Supporting Information

CONTENTS **Page No.**

Combining Multi-catalysis and Multi-component System for the Development of One-pot Asymmetric Reactions: Stereoselective Synthesis of Highly Functionalized Bicyclo[4.4.0]decane-1,6-diones

Dhevalapally B. Ramachary* and Rajasekar Sakthidevi

School of Chemistry, University of Hyderabad, Central University (P.O.), Hyderabad 500 046, India

ramsc@uohyd.ernet.in

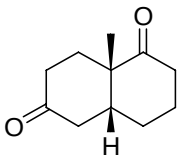
General Methods: The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. *In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment, and is given in parentheses.* The coupling constants *J* are given in Hz. Column chromatography was performed using Acme's silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Materials: All solvents and commercially available chemicals were used as received. Chiral bicyclic enones **5a-g** were prepared by using the literature procedures.[1]

General Experimental Procedures for the Bio-mimetic Reactions:

General Procedure for the Reduction of Unsaturated Cyclic Enones: (*S*)-(+)-1-(2-Pyrrolidinylmethyl)pyrrolidine **4e** (0.019g, 0.125 mmol) and 70% $HClO_4$ (8µL, 0.125 mmol) in dry CH_3CN (1.0 mL) were stirred at 25 °C for 10 minutes then 0.5 mmol of chiral enone **5** in CH_3CN (1.0 mL) were added slowly and stirring was continued at the same temperature for the 5 min. To the reaction mixture added Hantzsch ester **2** (0.253 g, 1mmol) and refluxed for 8h. The crude reaction mixture was worked up with aqueous NH_4Cl or $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure hydrogenated products **6** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

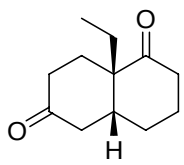
Amine/Amino Acid/Acid/Amine-Catalyzed One-Pot Michael/Robinson Annulation/Hydrogenation Reactions: In an ordinary glass vial equipped with a magnetic stirring bar, to 1.0 mmol of CH-acid **1** and 0.30 mmol of triethylamine was added 3.0 mL of CH_3CN, and then the freshly distilled methyl vinyl ketone (0.25 mL, 3.0 mmol) was added and the reaction mixture was stirred at 25 °C for the 24 h. To the reaction mixture added L-Proline **4a** (58 mg, 0.5 mmol) and 70% $HClO_4$ (15 µL, 0.25 mmol) and refluxed for 24 h. After the confirmation of complete conversion of Michael adduct into the enone **5** through TLC, added (*S*)-(+)-1-(2-pyrrolidinylmethyl)pyrrolidine **4e** (38 mg, 0.25 mmol) and Hantzsch ester **2** (253 mg, 1.0 mmol) and continued the reflux for 24 h. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure one-pot products **6** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).



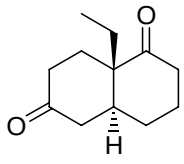
***cis*-6a**

(+)-*cis*-8a-Methyl-hexahydro-naphthalene-1,6-dione (6a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 48 °C; $[\alpha]_D^{25}$ = +8.911° (*c* = 1.0 g/100 mL, C_6H_6, 75% *ee*); IR (Neat): ν_{max} 2940, 1700 (*C*=O), 1698 (*C*=O), 1454, 1310, 1216, 1176, 1102 and 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65-2.35 (4H, m), 2.35-2.25 (4H, m), 2.20-2.05 (1H, m), 2.05-1.89 (2H, m), 1.60-1.50 (1H, m), 1.50-1.38 (1H, m), 1.36 (3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 214.0

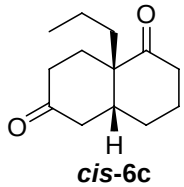
(C, *C*=O), 211.0 (C, *C*=O), 48.4 (C), 45.9 (CH), 43.6 (CH_2), 38.3 (CH_2), 37.4 (CH_2), 33.6 (CH_2), 26.6 (CH_2), 23.8 (CH_3), 22.8 (CH_2); LRMS m/z 181.00 ($M + H^+$), calcd for $C_{11}H_{16}O_2H$ 181.1150; Anal. calcd for $C_{11}H_{16}O_2$ (180.1150): C, 73.30; H, 8.95. Found: C, 73.274; H, 8.984%.


***cis*-6b**

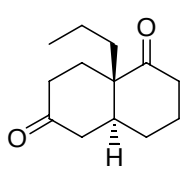
(–)-*cis*-8a-Ethyl-hexahydro-naphthalene-1,6-dione (6b): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 45 °C. $[\alpha]_D^{25}$ = –2.723° (*c* = 0.625 g/100 mL, $CHCl_3$, 75% *ee*); IR (Neat): ν_{max} 2954, 2876, 1708 (2 x *C*=O) and 1462 cm^{-1}; ^1H NMR ($CDCl_3$, major isomer) δ 2.60-2.40 (3H, m), 2.40-2.29 (3H, m), 2.29-2.05 (4H, m), 1.99-1.89 (2H, m), 1.60-1.45 (1H, m), 1.45-1.35 (1H, m), 1.30-1.23 (1H, m), 0.78 (3H, t, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 213.8 (C, *C*=O), 211.7 (C, *C*=O), 52.2 (C), 44.3 (CH), 43.6 (CH_2), 38.2 (CH_2), 38.0 (CH_2), 30.9 (CH_2), 30.3 (CH_2), 25.8 (CH_2), 22.2 (CH_2), 8.0 (CH_3); LRMS m/z 195.00 ($M + H^+$), calcd for $C_{12}H_{18}O_2H$ 195.1307; Anal. calcd for $C_{12}H_{18}O_2$ (194.1307): C, 74.19; H, 9.34. Found: C, 74.160; H, 9.357%.


***trans*-6b**

***Trans*-8a-Ethyl-hexahydro-naphthalene-1,6-dione (6b):** Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (Neat): ν_{max} 2953, 2875, 1717 (C=O), 1711 (C=O), 1441, 1287, 1229, 1105 and 1044 cm^{-1}; ^1H NMR ($CDCl_3$, minor isomer) δ 2.64-2.47 (3H, m), 2.43-2.07 (6H, m), 2.07-1.82 (3H, m), 1.73-1.39 (3H, m), 0.80 (3H, t, *J* = 8.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 213.7 (C, *C*=O), 209.6 (C, *C*=O), 51.2 (C), 46.1 (CH), 43.4 (CH_2), 38.0 (CH_2), 37.1 (CH_2), 27.3 (CH_2), 27.0 (CH_2), 26.2 (CH_2), 18.9 (CH_2), 7.5 (CH_3).

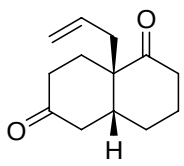

***cis*-6c**

(–)-*cis*-8a-Propyl-hexahydro-naphthalene-1,6-dione (6c): Purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25}$ = –4.449° (*c* = 0.135 g/100 mL, $CHCl_3$, 73% *ee*); IR (Neat): ν_{max} 2955, 2872, 1708 (2 x C=O), 1098 and 632 cm^{-1}; ^1H NMR ($CDCl_3$, major isomer) δ 2.71-2.47 (3H, m), 2.46-2.18 (7H, m), 2.15-1.85 (3H, m), 1.56-1.26 (4H, m), 0.92 (3H, t, *J* = 8.0 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 213.9 (C, *C*=O), 211.8 (C, *C*=O), 52.2 (C), 44.7 (CH), 43.7 (CH_2), 40.2 (CH_2), 38.4 (CH_2), 38.1 (CH_2), 31.6 (CH_2), 25.9 (CH_2), 22.3 (CH_2), 17.0 (CH_2), 14.7 (CH_3); LRMS m/z 209.10 ($M + H^+$), calcd for $C_{13}H_{20}O_2H$ 209.1463; Anal. calcd for $C_{13}H_{20}O_2$ (208.1463); C, 74.96; H, 9.86. Found: C, 75.057, H, 9.671%.

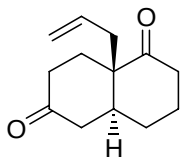

***trans*-6c**

***Trans*-8a-Propyl-hexahydro-naphthalene-1,6-dione (6c):** Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (Neat): ν_{max} 2955, 2871, 1707 (2 x *C*=O) cm^{-1}; ^1H NMR ($CDCl_3$, minor isomer) δ 2.66-2.47 (3H, m), 2.44-2.14 (7H, m), 2.03-1.89 (3H, m), 1.51-1.22 (4H, m), 0.97 (3H, t,

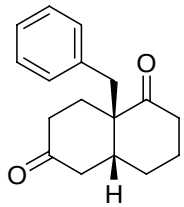
J = 8.0 Hz, C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 213.8 (C, *C*=O), 209.6 (C, *C*=O), 51.1 (C), 46.3 (CH), 43.4 (CH_2), 38.1 (CH_2), 37.2 (CH_2), 28.7 (CH_2), 28.1 (CH_2), 27.1 (CH_2), 26.3 (CH_2), 16.7 (CH_2), 14.8 (CH_3).


***cis*-6d**

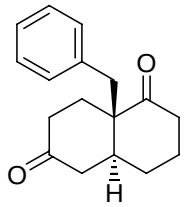
(–)-*cis*-8a-Allyl-hexahydro-naphthalene-1,6-dione (6d): Purified by column chromatography using EtOAc/hexane and isolated as a gummy solid. $[\alpha]_D^{25}$ = –29.233° (*c* = 1.0 g/100 mL, $CHCl_3$, 73% *ee*); IR (Neat): ν_{max} 2945, 2874, 1709 (2 x C=O), 1438, 1235, 1105, 996, 919, 666 and 619 cm^{-1}; ^{1}H NMR ($CDCl_3$, major isomer) δ 5.71-5.61 (1H, m, RC*H*=CH_2), 5.12 (1H, br d, *J* = 4.0 Hz), 5.09 (1H, br s) [RCH=C*H*$_2$]; 2.70 (1H, dd, *J* = 12.0, 8.0 Hz), 2.60-2.48 (3H, m), 2.45-2.10 (7H, m), 2.05-1.90 (2H, m), 1.55-1.35 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 213.0 (C, *C*=O), 211.2 (C, *C*=O), 132.4 (CH, R*C*H=CH_2), 118.8 (CH_2, RCH=*C*H_2), 51.9 (C), 43.6 (CH), 43.5 (CH_2), 41.0 (CH_2), 38.1 (CH_2), 38.0 (CH_2), 31.4 (CH_2), 26.1 (CH_2), 22.5 (CH_2); LRMS m/z 207.05 (M + H$^+$), calcd for $C_{13}H_{18}O_2H$ 207.1307; Anal. calcd for $C_{13}H_{18}O_2$ (206.1307): C, 75.69; H, 8.80. Found: C, 75.652, H, 8.794%.


***trans*-6d**

***Trans*-8a-Allyl-hexahydro-naphthalene-1,6-dione (6d):** Purified by column chromatography using EtOAc/hexane and isolated as a gummy solid. IR (Neat): ν_{max} 2946, 2252, 1708 (2 x C=O), 907, 730, 656 and 645 cm^{-1}; ^{1}H NMR ($CDCl_3$, minor isomer) δ 5.69-5.49 (1H, m, RC*H*=CH_2), 5.20-5.09 (2H, m, RCH=C*H*$_2$), 2.75-2.45 (4H, m), 2.45-2.25 (6H, m), 2.25-1.90 (3H, m), 1.90-1.65 (1H, m), 1.57-1.39 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 212.7 (C, *C*=O), 209.3 (C, *C*=O), 131.6 (CH, R*C*H=CH_2), 118.7 (CH_2, RCH=*C*H_2), 51.0 (C), 45.9 (CH), 43.4 (CH_2), 38.2 (CH_2), 36.9 (CH_2), 31.1 (CH_2), 28.3 (CH_2), 27.2 (CH_2), 26.2 (CH_2).

