Supporting information for

Stereoselective Ring Opening of *Meso* Bicyclic Hydrazines: a Straightforward Approach to Hydrazino Cyclopentenic Cores.

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3-oxo-2,3,7,7a-tetrahydro-4aH-cyclopenta[1,3,4] oxadiazine-1-carboxylic acid benzyl ester 6 : ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 2.54 (dm, *J* = 17.8 Hz, 1H), 2.66 (br d, *J* = 17.8 Hz, 1H), 4.52 (br s, 1H), 5.16 (d, *J* = 12.2 Hz, 1H), 5.20 (d, *J* = 12.2 Hz, 1H), 5.46 (m, 1H), 5.84 (m, 1H), 6.06 (m, 1H), 6.90 (br s, 1H), 7.36 (br s, 5 H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.9, 58.1, 68.0, 83.0, 128.0, 128.2, 128.4, 128.6, 135.2, 135.7, 155.4, 156.3 ; IR (cm^{-1}) 3411, 1777, 1746, 1488, 1324, 1028; MS (ESI) (Vc 55V) 297 (MNa^+), 253, 172, 162, 129, 118; Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21 Found: C, 61.47, H, 5.29; N, 10.05.

General Procedure for Asymmetric Allylic Alkylation.

Asymmetric allylic alkylation of **4** with phenol is representative: $Pd_2(dba)_3$-$CHCl_3$ (13.4 mg, 0.013 mmol), *R*(-)-2-[2-(Diphenylphosphino)phenyl]-4-phenyl-2-oxazoline (17.4 mg, 0.043 mmol) were placed in a Schlenk tube, dried under vacuum (0.1 mm Hg) for 1h, and then placed under argon. Freshly distilled THF (10 mL) was degassed and then added to the mixture at room temperature. The dark red solution was stirred for 30 min and gradually became orange. **4** (90 mg, 0.25 mmol) and phenol (117 mg, 1.25 mmol) dissolved in THF (1 mL) were next added, and the solution was stirred 2 h at room temperature. Sodium hydroxide (1 M, 5 mL) was added, and the organic layer was separated, washed with brine (5 mL) and concentrated. Purification by flash chromatography (cyclohexane/ethyl acetate = gradient) afforded **7a** as a slowly crystallizing white solid (92 mg, 82 %).

Dibenzyl diazane-1,2-dicarboxylate-1-[4-phenoxy-cyclopent-2-enyl] 7a: mp= 105-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ 1.96 (br s, 1H), 2.76 (br s, 1H), 5.13 (br s, 3H), 5.18 (br s, 2H), 5.37 (br s, 1H), 6.02 (br s, 1H), 6.13 (br s, 1H), 6.48 (br s, NH), 6.89 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 7.25-7.33 (m, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.3 (br), 62.1 (br), 67.7, 68.3, 79.8, 115.4, 120.9, 128.0, 128.2, 128.5, 129.5, 133.8, 135.8 (br), 155.5, 156.2, 157.7; IR ($CHCl_3$) 3400, 3030, 3022, 1754, 1714, 1598, 1586, 1494, 1408, 1236; MS 476 (MNH_4^+), 459 (MH^+), 365; Anal. Calcd for $C_{27}H_{26}N_2O_5$: C, 70.73; H, 5.72; N, 6.11. Found: C, 70.72, H, 5.72; N, 6.06.

Dibenzyl diazane-1,2-dicarboxylate-1-[4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-cyclopent-2-enyl] 7d: white solid; mp= 108-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ2.16 (br s, 1H), 2.85 (br s, 1H), 5.10-5.30 (m, 5H), 5.43 (br s, 1H), 5.85 (br s, 1H), 5.94 (br s, 1H), 7.31 (m, 10 H), 7.69 (m, 2H), 7.79 (m, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.9 (br), 53.7, 63.0

(br), 67.4, 68.0, 123.3, 127.9, 128.0, 128.3, 128.4, 131.8, 132.1, 133.4, 134.1, 136.0, 155.5, 156.5 168.1 ; IR (cm^{-1}) 3393, 3061, 2954, 1747, 1709, 1498, 1392, 1371, 1062; MS 529 (MNH_4^+) ; Anal. Calcd for $C_{29}H_{25}N_3O_6$: C, 68.09 ; H, 4.93 ; N, 8.21. Found: C, 67.86, H, 5.25; N, 7.88.

