Supporting Information

Efficient Merging of Copper and Photoredox Catalysis for the Asymmetric Cross-Dehydrogenative-Coupling of Alkynes and Tetrahydroisoquinolines

Inna Perepichka, Soumen Kundu, Zoë Hearne and Chao-Jun Li*

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, Quebec H3A 0B8, Canada. *E-mail*: cj.li@mcgill.ca

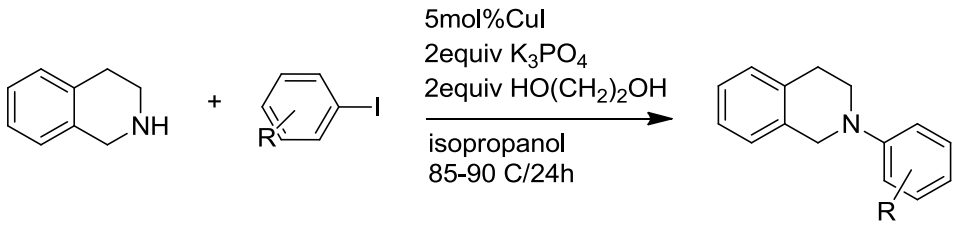
Contents

1. General remarks

All commercially available reagents were used as provided without further purification. Solvents were dried and distilled before use according to the standard procedure[i] and stored over molecular sieves. The glassware was oven-dried for at least 1 h prior to use. All reagents were weighed and handled in air, and backfilled under an inert atmosphere of nitrogen at room temperature. *N*-aryl-tetrahydroisoquinolines **1** (Scheme 3)[ii,iii,iv] $[Ru(bpy)_3](PF_6)_2$[v] and $Ir(ppy)_2(dtbbpy)PF_6$[vi,vii] were synthesized according to the published procedures and spectroscopic data were consistent (see text later) with those previously reported for these compounds. A sample of $[Ru(bpy)_3](PF_6)_2$ was provided as a gift from Professor Eli Zysman-Colman (Department of Chemistry, University of St. Andrews, United Kingdom).

^1H NMR and ^{13}C NMR were obtained using Varian MERCURY-300, 400, and 500 MHz spectrometer in deuterated NMR solvents ($CDCl_3$, d_6-acetone etc.). GC-MS and HR-MS (ESI) spectra were conducted at the Mass Spectroscopy Facility at the Department of Chemistry, McGill University on a Thermo PolarisQ GC System and a JEOL JMS-700 instrument, respectively. Enantiomeric excess was determined with HPLC, Agilent 1260 Infinity Diode Array detector (G 4212B) by using a Chiralcel OD-H column (25cm × 4.6mm, part. size 5μm) and 4:96 isopropanol/hexane as an eluent (flow rate 1.0 mL/min, UV detection at 254 nm). Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light.

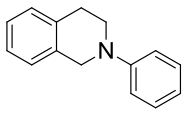
2. General procedure for the synthesis of *N*-Aryl-tetrahydroisoquinoline, 1[ii]



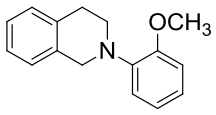
Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were placed into a 50 mL three-neck flask. The flask was evacuated and back filled with argon. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL), 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15 mmol) and iodobenzene (1.12 mL, 10.0 mmol) were added successively by syringe at room temperature. The reaction mixture was heated at 90 °C for 24 h and then allowed to cool to room temperature.

Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate (20:1) as an eluent.

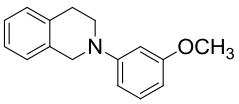
3. Characterization of starting materials:



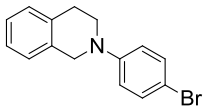
2-Phenyl-1,2,3,4-tetrahydrolisoquinoline,[ii] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 2 H), 7.21-7.15 (m, 4 H), 7.00 (d, J = 8.0 Hz, 2 H), 6.84 (t, J = 8.0 Hz, 1 H), 4.42 (s, 2 H), 3.58 (t, J = 6 Hz, 2 H), 3.00 (t, J= 5.6 Hz, 2 H).



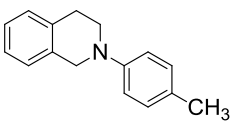
2-(2-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline,[ii] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.11 (m, 4 H), 7.03-7.0 (m, 2 H), 6.94-6.89 (m, 2 H), 4.31 (s, H), 3.89 (s, 3 H), 3.43 (t, J=6.0 Hz, 2 H), 2.99 (t, J = 6.0 Hz, 2 H).



2-(3-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline,[viii] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.15 (m, 4 H), 6.62–6.59 (m, 1 H), 6.53–6.52 (m, 1 H), 6.41-6.39 (m, 1 H), 4.42 (s, 2 H), 3.81 (s, 3 H), 3.56 (t, J=6.4 Hz, 2 H), 2.99 (t, J = 5.6 Hz, 2 H).

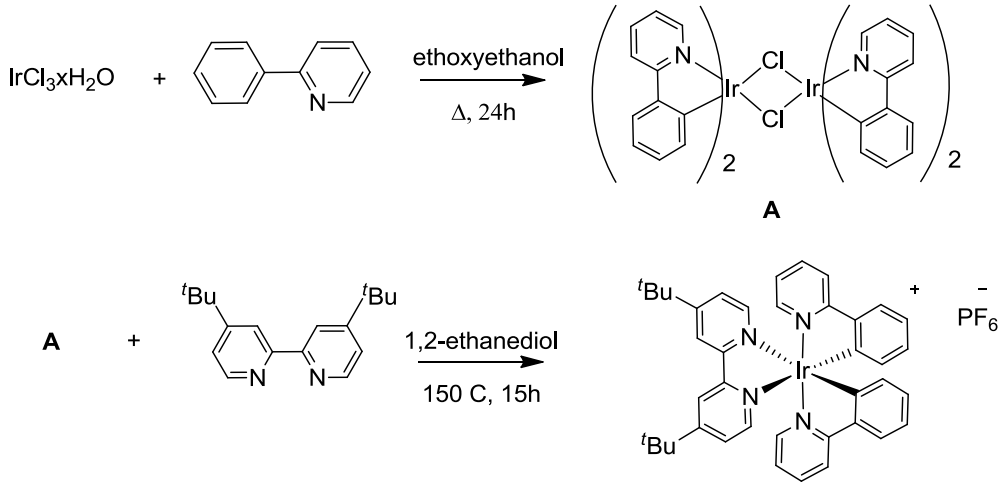


2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinoline,[iii] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.34 (d, J = 9.0 Hz, 2 H), 7.20-7.15 (m, 4 H), 6.84 (d, J = 9.0 Hz, 2 H), 4.38 (s, 2 H), 3.54 (t, J = 6.9 Hz, 2 H), 3.00 (t, J = 6.0 Hz, 2 H).



2-(4-Methylphenyl)-1,2,3,4-tetrahydroisoquinoline,[iii] **1k** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18-7.11 (m, 4 H), 7.00 (d, J = 5 Hz, 2 H), 6.93 (d, J = 5 Hz, 2 H), 4.37 (s, 2 H), 3.52 (t, J = 5 Hz, 2 H), 2.99 (t, J = 5.5 Hz, 2 H), 2.29 (s, 1 H).

4. Synthesis of $[Ir(ppy)_2(dtbbpy)](PF_6)$[vi,vii]



Scheme 1S Synthesis of **$[Ir(ppy)_2(dtbbpy)](PF_6)$**.

Tetrakis(2-phenylpyridine-C2,N') (μ-dichloro)diiridium, (A, Scheme 1S) Iridium trichloride hydrate (0.389 g, 1.31 mmol) was combined with 2- phenylpyridine (0.76 g, 4.9 mmol), dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL), and refluxed for 24 h. The solution was cooled to room temperature, and the yellow precipitate was collected on a glass filter frit. The precipitate was washed with ethanol (60 mL) and acetone (60 mL) and then dissolved in dichloromethane (75 mL) and filtered. Toluene (25 mL) and hexanes (10 mL) were added to the filtrate, which was then reduced in volume by evaporation to 50 mL, and cooled to give crystals of $[Ir(ppy)_2Cl]_2$ (0.44 g, 75%) (**A**, Scheme 1S).

Synthesis of $[Ir(ppy)_2(dtbbpy)](PF_6)$ was adapted from literature procedures[vi,vii] for the analogous unsubstituted complex. A stirred suspension of 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.44 g, 0.88 mmol) and tetrakis(2-phenylpyridine-C,N)(μ-dichloro)-diiridium, **A** (0.428g, 0.400 mmol) in 20 mL of 1,2-ethanediol under nitrogen was heated to 150 °C for 15 h. All the solids

dissolved to yield a clear, yellow solution. After cooling the mixture to room temperature, 200 mL of water was added. The excess of bipyridine ligand was removed through three extractions with diethyl ether (3×50 mL), and the aqueous layer was subsequently heated to 70 °C. NH_4PF_6 (2 g) in 20 mL of water was added, and the PF_6 salt of the iridium complex immediately precipitated. After cooling the suspension to 5 °C, the yellow solid was separated through filtration, dried, and recrystallized through acetonitrile/ether. Yield: 0.50 g (66%). ^{1}H NMR (acetone-d_6, 400 MHz): δ 8.88 (d, *J* =2.0 Hz, dtb-bpy-H3, 2H), 8.24 (ppy-H6, pyridine, 2H, d, *J* = 8), 7.99-7.93 (m, dtb-bpy-H6, 2H, ppy-H5, pyridine, 2H), 7.90 (ppy-H3, phenyl, 2H, dd, *J* = 7.2, 0.8 Hz), 7.79 (ppy-H6, phenyl, 2H, d, *J* = 6 Hz), 7.71 (dtb-bpy-H5, 2H, dd, *J* = 6.0, 2.0 Hz), 7.14 (ppy-H4, pyridine, 2H, dt, *J* = 7.2, 1.6 Hz), 7.04 (ppy-H4, phenyl, 2H, dt, *J*= 7.6, 0.8 Hz), 6.91 (ppy-H5, phenyl, 2H, dt, *J* = 6.8, 1.2 Hz), 6.34 (ppy-H3, pyridine, 2H, d, *J* = 8), 1.42 (18H, s).

HRMS (ESI) *m/z* calculated for $C_{40}H_{40}N_4Ir^+$ ([M - PF_6]$^+$) 769.2876, found 769.2866.

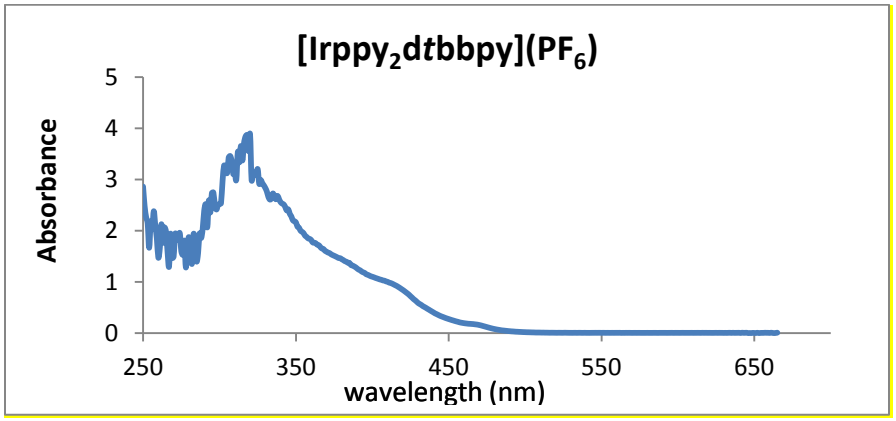


Figure 1S. UV/Visible Spectra of **[Ir(ppy)$_2$(d*t*bbpy)](PF$_6$)** in CH_3CN.

5a General procedure for the photoredox catalyzed synthesis of chiral 2-phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline using $(BzO)_2$ as a terminal oxidant (Table 1 and 2, entry 1-6):

An oven-dried sample vial (15×45 mm) was equipped with a magnetic stirring bar, *N*-aryl tetrahydroisoquinolines (0.100 mmol), photocatalyst (1 mol %), Cu-Catalyst (10 mol %), chiral ligand (15 mol %), and $(BzO)_2$ (0.120 mmol). The vial was fitted with a septa and degassed by

quickly alternating vacuum evacuation and argon backfill before anhydrous solvent (THF and MeCN) (1.0 mL) and terminal alkyne (0.150 mmol) were added under an atmosphere of argon. The reaction mixture was stirred under radiation of a 26-W household fluorescent bulb (daylight GE Energy Smart™ with 1600 lumens), at a distance of 10 cm from the reaction vial, at room temperature. After a particular period of time (for details see the footnotes of Table 1 and 2), the resulting mixture was filtered through a short silica gel pad and washed with 5 mL of ethyl acetate. The above solution was evaporated under vacuum, a known quantity of nitromethane (^{1}H NMR, $CDCl_3$: δ 4. 2 ppm) was added as an internal standard and product yield was determined by ^{1}H-NMR. The residue was purified by silica gel PTLC (hexane/DCM/ether, 3:2:0.5) to give the pure product. Enantioselectivity of isolated products were determined by the previously discussed method. Enantiomeric access (*ee* %) was calculated by the following[ix]:

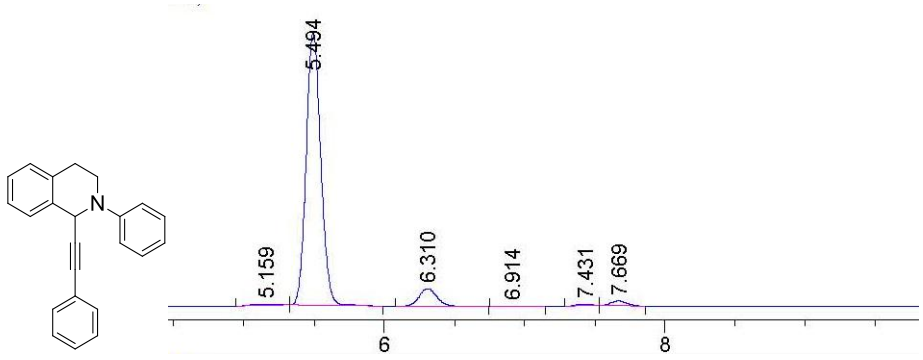
ee (%) = [(Major Isomer HPLC Area – Minor Isomer HPLC Area)/ (Major Isomer HPLC Area + Minor Isomer HPLC Area)] × 100

5b General procedure for photoredox catalyzed synthesis of the chiral C_1-alkynyl-*N*-aryl-1,2,3,4-tetrahydraisoquinoline derivatives (Table 2, entry 7-9 and Table 3):

An oven-dried sample vial (15×45 mm) was equipped with a magnetic stirring bar, *N*-aryl tetrahydroisoquinolines (0.100 mmol), photocatalyst (1 mol %), Cu-Catalyst (10 mol %) and chiral ligand (15 mol %). The vial was fitted with septa and degassed by quickly alternating vacuum evacuation and argon backfill before anhydrous THF (0.5 mL) was added under an atmosphere of argon. The reaction mixture was stirred for 15-20 min at RT covered by aluminium paper (light-protection). Phenylacetylene (0.150 mmol) was added following by 0.5 mL of CH_3CN. The reaction vial was placed in the cold room (4 °C) or placed into the chiller (-40 to 0 °C) under radiation of a 26-W household fluorescent bulb (daylight GE Energy Smart™ with 1600 lumens), at a distance of 10 cm from the vial. After a particular period of time, the resulting mixture was filtered through a short silica gel pad and washed with ethyl acetate. The above solution was evaporated under vacuum, a known quantity of nitromethane (^{1}H NMR, $CDCl_3$: δ 4. 1 ppm) was added as internal standard and product yield was determined by ^{1}H-NMR. The residue was purified by silica gel PTLC (hexane/DCM/ether, 3:2:0.5) to give the pure product. Enantioselectivity of isolated compounds were determined by the previously discussed method. Enantiomeric access (*ee* %) was calculated by the following[x]:

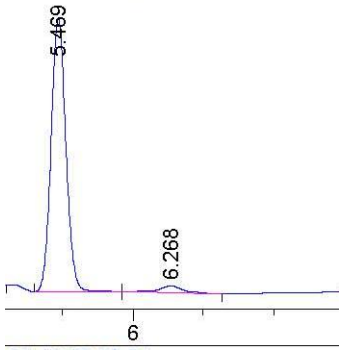
ee (%) = [(Major Isomer HPLC Area – Minor Isomer HPLC Area)/ (Major Isomer HPLC Area + Minor Isomer HPLC Area)] × 100

6. HPLC Chromatogram for the Chiral 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline at different temperatures.



Peak	Retention Time / min	Area / %
Major Enantiomer	5.494	90.0896
Minor Enantiomer	6.631	6.8380

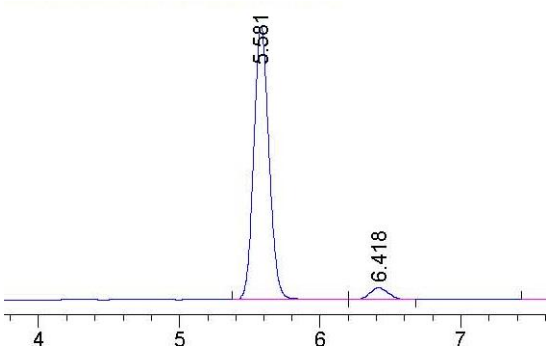
Figure 2S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 1 (Conditions: THF/ rt).



Peak	Retention Time/ min	Area/ %

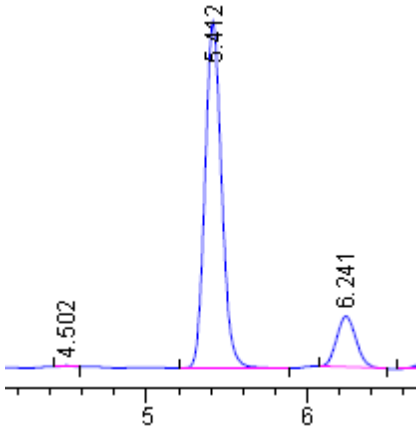
Major Enantiomer	5.469	68.0955
Minor Enantiomer	6.268	2.8232

Figure 3S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 2 (Conditions: THF/ 4 °C).



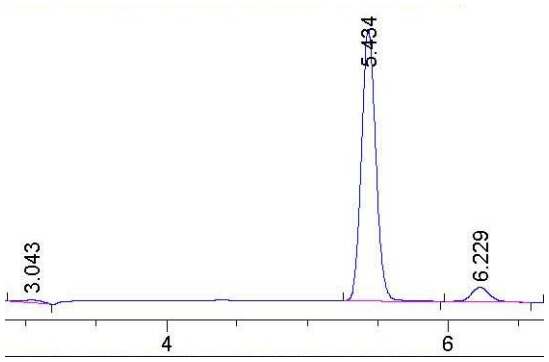
Peak	Retention Time, min	Area, %
Major Enantiomer	5.581	91.7012
Minor Enantiomer	6.418	4.6804

Figure 4S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 3 (Conditions: THF/ -20 °C).



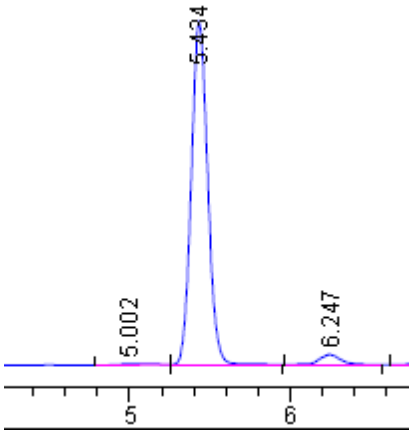
Peak	Retention Time, min	Area, %
Major Enantiomer	5.412	16.806
Minor Enantiomer	6.241	3.1585

Figure 5S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 1 , entry 10 and Table 2, entry 4 (conditions: CH_3CN/rt).



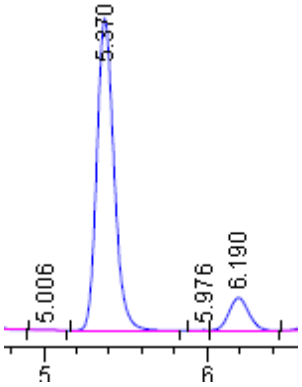
Peak	Retention Time, min	Area, %
Major Enantiomer	5.434	85.1587
Minor Enantiomer	6.229	5.6092

Figure 6S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 5 (conditions CH_3CN/ 4 °C).



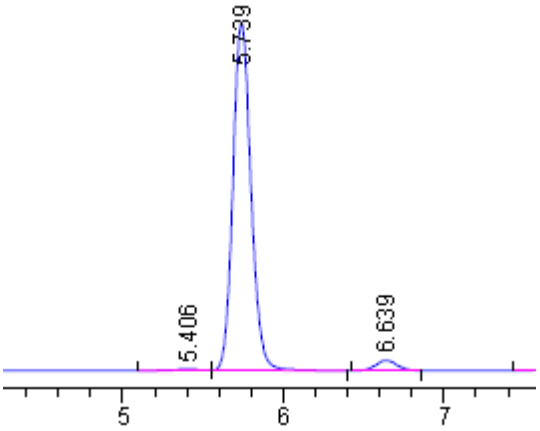
Peak	Retention Time, min	Area, %
Major Enantiomer	5.434	80.0010
Minor Enantiomer	6.247	2.9159

Figure 7S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 6 (conditions CH3CN/ -20 °C).



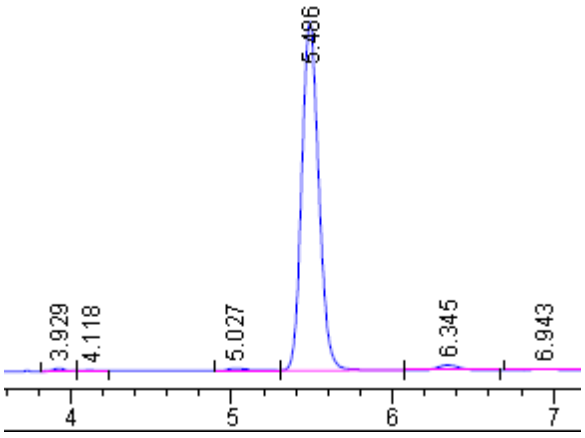
Peak	Retention Time, min	Area, %
Major Enantiomer	5.370	78.8269
Minor Enantiomer	6.190	9.4368

Figure 8S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 7 (conditions THF and CH_3CN(1:1)/rt).



