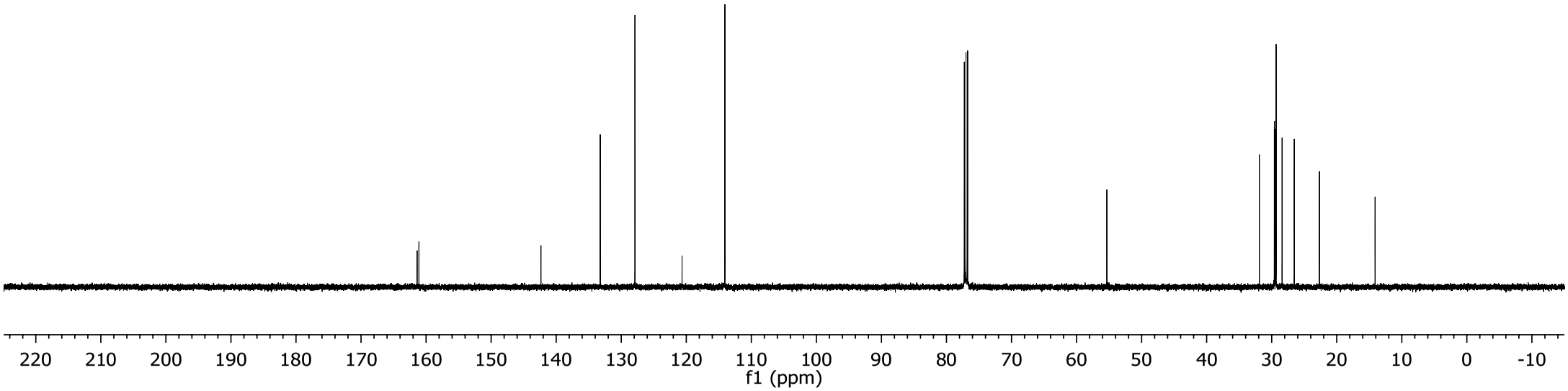
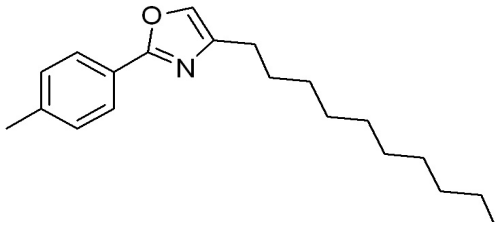


lyd-3-06152012pure

Parameter	Value
1 Title	lyd-3-06152012pure
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



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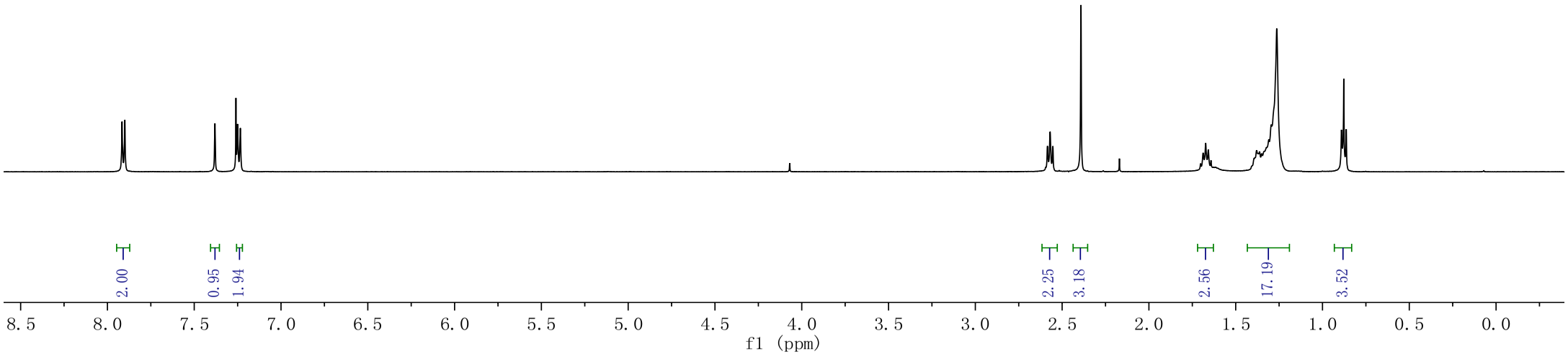
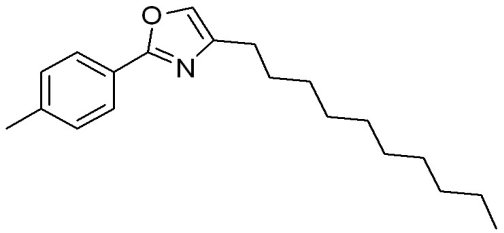


lyd-3-06152012-C
Std carbon



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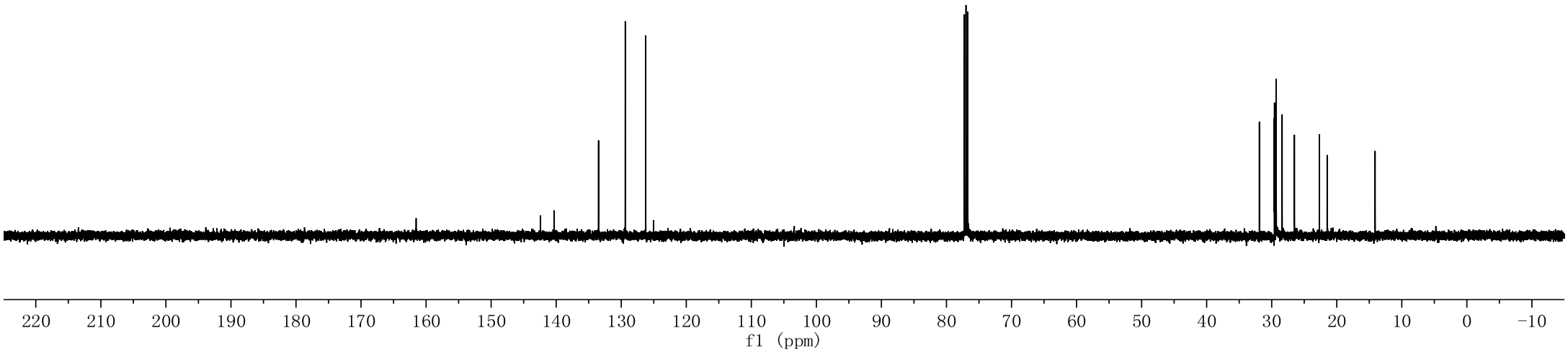
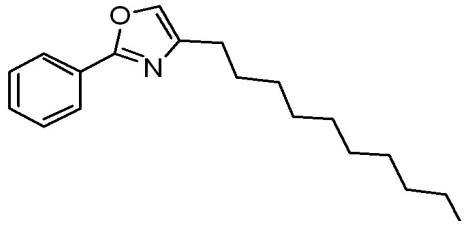
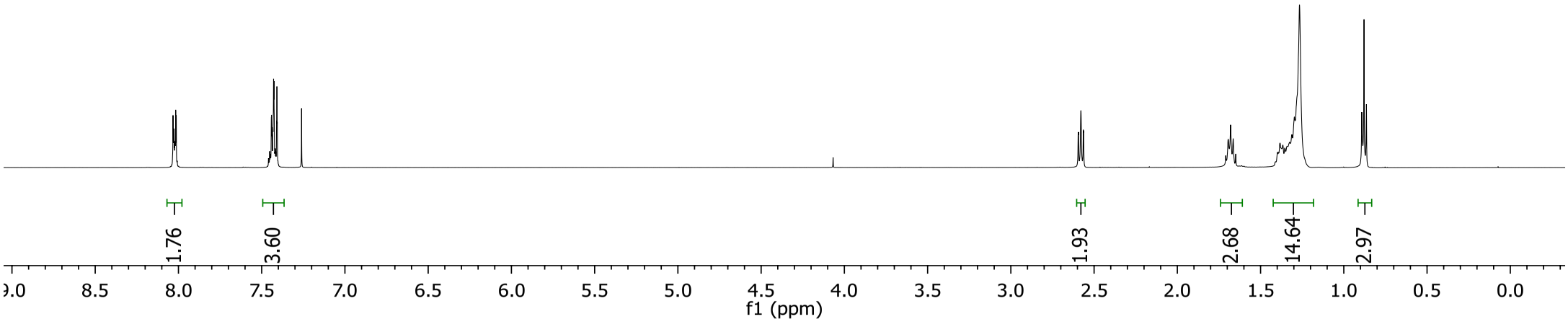


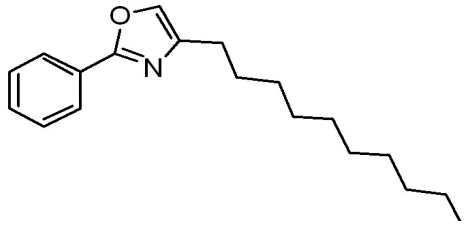
Title lyd-3-204
Solvent CDCl3
Spectrometer Frequency 499.86



3c



Title lyd-3-204-c-2
Solvent CDCl3
Spectrometer Frequency 125.70



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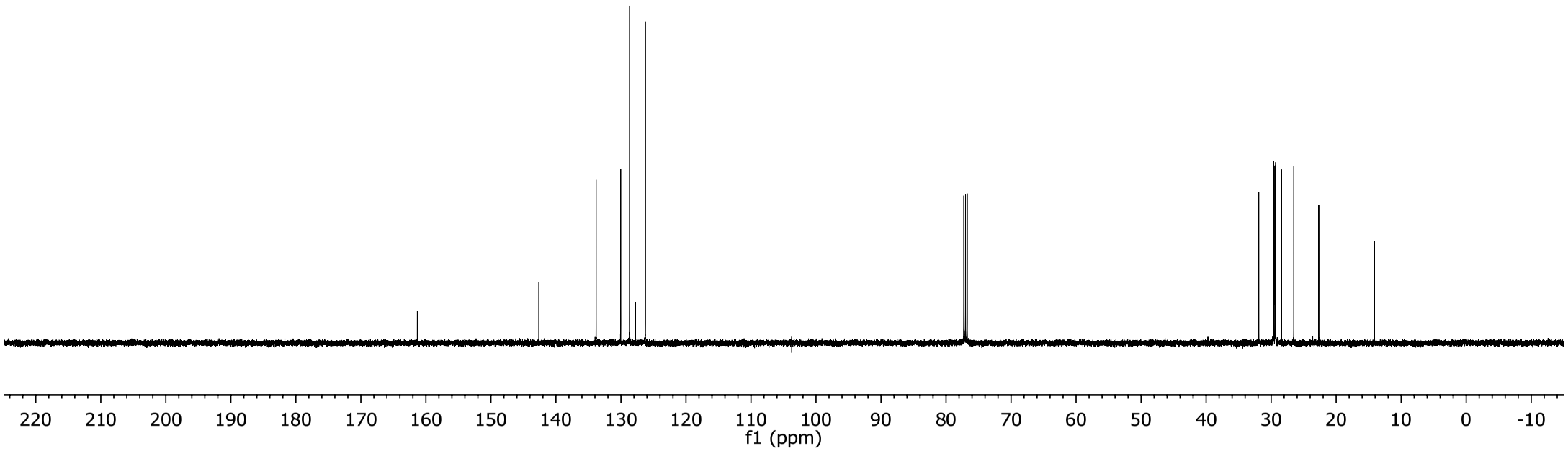
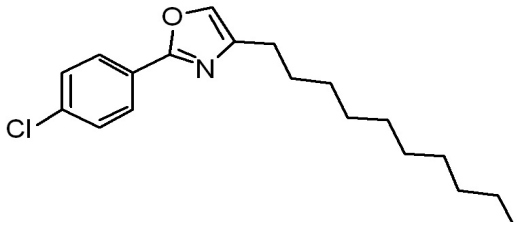
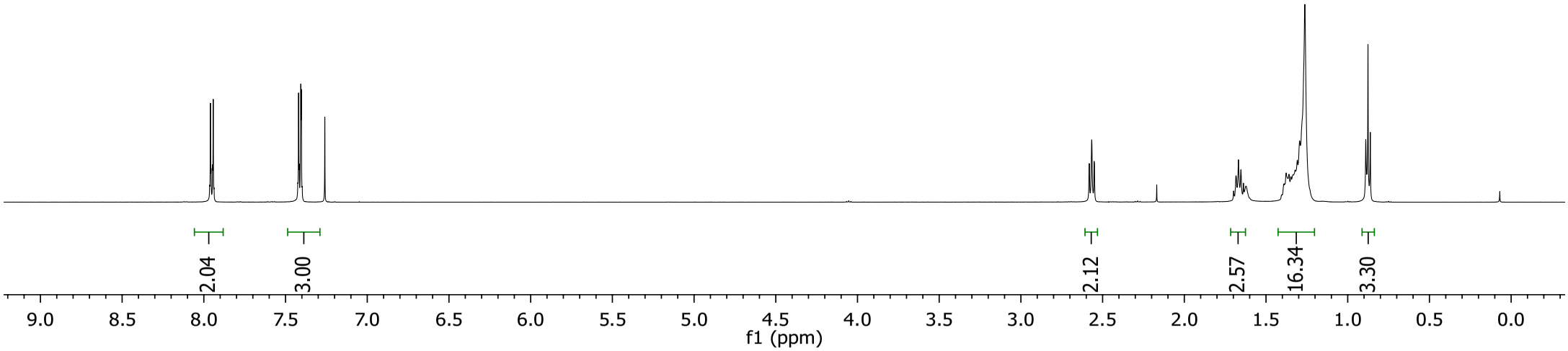