Dibenzyl diazane-1,2-dicarboxylate-1-[4-nitromethyl-cyclopent-2-enyl] 7e: white solid; mp= 115-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ1.66 (br s, 1H), 2.54 (br s, 1H), 3.33 (br s, 1H), 4.26 (br s, 2H), 5.16 (br s, 4H), 5.39 (br s, 1H), 5.80 (br s, 2H), 6.51 (br s, NH), 7.33 (br s, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.1 (br), 42.7, 64.2 (br), 68.1, 79.3, 128.1, 128.4, 128.7, 132.5 (br), 135.6, 135.8, 155.5, 156.6 ; IR (cm^{-1}) 3389, 3066, 2961, 1755, 1714, 1552, 1488, 1406, 1311, 1070; MS 443 (MNH_4^+), 426 (MH^+) ; Anal. Calcd for $C_{22}H_{23}N_3O_6$: C, 62.11 ; H, 5.45 ; N, 9.88. Found: C, 62.04, H, 5.47; N, 9.82.

2-(4-Dibenzyl diazane-1,2-dicarboxylate-cyclopent-2-enyl)-malonic acid diethyl ester 7f: white solid; mp= 102-104 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ1.25 (m, 6H), 1.66 (br s, 1H), 2.53 (br s, 1H), 3.33 (m, 2H), 4.17 (m, 4H), 5.15 (br s, 4H), 5.37 (br s, 1H), 5.75 (br s, 1H), 5.87 (br s, 1H), 6.57 (br s, NH), 7.32 (br s, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 31.8 (br), 43.4, 56.6, 61.4, 64.1 (br), 67.7, 68.1, 127.9, 128.0, 128.2, 128.3, 128.4, 130.9, 135.6 , 135.8, 155.5, 156.4, 168.2, 168.3; IR (cm^{-1}) 3393, 2983, 2842, 1748, 1724, 1497, 1455, 1407, 1315, 1231, 1028; MS 542 (MNH_4^+), 525 (MH^+); Anal. Calcd for $C_{28}H_{32}N_2O_8$: C, 64.11 ; H, 6.15 ; N, 5.34. Found: C, 64.18, H, 6.23; N, 5.20.

2-(4-Dibenzyl diazane-1,2-dicarboxylate-cyclopent-2-enyl)-malonic acid di-*ter*-butyl ester 7g: colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$, 50 °C) δ1.46 (m, 18H), 1.62 (br s, 1H), 2.50 (m, 1H), 3.09 (m, 1H), 3.19 (m, 1H), 5.15 (br s, 4H), 5.37 (br s, 1H), 5.74 (br s, 1H),

5.89 (br s, 1H), 6.57 (br s, NH), 7.32 (br s, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.9, 31.9 (br), 43.3, 58.6, 64.0 (br), 67.7, 68.1, 81.6, 127.9, 128.0, 128.2, 128.3, 128.4, 130.5, 135.6, 135.8, 155.5, 156.4, 167.5 ; IR (cm^{-1}) 3392, 3030, 2981, 1744, 1718, 1497, 1455, 1407, 1314, 1255; MS 598 (MNH_4^+), 581 (MH^+).

Di-*iso*-propyl diazane-1,2-dicarboxylate-1-[4-phenoxy-cyclopent-2-enyl] 11: ^{1}H NMR (400 MHz, $CDCl_3$) δ1.24 (m, 12H), 1.80-2.20 (m, 1H), 2.78 (m, 1H), 4.85-5.00 (m, 2H), 5;15 (br s, 1H), 5.37 (br s, 1H), 6.00-6.20 (m, 2H), 6.30 (br s, NH), 6.93 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 22.0, 35.6 (br), 61.5 (br), 69.6, 70.2, 79.8, 115.4, 120.9, 129.5, 133.6, 134.3, 155.3, 156.2, 157.8; IR (cm^{-1}) 3400, 3029, 2984, 1747, 1705, 1598, 1585, 1493, 1404, 1311 ; MS 380 (MNH_4^+), 363 (MH^+).