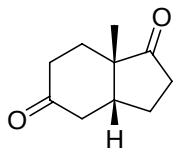

***cis*-6e**

(–)-*cis*-8a-Benzyl-hexahydro-napthalene-1,6-dione (6e): Purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25}$ = –30.834° (*c* = 0.25 g/100 mL, $CHCl_3$, 70% *ee*); IR (Neat): ν_{max} 2949, 2875, 1717 (*C*=O), 1710 (*C*=O), 1446, 1189, 1157 and 704 cm^{-1}; ^{1}H NMR ($CDCl_3$, major isomer) δ 7.28-7.23 (3H, m), 7.06 (2H, d, *J* = 6.3 Hz) [Ph-*H*]; 3.23 (1H, d, *J* = 13.7 Hz), 3.03 (1H, d, *J* = 13.7 Hz) [PhC*H*$_2$]; 2.83 (1H, td, *J* = 15.08, 9.5 Hz), 2.55-2.15 (8H, m), 2.10-1.95 (2H, m), 1.57-1.52 (1H, m), 1.44-1.37 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 213.2 (C, *C*=O), 211.3 (C, *C*=O), 136.1 (C), 129.9 (2 x CH), 128.3 (2 x CH), 127.0 (CH), 52.9 (C), 43.53 (CH), 43.47 (CH_2), 42.8 (CH_2), 38.2 (CH_2), 38.1 (CH_2), 31.6 (CH_2), 26.0 (CH_2), 22.2 (CH_2); LRMS m/z 257.00 (M + H$^+$), calcd for $C_{17}H_{20}O_2H$ 257.1463; Anal. calcd for $C_{17}H_{20}O_2$ (256.1463): C, 79.65; H, 7.86. Found: C, 79.676; H, 7.840%.



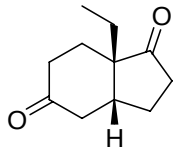
***trans*-6e**

***Trans*-8a-Benzyl-hexahydro-napthalene-1,6-dione (6e):** Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (Neat): ν_{max} 1720 (*C*=O), 1703 (*C*=O), 1697, 1275, 1266, 1259, 750 and 628 cm^{-1}; ^1H NMR ($CDCl_3$, minor isomer) δ 7.26-7.23 (3H, m), 7.07-7.03 (2H, m) [Ph-*H*]; 3.41 (1H, d, *J* = 16.0 Hz), 3.13 (1H, d, *J* = 16.0 Hz) [PhCH_2]; 2.64 (1H, t, *J* = 16.0 Hz), 2.56-2.21 (8H, m), 2.13-1.93 (2H, m), 1.84-1.52 (1H, m), 1.44-1.36 (1H, m); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 212.9 (C, *C*=O), 209.3 (C, *C*=O), 136.0 (C), 128.9 (2 x CH), 128.6 (2 x CH), 127.1 (CH), 52.3 (C), 46.8 (CH), 43.4 (CH_2), 38.7 (CH_2), 37.4 (CH_2), 32.6 (CH_2), 28.4 (CH_2), 27.3 (CH_2), 26.7 (CH_2).



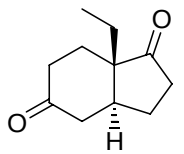
***cis*-6f**

(+)-*cis*-7a-Methyl-hexahydro-indene-1,5-dione (6f): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 68°C; $[\alpha]_D^{25}$ = +78.546° (*c* = 0.283 g/100 mL, $CHCl_3$, 86% *ee*); IR (Neat): ν_{max} 2951, 2914, 2877, 1736 (*C*=O), 1729 (*C*=O), 1707, 1253, 1151 and 1057 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60 (1H, dd, *J* = 15.0, 6.2 Hz), 2.50-2.00 (6H, m), 2.20-1.95 (2H, m), 1.70-1.55 (2H, m), 1.25 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 220.2 (C, *C*=O), 210.7 (C, *C*=O), 47.2 (C), 44.6 (CH), 41.8 (CH_2), 37.1 (CH_2), 35.2 (CH_2), 29.9 (CH_2), 25.1 (CH_2), 20.6 (CH_3); LRMS (MALDI-TOF) m/z 167.026 (M + H^+), calcd for $C_{10}H_{14}O_2$ 166.0994; Anal. calcd for $C_{10}H_{14}O_2$ (166.10): C, 72.26; H, 8.49. Found: C, 72.252, H, 8.493%.



***cis*-6g**

(+)-*cis*-7a-Ethyl-hexahydro-indene-1,5-dione (6g): Purified by column chromatography using EtOAc/hexane and isolated as liquid. $[\alpha]_D^{25}$ = +44.495° (*c* = 0.297 g/100 mL, $CHCl_3$, 85% *ee*); IR (Neat): ν_{max} 2963, 1720 (2 x C=O), 1237 and 642 cm^{-1}; ^1H NMR ($CDCl_3$, major isomer) δ 2.63-2.52 (2H, m), 2.45-2.24 (4H, m), 2.20-2.11 (2H, m), 2.09-2.02 (1H, m), 1.75-1.65 (3H, m), 1.60-1.51 (1H, m), 0.90 (3H, t, *J* = 8.0 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, major isomer) δ 220.4 (C, *C*=O), 211.2 (C, *C*=O), 51.0 (C), 42.1 (CH_2), 40.1 (CH), 37.0 (CH_2), 36.3 (CH_2), 28.6 (CH_2), 27.3 (CH_2), 25.4 (CH_2), 8.6 (CH_3); LRMS (MALDI-TOF) m/z 180.008, calcd for $C_{11}H_{16}O_2$ 180.1150; Anal. calcd for $C_{11}H_{16}O_2$ (180.12): C, 73.30; H, 8.95;. Found: C, 73.310, H, 8.948%.



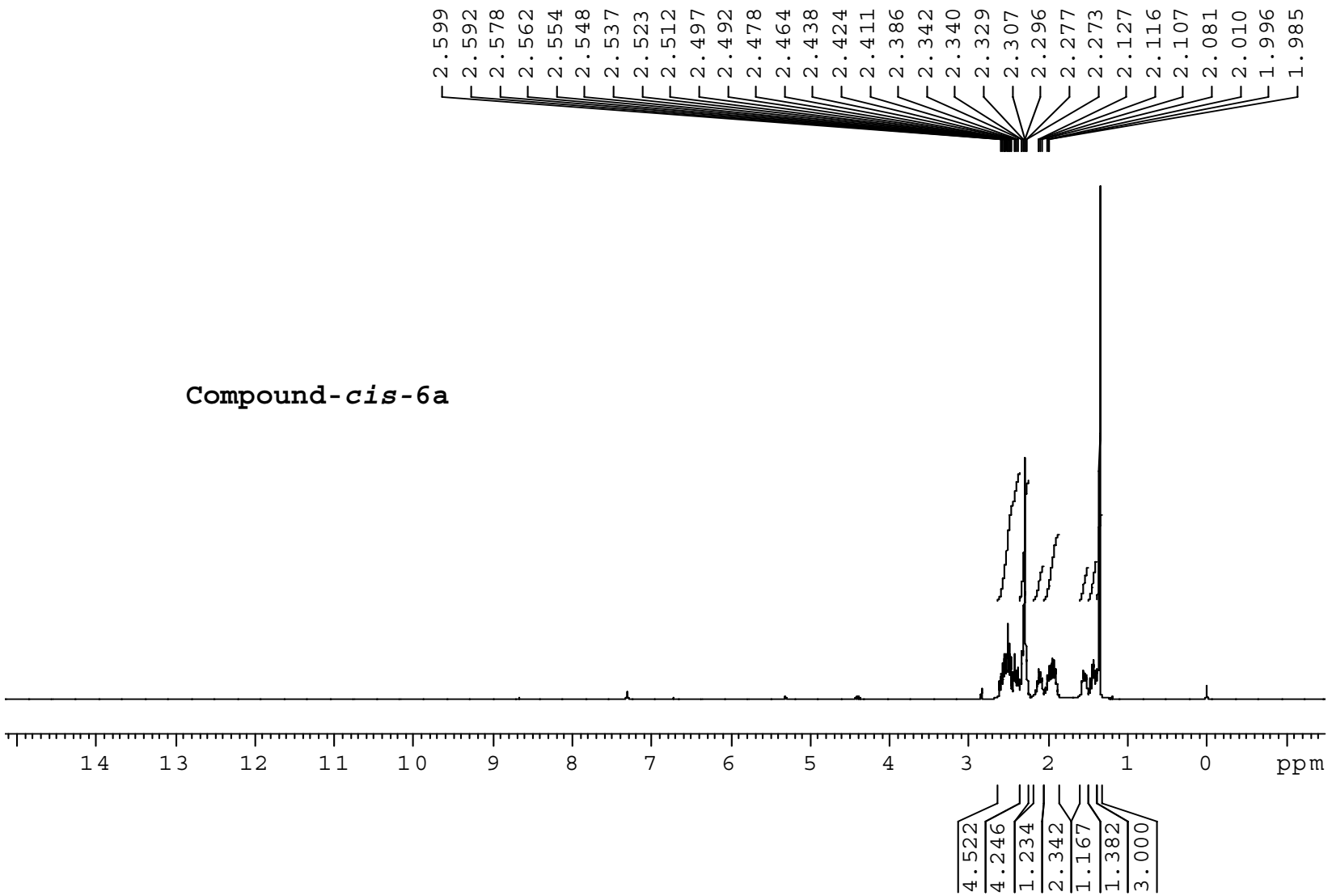
***trans*-6g**

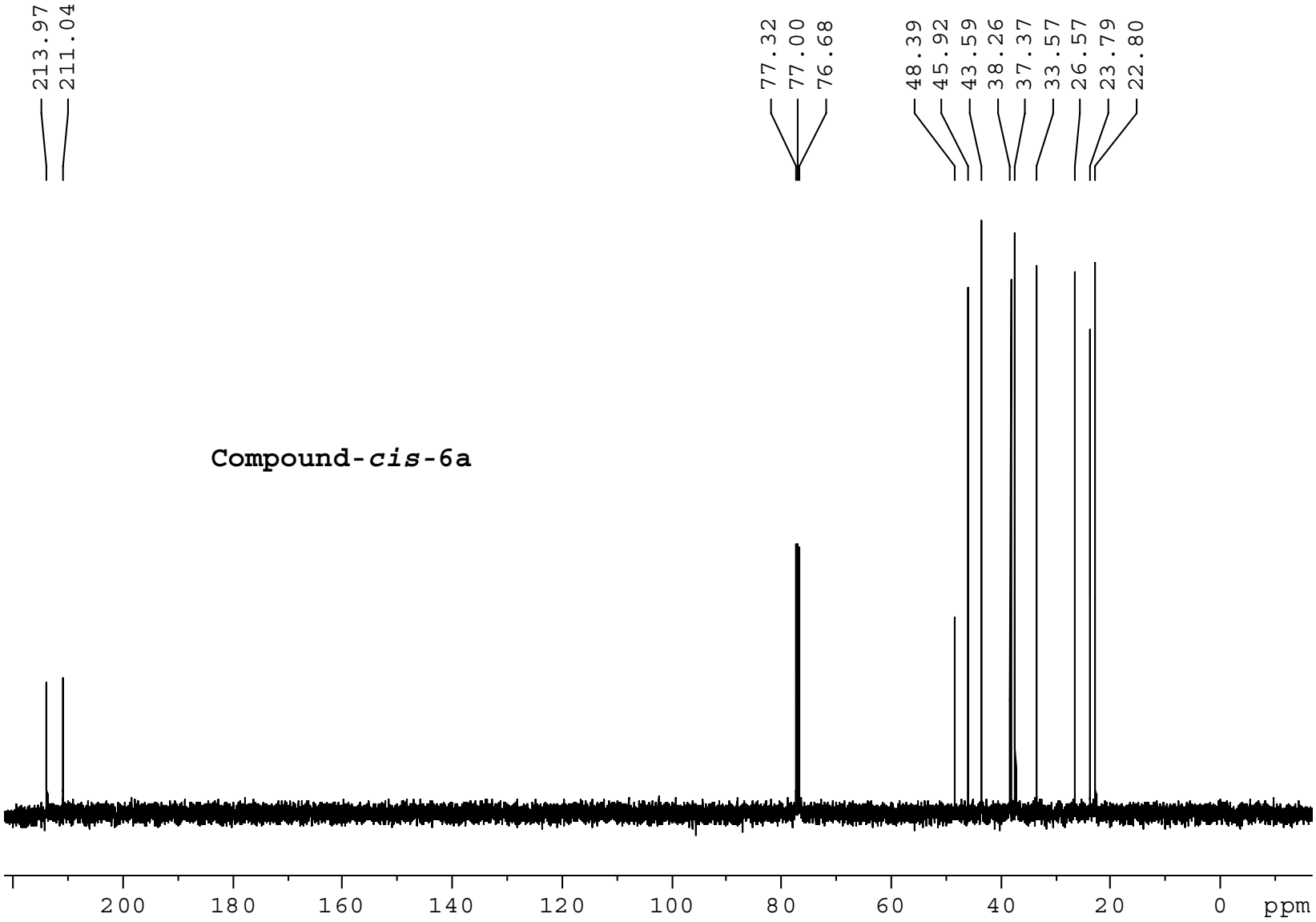
***Trans*-7a-Ethyl-hexahydro-indene-1,5-dione (6g):** Purified by column chromatography using EtOAc/hexane and isolated as liquid. IR (Neat): ν_{max} 2960, 1729 (*C*=O) and 1714 (*C*=O) cm^{-1}; ^1H NMR ($CDCl_3$, minor isomer) δ 2.63-2.50 (2H, m), 2.45-1.92 (6H, m), 1.86-1.44 (4H, m), 1.40-1.19 (1H, m),

