

The Palladium-Mediated Intramolecular Carbonylative Annulation of *o*-Alkynylphenols to Synthesize Benzo[*b*]furo[3,4-*d*]furan-1-ones

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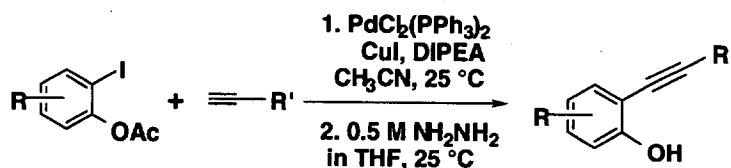
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Supporting Information

General Methods

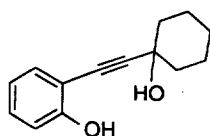
Unless stated otherwise, reactions were performed in flame-dried glassware under nitrogen or an argon atmosphere. Reaction solvents were commercially purchased from *Aldrich* without further purification and reagents were used as received. Reaction were monitored by thin-layer chromatography (TLC) on 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. ¹H and ¹³C NMR spectra were recorded on a Varian Unity INPVA 500MHz spectrometer and are referenced to residual solvent peaks or to an internal reference of tetramethylsilan 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). IR spectra were recorded on a Bruker Vector 22 with Harrick SplitPea™. MS spectra were obtained on a Micromass Platform LCZ with Alliance 2690. High-resolution mass spectra were submitted to Harvard University Mass Spectrometry, and will provide later.

General Procedure for Synthesis of *o*-Alkynylphenols



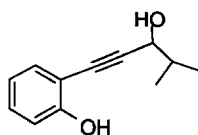
A mixture of phenyl iodide **A** (1 mmol), acetylene **B** (2.0 mmol), copper (I) iodide (0.05 mmol) and dichlorobis(triphenylphosphine)palladium (0.05 mmol) in dry acetonitrile (15 mL)

was degassed with argon for 10 min., and the reaction mixture was treated with DIPEA (0.9 mL, 5.0 mmol), then stirred at 25 °C for 24 hours. The reaction mixture was concentrated and the residue was purified by flash column chromatography to afford the corresponding *o*-alkynylphenol acetate. This acetate was treated with 0.5M NH₂NH₂ in THF (5 mL) at 25 °C for 30 min., and then purified by flash chromatography.



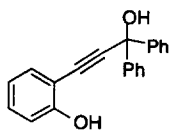
Compound 1

Purification by flash chromatography (Hexane/EtOAc = 2/1) gave **1** in 98% yield; ¹H NMR: δ 7.28 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.19 (m, 1H), 7.00 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.81 (m, 1H), 3.8 (s, 1H), 2.05 (m, 2H), 1.90 (m, 1H), 1.74-1.50 (bm, 6H), 1.23 (m, 1H); ¹³C NMR: δ 156.87, 131.86, 130.07, 119.91, 115.22, 109.23, 98.88, 79.20, 69.55, 39.86, 39.51, 25.01, 24.91, 23.36.



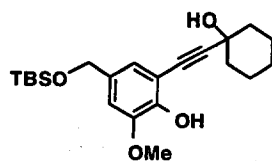
Compound 3a

Purification by flash chromatography (Hexane/EtOAc = 2/1) gave **3a** in 78% yield; ¹H NMR: δ 7.30 (d, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 8.5 Hz, 1H), 7.03 (s, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 7.5 Hz, 1H), 4.49 (s, 1H), 3.70 (s, 1H), 2.00 (m, 1H), 1.09 (d, *J* = 6.5 Hz, 3H), 1.06 (d, *J* = 6.5 Hz, 3H); ¹³C NMR: δ 157.01, 131.92, 130.26, 120.07, 115.29, 109.18, 94.88, 80.53, 68.47, 34.56, 18.21, 17.53.



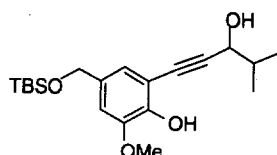
Compound 3b

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **3b** in 70 % yield; ¹H NMR: δ 7.68 (s, 2H), 7.67 (s, 2H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.43 (d, *J* = 7.0 Hz, 1H), 7.39-7.25 (bm, 6H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.91 (dd, *J* = 7.5 Hz, 1H), 6.21 (s, 1H); ¹³C NMR: δ 157.04, 144.59, 131.91, 130.77, 128.41, 128.35, 128.03, 127.91, 126.04, 125.97, 120.27, 115.11, 108.72, 98.50, 81.76, 75.10.



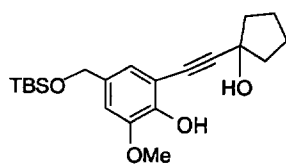
Compound 3c

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **3c** in 78 % yield; ^1H NMR: δ 6.88 (s, 2H), 5.91 (s, 1H), 4.63 (s, 2H), 3.89 (s, 3H), 2.06 (m, 2H), 1.75 (m, 2H), 1.66 (m, 2H), 1.58 (m, 1H), 1.27 (m, 1H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR: δ 146.78, 145.79, 133.22, 122.22, 109.83, 109.29, 98.07, 79.74, 69.31, 64.70, 56.23, 40.20, 26.08, 25.42, 23.63, 18.54, -5.03.



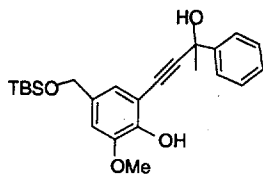
Compound 3d

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **3d** in 80 % yield; ^1H NMR: δ 6.89 (s, 2H), 6.16 (s, 1H), 4.63 (s, 2H), 4.46 (d, J = 5.5 Hz, 1H), 3.89 (s, 3H), 2.00 (m, 1H), 1.10 (d, J = 6.5 Hz, 3H), 1.07 (d, J = 6.5 Hz, 3H), 0.96 (s, 9H), 0.11 (s, 6H); ^{13}C NMR: δ 146.52, 145.78, 133.07, 121.92, 109.70, 108.74, 93.82, 80.74, 68.34, 64.49, 56.03, 34.57, 25.88, 18.35, 18.16, 17.50, -5.24.



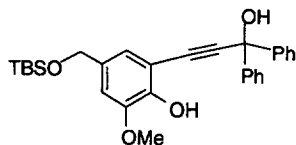
Compound 3e

Purification by flash chromatography (Hexane/EtOAc = 2/1) gave **3e** in 77 % yield; ^1H NMR: δ 6.88 (s, 1H), 6.86 (s, 1H), 6.29 (s, 1H), 4.62 (s, 2H), 3.87 (s, 3H), 2.00 (m, 1H), 3.15 (s, 1H), 2.07 (m, 4H), 1.88 (m, 2H), 1.77 (m, 2H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR: δ 139.51, 138.53, 126.02, 114.79, 102.66, 102.03, 91.02, 71.18, 67.77, 57.52, 49.00, 35.44, 18.88, 16.48, 11.33, -12.24.



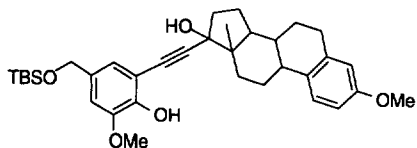
Compound 3f

Purification by flash chromatography (Hexane/EtOAc = 2/1) gave **3f** in 88 % yield; ^1H NMR: δ 7.78 (d, J = 7.5 Hz, 2H), 7.38 (dd, J = 7.0 Hz, 2H), 7.31 (d, J = 7.5 Hz, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 4.65 (s, 2H), 3.89 (s, 3H), 1.90 (s, 3H), 0.97 (s, 9H), 0.12 (s, 6H); ^{13}C NMR: δ 146.54, 145.89, 145.73, 133.10, 128.22, 127.54, 125.07, 121.87, 109.82, 108.59, 97.31, 80.21, 70.40, 64.51, 56.04, 33.30, 25.91, 18.37, -5.21.



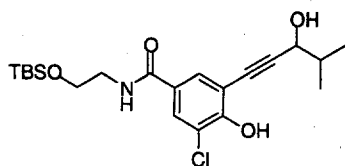
Compound 3g

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **3g** in 85 % yield; ^1H NMR: δ 7.75 (s, 1H), 7.74 (s, 1H), 7.73 (s, 2H), 7.35 (m, 4H), 7.30 (m, 1H), 7.29 (m, 1H), 6.96 (s, 1H), 6.93 (s, 1H), 6.02 (s, 1H), 4.66 (s, 2H), 3.90 (s, 3H), 0.98 (s, 9H), 0.14 (s, 6H); ^{13}C NMR: δ 146.77, 146.42, 145.32, 133.34, 128.60, 128.50, 128.45, 128.27, 127.80, 126.34, 126.27, 126.18, 122.04, 110.16, 108.64, 96.67, 82.97, 75.17, 64.72, 56.30, 26.16, 18.62, -4.97.

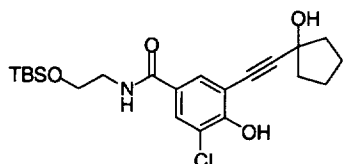


Compound 3h

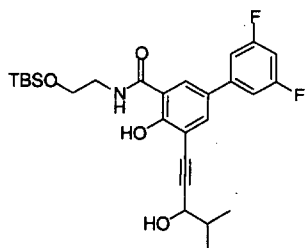
Purification by flash chromatography (Hexane/EtOAc = 2/1) gave **3h** in 94 % yield; ^1H NMR: δ 7.22 (d, J = 8.5 Hz, 1H), 6.89 (s, 1H), 6.87 (s, 1H), 6.71 (d, J = 8.5 Hz, 1H), 6.63 (s, 1H), 6.01 (s, 1H), 4.63 (s, 2H), 3.88 (s, 3H), 3.78 (s, 3H), 2.86 (m, 2H), 2.40 (m, 1H), 2.37 (m, 1H), 2.25 (m, 1H), 2.11 (m, 1H), 2.05 (m, 1H), 1.90-1.72 (bm, 4H), 1.52-1.36 (bm, 4H), 0.93 (s, 9H), 0.09 (s, 6H); ^{13}C NMR: δ 157.65, 146.90, 146.06, 138.23, 133.35, 132.94, 126.63, 122.01, 114.01, 111.72, 109.86, 109.42, 98.19, 81.26, 80.56, 64.76, 56.33, 55.41, 49.93, 47.94, 43.87, 39.80, 33.29, 30.13, 27.54, 26.82, 26.18, 23.20, 21.27, 18.64, 13.20, -4.94.

**Compound 3i**

Purification by flash chromatography (Hexane/EtOAc = 1/1) gave **3i** in 88 % yield; ^1H NMR: δ 7.71 (d, J = 2.0 Hz, 1H), 7.59 (d, J = 2.0 Hz, 1H), 6.61 (m, 1H), 4.44 (d, J = 6.0 Hz, 1H), 3.78 (t, J = 5.0 Hz, 2H), 3.54 (m, 2H), 1.98 (m, 1H), 1.07 (d, J = 6.5 Hz, 3H), 1.05 (d, J = 6.5 Hz, 3H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR: δ 165.94, 155.62, 129.64, 129.43, 127.15, 121.11, 111.32, 96.80, 79.21, 68.44, 61.84, 42.45, 34.68, 26.08, 18.46, 17.76, 14.36, -5.15.

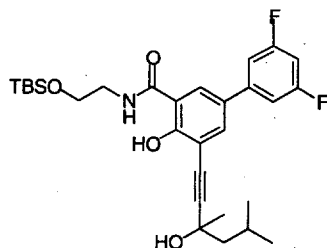
**Compound 3j**

Purification by flash chromatography (Hexane/EtOAc = 1/1) gave **3j** in 62 % yield; ^1H NMR: δ 7.71 (s, 1H), 7.60 (s, 1H), 6.51 (m, 1H), 3.77 (t, J = 5.0 Hz, 2H), 3.55 (m, 2H), 2.06 (m, 4H), 1.89 (m, 2H), 1.79 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C NMR: δ 165.46, 155.03, 129.34, 129.10, 127.13, 120.70, 111.16, 100.80, 96.51, 76.47, 74.78, 61.65, 42.42, 42.17, 25.87, 23.48, 18.26, -5.35.

**Compound 3k**

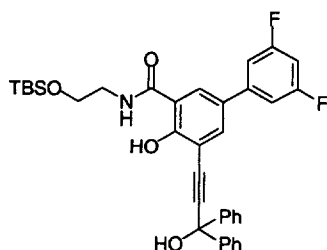
Purification by flash chromatography (Hexane/EtOAc = 1/1) gave **3k** in 90 % yield; ^1H NMR: δ 7.64 (s, 1H), 7.48 (s, 1H), 7.32 (m, 1H), 7.01 (m, 1H), 6.93-6.86 (m, 2H), 4.47 (d, J = 5.0 Hz, 2H), 3.79 (t, J = 5.0 Hz, 2H), 3.56 (m, 2H), 2.06 (m, 1H), 1.12 (d, J = 6.5 Hz, 3H), 1.08 (d, J = 6.5 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR: δ 169.31, 161.93, 137.80, 131.19, 126.41, 125.34,

114.78, 113.68, 112.09, 111.92, 104.89, 104.69, 104.48, 94.94, 80.63, 68.68, 61.48, 41.80, 34.90, 26.03, 18.39, 17.85, -5.20.



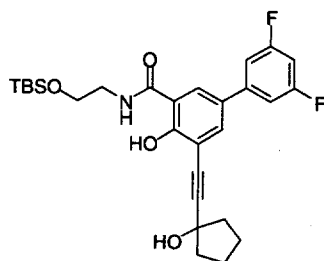
Compound 3l

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **3l** in 89 % yield; ^1H NMR: δ 7.60 (s, 1H), 7.50 (s, 1H), 7.33 (m, 1H), 6.98 (m, 1H), 6.92 (m, 2H), 3.78 (m, 2H), 3.56 (m, 2H), 2.03 (m, 1H), 1.72 (s, 2H), 1.61 (s, 3H), 1.05 (s, 6H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR: δ 168.97, 161.36, 137.30, 130.86, 126.16, 125.05, 114.60, 113.52, 111.78, 111.57, 104.57, 104.36, 104.16, 99.11, 78.33, 68.51, 61.22, 51.84, 41.55, 30.76, 25.76, 25.11, 24.24, 24.10, 18.12, -5.48.



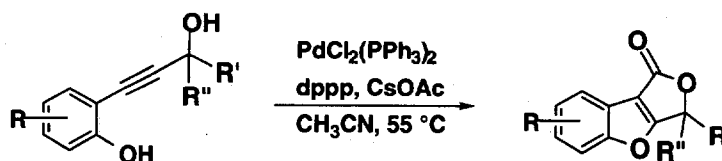
Compound 3m

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **3m** in 98 % yield; ^1H NMR: δ 7.78 (s, 2H), 7.76 (s, 2H), 7.68 (s, 1H), 7.51 (s, 1H), 7.38-7.28 (bm, 7H), 6.94 (m, 3H), 3.82 (m, 2H), 3.60 (m, 2H), 3.15 (s, 1H), 0.91 (s, 9H), 0.09 (s, 6H); ^{13}C NMR: δ 169.20, 162.31, 145.05, 137.47, 131.05, 128.48, 128.38, 128.17, 127.76, 126.45, 126.27, 126.16, 125.17, 114.63, 113.38, 111.98, 111.79, 104.77, 104.57, 97.33, 74.90, 82.42, 75.09, 61.33, 41.67, 25.91, 18.27, -5.31.