Peak	Retention Time, min	Area, %
Major Enantiomer	5.739	95.2147
Minor Enantiomer	6.639	3.2565

Figure 9S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 8 (conditions THF and CH_3CN(1;1)/ -20 °C).



Peak	Retention Time, min	Area, %

Major Enantiomer	5.486	28.4170
Minor Enantiomer	6.345	0.5622

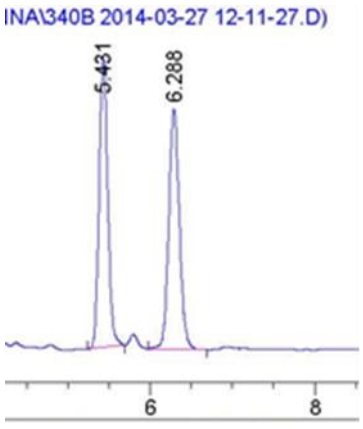
Figure 10S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 2, entry 9 (conditions THF and CH_3CN(1;1)/ -40 °C).

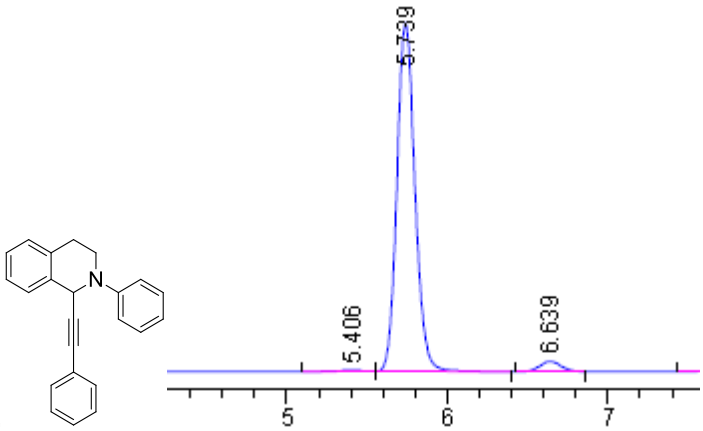
7. Characterization Data and HPLC Chromatogram for the Racemic- and Chiral C_1-Alkynyl-*N*-Aryl-Tetrahydraisoquinoline Derivatives.

2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline, 3a

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, R_f = 0.7).^{1}H NMR (400 MHz, ppm) δ 7.35-7.25(m, 5H), 7.22-7.14(m, 6H), 7.09(dd, J = 8.4, 0.8 Hz, 2H), 6.86(dt, J = 7.2, 0.8 Hz, 1H), 5.62(s, 1H), 3.75-3.61(m, 2H), 3.09(ddd, J = 16.8, 10.4, 6.4 Hz, 1H), 2.95(dt, J = 16.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ; 149.55 HRMS calcd for C23H19N: 309.1517; found: 309.1511.

RACEMIC





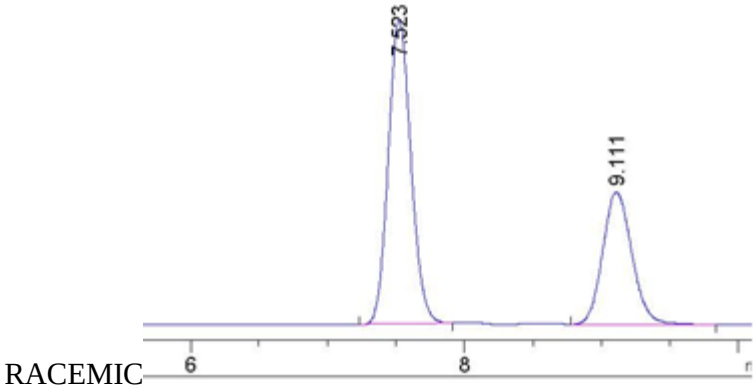
CHIRAL

Peak	Retention Time, min	Area, %
Major Enantiomer	5.739	95.2147
Minor Enantiomer	6.639	3.2565

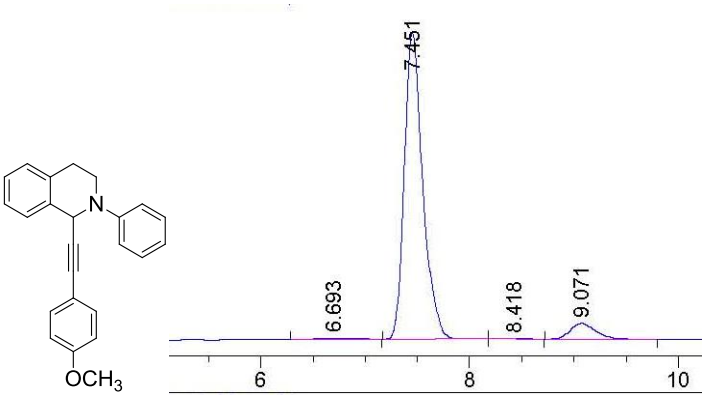
Figure 9S. HPLC Chromatogram for the two enantiomers of 2-Phenyl-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline synthesized according to the procedure described in Table 3, entry 1.

1-(4-Methoxy-phenylethynyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline, 3b

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, R_f = 0.4). ^{1}H NMR (400 MHz, ppm) δ 7.34-7.31(m, 1H), 7.30- 7.26(m, 2H), 7.21-7.16(m, 4H), 7.15-7.12(m, 1H), 7.08(d, J = 8.0 Hz, 2H), 6.84(dd, J = 7.6, 7.6 Hz, 1H), 6.69(dt, J = 8.8, 2.4 Hz, 2H), 5.60(s, 1H), 3.73-3.60(m, 2H), 3.68(s, 3H), 3.09(ddd, J = 16.0, 9.6, 6.0 Hz, 1H), 2.92(dt, J = 16.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 159.10, 149.32, 135.40, 134.14, 132.93, 128.92, 128.70, 127.23, 126.94, 126.04, 119.34, 116.46, 114.95, 113.54, 87.03, 84.52, 55.17, 52.25, 43.41, 28.95; MS (EI) *m/z* (%) 340, 339, 338(100), 324, 223, 220, 219, 208, 191, 189, 118, 104, 77; HRMS calcd for C24H21NO: 339.1623; found: 339.1604.



RACEMIC



CHIRAL

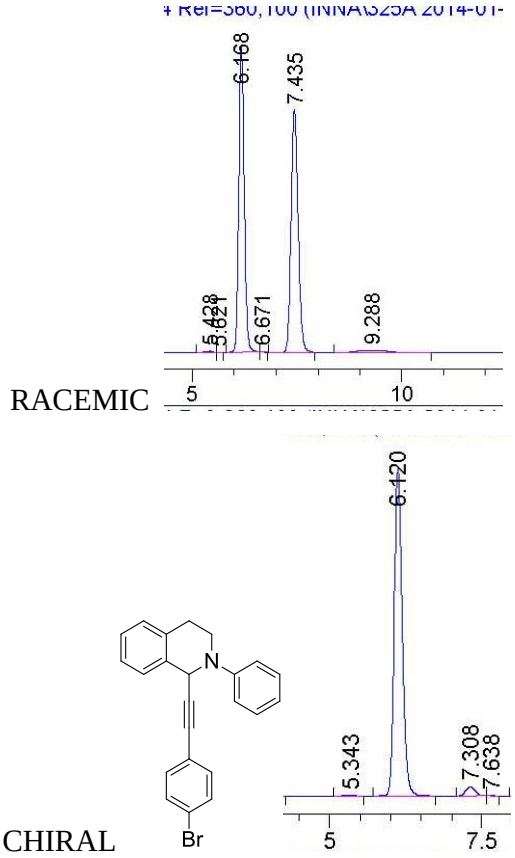
Peak	Retention Time, min	Area, %
Major Enantiomer	7.451	90.1879
Minor Enantiomer	9.071	6.4559

Figure 10S. HPLC Chromatogram for the two enantiomers of **1-(4-Methoxy-phenylethynyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline, 3b** synthesized according to the procedure described in Table 3, entry 2.

1-(4-Bromo-phenylethynyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline, 3c.

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.5). ^{1}H NMR (300 MHz, ppm) δ 7.35-7.29(m, 4H), 7.24-7.15(m, 4H), 7.14-7.07(m, 4H), 6.87(dt, J = 7.2, 1.2 Hz, 1H), 5.61(s, 1H), 3.77-3.58(m, 2H), 3.13(ddd, J = 15.6, 9.9, 5.7 Hz, 1H), 2.95(dt, J = 15.9, 4.2 Hz, 1H); ^{13}C NMR (75 MHz, ppm) δ 149.29, 134.93, 134.26, 133.06, 131.20, 129.04, 128.85, 127.26, 127.20, 126.20, 122.11, 121.81, 119.64, 116.58, 89.78, 83.67, 52.35,

43.47, 28.94; MS (EI) *m/z* (%) 389, 388(100), 387, 386(100), 373, 360, 307, 284, 258, 206, 182, 153, 140, 75, 50; HRMS calcd for 386.0544; $C_{23}H_{18}BrN$: 387.0631; found: 387.0623.



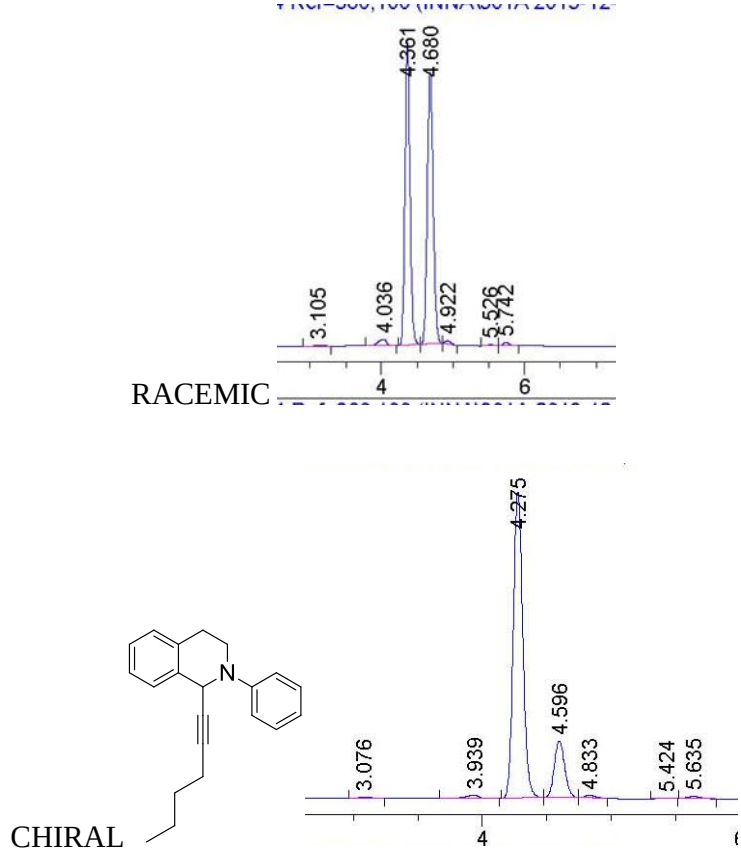
Peak	Retention Time, min	Area, %
Major Enantiomer	6.120	93.6750
Minor Enantiomer	7.308	3.1405

Figure 11S. HPLC Chromatogram for the two enantiomers of **1-(4-Bromo-phenylethynyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline 3c** synthesized according to the procedure described in Table 3, entry 3.

1-(hex-1-yn-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline, 3d

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33- 7.29(m, 3H), 7.24-7.16(m, 3H), 7.09-7.07(m, 2H), 6.87(t, *J* = 7.4 Hz, 1H), 5.43(s, 1H), 3.73-3.69(m, 1H), 3.62-3.55(m, 1H), 3.14-3.06(m, 1H), 2.96-2.91(m, 1H), 2.13-2.09(m, 2H), 1.41-1.38(m, 2H), 1.37-1.24(m, 2H), 0.84-0.81(m, 3H).

^{13}C NMR (75 MHz, ppm) δ 149.64, 136.21, 134.13, 129.01, 128.81, 127.30, 126.93, 126.11, 119.32, 116.58, 85.22, 79.08, 51.78, 43,15, 30.77, 28.88, 21.78, 18.44, 13.55. HRMS (ESI) *m/z* calculated for $C21H23N^+$ ($[M + H]^+$) 290.19033, found 290.19031.



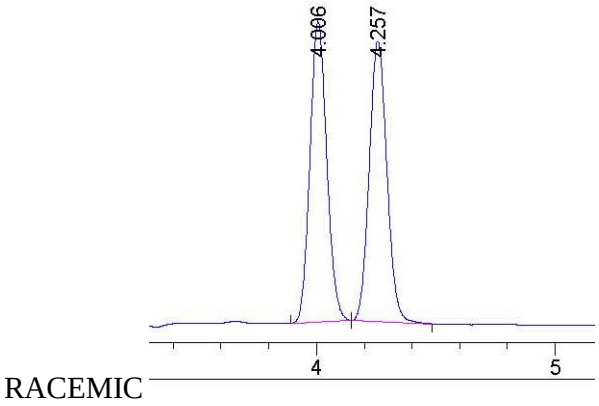
Peak	Retention Time, min	Area, %
Major Enantiomer	4.275	79.1011
Minor Enantiomer	4.596	16.1434

Figure 12S. HPLC Chromatogram for the two enantiomers of **1-(hex-1-yn-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline 3d** synthesized according to the procedure described in Table 3, entry 4.

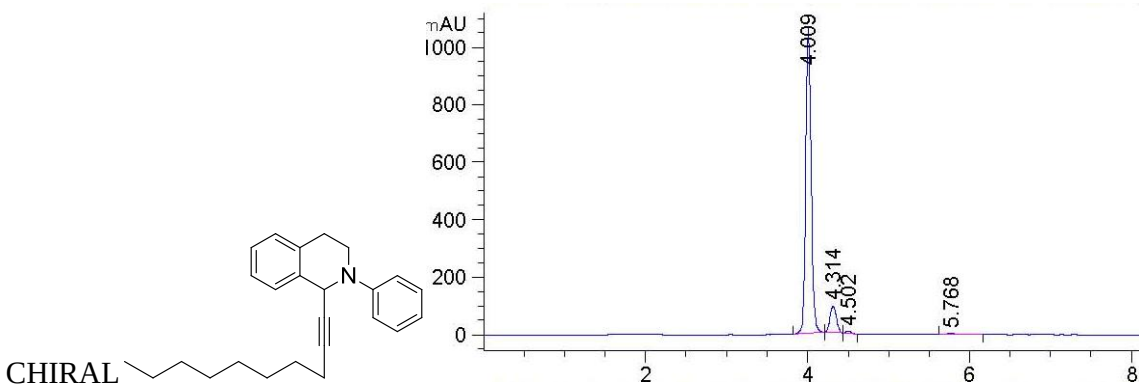
1-(dec-1-yn-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline, 3e

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.85). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34- 7.26(m, 3H), 7.24-7.18(m, 3H), 7.11-7.09(d, *J* = 8.0 Hz, 2H), 6.90(t, *J* = 8.0 Hz, 1H), 5.45(s, 1H), 3.77-3.71(m, 1H), 3.66-3.59(m, 1H), 3.17-

3.09(m, 1H), 2.99-2.94(m, 1H), 2.15-2.11(m, 2H), 1.43-1.39(m, 2H), 1.33-1.20(m, 2H), 0.925 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (75 MHz, ppm) δ 149.62, 136.24, 134.14, 129.03, 128.82, 127.32, 126.96, 126.14, 119.37, 116.60, 85.38, 79.13, 51.80, 43. 22, 31.83, 29.20, 29.05, 28.90, 28.71, 22.69, 18.77, 14.14. HRMS (ESI) *m/z* calculated for $C25H32N^+$ ($[M + H]^+$) 346.25293, found 346.25241.



RACEMIC



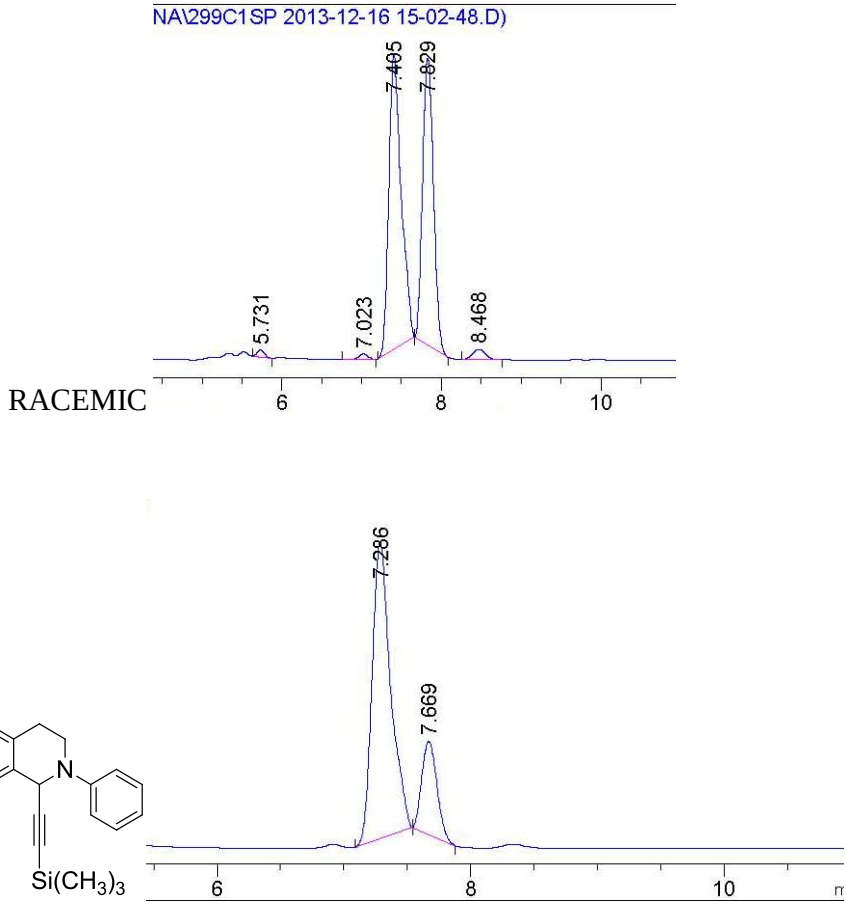
CHIRAL

Peak	Retention Time, min	Area, %
Major Enantiomer	4.009	90.0230
Minor Enantiomer	4.314	8.9096

Figure 13S. HPLC Chromatogram for the two enantiomers of **1-(dec-1-yn-1-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline, 3e** synthesized according to the procedure described in Table 3, entry 5.

2-Phenyl-1-trimethylsilanylethynyl-1,2,3,4-tetrahydroisoquinoline, 3f

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.8). ^{1}H NMR (400 MHz, ppm) δ 7.29-7.25(m, 3H), 7.21-7.13(m, 3H), 7.04(d, J = 6.0 Hz, 2H), 6.86(t, J = 5.4 Hz, 1H), 5.40(s, 1H), 3.69-3.64(m, 1H), 3.60-3.54(m, 1H), 3.09(ddd, J = 16.2, 10.2, 6.0 Hz, 1H), 2.91(dt, J = 16.0, 3.6 Hz, 1H), 0.05(s, 9H); ^{13}C NMR (100 MHz, ppm) δ 149.37, 135.04, 134.17, 128.85, 128.73, 127.29, 126.97, 126.04, 119.52, 116.80, 104.61, 88.98, 52.72, 43.38, 28.87, 0.13; HRMS calcd for C20H23NSi: 305.1600; found: 305.1611.



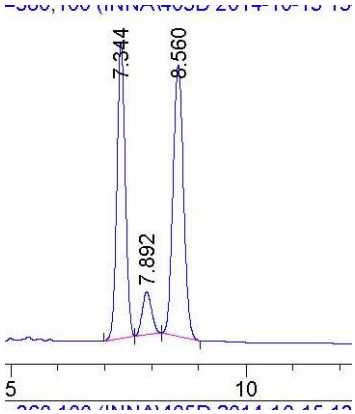
Peak	Retention Time, min	Area, %
Major Enantiomer	7.286	72.5227
Minor Enantiomer	7.669	18.4973

Figure 14S. HPLC Chromatogram for the two enantiomers of **2-Phenyl-1-trimethylsilanylethynyl-1,2,3,4-tetrahydroisoquinoline 3f** synthesized according to the procedure described in Table 3, entry 6.

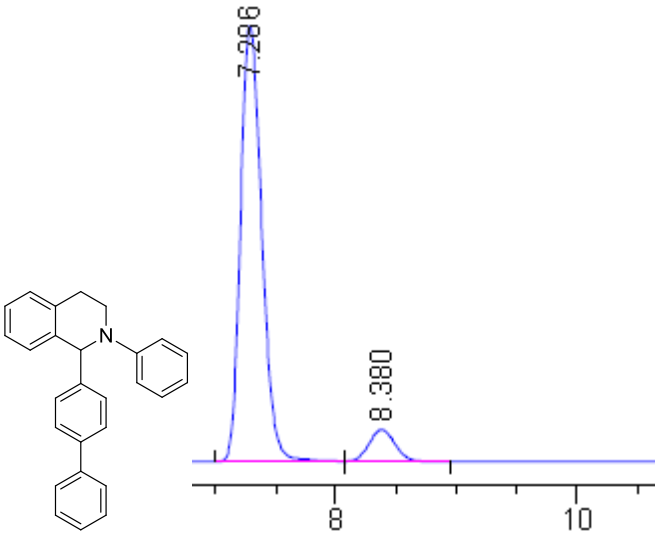
1-([1,1'-biphenyl]-4-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline, 3g

Isolated by Thin Layer Chromatography (Hexane/Ethyl Acetate = 10:1, Rf = 0.4).^{1}H NMR (400 MHz, ppm) δ 7.56-7.54(m, 2H), 7.49-7.32(m, 10H), 7.28-7.22(m, 3H), 7.17-7.15(m, 2H), 6.91(t, J = 7.4, 1H), 5.68(s, 1H), 3.78-3.70(m, 2H), 3.17-3.14(m, 1H), 3.04-2.90(m, 1H); ^{13}C NMR (75 MHz, ppm) δ 149.55, 140.75, 140.36, 135.37, 134.39, 132.16, 129.15, 128.95, 128.81, 127.55, 127.44, 127.24, 126.98, 126.76, 126.29, 121.91, 119.68, 118.15, 116.74, 89.28, 84.65, 52.40, 43.47, 28.92.