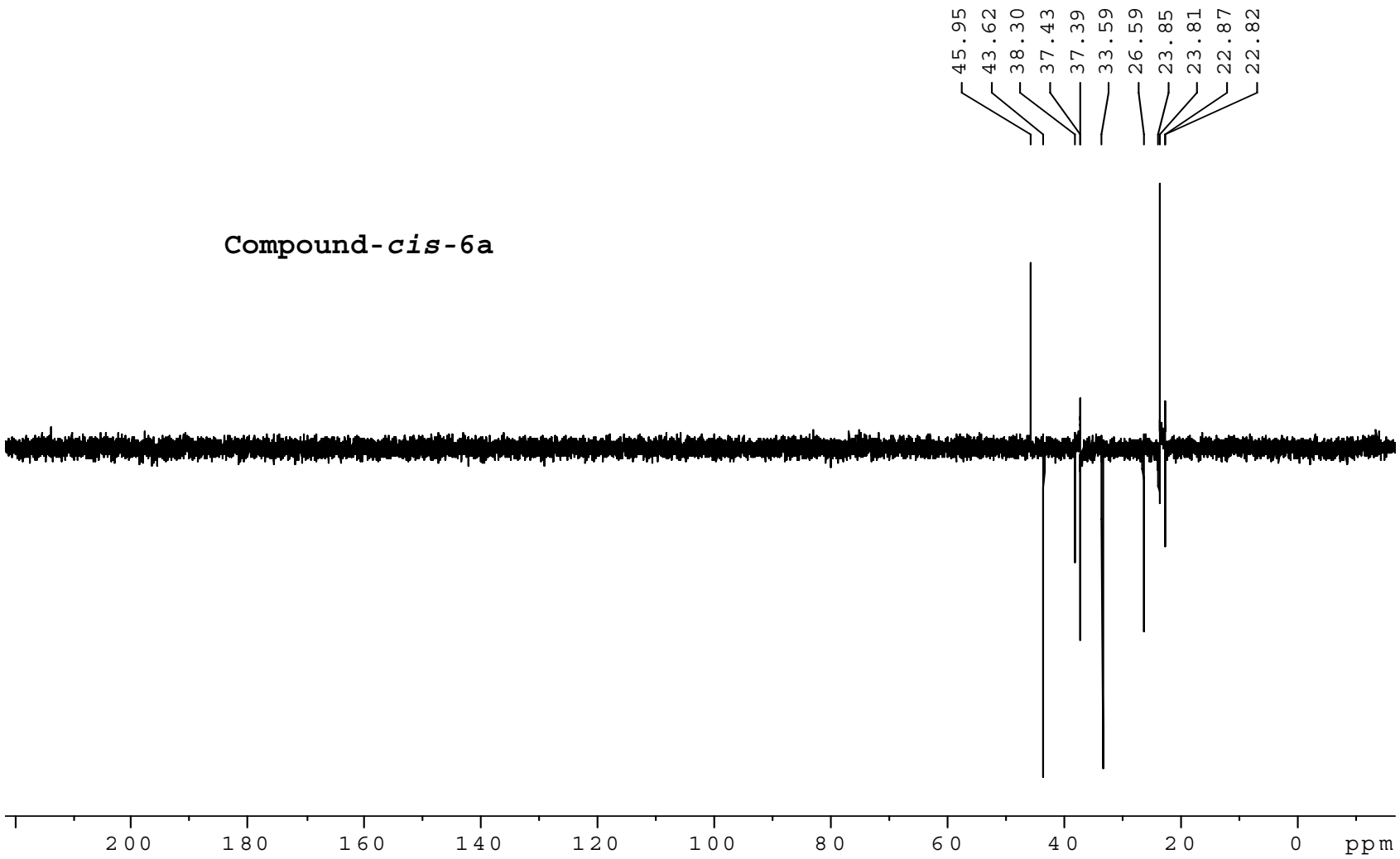
0.90 (3H, t, J = 8.0 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135, minor isomer) δ 216.7 (C, *C*=O), 209.6 (C, *C*=O), 49.7 (C), 45.2 (CH), 42.1 (CH_2), 36.5 (CH_2), 36.1 (CH_2), 25.3 (CH_2), 23.2 (CH_2), 16.4 (CH_2), 7.5 (CH_3).

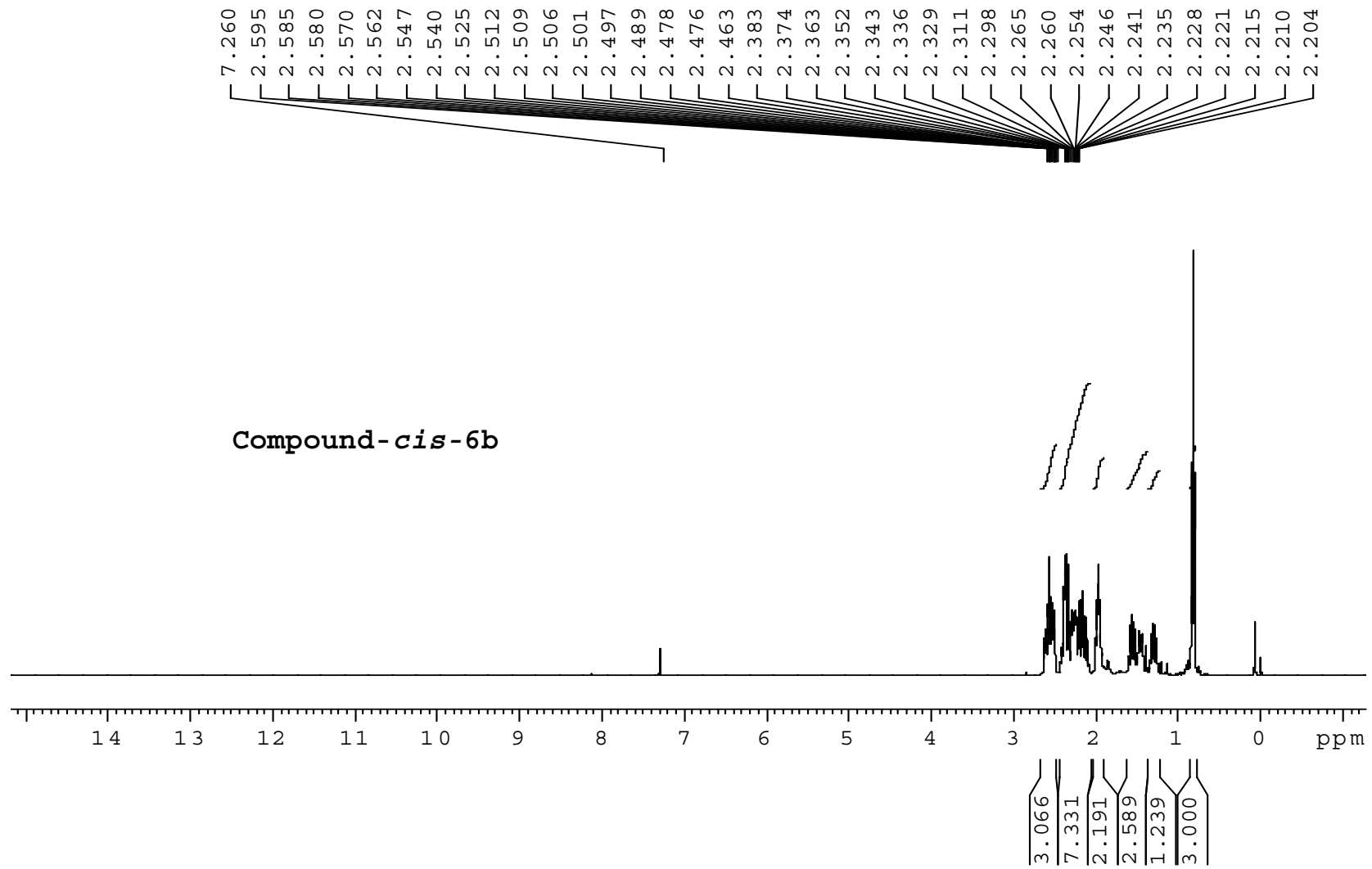
References:

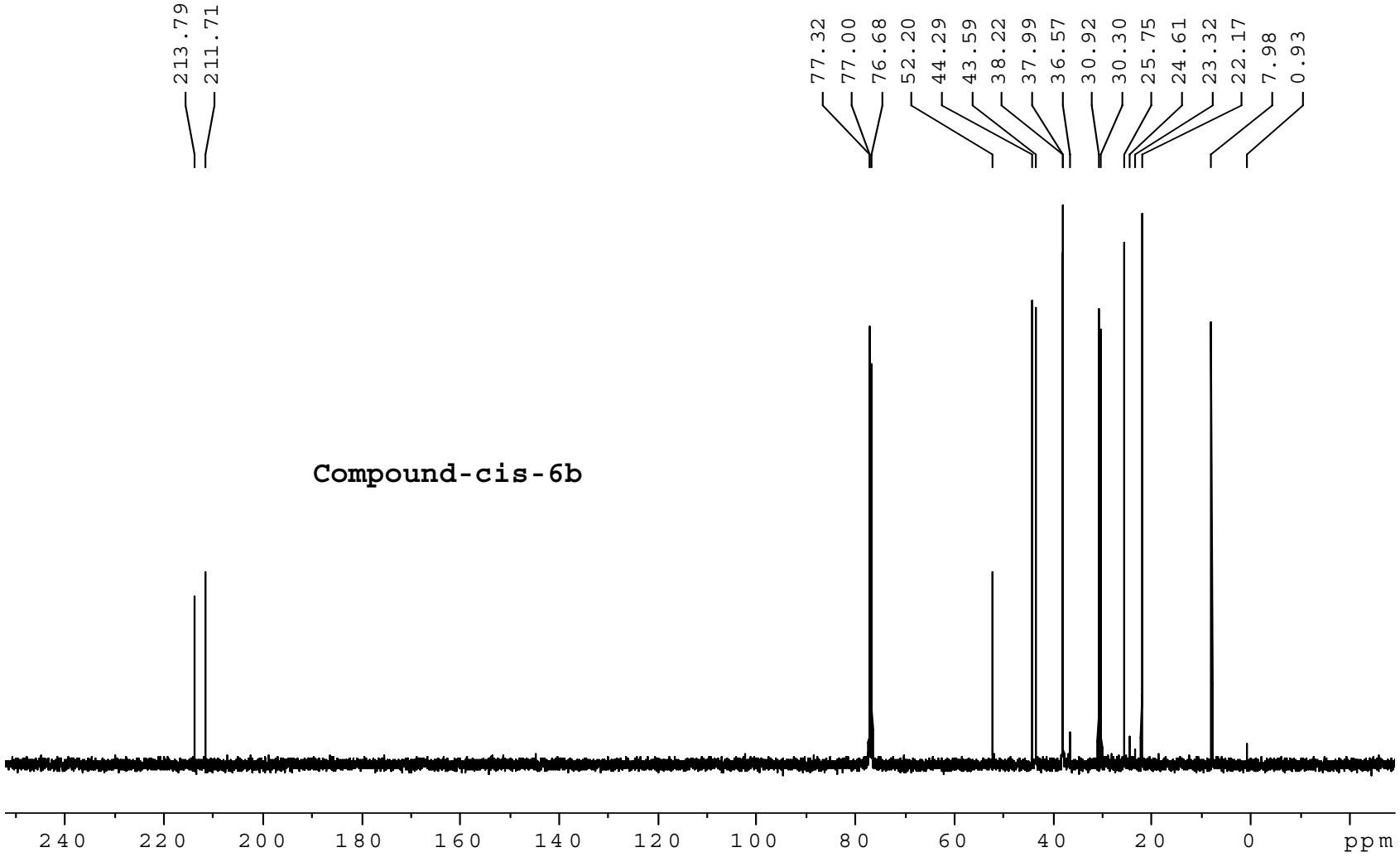
1. (a) D. B. Ramachary and M. Kishor *J. Org. Chem., 72*, 14, **2007**, 5061-5068. (b) R. Narayanan and S. Swaminathan *Tetrahedron Letters.*, *42*, **2001**, 4887–4890. (c) Z. G. Hajos and D. R. Parrish *J. Org. Chem.*, *39,* 12, **1974**, 1615-1621. (d) M. A. Stealey, R. L. Shone and M. Miyano *Synthetic Communications 20*, 12, **1990**, 1869-1876. (e) R. Hanselmann and M. Benn, *Synthetic Communications 26*, 5, **1996**, 945.