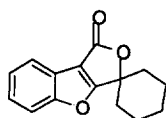


Compound 3n

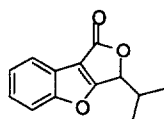
Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **3n** in 86 % yield; ^1H NMR: δ 7.61 (s, 1H), 7.48 (s, 1H), 7.31 (m, 1H), 6.95 (m, 1H), 6.92-6.86 (m, 2H), 3.79 (t, J = 5.0 Hz, 2H), 3.56 (m, 2H), 2.10 (m, 4H), 1.86 (m, 2H), 1.78 (m, 2H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR: δ 169.04, 161.32, 137.47, 131.01, 126.15, 125.10, 114.56, 113.58, 111.81, 111.61, 104.62, 104.40, 104.20, 98.68, 77.95, 74.91, 61.25, 42.53, 41.58, 25.79, 23.54, 18.16, -5.44.



A mixture of *o*-alkynylphenol (1.0 mmol), dppp (1.0 mmol), CsOAc (4.0 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (1.0 mmol) was dissolved in dry acetonitrile (5 mL), and the reaction mixture was degassed by CO for 10 minutes, and then was stirred at 55°C under CO balloon for 12 hours. The reaction mixture was concentrated and the residue was filtered through silical gel bed and washed by EtOAc. The solvent was evaporated and the residue was purified by flash chromatography.

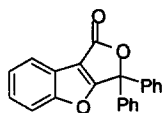
**Compound 2**

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **2** in 68 % yield; ^1H NMR: δ 7.83 (dd, J = 6.5, 3.0 Hz, 1H), 7.60 (dd, J = 6.0, 2.0 Hz, 1H), 7.41 (m, 2H), 2.00 (m, 4H), 1.91 (m, 2H), 1.87 (m, 2H), 1.62 (m, 2H); ^{13}C NMR: δ 183.39, 163.71, 161.36, 125.64, 124.96, 121.16, 112.63, 111.26, 83.52, 34.61, 24.43, 22.38; IR (cm^{-1}): 2939, 1771, 1613, 1482, 1406, 1311, 1116, 1015, 958, 804, 778, 609; MS (APCI) [$\text{C}_{15}\text{H}_{14}\text{O}_3$], m/z (M^+ +1) calcd 243, found 243.

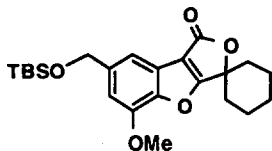


Compound 4a

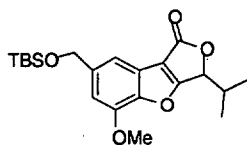
Purification by flash chromatography (Hexane/EtOAc = 5/1) gave in **4a** 53 % yield; ^1H NMR: δ 7.81 (dd, J = 6.0, 2.0 Hz, 1H), 7.60 (dd, J = 7.0, 1.5 Hz, 1H), 7.40 (m, 2H), 5.24 (d, J = 6.0 Hz, 1H), 2.30 (m, 1H), 1.12 (d, J = 7.0 Hz, 3H), 1.09 (d, J = 7.0 Hz, 3H); ^{13}C NMR: δ 178.99, 164.17, 161.68, 125.80, 124.98, 121.03, 120.88, 113.46, 112.65, 81.46, 31.42, 17.38; 17.09; IR (cm^{-1}): 2966, 1771, 1611, 1483, 1321, 1249, 1088, 990, 795, 669; MS (APCI) [$\text{C}_{13}\text{H}_{12}\text{O}_3$], m/z ($\text{M}^+ + 1$) calcd 217, found 217.

**Compound 4b**

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **4b** in 52 % yield; ^1H NMR: δ 7.87 (dd, J = 7.5, 2.0 Hz, 1H), 7.65 (dd, J = 7.5, 2.0 Hz, 1H), 7.55 (m, 4H), 7.47-7.39 (bm, 8H); ^{13}C NMR: δ 179.83, 162.99, 161.99, 137.96, 129.03, 128.76, 126.51, 126.11, 125.26, 121.36, 120.96, 112.92, 112.15, 87.49; IR (cm^{-1}): 2970, 1776, 1614, 1483, 1443, 1401, 1147, 1092, 805, 773, 647, 611; MS (APCI) [$\text{C}_{22}\text{H}_{14}\text{O}_3$], m/z ($\text{M}^+ + 1$) calcd 327, found 327.

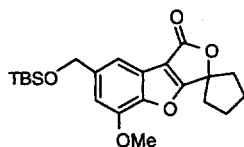
**Compound 4c**

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **4c** in 67 % yield; ^1H NMR: δ 7.30 (s, 1H), 7.00 (s, 1H), 4.81 (s, 2H), 4.03 (s, 3H), 2.03 (m, 2H), 1.96 (m, 1H), 1.85 (m, 3H), 1.67 (m, 1H), 1.51 (m, 1H), 0.96 (s, 9H), 0.12 (s, 6H); ^{13}C NMR: δ 183.55, 163.94, 149.64, 145.60, 140.15, 122.65, 111.85, 110.45, 106.72, 83.67, 65.14, 56.29, 34.70, 26.16, 24.67, 22.51, 19.59, 18.62, -4.98; IR (cm^{-1}): 2936, 1772, 1616, 1464, 1370, 1280, 1250, 1138, 1014, 932, 777, 613; MS (APCI) [$\text{C}_{23}\text{H}_{32}\text{O}_5\text{Si}$], m/z (M^+) calcd 416, found 416.

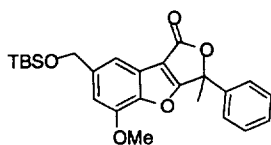


Compound 4d

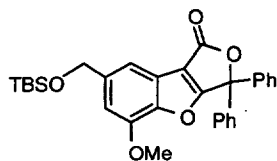
Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **4d** in 62 % yield; ^1H NMR: δ 7.32 (s, 1H), 7.02 (s, 1H), 5.25 (d, J = 5.5 Hz, 1H), 4.83 (s, 2H), 4.04 (s, 3H), 2.31 (m, 1H), 1.12 (d, J = 6.5 Hz, 3H), 1.10 (d, J = 6.5 Hz, 3H), 0.96 (s, 9H), 0.14 (s, 6H); ^{13}C NMR: δ 178.91, 164.22, 149.79, 145.38, 139.95, 122.16, 113.84, 110.11, 106.65, 81.48, 64.87, 56.06, 31.40, 25.93, 18.40, 17.37, 17.20, -5.23; IR (cm^{-1}): 2929, 1774, 1612, 1464, 1391, 1368, 1282, 1253, 1137, 1049, 983, 735, 614; MS (APCI) [$\text{C}_{21}\text{H}_{30}\text{O}_5\text{Si}$], m/z (M^+ +1) calcd 391, found 391.

**Compound 4e**

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **4e** in 92 % yield; ^1H NMR: δ 7.29 (s, 1H), 7.01 (s, 1H), 4.82 (s, 2H), 4.04 (s, 3H), 2.31 (m, 2H), 2.18 (m, 2H), 2.07 (m, 2H), 1.95 (m, 2H), 0.96 (s, 9H), 0.12 (s, 6H); ^{13}C NMR: δ 180.51, 163.52, 149.59, 145.31, 139.91, 122.52, 112.40, 110.10, 106.40, 90.53, 64.86, 56.04, 36.91, 25.89, 24.79, 18.35, -5.25; IR (cm^{-1}): 2955, 1772, 1616, 1464, 1362, 1277, 1138, 1016, 837, 776, 668; MS (APCI) [$\text{C}_{22}\text{H}_{30}\text{O}_5\text{Si}$], m/z (M^+ -1) calcd 401, found 401.

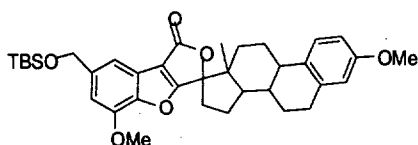
**Compound 4f**

Purification by flash chromatography (Hexane/EtOAc = 2/1) gave **4f** in 70 % yield; ^1H NMR: δ 7.62 (m, 2H), 7.42 (m, 2H), 7.36 (m, 1H), 7.33 (s, 1H), 7.03 (s, 1H), 4.83 (s, 2H), 4.05 (s, 3H), 2.10 (s, 3H), 0.94 (s, 9H), 0.14 (s, 6H); ^{13}C NMR: δ 181.42, 163.09, 145.41, 140.12, 137.97, 128.81, 128.74, 124.94, 122.29, 111.66, 110.22, 106.67, 83.91, 64.83, 56.03, 26.61, 25.89, 18.36, -5.24; IR (cm^{-1}): 2954, 1779, 1616, 1463, 1365, 1277, 1133, 1095, 986, 699, 613; MS (APCI) [$\text{C}_{25}\text{H}_{30}\text{O}_5\text{Si}$], m/z (M^+) calcd 438, found 438.

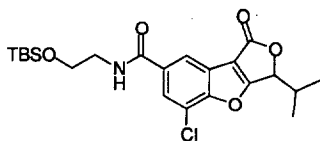


Compound 4g

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **4g** in 73 % yield; ^1H NMR: δ 7.53 (m, 4H), 7.37 (m, 7H), 7.03 (s, 1H), 4.83 (s, 2H), 4.04 (s, 3H), 0.96 (s, 9H), 0.13 (s, 6H); ^{13}C NMR: δ 180.05, 163.28, 150.34, 145.76, 140.48, 138.13, 129.22, 128.95, 128.25, 128.09, 127.64, 127.60, 126.86, 122.40, 112.74, 110.47, 107.12, 87.84, 65.08, 56.27, 26.15, 18.62, -4.98; IR (cm^{-1}): 2928, 1782, 1614, 1136, 1094, 1064, 1017, 813, 778, 668, 615; MS (APCI) [$\text{C}_{30}\text{H}_{32}\text{O}_5\text{Si}$], m/z ($\text{M}^+ + 1$) calcd 501, found 501.

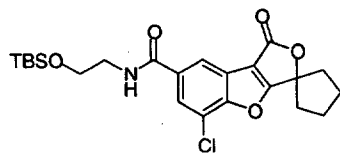
**Compound 4h**

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **4h** in 85 % yield; ^1H NMR: δ 7.32 (s, 1H), 7.14 (d, $J = 9.0$ Hz, 1H), 7.02 (s, 1H), 6.70 (dd, $J = 8.0, 2.5$ Hz, 1H), 6.66 (d, $J = 2.0$ Hz, 1H), 4.83 (s, 2H), 4.04 (s, 3H), 3.79 (s, 3H), 2.92 (m, 2H), 2.54 (dd, $J = 11.5$ Hz, AB, 1H), 2.32 (m, 1H), 2.23 (m, 1H), 2.08 (m, 1H), 1.98 (m, 1H), 7.75-1.45 (bm, 4H), 1.21 (s, 3H), 1.07 (m, 1H), 0.98 (s, 9H), 0.94 (m, 1H), 0.13 (s, 6H); ^{13}C NMR: δ 182.20, 164.03, 157.52, 149.49, 145.34, 139.95, 137.75, 131.84, 126.28, 122.32, 113.80, 111.52, 111.38, 110.08, 106.41, 94.08, 64.89, 55.93, 55.14, 49.61, 47.60, 43.23, 38.99, 32.92, 31.44, 29.75, 27.16, 25.92, 18.39, 14.56, -5.23; IR (cm^{-1}): 2929, 1771, 1611, 1463, 1362, 1279, 1249, 1136, 1060, 974, 775, 609; MS (APCI) [$\text{C}_{36}\text{H}_{46}\text{O}_6\text{Si}$], m/z ($\text{M}^+ + 1$) calcd 603, found 603.

**Compound 4i**

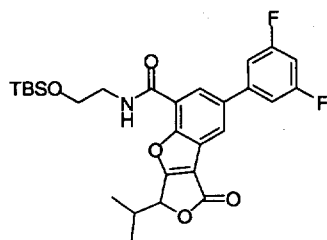
Purification by flash chromatography (Hexane/EtOAc = 2/1) gave **4i** in 52 % yield; ^1H NMR: δ 8.07 (s, 1H), 7.98 (s, 1H), 6.67 (m, 1H), 5.32 (d, $J = 6.0$ Hz, 1H), 3.83 (t, $J = 5.0$ Hz, 2H), 3.62 (m, 2H), 2.34 (m, 1H), 1.15 (d, $J = 5.5$ Hz, 3H), 1.14 (d, $J = 5.5$ Hz, 3H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR: δ 180.39, 165.73, 163.29, 158.77, 133.62, 126.34, 122.61, 118.73, 117.86, 114.81, 82.04, 61.87, 42.74, 31.75, 26.15, 18.55, 17.65, 17.52, -5.05; IR (cm^{-1}): 3368, 2930, 1778, 1646,

1612, 1470, 1362, 1300, 1162, 1098, 981, 776, 668, 617; MS (APCI) [C₂₂H₃₀ClNO₅Si], *m/z* (M⁺+1) calcd 452, found 452.



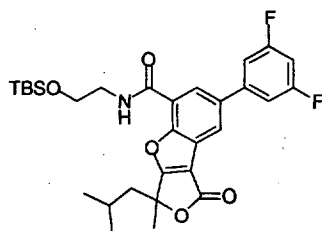
Compound 4j

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **4j** in 83 % yield; ¹H NMR: δ 8.05 (s, 1H), 7.97 (s, 1H), 6.63 (m, 1H), 3.83 (t, *J* = 5.0 Hz, 2H), 3.61 (m, 2H), 2.35 (m, 2H), 2.22 (m, 2H), 2.11 (m, 2H), 1.20 (m, 2H), 0.91 (s, 9H), 0.08 (s, 6H); ¹³C NMR: δ 181.79, 165.49, 162.43, 158.45, 133.26, 125.92, 122.83, 118.46, 117.48, 113.09, 90.92, 61.60, 42.47, 37.03, 25.89, 24.80, 18.29, -5.32; IR (cm⁻¹): 3359, 2929, 1761, 1646, 1615, 1582, 1471, 1301, 1255, 1180, 1027, 901, 775, 668, 622; MS (APCI) [C₂₃H₃₀ClNO₅Si], *m/z* (M⁺+1) calcd 464, found 464.



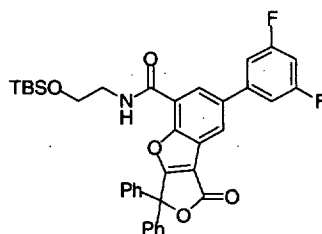
Compound 4k

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **4k** in 55 % yield; ¹H NMR: δ 8.28 (s, 1H), 8.09 (s, 1H), 7.48 (m, 1H), 7.40 (m, 1H), 7.00 (m, 2H), 5.34 (d, *J* = 5.5 Hz, 1H), 3.89 (m, 2H), 3.74 (m, 1H), 3.68 (m, 1H), 2.38 (m, 1H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.92 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ¹³C NMR: δ 178.98, 163.22, 162.41, 157.85, 132.91, 131.69, 128.61, 124.67, 121.73, 119.68, 114.31, 111.95, 111.78, 104.78, 104.58, 104.39, 81.51, 61.81, 42.54, 31.44, 25.86, 18.25, 17.75, 16.91, -5.32; IR (cm⁻¹): 3359, 2930, 1777, 1668, 1616, 1512, 1471, 1422, 1257, 1174, 1023, 969, 777, 668, 609; MS (APCI) [C₂₈H₃₃F₂NO₅Si], *m/z* (M⁺+1) calcd 530, found 530.