RACEMIC



CHIRAL

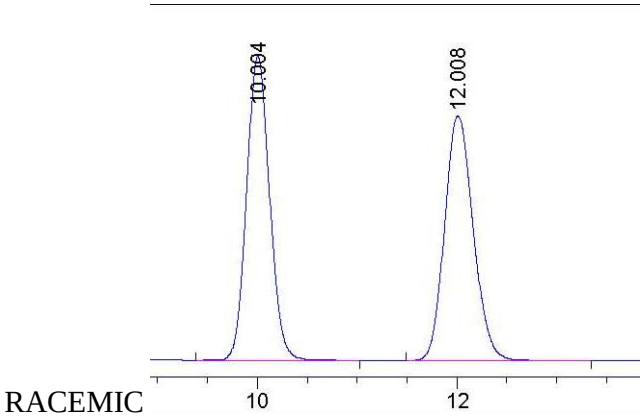


Peak	Retention Time, min	Area, %
Major Enantiomer	7.286	80.002
Minor Enantiomer	8.380	7.212

Figure 15S. HPLC Chromatogram for the two enantiomers of **1-([1,1'-biphenyl]-4-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline**, **3g** synthesized according to the procedure described in Table 3, entry 7.

2-(3-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline, 3h

Isolated by Thin Layer Chromatography Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.5). ^{1}H NMR (400 MHz, ppm) δ 7.39-7.36(m, 1H), 7.34-7.31(m, 2H), 7.27-7.19(7H), 6.75-6.73(m, 1H), 6.70-6.69(m, 1H), 6.48-6.45(m, 1H), 5.65(s, 1H), 3.83(s, 3H), 3.79-3.71(m, 2H), 3.19-3.11(m, 1H), 3.03-2.96(m, 1H). ^{13}C NMR (75 MHz, ppm) 160.63, 150.79, 135.36, 134.42, 131.75, 129.81, 128.88, 128.07, 128.03, 127.38, 127.24, 126.31, 122.98, 109.23, 104.48, 102.84, 88.52, 84.72, 55.24, 52.17, 43.52, 28.84.

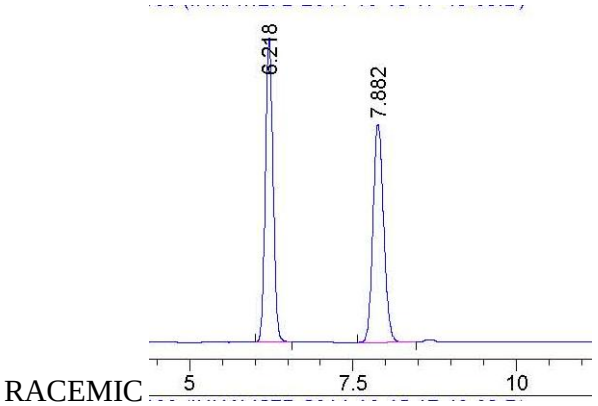


Peak	Retention Time, min	Area, %
Major Enantiomer	10.187	95.7409
Minor Enantiomer	12.301	2.9895

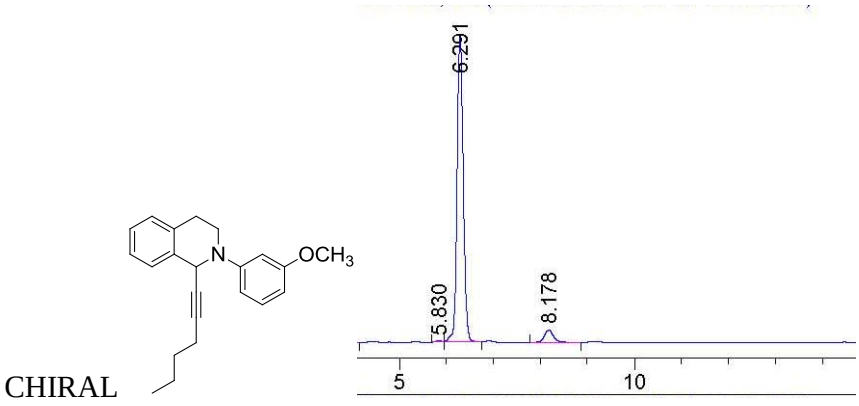
Figure 16S. HPLC Chromatogram for the two enantiomers of **2-(3-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline, 3h** synthesized according to the procedure described in Table 3, entry 8.

1-(hex-1-yn-1-yl)-2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline, 3i

Isolated by Thin Layer Chromatography Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.6). ^{1}H NMR (300 MHz, ppm) δ 7.31-7.14(m, 5H), 6.69-6.62(m, 2H), 6.45-6.41(m, 1H), 5.41(s, 1H), 3.82(s, 3H), 3.72-3.67(m, 1H), 3.61-3.14(m, 1H), 3.12-3.04(m, 1H), 2.97-2.89(m, 1H), 2.14-2.08(m, 2H), 1.41-1.24(m, 4H), 0.83(t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, ppm) 160.57, 150.92, 136.15, 134.17, 129.66, 128.76, 127.26, 126.96, 126.14, 109.21, 104.21, 102.75, 85.18, 79.05, 55.18, 51.69, 43.24, 30.78, 28.81, 21.81, 18.46, 13.55.



RACEMIC



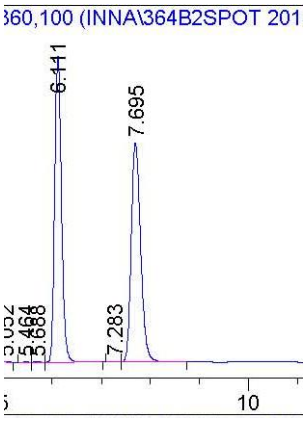
CHIRAL

Peak	Retention Time, min	Area, %
Major Enantiomer	6.291	93.2168
Minor Enantiomer	8.178	5.0439

Figure 17S. HPLC Chromatogram for the two enantiomers of **1-(hex-1-yn-1-yl)-2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline, 3i** synthesized according to the procedure described in Table 3, entry 9.

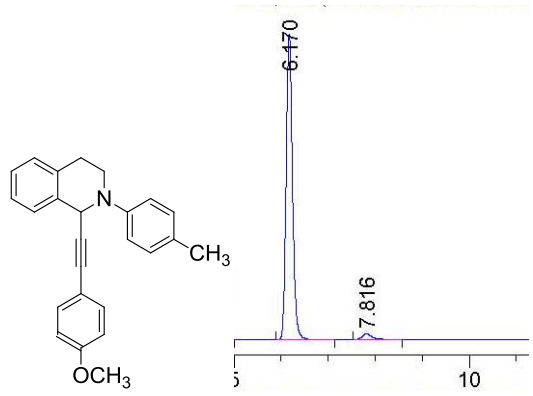
1-((4-methoxyphenyl)ethynyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline, 3j

Isolated by Thin Layer Chromatography Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.7). ^{1}H NMR (400 MHz, ppm) δ 7.37-7.34(m, 1H), 7.24-7.17(m, 5H), 7.14-7.11(m, 2H), 7.06-7.04(m, 2H), 6.75-6.72(m, 2H), 5.57(s, 1H), 3.76(s, 1H), 3.71-3.62(m, 2H), 319-3.11(m, 1H), 2.98-2.92(m, 1H), 2.33(s, 3H). ^{13}C NMR (75 MHz, ppm) 159.34, 154.36, 135.58, 134.17, 133.13, 129.61, 128.95, 127.46, 127.11, 126.16, 117.54, 115.18, 113.66, 86.94, 85.03, 55.22, 53.06, 43.80, 28.83, 20.52.



RACEMIC

CHIRAL



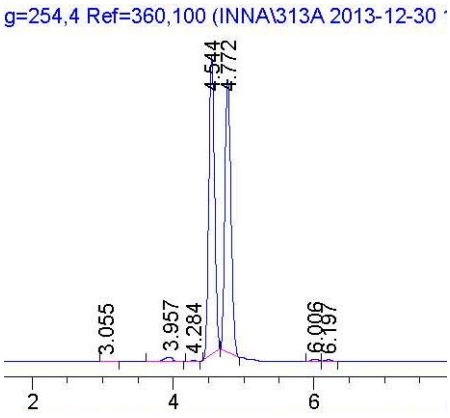
Peak	Retention Time, min	Area, %
Major Enantiomer	6.170	83.4949
Minor Enantiomer	7.816	2.4972

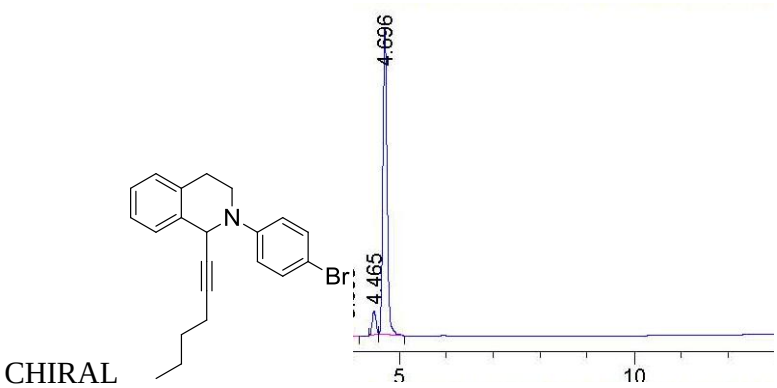
Figure 18S. HPLC Chromatogram for the two enantiomers of **1-((4-methoxyphenyl)ethynyl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline, 3j** synthesized according to the procedure described in Table 3, entry 10 .

2-(4-bromophenyl)-1-(hex-1-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline, 3k

Isolated by Thin Layer Chromatography Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.7). ^{1}H NMR (500 MHz, ppm) δ 7.40-7.38(m, 2H), 7.31-7.28(m, 1H), 7.24-7.23(m, 2H), 7.22-7.18(m,1H), 6.97-6.95(m, 2H), 5.38(s, 1H), 3.66-3.59(m, 1H), 3.58-3.54(m, 1H), 3.11-3.08(m, 1H), 2.99-2.95(m, 1H), 2.13-2.11(m, 2H), 1.41-1.36(m, 2H), 1.31-1.26(m, 2H), 0.85(t, , J = 10 Hz, 3H). ^{13}C NMR (125 MHz, ppm) δ 148.49, 135.69, 133.86, 131.79, 128.79, 127.29, 127.14, 126.28, 118.21, 111.65, 85.63, 78.54, 51.74, 43.34, 30.73, 28.73, 21.80, 18.41, 13.55.

RACEMIC



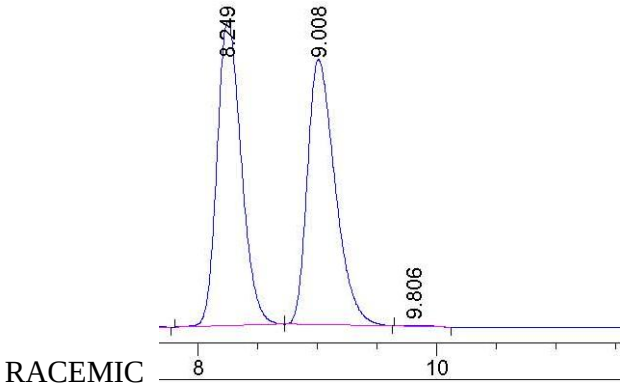


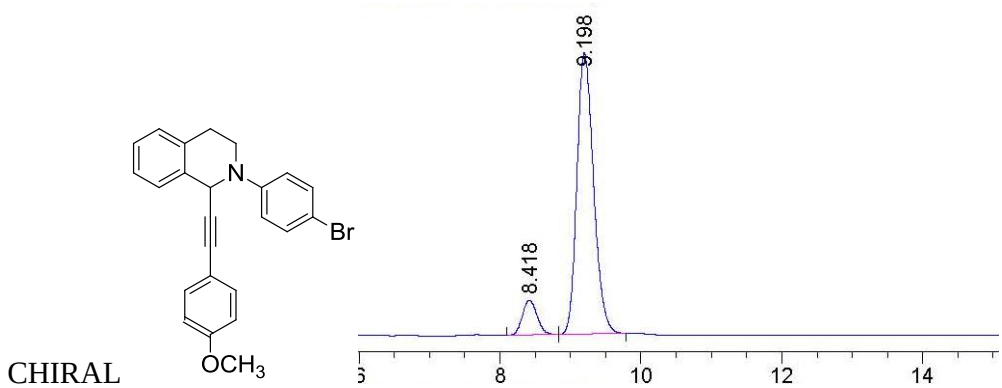
Peak	Retention Time, min	Area, %
Major Enantiomer	4.465	89.3509
Minor Enantiomer	4.696	6.1649

Figure 19S. HPLC Chromatogram for the two enantiomers of **2-(4-bromophenyl)-1-(hex-1-yn-1-yl)-1,2,3,4-tetrahydroisoquinoline, 3k** synthesized according to the procedure described in Table 3, entry 11.

2-(4-bromophenyl)-1-((4methoxyphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline, 3l

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, Rf = 0.6). 1H NMR (400 MHz, ppm) δ 7.44-7.33(m, 3H), 7.25-7.18(m, 5), 7.01-6.98(m, 2H), 6.77-5.56(m, 2H), 5.56(s, 1H), 3.77(s, 3H), 3.73-3.69(m, 2H), 3.17-3.01(m, 1H), 3.00-2.96(m, 1H). ^{13}C NMR (100 MHz, ppm) δ159.53, 148.41, 135.16, 134.09, 133.60, 133.17, 131.88, 128.86, 127.40, 127.33, 126.39, 118.22, 114.84, 113.76, 86.43, 84.91, 55.26, 52.19, 43.59, 28.76.





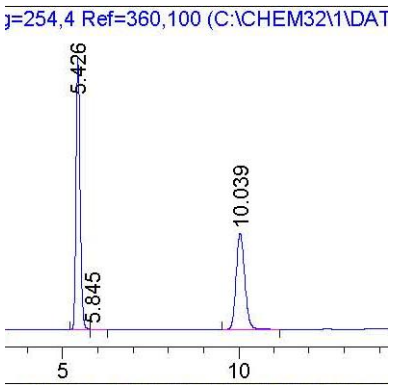
Peak	Retention Time, min	Area, %
Major Enantiomer	8.418	68.1386
Minor Enantiomer	9.198	7.3856

Figure 20S. HPLC Chromatogram for the two enantiomers of **2-(4-bromophenyl)-1-((4methoxyphenyl)ethynyl)-1,2,3,4-tetrahydroisoquinoline, 3l** synthesized according to the procedure described in Table 3, entry 12 .

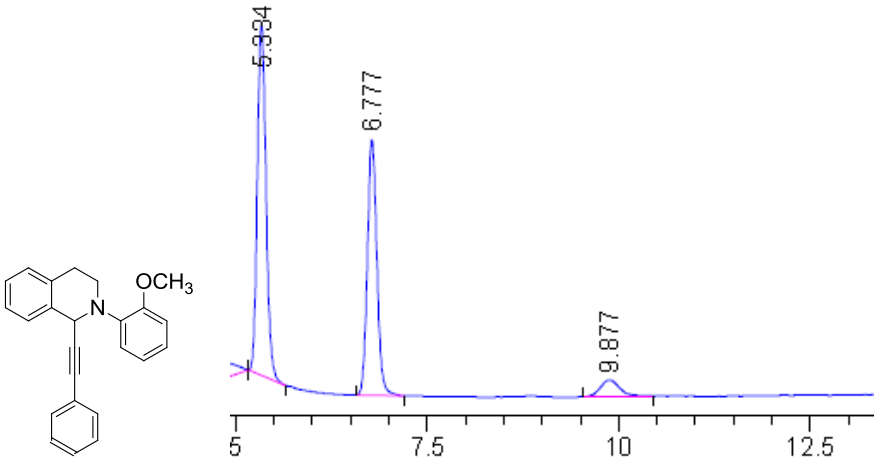
2-(2-Methoxy-phenyl)-1-phenylethynyl-1,2,3,4-tetrahydroisoquinoline, (3m).

Isolated by Thin Layer Chromatography (Hexane/Methylene Chloride/Diethyl ether = 100:60:1, *R*f = 0.3). ^{1}H NMR (400 MHz, ppm) δ 7.32-7.30(m, 1H), 7.22-7.15(m, 9H), 7.05(dt, *J* = 7.6, 1.6 Hz, 1H), 6.96(dt, *J* = 7.6, 1.6 Hz, 1H), 6.89(dd, *J* = 8.0, 0.8 Hz, 1H), 5.74(s, 1H), 3.87(s, 3H), 3.68(dt, *J* = 11.6, 4.0 Hz, 1H), 3.43(dd, *J* = 11.6, 11.6 Hz, 1H), 3.24(ddd, *J* = 16.8, 11.2, 5.6 Hz, 1H), 2.90(dt, *J* = 16.4, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, ppm) δ 159.10, 149.32, 135.40, 134.14, 132.93, 128.92, 128.70, 127.23, 126.94, 126.04, 119.34, 116.46, 114.95, 113.54, 87.03, 84.52, 55.17, 52.25, 43.41, 28.95; MS (EI) *m/z* (%) 339, 338, 322, 308(100), 293, 262, 246, 232, 217, 203, 202, 189, 165, 152, 115, 92, 91, 77, 64; HRMS calcd for C24H20NO: 339.1623; found: 339.1627.

RACEMIC



CHIRAL

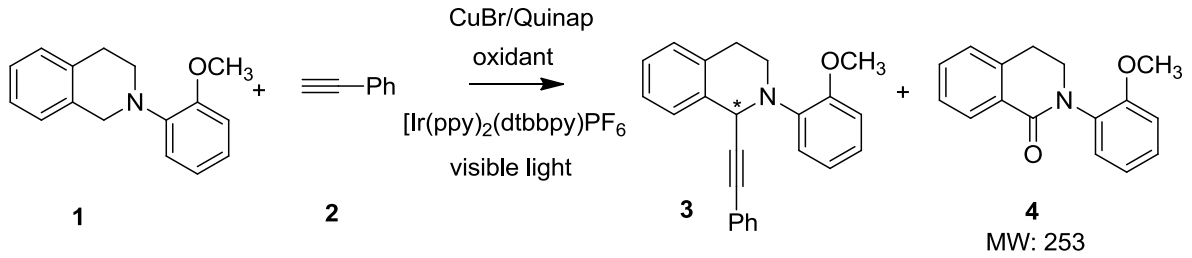


Peak	Retention Time, min	Area, %
Major Enantiomer	5.334	40.0343
Minor Enantiomer	6.777 (Starting material)	32.3233
	9.877	4.3070

Figure 21S. HPLC Chromatogram for the two enantiomers of **2-(2-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline, 3m** synthesized according to the procedure described in Table 3, entry 13 .

8. Effect of conditions on the enantioselectivity of coupling of *N*-aryl-1,2,3,4-tetrahydroisoquinolines with phenylacetylene

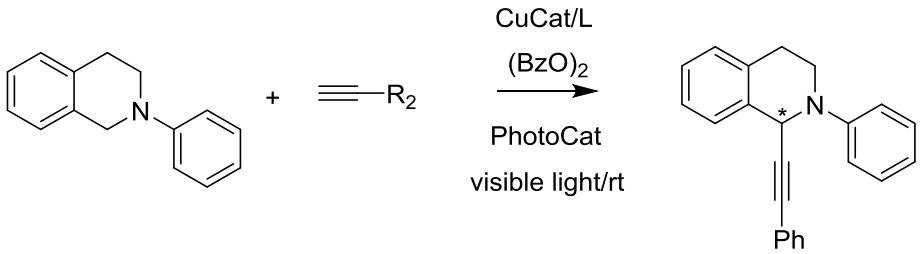
Table S1. Photoredox catalyzed synthesis of chiral **2-(2-methoxyphenyl)-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline, 3m.**



Entry[a]	Oxidant	**1,** %	**3,** Yield,%	**4**
1	O_2	80	16	ND[b]
2	$(BzO)_2$	trace	trace	D[c]

[a] Conditions: 0.1 mmol *N*-(2-methoxyphenyl)-tetrahydroisoquinoline, 0.15 mmol phenylacetylene, 1 mol % $[Ir(ppy)_2(dtbbpy)PF_6$, 10 mol % Copper Salt, 15 mol % chiral ligand (**L**) and 0.12 mmol $(BzO)_2$ or ballon with O_2, CH_3CN/THF (1:1), 48 h, 4° C. The yield was calculated by ^1H NMR integration method using CH_3NO_2 as an internal standard. [b] The desired product was not detected. [c] Detected by GCMS (dominant peak in the chromatogram) calculated for $C_{16}H_{15}NO$ [M] 253, found 253. Molecular weight of **4** was confirmed by HRMS (ESI): *m/z* calculated for $C_{16}H_{15}NNaO_2^+$ ($[M + Na]^+$) 276.0995, found 276.1001.

Table S2. Effect of conditions on the enantioselectivity of coupling of N-benzene tetrahydroisoquinoline with phenylacetylene.