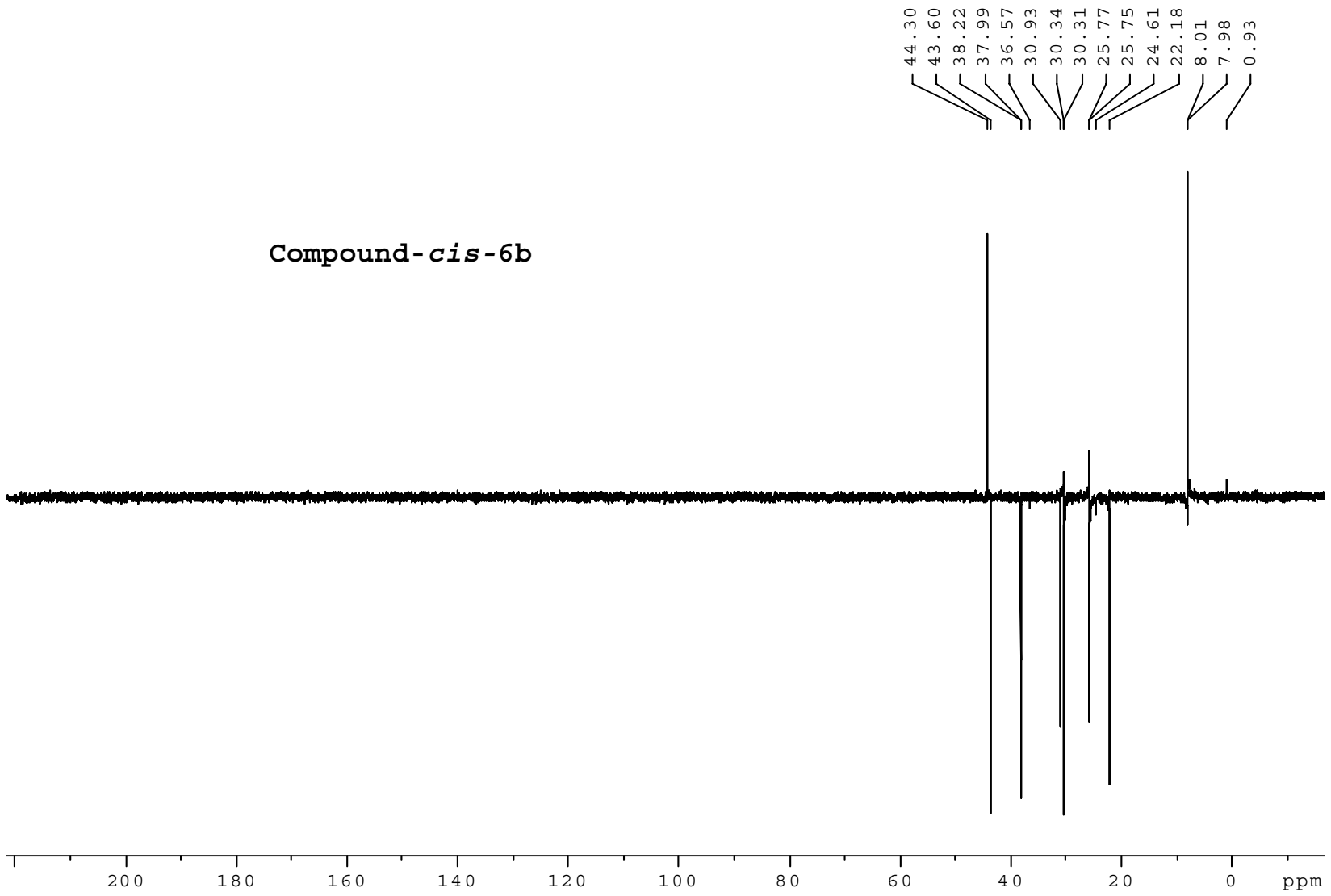

2.599
2.592
2.578
2.562
2.554
2.548
2.537
2.523
2.512
2.497
2.492
2.478
2.464
2.438
2.424
2.411
2.386
2.342
2.340
2.329
2.307
2.296
2.277
2.273
2.127
2.116
2.107
2.081
2.010
1.996
1.985
Compound-*cis*-6a
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.522
4.246
1.234
2.342
1.167
1.382
3.000

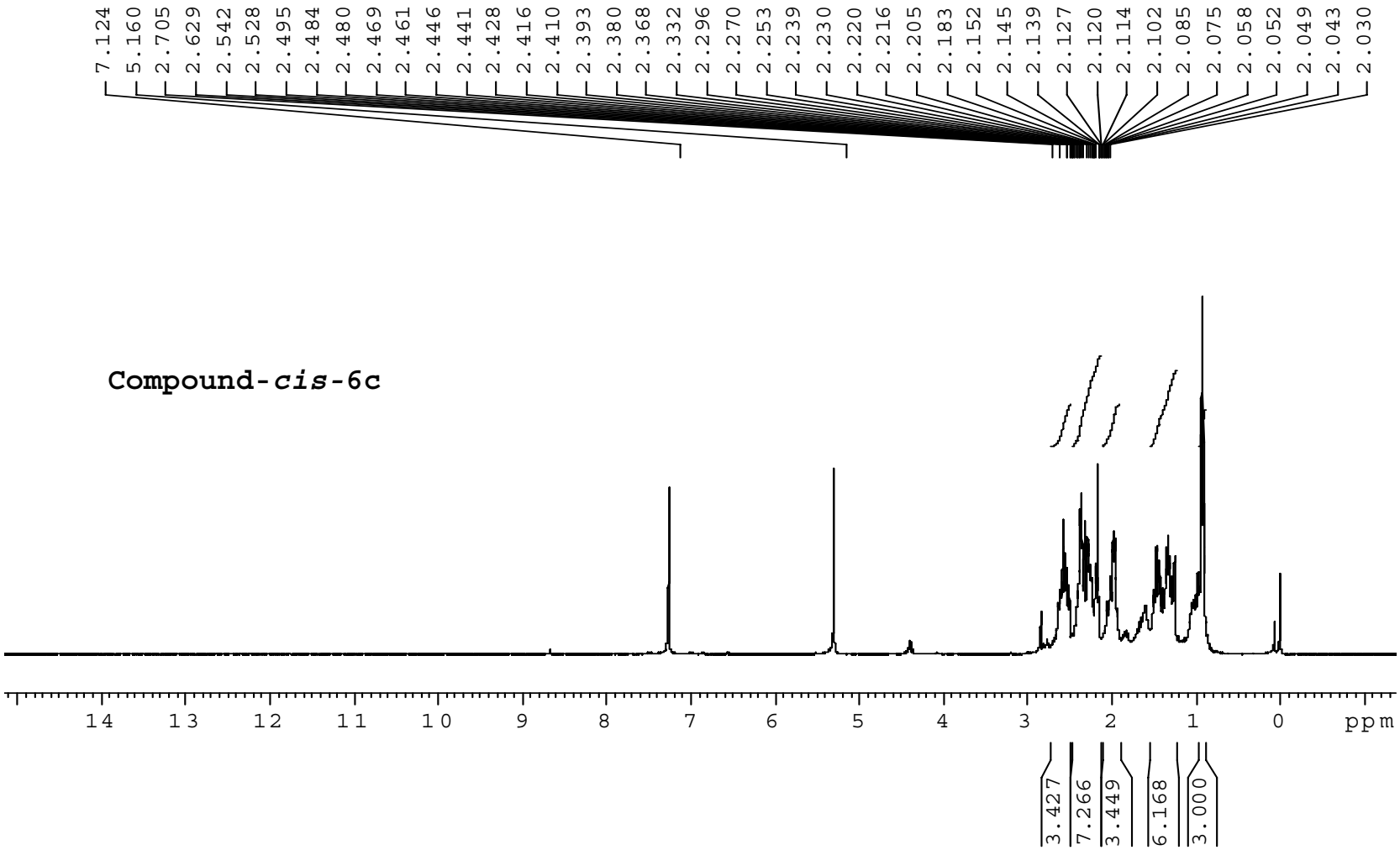

213.97
211.04
77.32
77.00
76.68
48.39
45.92
43.59
38.26
37.37
33.57
26.57
23.79
22.80
Compound-*cis*-6a
200
180
160
140
120
100
80
60
40
20
0
ppm

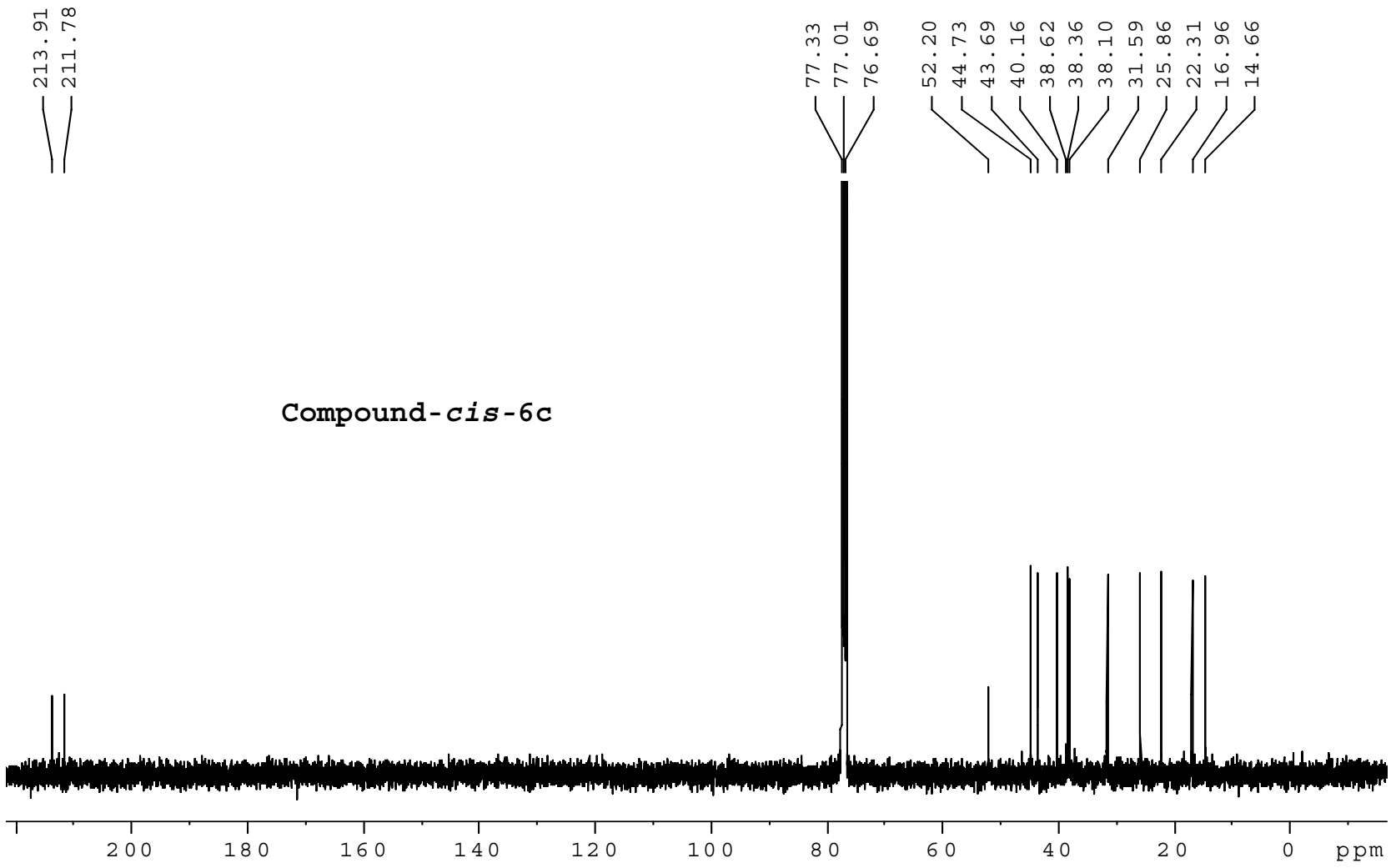

45.95
43.62
38.30
37.43
37.39
33.59
26.59
23.85
23.81
22.87
22.82
Compound-*cis*-6a
200
180
160
140
120
100
80
60
40
20
0
ppm