Di-*ter*-butyl diazane-1,2-dicarboxylate-1-[4-phenoxy-cyclopent-2-enyl] 12: white solid; mp= 96-98 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ1.48 (s, 18H), 1.80-2.20 (m, 1H), 2.77 (m, 1H), 5;15 (br s, 1H), 5.35 (br s, 1H), 6.00-6.20 (m, 2H), 6.48 (br s, NH), 6.93 (m, 3H), 7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3, 36.1 (br), 60.8 (br), 80.0, 81.0, 81.5, 115.5, 120.9, 129.5, 133.2, 134.7, 154.8, 155.6, 158.0; IR (cm^{-1}) 3402, 3025, 2933, 1742, 1702, 1598, 1585, 1494, 1393, 1368 ; MS 390 (MH^+).

General parameters for analyses : Chiralpack AD column (0.46 cm I.D. × 25 cm), Flow 0.8 $mL.min^{-1}$, Detection λ = 220 nm. Samples were injected at 0.05 $g.L^{-1}$ concentration with a 20 μL inlet.

Compound **7a**:

hexane/*i*PrOH = 90/10, retention times = 45.1 (1*R*, 4*S*), 47.9 (1*S*, 4*R*) (min).

Compound **7b**:

hexane/*i*PrOH = 90/10, retention times = 49.7 (1*S*, 4*R*), 51.8 (1*R*, 4*S*) (min).

*Crystal Data for compound **7b***: [Br $C_{27}N_2O_5H_{25}$] M = 537.40, triclinic, space group P1, a = 5.656(2) Å, b = 10.666(4), c = 10.995(4),α =98.30(4)°, β =103.98(4)°, γ =103.41(4)°, V = 611.8(4) $Å^3$, Z = 1, λ = 0.71073 Å, d_c = 1.458 gcm^{-3}, F(000) = 276, μ = 1.721 mm^{-1}, T = 296(2)K.

A colourless crystal of 0. 45 x 0.17 x 0.15 mm was mounted on an Enraf-Nonius Kappa-CCD diffractometer, with graphite monochromated MoKα radiation. A full sphere of data was collected by φ axis rotation with an increment of 2° over 360° and 25 s exposure per degree. ¨Denzingering ¨was accomplished by measuring each frame twice. The crystal to detector distance was 40 mm. The theta range for data collection was 1.95 to 27.61°. Data were analyzed using Kappa-CCD software(**1**). Cell dimensions were refined with HKL-scalepack (**2**) and data reduction performed with Denzo (**2**).Of a total of 4976 reflections collected, 4327 were independent and 3823 were larger than 2σ(I).

The structure was solved by direct methods (SHELX-S86) (**3**) and was refined on F^2 for all reflections by least-squares methods using SHELXL-93 (**4)**

All hydrogen atoms were located on difference - Fourier syntheses. They were modelled at their theoretical positions using an isotropic thermal factor equal to 1.2 times that of the bonded atom and introduced in the refinement cycles. The final conventional R is 0.0379 for 3823 Fo > 4σ(Fo), 319 parameters and 3 restraints, and 0.0834 for all data, $wR(F^2)$ = 0.0905 for all, $w = 1 / [\sigma^2(Fo)^2 + (0.0228 P)^2 + 0.23P]$ where $P = (Fo^2 + 2Fc^2) / 3$. The largest difference peak and hole are 0.19 and –0.25 $eÅ^{-3}$. The correctness of the chosen polarity was confirmed by a near zero Flack absolute structure parameter of 0.037(8) **[5]**. Crystal data and experimental details, list of atomic coordinates , bond lengths and angles, anisotropic thermal parameters of non hydrogen atoms, atomic coordinates of hydrogen atoms are reported in

supplementary material. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

Structural data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under the depository number CCDC **214051.**

References :

[1] Enraf-Nonius, *Kappa-CCD software*,**1997**, Enraf-Nonius, Delft, The Netherlands.