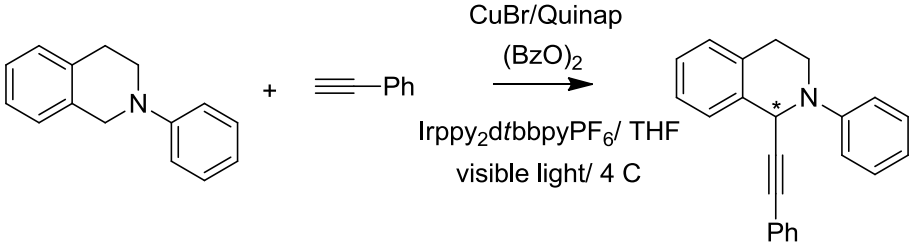


Entry[a]	PhotoCat (1 mol %)	CuCat,	Ligand	Solvent	*ee* (%)
1	$Ru(bpy)_3(PF6)_2$	none	PyBox	CH_3CN	ND[b]
2	$Ru(bpy)_3(PF6)_2$	CuBr	none	CH_3CN	5.0
3	none	CuBr	R-Quinap	THF	80(24)

4[c]	$[Ir(ppy)_2(dtbbpy)PF_6$	CuBr	R-Quinap	THF	77(16)

[a] Conditions: 0.1 mmol *N*-phenyl-tetrahydroisoquinoline, 0.1 mmol phenylacetylene, 10 mol % Copper Salt, 15 mol % chiral ligand (**L**) and 0.12 mmol $(BzO)_2$, 20 h . The *ee* values were determined with HPLC by using a Chiral cel OD-H column and 4:96 hexane/isopropanol as an eluent. The yield in parenthesis was calculated by ^{1}H NMR integration method using CH_3NO_2 as an internal standard. [b] The desired product was not detected. [c] The reaction was done in dark at 4 °C.

Table S3. Effect of conditions on the enantioselectivity of coupling of N-benzene tetrahydroisoquinoline with phenylacetylene.



Entry[a]	PhCCH, equiv.	Ligand, mol %	Time, h	Yield, %	ee, %
1	1	15	46	53	92
2	1	20	91	51	93
3	1.5	15	91	64	93
4	3	15	46	47	94

[a] Conditions: 0.1 mmol *N*-phenyl-tetrahydroisoquinoline, 10 mol % Copper Salt, 1 mol % $[Ir(ppy)_2(dtbbpy)PF_6$, and 0.12 mmol $(BzO)_2$. [d] The *ee* values were determined with HPLC by using a Chiral cel OD-H column and 4:96 hexane/isopropanol as an eluent. The yields were calculated by ^{1}H NMR integration method using CH_3NO_2 as an internal standard.

[i] Perrin, D.D.; Armarego, W. L. F. in *Purification of laboratory Chemicals.* Pergamon Press plc. Great Britain by BPCC Wheatons Ltd, 3rd ed. **1989**.

[ii] Zhiping Li, Z.; MacLeod, P. D.; Li, C.-J. *Tetrahedron Lett.* **2002**, *43*, 5731.

[iii] Rueping, M.; Koenigs, R. M.; Poscharny, K.; Fabry, D. C.; Leonori,D.; Carlos Vila, C. *Chem. Eur. J.* **2012,**, 18, 5170.

[iv] Kwong, F. Y.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 581–584.

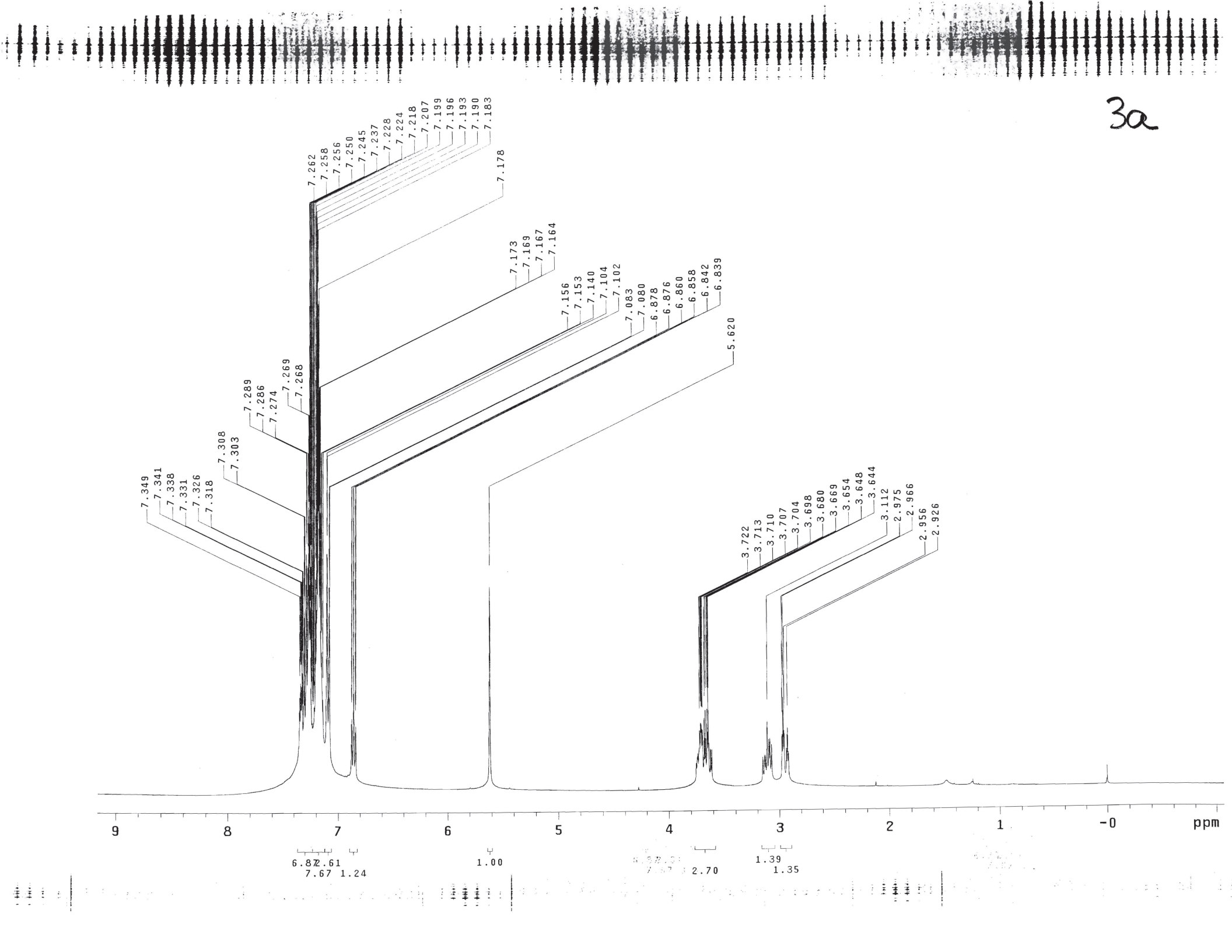
[v] Palmer, R.A.; Piper T. S. *Inorg. Chem.* **1966**, *5 (5),* 864-878.

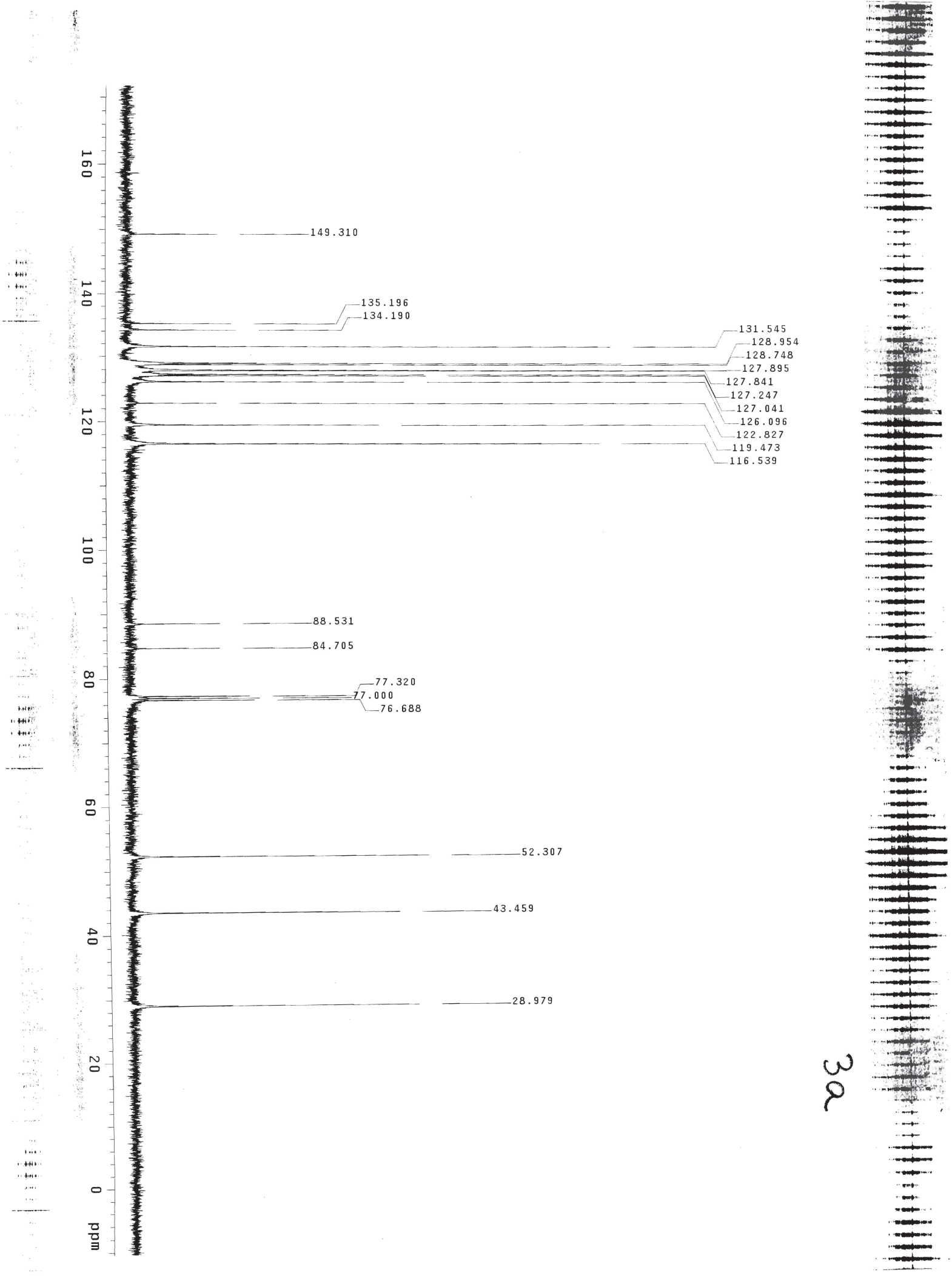
[vi] Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. *J. Am. Chem. Soc.* **2004**, *126*, 2763.

[vii] Sprouse, S.; K. A. King, K. A.; P. J. Spellane, P. J.; Watts, R. J. *J . Am. Chem. SOC.* **1984,** *106*, 6647-665.

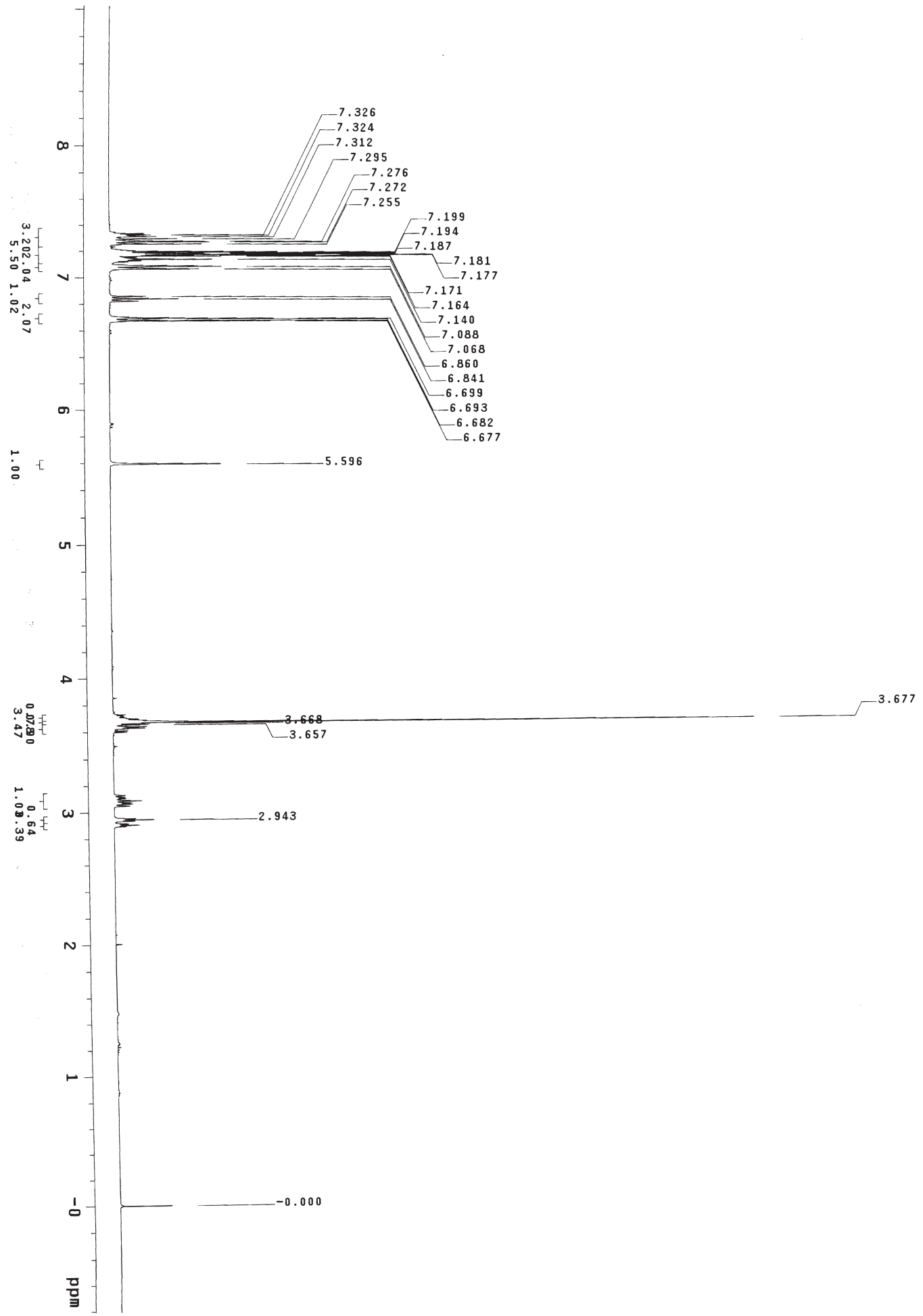
[viii] Zeng, T.; Song, G.; Moores, A.; Li, C.-J. *Synlett.* **2010**, *13*, pp 2002–2008

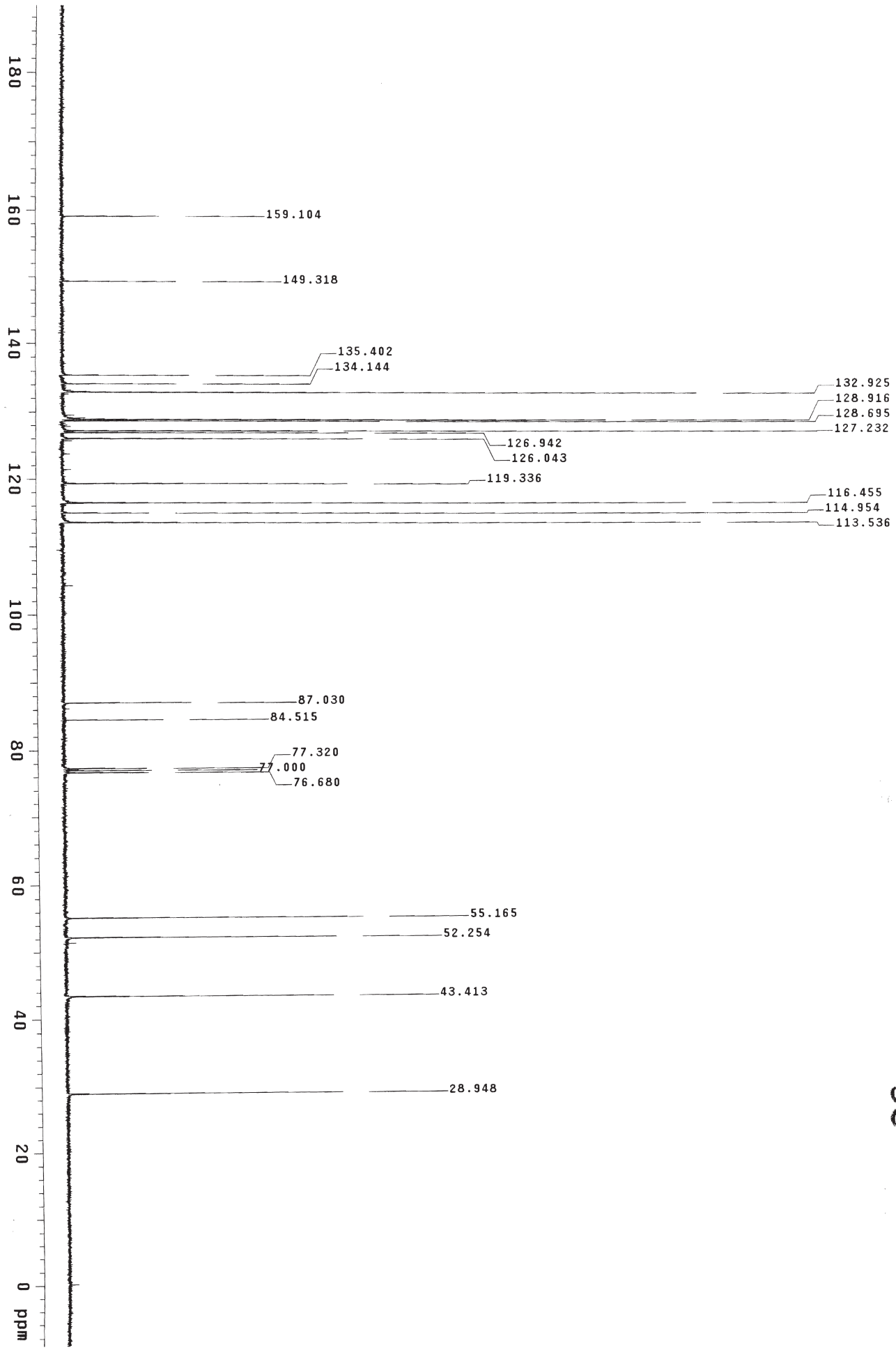
[ix] Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; Prentice Hall: Englewood Cliffs, NJ, **1971**.

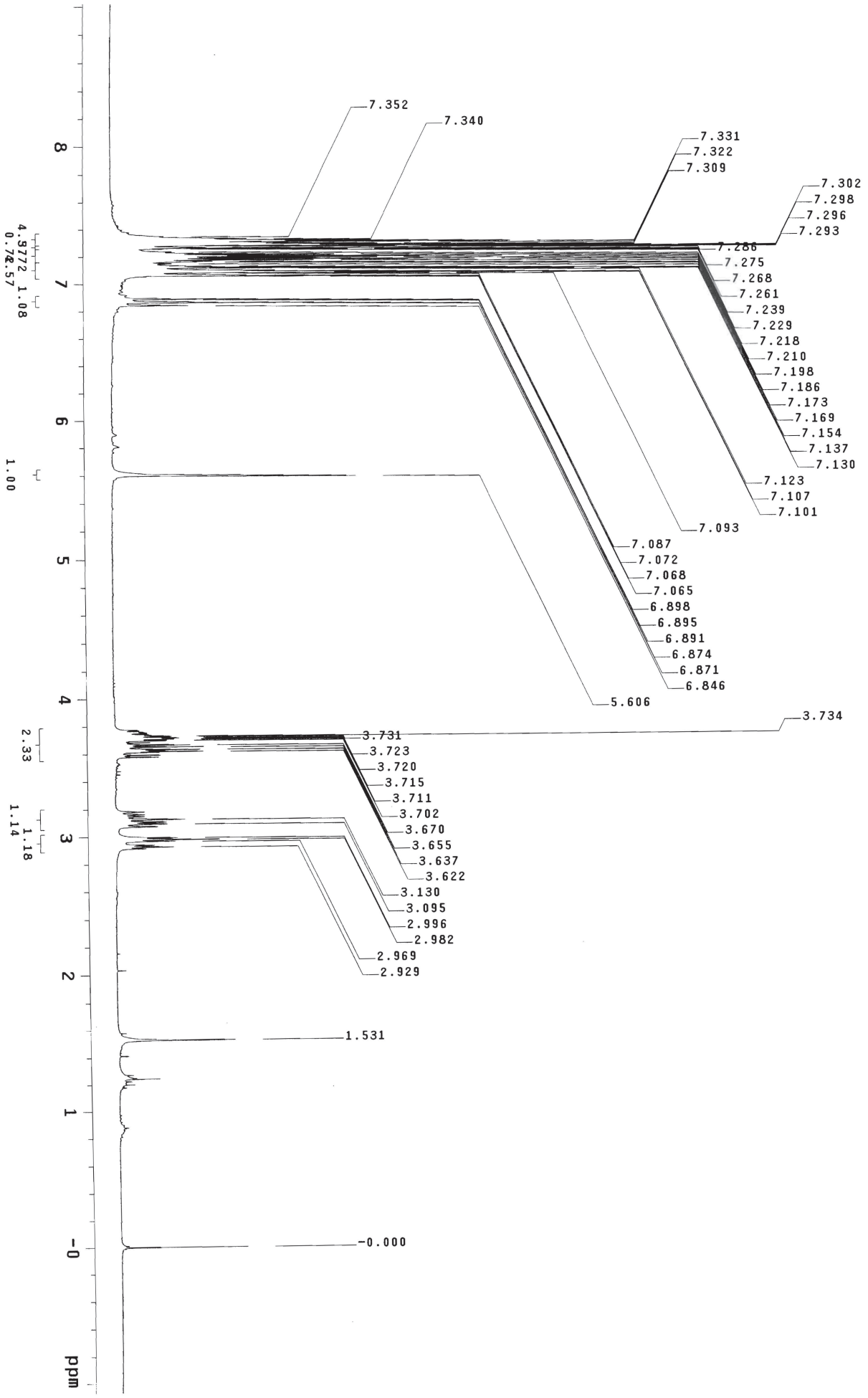

3a
7.262
7.258
7.256
7.250
7.245
7.237
7.228
7.224
7.218
7.207
7.199
7.196
7.193
7.190
7.183
7.178
7.173
7.169
7.167
7.164
7.156
7.153
7.140
7.104
7.102
7.083
7.080
6.878
6.876
6.860
6.858
6.842
6.839
5.620
7.289
7.286
7.274
7.269
7.268
7.308
7.303
7.349
7.341
7.338
7.331
7.326
7.318
3.722
3.713
3.710
3.707
3.704
3.698
3.680
3.669
3.654
3.648
3.644
3.112
2.975
2.966
2.956
2.926
9
8
7
6
5
4
3
2
1
-0
ppm
6.87
2.61
7.67
1.24
1.00
2.70
1.39
1.35