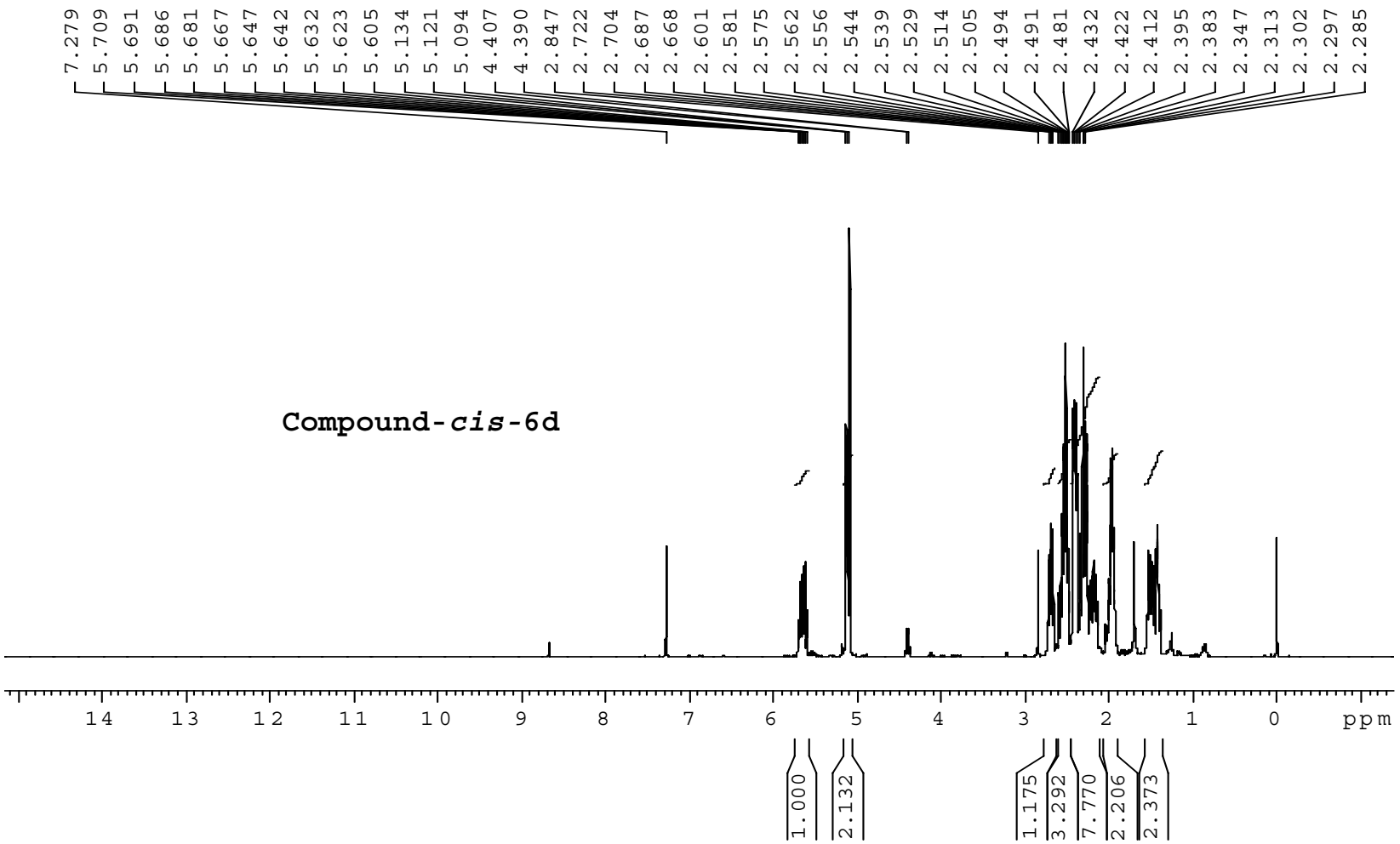

7.260
2.595
2.585
2.580
2.570
2.562
2.547
2.540
2.525
2.512
2.509
2.506
2.501
2.497
2.489
2.478
2.476
2.463
2.383
2.374
2.363
2.352
2.343
2.336
2.329
2.311
2.298
2.265
2.260
2.254
2.246
2.241
2.235
2.228
2.221
2.215
2.210
2.204
Compound-*cis*-6b
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
3.066
7.331
2.191
2.589
1.239
3.000

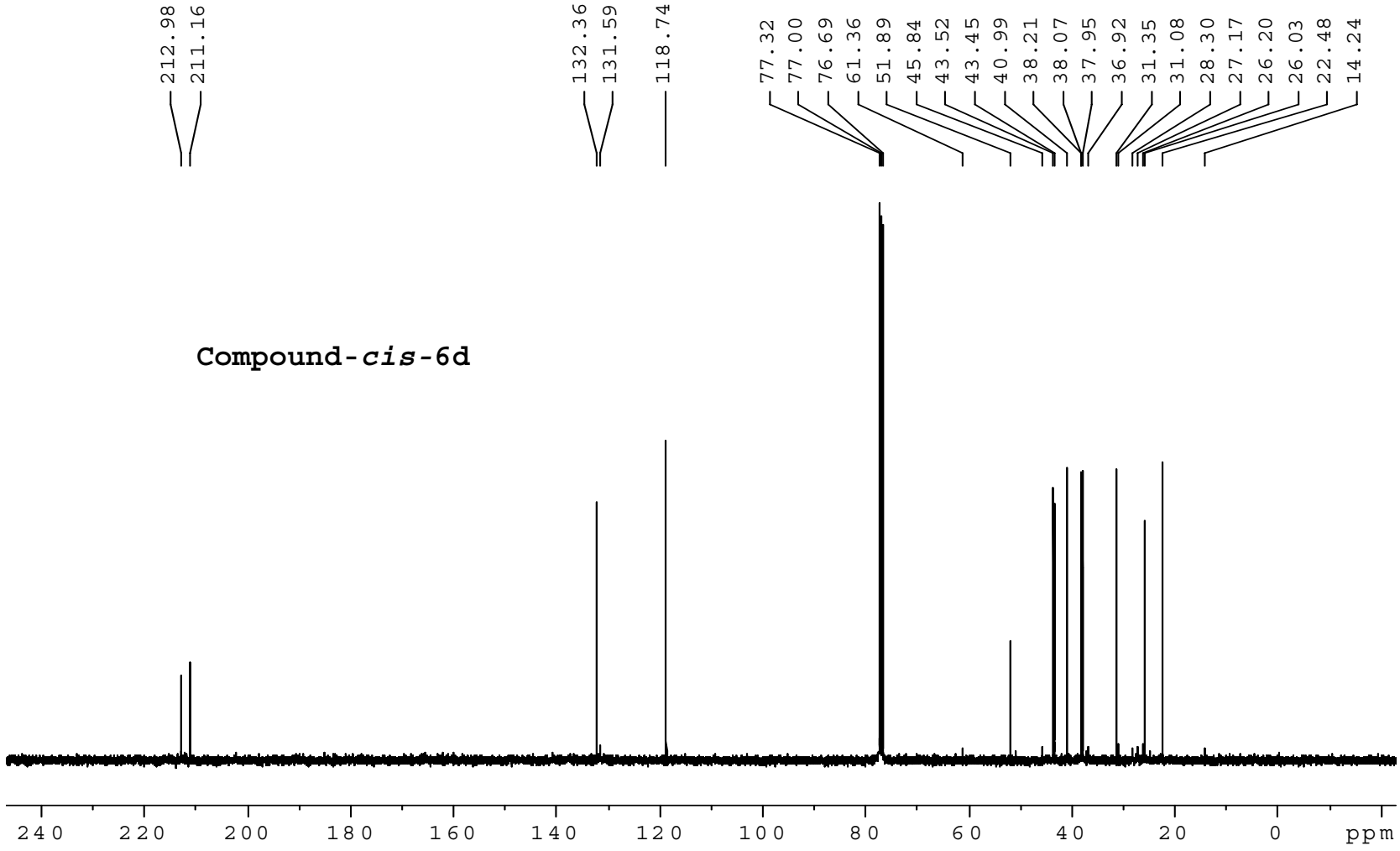

213.79
211.71
77.32
77.00
76.68
52.20
44.29
43.59
38.22
37.99
36.57
30.92
30.30
25.75
24.61
23.32
22.17
7.98
0.93
Compound-cis-6b
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

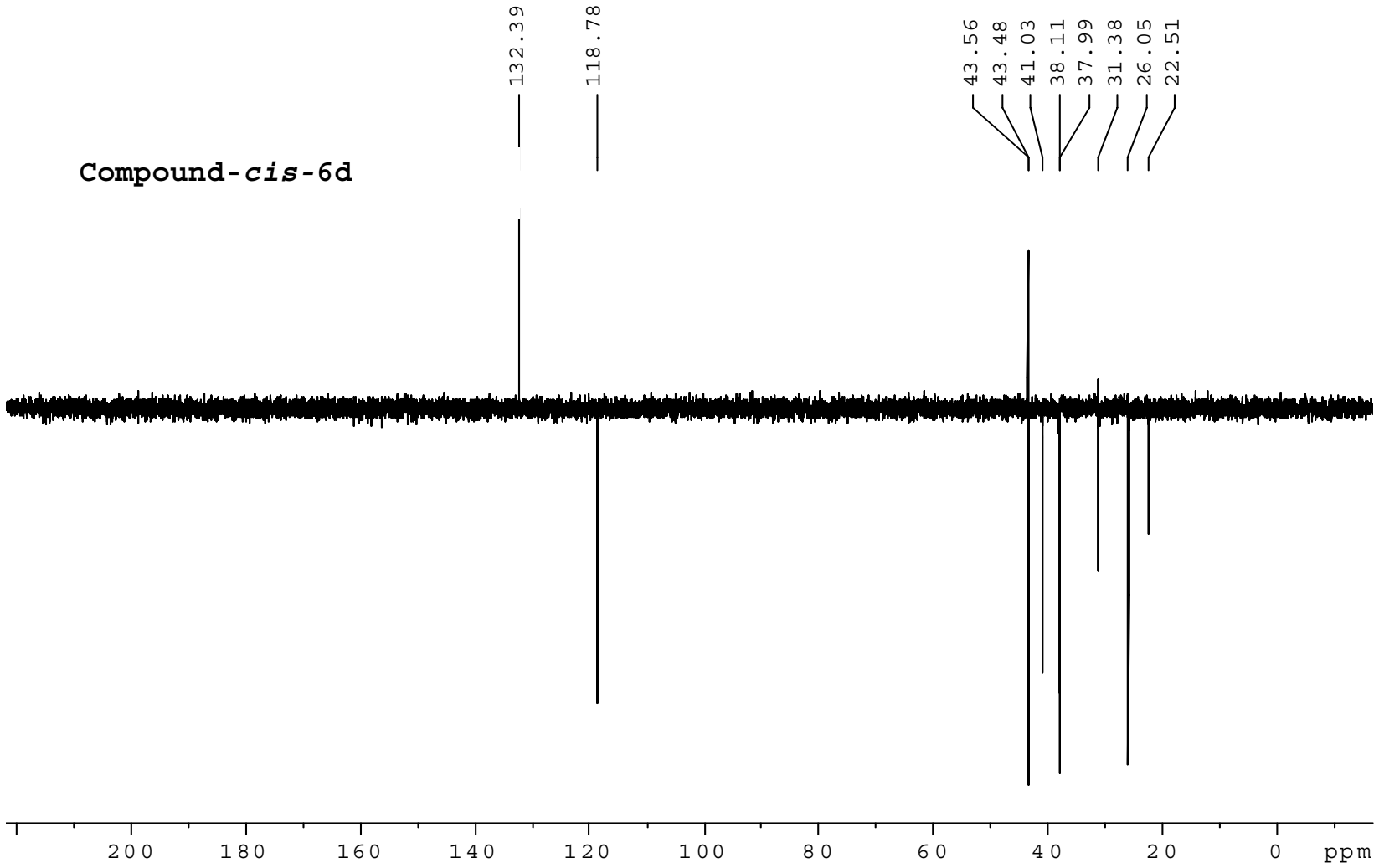

44.30
43.60
38.22
37.99
36.57
30.93
30.34
30.31
25.77
25.75
24.61
22.18
8.01
7.98
0.93
Compound-*cis*-6b
200
180
160
140
120
100
80
60
40
20
0
ppm