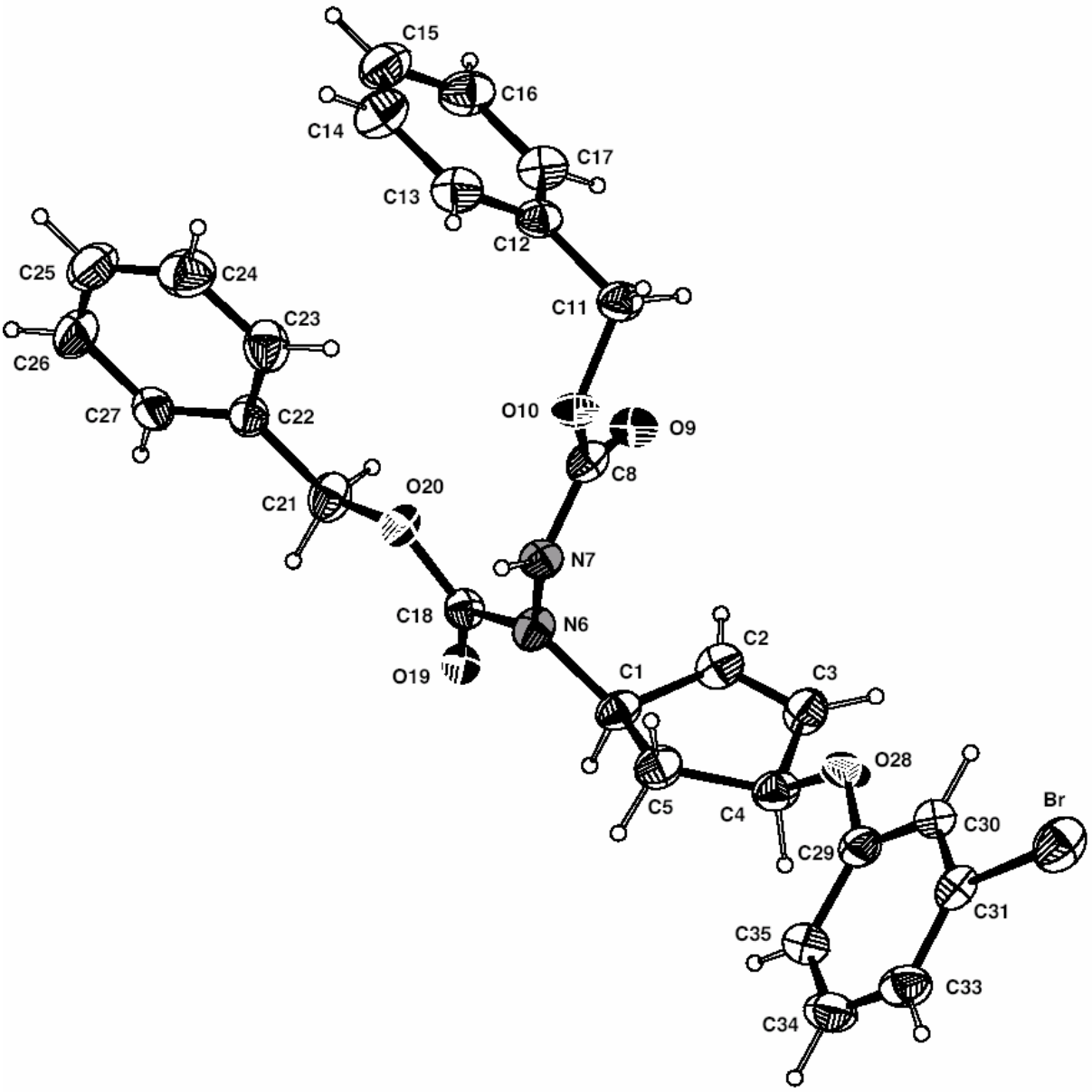
[2] Otvinowski, Z., Minor, W.,**1997**, *Methods in Enzymology*, Vol 276 : *Macromolecular Crystallography*, Part A, pp 307-26.

[3] Sheldrick, G.M., *Acta Crystallogr*., Sec. A, **1990**, *46*,467.

[4] Sheldrick, G. M., SHELX-93 : *Program fot the refinement of crystal structures*, University of Göttingen, Germany, **1993**.