149.310
135.196
134.190
131.545
128.954
128.748
127.895
127.841
127.247
127.041
126.096
122.827
119.473
116.539
88.531
84.705
77.320
77.000
76.688
52.307
43.459
28.979
160
140
120
100
80
60
40
20
0
ppm

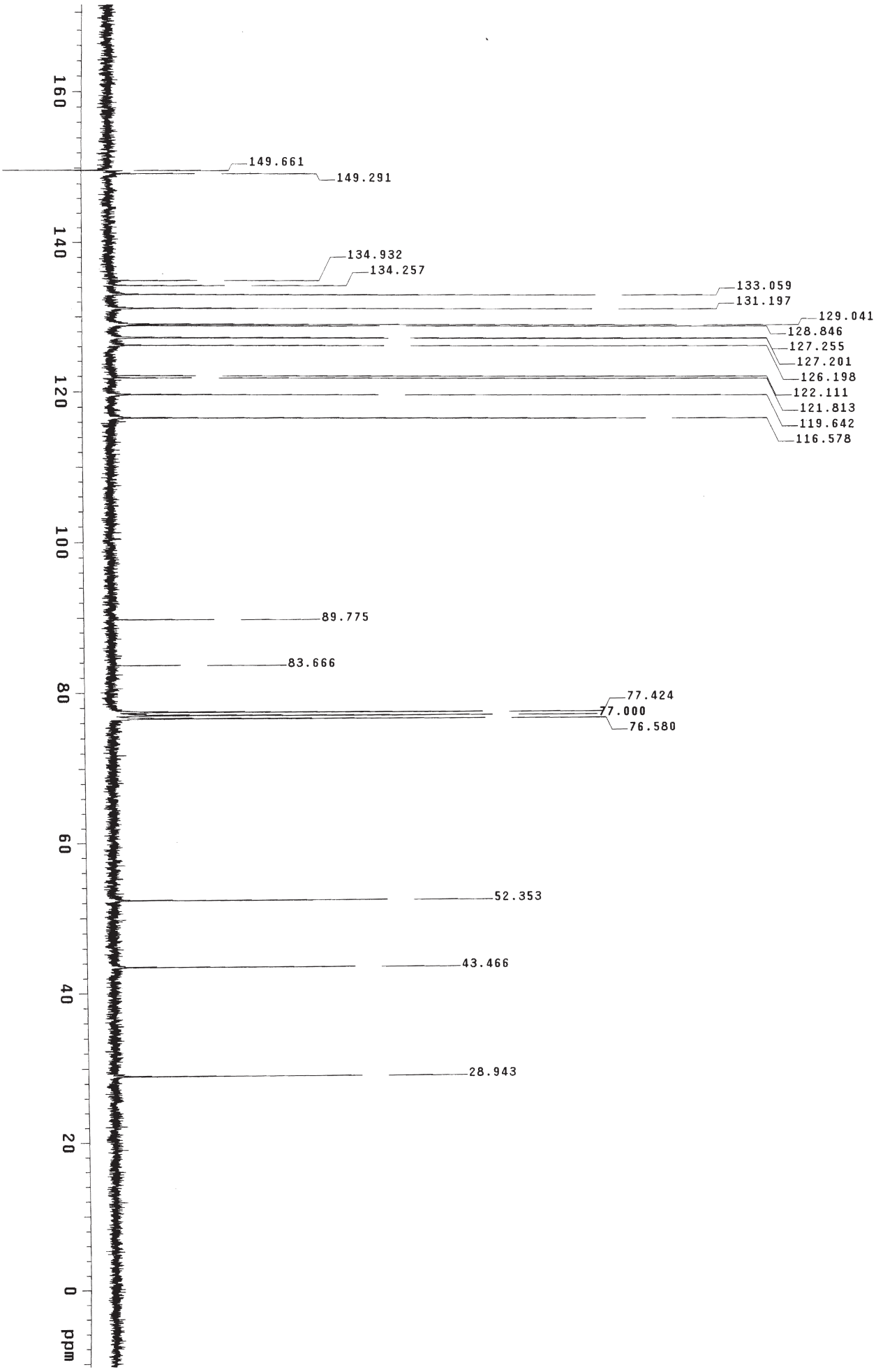
3a


7.326
7.324
7.312
7.295
7.276
7.272
7.255
7.199
7.194
7.187
7.181
7.177
7.171
7.164
7.140
7.088
7.068
6.860
6.841
6.699
6.693
6.682
6.677
5.596
3.677
3.668
3.657
2.943
-0.000
ppm

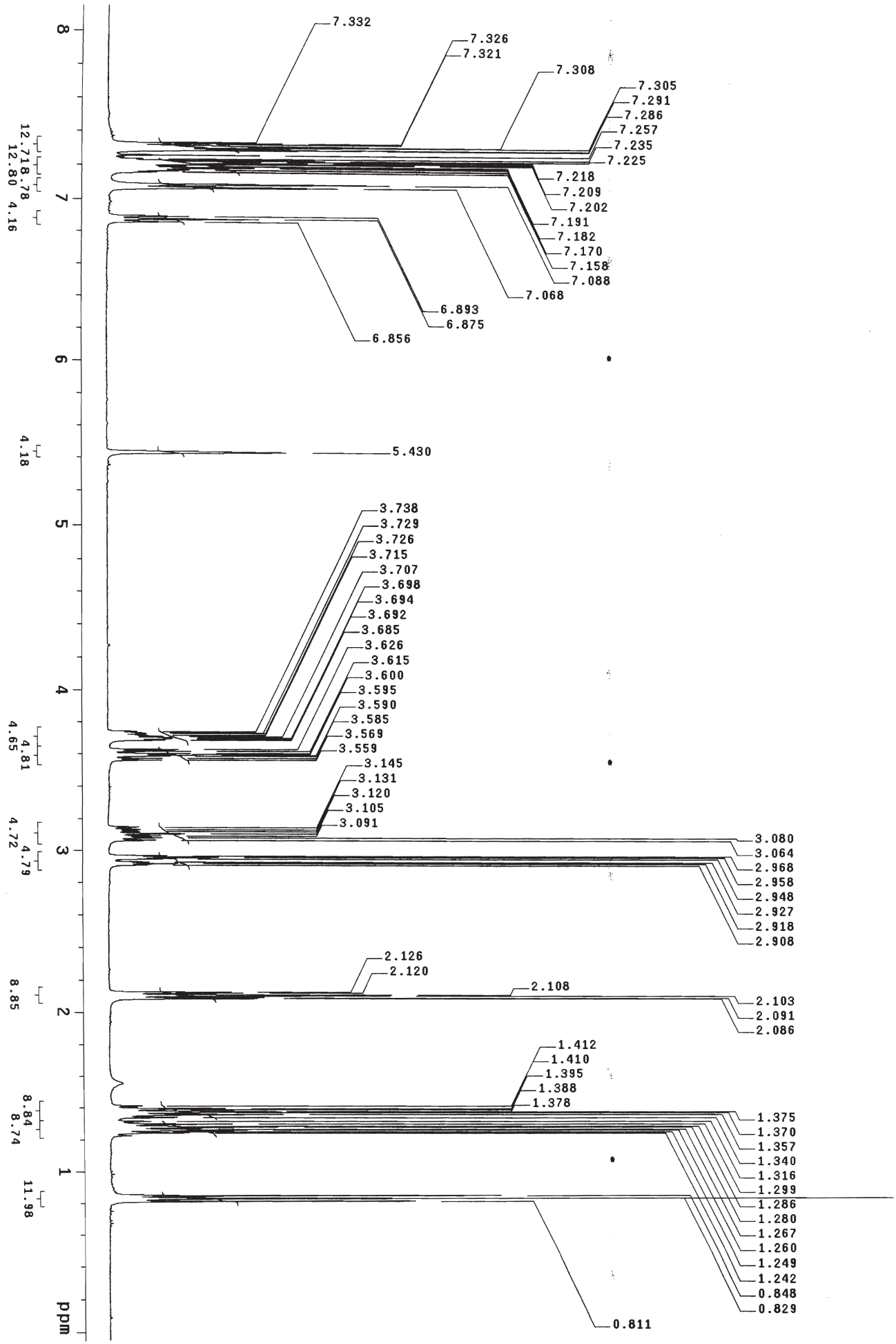

180
160
140
120
100
80
60
40
20
0 ppm
159.104
149.318
135.402
134.144
132.925
128.916
128.695
127.232
126.942
126.043
119.336
116.455
114.954
113.536
87.030
84.515
77.320
77.000
76.680
55.165
52.254
43.413
28.948


7.352
7.340
7.331
7.322
7.309
7.302
7.298
7.296
7.293
7.286
7.275
7.268
7.261
7.239
7.229
7.218
7.210
7.198
7.186
7.173
7.169
7.154
7.137
7.130
7.123
7.107
7.101
7.093
7.087
7.072
7.068
7.065
6.898
6.895
6.891
6.874
6.871
6.846
5.606
3.734
3.731
3.723
3.720
3.715
3.711
3.702
3.670
3.655
3.637
3.622
3.130
3.095
2.996
2.982
2.969
2.929
1.531
-0.000
4.9772 1.08
0.74 2.57
1.00
2.33
1.14 1.18
ppm

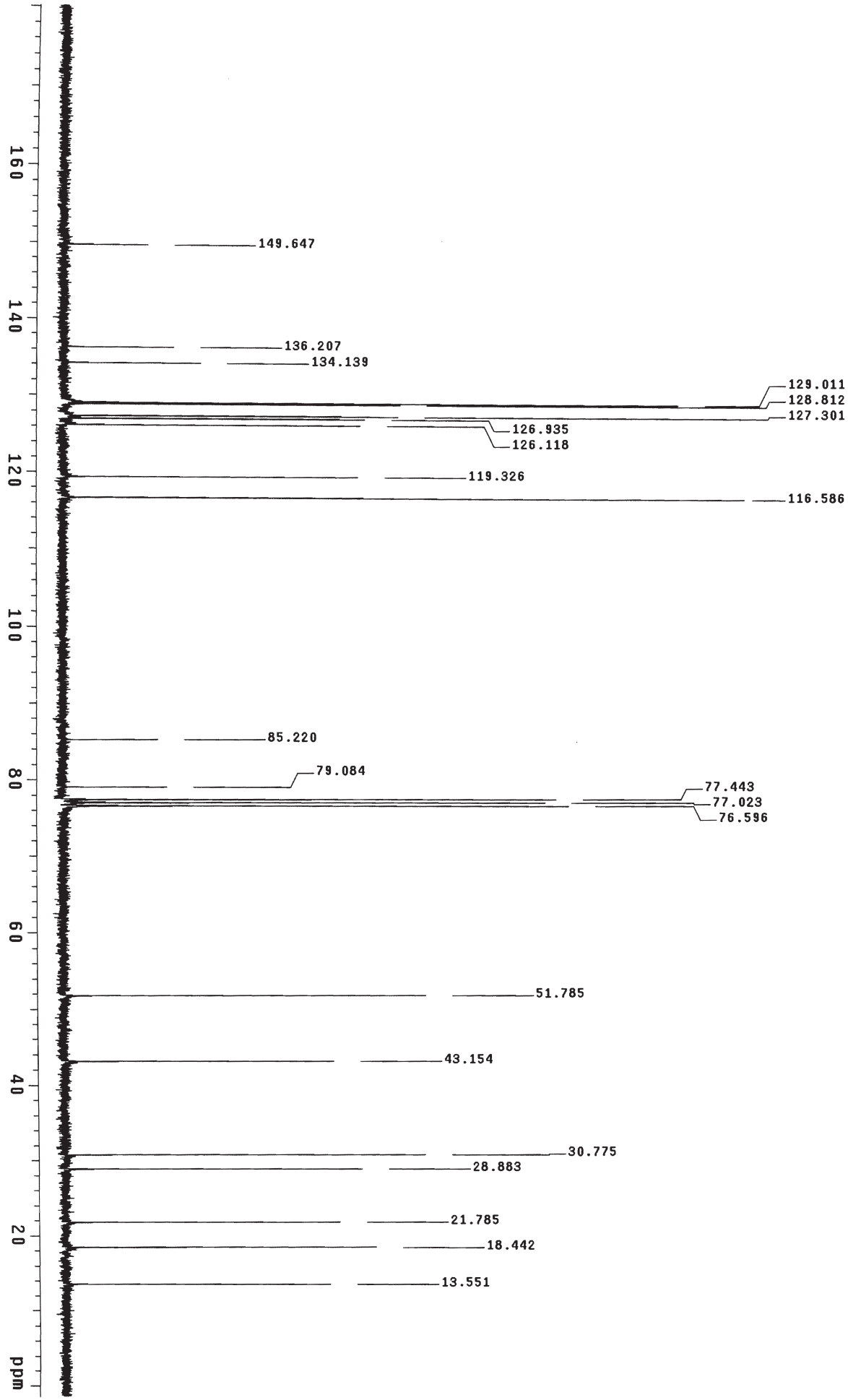
3C


160
140
120
100
80
60
40
20
0
ppm
149.661
149.291
134.932
134.257
133.059
131.197
129.041
128.846
127.255
127.201
126.198
122.111
121.813
119.642
116.578
89.775
83.666
77.424
77.000
76.580
52.353
43.466
28.943

3C


7.332
7.326
7.321
7.308
7.305
7.291
7.286
7.257
7.235
7.225
7.218
7.209
7.202
7.191
7.182
7.170
7.158
7.088
7.068
6.893
6.875
6.856
5.430
3.738
3.729
3.726
3.715
3.707
3.698
3.694
3.692
3.685
3.626
3.615
3.600
3.595
3.590
3.585
3.569
3.559
3.145
3.131
3.120
3.105
3.091
3.080
3.064
2.968
2.958
2.948
2.927
2.918
2.908
2.126
2.120
2.108
2.103
2.091
2.086
1.412
1.410
1.395
1.388
1.378
1.375
1.370
1.357
1.340
1.316
1.299
1.286
1.280
1.267
1.260
1.249
1.242
0.848
0.829
0.811
12.71
8.78
12.80
4.16
4.18
4.65
4.81
4.72
4.79
8.85
8.84
8.74
11.98
8
7
6
5
4
3
2
1
ppm

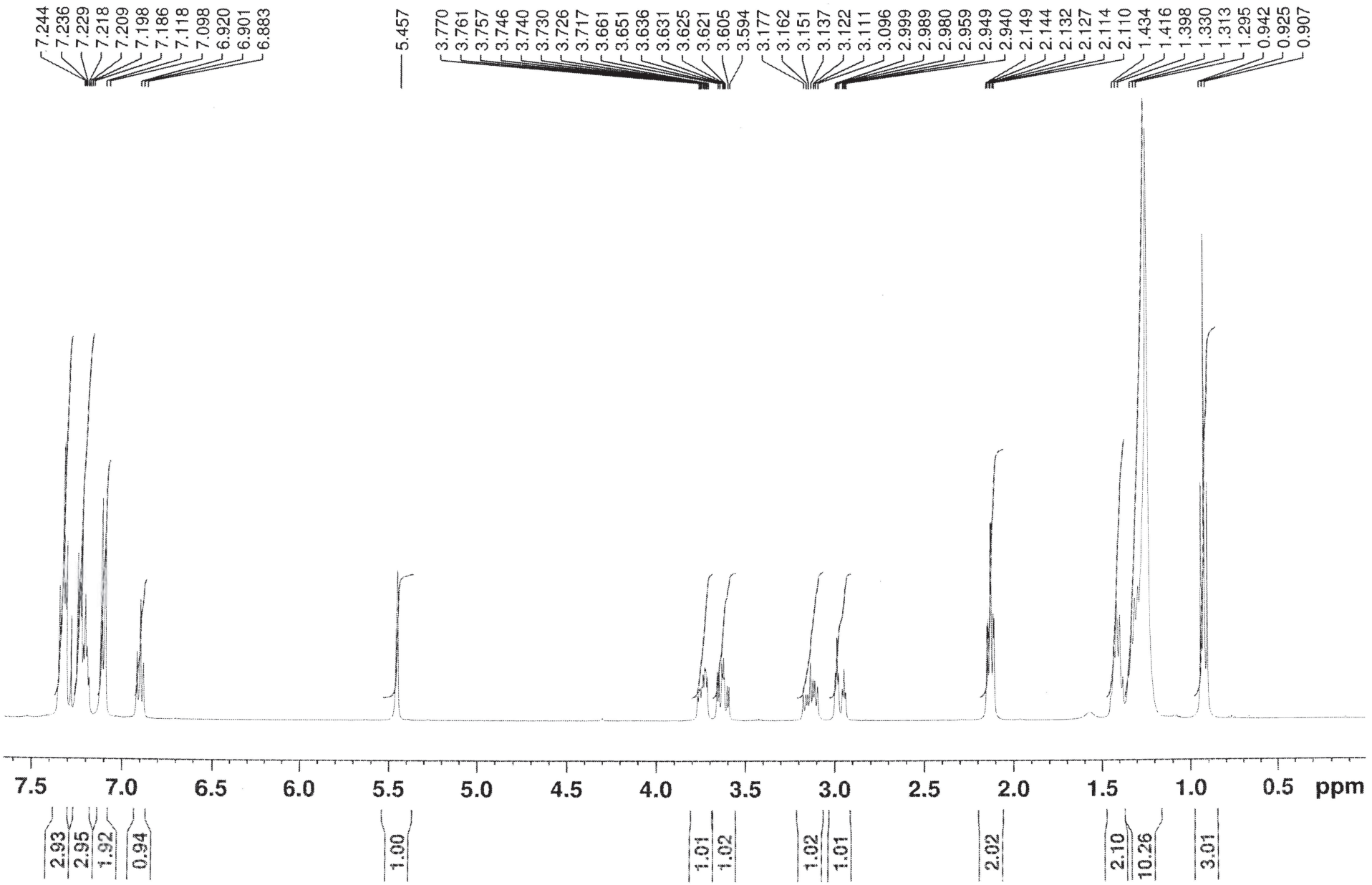
3d


160
140
120
100
80
60
40
20
ppm
149.647
136.207
134.139
129.011
128.812
127.301
126.935
126.118
119.326
116.586
85.220
79.084
77.443
77.023
76.596
51.785
43.154
30.775
28.883
21.785
18.442
13.551

3d

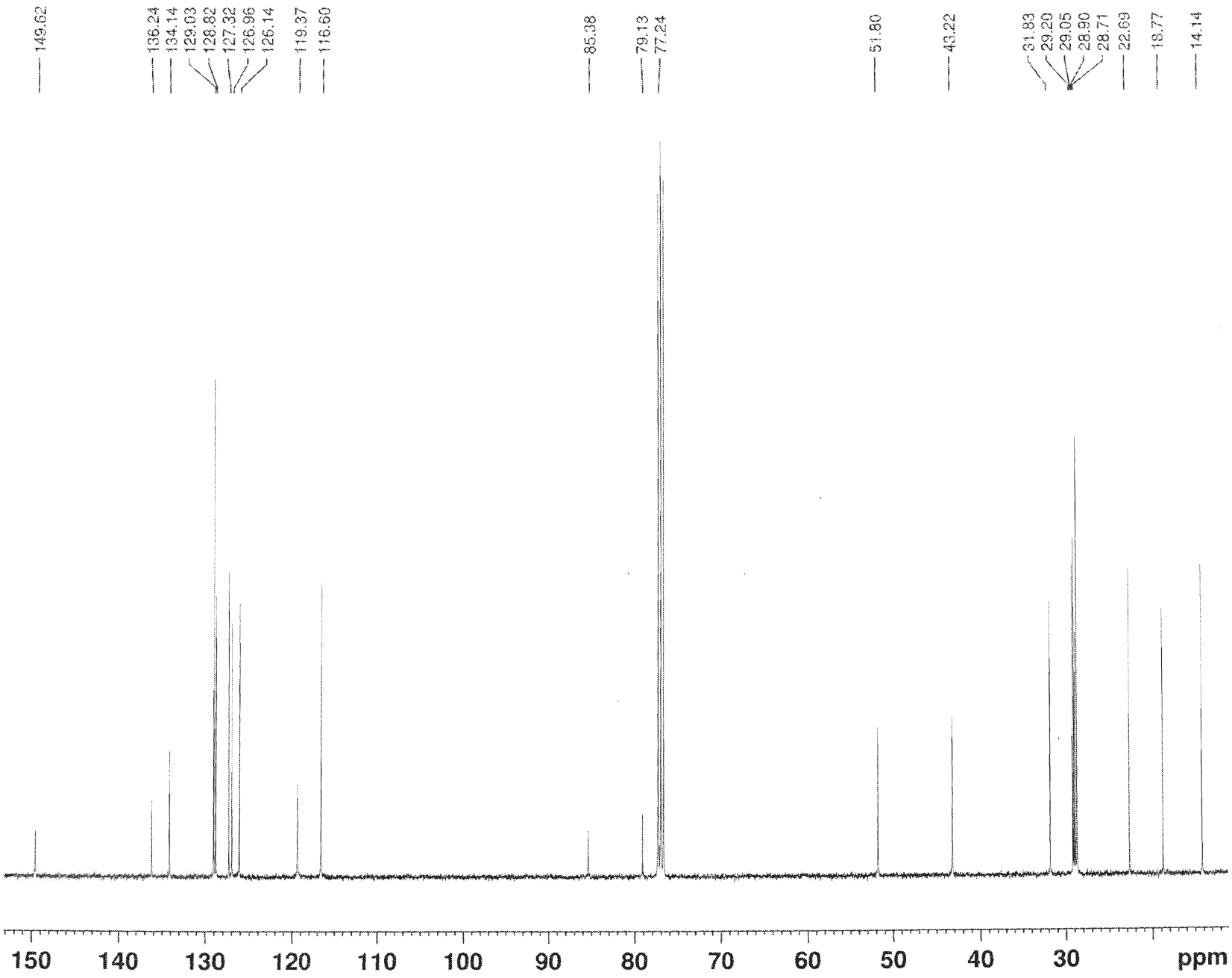
435-H

3e


7.244
7.236
7.229
7.218
7.209
7.198
7.186
7.118
7.098
6.920
6.901
6.883
5.457
3.770
3.761
3.757
3.746
3.740
3.730
3.726
3.717
3.661
3.651
3.636
3.631
3.625
3.621
3.605
3.594
3.177
3.162
3.151
3.137
3.122
3.111
3.096
2.999
2.989
2.980
2.959
2.949
2.940
2.149
2.144
2.132
2.127
2.114
2.110
1.434
1.416
1.398
1.330
1.313
1.295
0.942
0.925
0.907
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.93
2.95
1.92
0.94
1.00
1.01
1.02
1.02
1.01
2.02
2.10
10.26
3.01