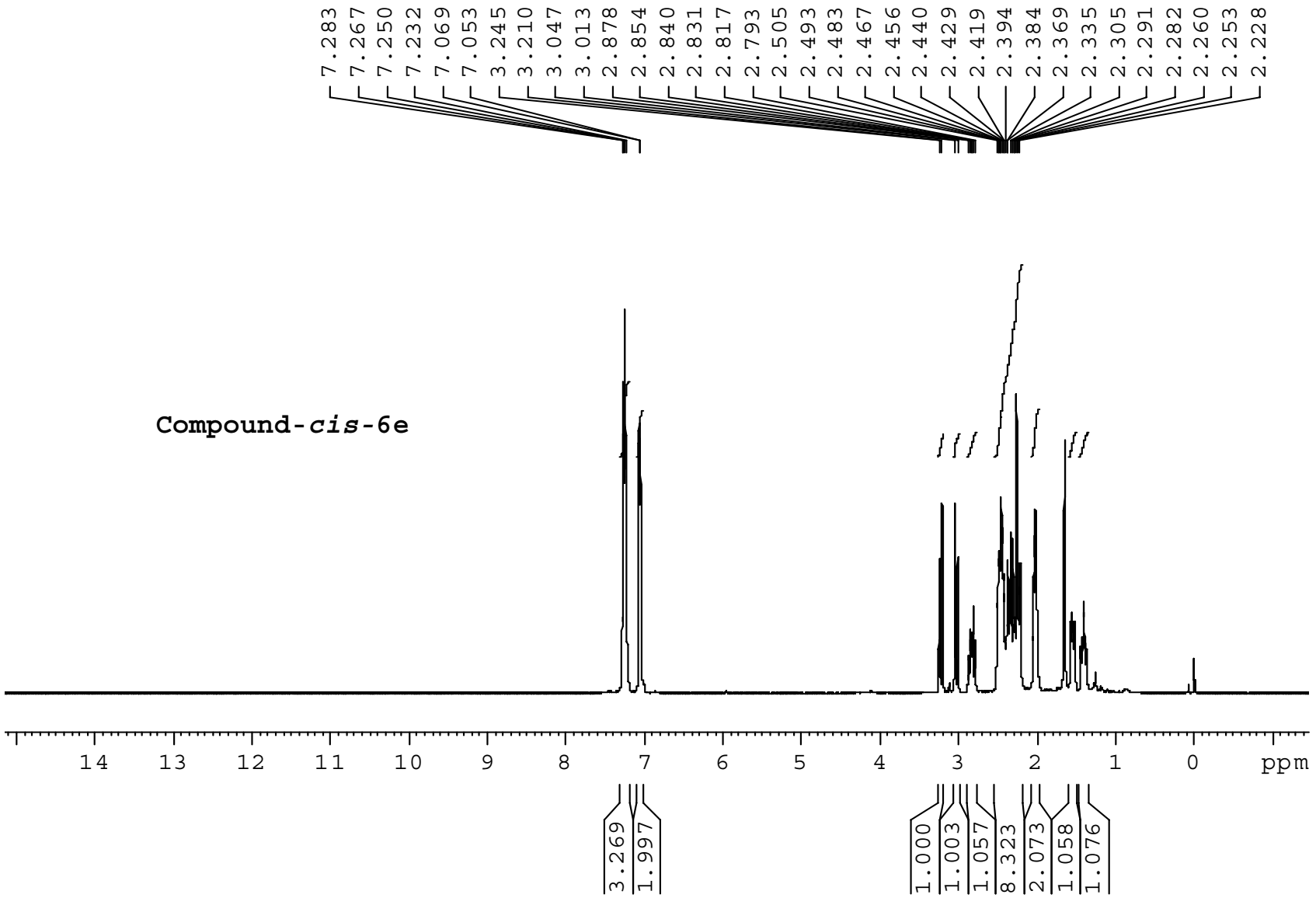

7.124
5.160
2.705
2.629
2.542
2.528
2.495
2.484
2.480
2.469
2.461
2.446
2.441
2.428
2.416
2.410
2.393
2.380
2.368
2.332
2.296
2.270
2.253
2.239
2.230
2.220
2.216
2.205
2.183
2.152
2.145
2.139
2.127
2.120
2.114
2.102
2.085
2.075
2.058
2.052
2.049
2.043
2.030
Compound-*cis*-6c
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
3.427
7.266
3.449
6.168
3.000

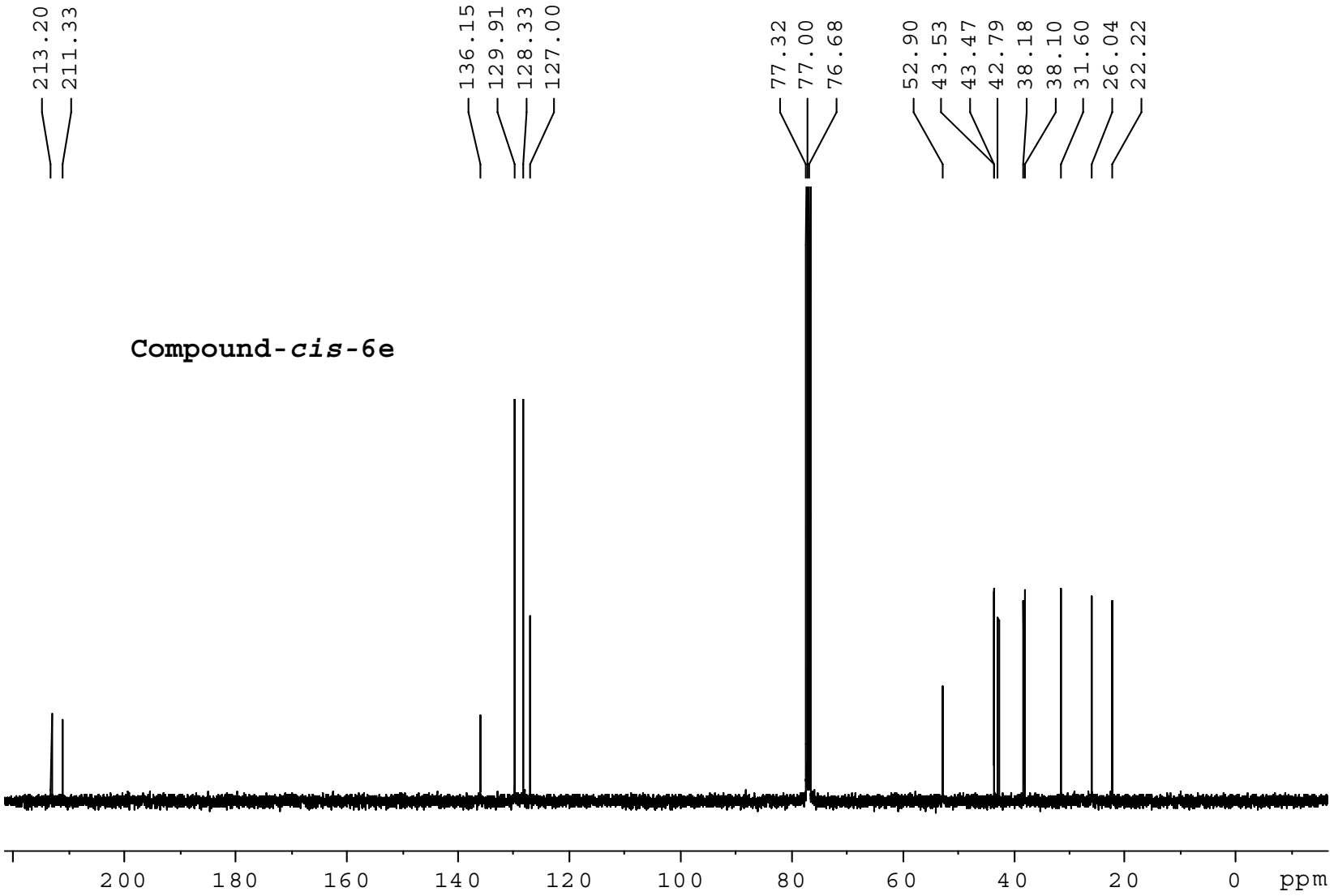

213.91
211.78
77.33
77.01
76.69
52.20
44.73
43.69
40.16
38.62
38.36
38.10
31.59
25.86
22.31
16.96
14.66
Compound-*cis*-6c
200
180
160
140
120
100
80
60
40
20
0
ppm

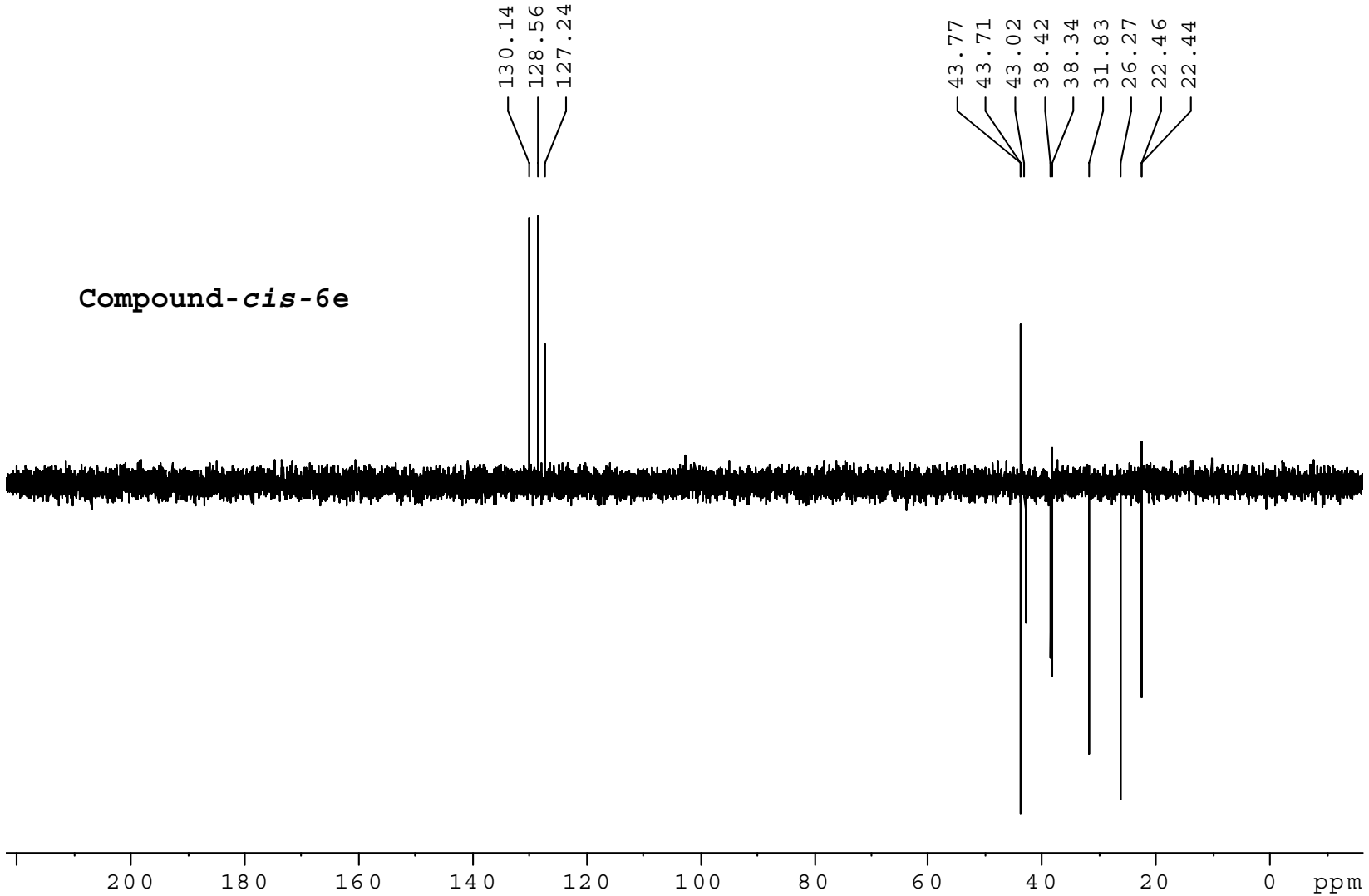

7.279
5.709
5.691
5.686
5.681
5.667
5.647
5.642
5.632
5.623
5.605
5.134
5.121
5.094
4.407
4.390
2.847
2.722
2.704
2.687
2.668
2.601
2.581
2.575
2.562
2.556
2.544
2.539
2.529
2.514
2.505
2.494
2.491
2.481
2.432
2.422
2.412
2.395
2.383
2.347
2.313
2.302
2.297
2.285
Compound-*cis*-6d
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
2.132
1.175
3.292
7.770
2.206
2.373