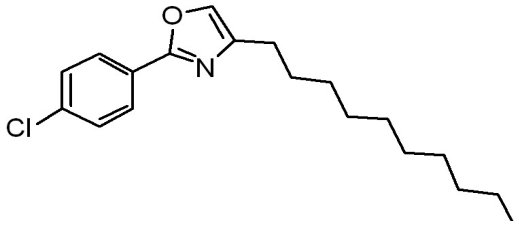
Title lyd-3-221-2-pure
Solvent CDCl3
Spectrometer Frequency 499.86



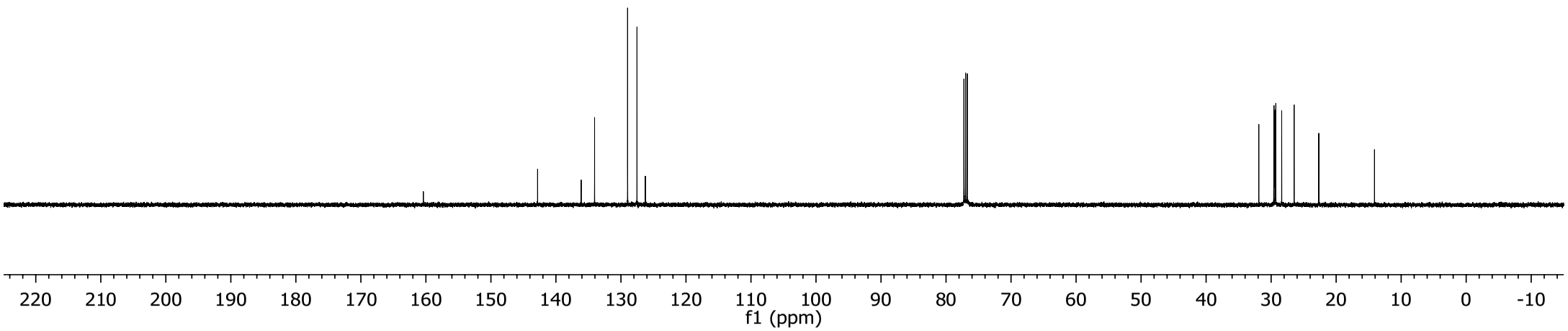
3d



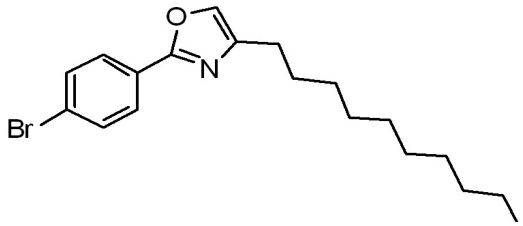
Title lyd-3-221-2-pure-C
Solvent CDCl3
Spectrometer Frequency 125.70



3d



Title lyd-3-226-2-pro
Solvent CDCl3
Spectrometer Frequency 499.86



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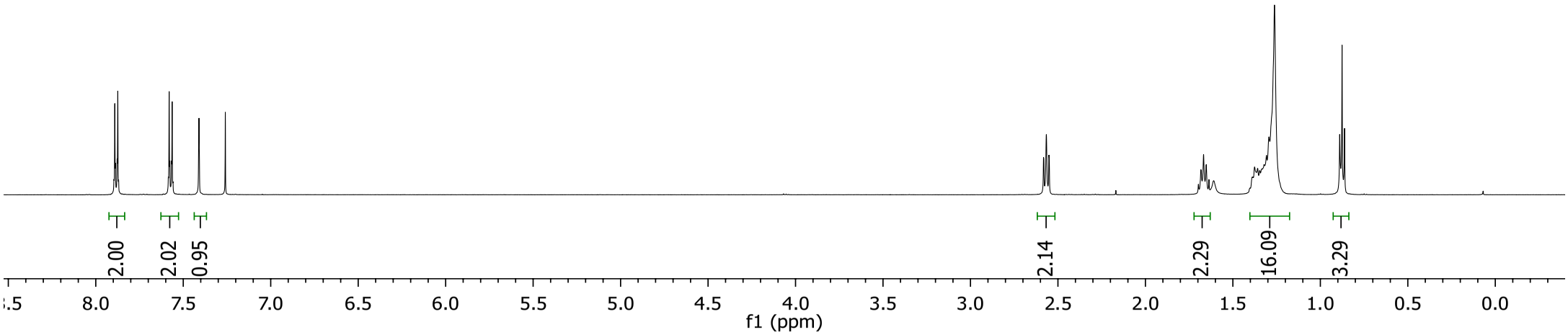
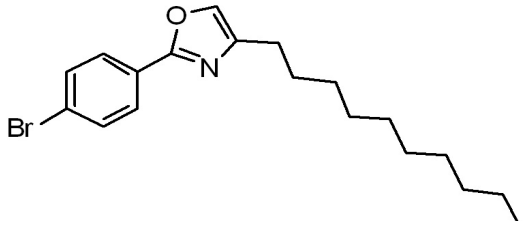
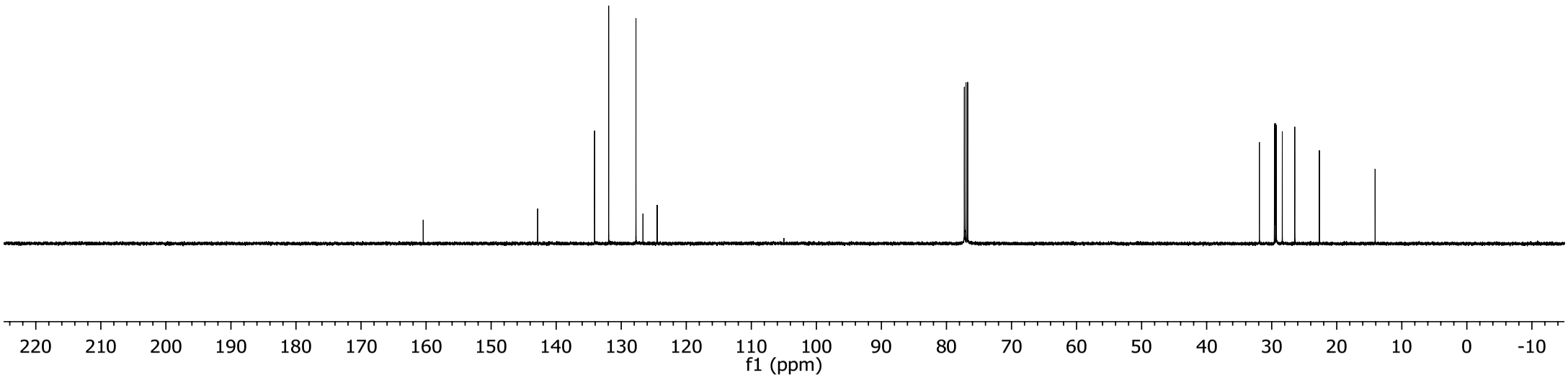


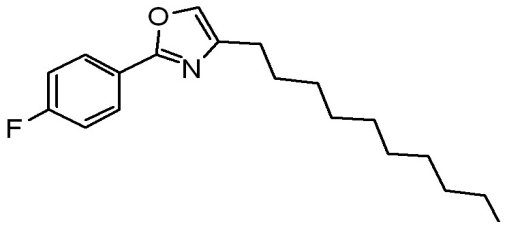
Title lyd-3-226-2-pro-C
Solvent CDCl3
Spectrometer Frequency 125.70



3e



Title lyd-3-210
Solvent CDCl3
Spectrometer Frequency 499.86



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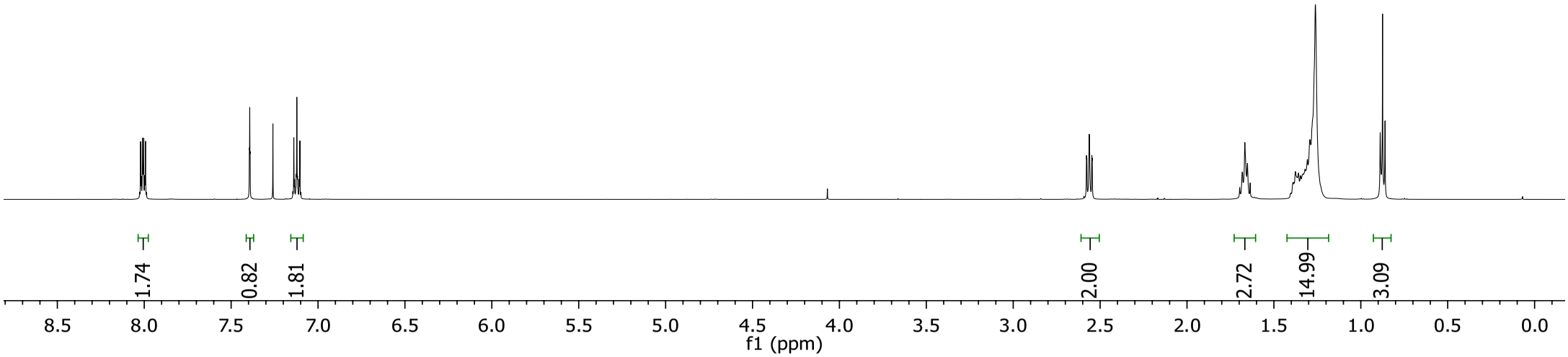
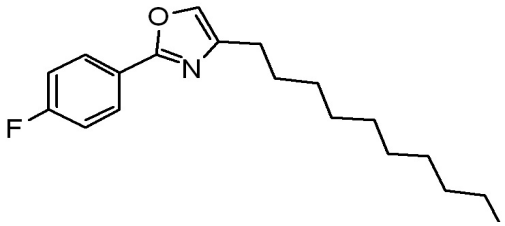