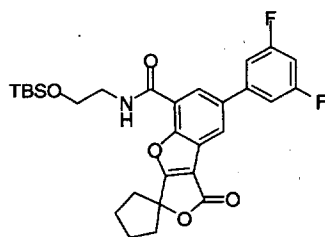
Compound 4l

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **4l** in 69 % yield; ^1H NMR: δ 8.28 (s, 1H), 8.10 (s, 1H), 7.49 (m, 1H), 7.35 (m, 1H), 7.02 (m, 2H), 3.89 (m, 2H), 3.74 (m, 2H), 2.13 (dd, $J = 15.0, 5.0$ Hz, 1H), 1.92 (dd, $J = 15.0, 7.5$ Hz, 1H), 1.81 (s, 3H), 1.78 (m, 1H), 1.01 (d, $J = 6.0$ Hz, 3H), 0.94 (s, 9H), 0.84 (d, $J = 6.0$ Hz, 3H), 0.12 (s, 6H); ^{13}C NMR: δ 182.49, 162.56, 162.50, 157.58, 132.84, 131.65, 128.54, 128.01, 124.66, 122.10, 119.70, 112.89, 111.85, 104.75, 104.54, 104.34, 83.94, 61.97, 46.22, 42.69, 25.92, 24.45, 24.18, 24.03, 23.16, 18.29, -5.25; IR (cm^{-1}): 3359, 2930, 1779, 1669, 1616, 1512, 1471, 1316, 1270, 1144, 1009, 918, 775, 618, 607; MS (APCI) [$\text{C}_{30}\text{H}_{37}\text{F}_2\text{NO}_5\text{Si}$], m/z ($\text{M}^+ + 1$) calcd 558, found 558.



Compound 4m

Purification by flash chromatography (Hexane/EtOAc = 4/1) gave **4m** in 67 % yield; ^1H NMR: δ 8.27 (d, $J = 1.5$ Hz, 1H), 8.13 (d, $J = 1.5$ Hz, 1H), 7.48 (m, 4H), 7.43 (m, 6H), 7.28 (m, 2H), 6.99 (m, 2H), 3.89 (t, $J = 5.0$ Hz, 2H), 3.72 (m, 2H), 0.82 (s, 9H), 0.02 (s, 6H); ^{13}C NMR: δ 180.24, 162.82, 162.34, 158.38, 137.44, 133.33, 131.98, 131.95, 131.91, 131.87, 129.66, 129.23, 128.97, 128.59, 126.94, 126.27, 125.07, 122.08, 120.25, 113.37, 112.24, 112.21, 112.07, 112.04, 105.04, 104.84, 104.63, 88.27, 62.23, 43.15, 26.08, 18.51, -5.09. IR (cm^{-1}): 3490, 2929, 1781, 1668, 1616, 1451, 1257, 1133, 907, 835, 755, 699, 637, 613; MS (APCI) [$\text{C}_{37}\text{H}_{35}\text{F}_2\text{NO}_5\text{Si}$], m/z ($\text{M}^+ + 1$) calcd 640, found 640.

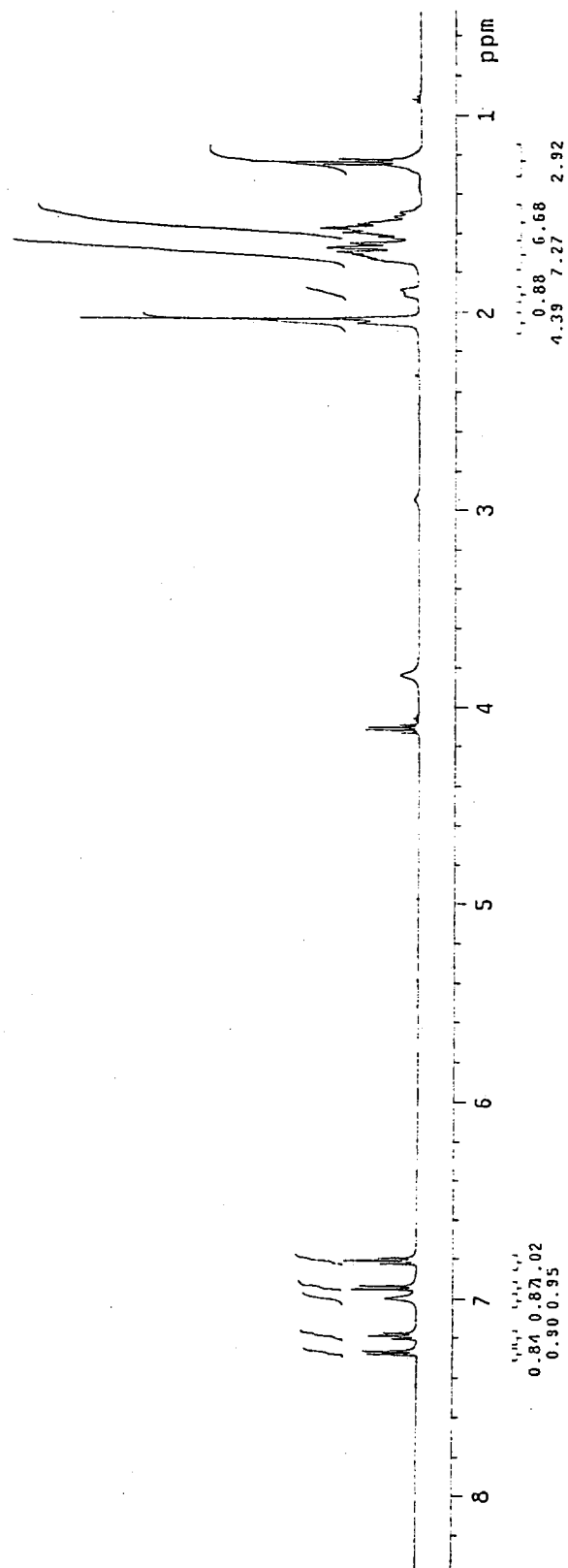
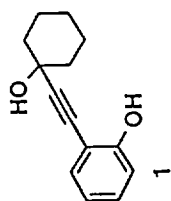


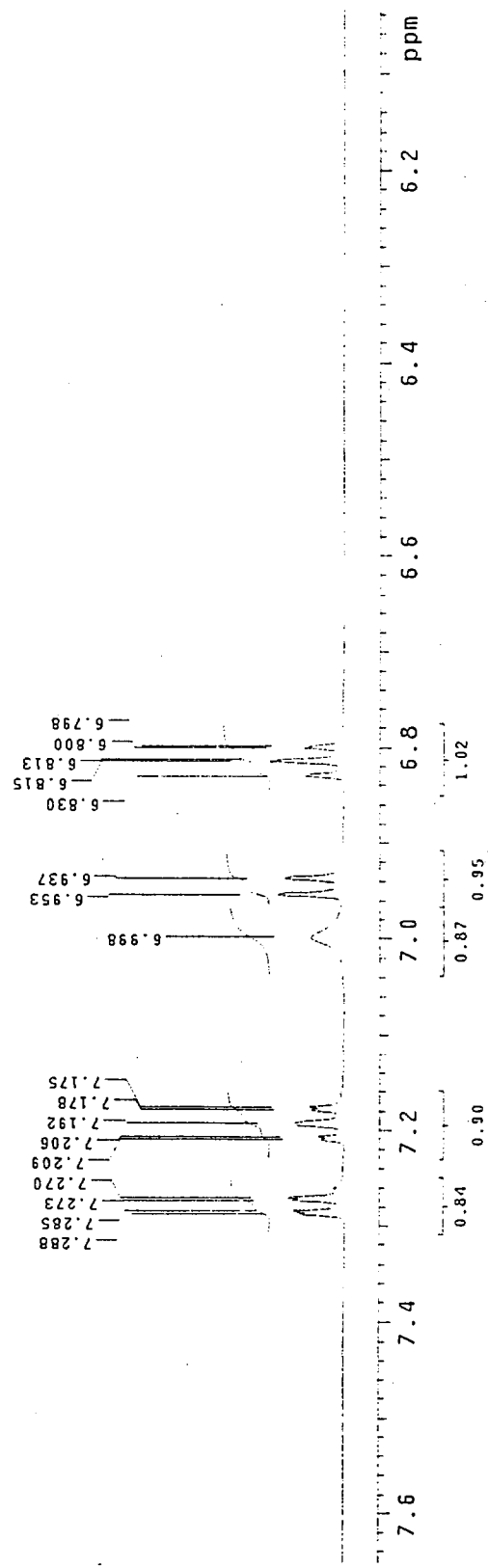
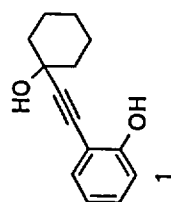
Compound 4n

Purification by flash chromatography (Hexane/EtOAc = 3/1) gave **4n** in 76 % yield; ^1H NMR: δ 8.25 (s, 1H), 8.06 (s, 1H), 7.46 (m, 1H), 7.35 (m, 1H), 6.96 (m, 2H), 3.86 (m, 2H), 3.71 (m, 2H), 2.35 (m, 2H), 2.23 (m, 2H), 2.12 (m, 2H), 1.99 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR: δ 180.54, 162.55, 157.81, 132.79, 131.75, 128.44, 124.56, 122.24, 119.68, 113.07, 111.95, 111.78, 104.77, 104.56, 104.35, 90.89, 61.99, 42.61, 37.09, 25.85, 24.60, 18.26, -5.31; IR (cm^{-1}): 3441, 2954, 1771, 1668, 1616, 1512, 1471, 1422, 1257, 1169, 1139, 969, 755, 668; MS (APCI) [$\text{C}_{29}\text{H}_{33}\text{F}_2\text{NO}_5\text{Si}$], m/z ($\text{M}^+ + 1$) calcd 542, found 542.

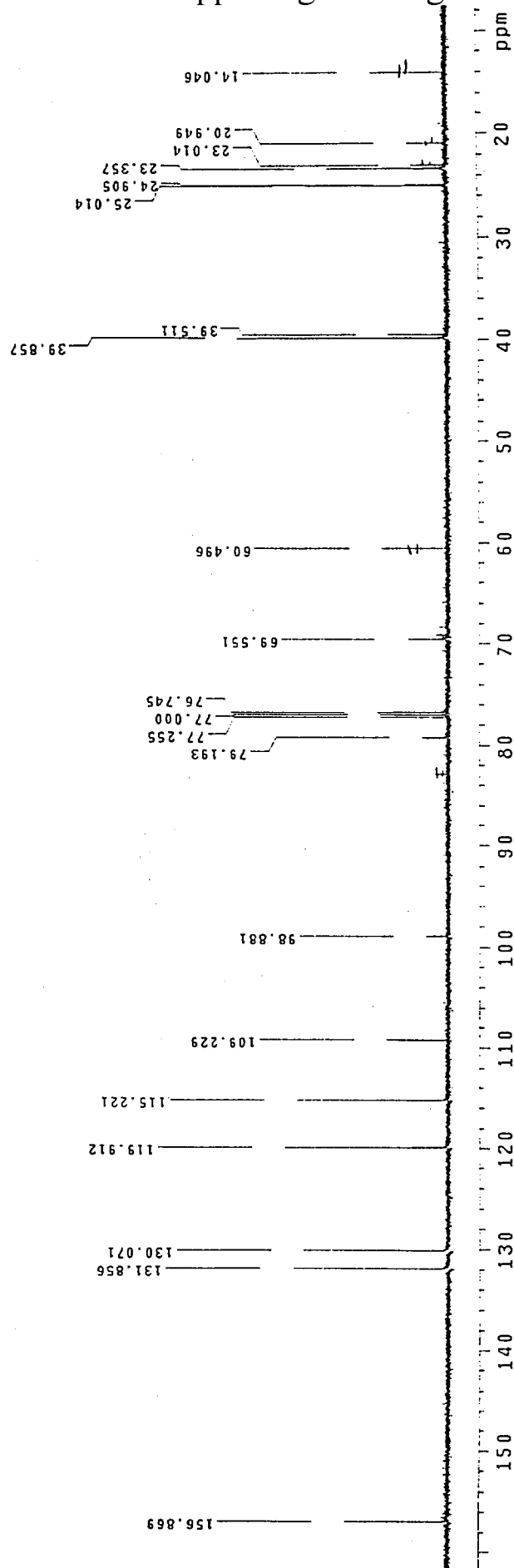
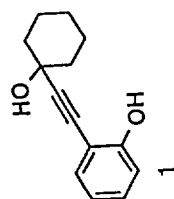
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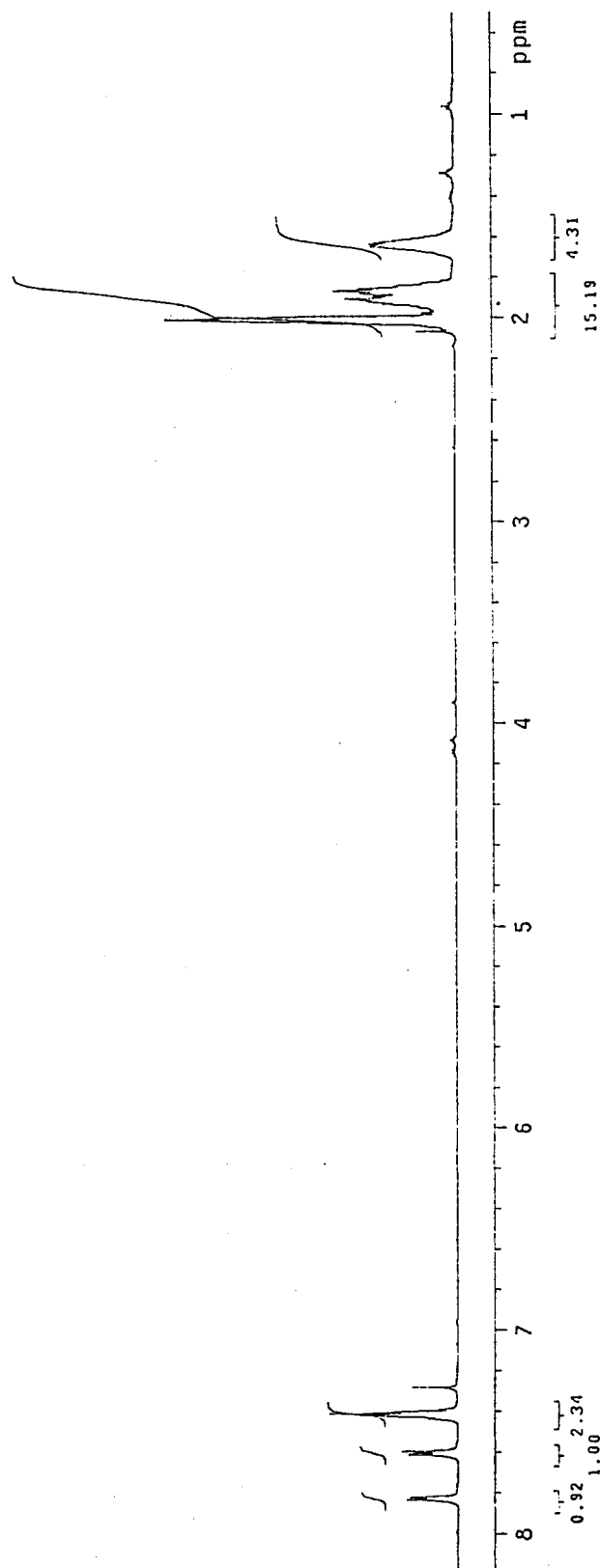
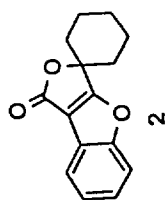
1. ^1H NMR and ^{13}C NMR spectra of compound 1 (Page 1-3)
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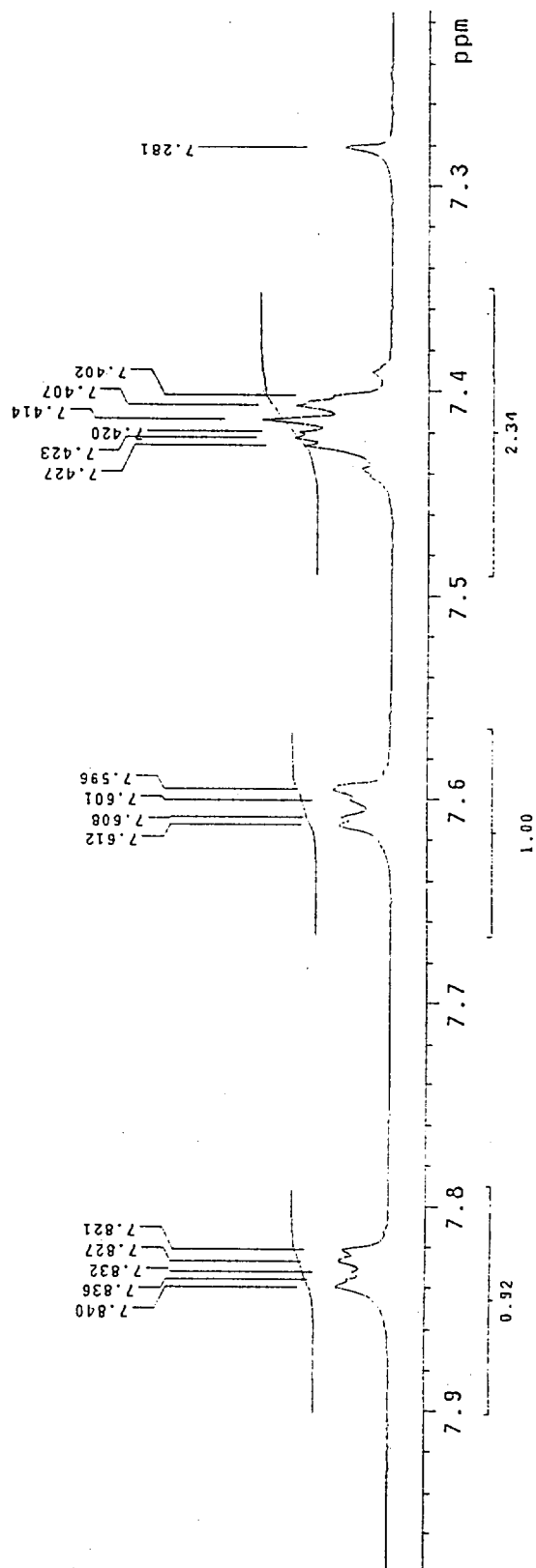
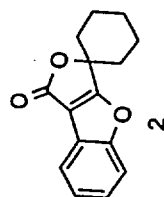


