

### Experimental Section

p-Bromanil was supplied by Lancaster. Solutions were evaporated under reduced pressure with a rotary evaporator. Flash chromatography was performed using silica gel (EM 60, 230-400 mesh). A Rainin Dynamax SD200 instrument was used for preparative reverse phase HPLC (0.1% TFA/CH<sub>3</sub>CN and 0.1% TFA/H<sub>2</sub>O were used as eluants, 12 mL/min flow rate). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 300 MHz.

2-[2-(3-methylbutyl)indol-3-yl]-3,5,6-tribromocyclohexa-2,5-diene-1,4-dione (**7a**): A mixture of 2-(3-methyl-n-butyl) indole (**4**) (0.044 g, 0.236 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.154 g, 0.472 mmol), p-bromanil (**3**) (0.100 g, 0.236 mmol), and CH<sub>3</sub>CN (2 ml) was stirred at room temperature for 3.5 hours. Following filtration of the mixture, the residue was purified by prep thin layer chromatography (20% EtOAc/hexane) to afford **7a** (0.103 g, 82%) as a blue crystalline solid: m.p. 184.4-185.7 °C; <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>): δ=8.34 (s, 1H), 7.34 (m, 1H), 7.15 (m, 3H), 2.61 (t, 2H, J=7.6 Hz), 1.56 (m, 3H), 0.88 (d, 6H, J=6.1 Hz); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ=174.8, 171.9, 144.2, 143.9, 141.1, 140.4, 138.5, 135.7, 134.7, 126.7, 122.6, 121.0, 120.2, 111.3, 38.4, 28.2, 26.3, 22.6; EI MS m/z 527, 529, 531, 533.

2,5-bis[2-(3-methylbutyl)indol-3-yl]-3,6-dibromocyclohexa-2,5-diene-1,4-dione (**7**) and 2,6-bis[2-(3-methylbutyl)indol-3-yl]-3,5-dibromocyclohexa-2,5-diene-1,4-dione (**8**): A mixture of 2-(3-methyl-n-butyl) indole (**4**) (30.0 g, 160 mmol), Cs<sub>2</sub>CO<sub>3</sub> (62.6 g, 192 mmol), p-bromanil (**3**) (27.2 g, 64 mmol), and CH<sub>3</sub>CN (64 ml) was stirred at room temperature for 20 hours. Following dilution with 0.5N HCl (500 ml), the crude mixture was extracted with EtOAc (1 L). The organic layer was washed with brine (400 ml) and dried with Na<sub>2</sub>SO<sub>4</sub>. Purification of the residue by flash chromatography (30% EtOAc/hexane) yielded a 1:1 mixture of **7** and **8** (36.3 g, 90%) as a blue crystalline solid.<sup>1</sup> In order to obtain spectral data of the regioisomers **7** and **8**, a small amount of the mixture

was further purified by flash chromatography (15% EtOAc/hexanes) to separate the isomers. **7**<sup>2</sup>: blue crystalline solid; m.p. 204.7-205.8 °C; <sup>1</sup>H NMR(300 MHz, DMSO-d<sub>6</sub>): δ=11.49 (major isomer) (s, 2H), 11.48 (minor isomer) (s, 2H), 7.37-6.98 (m, 8H), 2.68-2.59 (m, 4H), 1.63-1.42 (m, 6H), 0.88 (minor isomer) (d, 12H, *J*=6.6 Hz), 0.83 (major isomer) (d, 12H, *J*=5.9 Hz); <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>): δ=177.2, 143.6, 141.1, 140.9, 136.0 (major isomer), 135.9 (minor isomer), 126.9, 121.2, 120.1, 119.6, 111.5, 106.7 (major isomer), 106.6 (minor isomer), 38.1, 27.4 (minor isomer), 27.3 (major isomer), 25.6, 22.5 (minor isomer), 22.4 (major isomer); MS m/z (positive electrospray) 635, 637, 639; elemental analysis calcd for C<sub>32</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (636.43): C 60.39, H 5.07, Br 25.11, N 4.40; found: C 60.31, H 5.19, Br 25.72, N 4.35. **8**<sup>3</sup> <sup>1</sup>H NMR(300 MHz, DMSO-d<sub>6</sub>): δ=11.41 (s, 2H), 7.35-6.93 (m, 8H), 2.64-2.57 (m, 4H), 1.58-1.45 (m, 6H), 0.84 (one isomer) (d, 12H, *J*=5.6 Hz), 0.83 (one isomer) (d, 12H, *J*=5.9 Hz); <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>): δ=180.0, 173.3, 143.5, 140.3 (one isomer), 140.0 (one isomer), 135.3, 134.1, 126.3, 120.4, 119.2, 118.8, 110.7, 106.0, 37.4, 26.8, 25.0, 21.8; MS m/z (positive electrospray) 635, 637, 639; elemental analysis calcd for C<sub>32</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub> (636.43): C 60.39, H 5.07, Br 25.11, N 4.40; found: C 60.64, H 5.43, Br 24.78, N 4.28.