Title lyd-3-210-C-1
Solvent CDCl3
Spectrometer Frequency 125.70



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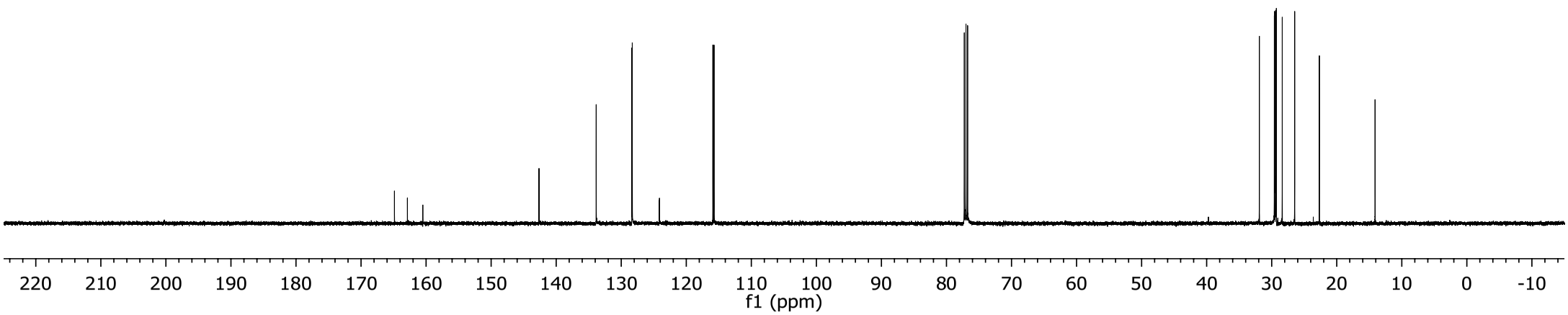
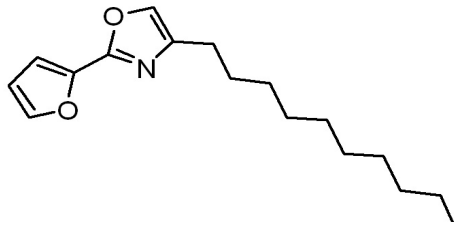
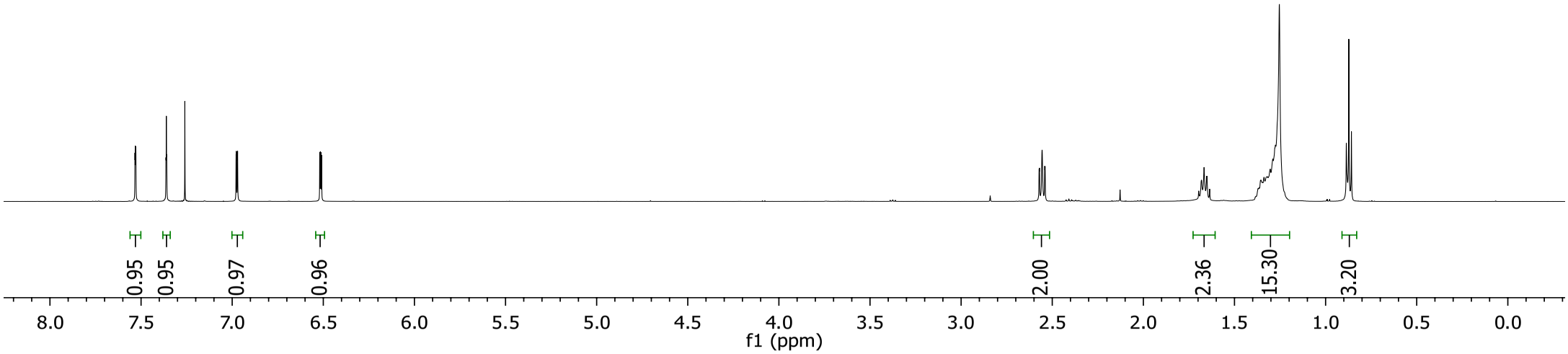


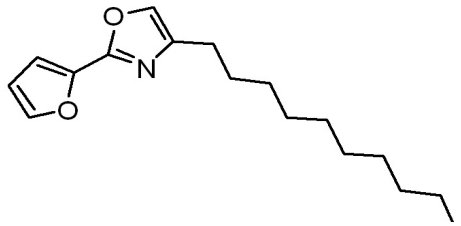
Title lyd-3-211-pure
Solvent CDCl3
Spectrometer Frequency 499.86



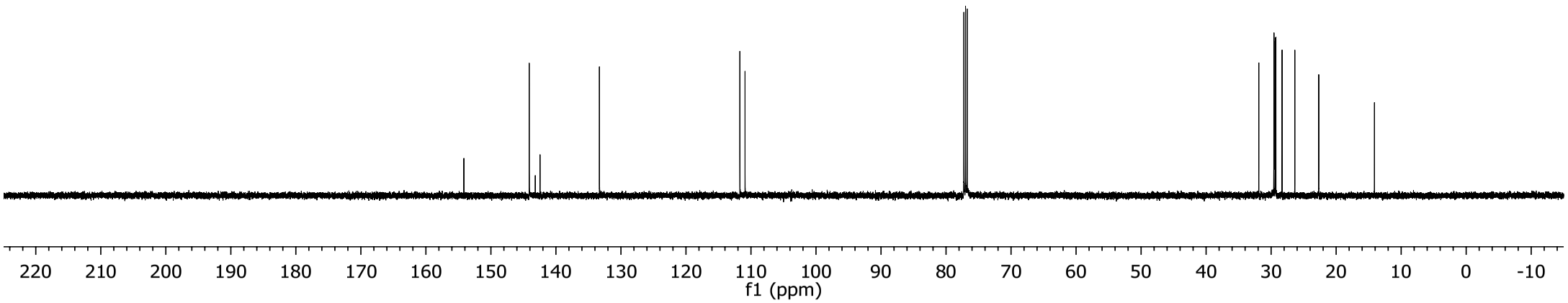
3g



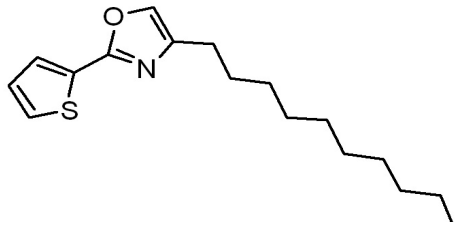
Title lyd-3-211-pure-C2
Solvent CDCl3
Spectrometer Frequency 125.70



3g



Title lyd-3-221-1-pure
Solvent CDCl3
Spectrometer Frequency 499.86



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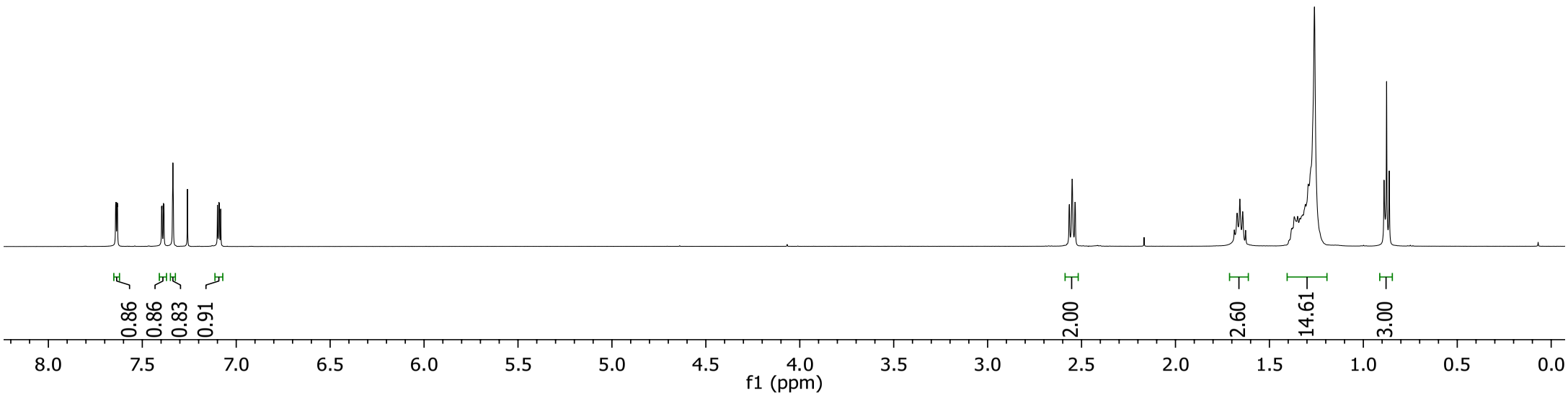
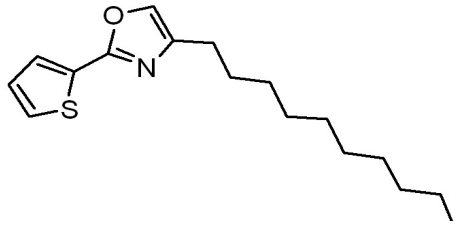


Title lyd-3-221-1-pure-C
Solvent CDCl3
Spectrometer Frequency 125.70



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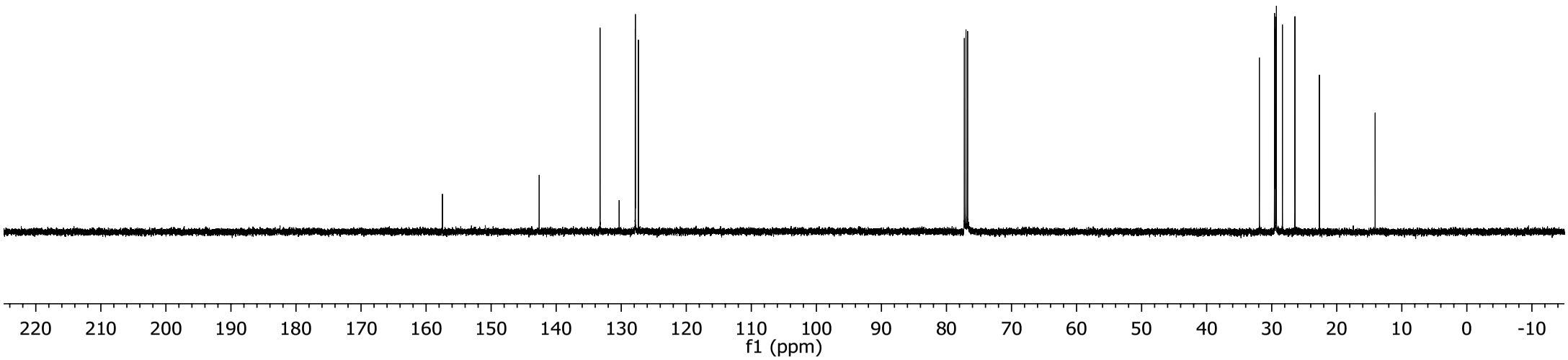
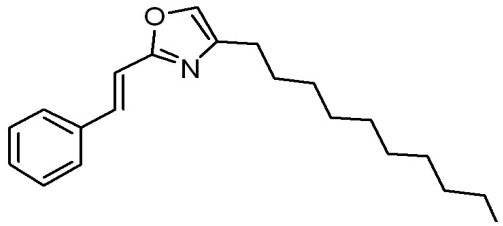
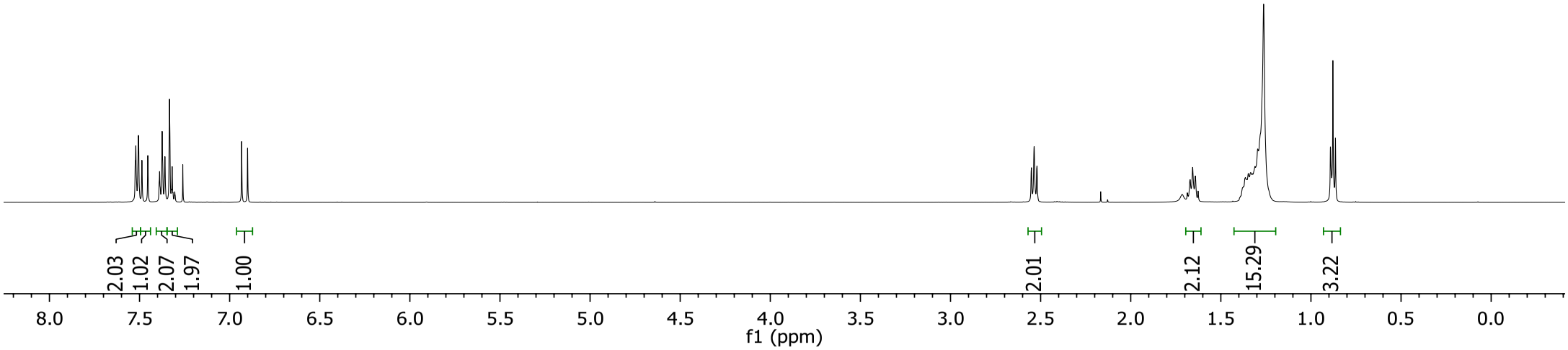