[5] Flack, H. D., *Acta Crystallogr*., Sec. A, **1983**,876-81

Figure caption: The molecular structure of compound **7b** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability.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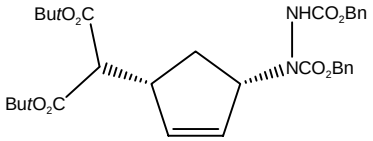
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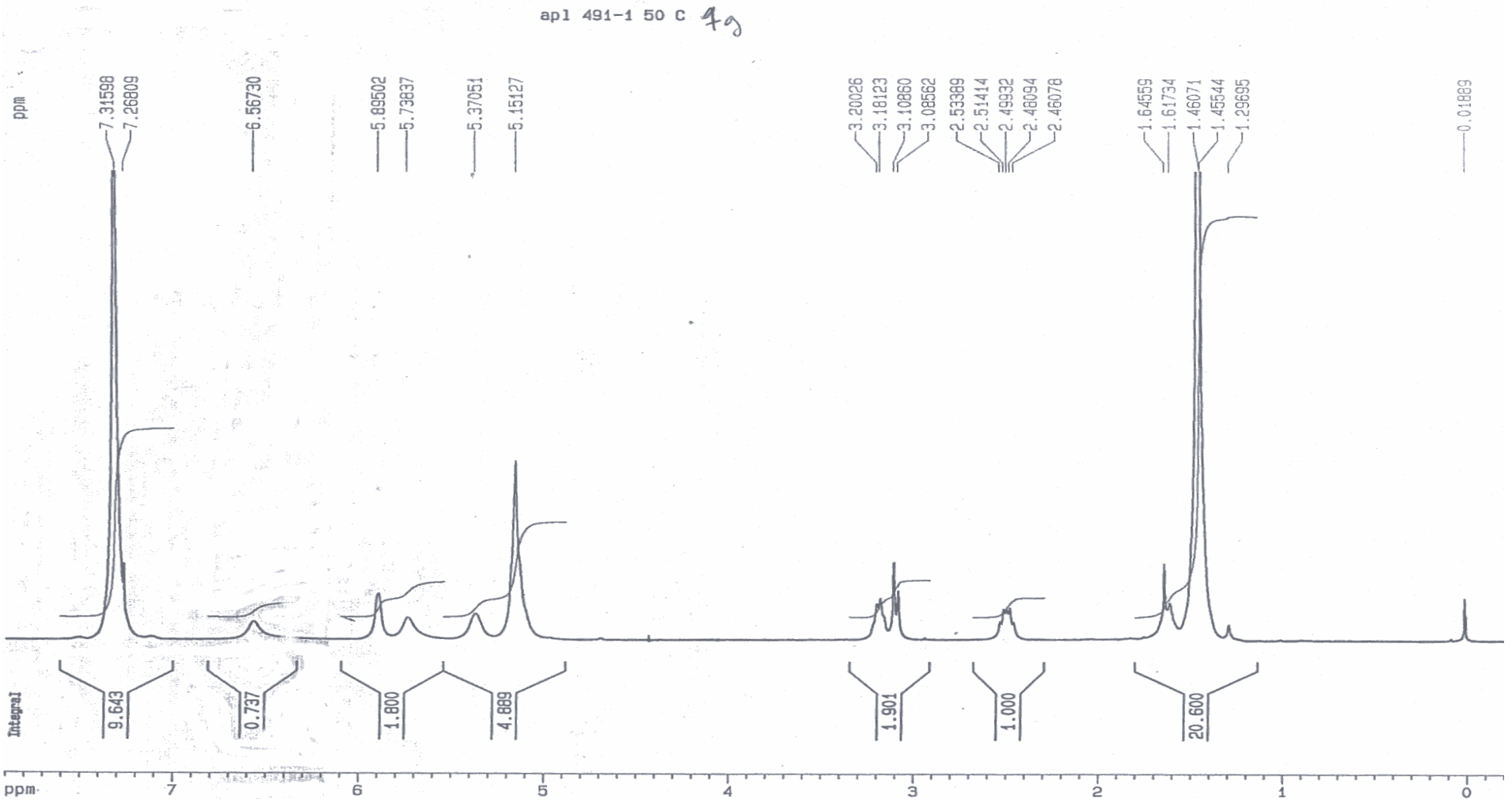
7g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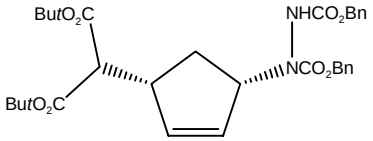
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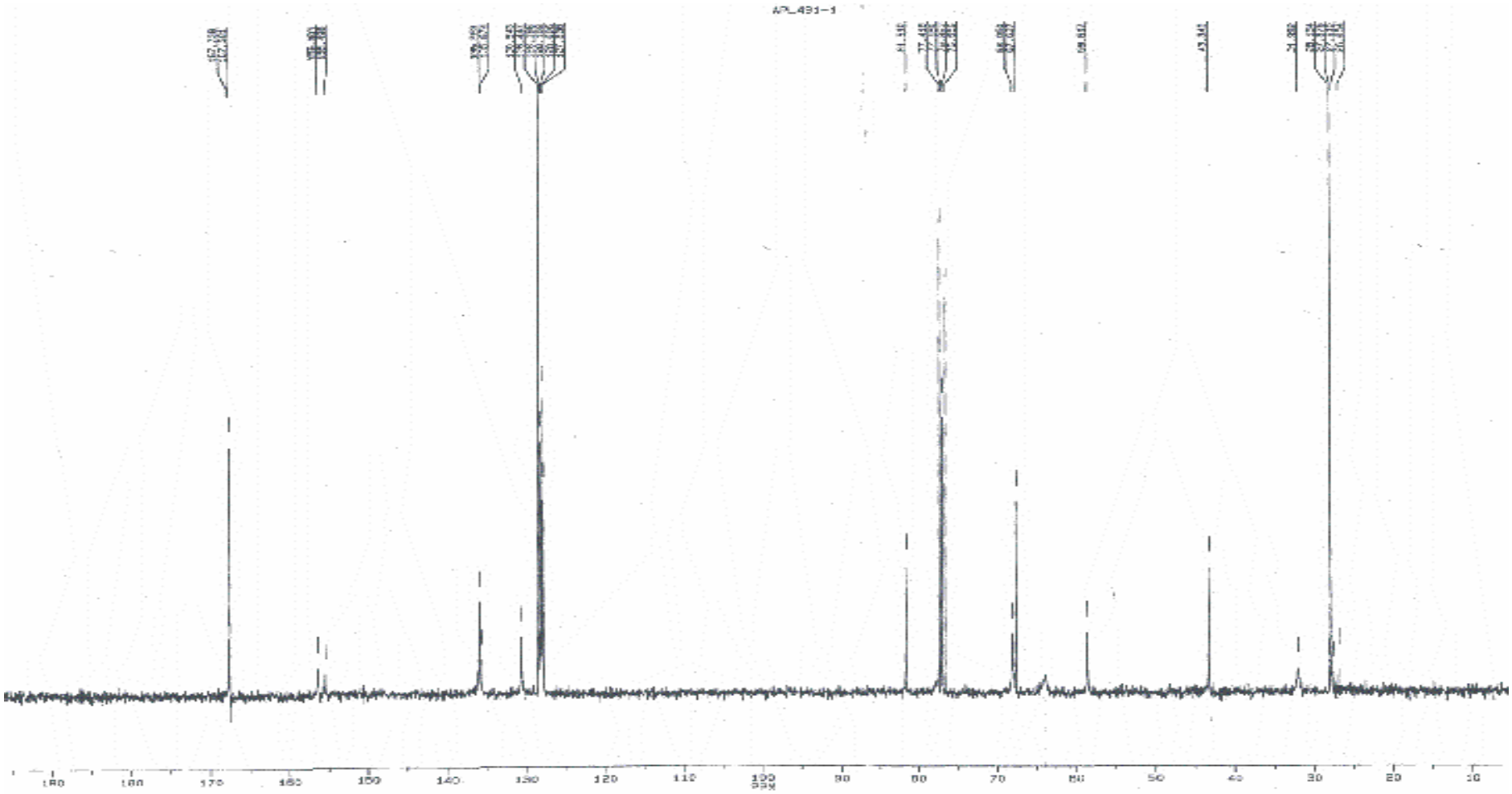