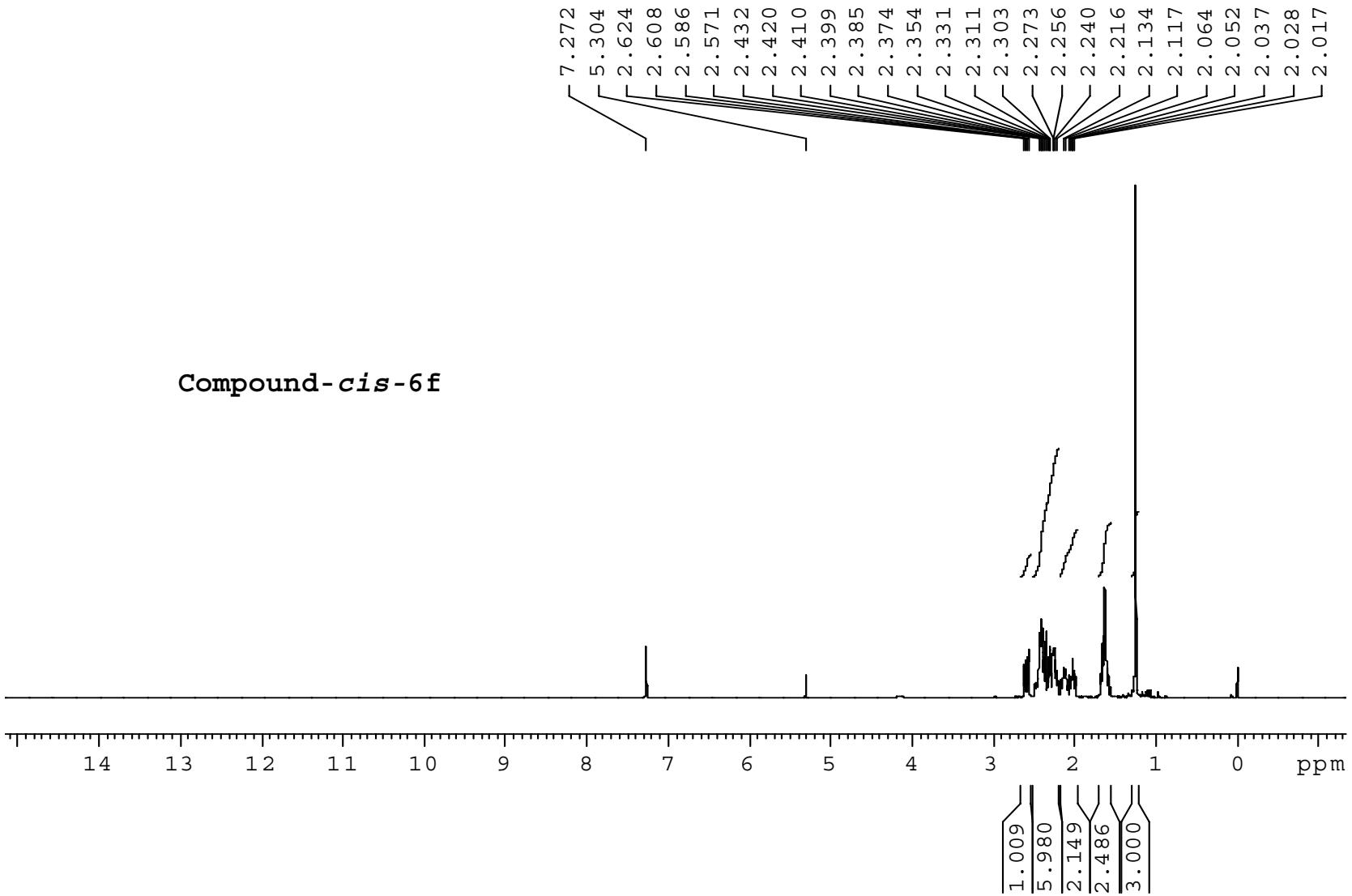

212.98
211.16
132.36
131.59
118.74
77.32
77.00
76.69
61.36
51.89
45.84
43.52
43.45
40.99
38.21
38.07
37.95
36.92
31.35
31.08
28.30
27.17
26.20
26.03
22.48
14.24
Compound-cis-6d
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

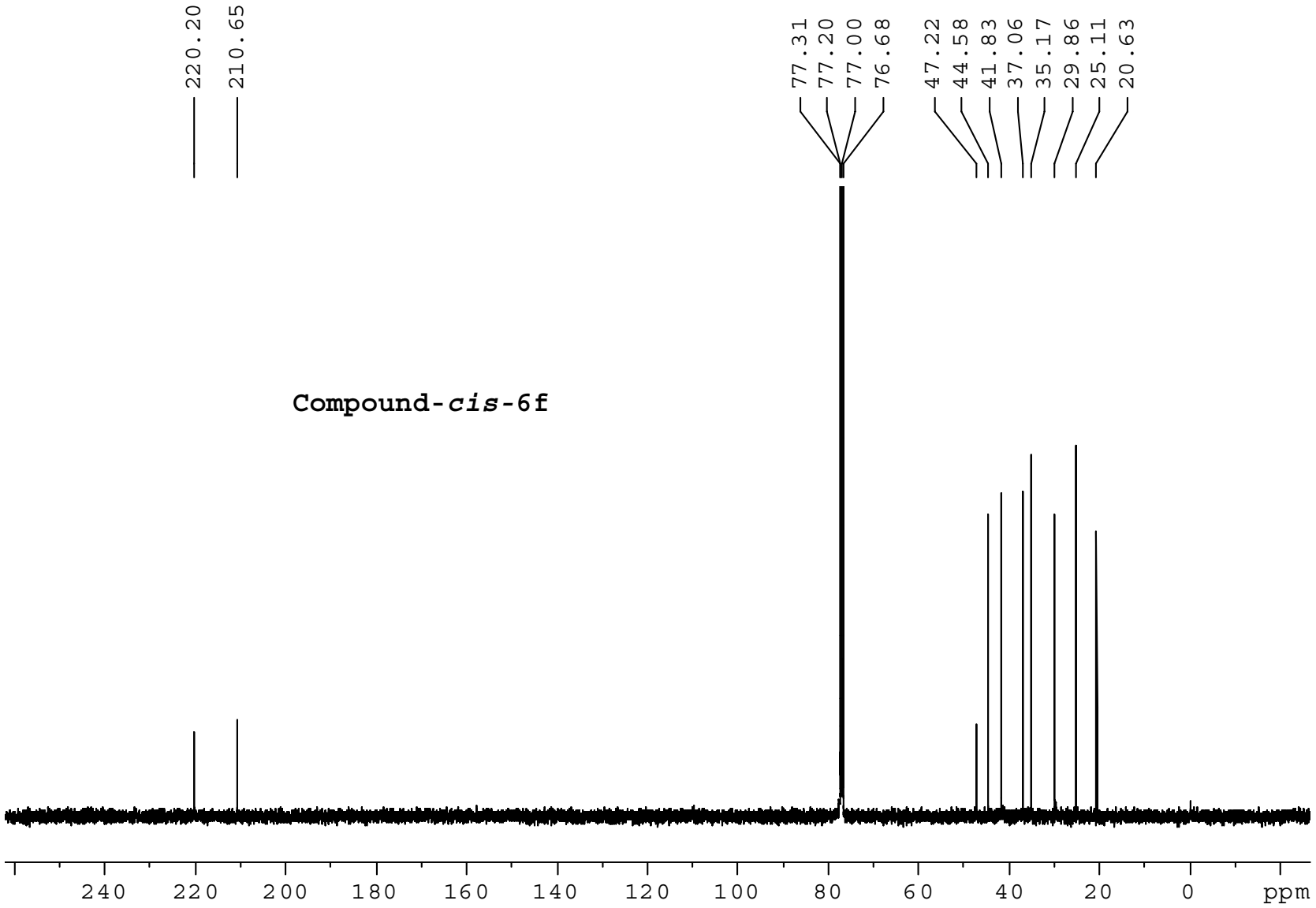

Compound-*cis*-6d
132.39
118.78
43.56
43.48
41.03
38.11
37.99
31.38
26.05
22.51
200
180
160
140
120
100
80
60
40
20
0
ppm

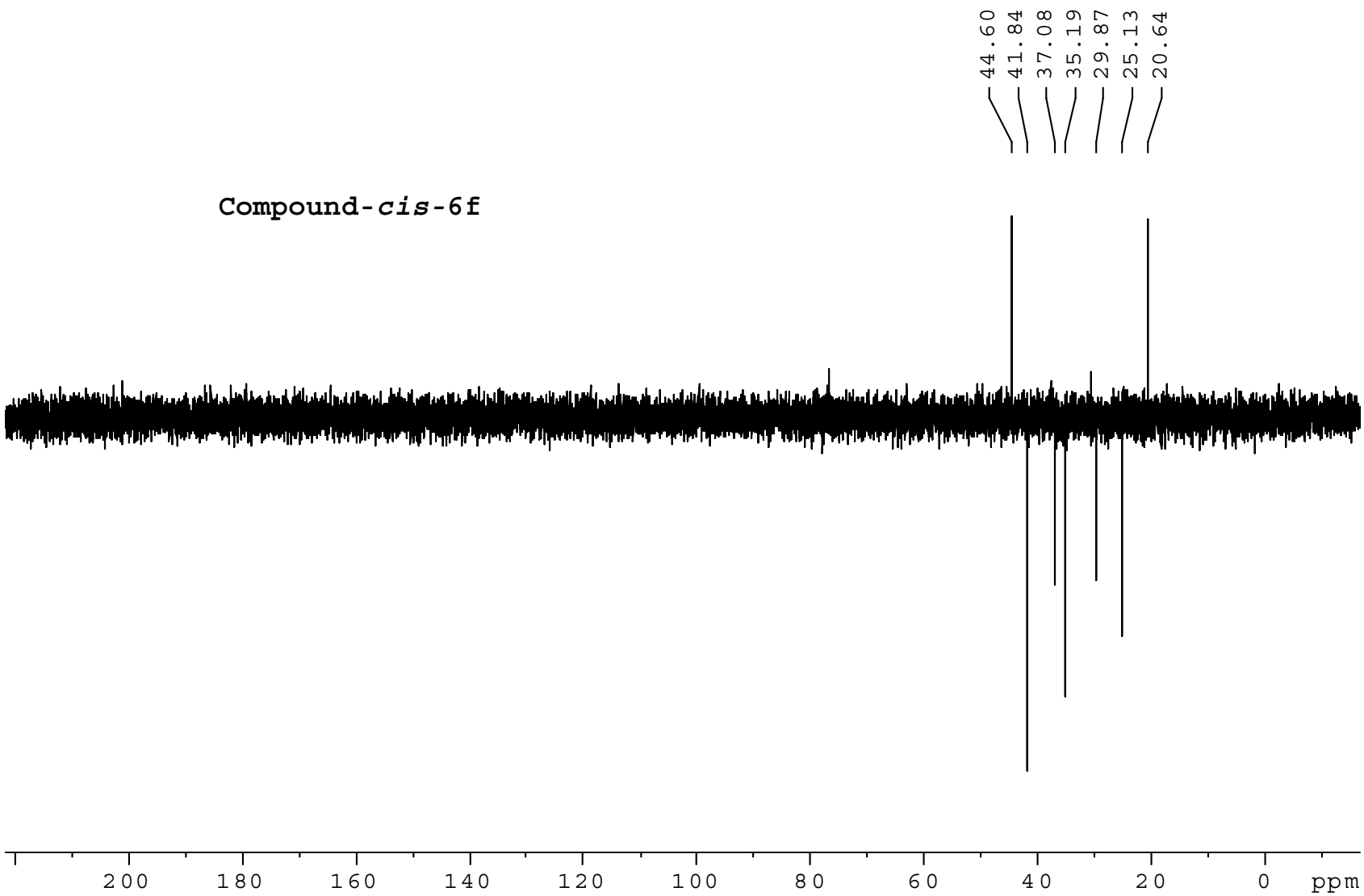

7.283
7.267
7.250
7.232
7.069
7.053
3.245
3.210
3.047
3.013
2.878
2.854
2.840
2.831
2.817
2.793
2.505
2.493
2.483
2.467
2.456
2.440
2.429
2.419
2.394
2.384
2.369
2.335
2.305
2.291
2.282
2.260
2.253
2.228
Compound-*cis*-6e
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.269
1.997
1.000
1.003
1.057
8.323
2.073
1.058
1.076

