

**Regio-specific carbonylative Annulation of Iodophenol Acetates and
Acetylenes to Construct the Flavones by a New Catalyst of Palladium-
Thiourea-dppp Complex**

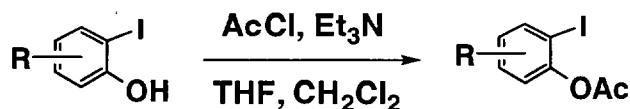
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Boston, Massachusetts 02115-5731*

Supporting Information

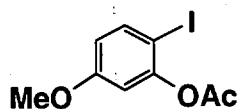
General Methods

Unless stated otherwise, reaction were performed in flame-dried glassware under nitrogen or an argon atmosphere. Reaction solvents were commercially purchased from *Aldrich* without further purification and reagents were used as received. Reaction were monitored by thin-layer chromatography (TLC) on 0.25 mm precoated Merck Silica Gel 60 F₂₅₄, visualizing with ultraviolet light, p-anisaldehyde stain, or phosphomolybdic acid stain. Flash column chromatography was performed on Merck Silica Gel 60 (230-400 mesh) using reagent grade hexanes, dichloromethane, and ACS grade ethyl acetate, methanol and diethyl ether. High-resolution mass spectra were performed at Harvard University Mass Spectrometry. ¹H and ¹³C NMR spectra were recorded on a Varian Unity INPVA 500MHz spectrometer and are referenced to residual solvent peaks (CDCl₃: ¹H: δ 7.27, ¹³C: δ 77.23) or to an internal reference of tetramethylsilane in CDCl₃ (¹H: δ 0.00). ¹H-¹H coupling are assumed to be first order, and peak multiplicity is reported as a s (single), d (doublet), t (triplet), q (quartet), m (multiplet), or b (broad).

General procedure for synthesis of compounds 9, 12, 15 - 20.

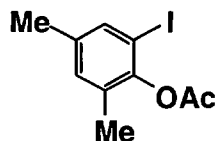
Compounds 9, 12, 15-22 are synthesized followed a general procedure as illustrated below.

Acetyl chloride (0.71 mL, 10 mmol) was added to a mixture of 2-iodophenol **5** (2g, 9 mmol), triethyl amine (2.8 ml, 20 mmol) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (3 mL/ 3mL) at 0 °C and then the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with water (5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The organic layer was washed with saturated sodium chloride solution (5 mL), and dried (Na_2SO_4). The solvent was removed and the residue was purified



compound 9

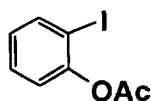
Compound 9: Purification by flash chromatography (EtOAc/hexanes = 1/9) gave **9** in 97% yield as a colorless oil (prepared according to the literature^{10d}); R_f = 0.6 (EtOAc/hexanes = 4/6); ^1H NMR (500 MHz, CDCl_3): δ 7.66 (d, J = 9.0 Hz, 1H), 6.69 (d, J = 2.0 Hz, 1H), 6.61 (dd, J_1 = 9.0, J_2 = 2.0 Hz, 1H), 3.79 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 168.7, 161.1, 152.1, 139.3, 114.5, 109.5, 79.1, 55.8, 21.5.



compound 12

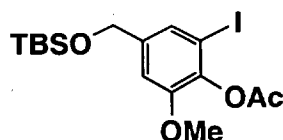
Compound 12: Purification by flash chromatography (CH_2Cl_2 /hexanes = 2:8) gave **12** in 99% yield as a colorless semi solid (prepared according to the literature^{11e}); R_f = 0.5 (CH_2Cl_2 /hexanes = 1/1); ^1H NMR (500 MHz, CDCl_3): δ 7.48 (s, 1H), 7.01 (s, 1H), 2.38 (s, 3H), 2.28 (s, 3H), 2.18

(s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 168.5, 147.8, 137.8, 137.4, 132.1, 131.5, 91.0, 21.18, 20.50, 17.36.



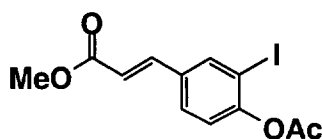
compound 15

Compound 15: Purification by flash chromatography (EtOAc/hexanes = 1/9) gave **15** in 97% yield as a colorless oil; R_f = 0.6 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 7.84 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 168.7, 151.3, 139.5, 129.5, 127.8, 123.2, 90.7, 21.4.



compound 16

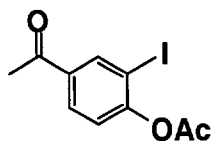
Compound 16: Purification by flash chromatography (EtOAc/hexanes = 1:9) gave **16** in 99% yield as white solid (prepared according to the literature^{11f}); R_f = 0.6 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 7.31 (s, 1H), 6.96 (s, 1H), 4.68 (s, 2H), 3.82 (s, 3H), 2.37 (s, 3H), 0.96 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 168.2, 151.6, 142.1, 139.6, 127.5, 110.3, 91.5, 63.9, 56.2, 26.1, 21.0, 18.6, -5.1.



compound 17

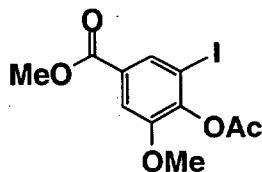
Compound 17: Purification by flash chromatography (EtOAc/hexanes = 1:9) gave **17** as a white solid (prepared according to the literature^{11c}); R_f = 0.6 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 7.99 (d, J = 2.0 Hz, 1H), 7.60 (d, J = 16.0 Hz, 1H), 7.52 (dd, J_1 = 8.0, J_2 = 2.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.40 (d, J = 16.0 Hz, 1H), 3.82 (s, 3H), 2.39 (s, 3H); ^{13}C NMR

(125.7 MHz, CDCl₃): δ 168.6, 167.1, 152.7, 142.3, 139.0, 134.3, 129.2, 123.5, 119.5, 91.3, 52.1, 21.4.



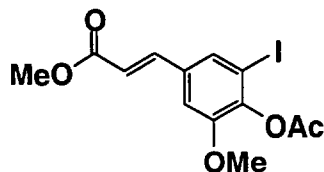
compound 18

Compound 18: Purification by flash chromatography (EtOAc/hexanes = 2/8) gave **18** in 95% yield as a yellow oil (prepared according to the literature^{11b}); R_f = 0.5 (EtOAc/hexanes = 3/7); ¹H NMR (500 MHz, CDCl₃): δ 8.42 (d, J = 2.0 Hz, 1H), 7.96 (dd, J_1 = 8.0, J_2 = 2.0 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 2.60 (s, 3H), 2.40 (s, 3H); ¹³C NMR (125.7 MHz, CDCl₃): δ 195.6, 168.1, 154.9, 139.8, 136.3, 129.7, 123.2, 91.0, 26.6, 21.3.



compound 19

Compound 19: Purification by flash chromatography (EtOAc/hexanes = 1:9) gave **19** in 70% yield as a white solid (prepared according to the literature^{11c}); R_f = 0.5 (EtOAc/hexanes = 3/7); ¹H NMR (500 MHz, CDCl₃): δ 8.09 (d, J = 2.0 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 3.92 (s, 3H), 3.88 (s, 3H), 2.39 (s, 3H); ¹³C NMR (125.7 MHz, CDCl₃): δ 167.5, 165.3, 151.6, 144.7, 132.1, 130.1, 113.5, 91.6, 56.5, 52.7, 21.0.

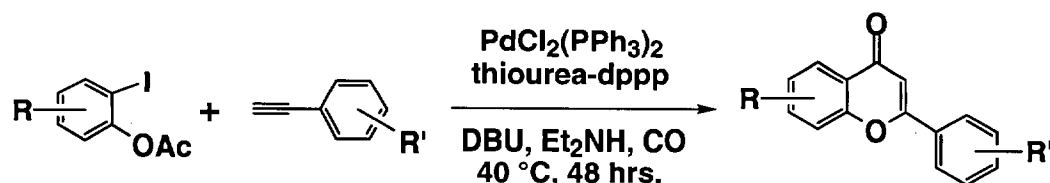


compound 20

Compound 20: Purification by flash chromatography (EtOAc/hexanes = 2:8) gave **20** in 99% yield as a white solid (prepared according to the literature^{11c}); R_f = 0.5 (EtOAc/hexanes = 3/7);

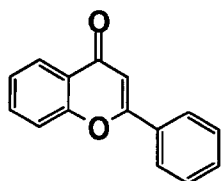
^1H NMR (500 MHz, CDCl_3): δ 7.56 (d, $J = 16.0$ Hz, 1H), 7.55 (d, $J = 2.0$ Hz, 1H), 7.04 (d, $J = 2.0$ Hz, 1H), 6.38 (d, $J = 16$ Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 167.8, 167.1, 151.9, 142.8, 142.5, 134.8, 130.5, 119.4, 111.4, 92.4, 56.4, 52.0, 21.0.

General procedure for the synthesis of compounds 15a –20a, 15b and 16b.



Compounds **15a-20a**, **15b** and **16b** are synthesized followed a general procedure as illustrated below.

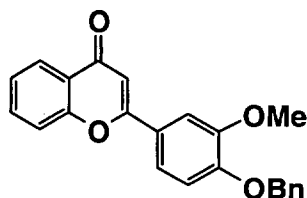
A mixture of o-iodophenylacetate (1.0 mmol), Phenylacetylene (2.0 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (35.0 mg, 5×10^{-2} mmol), Thiourea (3.8 mg, 5×10^{-2} mmol), 1,3-Bis(diphenylphosphino)propane (20.6 mg, 0.05×10^{-2} mmol) and DBU (748 μl , 5.0 mmol) in HNEt_2 (5.0 mL) was degassed with CO for 10 min and then stirred at 40 $^\circ\text{C}$ for 48 h. The solvent was removed under vacuum and the residue was diluted with brine and adjusted to neutral with 3N HCl, extracted with dichloromethane, and dried (Na_2SO_4). The solvent was evaporated and the residue was subjected to flash chromatography.



compound 15a

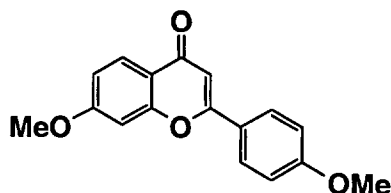
Compound 15a: Purification by flash chromatography (EtOAc/hexanes = 3/7) gave **15a** in 92% yield as a white solid⁶; $R_f = 0.5$ (EtOAc/hexanes = 4/6); ^1H NMR (500 MHz, CDCl_3): δ 8.24 (dd,

$J_1 = 8.0$, $J_2 = 1.5$ Hz, 1H), 7.93-7.95 (m, 2H), 7.71(m, 1H), 7.50-7.60 (m, 4H), 7.43 (m, 1H), 6.84 (s, 1H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 178.7, 163.6, 156.4, 133.9, 131.9, 131.8, 129.2, 126.4, 125.9, 125.4, 124.2, 118.3, 107.8; HRMS (EI) for $[\text{C}_{15}\text{H}_{10}\text{O}_2]^+$, m/z calcd 222.0681, found: 222.0676.



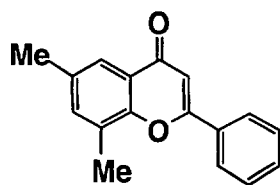
compound 15b

Compound 15b: Purification by flash chromatography (EtOAc/hexanes = 3/7) gave **15b** in 88% yield as a white solid; $R_f = 0.4$ (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 8.24 (dd, $J_1 = 7.5$, $J_2 = 1.5$ Hz, 1H), 7.69 (t, $J = 10.0$ Hz, 1H), 7.56 (d, $J = 10.0$ Hz, 1H), 7.31-7.52 (m, 8H), 7.01 (d, $J = 10.0$ Hz, 1H), 6.76 (s, 1H), 5.26 (s, 2H), 4.00 (s, 3H), ^{13}C NMR (125.7 MHz, CDCl_3): δ 178.3, 163.3, 156.2, 151.3, 149.9, 136.4, 139.6, 128.8, 128.2, 127.3, 125.7, 125.2, 124.6, 123.9, 119.9, 118.0, 113.5, 109.4, 106.5, 70.9, 56.2; HRMS (EI) for $[\text{C}_{23}\text{H}_{18}\text{O}_4]^+$, m/z calcd 358.1205, found: 358.1219.



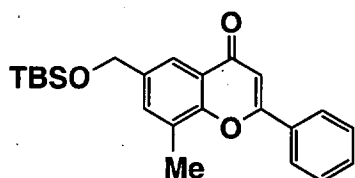
compound 11

Compound 11: Purification by flash chromatography (EtOAc/hexanes = 1/9) gave **11** in 79% yield as a white solid; $R_f = 0.3$ (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 8.11 (d, $J = 9.0$ Hz, 1H), 7.84 (d, $J = 8.5$ Hz, 2H), 7.00 (d, $J = 9.0$ Hz, 2H), 6.96 (dd, $J_1 = 9.0$, $J_2 = 2.5$ Hz, 1H), 6.93 (d, $J = 2.5$ Hz, 1H), 6.67 (s, 1H), 3.92 (s, 3H), 3.88 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 178.0, 164.2, 163.2, 162.4, 158.1, 128.0, 127.2, 124.3, 118.0, 114.6, 114.3, 106.3, 100.6, 56.0, 55.7; HRMS (EI) for $[\text{C}_{17}\text{H}_{14}\text{O}_4]^+$, m/z calcd 282.0892, found: 282.0894.



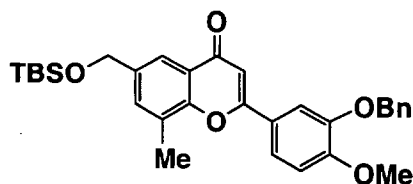
compound 14

Compound 14: Purification by flash chromatography (EtOAc/hexanes = 1/9) gave **14** in 66% yield as a white solid; R_f = 0.3 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 7.83–7.91 (m, 2H), 7.83 (s, 1H), 7.50–7.53 (m, 3H), 7.33 (s, 1H), 6.79 (s, 1H), 2.55 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 179.0, 162.8, 153.1, 136.2, 134.8, 132.3, 131.6, 129.2, 127.4, 126.3, 123.7, 122.8, 107.3, 21.0, 15.9; HRMS (EI) for $[\text{C}_{17}\text{H}_{14}\text{O}_2]^+$, m/z calcd 250.0994, found: 250.0987.