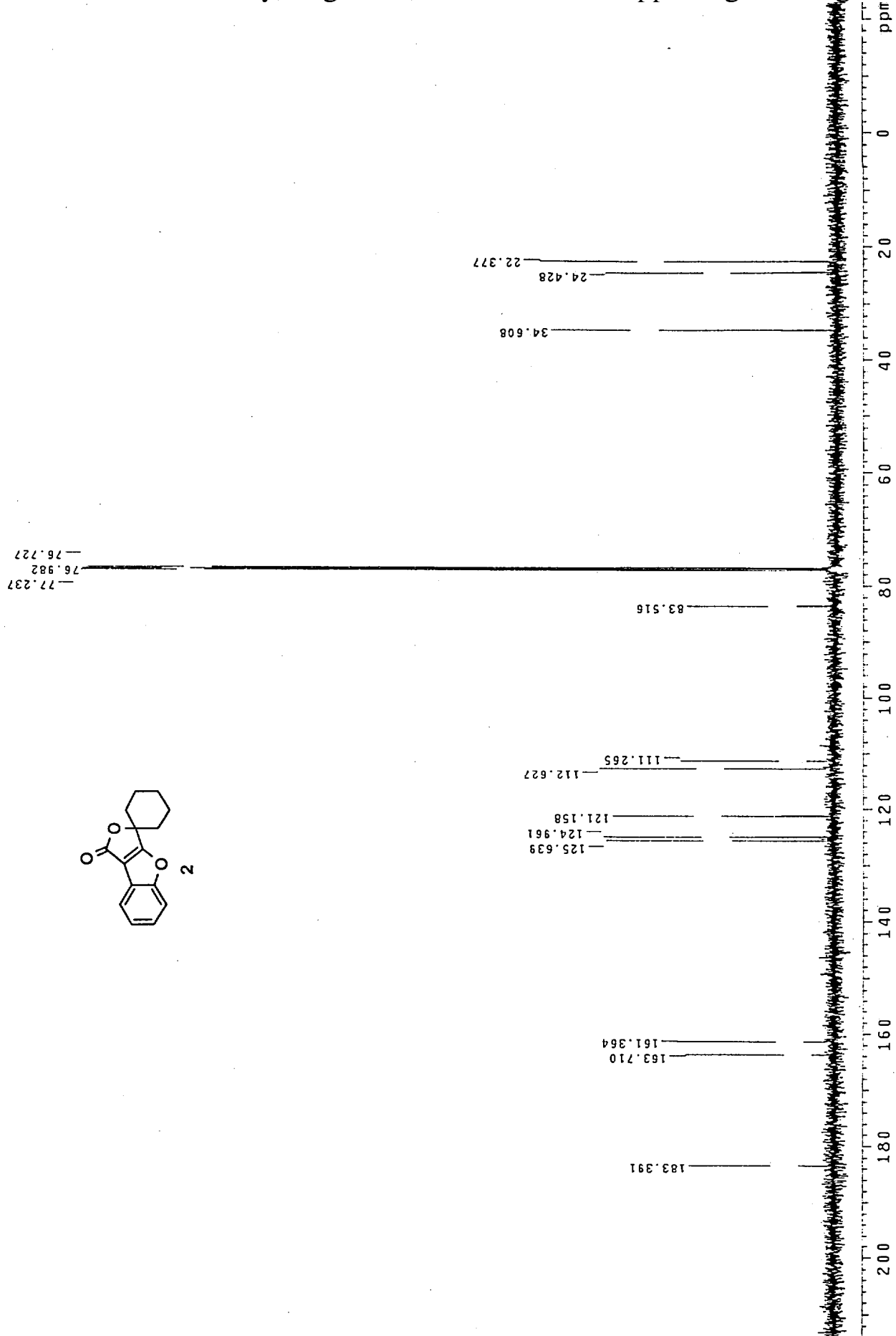


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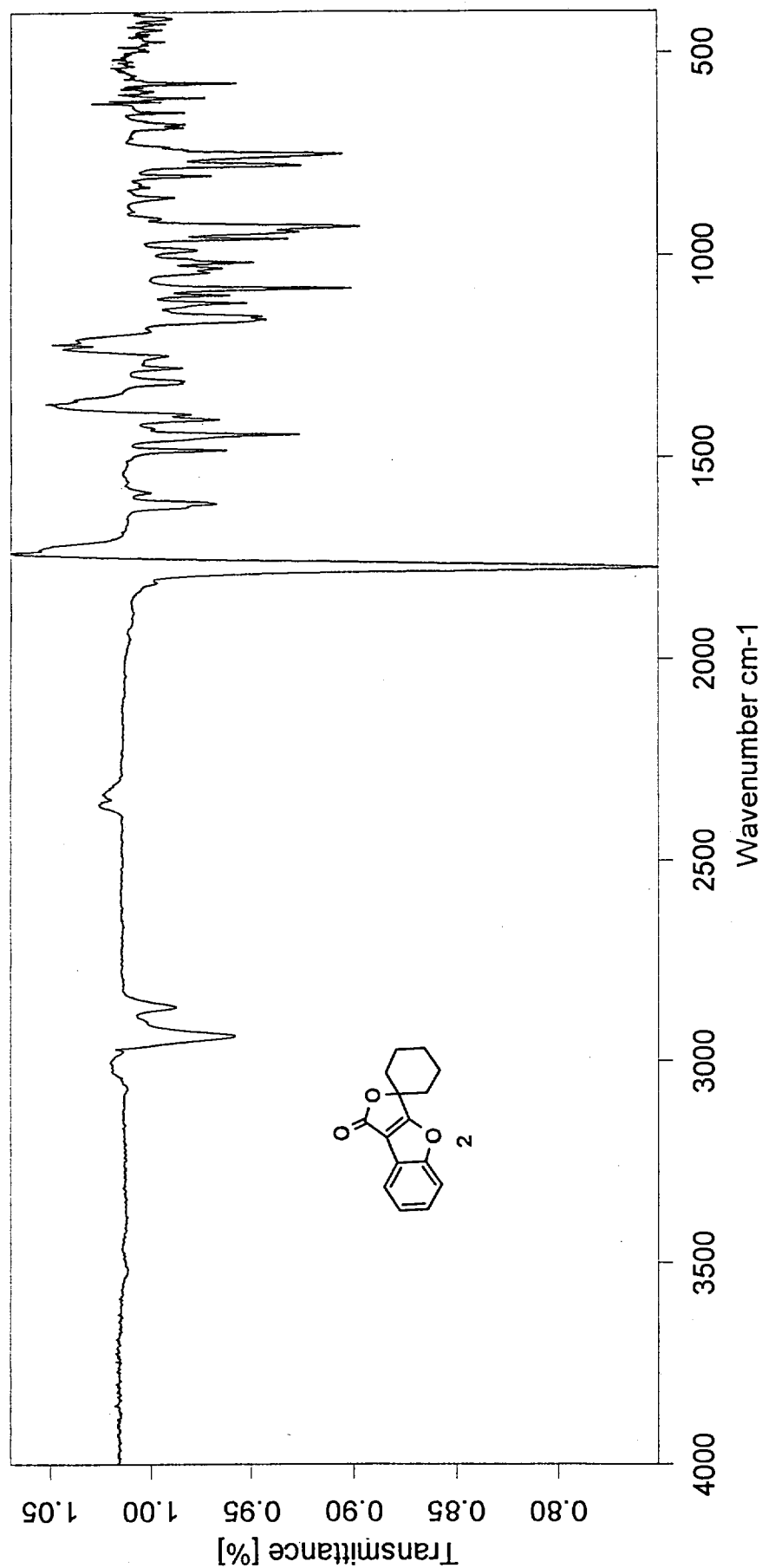