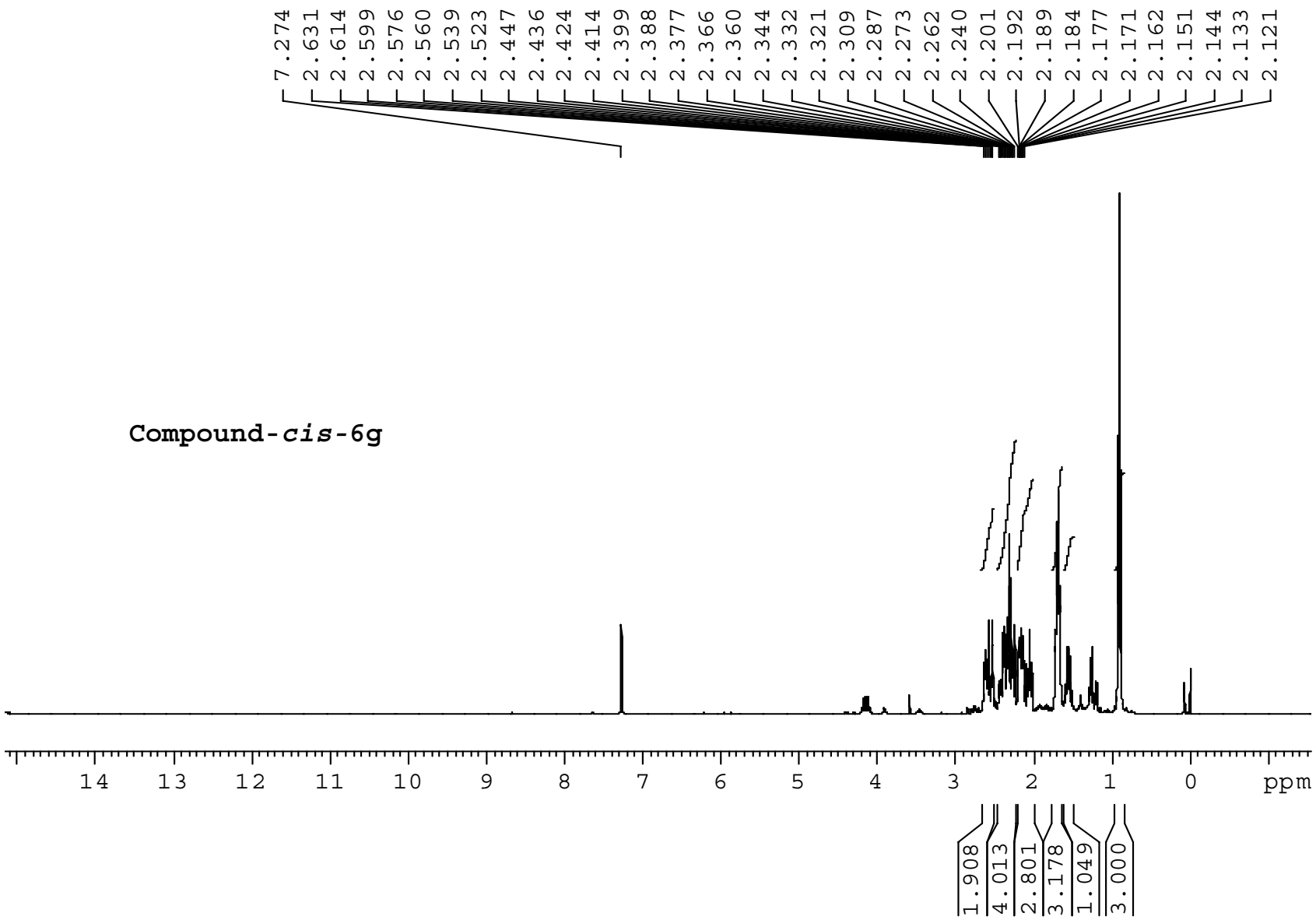

213.20
211.33
136.15
129.91
128.33
127.00
77.32
77.00
76.68
52.90
43.53
43.47
42.79
38.18
38.10
31.60
26.04
22.22
Compound-*cis*-6e
200
180
160
140
120
100
80
60
40
20
0
ppm

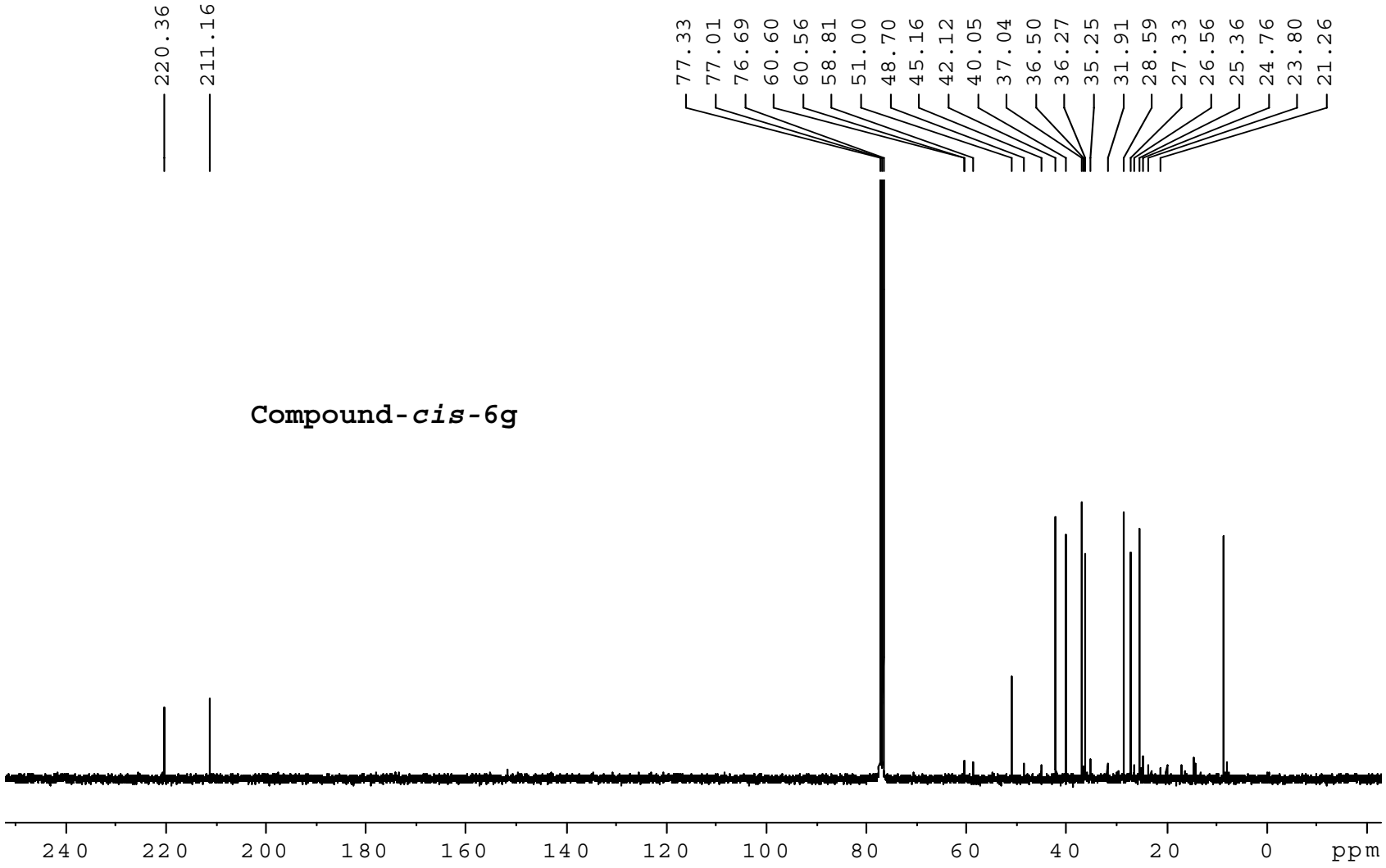

130.14
128.56
127.24
43.77
43.71
43.02
38.42
38.34
31.83
26.27
22.46
22.44
Compound-*cis*-6e
200
180
160
140
120
100
80
60
40
20
0
ppm

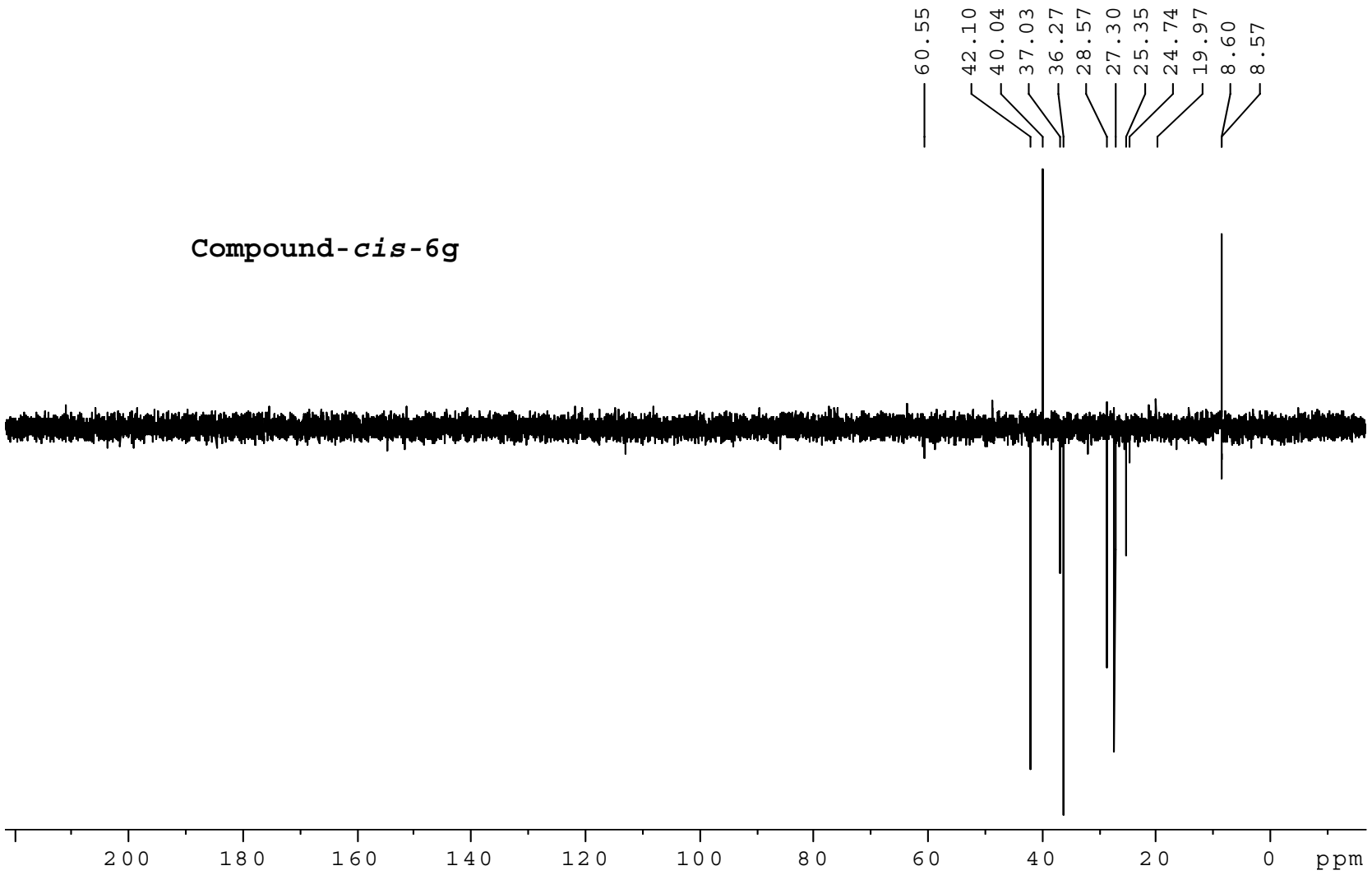

7.272
5.304
2.624
2.608
2.586
2.571
2.432
2.420
2.410
2.399
2.385
2.374
2.354
2.331
2.311
2.303
2.273
2.256
2.240
2.216
2.134
2.117
2.064
2.052
2.037
2.028
2.017
Compound-cis-6f
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.009
5.980
2.149
2.486
3.000


220.20
210.65
77.31
77.20
77.00
76.68
47.22
44.58
41.83
37.06
35.17
29.86
25.11
20.63
Compound-cis-6f
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


44.60
41.84
37.08
35.19
29.87
25.13
20.64
Compound-*cis*-6f
200
180
160
140
120
100
80
60
40
20
0
ppm


7.274
2.631
2.614
2.599
2.576
2.560
2.539
2.523
2.447
2.436
2.424
2.414
2.399
2.388
2.377
2.366
2.360
2.344
2.332
2.321
2.309
2.287
2.273
2.262
2.240
2.201
2.192
2.189
2.184
2.177
2.171
2.162
2.151
2.144
2.133
2.121
Compound-*cis*-6g
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.908
4.013
2.801
3.178
1.049
3.000


220.36
211.16
77.33
77.01
76.69
60.60
60.56
58.81
51.00
48.70
45.16
42.12
40.05
37.04
36.50
36.27
35.25
31.91
28.59
27.33
26.56
25.36
24.76
23.80
21.26
Compound-cis-6g
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm


60.55
42.10
40.04
37.03
36.27
28.57
27.30
25.35
24.74
19.97
8.60
8.57
Compound-*cis*-6g
200
180
160
140
120
100
80
60
40
20
0
ppm