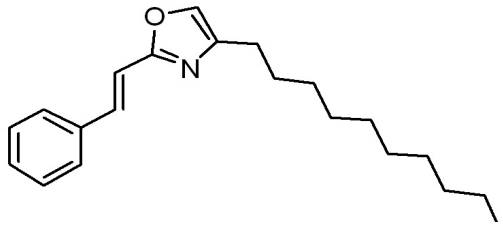
Title lyd-3-212-3-pure
Solvent CDCl3
Spectrometer Frequency 499.86



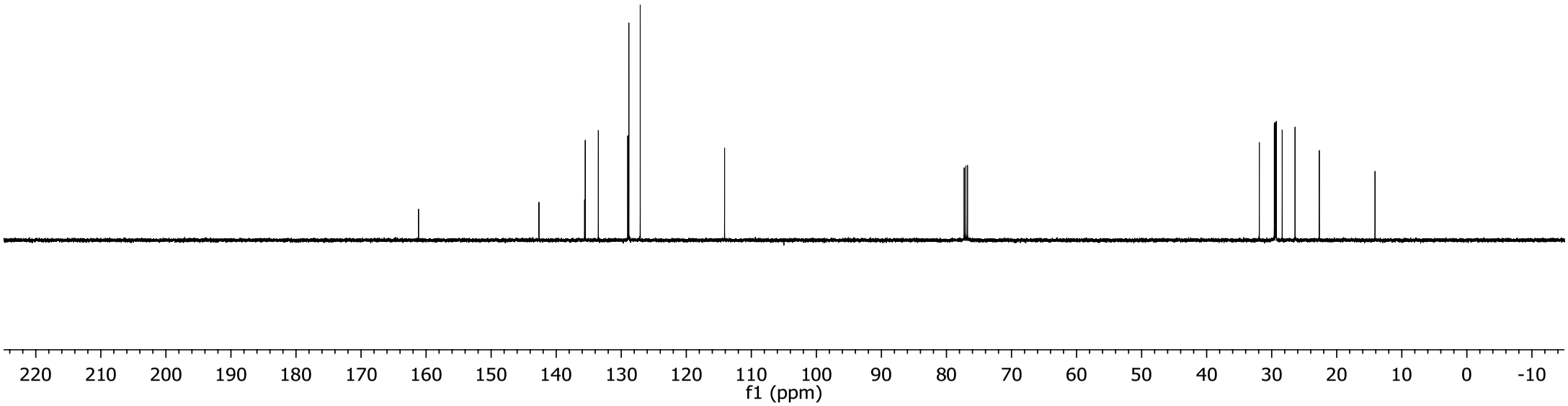
3i



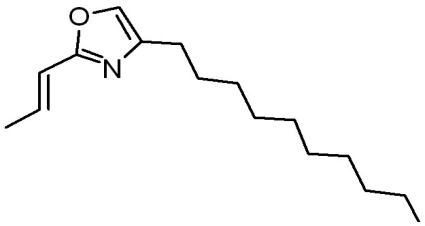
Title lyd-3-212-3-C
Solvent CDCl3
Spectrometer Frequency 125.70



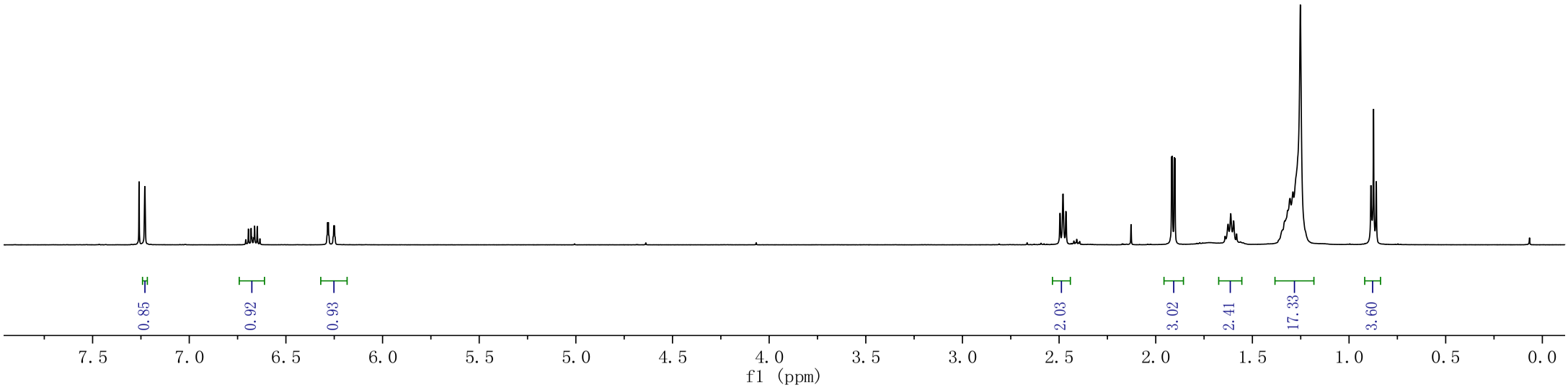
3i



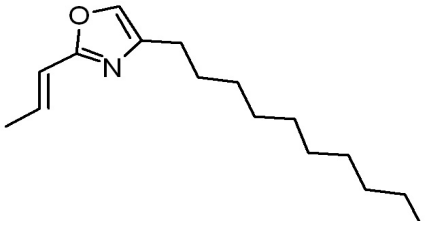
Parameter	Value
1 Title	lyd-3-237-1
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



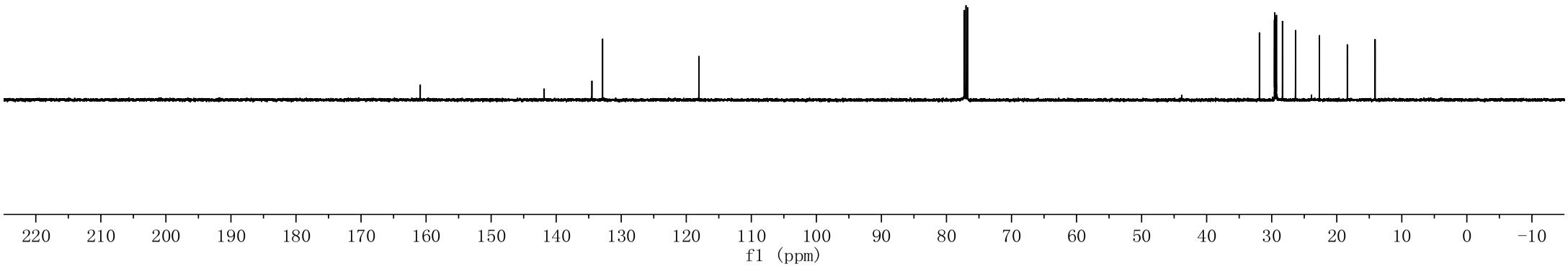
3j



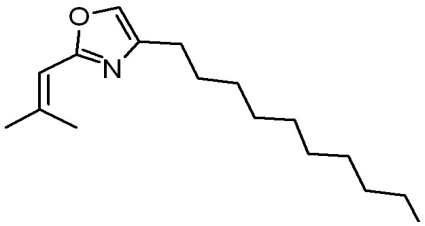
Parameter	Value
1 Title	lyd-3-237-1-C
2 Solvent	CDCl3
3 Spectrometer Frequency	125.70



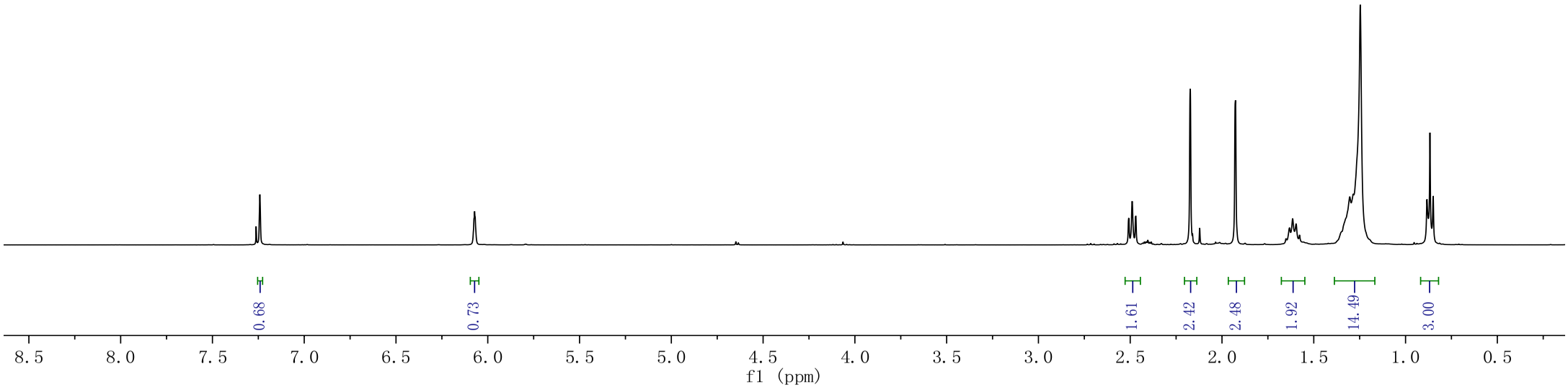
3j



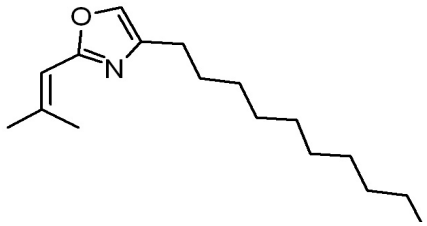
Parameter	Value
1 Title	lyd-3-237-2
2 Solvent	cdcl3
3 Spectrometer Frequency	399.95