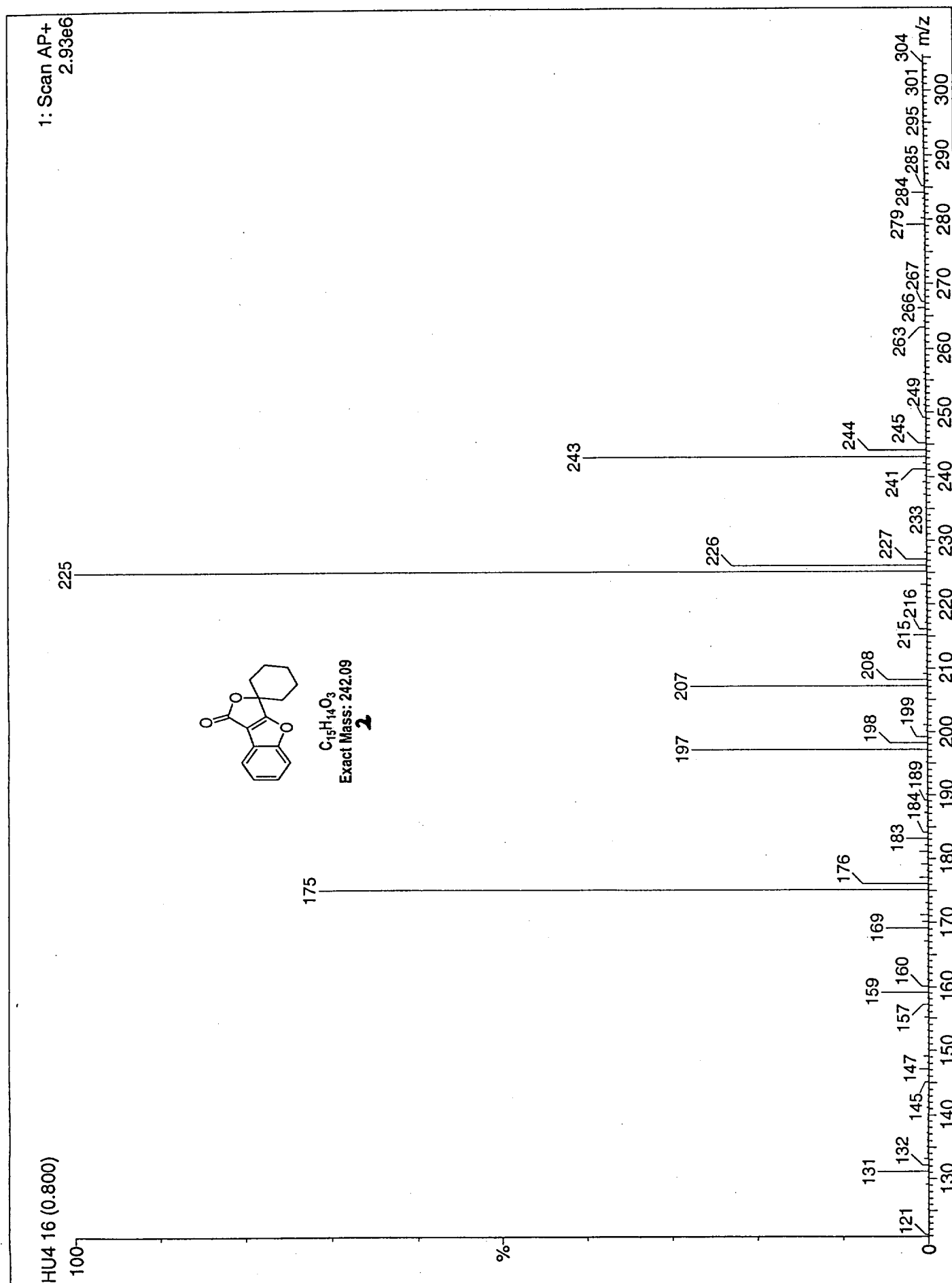
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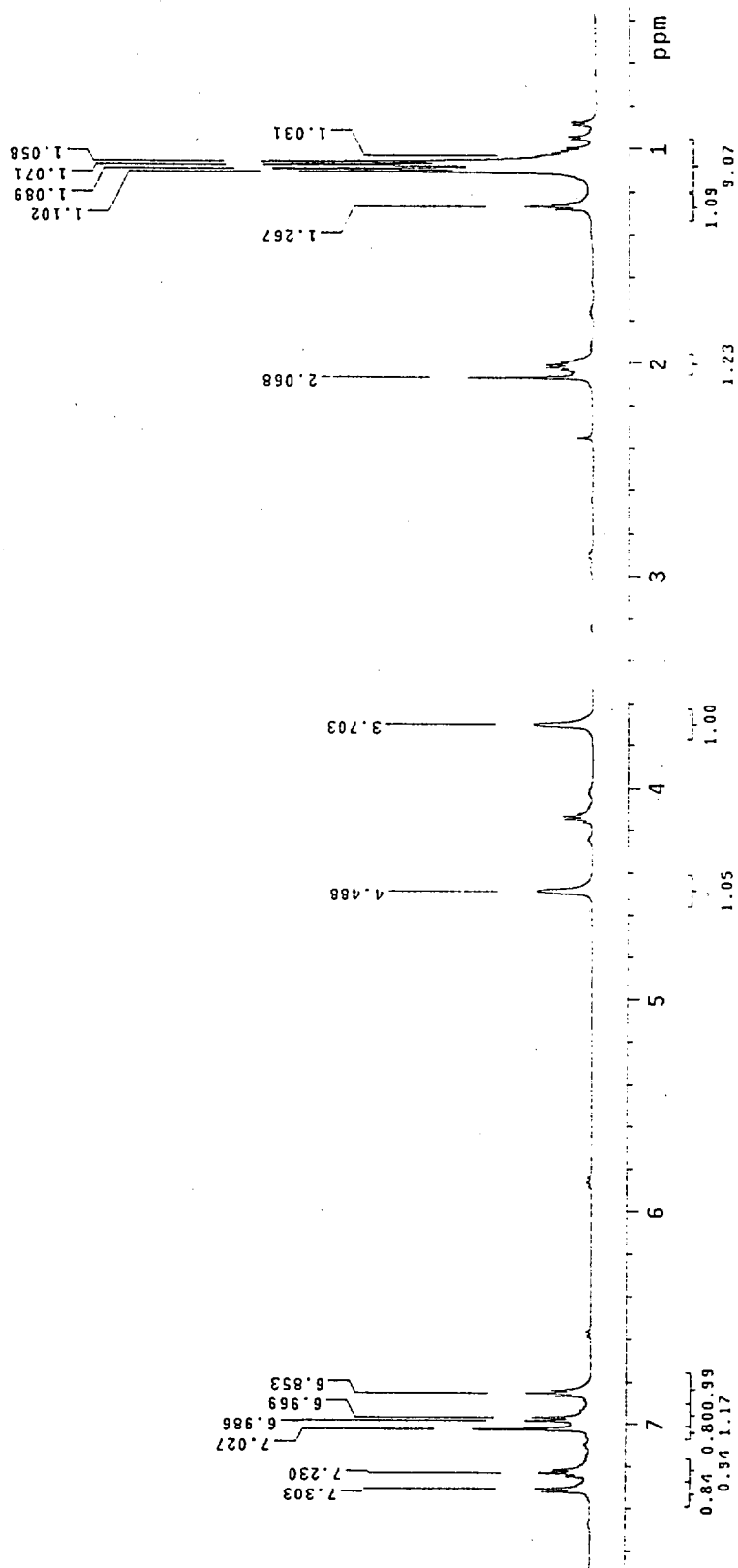
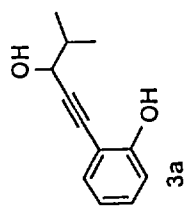
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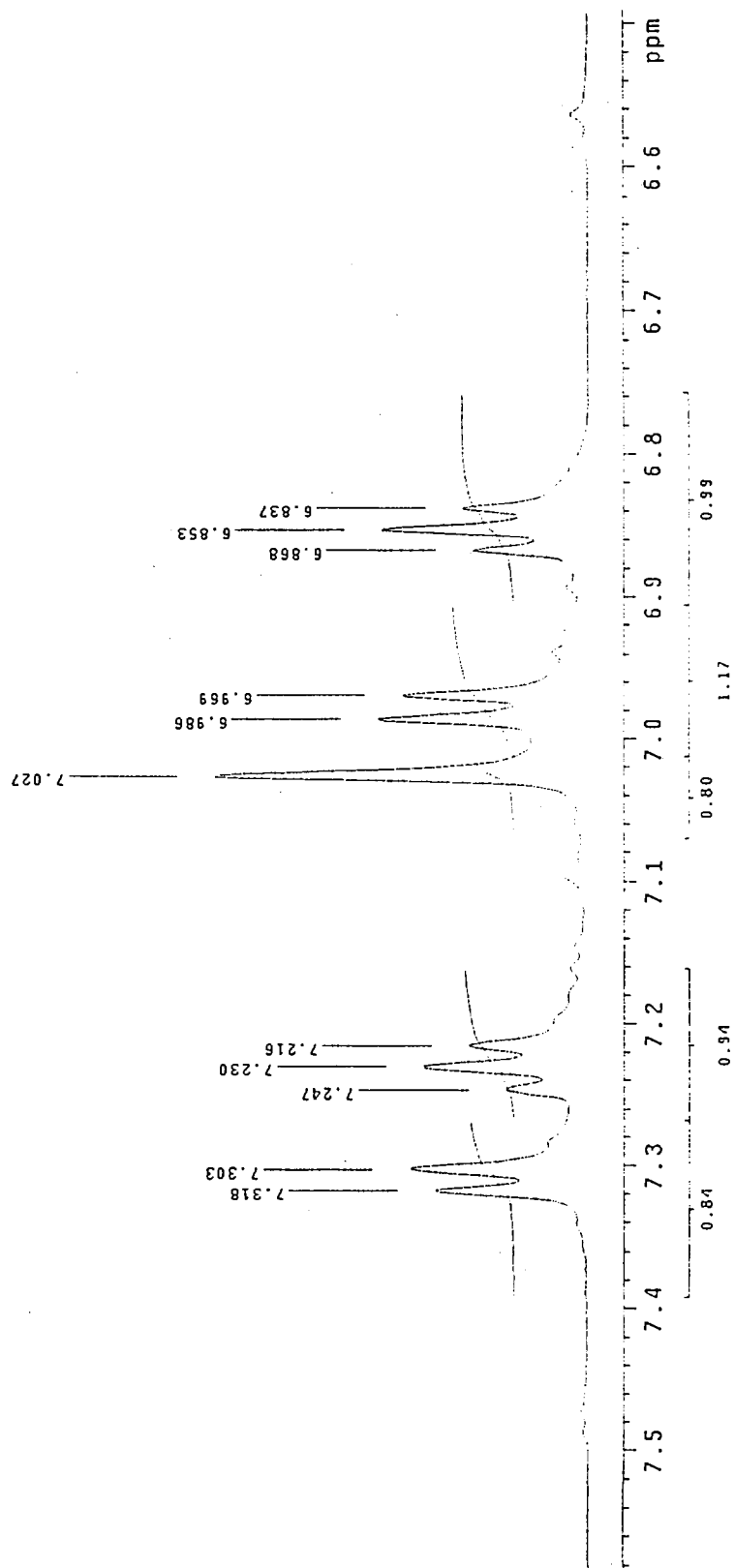
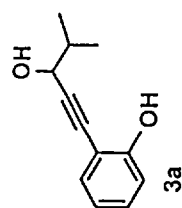


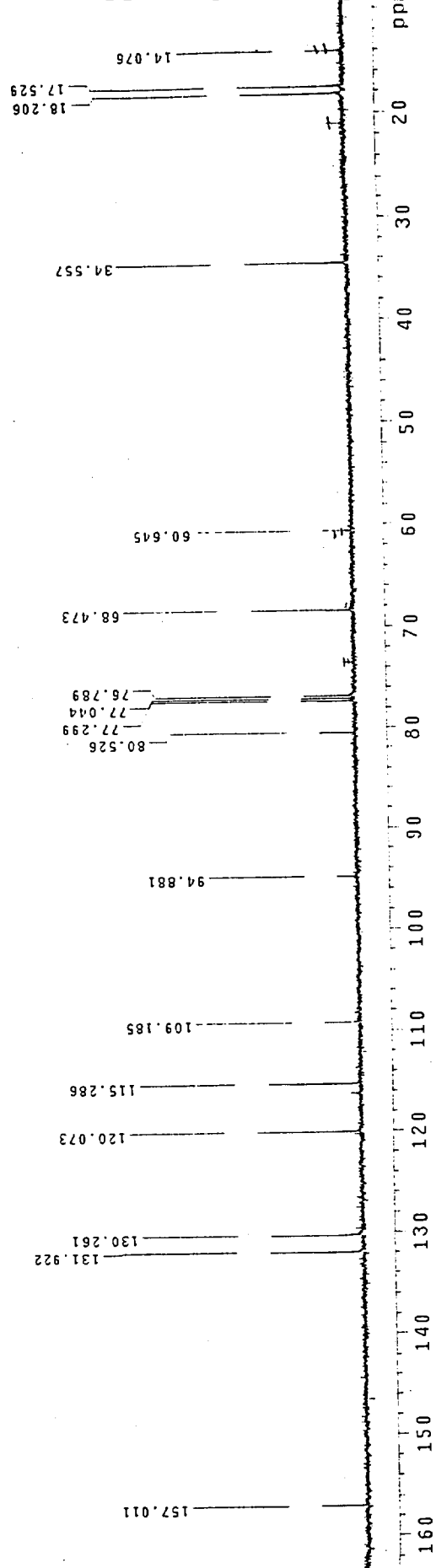
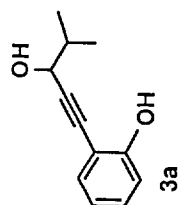
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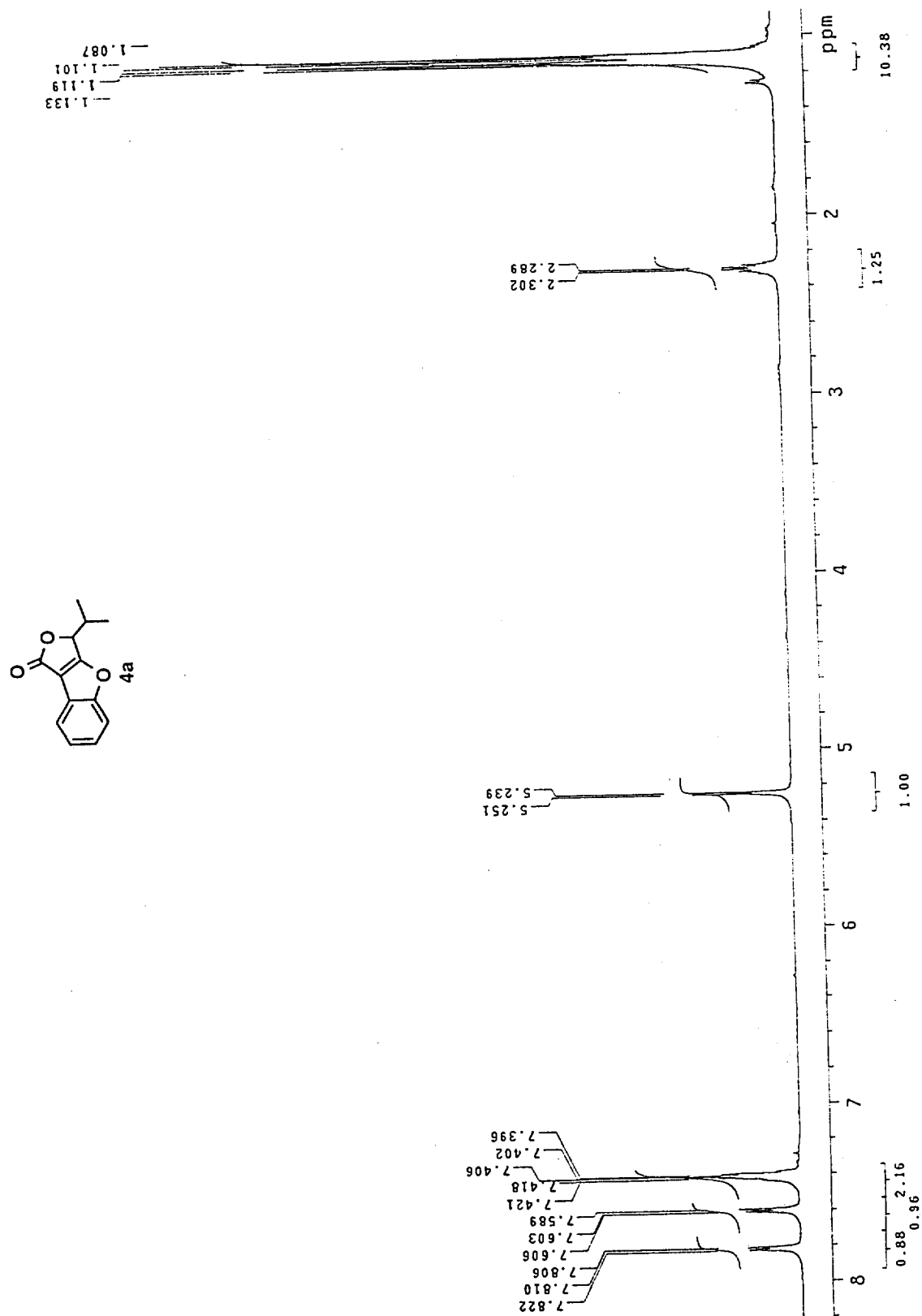