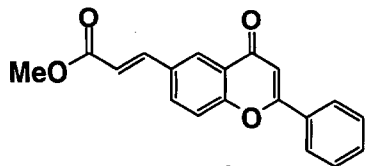
compound 16a

Compound 16a: Purification by flash chromatography (EtOAc/hexanes = 2/8) gave **16a** in 83% yield as a white solid; R_f = 0.4 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 7.99 (dd, J_1 = 5.0, J_2 = 2.0, 2H), 7.67 (s, 1H), 7.51–7.54 (m, 3H), 7.33 (s, 1H), 6.85 (s, 1H), 4.83 (s, 2H), 4.05 (s, 3H), 1.01 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 178.7, 163.2, 149.4, 145.9, 138.9, 132.1, 131.7, 129.2, 126.6, 124.7, 113.2, 112.9, 107.5, 64.7, 56.5, 26.1, 18.6, -5.0; HRMS (ES) for $[\text{C}_{31}\text{H}_{36}\text{O}_6\text{Si} + \text{H}]^+$, m/z calcd 397.1835, found: 397.1850



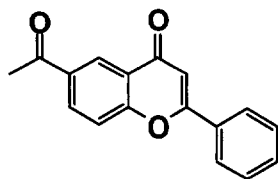
compound 16b

Compound 16b: Purification by flash chromatography (EtOAc/hexanes = 2:8) gave **16b** in 76% yield as a white solid; R_f = 0.4 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 7.65 (s, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.47 (s, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0, 2H), 7.33 (t, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.75 (s, 1H), 5.26 (s, 2H), 4.82 (s, 2H), 4.03 (s, 3H), 4.00 (s, 3H), 0.97 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 178.6, 163.1, 151.3, 150.0, 149.3, 145.8, 138.7, 136.6, 128.9, 128.3, 127.4, 124.9, 124.6, 120.1, 113.7, 113.2, 112.8, 109.7, 106.5, 71.1, 64.7, 56.5, 56.4, 26.1, 18.0, -5.0; HRMS (ES) for $[\text{C}_{31}\text{H}_{36}\text{O}_6\text{Si} + \text{H}]^+$, m/z calcd 533.2359, found: 533.2362



compound 17a

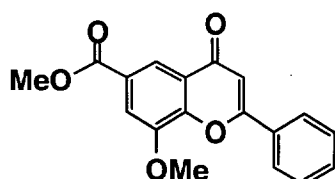
Compound 17a: Purification by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$ = 9/1) gave **17a** in 85% yield as a white solid^{11a}; R_f = 0.4 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3) δ 8.37 (d, J = 2.0 Hz, 1H), 7.93 (dd, J = 8.0, 2.0 Hz, 2H), 7.85 (dd, J_1 = 8.0, J_2 = 2.0 Hz, 1H), 7.76 (d, J = 16.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.51-7.58 (m, 3H), 6.84 (s, 1H), 6.54 (d, J = 16.0 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 178.1, 167.2, 163.8, 157.2, 143.1, 132.9, 132.1, 131.9, 131.6, 129.3, 126.5, 125.8, 124.4, 119.5, 119.2, 107.9, 52.1; HRMS (EI) for $[\text{C}_{19}\text{H}_{14}\text{O}_4]^+$, m/z calcd 306.0892, found: 306.0887.



compound 18a

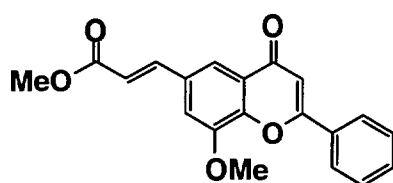
Compound 18a: Purification by flash chromatography (EtOAc/hexanes = 2/8) gave **18a** in 70% yield as a white solid^{11b}; R_f = 0.4 (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3): δ 8.78 (d,

$J = 2.0$ Hz, 1H), 8.36 (dd, $J_1 = 8.0$, $J_2 = 2.0$ Hz, 1H), 7.94 (m, 2H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.52-7.60 (m, 3H), 6.88 (s, 1H), 2.72 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 196.7, 178.0, 164.0, 159.0, 134.2, 133.1, 132.2, 131.4, 129.4, 127.4, 126.6, 123.6, 119.1, 108.1, 26.9; HRMS (EI) for $[\text{C}_{17}\text{H}_{12}\text{O}_5]^+$, m/z calcd 264.0786, found: 264.0775.



compound 19a

Compound 19a: Purification by flash chromatography (EtOAc/hexanes = 2:8) gave **19a** in 68% yield as a white solid; $R_f = 0.3$ (EtOAc/hexanes = 3/7); ^1H NMR (500 MHz, CDCl_3) δ 8.52 (s, 1H), 8.01-7.97 (m, 2H), 7.86 (s, 1H), 7.58-7.55 (m, 3H), 6.89 (s, 1H), 4.11 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3) δ 178.1, 166.4, 163.5, 149.5, 132.1, 131.6, 129.4, 128.9, 127.0, 126.6, 124.7, 119.2, 114.6, 107.9, 56.8, 52.7; HRMS (EI) for $[\text{C}_{18}\text{H}_{14}\text{O}_5]^+$, m/z calcd 310.0841, found: 310.0827.



compound 20a

Compound 20a: Purification by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{EtOAc} = 8/2$) gave **20a** in 78% yield as a white solid; $R_f = 0.5$ (EtOAc/hexanes = 4/6); ^1H NMR (500 MHz, CDCl_3): δ 7.94-7.98 (m, 2H), 7.94 (s, 1H), 7.73 (d, $J = 16.0$ Hz, 1H), 7.41-7.59 (m, 3H), 7.29 (s, 1H), 6.85 (s, 1H), 6.51 (d, $J = 16.0$ Hz, 1H), 4.07 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (125.7 MHz, CDCl_3): δ 178.1, 167.2, 163.4, 149.8, 147.9, 143.7, 131.9, 131.7, 131.5, 129.3, 126.6, 125.2, 119.3, 117.3, 112.6, 107.8, 56.7, 52.1; HRMS (EI) for $[\text{C}_{20}\text{H}_{16}\text{O}_5]^+$, m/z calcd 336.0998, found: 336.0983.

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7. ^1H NMR and ^{13}C NMR spectra of compounds **19** (pages 13-14)
8. ^1H NMR and ^{13}C NMR spectra of compounds **20** (pages 15-16)
9. ^1H NMR and ^{13}C NMR spectra of compounds **11** (pages 17-18)
10. ^1H NMR and ^{13}C NMR spectra of compounds **14** (pages 19-20)
11. ^1H NMR and ^{13}C NMR spectra of compounds **15a** (pages 21-23)
12. ^1H NMR and ^{13}C NMR spectra of compounds **15b** (pages 24-26)
13. ^1H NMR and ^{13}C NMR spectra of compounds **16a** (pages 27-28)
14. ^1H NMR and ^{13}C NMR spectra of compounds **16b** (pages 29-30)
15. ^1H NMR and ^{13}C NMR spectra of compounds **17a** (pages 31-32)
16. ^1H NMR and ^{13}C NMR spectra of compounds **18a** (pages 33-34)
17. ^1H NMR and ^{13}C NMR spectra of compounds **19a** (pages 35-36)
18. ^1H NMR and ^{13}C NMR spectra of compounds **20a** (pages 37-38)

I

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 °C / 298.1 K

INNOVA-500 "1ccb-nmr"

PULSE SEQUENCE

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 8000.0 Hz

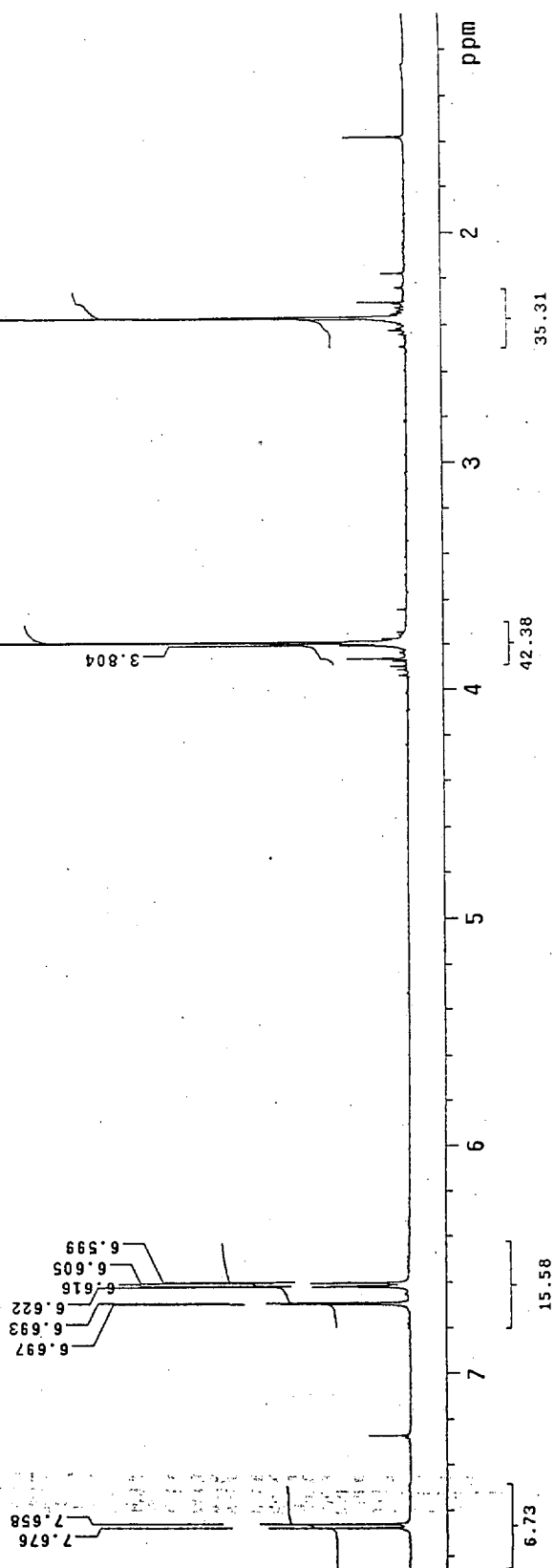
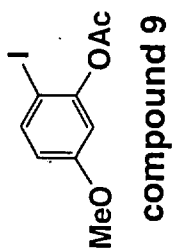
8 repetitions

OBSERVE H1, 499.7355370 MHz

DATA PROCESSING

FT size 32768

Total time 0 min, 15 sec



2

JA A 172B

Pulse Sequence: s2pul

Solvent: cdc13

Temp. 25.0 C / 298.1 K

INOVA-500 "jccb-nmr"

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

704 repetitions

OBSERVE C13, 125.6585743 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

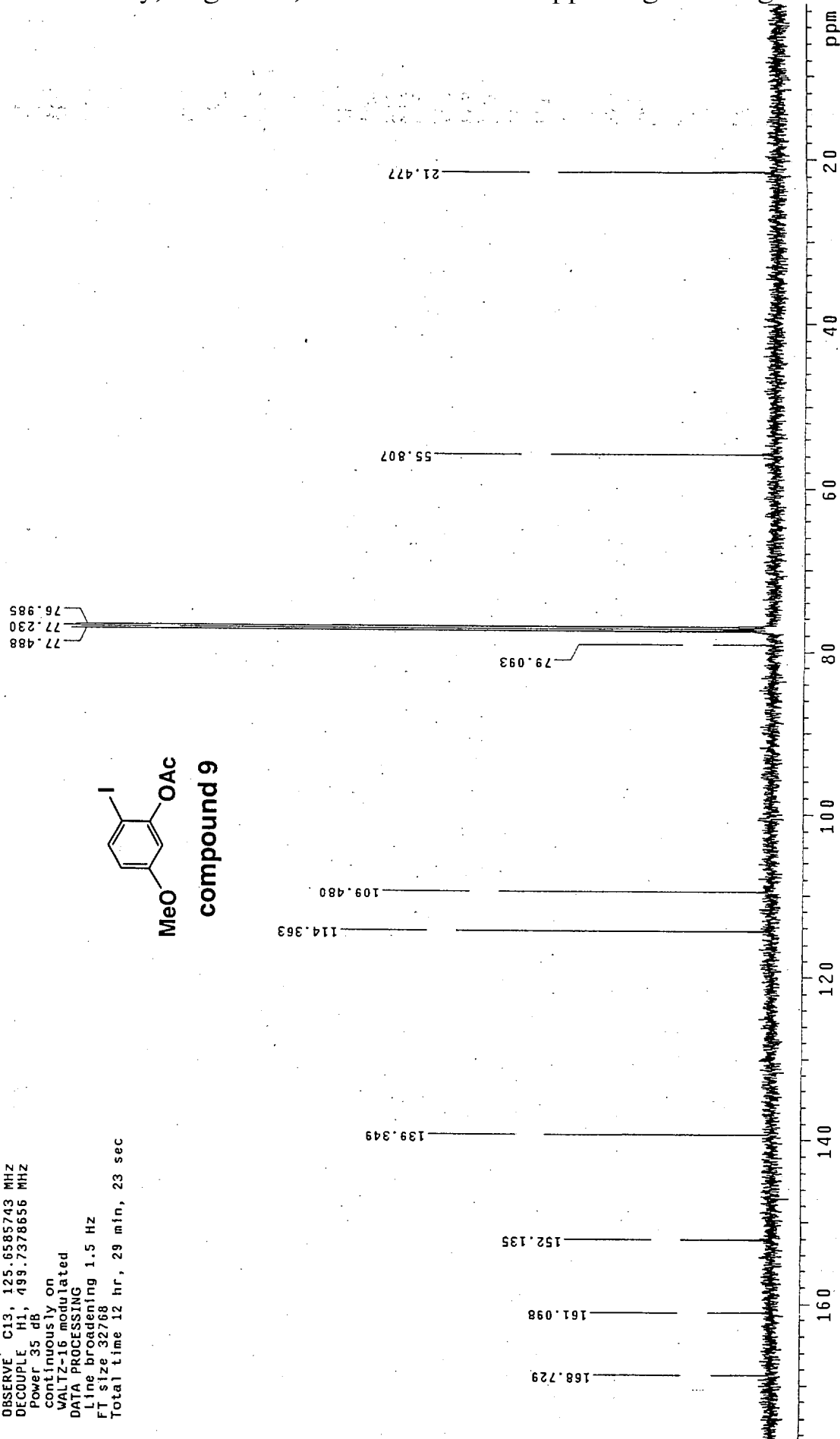
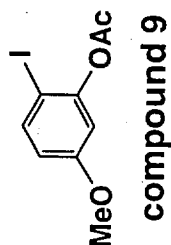
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

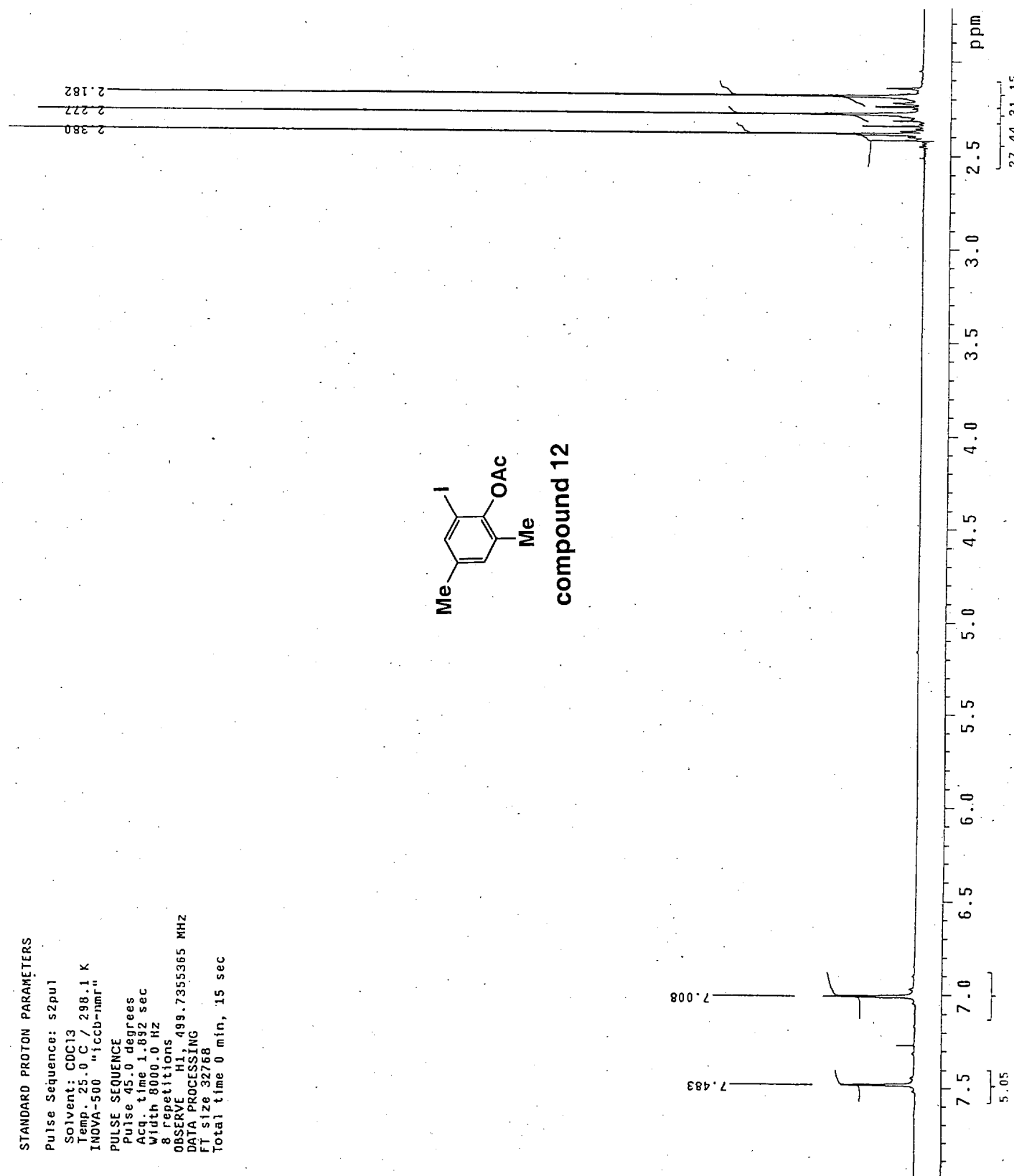
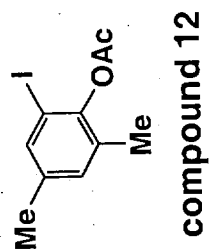
FT size 32768