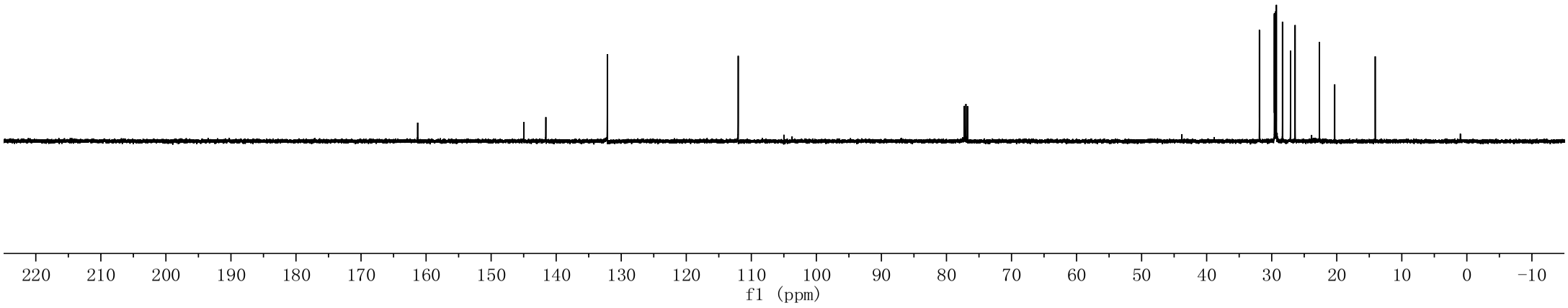
3k



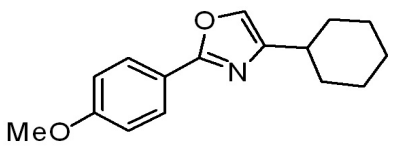
lyd-3-237-2-pure-C
Std carbon



3k

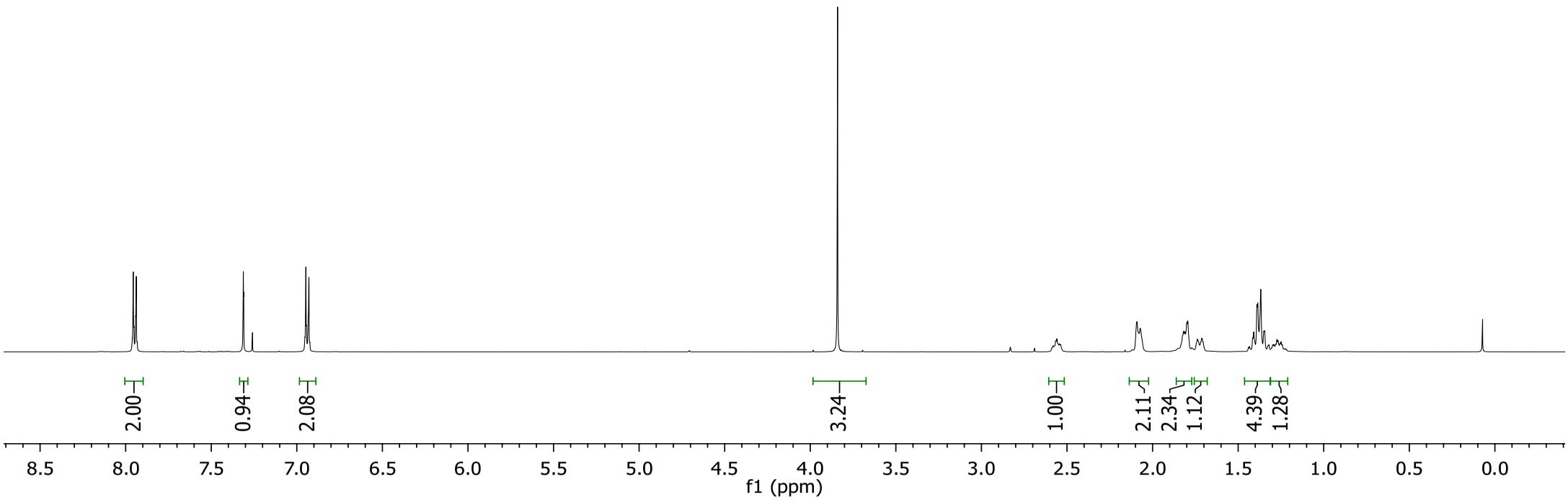


Title lyd-3-225
Solvent CDCl3
Spectrometer Frequency 499.86

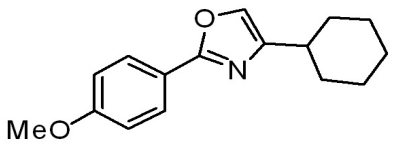


3l

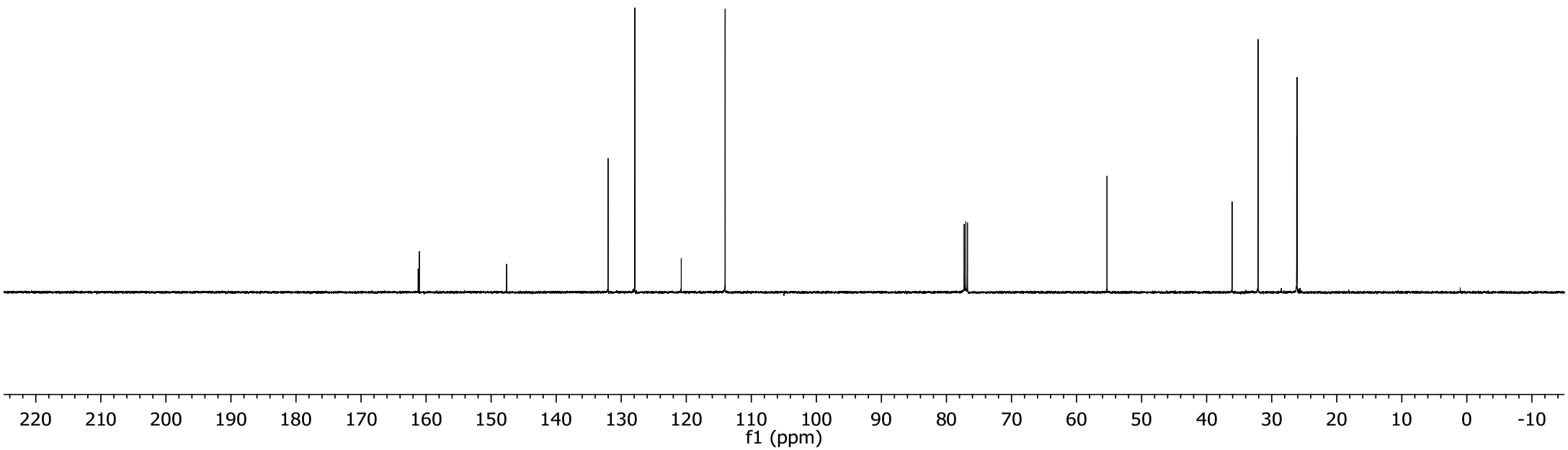
S58



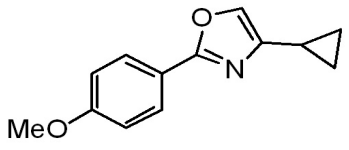
Title lyd-3-225-C
Solvent CDCl3
Spectrometer Frequency 125.70



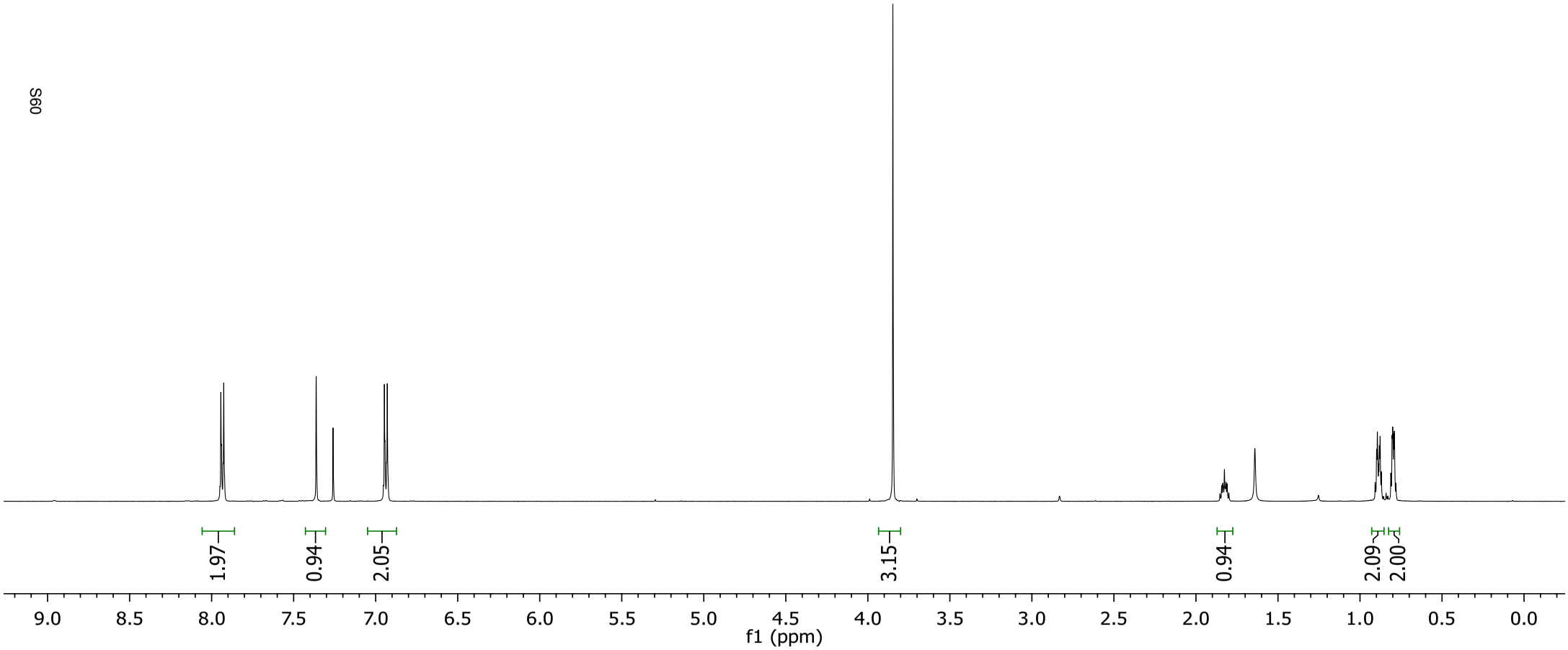
3l



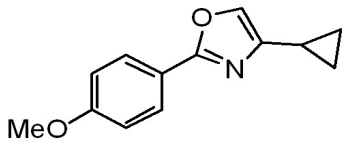
Title lyd-3-226-1-pro
Solvent CDCl3
Spectrometer Frequency 499.86