2,5-bis[2-(3-methylbutyl)indol-3-yl]-3,6-dihydroxycyclohexa-2,5-diene-1,4-dione (**2**): To a stirred solution of a 1:1 mixture of **7** and **8** (42.3 g, 66.4 mmol) in EtOH (166 ml), and THF (166 ml) was added 4N KOH. After heating at 85 °C for 10 h, the mixture was diluted with 1N HCl (500 ml) and extracted with EtOAc (1L). The organic layer was washed with brine (250 ml) and dried with sodium sulfate. HPLC purification provided pure **2**<sup>4,5</sup> (8.78 g, 52% based on **7**) as a reddish-purple crystalline solid: m.p. 229.8-230.3 °C; <sup>1</sup>H NMR(300 MHz, DMSO-d<sub>6</sub>): δ=11.05 (s, 2H), 10.61 (br s, 2H), 7.31-6.89 (m, 8H), 2.65-2.56 (m, 4H), 1.60-1.43 (m, 6H), 0.88 (minor isomer) (d, 12H, *J*=5.5

Hz), 0.83 (major isomer) (d, 12H,  $J=6.0$  Hz);  $^{13}\text{C}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta=139.8$  (major isomer), 139.6 (minor isomer), 135.5, 135.4, 127.5, 121.6, 120.0 (major isomer), 119.8 (minor isomer), 119.6, 119.5, 110.6, 38.0, 27.9 (minor isomer), 27.8 (major isomer), 25.6, 22.4 (major isomer), 22.2 (minor isomer); MS  $m/z$  (positive electrospray) 511; FAB HRMS  $[M + 1]$   $m/z$  511.2593, calcd for  $\text{C}_{32}\text{H}_{35}\text{N}_2\text{O}_4$  511.2597. The compound exists as a multiple hydrate, complicating the elemental analysis. The  $^1\text{H}$  NMR spectrum and an HPLC chromatogram of **2** have been included to indicate purity.

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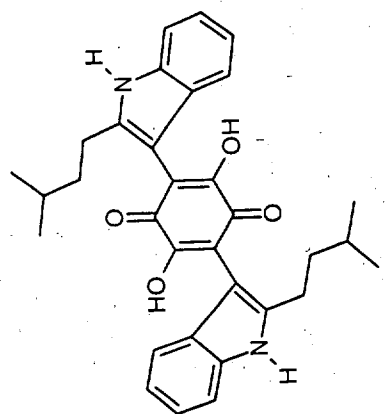
(1) The yields of **7** and **8** were based on HPLC analysis of the mixture. The HPLC chromatogram indicated that 10% of the mixture consisted of unidentified impurities.

(2) Compound **7** consists of two rotational isomers in a 1.5:1 ratio.