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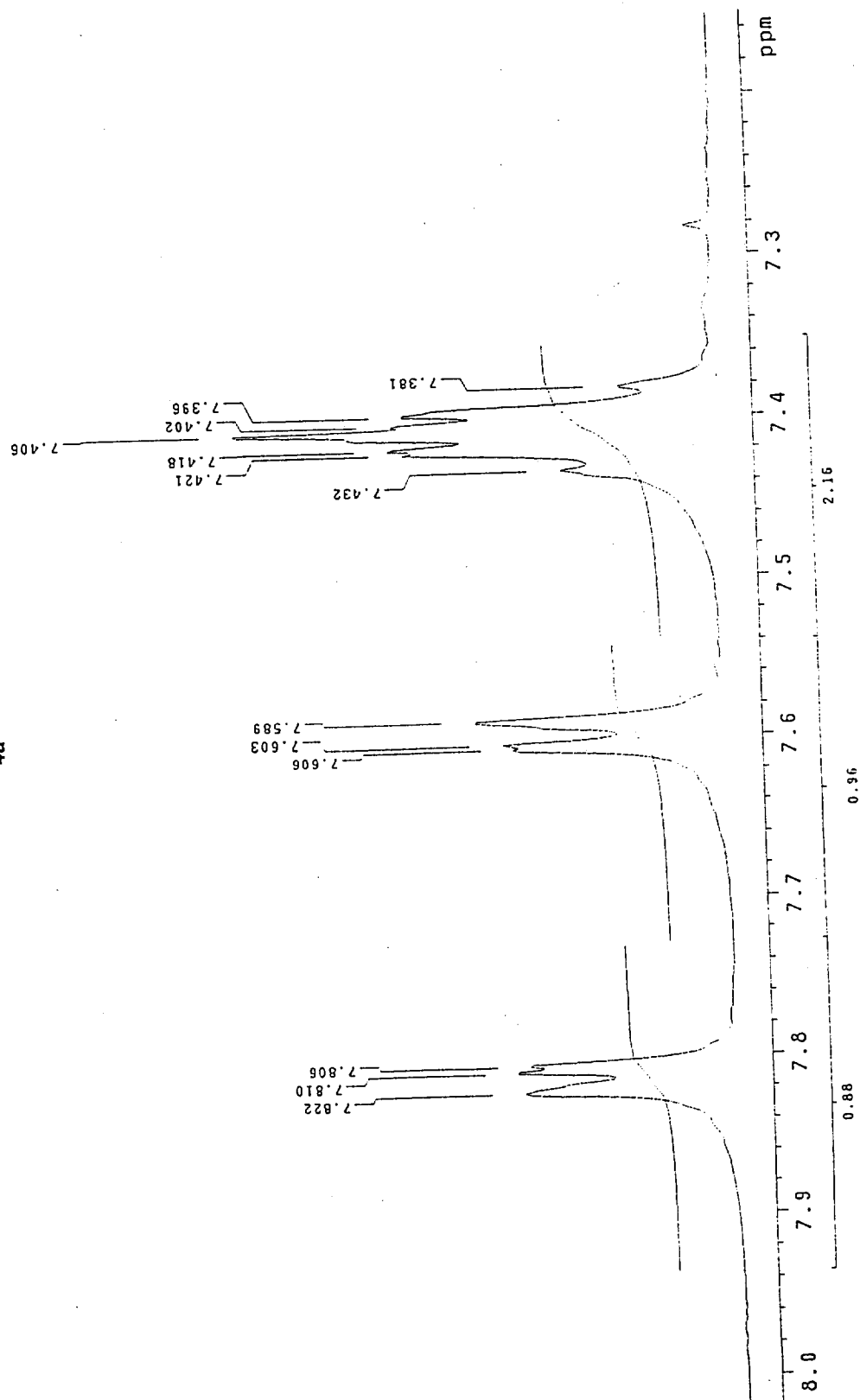
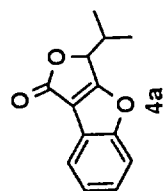




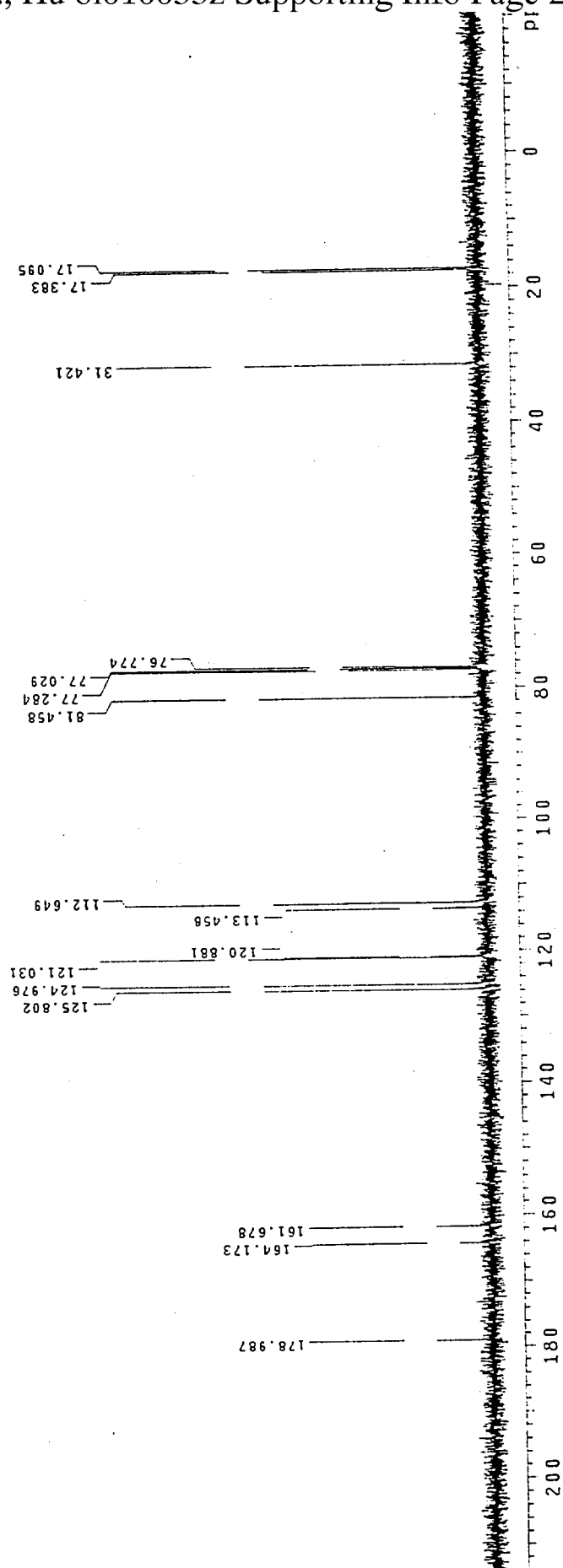
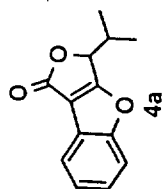
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13

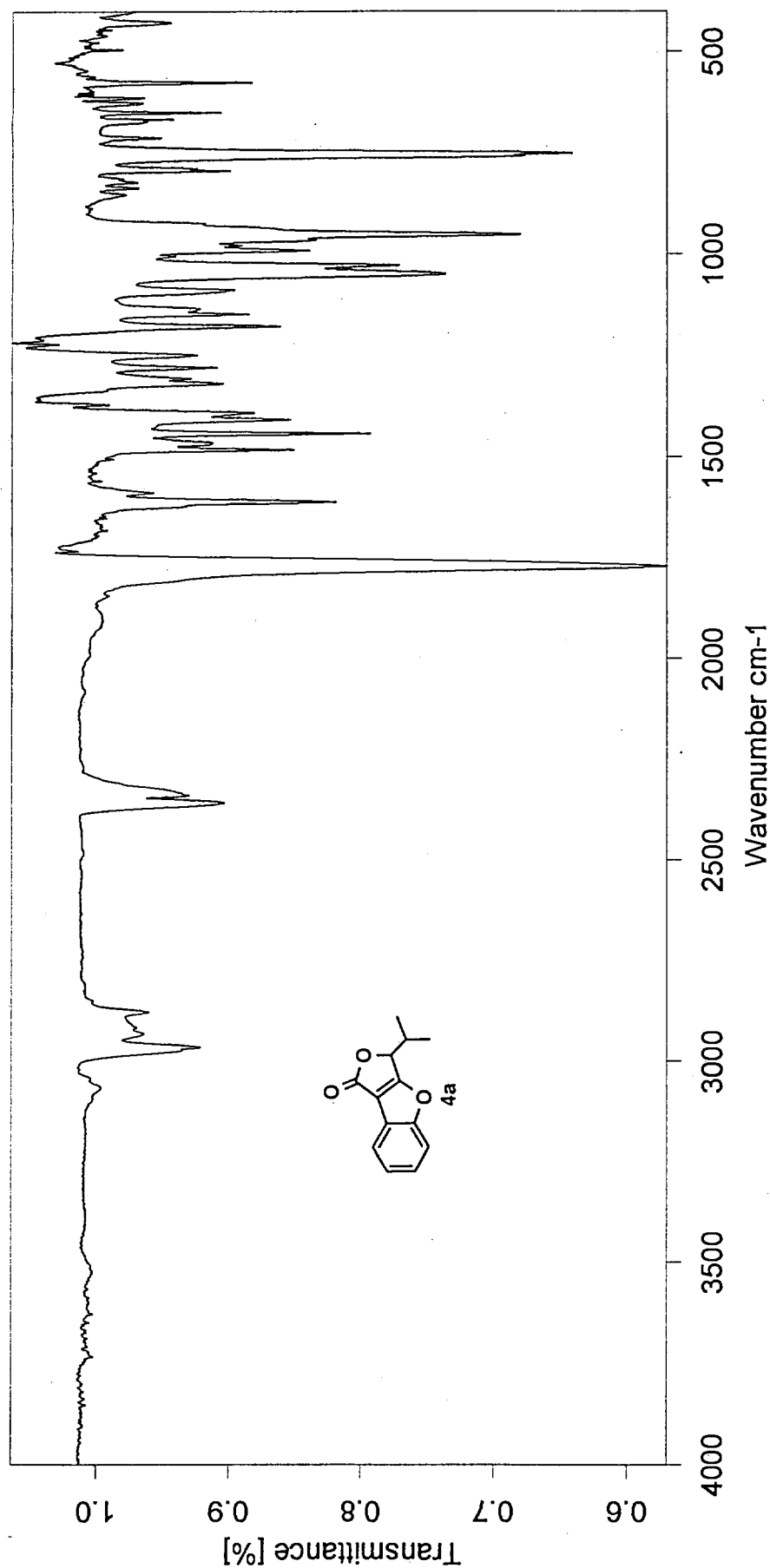


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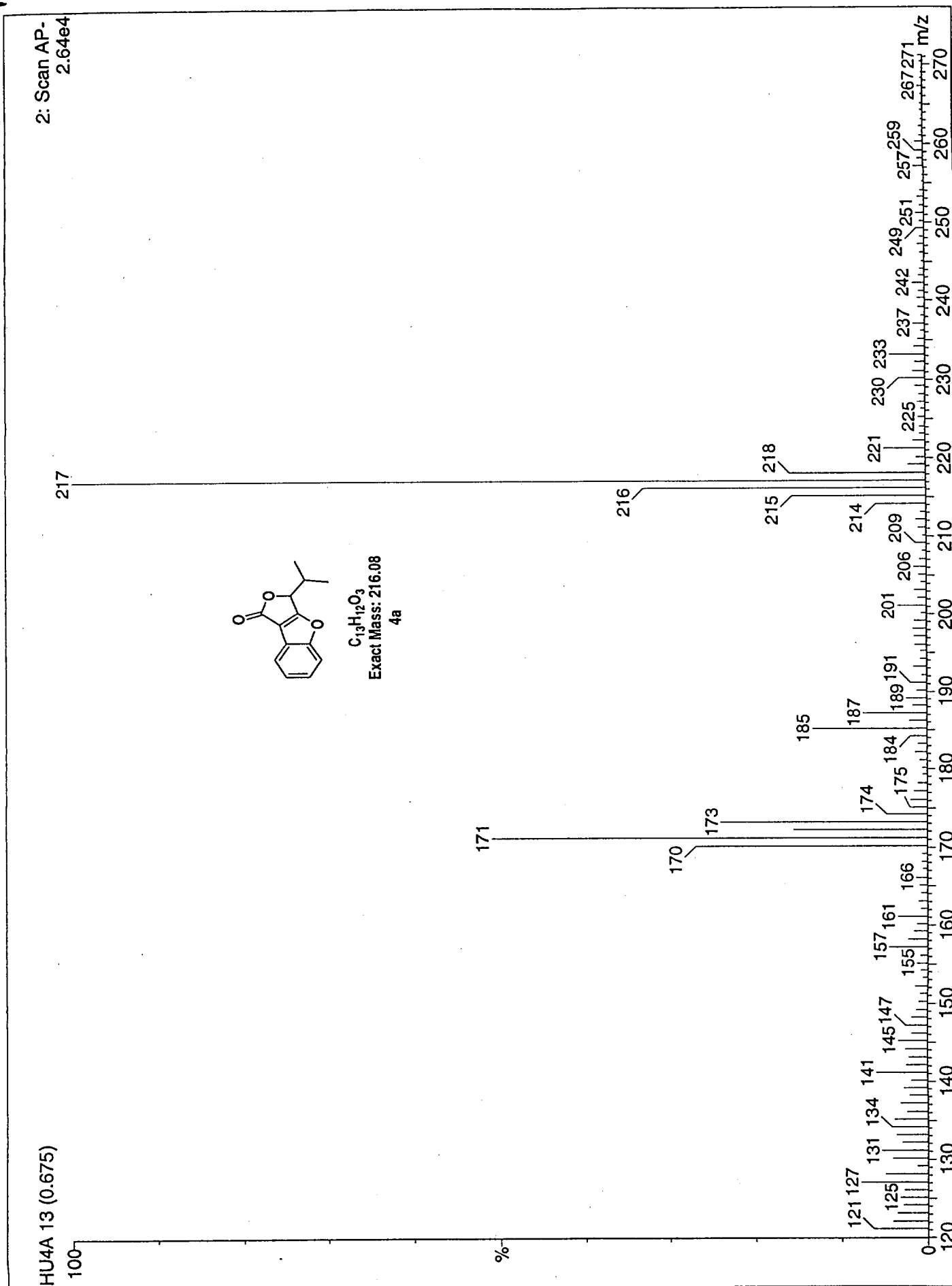