Total time 12 hr, 29 min, 23 sec



3

STANDARD PROTON PARAMETERS
 Pulse Sequence: s2pul
 Solvent: CDCl₃
 Temp: 25.0 C / 298.1 K
 INOVA-500 "iccb-nmr"
 PULSE SEQUENCE
 Pulse 45.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 repetitions
 OBSERVE H1, 499.7355365 MHz
 DATA PROCESSING
 FT size 32768
 Total time 0 min, 15 sec



4

JA A 172B

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

INNOVA-500 "iccb-nmr"

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

304 repetitions

OBSERVE C13, 125.6585794 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

Continuously on

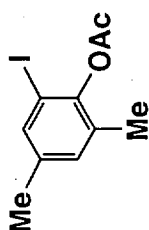
WALTZ-16 modulated

DATA PROCESSING

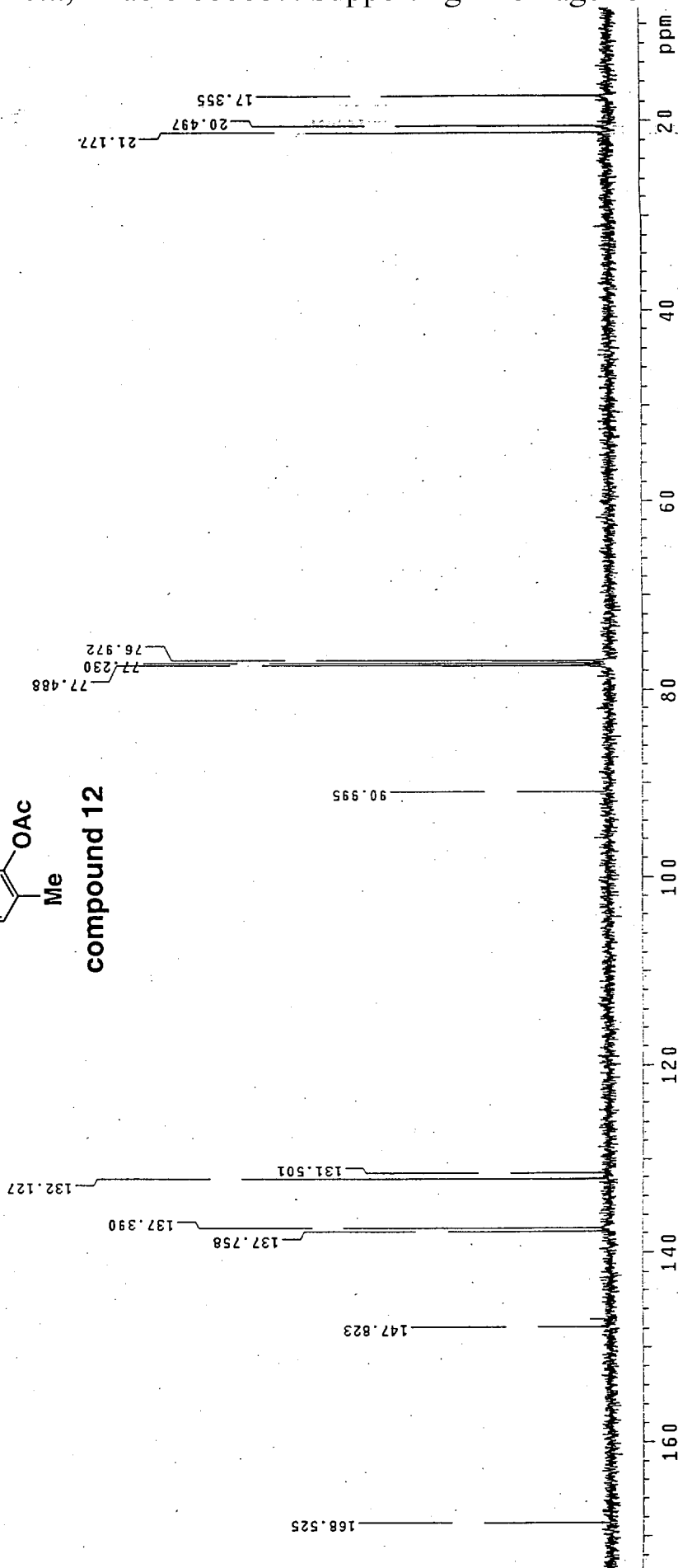
Line broadening 1.5 Hz

FI size 32768

Total time 12 hr, 29 min, 23 sec

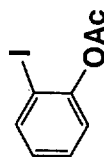


compound 12

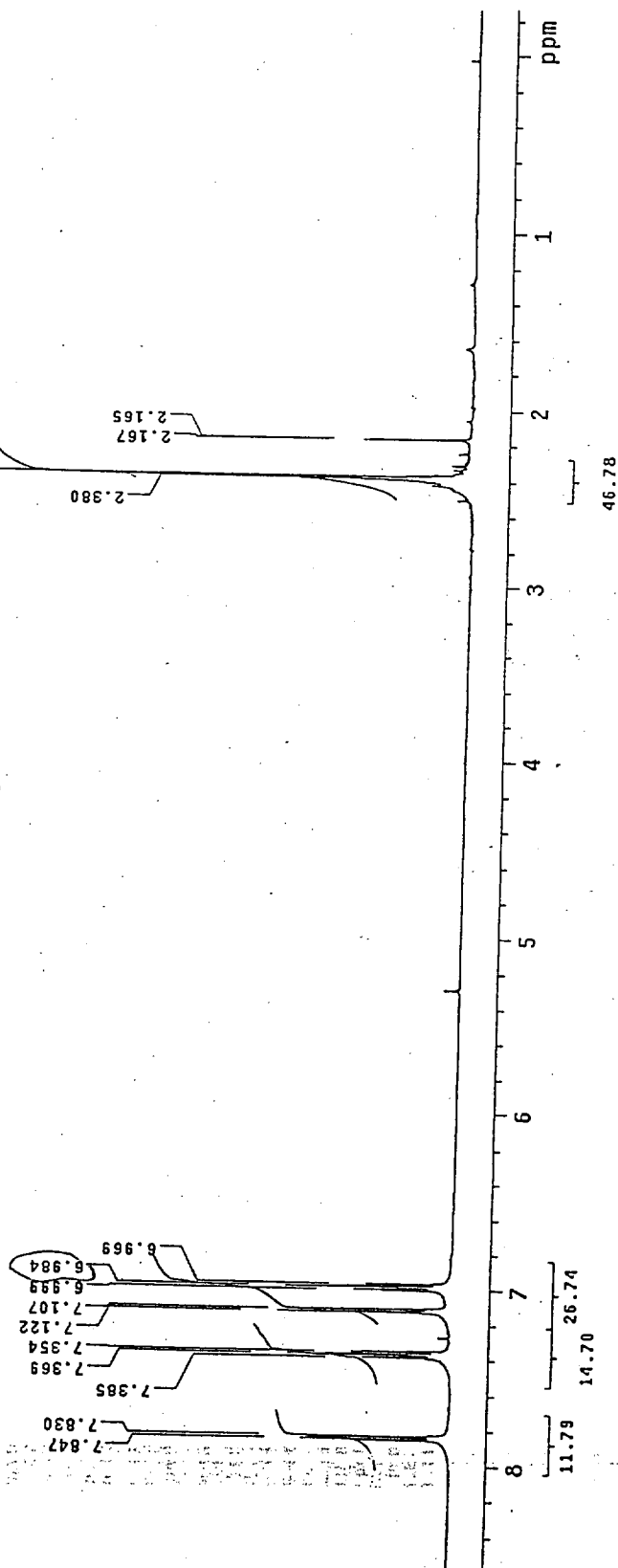


5

STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
Solvent: CDCl₃
Temp: 25.0 C / 298.1 K
INOVA-500 "f1ccb-nmr"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7355370 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 15 sec



compound 15



6

JA: A 1728

Pulse Sequence: s2pul

Solvent: cdc13

Temp: 25.0 C / 298.1 K

INQVA-500 "1ccb-nmr"

PULSE SEQUENCE

Relax delay 2.000 sec

Pulse 52.7 degrees

Acq time 0.800 sec

Width 28001.4 Hz

64 repetitions

OBSERVE C13, 125.6585879 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

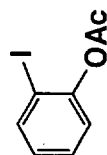
WALTZ-16 modulated

DATA PROCESSING

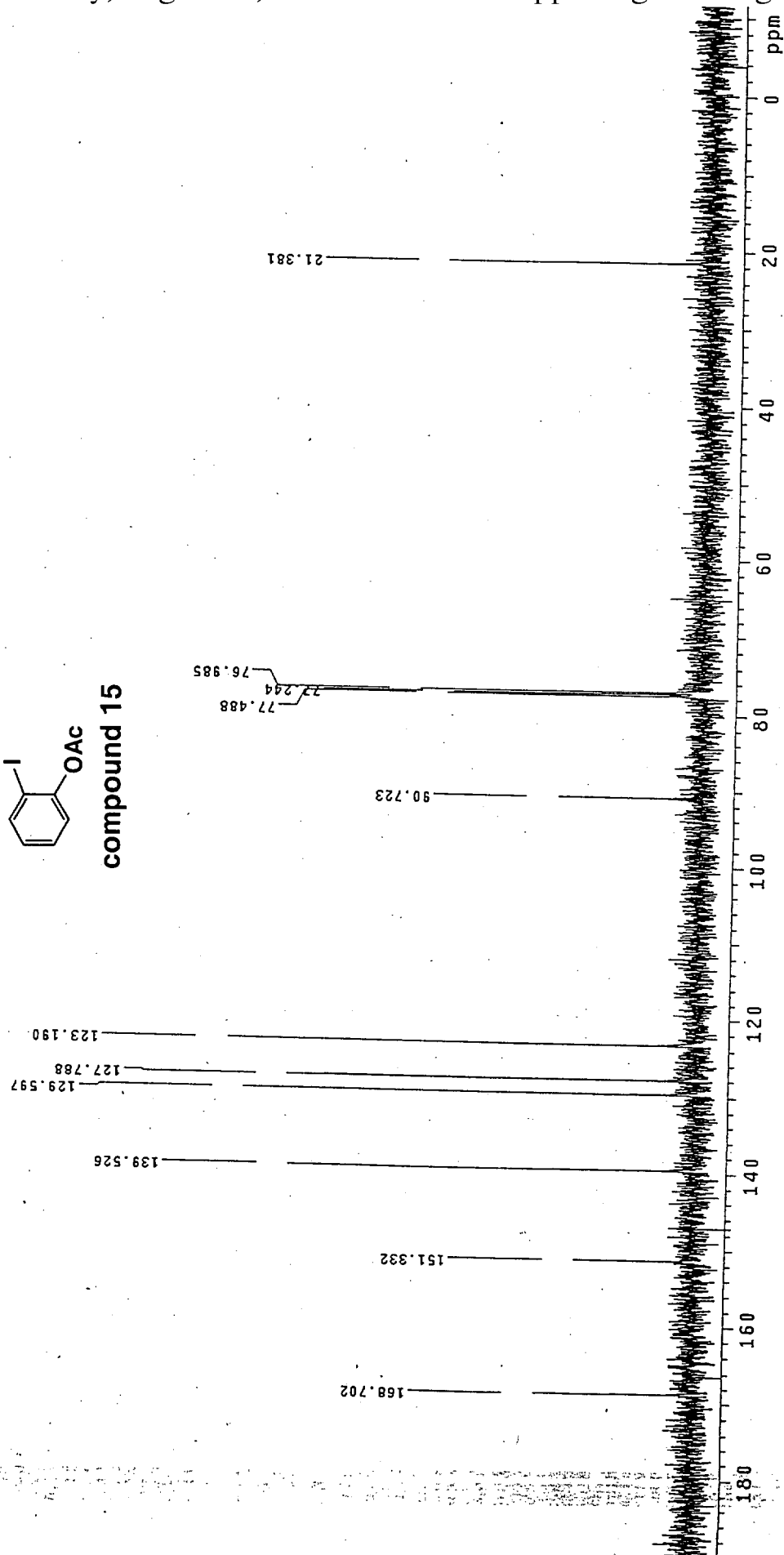
Line broadening 2.0 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



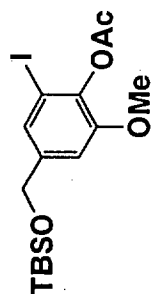
compound 15



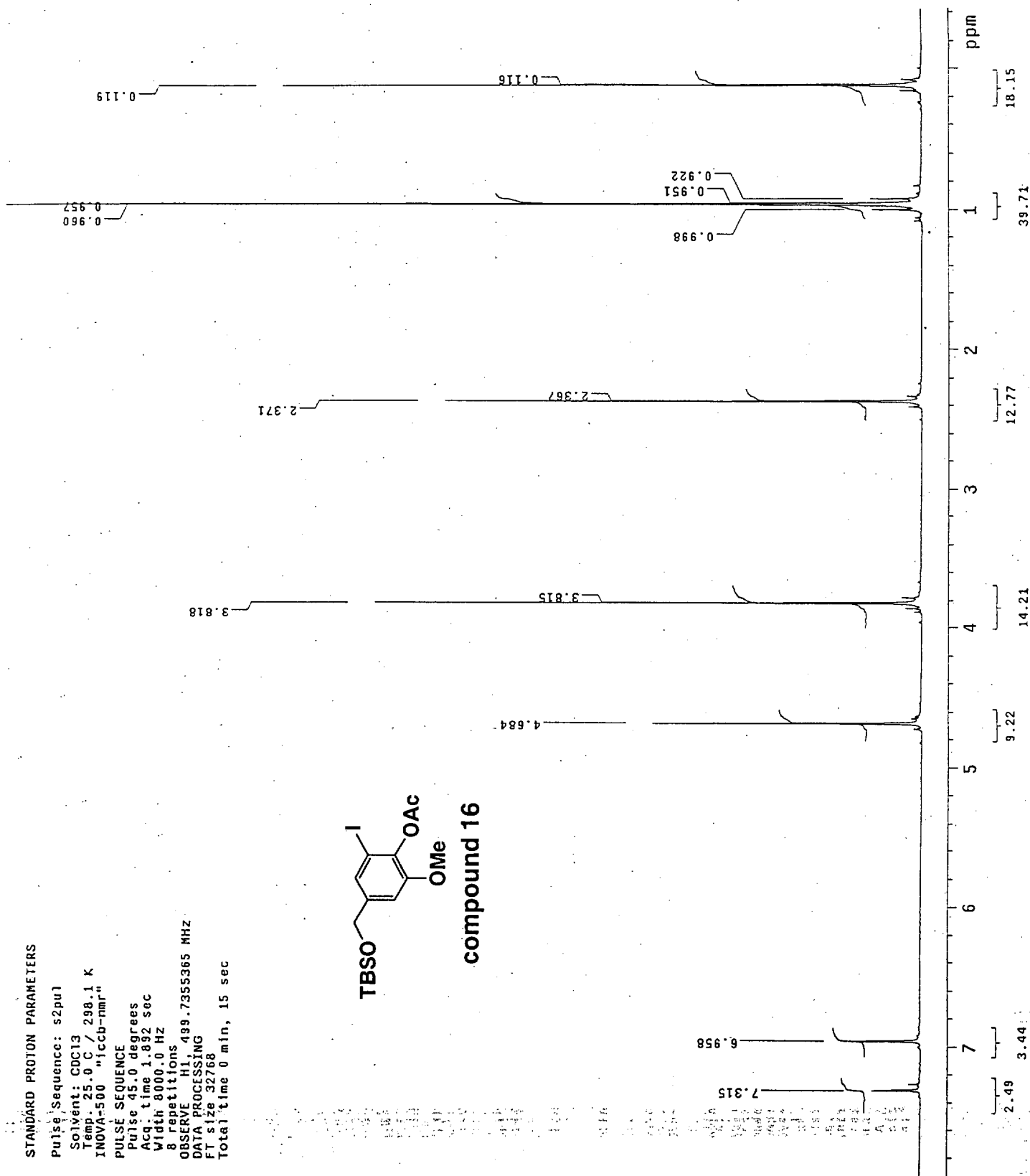
7

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl₃
 Temp: 25.0 C / 298.1 K
 INOVA-500 "iccb-nmr"
 PULSE SEQUENCE
 Pulse 45.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 repetitions
 OBSERVE H1, 499.735365 MHz
 DATA PROCESSING
 FI size 32768
 Total time 0 min, 15 sec



compound 16



8

JA A 172B

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

INNOVA-500 "iccb-nmr"