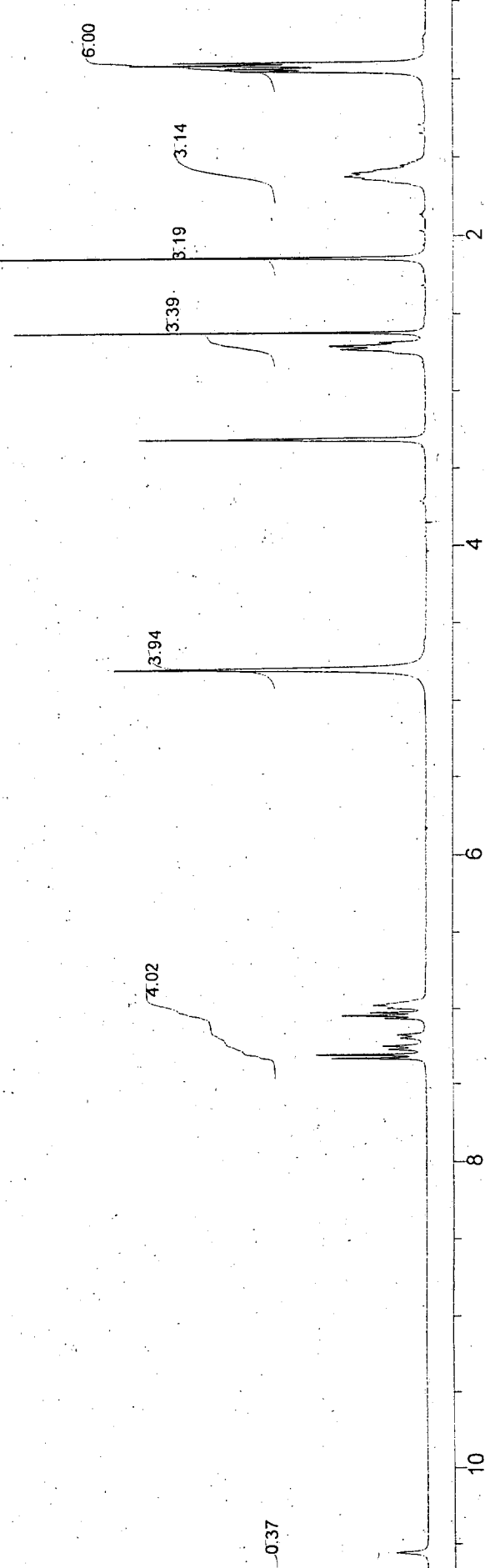
(3) Compound **8** consists of two rotational isomers in a 1:1 ratio.

(4) Compound **2** consists of two rotational isomers in a 1.3:1 ratio.

(5) The crude quinone can be bis-acetylated, purified by flash chromatography, hydrolyzed under acidic conditions, and subjected to acid/base extraction to provide **2** in >95% pure form without HPLC purification.



2



DH-CMPD-2 IN MEOH

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PD: 2.0 sec

OF1: 1423.5

NA: 16

LB: 0.2

PTSId: 16384

USER: JIF

DATE: 12FE 4

WinNuts - \$Nfe12.001

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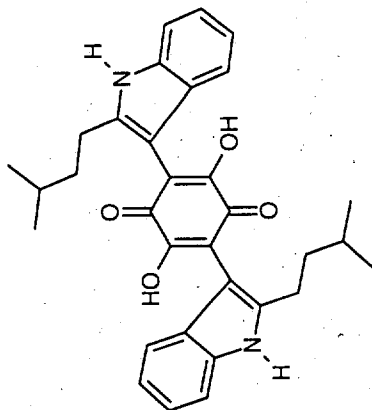
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REL. HT  
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Interpolated Peak Listing