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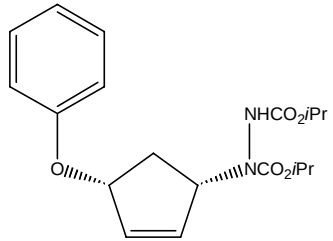
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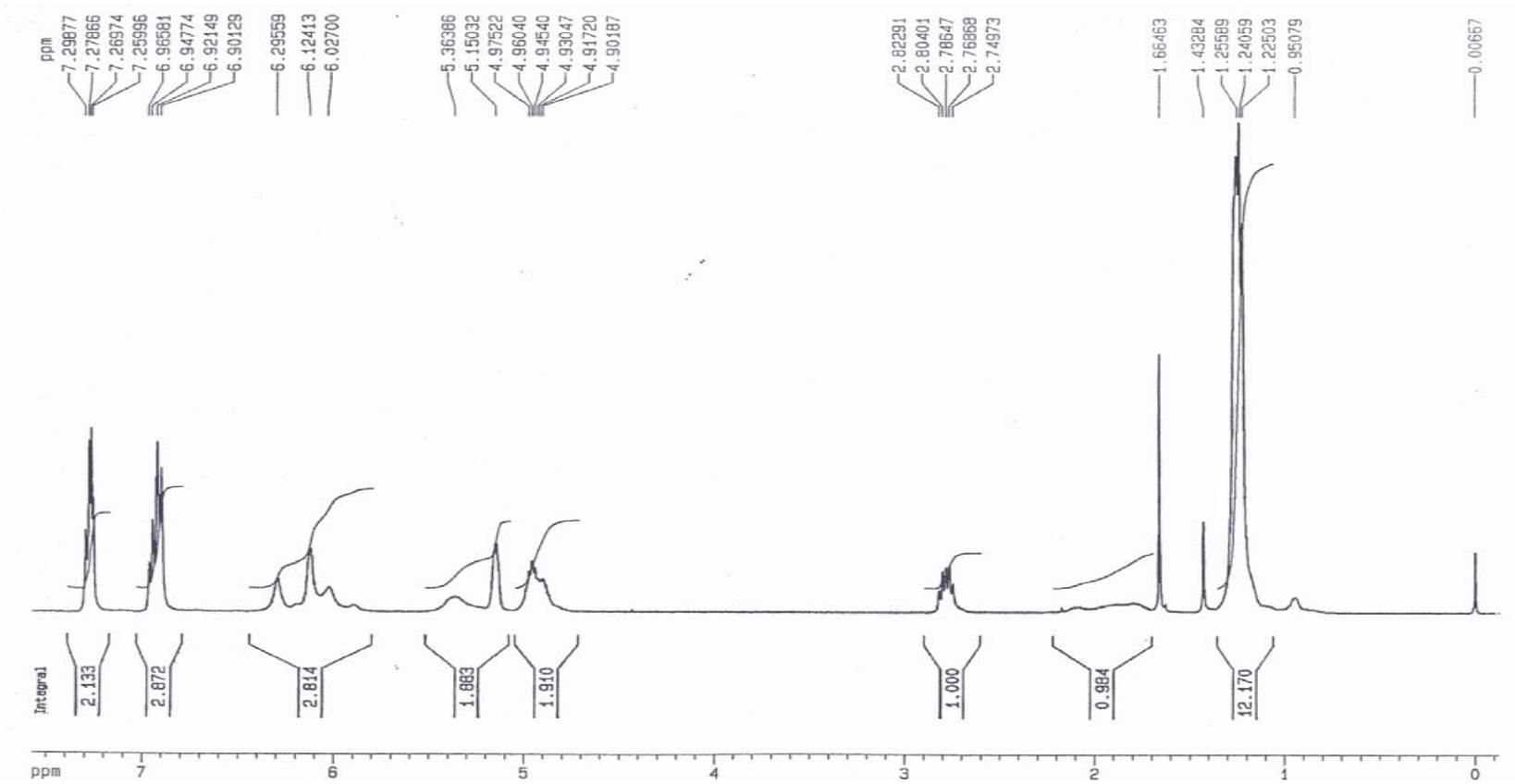
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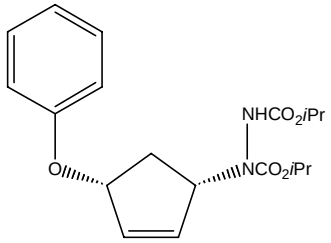