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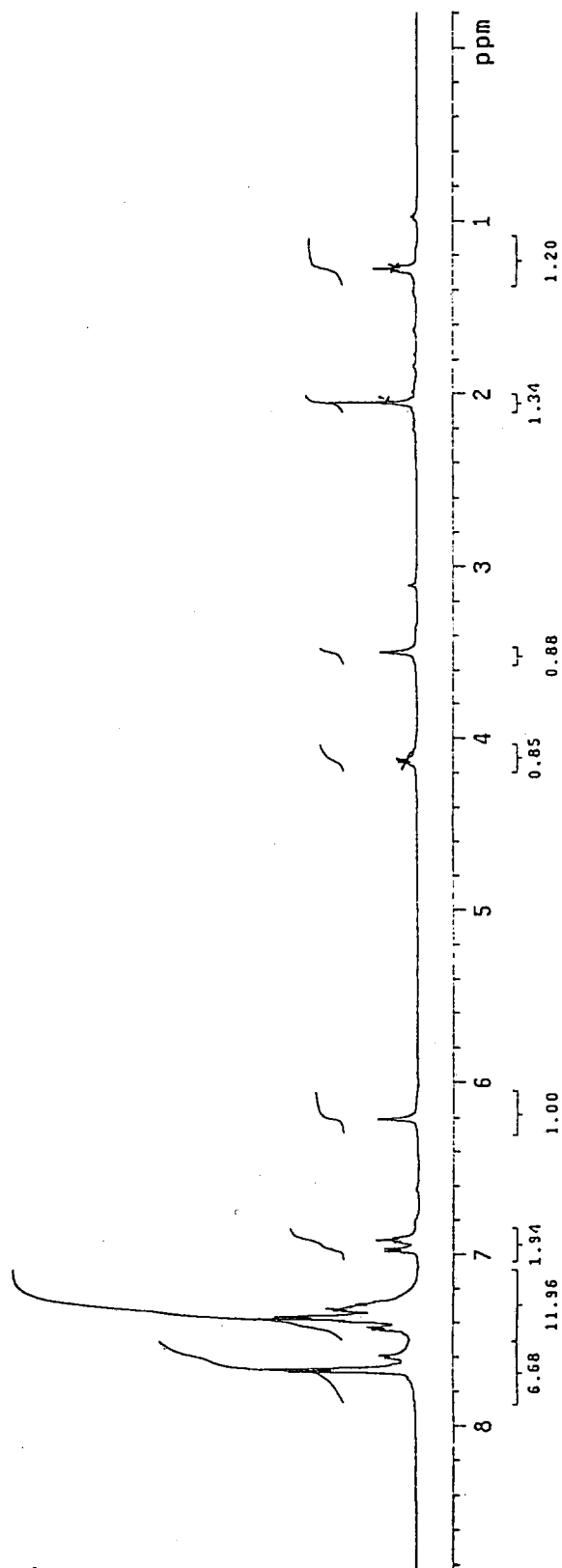
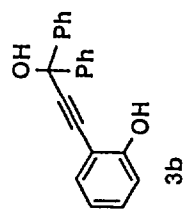
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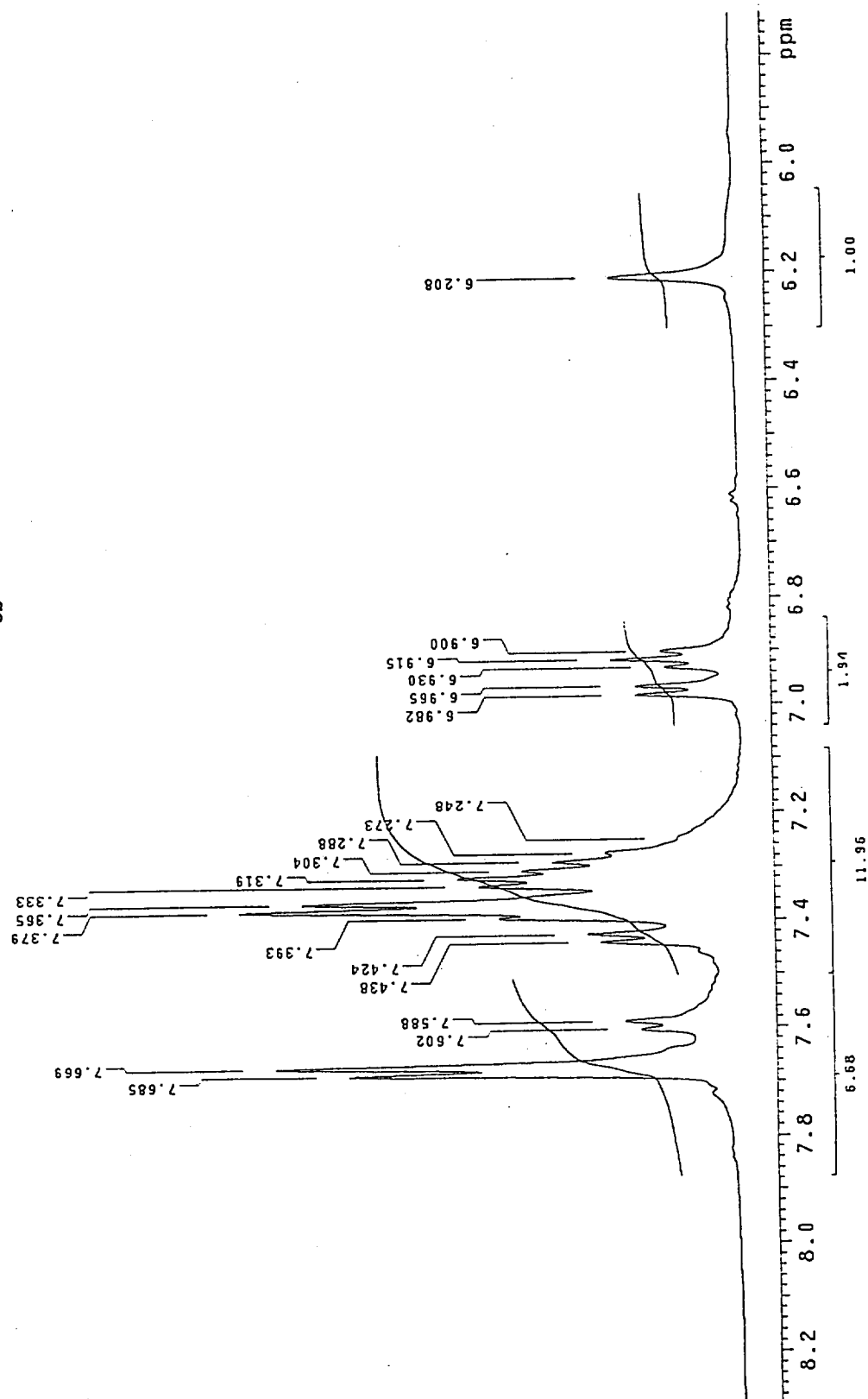
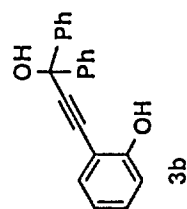
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Number of Scans 32	Result Spectrum Transmittance



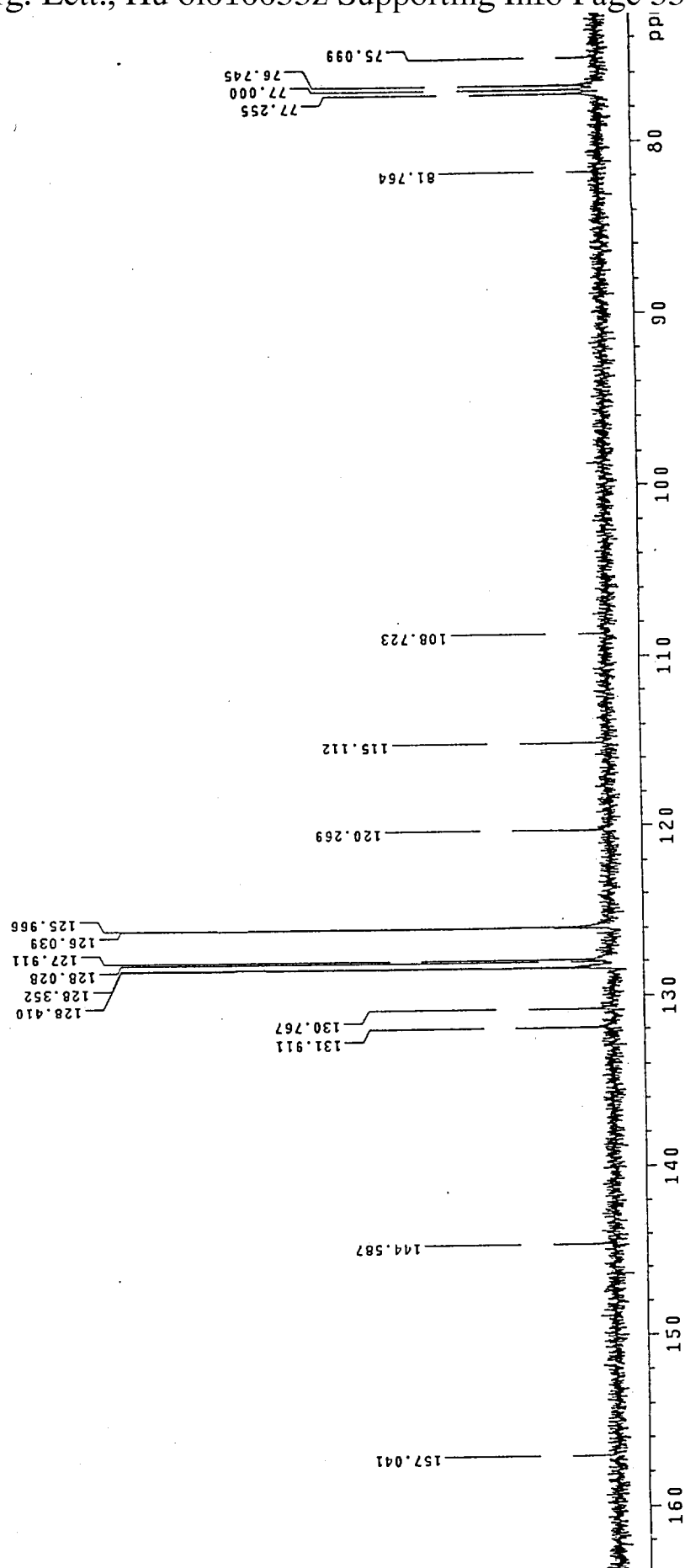
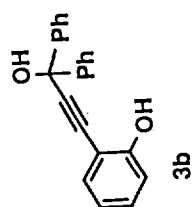
17



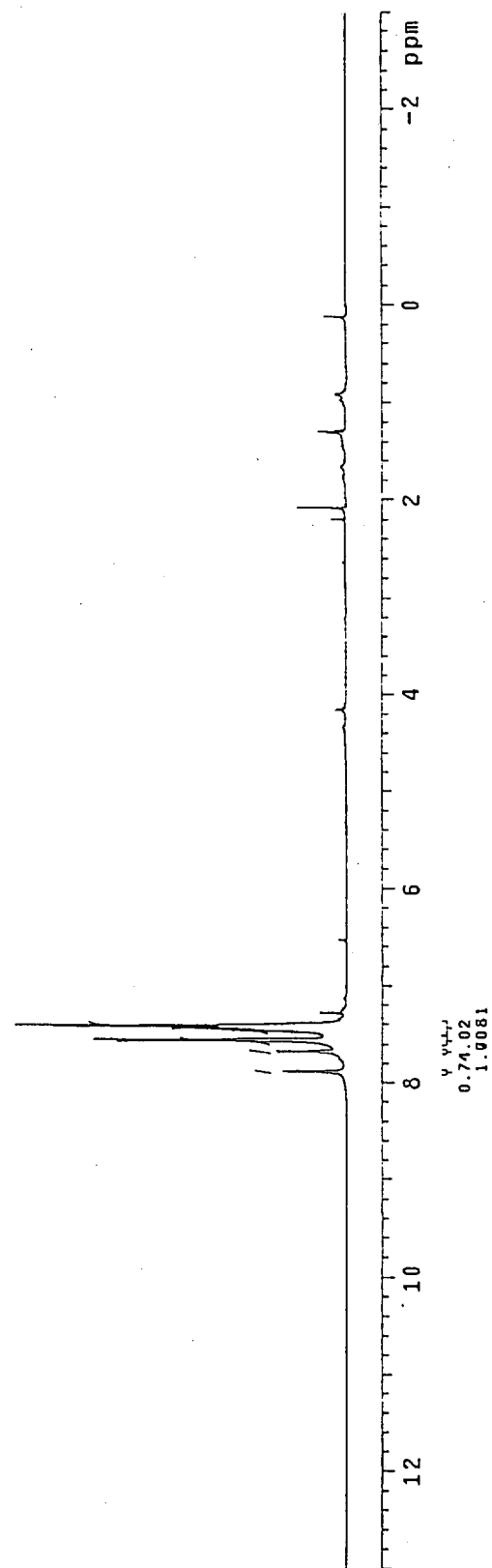
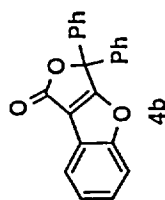
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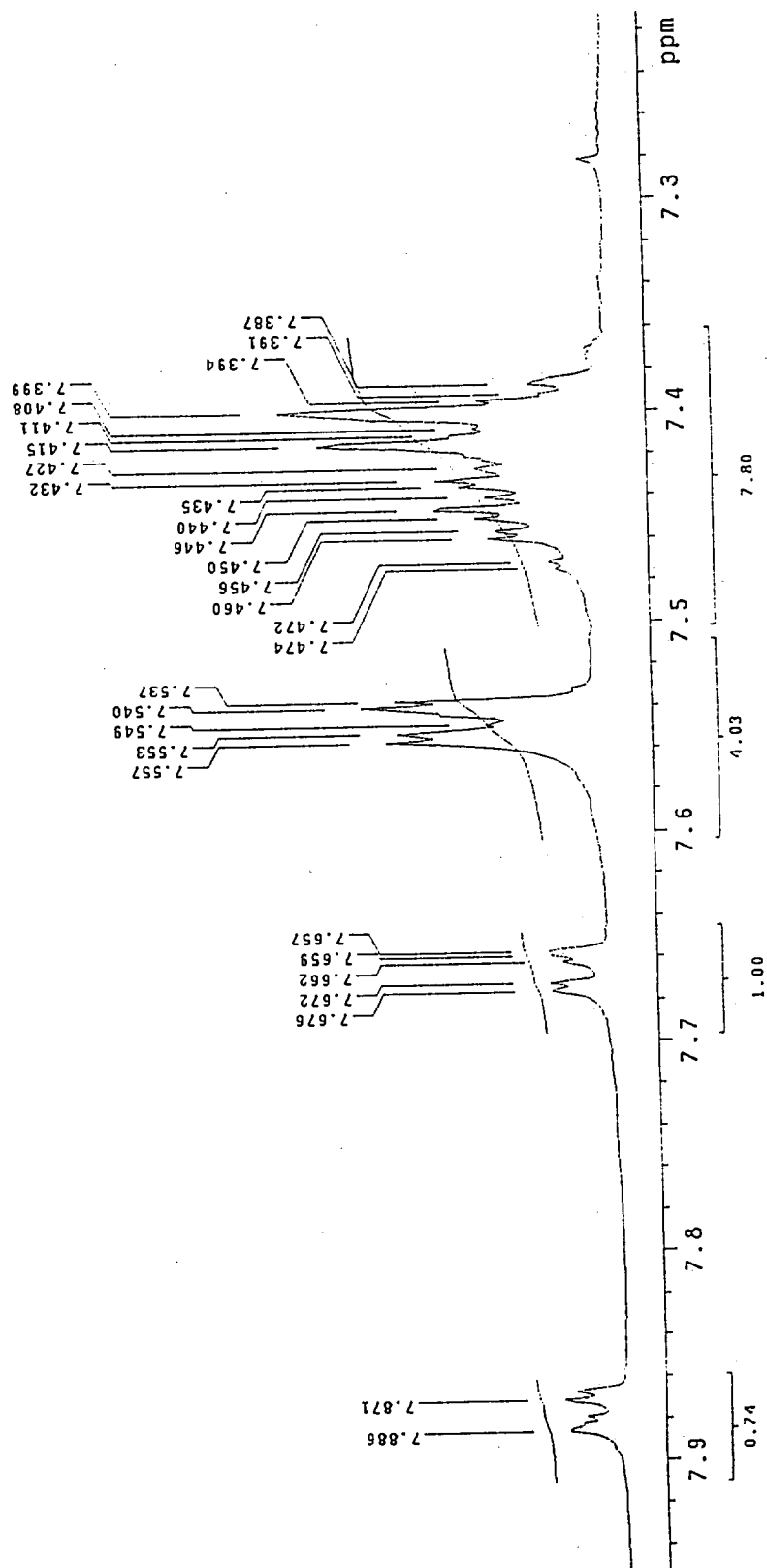
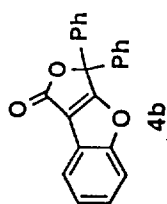
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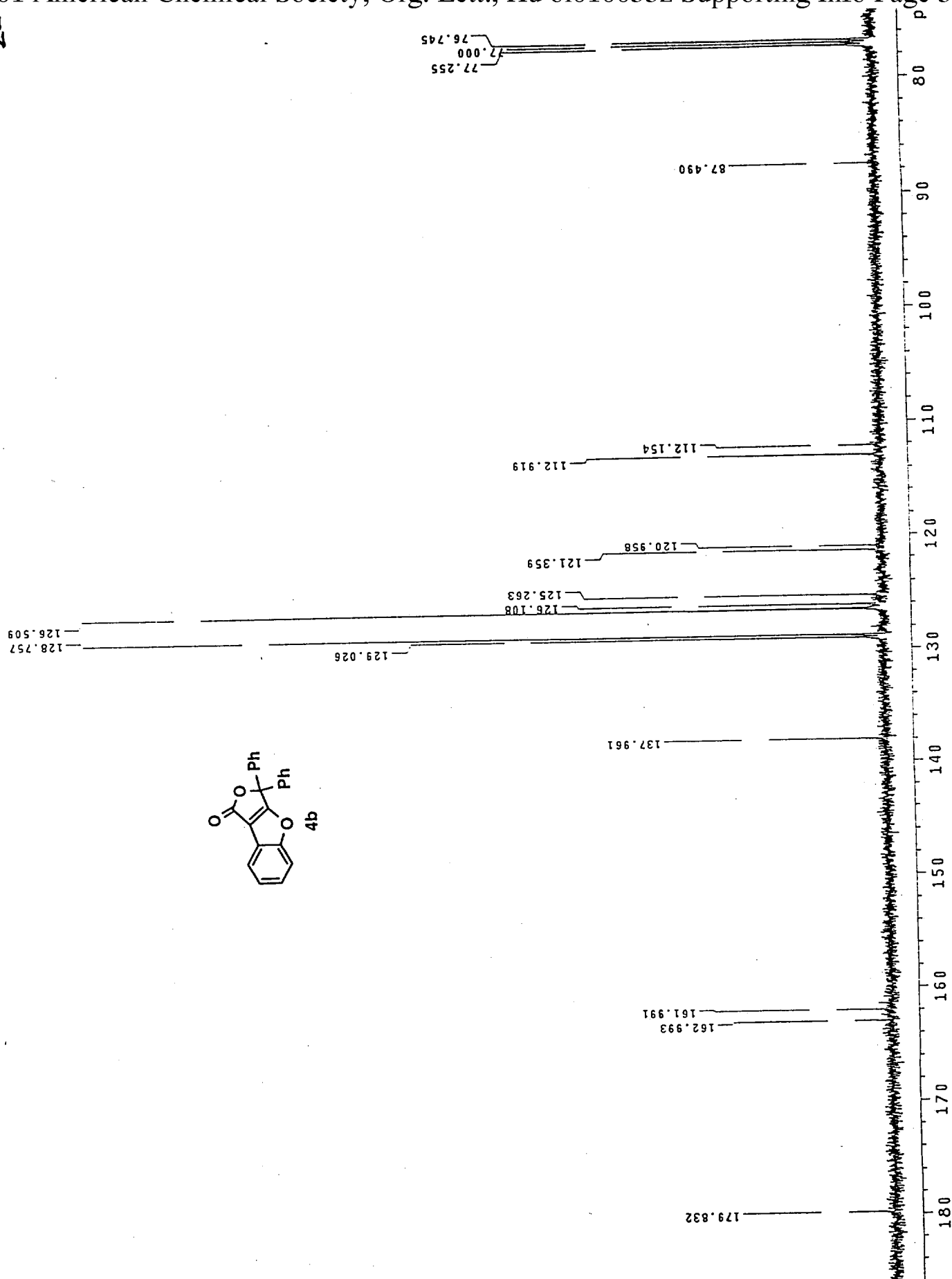
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21