3e

435-C



Current Data Parameters
NAME 435-C
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140828
Time 17.44
INSTRUM AVIII400HD
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 202.76
DW 20.800 usec
DE 22.57 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

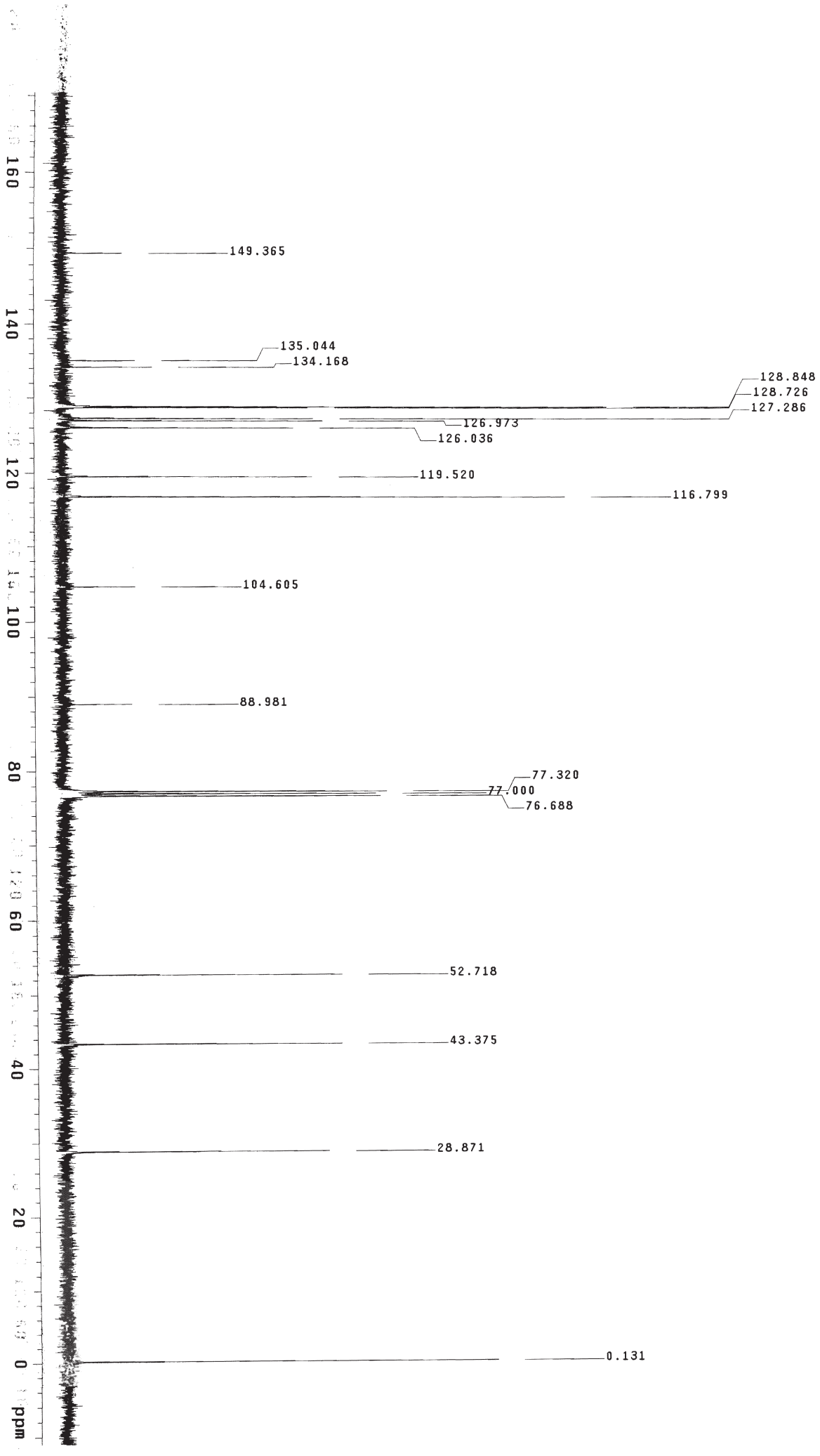
======== CHANNEL f1 ========
SFO1 100.6781539 MHz
NUC1 13C
P1 10.00 usec
PLW1 67.00000000 W

======== CHANNEL f2 ========
SFO2 400.3516014 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 18.07999992 W
PLW12 0.19430000 W
PLW13 0.15738000 W

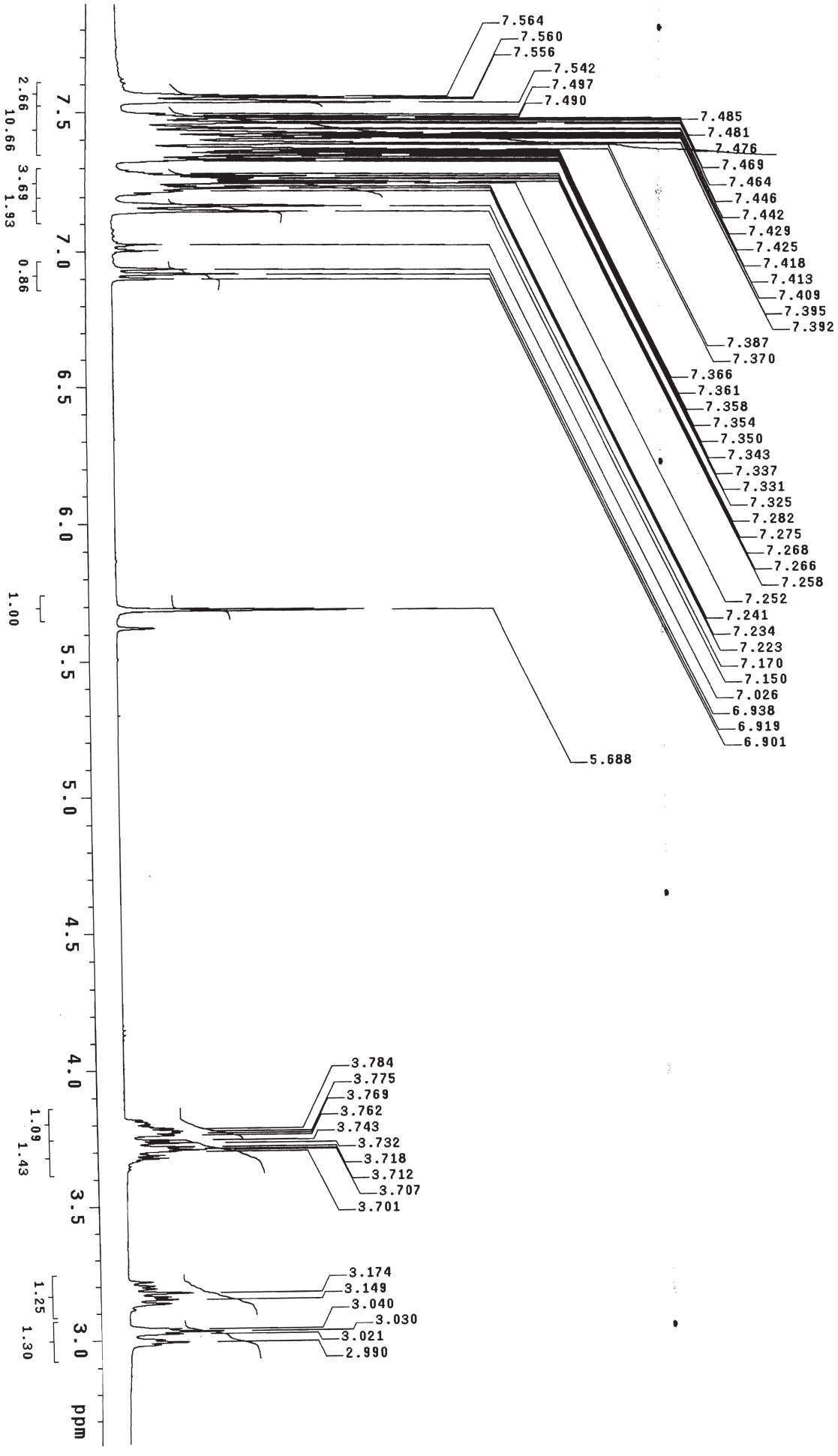
F2 - Processing parameters
SI 32768
SF 100.6680880 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

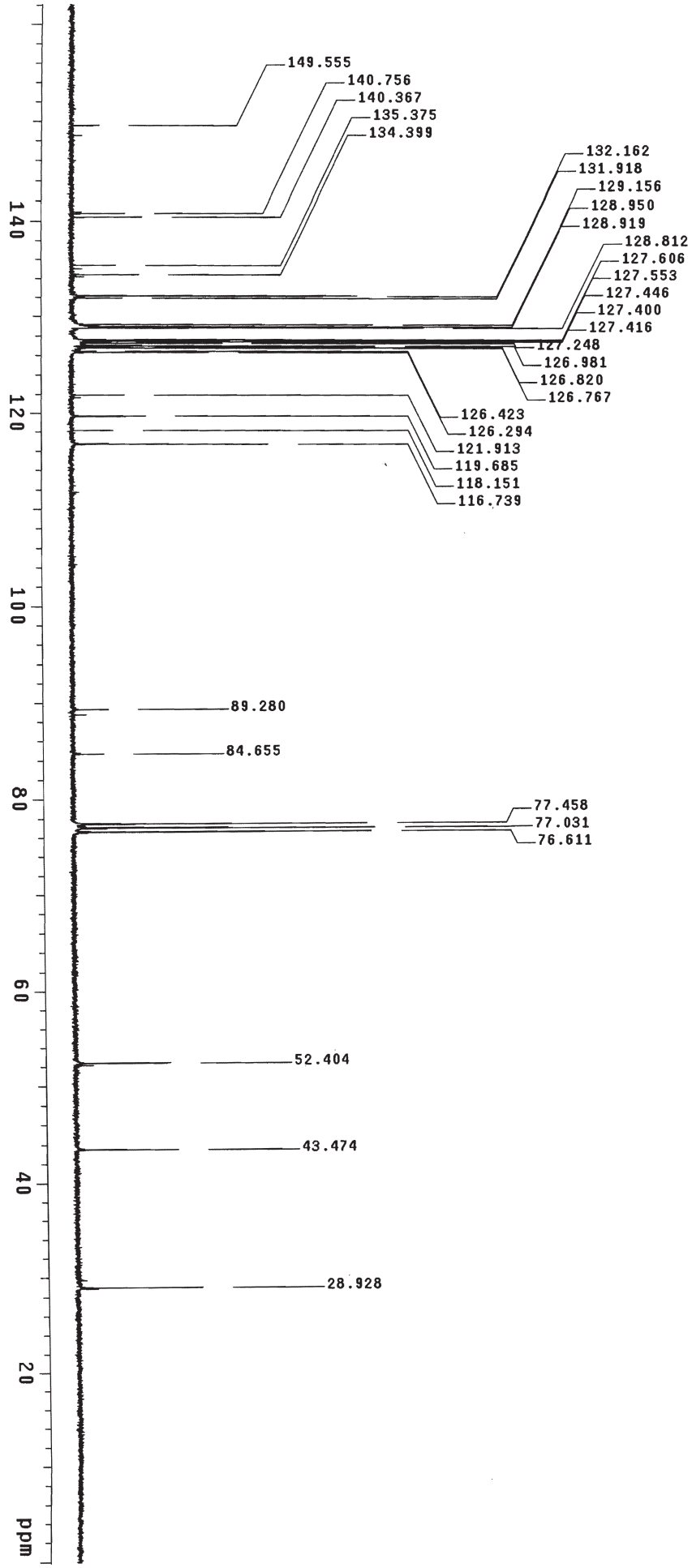
7.275
7.272
7.254
7.225
7.201
7.191
7.187
7.178
7.048
7.028
5.399
0.060
0.042
0.051
3.8911 1.01
0.48.10
1.00
1.30
1.13
1.23
1.19
8.11
ppm

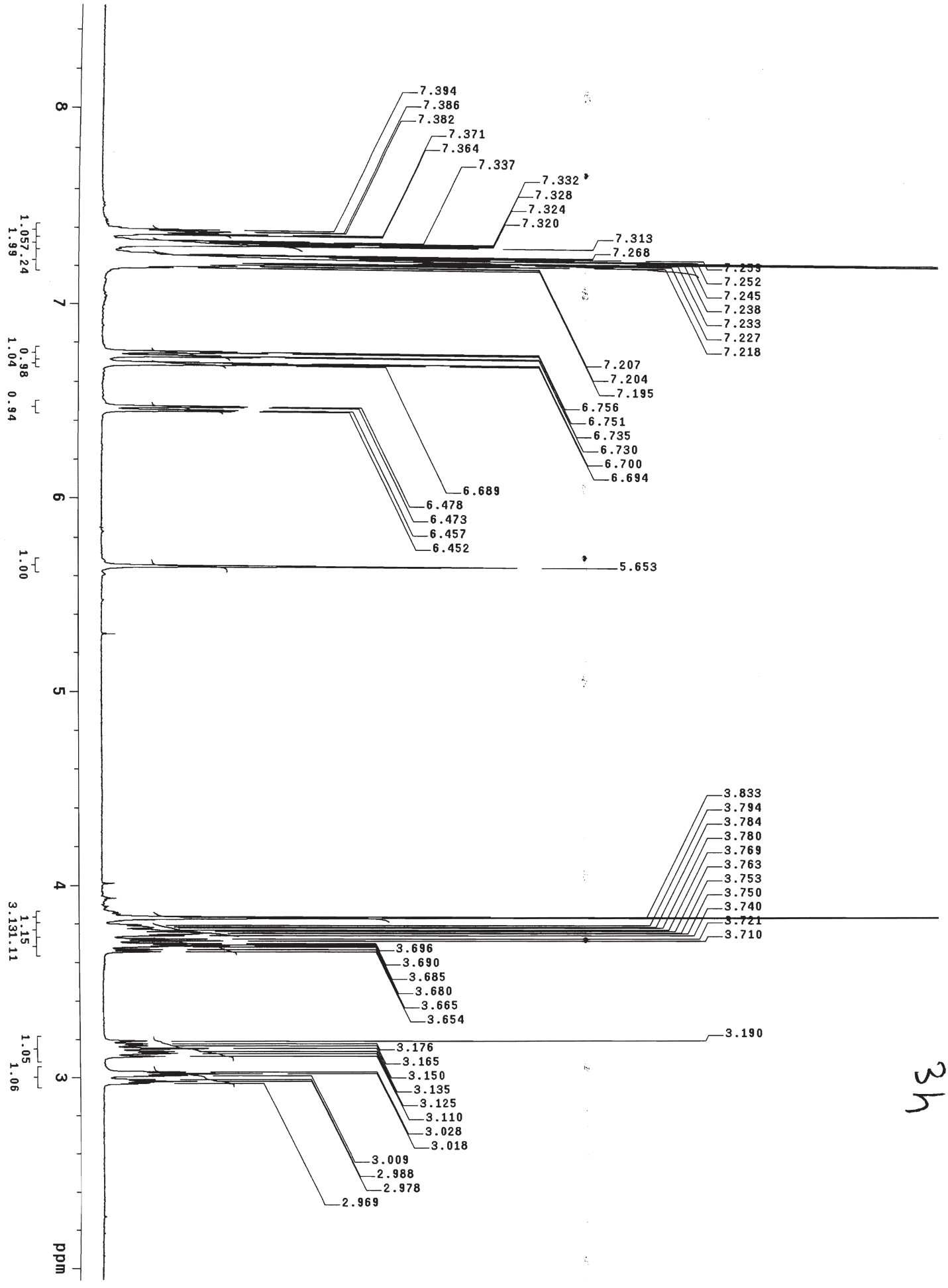
3p


160
140
120
100
80
60
40
20
0
ppm
149.365
135.044
134.168
128.848
128.726
127.286
126.973
126.036
119.520
116.799
104.605
88.981
77.320
77.000
76.688
52.718
43.375
28.871
0.131

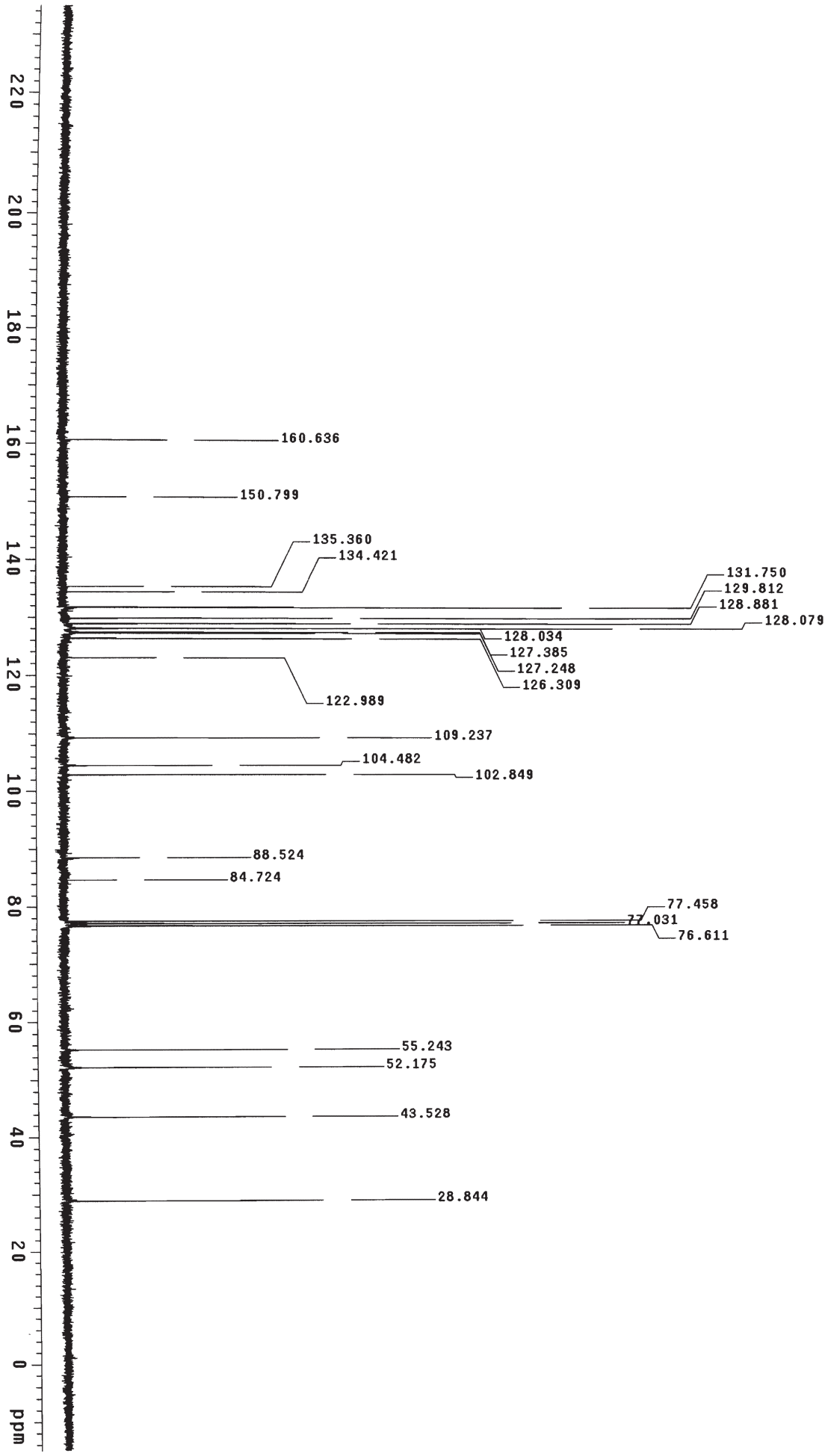
3f


7.564
7.560
7.556
7.542
7.497
7.490
7.485
7.481
7.476
7.469
7.464
7.446
7.442
7.429
7.425
7.418
7.413
7.409
7.395
7.392
7.387
7.370
7.366
7.361
7.358
7.354
7.350
7.343
7.337
7.331
7.325
7.282
7.275
7.268
7.266
7.258
7.252
7.241
7.234
7.223
7.170
7.150
7.026
6.938
6.919
6.901
5.688
3.784
3.775
3.769
3.762
3.743
3.732
3.718
3.712
3.707
3.701
3.174
3.149
3.040
3.030
3.021
2.990
2.66
10.66
3.69
1.93
0.86
1.00
1.09
1.43
1.25
1.30
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm