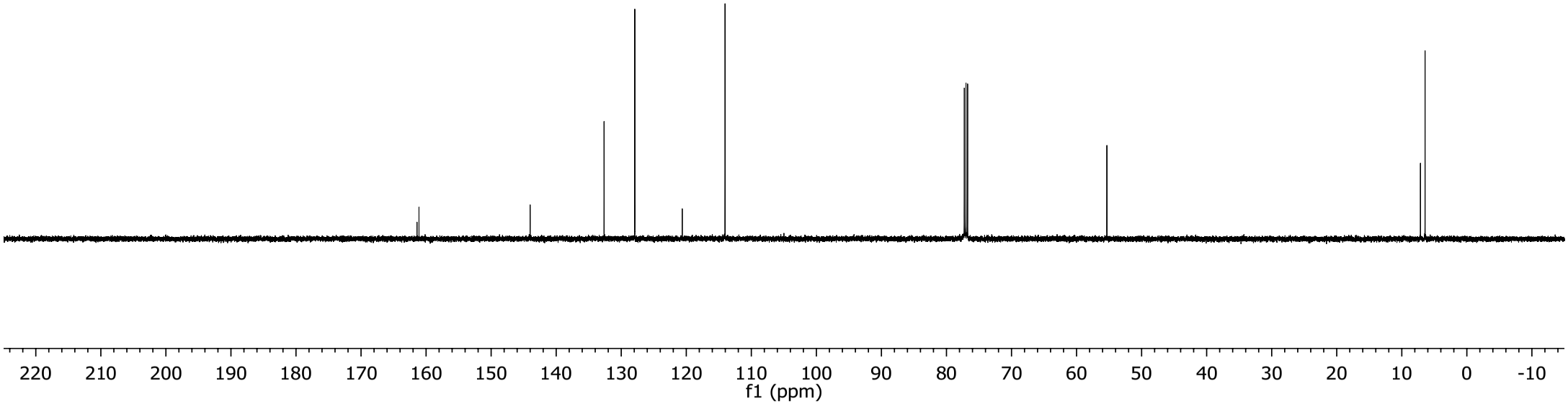
3m



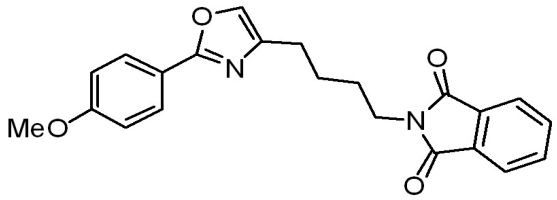
Parameter	Value
1 Title	lyd-3-226-1-pro-C
2 Solvent	CDCl3
3 Spectrometer Frequency	125.70



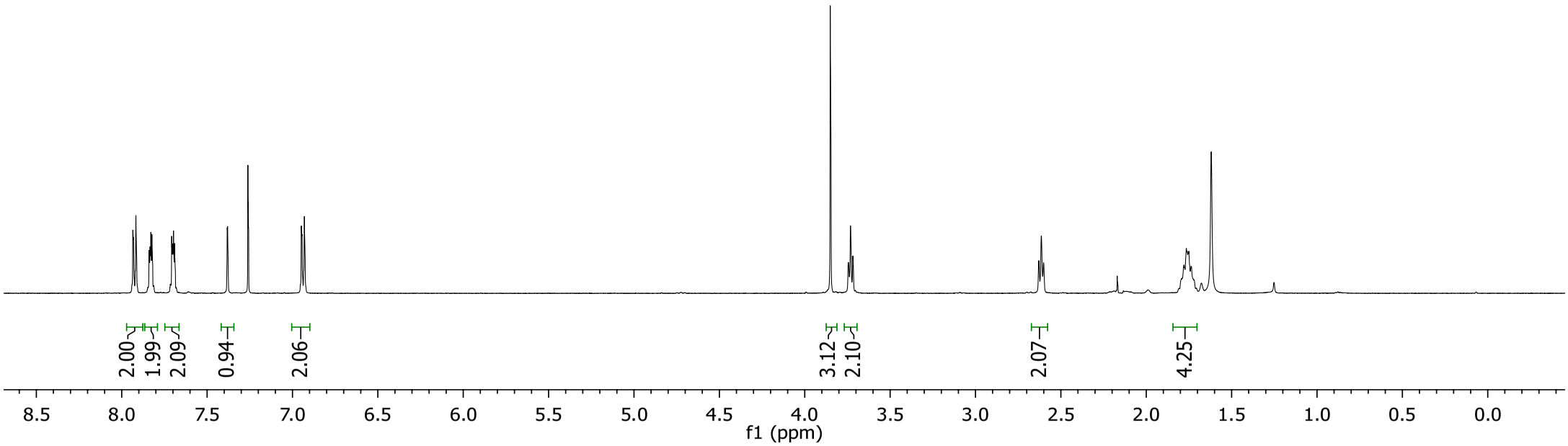
3m



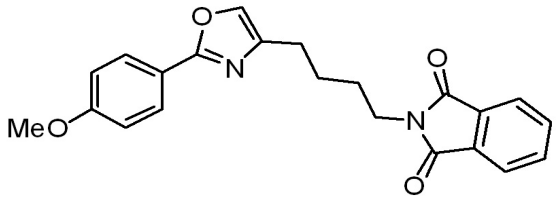
Title lyd-3-228-2-pure
Solvent CDCl3
Spectrometer Frequency 499.86



3n



Title lyd-3-228-2-pure-C
Solvent CDCl3
Spectrometer Frequency 125.70



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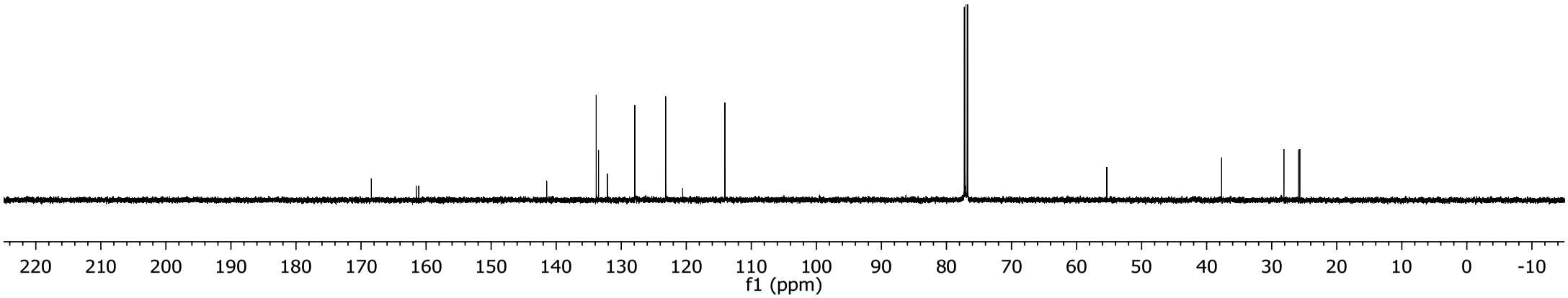
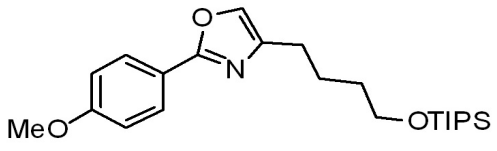
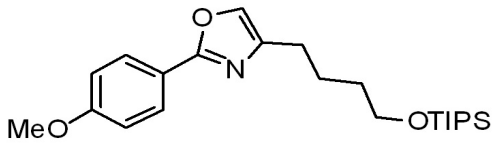


Parameter	Value
1 Title	lyd-3-232-2-pro
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



3o

Parameter	Value
1 Title	lyd-3-211-pure
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



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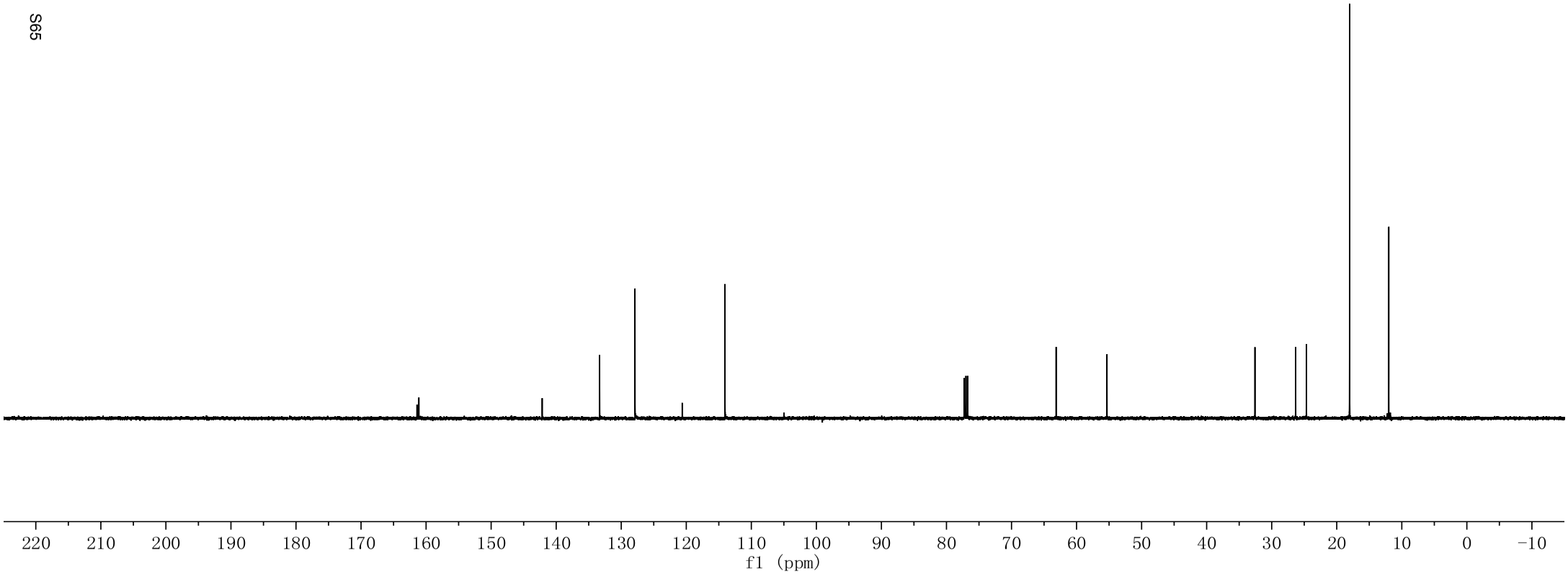
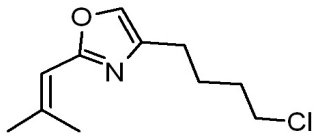


Parameter	Value
1 Title	lyd-3-241-pure
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