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

144 repetitions

OBSERVE C13, 125.6585760 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

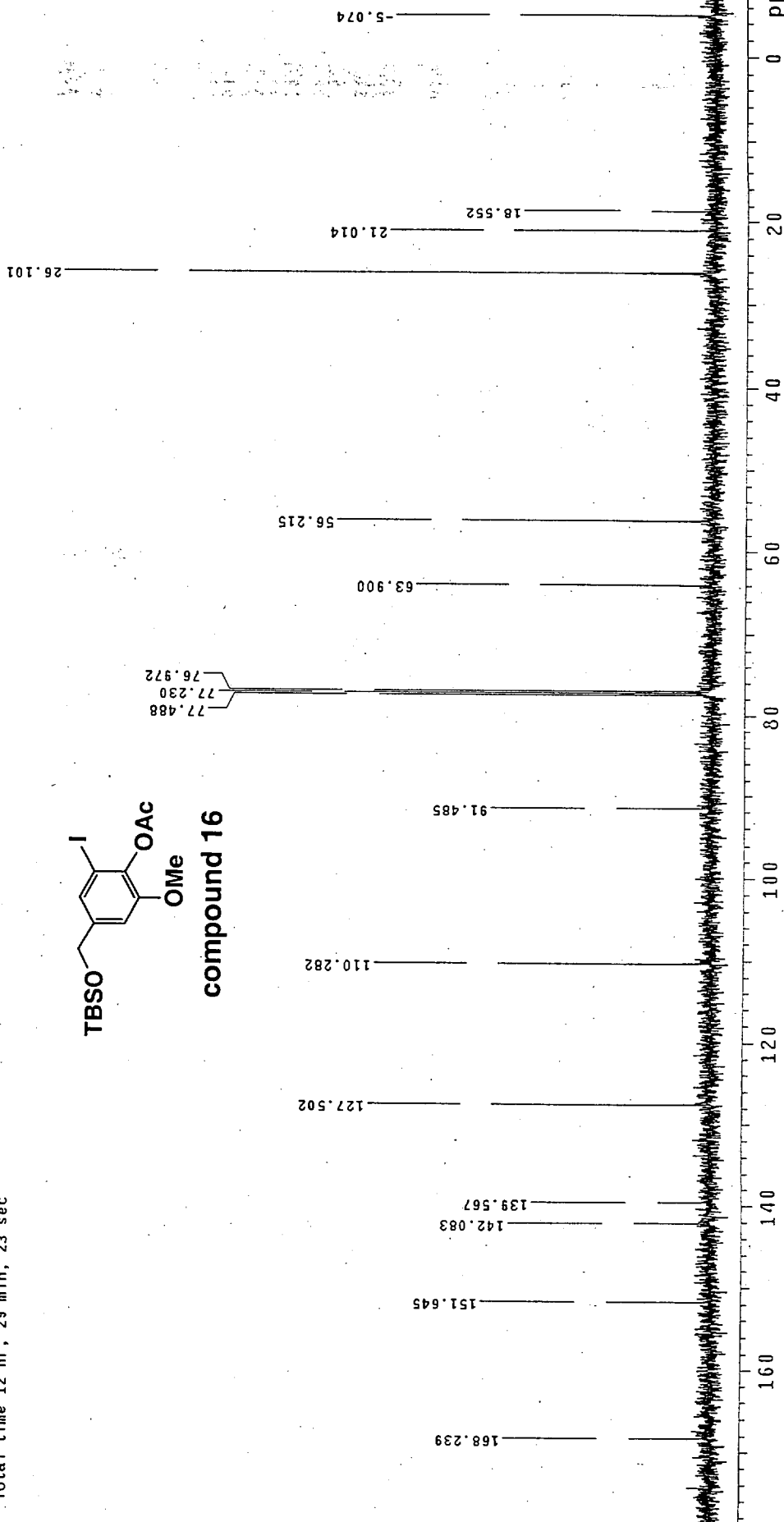
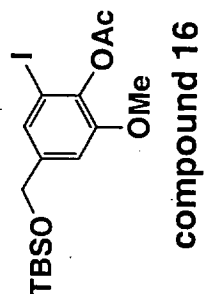
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



9

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp.: 25.0 C / 298.1 K

INVA-500 "1ccu-nmr"

PULSE SEQUENCE

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 8000.0 Hz

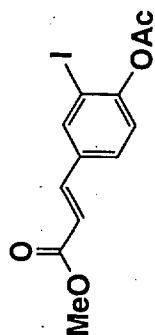
8 repetitions

OBSERVE H1: 499.7355360 MHz

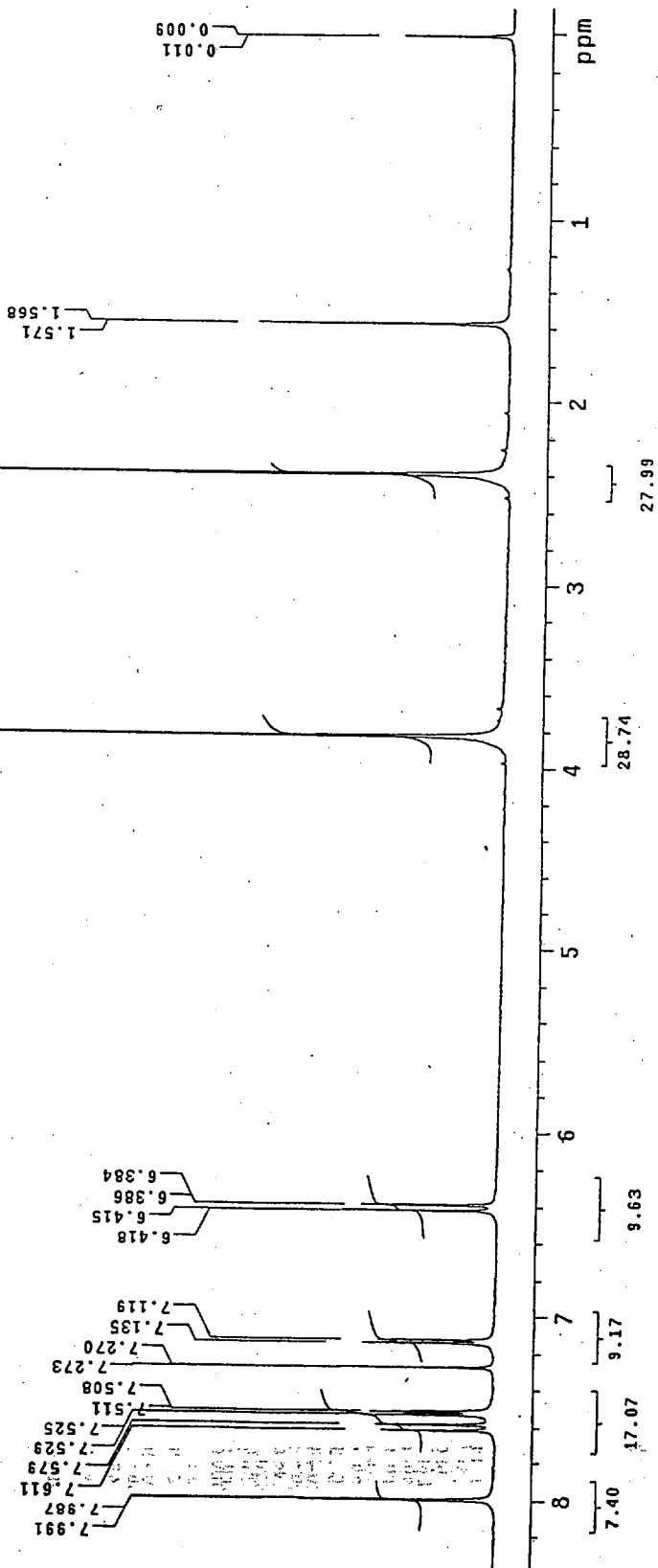
DATA PROCESSING

FT size 32768

Total time 0 min, 15 sec



compound 17



10

JA A 172B

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

INOVA-500 "1ccb-nmr"

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

16000 repetitions

OBSERVE C13, 125.6585726 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

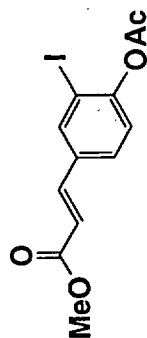
WALTZ-16 modulated

DATA PROCESSING

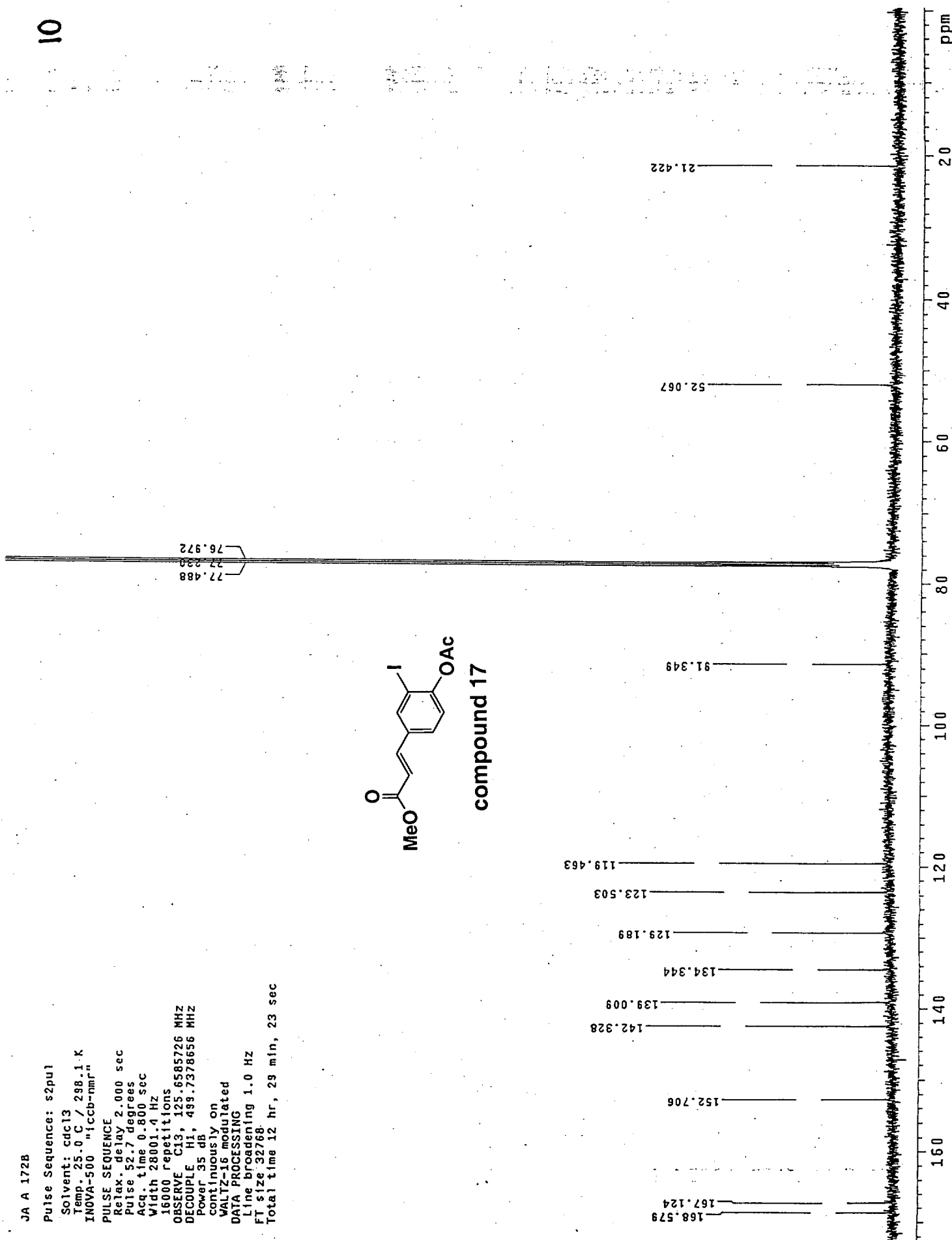
Line broadening 1.0 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



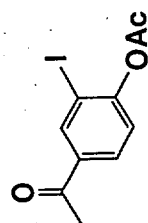
compound 17



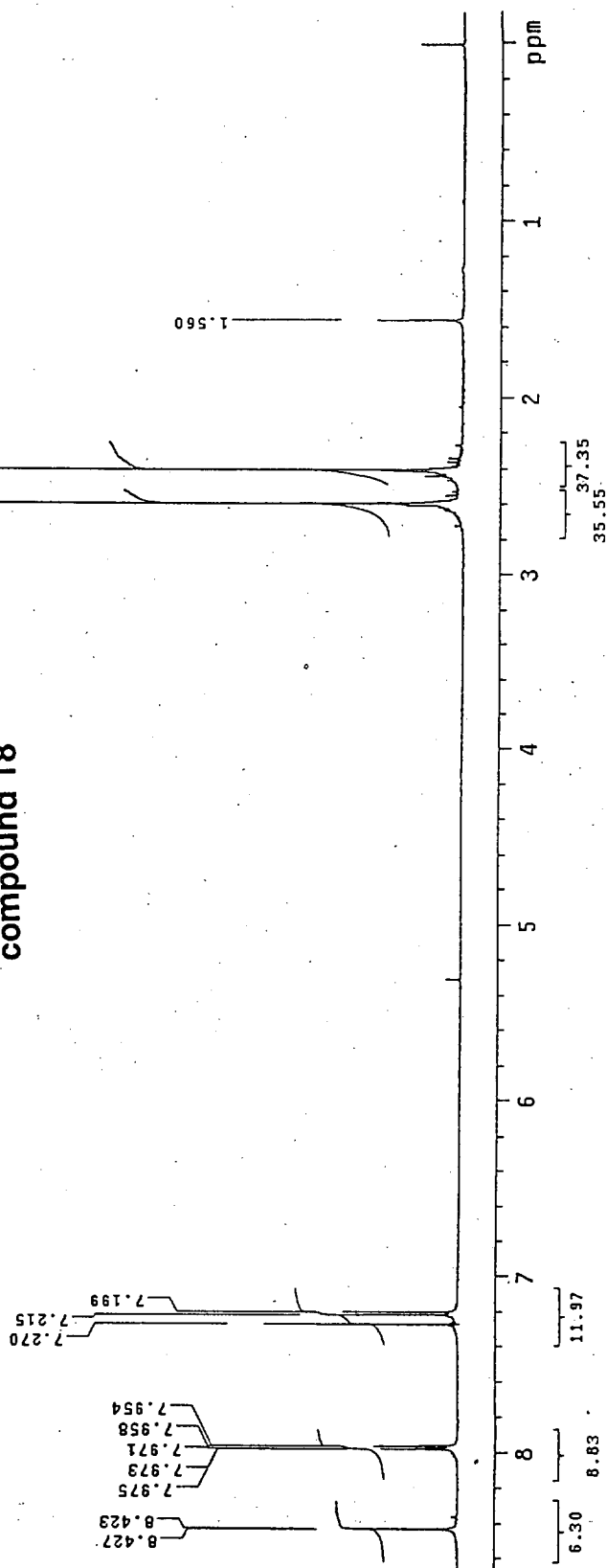
11

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl₃
 Temp: 25.0 C / 298.1 K
 INOVA-500 "1cch-nmr"
 PULSE SEQUENCE
 Pulse 45.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 Repetitions
 OBSERVE H1, 499.7355370 MHz
 DATA PROCESSING
 FT size 32768
 Total time 0 min, 15 sec



compound 18



12

JA A 172B

Pulse Sequence: s2pu1

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

INOVIA-500 "iccb-nmr"