149.555
140.756
140.367
135.375
134.399
132.162
131.918
129.156
128.950
128.919
128.812
127.606
127.553
127.446
127.400
127.416
127.248
126.981
126.820
126.767
126.423
126.294
121.913
119.685
118.151
116.739
89.280
84.655
77.458
77.031
76.611
52.404
43.474
28.928
140
120
100
80
60
40
20
ppm


7.394
7.386
7.382
7.371
7.364
7.337
7.332
7.328
7.324
7.320
7.313
7.268
7.259
7.252
7.245
7.238
7.233
7.227
7.218
7.207
7.204
7.195
6.756
6.751
6.735
6.730
6.700
6.694
6.689
6.478
6.473
6.457
6.452
5.653
3.833
3.794
3.784
3.780
3.769
3.763
3.753
3.750
3.740
3.721
3.710
3.696
3.690
3.685
3.680
3.665
3.654
3.190
3.176
3.165
3.150
3.135
3.125
3.110
3.028
3.018
3.009
2.988
2.978
2.969
1.057.24
1.99
0.98
1.04
0.94
1.00
1.15
3.131.11
1.05
1.06
8
7
6
5
4
3
ppm

34


220
200
180
160
140
120
100
80
60
40
20
0
ppm
160.636
150.799
135.360
134.421
131.750
129.812
128.881
128.079
128.034
127.385
127.248
126.309
122.989
109.237
104.482
102.849
88.524
84.724
77.458
77.031
76.611
55.243
52.175
43.528
28.844

3h

3i

STANDARD PROTON PARAMETERS

Sample Name:
433
Data Collected on:
m300-mercury300
Archive directory:

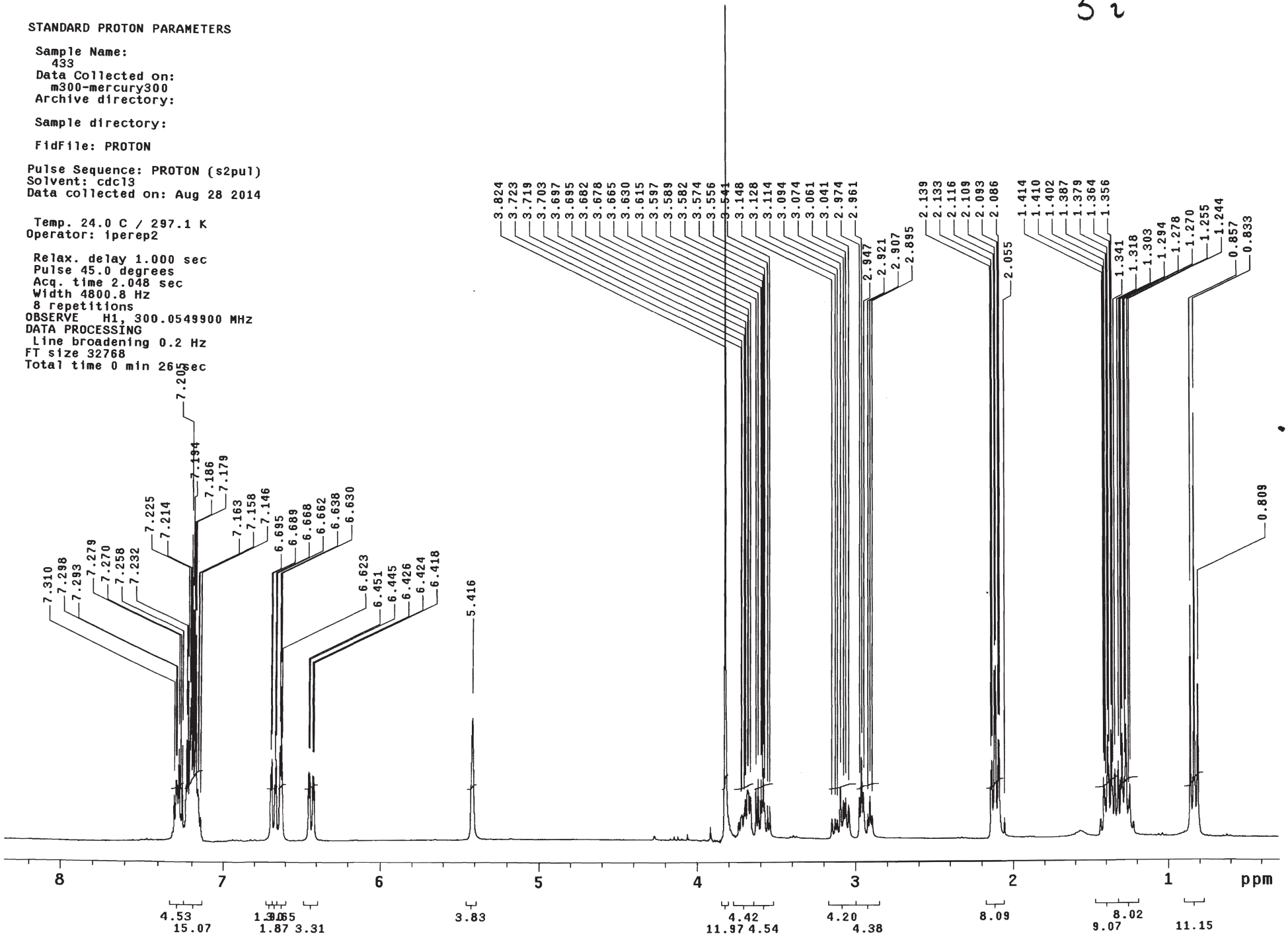
Sample directory:

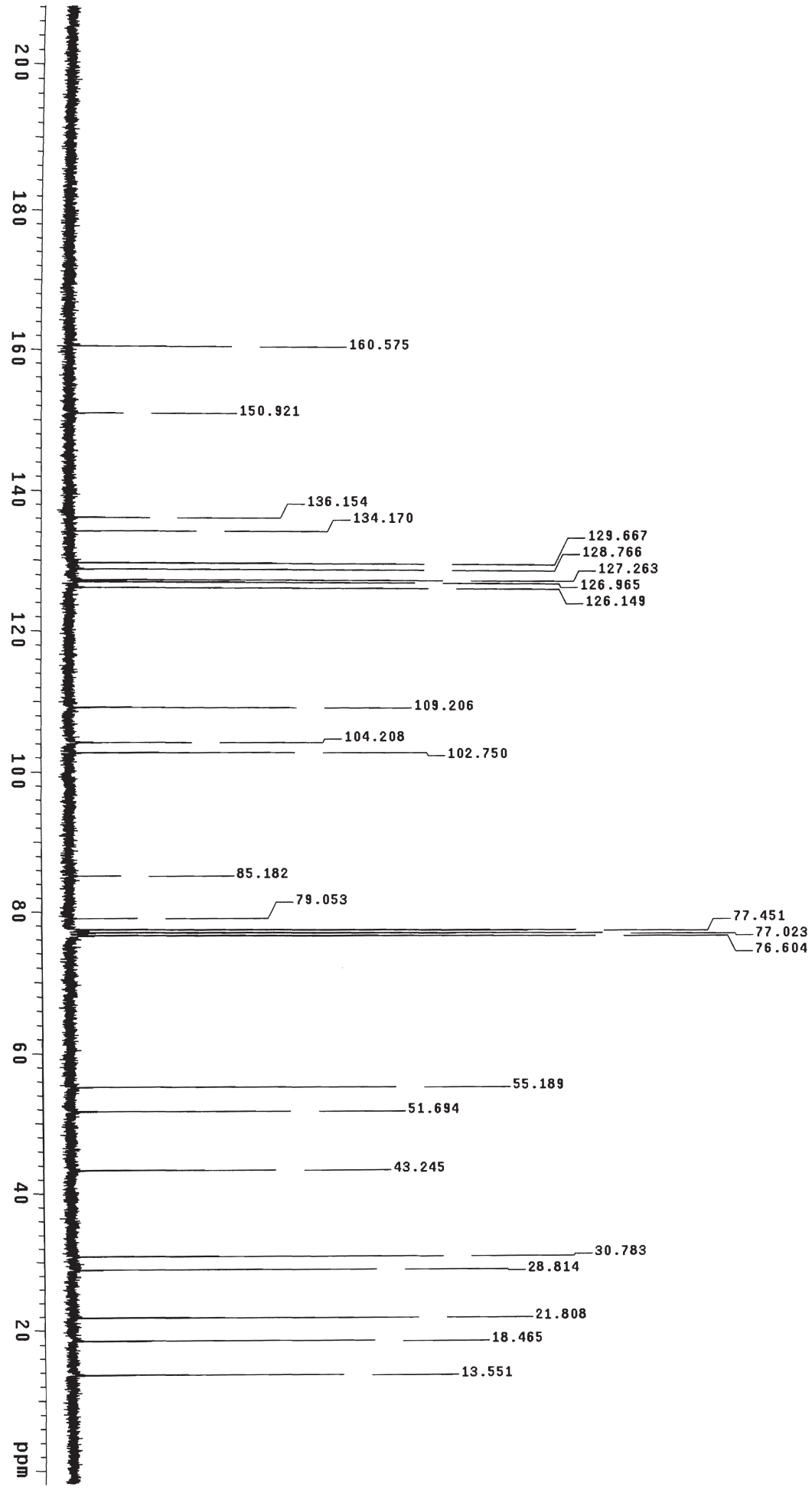
FidFile: PROTON

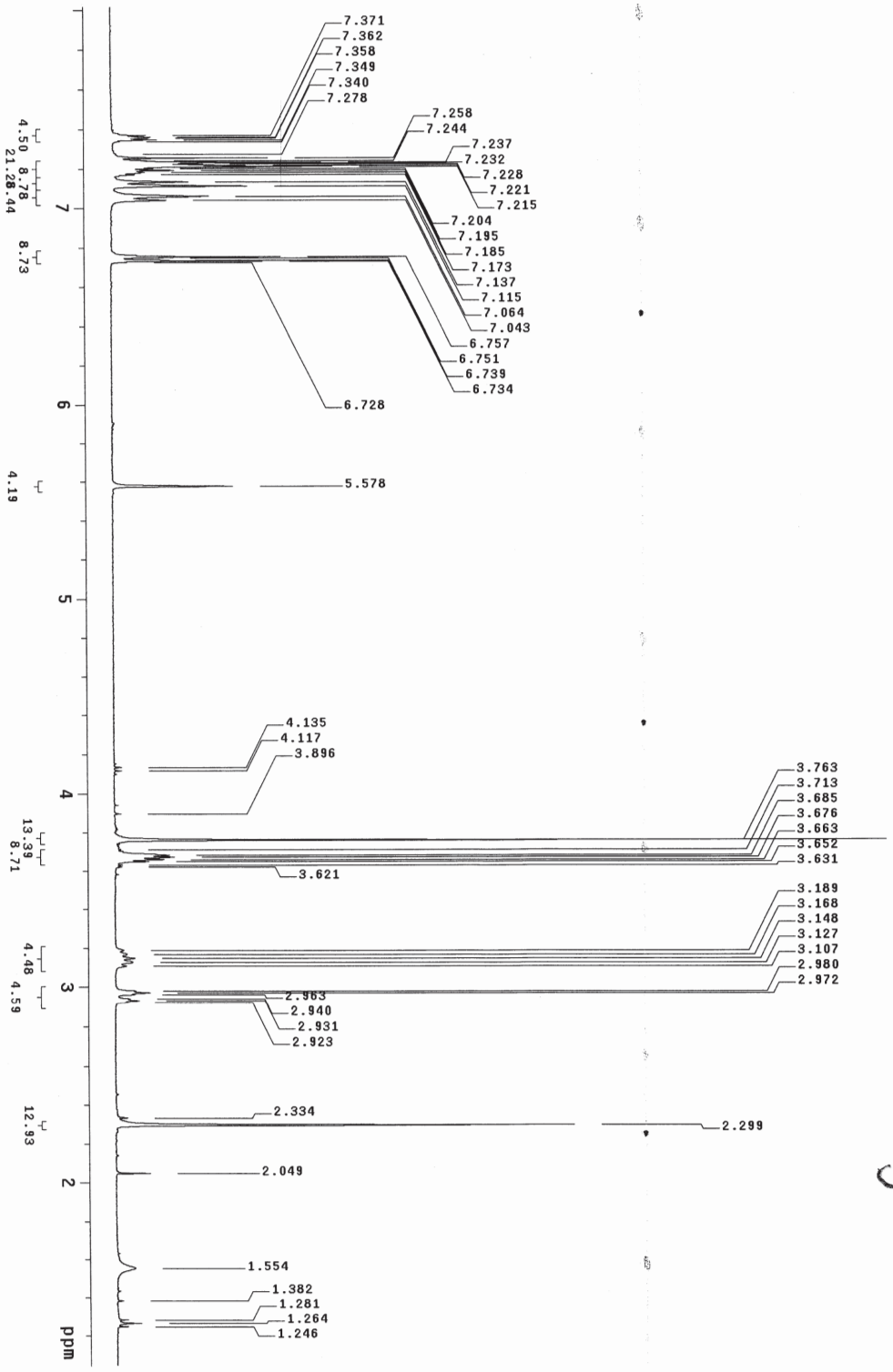
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 28 2014

Temp. 24.0 C / 297.1 K
Operator: iperep2

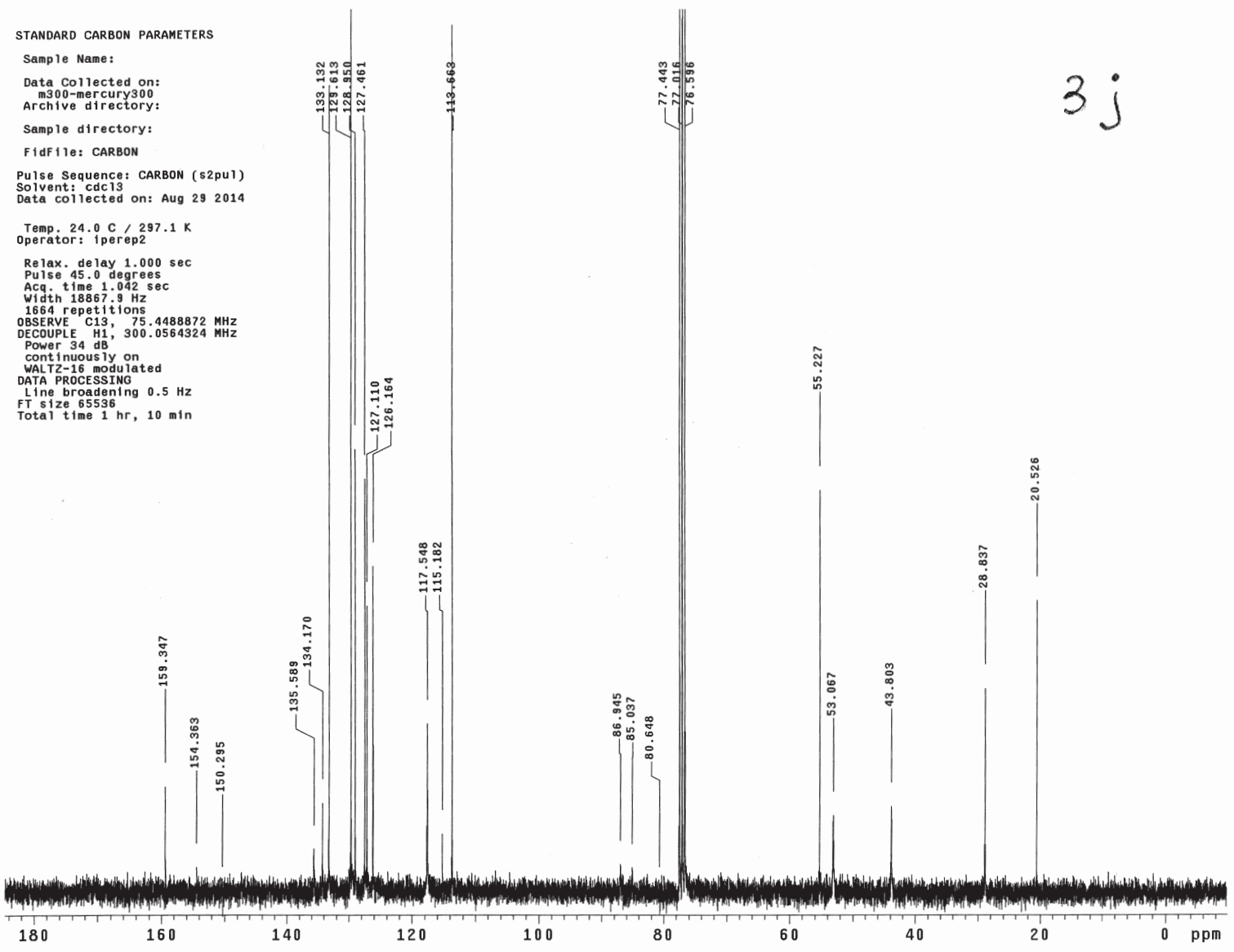
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 4800.8 Hz
8 repetitions
OBSERVE H1, 300.0549900 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 0 min 26 sec




200
180
160
140
120
100
80
60
40
20
ppm
160.575
150.921
136.154
134.170
129.667
128.766
127.263
126.965
126.149
109.206
104.208
102.750
85.182
79.053
77.451
77.023
76.604
55.189
51.694
43.245
30.783
28.814
21.808
18.465
13.551


7.371
7.362
7.358
7.349
7.340
7.278
7.258
7.244
7.237
7.232
7.228
7.221
7.215
7.204
7.195
7.185
7.173
7.137
7.115
7.064
7.043
6.757
6.751
6.739
6.734
6.728
5.578
4.135
4.117
3.896
3.763
3.713
3.685
3.676
3.663
3.652
3.631
3.621
3.189
3.168
3.148
3.127
3.107
2.980
2.972
2.963
2.940
2.931
2.923
2.334
2.299
2.049
1.554
1.382
1.281
1.264
1.246
4.50
8.78
21.28
44
8.73
4.19
13.39
8.71
4.48
4.59
12.93
ppm

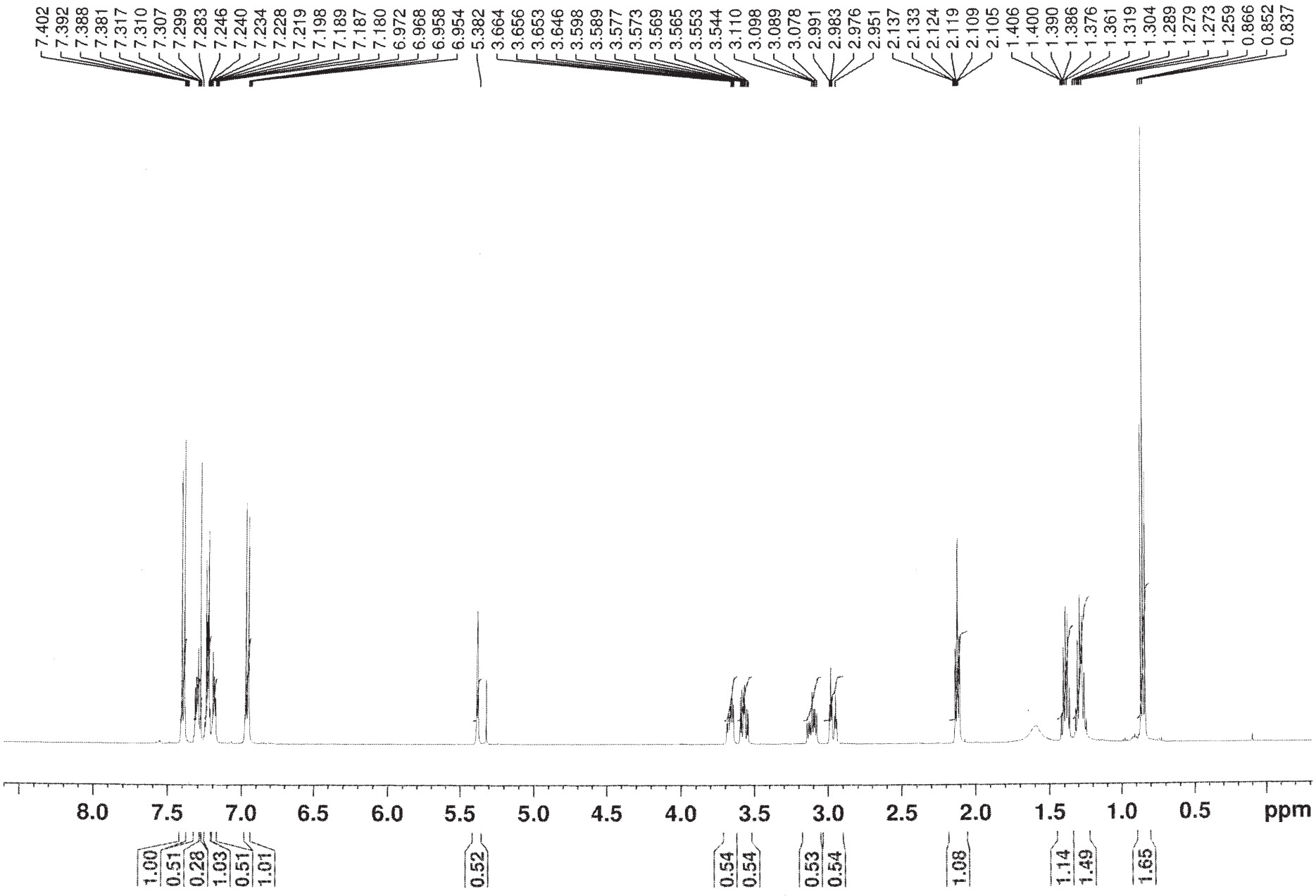
3.