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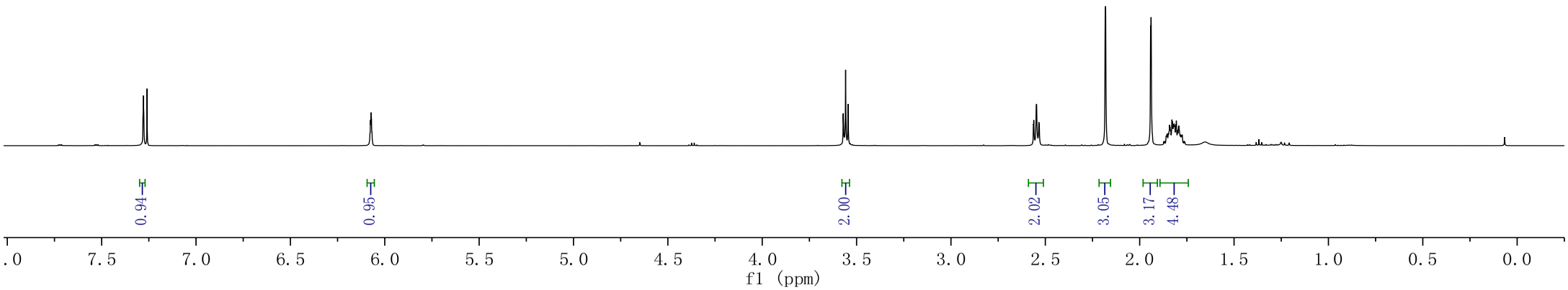
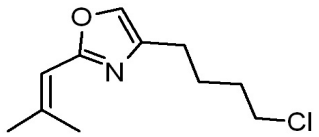
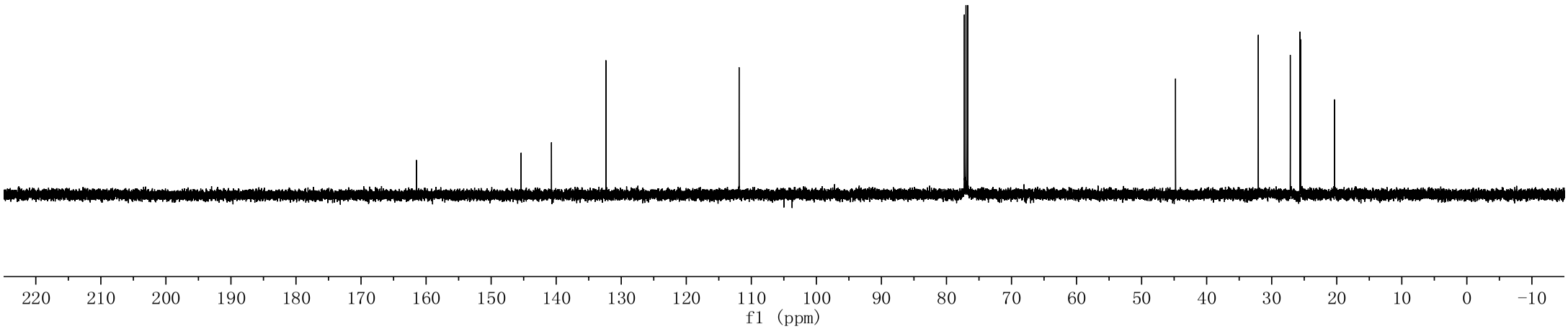


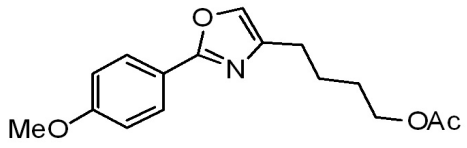
Parameter	Value
1 Title	lyd-3-241-pure-C
2 Solvent	CDCl3
3 Spectrometer Frequency	125.70



3p



Title lyd-3-216-pure
Solvent CDCl3
Spectrometer Frequency 499.86



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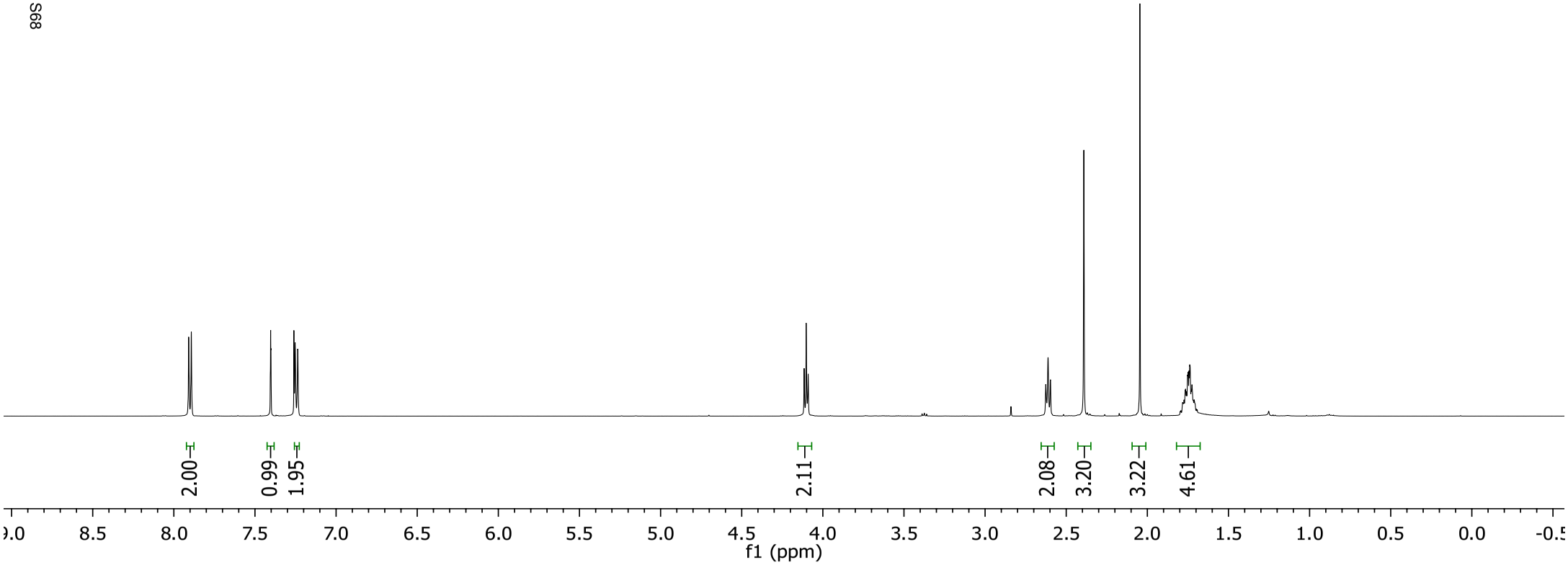
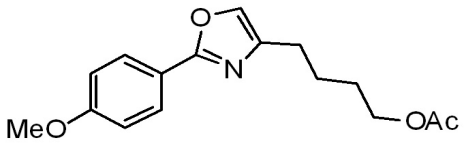


Title lyd-3-216-pure-C
Solvent CDCl3
Spectrometer Frequency 125.70



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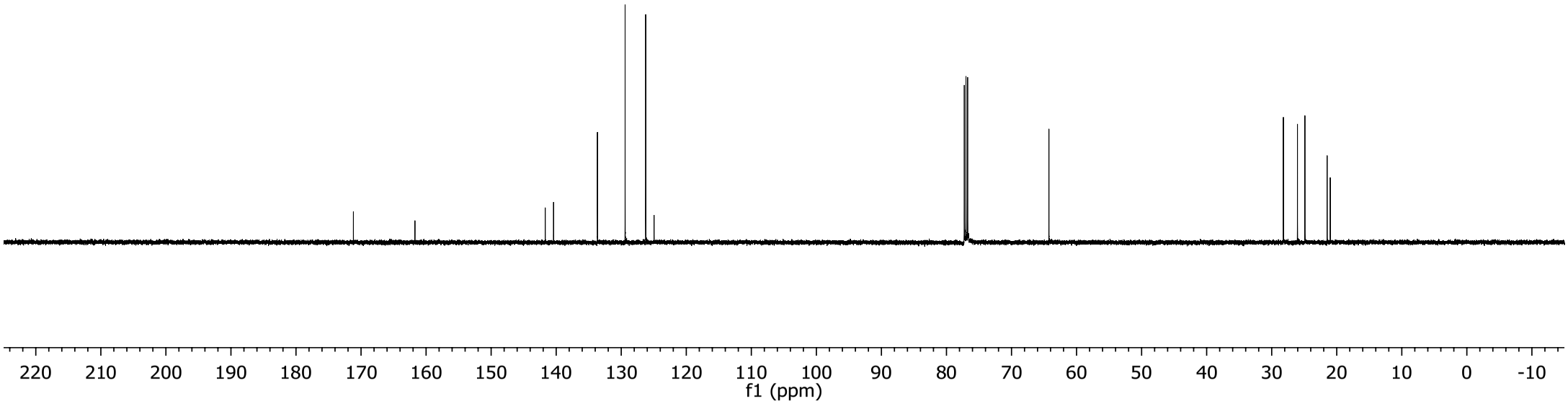
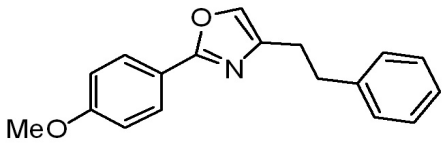


Title lyd-3-228-1-pro
Solvent CDCl3
Spectrometer Frequency 499.86



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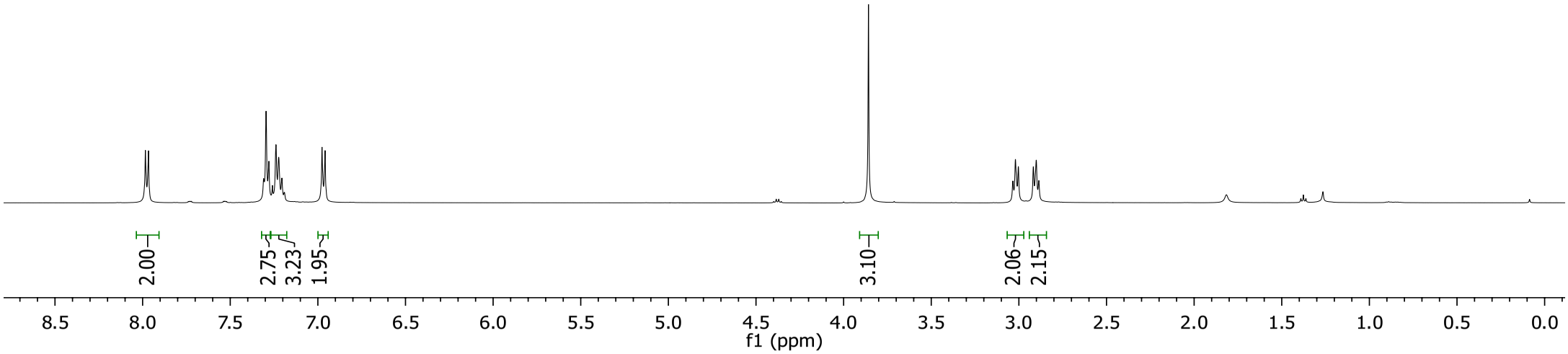
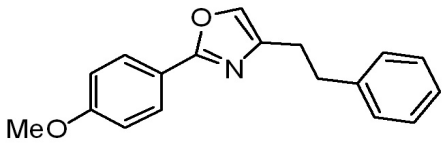


Title lyd-3-228-1-pure-C
Solvent CDCl3
Spectrometer Frequency 125.70



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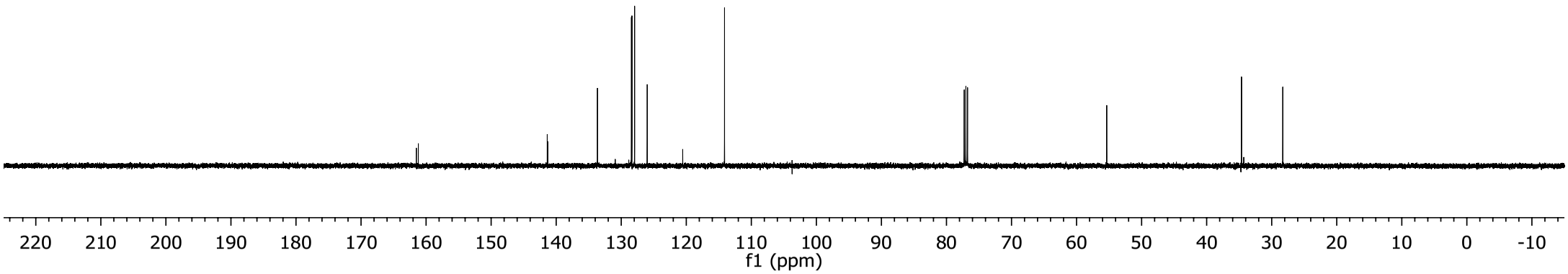
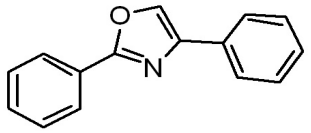