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

232 repetitions

OBSERVE C13, 125.6585879 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

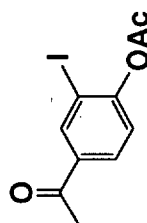
WALTZ-16 modulated

DATA PROCESSING

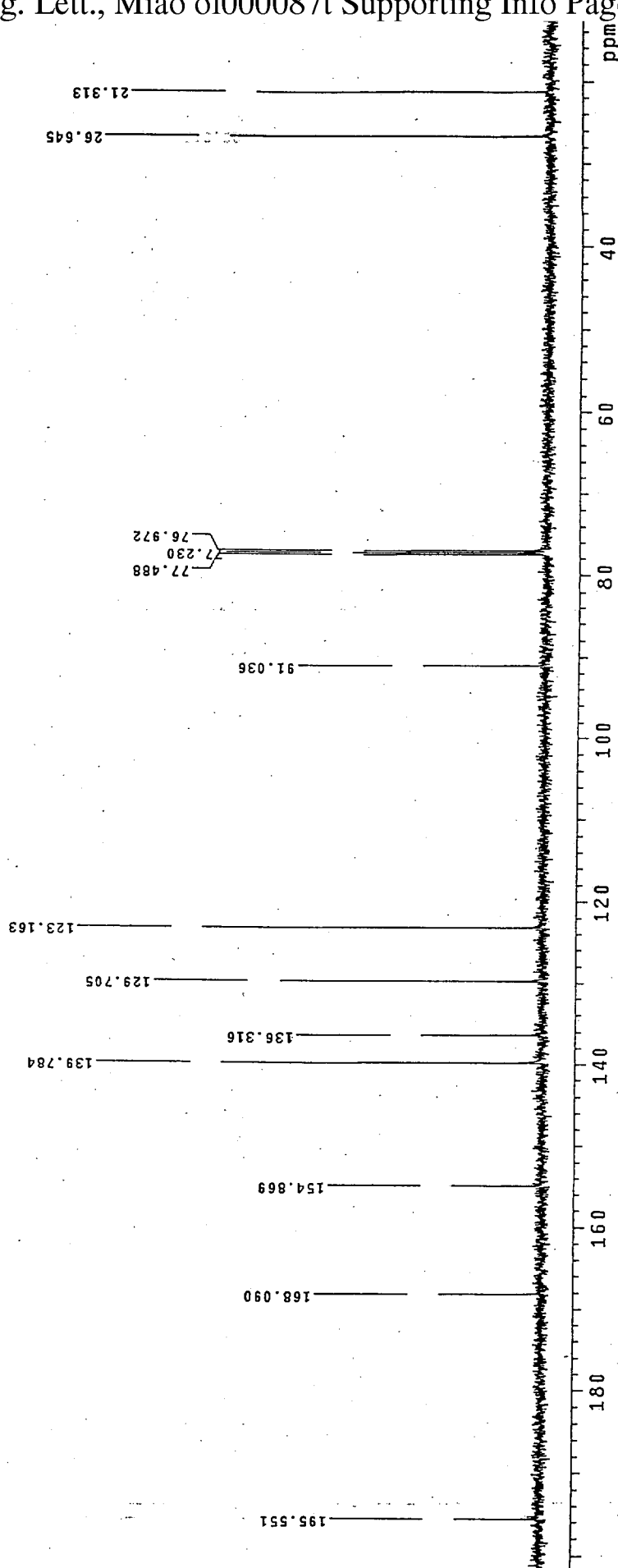
Line broadening 1.5 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



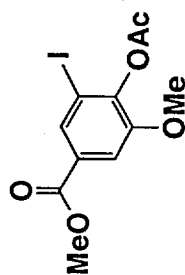
compound 18



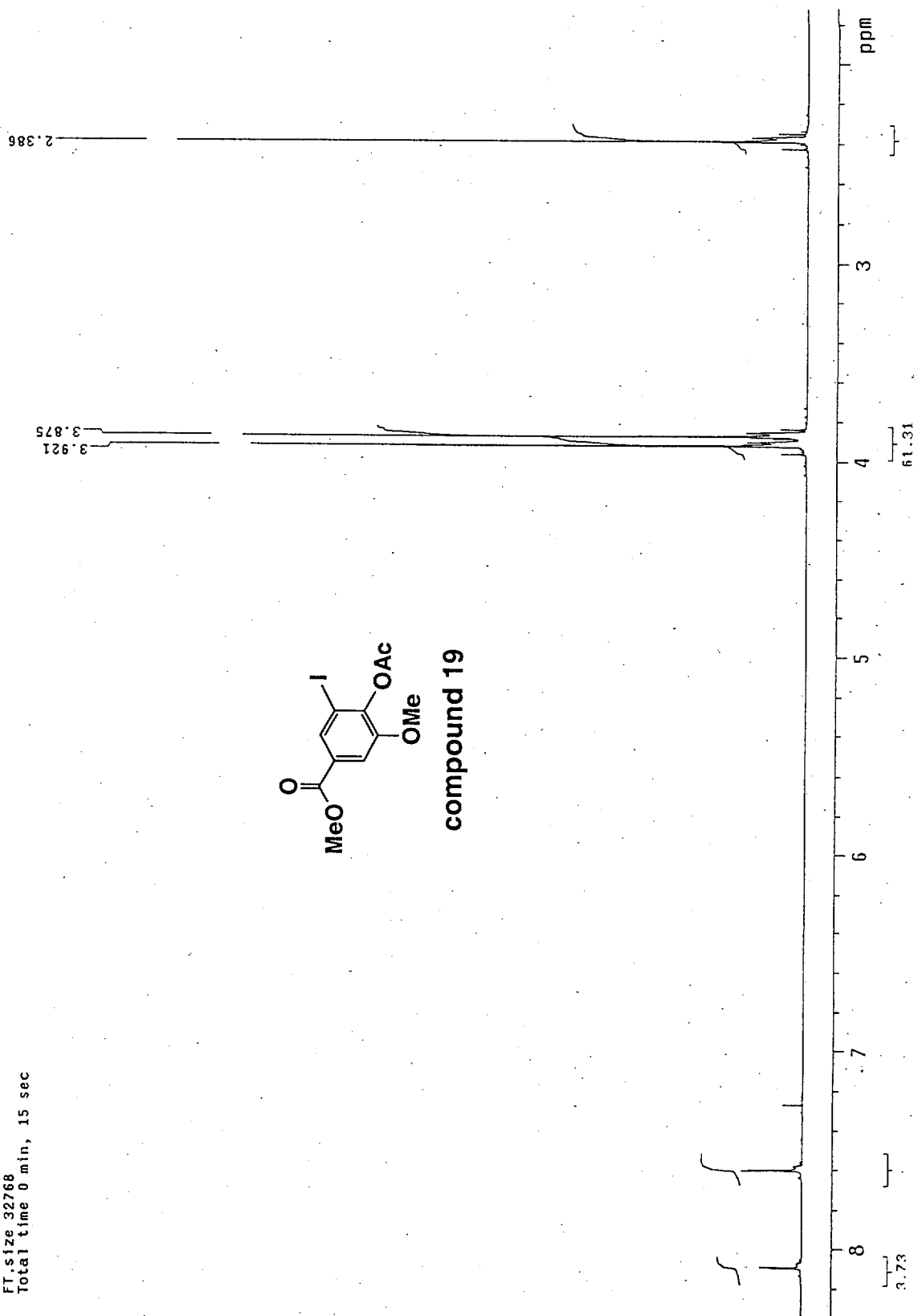
13

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pu1
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
INOVA-500 "1ccu-nmr"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
8 Repetitions
OBSERVE H1, 499.7355365 MHZ
DATA PROCESSING
FI size 32768
Total time 0 min, 15 sec



compound 19



14

JA A 172B

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C / 298.1 K

INNOVA-500 "iccb-nmr"

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

296 repetitions

OBSERVE C13, 125.6585760 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

Continuously on

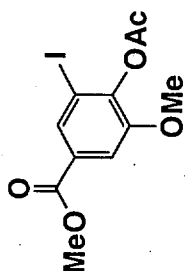
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



compound 19

77.475
77.230
76.972

56.542

52.733

20.960

91.593

113.519

132.086
130.073

144.749

151.645

165.328

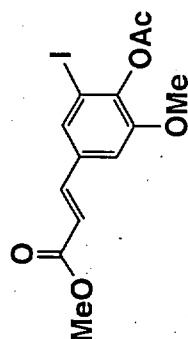
167.532

ppm

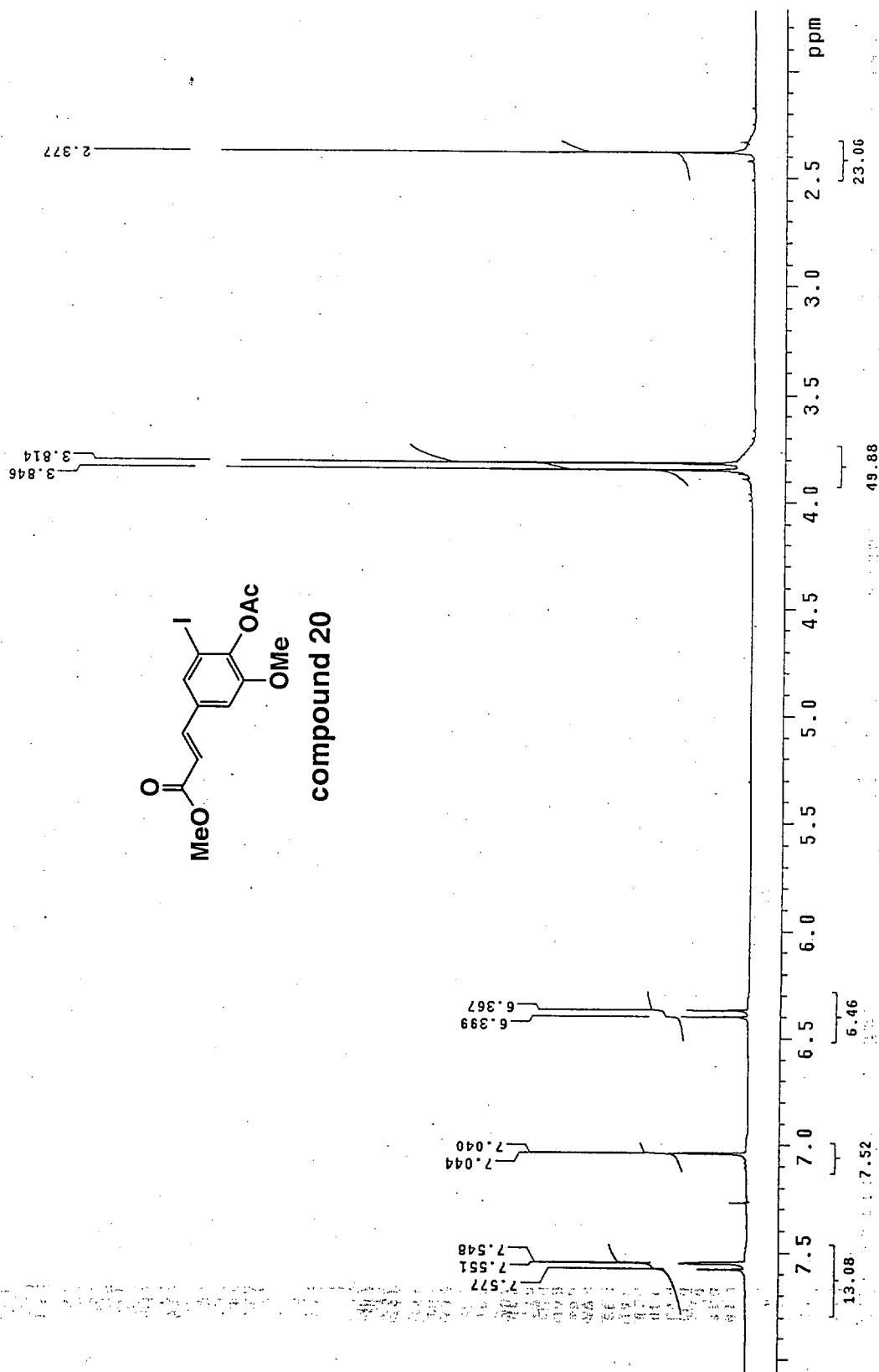
15

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp.: 25.0 C / 298.1 K
INOVA-500 "1ccy-nmr"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7355370 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 15 sec



compound 20



16

JA A 172B

Pulse Sequence: s2pul

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

INOVA-500 "iccb-nmr"

PULSE SEQUENCE

Relax: delay 2.000 sec

Pulse: 52.7 degrees

Acq. time 0.800 sec

Width: 28001.4 Hz

336 repetitions

OBSERVE C13, 125.6585760 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

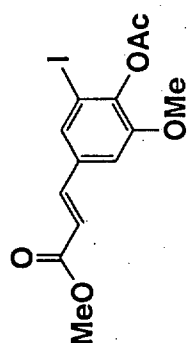
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.5 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



compound 20

77.475
77.216
76.972142.831
142.532

134.847

130.481

119.368

111.438

92.369

56.379

52.040

20.960

167.845
167.056

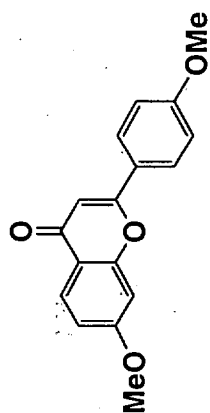
151.931

ppm

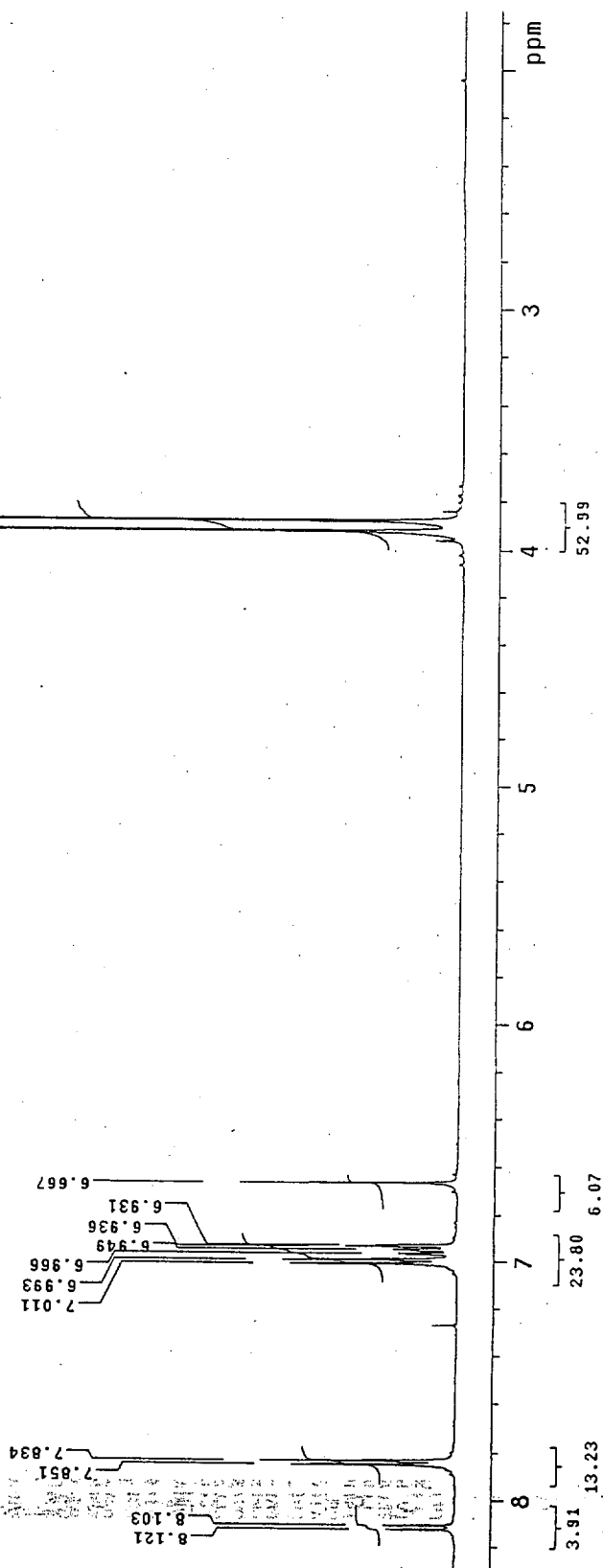
17

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp: 25.0 C / 298.1 K
INOVIA-500 "iccb-nmr"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7355380 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 15 sec



compound 11



18

JA A 172B

Pulse Sequence: s2pu1

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

INNOVA-500 "1ccb-nmr"