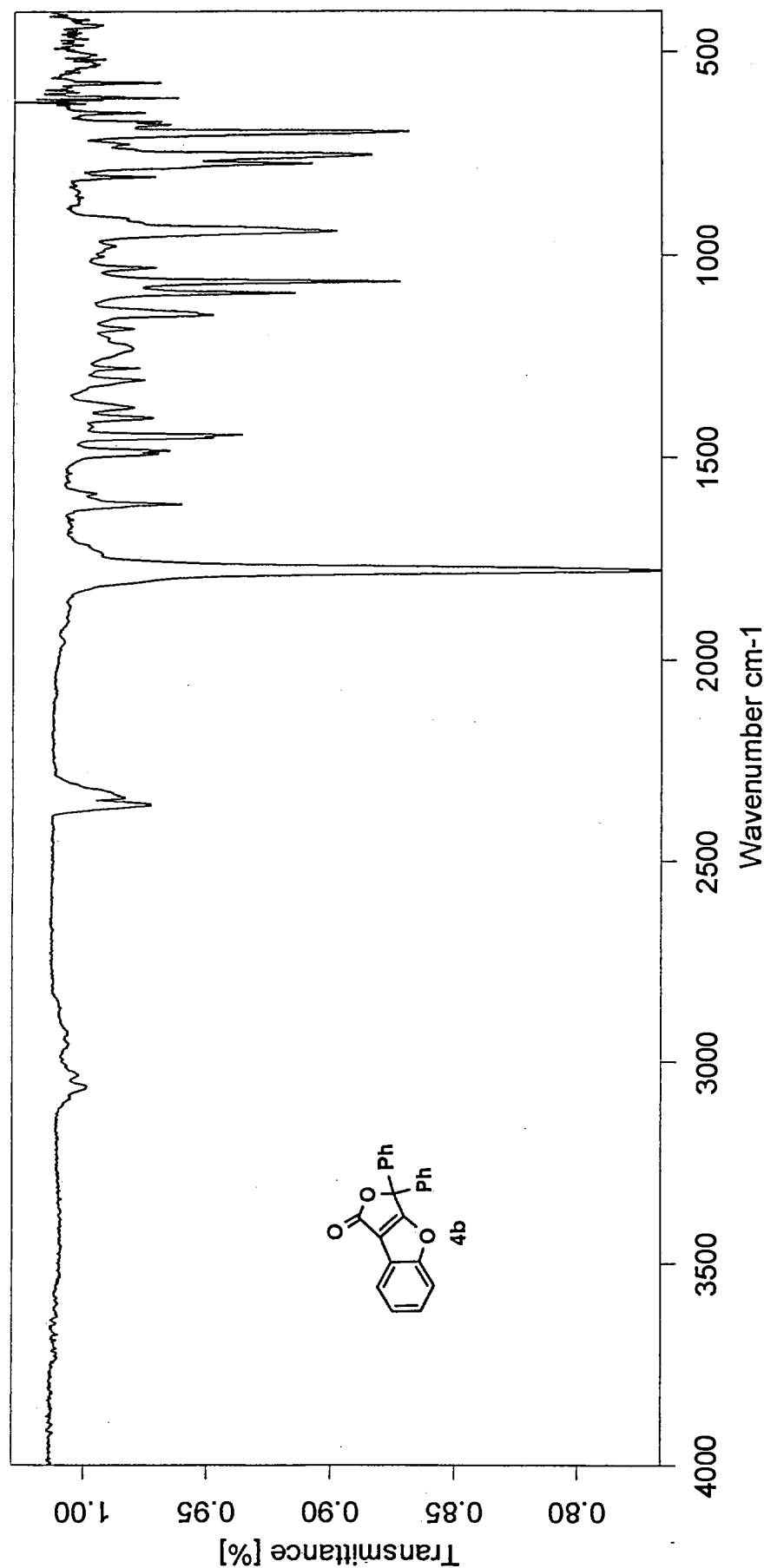


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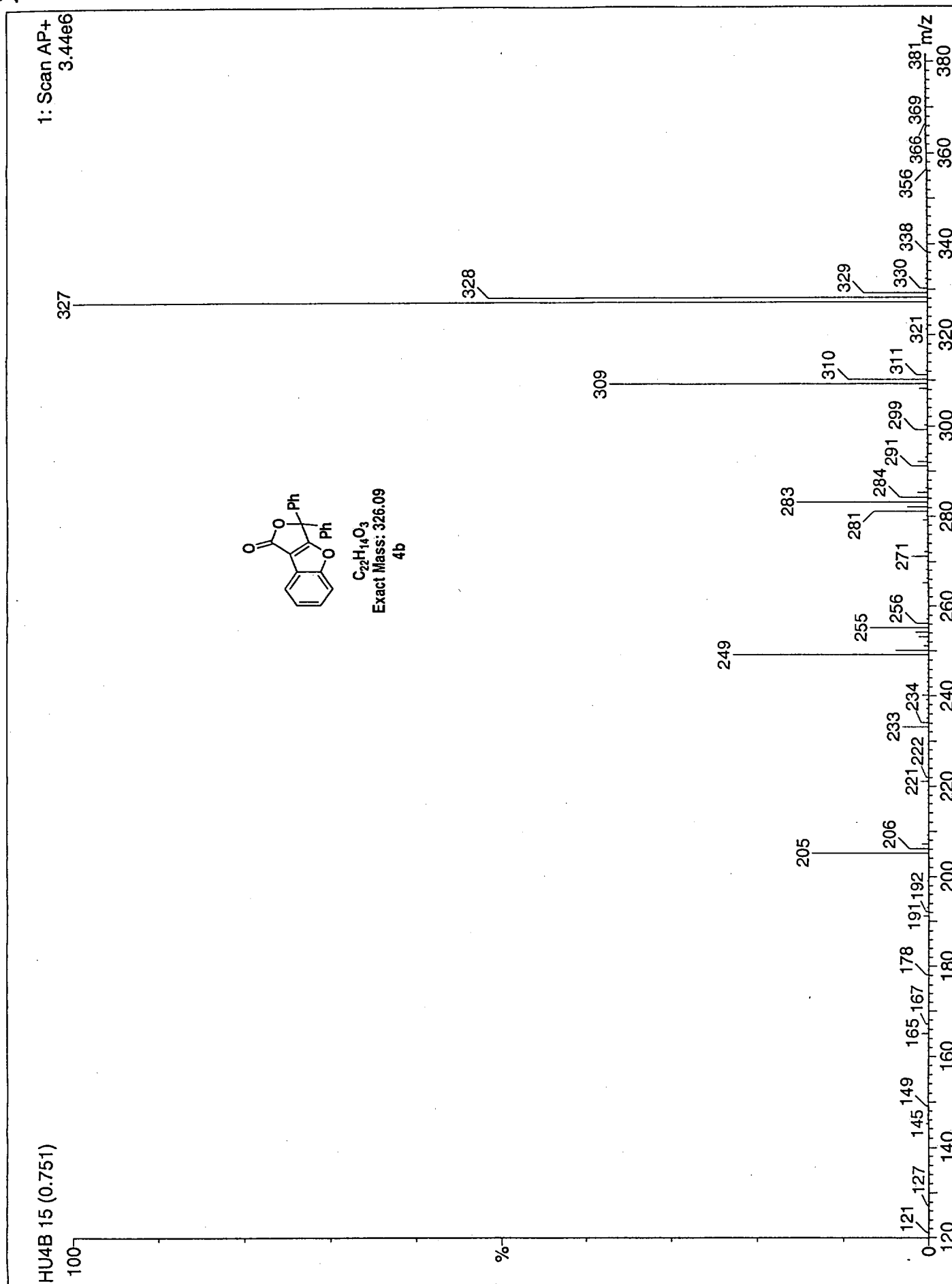


C:\OPUS_NT\HU4B.0

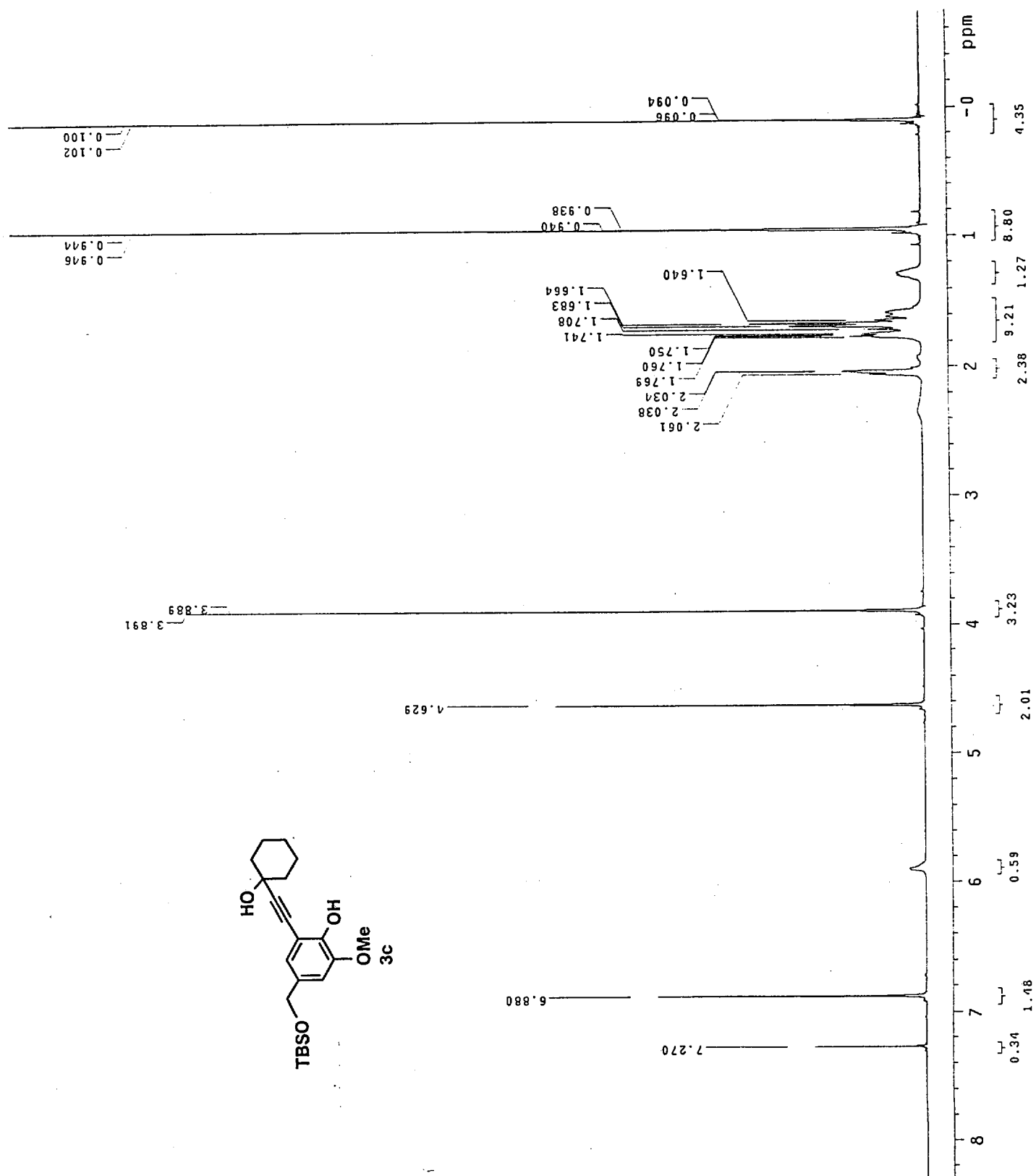
2/16/01 04:52:34



Filename HU4B.0	Date of Measurement 16/02/2001
Path of File C:\OPUS_NT\HU	Sample Name lactone
Number of Scans 32	Result Spectrum Transmittance



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