STANDARD CARBON PARAMETERS
Sample Name:
Data Collected on:
m300-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 29 2014
Temp. 24.0 C / 297.1 K
Operator: iperep2
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 18867.9 Hz
1664 repetitions
OBSERVE C13, 75.4488872 MHz
DECOUPLE H1, 300.0564324 MHz
Power 34 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 10 min
159.347
154.363
150.295
135.589
134.170
133.132
129.613
128.850
127.461
127.110
126.164
117.548
115.182
113.663
86.845
85.037
80.648
77.443
77.016
76.596
55.227
53.067
43.803
28.837
20.526
180
160
140
120
100
80
60
40
20
0
ppm

3j

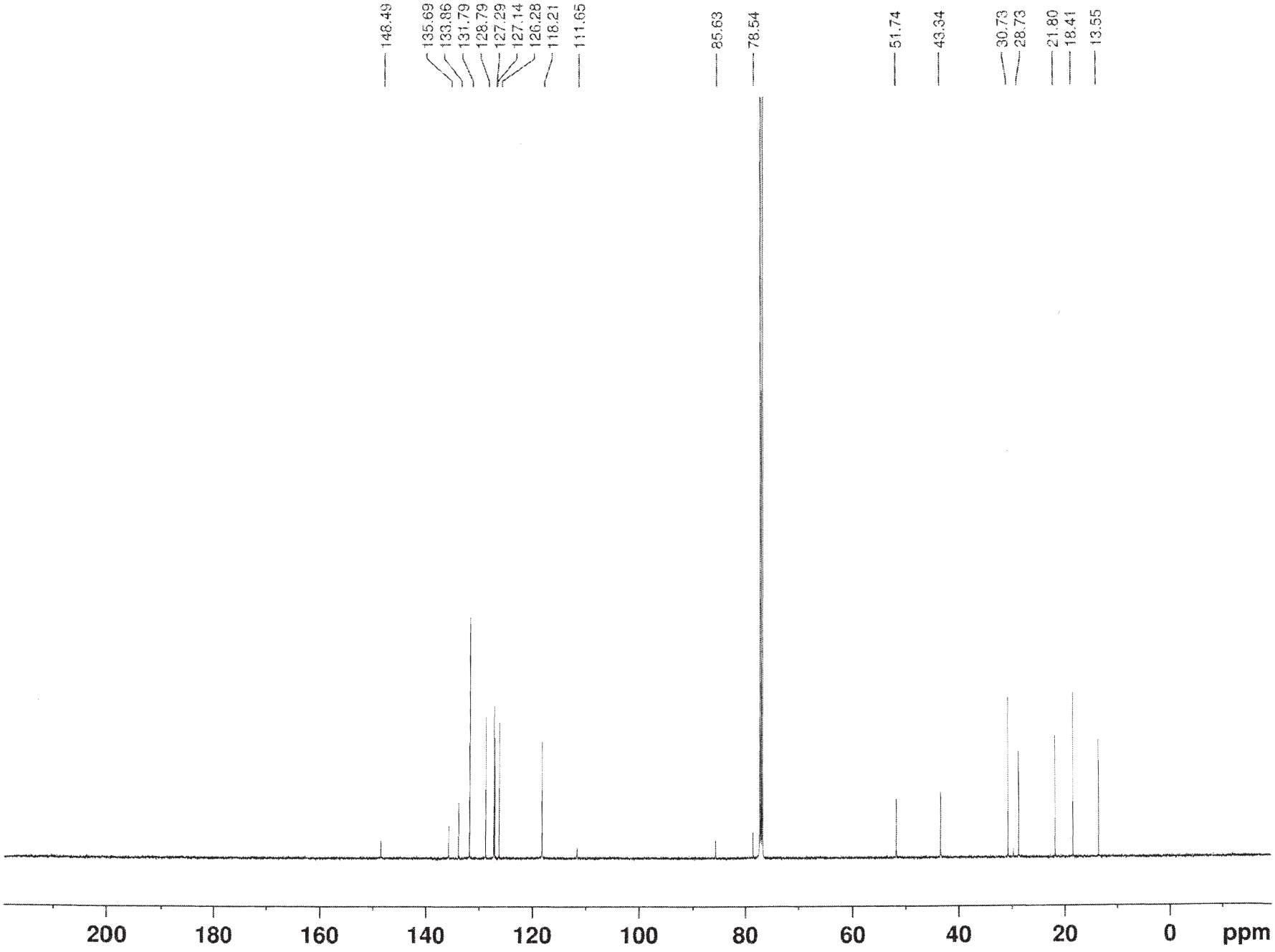
434-H

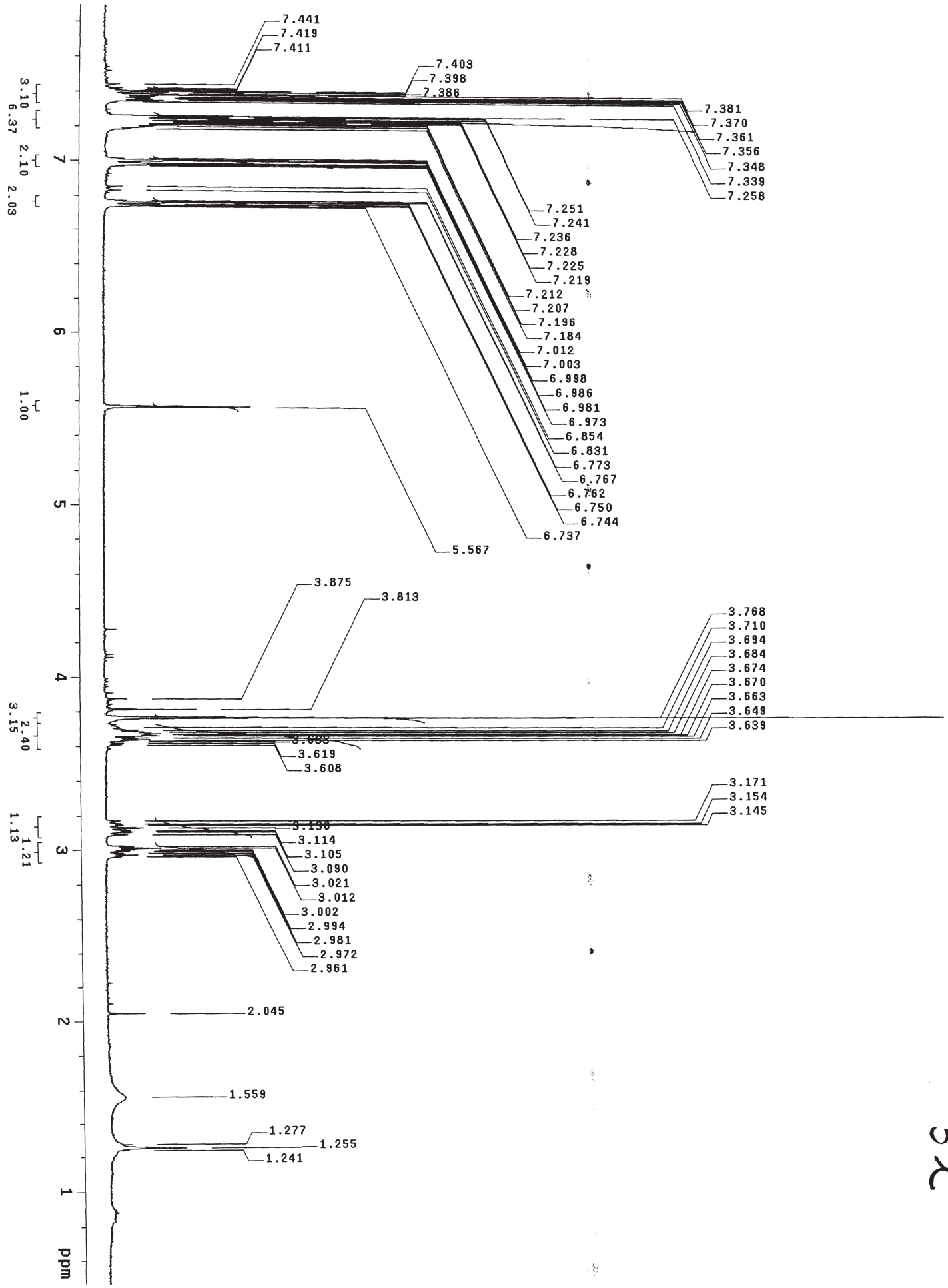
3K


7.402
7.392
7.388
7.381
7.317
7.310
7.307
7.299
7.283
7.246
7.240
7.234
7.228
7.219
7.198
7.189
7.187
7.180
6.972
6.968
6.958
6.954
5.382
3.664
3.656
3.653
3.646
3.598
3.589
3.577
3.573
3.569
3.565
3.553
3.544
3.110
3.098
3.089
3.078
2.991
2.983
2.976
2.951
2.137
2.133
2.124
2.119
2.109
2.105
1.406
1.400
1.390
1.386
1.376
1.361
1.319
1.304
1.289
1.279
1.273
1.259
0.866
0.852
0.837
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
0.51
0.28
1.03
0.51
1.01
0.52
0.54
0.54
0.53
0.54
1.08
1.14
1.49
1.65

3k

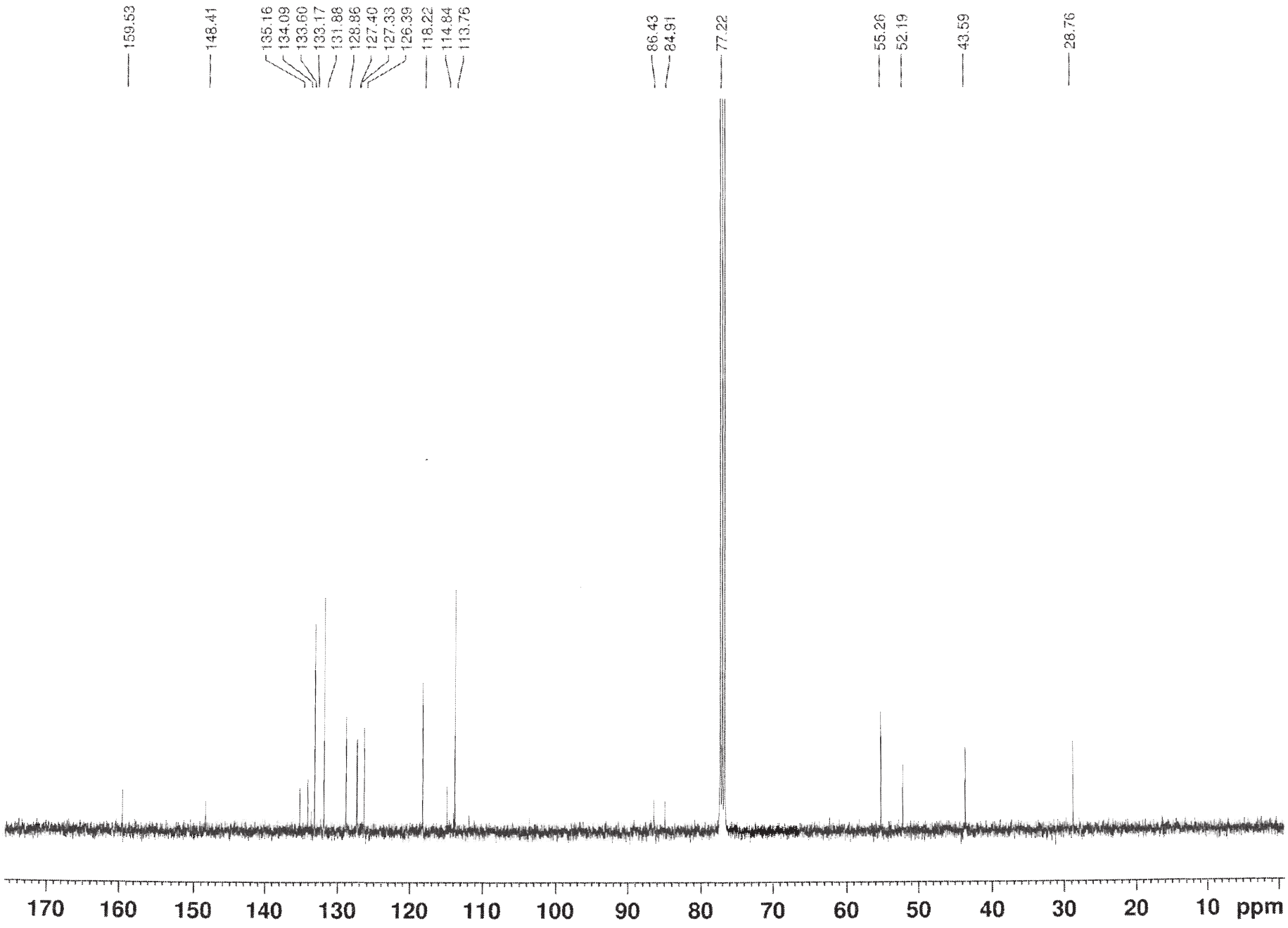
434-H

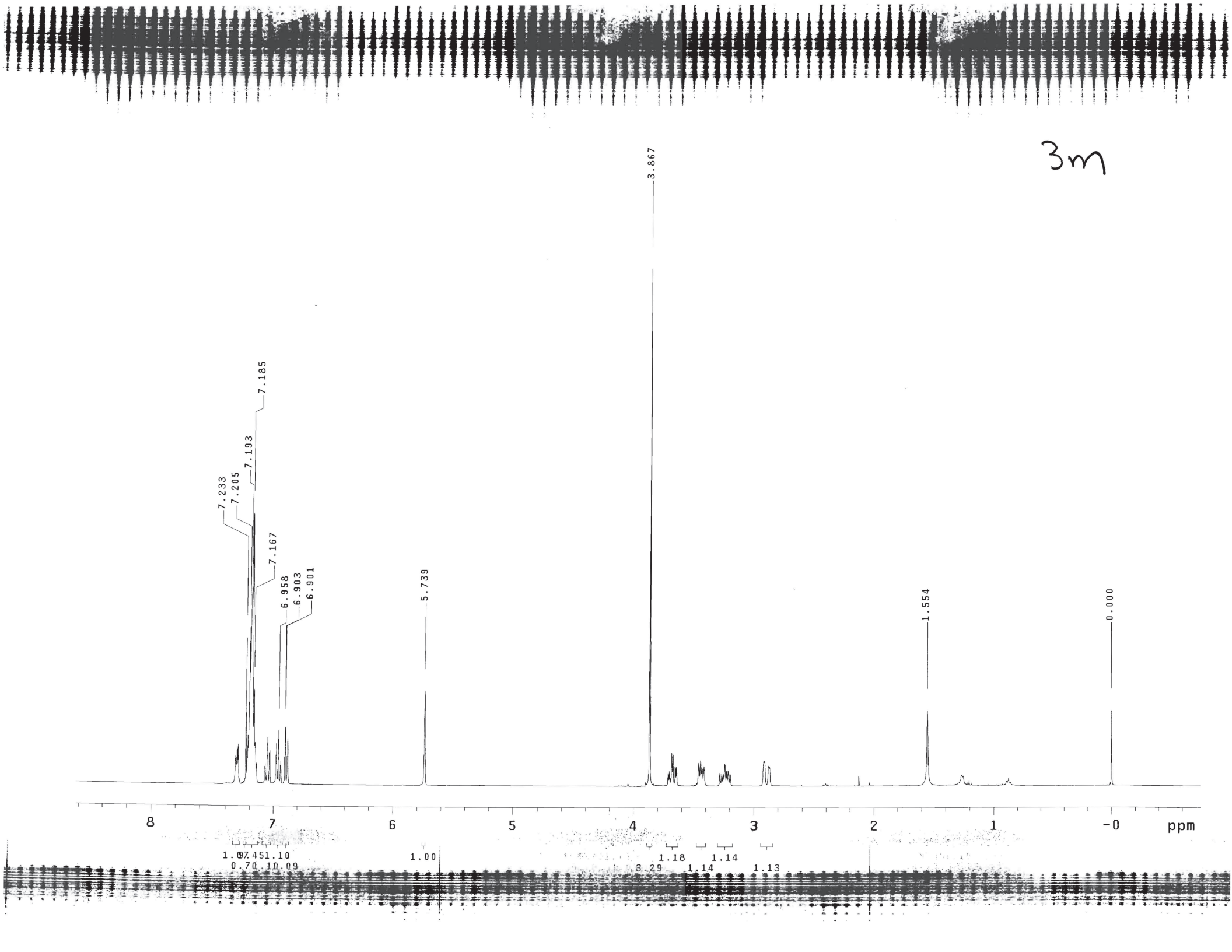

148.49
135.69
133.86
131.79
128.79
127.29
127.14
126.28
118.21
111.65
85.63
78.54
51.74
43.34
30.73
28.73
21.80
18.41
13.55
200
180
160
140
120
100
80
60
40
20
0
ppm

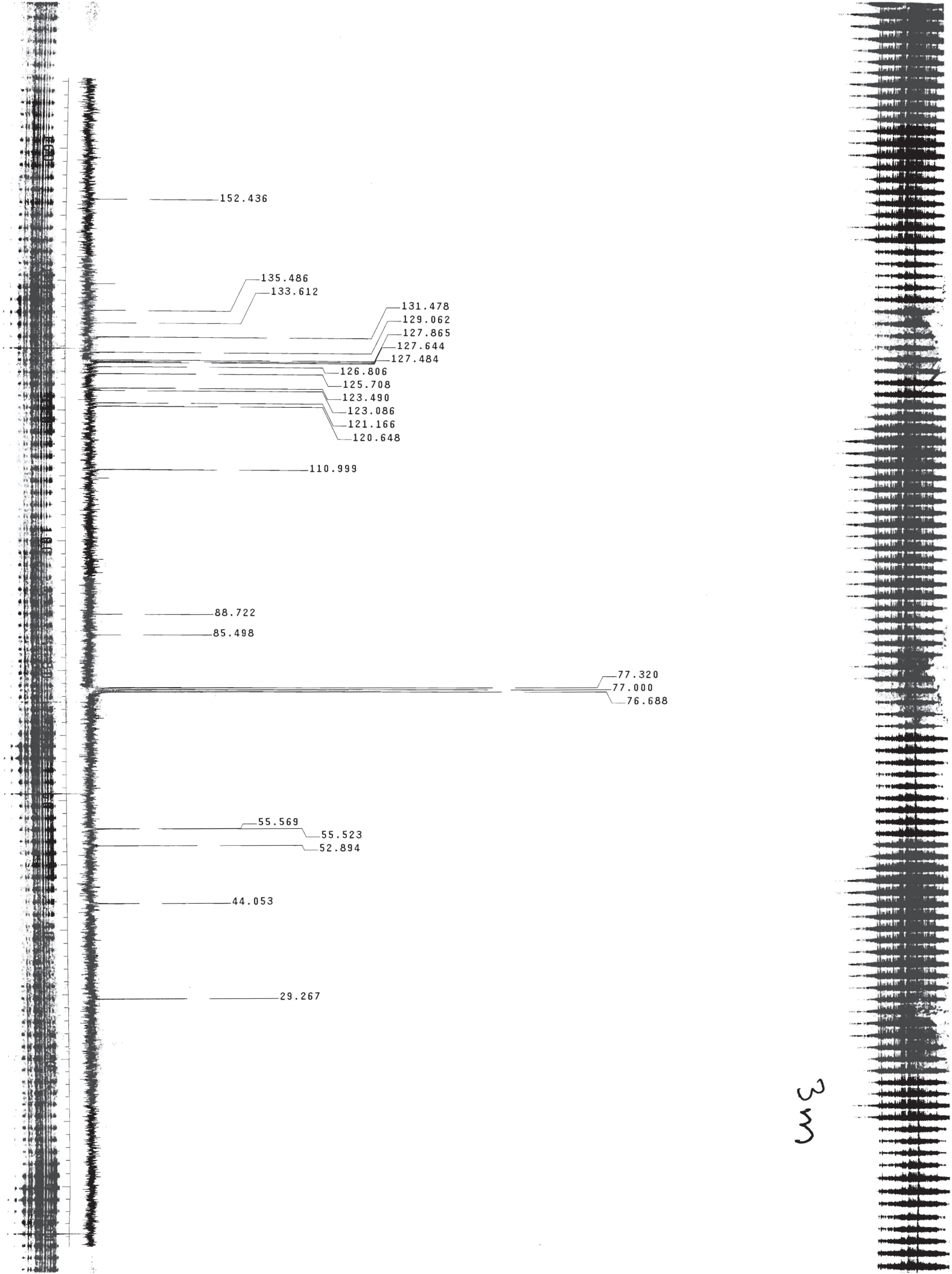

7.441
7.419
7.411
7.403
7.398
7.386
7.381
7.370
7.361
7.356
7.348
7.339
7.258
7.251
7.241
7.236
7.228
7.225
7.219
7.212
7.207
7.196
7.184
7.012
7.003
6.998
6.986
6.981
6.973
6.854
6.831
6.773
6.767
6.762
6.750
6.744
6.737
5.567
3.875
3.813
3.768
3.710
3.694
3.684
3.674
3.670
3.663
3.649
3.639
3.619
3.608
3.171
3.154
3.145
3.130
3.114
3.105
3.090
3.021
3.012
3.002
2.994
2.981
2.972
2.961
2.045
1.559
1.277
1.255
1.241
3.10
6.37
2.10
2.03
1.00
2.40
3.15
1.21
1.13
7
6
5
4
3
2
1
ppm

3l

Z-048


159.53
148.41
135.16
134.09
133.60
133.17
131.88
128.86
127.40
127.33
126.39
118.22
114.84
113.76
86.43
84.91
77.22
55.26
52.19
43.59
28.76
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


3m
3.867
7.185
7.193
7.233
7.205
7.167
6.958
6.903
6.901
5.739
1.554
0.000
8
7
6
5
4
3
2
1
-0
ppm
1.00
1.18
1.14
1.14
1.13


152.436
135.486
133.612
131.478
129.062
127.865
127.644
127.484
126.806
125.708
123.490
123.086
121.166
120.648
110.999
88.722
85.498
77.320
77.000
76.688
55.569
55.523
52.894
44.053
29.267