PULSE SEQUENCE

Relax delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

760 repetitions

OBSERVE C13, 125.6585760 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

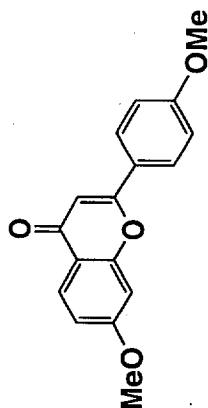
WALTZ-16 modulated

DATA PROCESSING

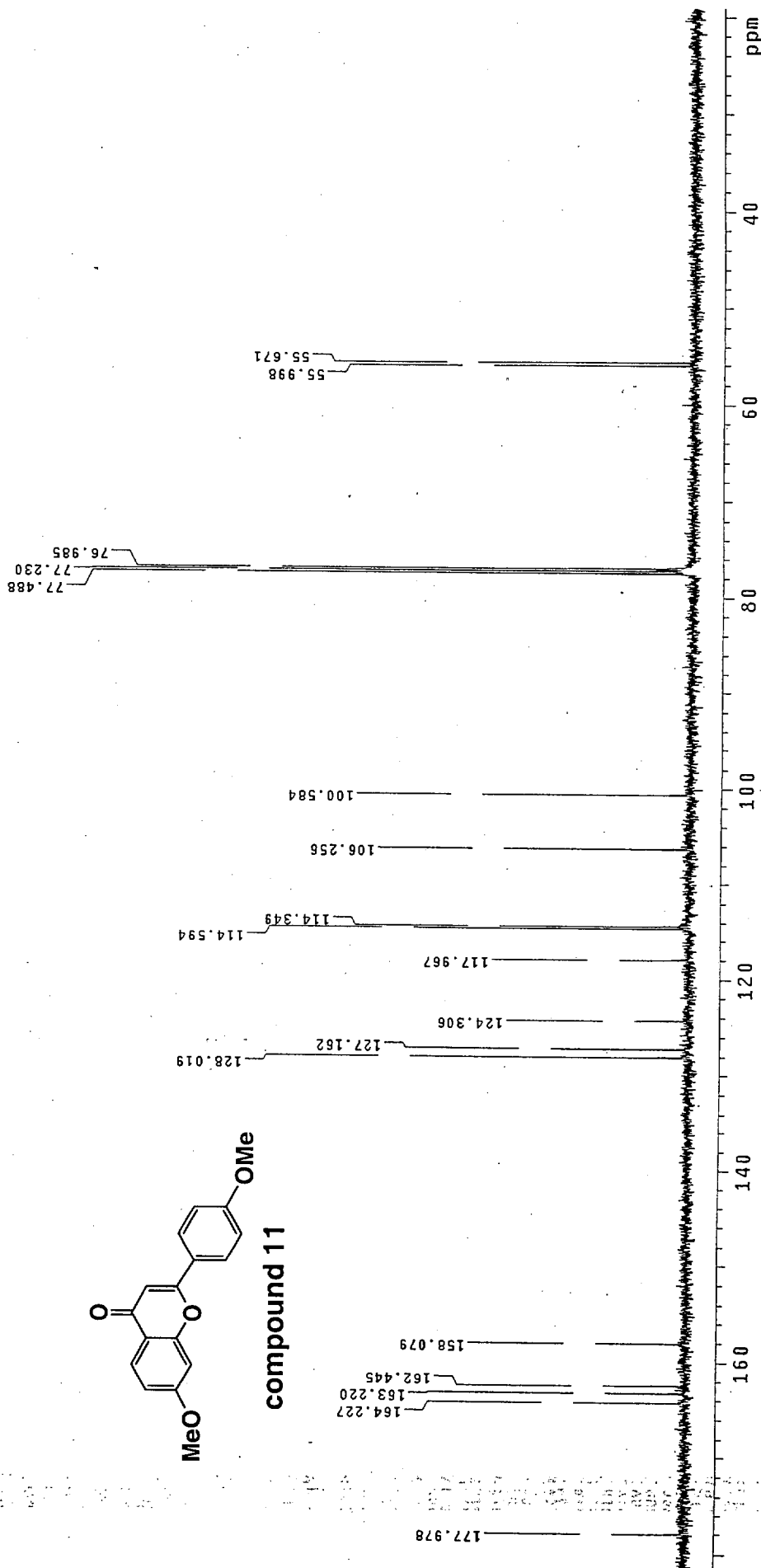
Line broadening 1.5 Hz

FI size 32768

Total time 12 hr, 29 min, 23 sec



compound 11



19

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp: 25.0 C / 298.1 K

INOVA-500 "1ccB-nmr"

PULSE SEQUENCE

Pulse 45.0 degrees

Acq. time 1.892 sec

Width 8000.0 Hz

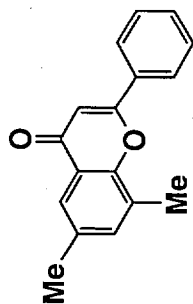
8 repetitions

OBSERVE H1, 499.7355375 MHz

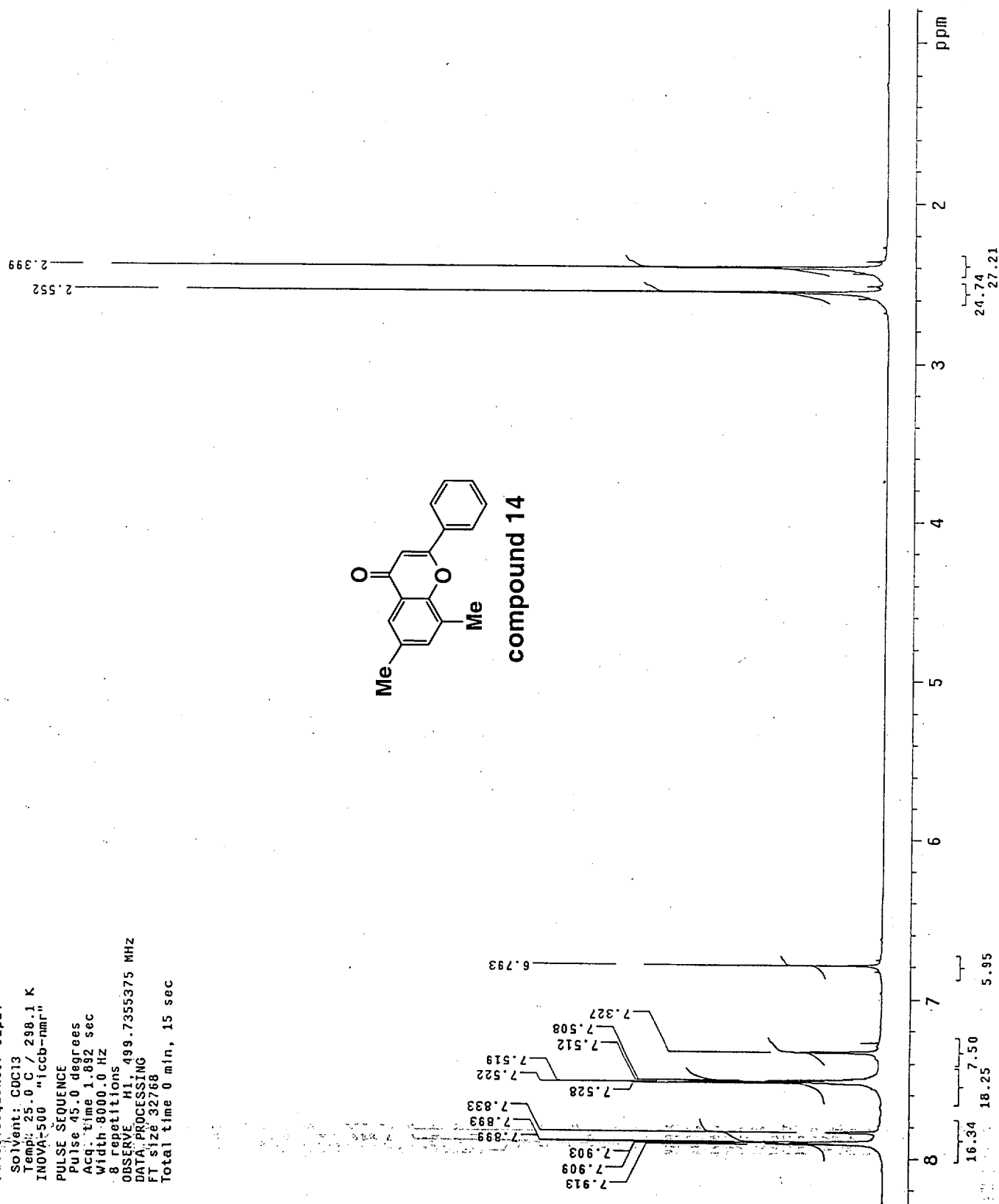
DATA PROCESSING

FT size 32768

Total time 0 min, 15 sec



compound 14



20

JA A 172B

Pulse Sequence: s2pul

Solvent: cdc13

Temp: 25.0 C / 298.1 K

INNOVA-500 "iccb-nmr"

PULSE SEQUENCE

Relax: delay 2.000 sec

Pulse: 52.7 degrees

Acq. time 0.800 sec

Width: 28001.4 Hz

312 repetitions

OBSERVE: C13, 125.6585794 MHz

DECOUPLE: H1, 499.7378656 MHz

Power 35 dB

continuously on

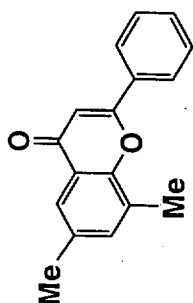
WALTZ-16 modulated

DATA PROCESSING

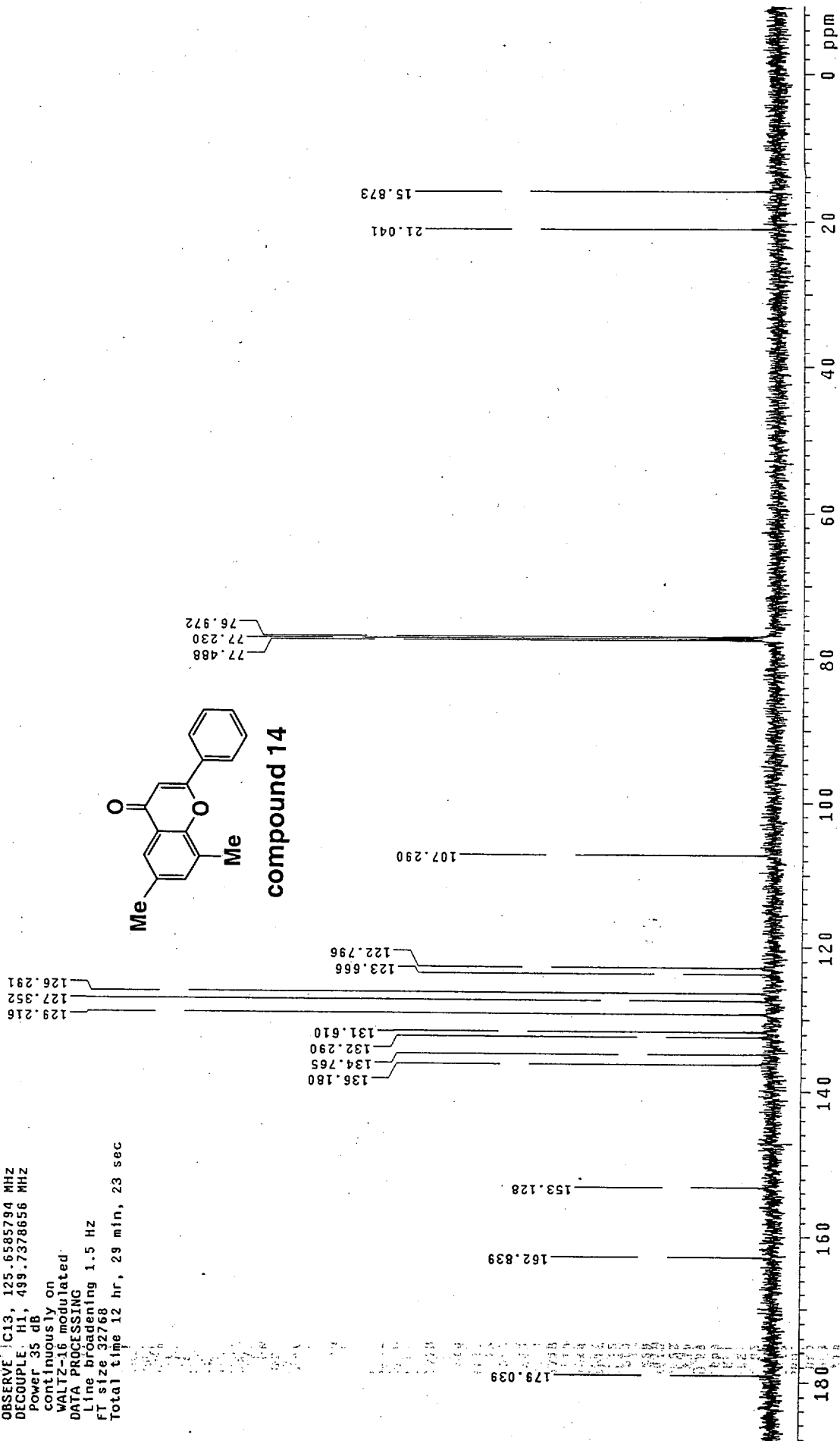
Line broadening 1.5 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