Title lyd-3-115-1-pro-pure
Solvent cdcl3
Spectrometer Frequency 599.63



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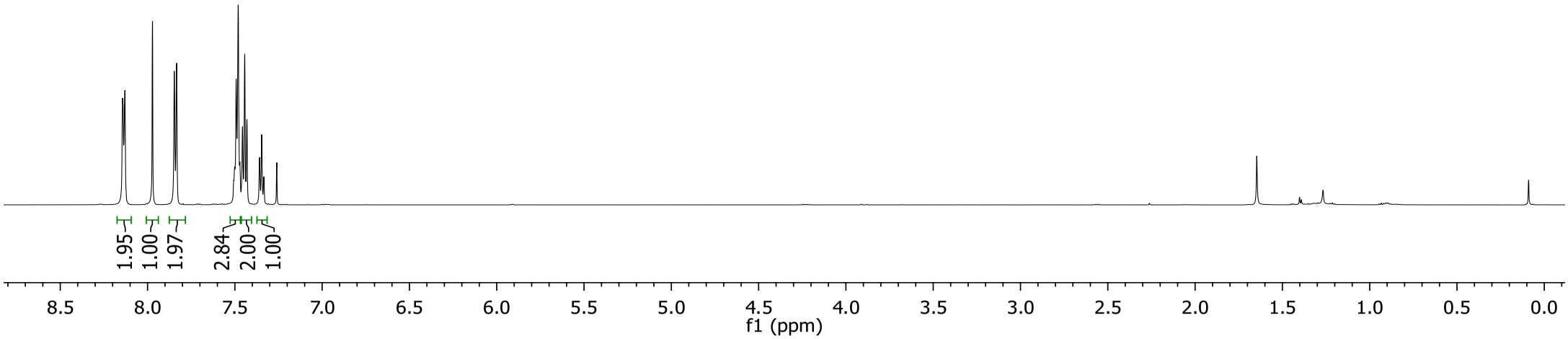
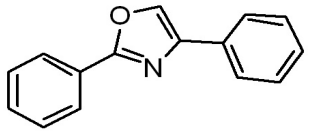
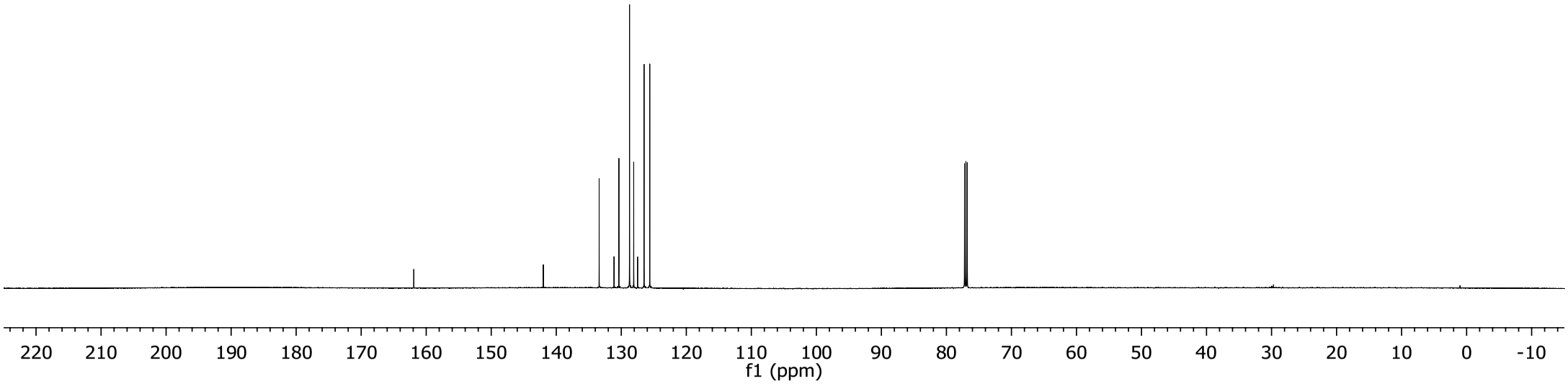


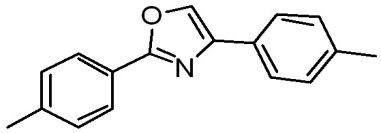
Title lyd-3-115-pro-pure-c
Solvent cdcl3
Spectrometer Frequency 150.79



3s



Title lyd-3-214
Solvent CDCl3
Spectrometer Frequency 499.86



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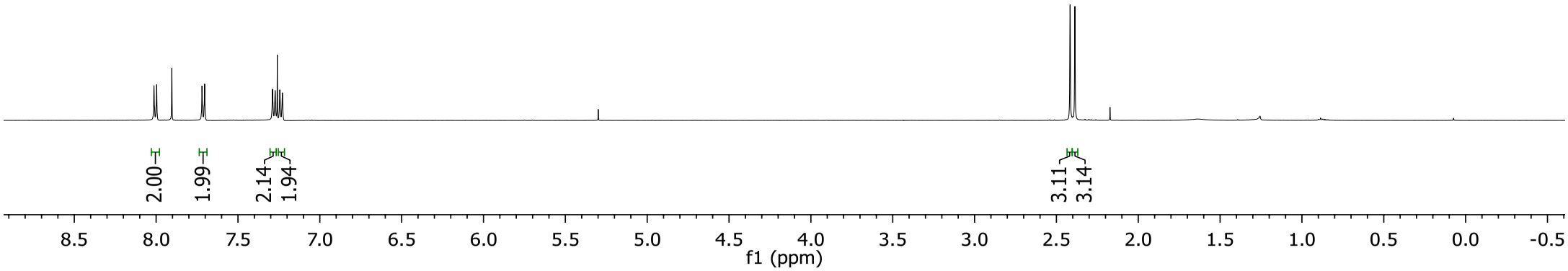
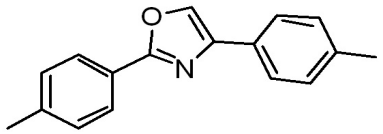


Title lyd-3-214-C
Solvent CDCl3
Spectrometer Frequency 125.70



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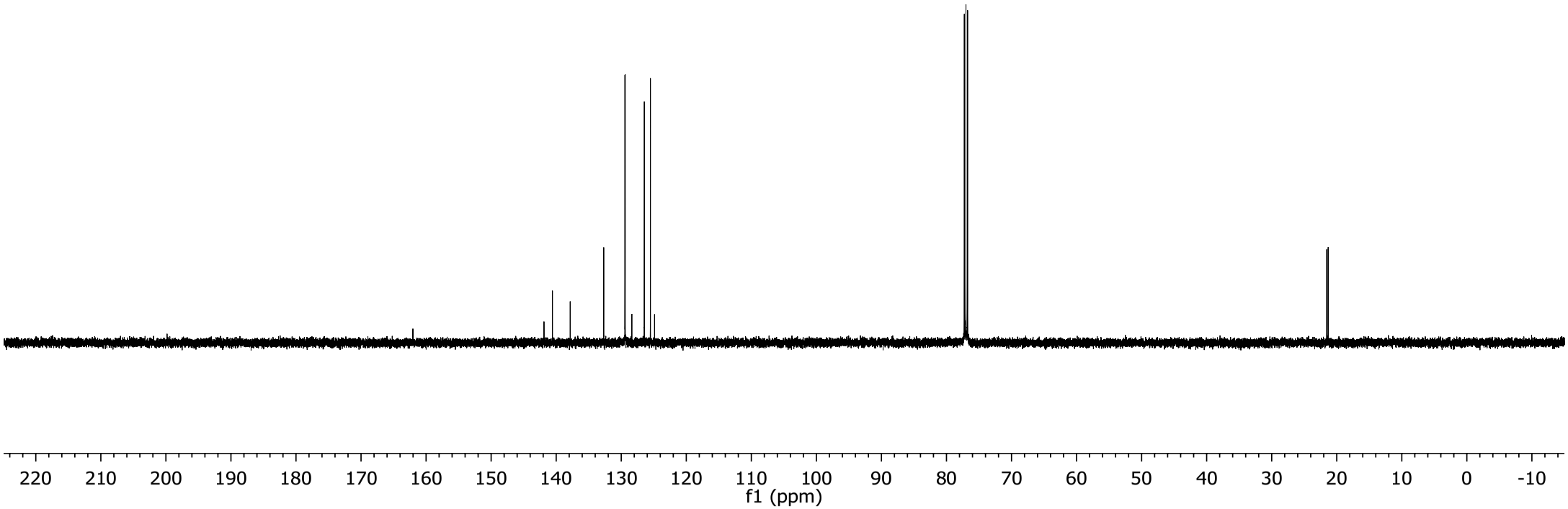
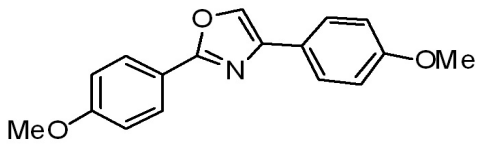


Title lyd-3-224
Solvent CDCl3
Spectrometer Frequency 499.86



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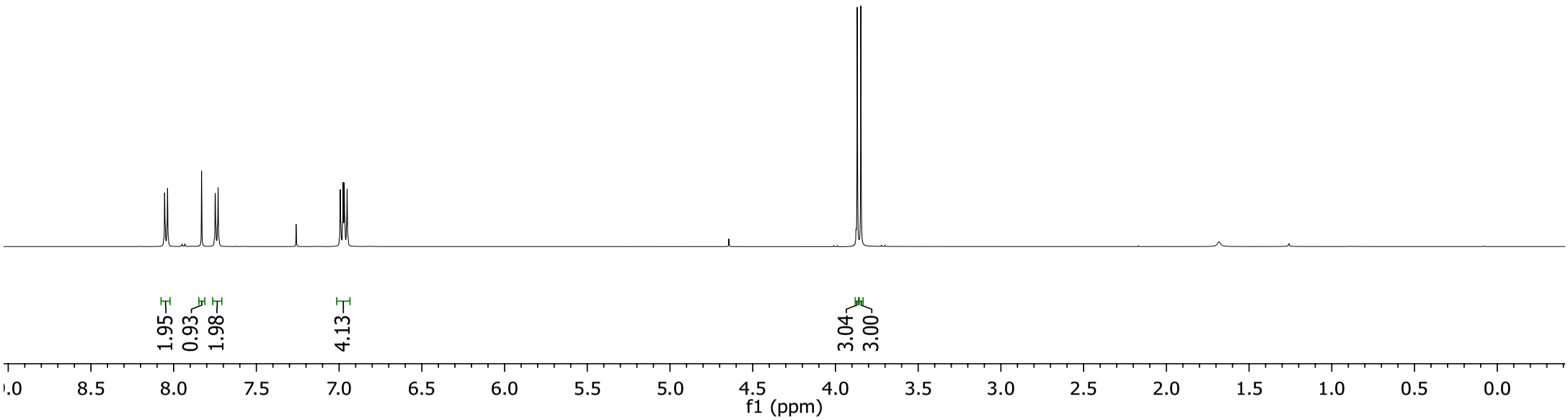
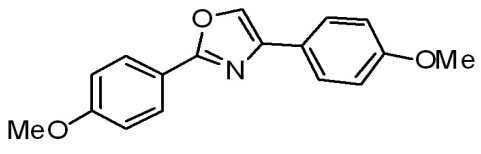


Parameter	Value
1 Title	lyd-3-224-C-2
2 Solvent	CDCl3
3 Spectrometer Frequency	125.70



3u