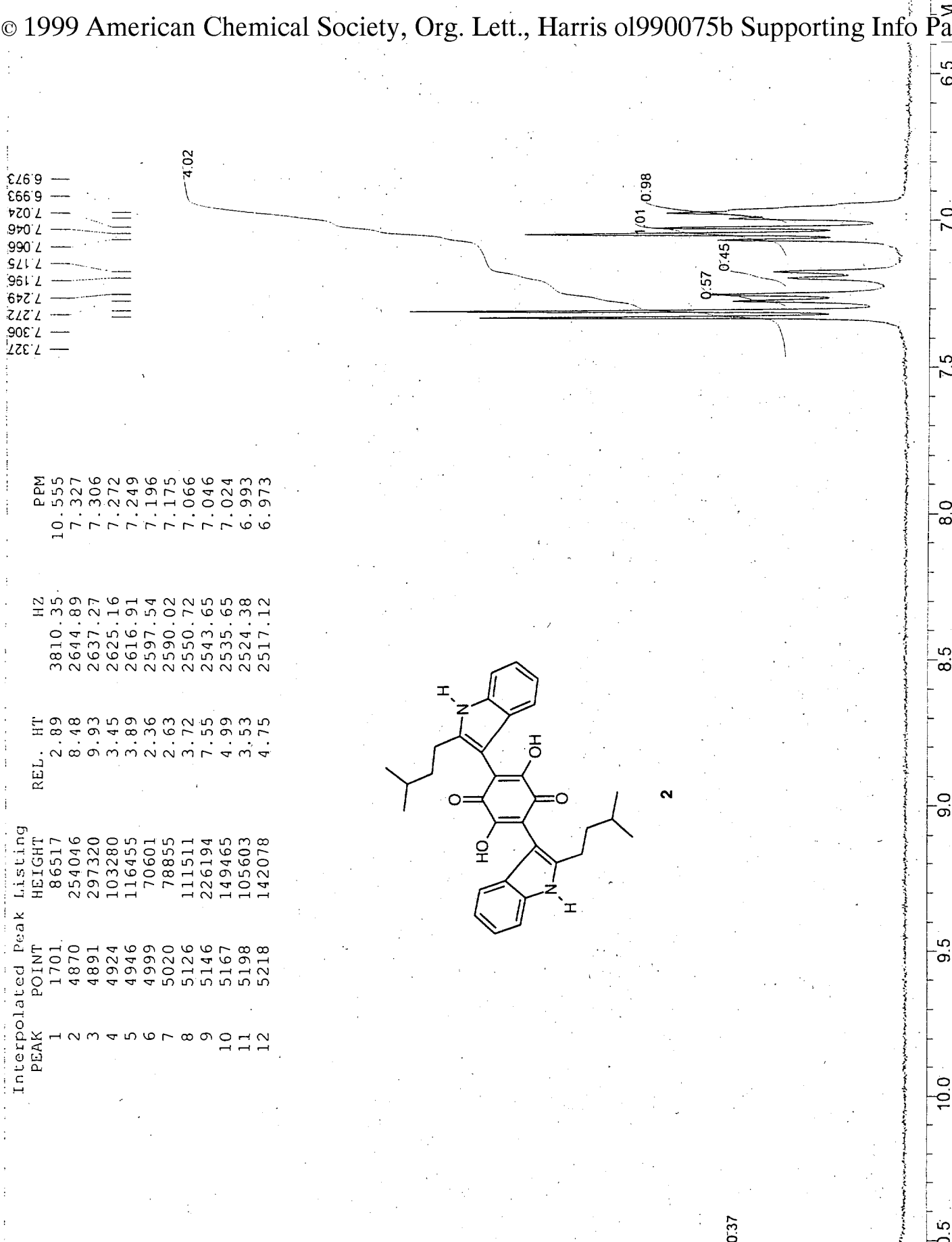
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5	4946	116455	3.89
6	4999	70601	2.36
7	5020	78855	2.63
8	5126	111511	3.72
9	5146	226194	7.55
10	5167	149465	4.99
11	5198	105603	3.53
12	5218	142078	4.75