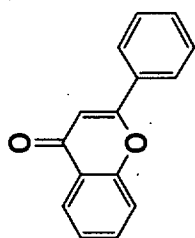
compound 14



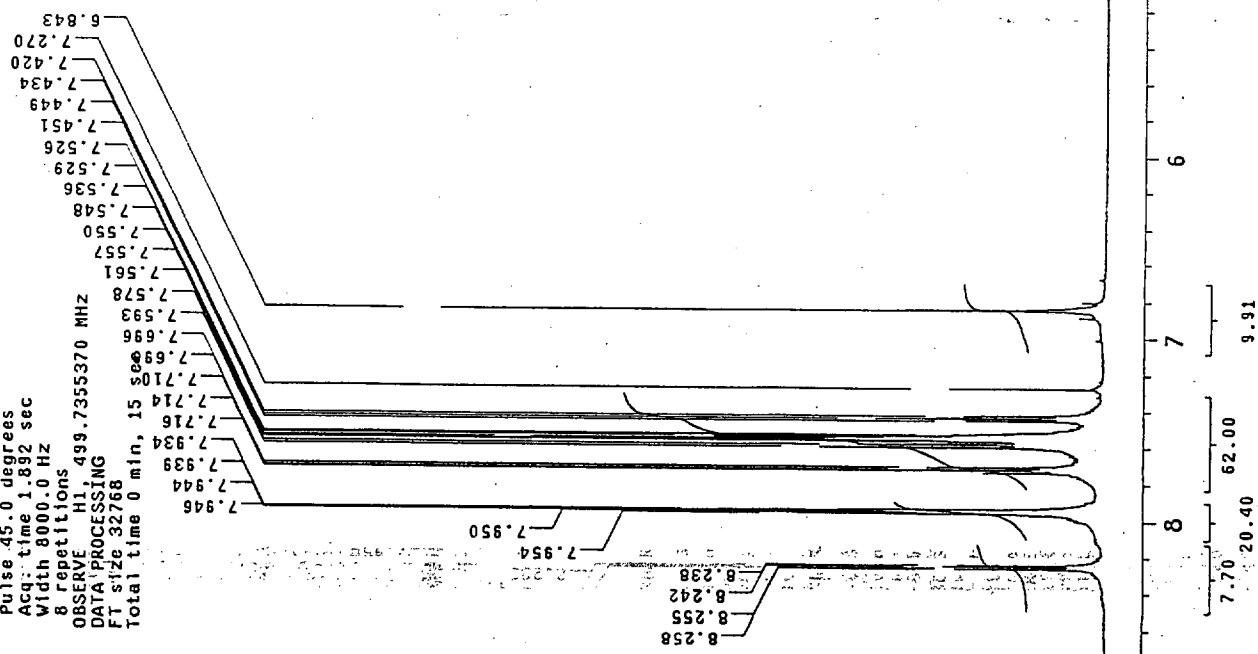
21

STANDARD PROTON PARAMETERS

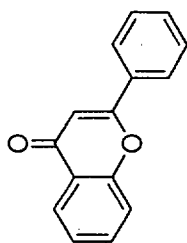
Pulse Sequence: s2pul
Solvent: CDCl₃
Temp: 25.0 C / 298.1 K
INOVA-500 "1ccd-nmr"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq: time 1.892 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7355370 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 15 sec



compound 15a

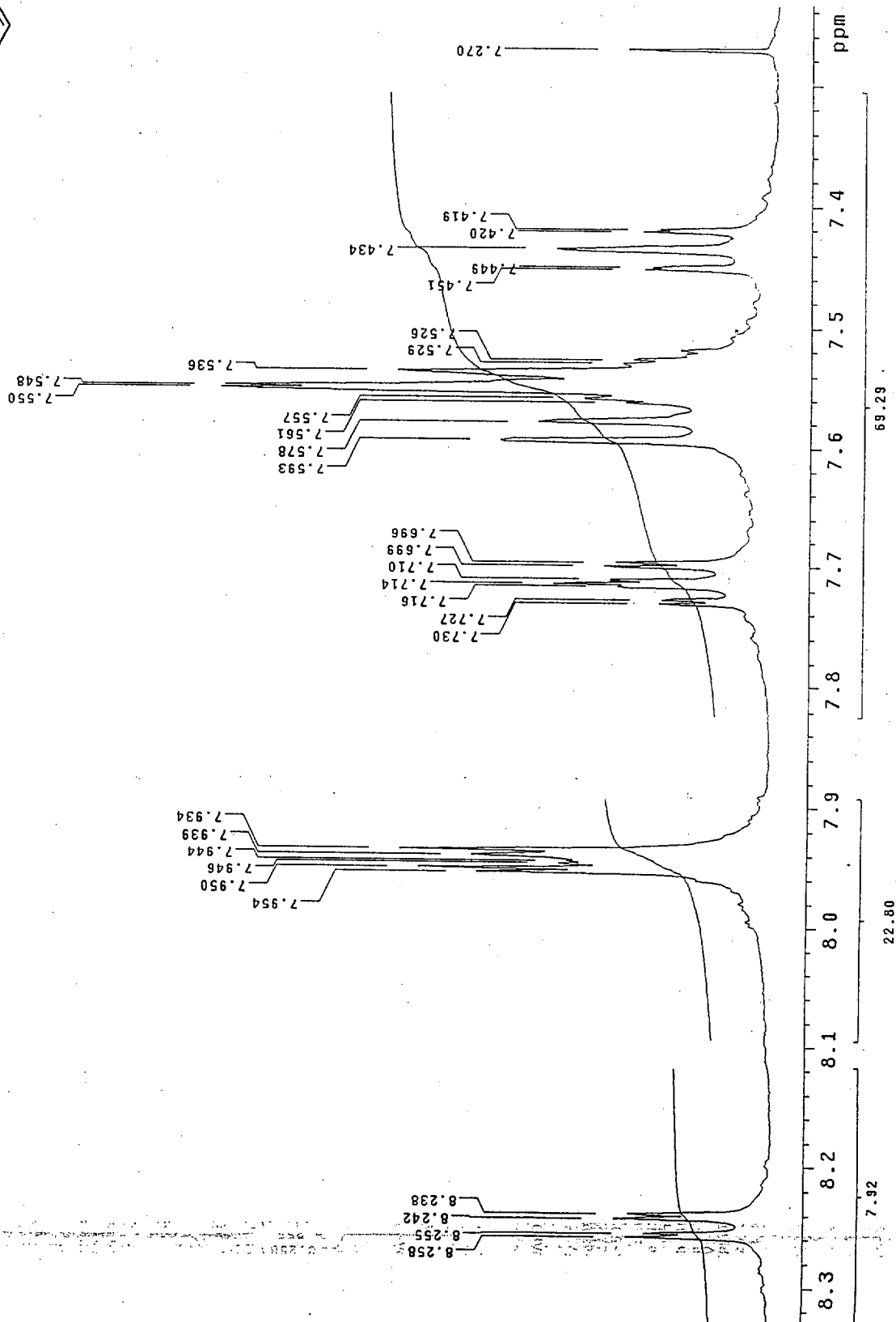


22



STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
Solvent: CDCl₃
Temp: 25.0 C / 298.1 K
INOVA-500 "iccb-nmr"
PULSE SEQUENCE
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.7355370 MHz
DATA PROCESSING
Ft size 32768
Total time 0 min, 15 sec



23

JA A 1728

Pulse Sequence: s2pul

Solvent: cdcl3

Temp: 25.0 C / 298.1 K

INNOVA-500 "iccb-nmr"

PULSE SEQUENCE

Relax: delay 2.000 sec

Pulse: 52.7 degrees

Acq: time 0.800 sec

Width: 28001.4 Hz

376 repetitions

OBSERVE C13, 125.6585777 MHZ

DECOUPLE H1, 499.7378656 MHZ

Power 35 dB

continuously on

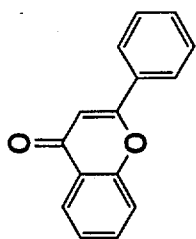
WALTZ-16 modulated

DATA PROCESSING

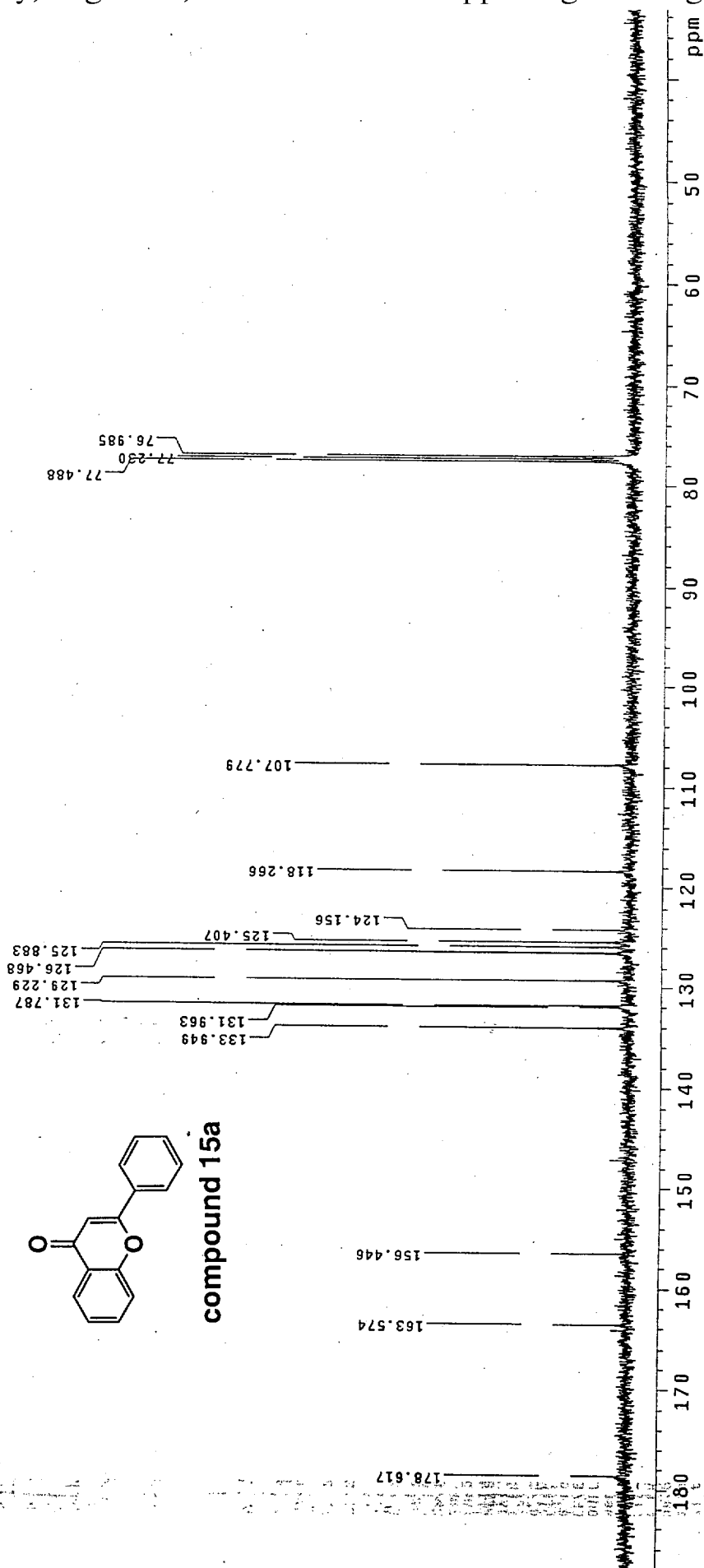
Line broadening 1.5 Hz

FT size 32768

Total time 12 hr, 29 min, 23 sec



compound 15a



24

STANDARD PROTON PARAMETERS

Solvent: CDCl₃

Temp: 25 °C / 298.1 K

INVOA-500 "1ccb-mm"

PULSE SEQUENCE

Relax: delay 2.000 sec

Pulse: 73.0 degrees

Acq. time: 1.832 sec

Width: 8000.0 Hz

8 repetitions

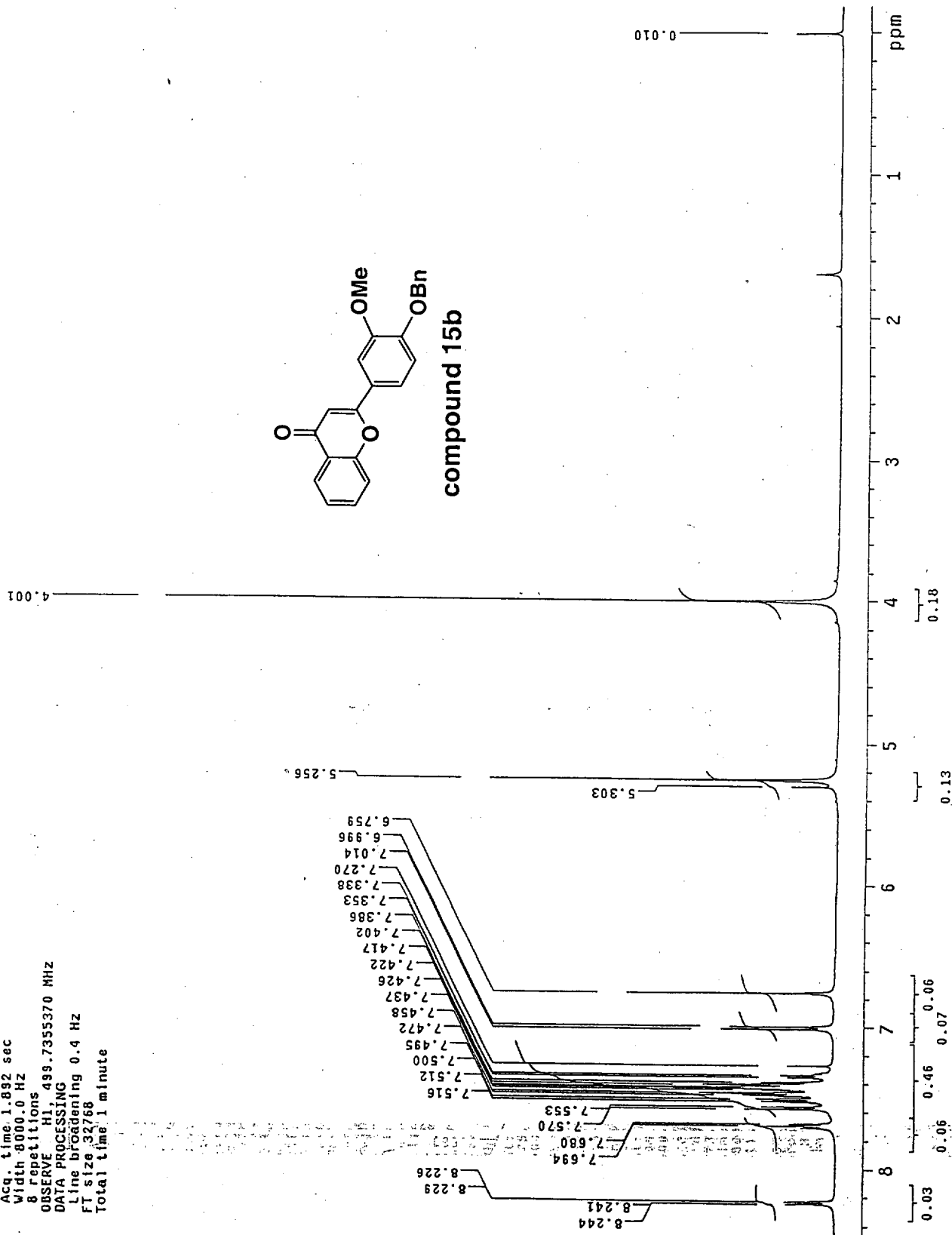
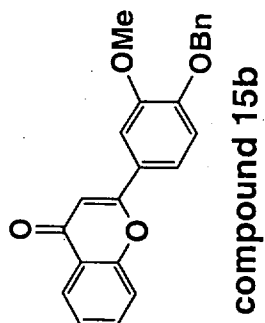
OBSERVE: H1, 499.7355370 MHz

DATA PROCESSING

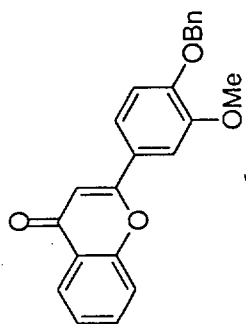
Line broadening 0.4 Hz

FT size 32768

Total time 1 minute

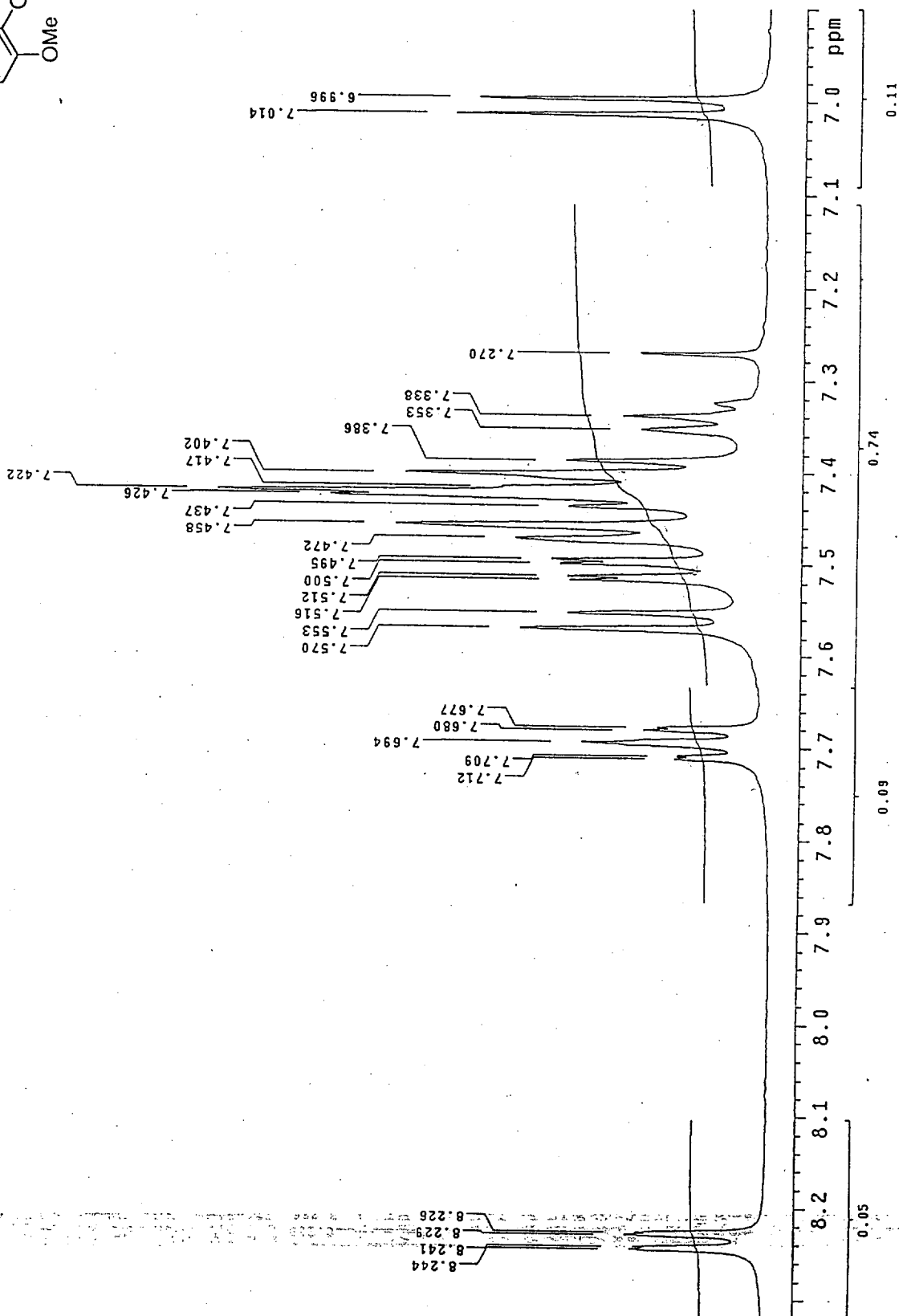


25



STANDARD PROTON PARAMETERS

Solvent: CDCl₃
 Temp: 25.0 C / 298.1 K
 INOVA-500 "iccb-nmr"
 PULSE SEQUENCE
 Relax delay 2.000 sec
 Pulse 73.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 repetitions
 OBSERVE: H1, 499.7955370 MHz
 DATA PROCESSING
 Line broadening 0.4 Hz
 FT size 32768
 Total time 1 minute



26

JA A 172B

Solvent: cdcl3

Temp: 25.0 C / 290.1 K

INNOVA-500 "fcdl-nmr"

PULSE SEQUENCE

Relax. delay 2.000 sec

Pulse 52.7 degrees

Acq. time 0.800 sec

Width 28001.4 Hz

688 repetitions

OBSERVE: C13, 125.6585872 MHz

DECOUPLE: H1, 499.7378656 MHz

Power 55 dB

continuously on

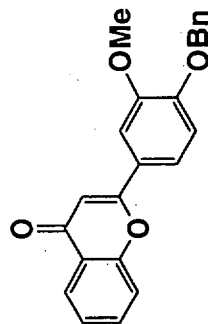
WALTZ-16 modulated

DATA PROCESSING

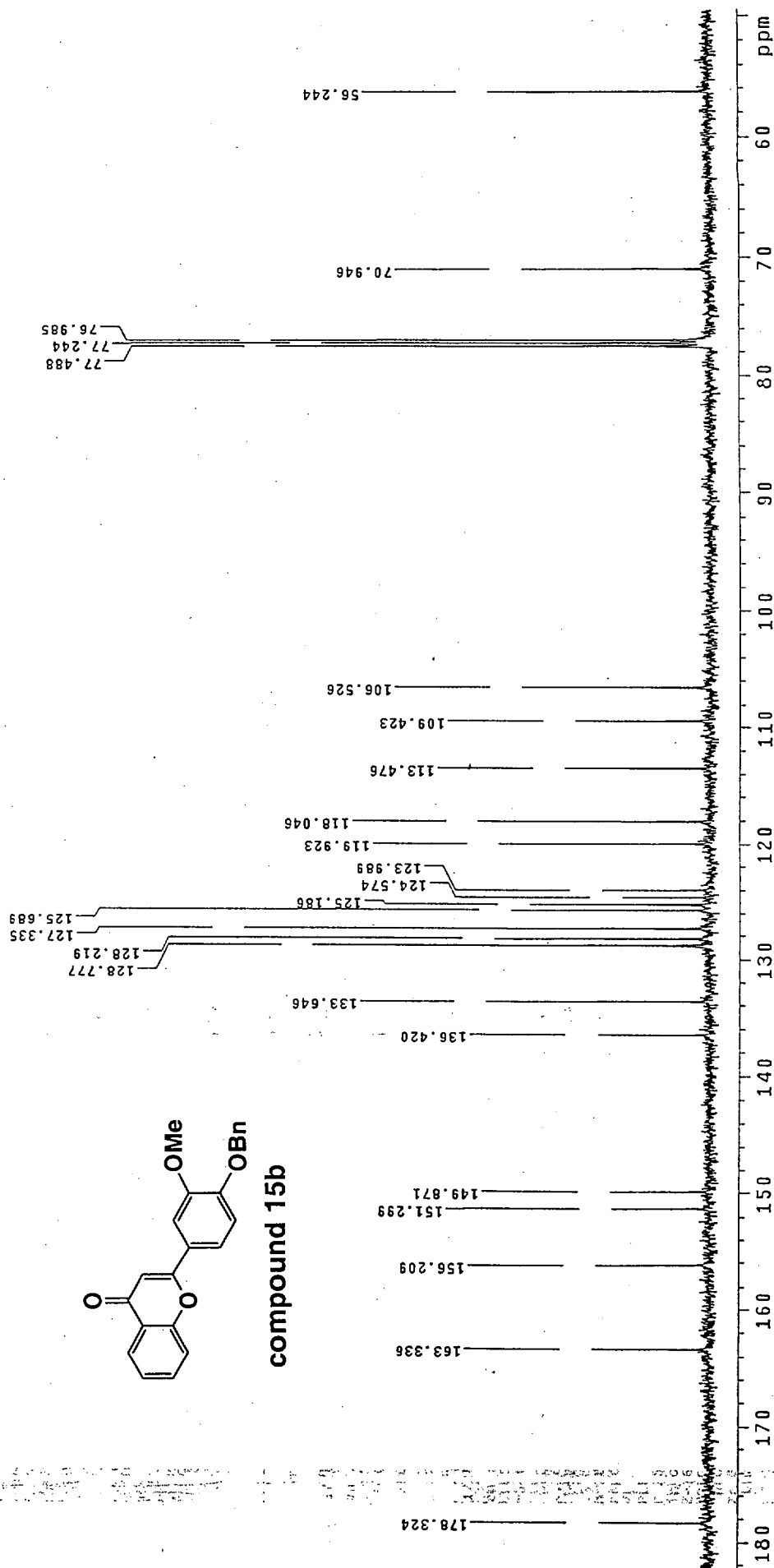
Line broadening 2.0 Hz

FT size 32768

Total time 32 minutes



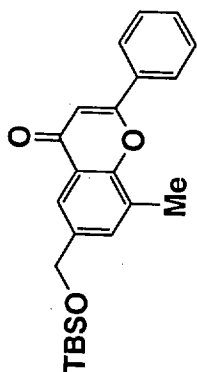
compound 15b



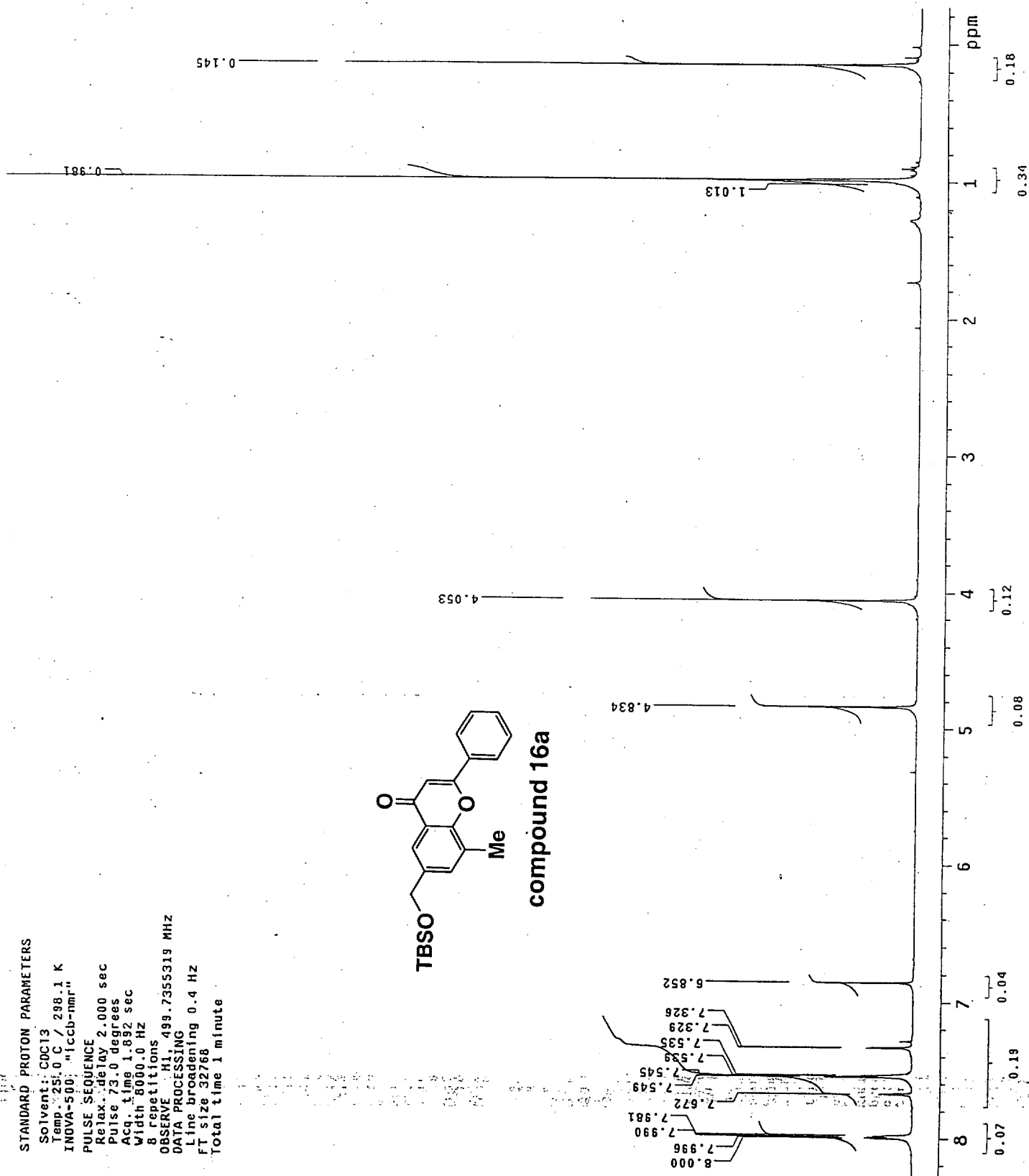
27

STANDARD PROTON PARAMETERS

Solvent: CDCl₃
 Temp: 25.0 °C / 298.1 K
 INOVA-500, "1ccb-nmr"
 PULSE SEQUENCE
 Relax delay 2.000 sec
 Pulse 73.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 repetitions
 OBSERVE H1, 499.7355319 MHz
 DATA PROCESSING
 Line broadening 0.4 Hz
 FT size 32768
 Total time 1 minute



compound 16a



28

JA A 1728

Solvent: cdcl3
Temp: 25.0 C / 298.1 K
INOVA-500 "1ccB-nmr"

PULSE SEQUENCE

Relax: delay 2.000 sec

Pulse: 52.7 degrees

Acq: time 0.800 sec

Width: 28001.4 Hz

576 repetitions

OBSERVE C13, 125.6585735 MHz

DECOUPLE H1, 499.7378656 MHz

Power 35 dB

continuously on

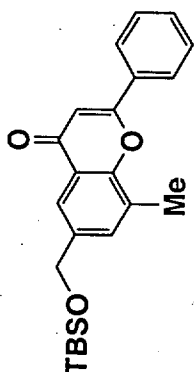
WALTZ-16 modulated

DATA PROCESSING

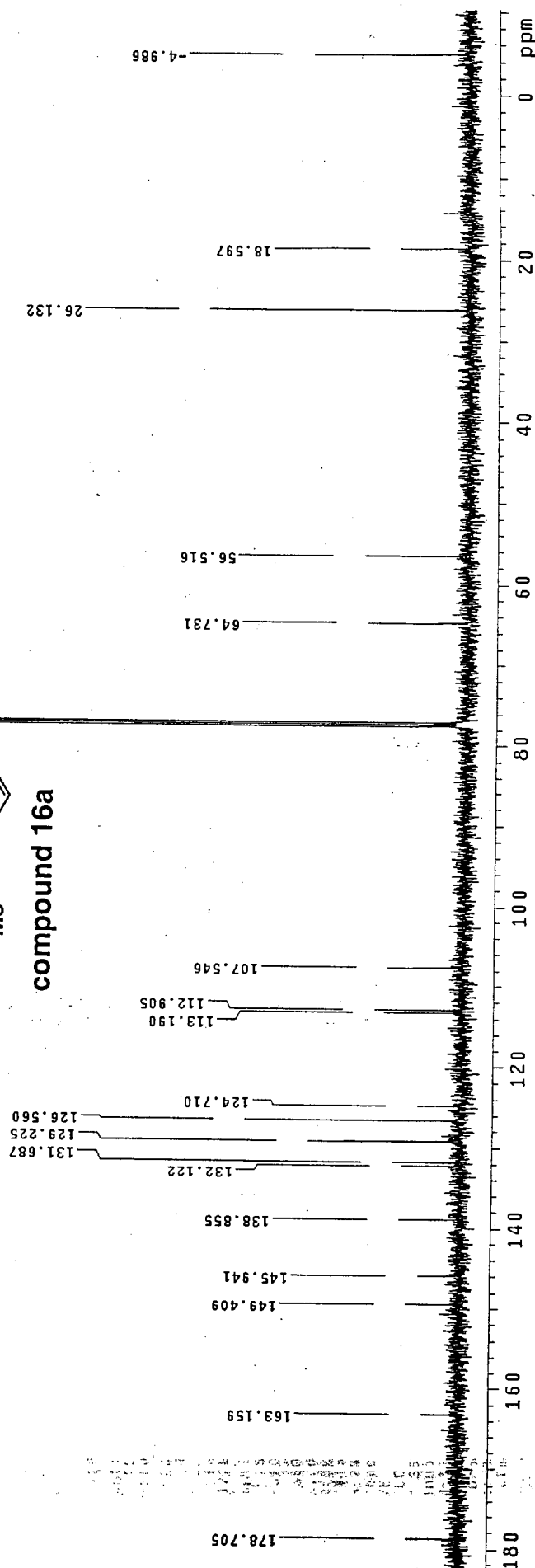
Line broadening 1.5 Hz

FT size 32768

Total time 27 minutes



compound 16a



29

STANDARD PROTON PARAMETERS

Solvent: CDCl₃
 Temp: 25.0 C / 298.1 K
 INOVA-500 "1ccb-nmr"
 PULSE SEQUENCE
 Relax delay 2.000 sec
 Pulse 73.0 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 repetitions
 OBSERVE H1, 499.7355375 MHz
 DATA PROCESSING
 Line broadening 0.4 Hz
 FT size 32768
 Total time 1 minute