2

10.555

5



DH-CMPD-2 IN MEOH

EX: 1PULS  
F1: 360.993  
F2: 200.000

SWI: 6024  
PW: 16.0 usec

PD: 2.0 sec

OFI: 1423.5  
NA: 16

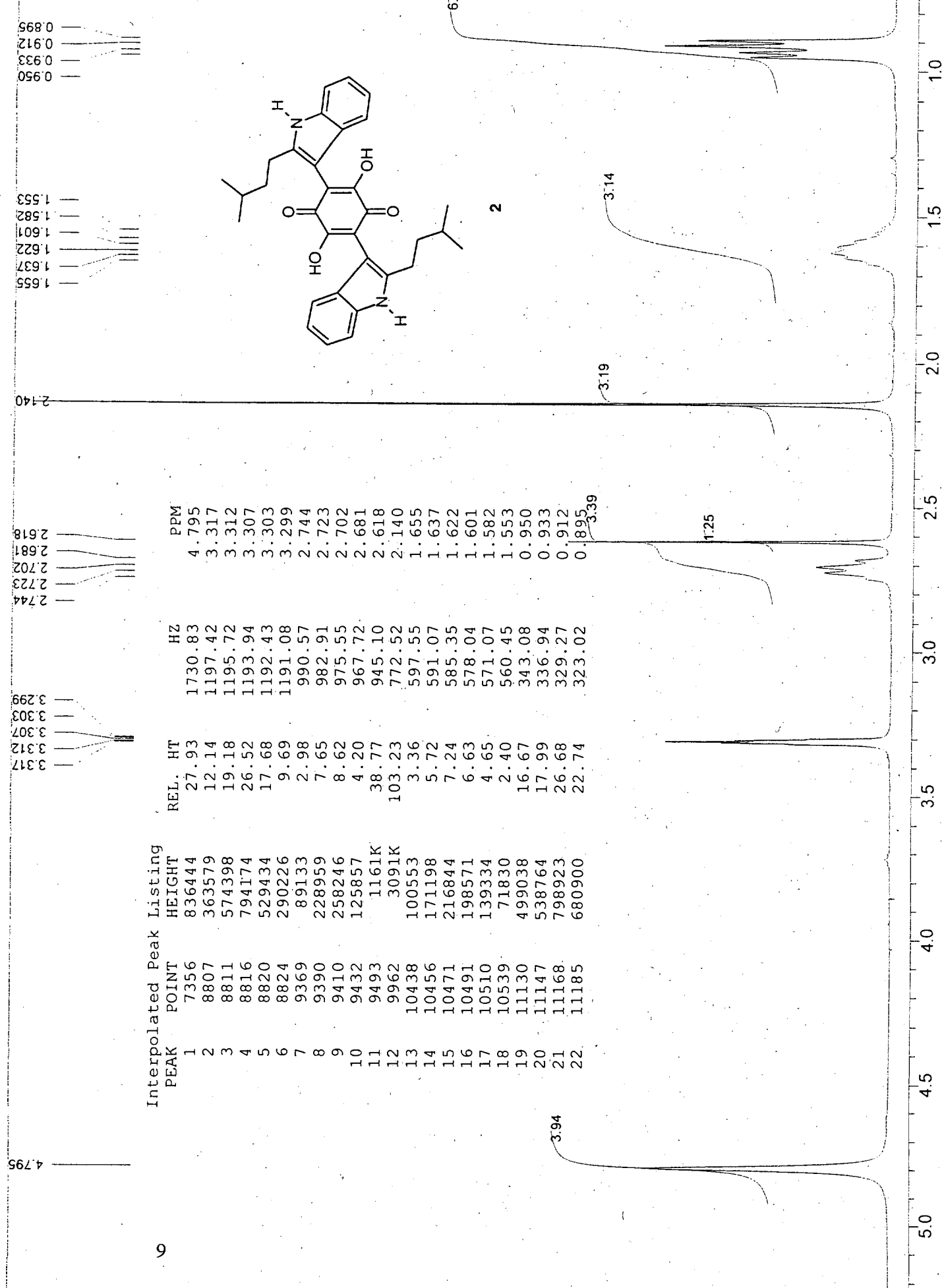
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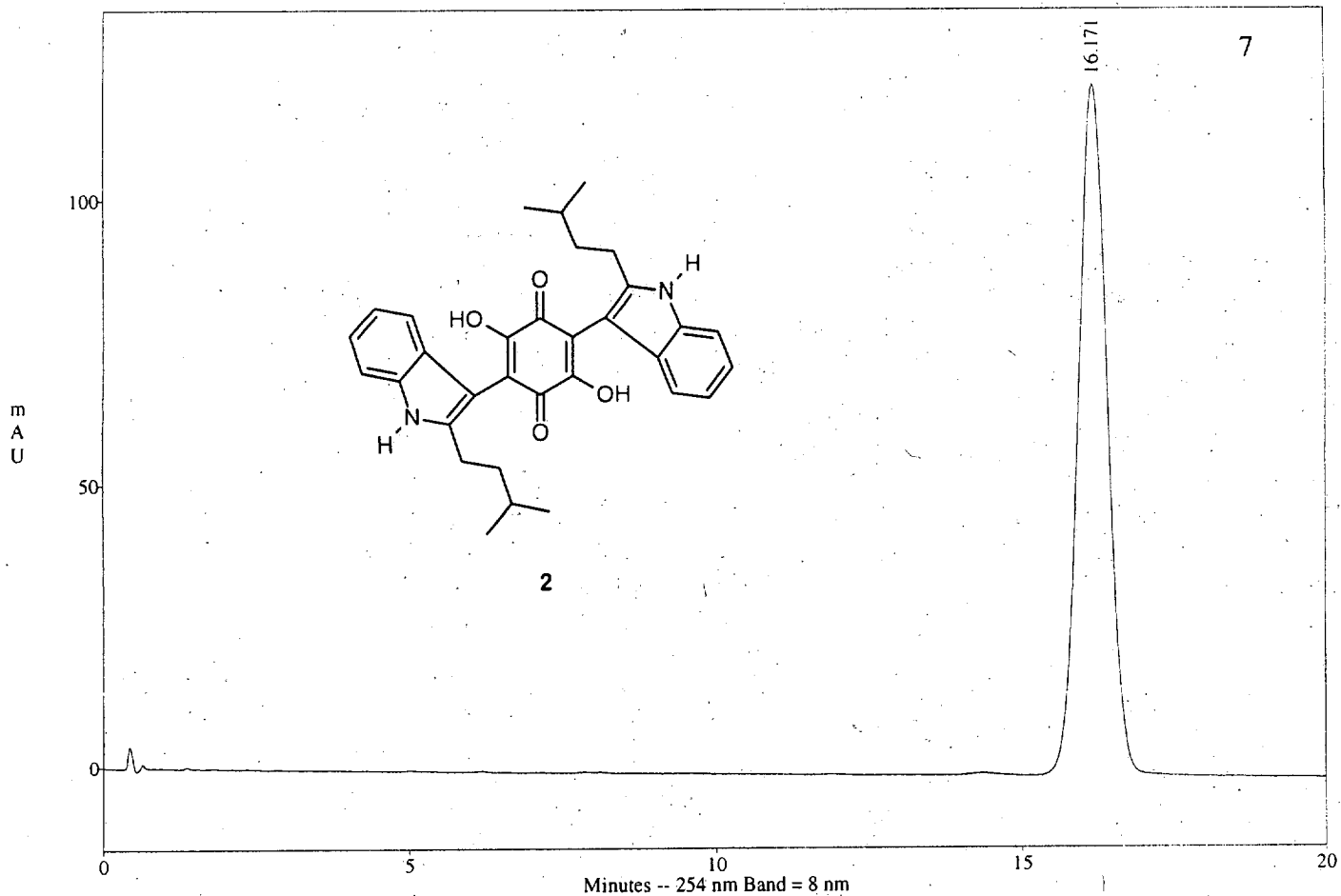
DATE: 12FE 95

WinNuts - \$Nfc12.001



Interpolated Peak Listing

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3	8811	574398	19.18	1195.72	3.312
4	8816	794174	26.52	1193.94	3.307
5	8820	529434	17.68	1192.43	3.303
6	8824	290226	9.69	1191.08	3.299
7	9369	89133	2.98	990.57	2.744
8	9390	228959	7.65	982.91	2.723
9	9410	258246	8.62	975.55	2.702
10	9432	125857	4.20	967.72	2.681
11	9493	1161K	38.77	945.10	2.618
12	9962	3091K	103.23	772.52	2.140
13	10438	100553	3.36	597.55	1.655
14	10456	171198	5.72	591.07	1.637
15	10471	216844	7.24	585.35	1.622
16	10491	198571	6.63	578.04	1.601
17	10510	139334	4.65	571.07	1.582
18	10539	71830	2.40	560.45	1.553
19	11130	499038	16.67	343.08	0.950
20	11147	538764	17.99	336.94	0.933
21	11168	798923	26.68	329.27	0.912
22	11185	680900	22.74	323.02	0.895



Channel A Results -- PDA Channel 1, 254 nm, 8 nm Band

PEAK #	Ret TIME	AREA	% of Area	ASYM
--	1.845	0	0	0.000
--	2.155	0	0	0.000
--	2.528	0	0	0.000
--	2.816	0	0	0.000
--	3.552	0	0	0.000
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Totals :

4036586 100

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 Printed : Feb 25, 1999 13:45:43  
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 B=95% MeCN Containing 10mM H3PO4  
 Flow Rate: 1.2mL/min  
 Method Name: 50b-20.met  
 Detector: PDA  
 DH-SU5519-A99000054  
 Sul of 1mg/ml in DMSO/90% CH3OH(1:9)