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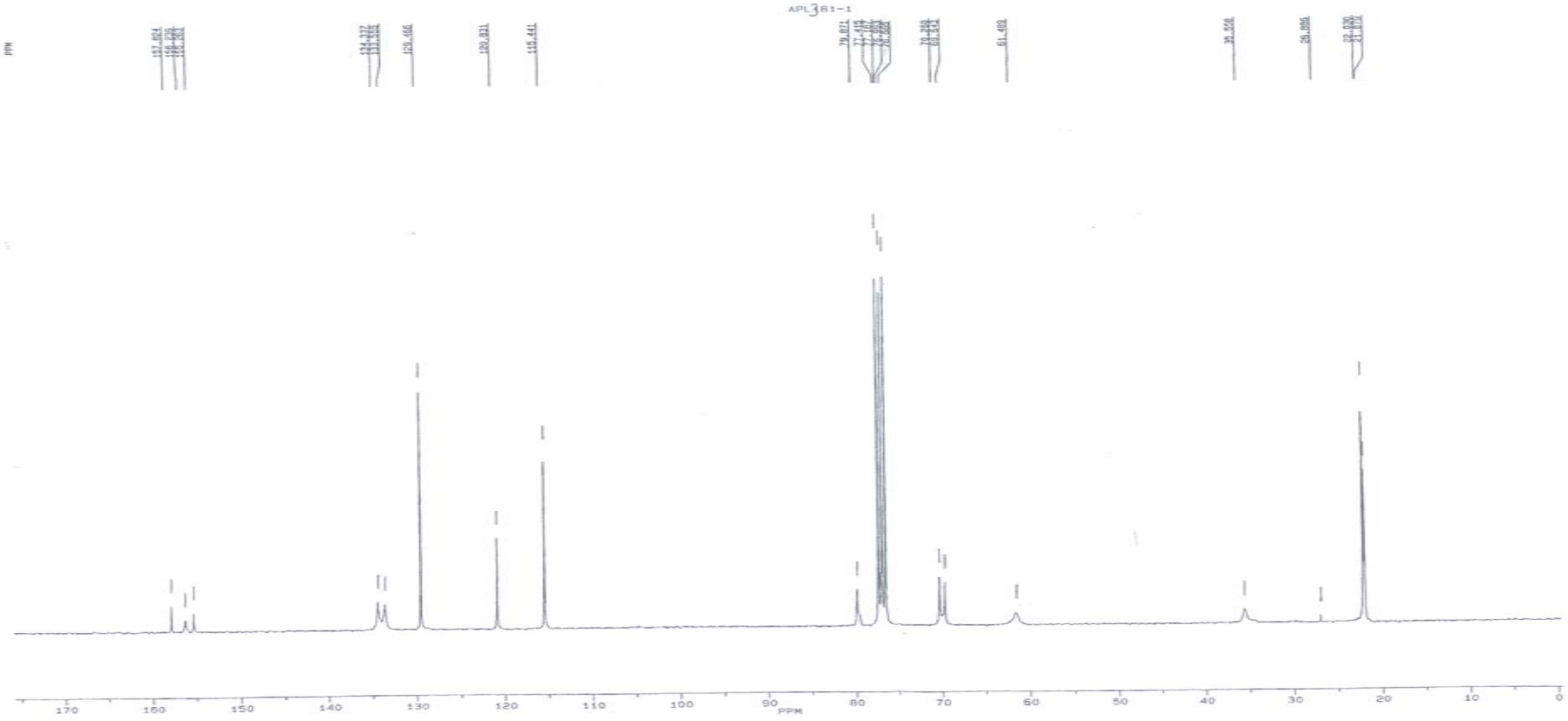
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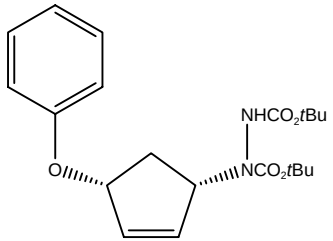
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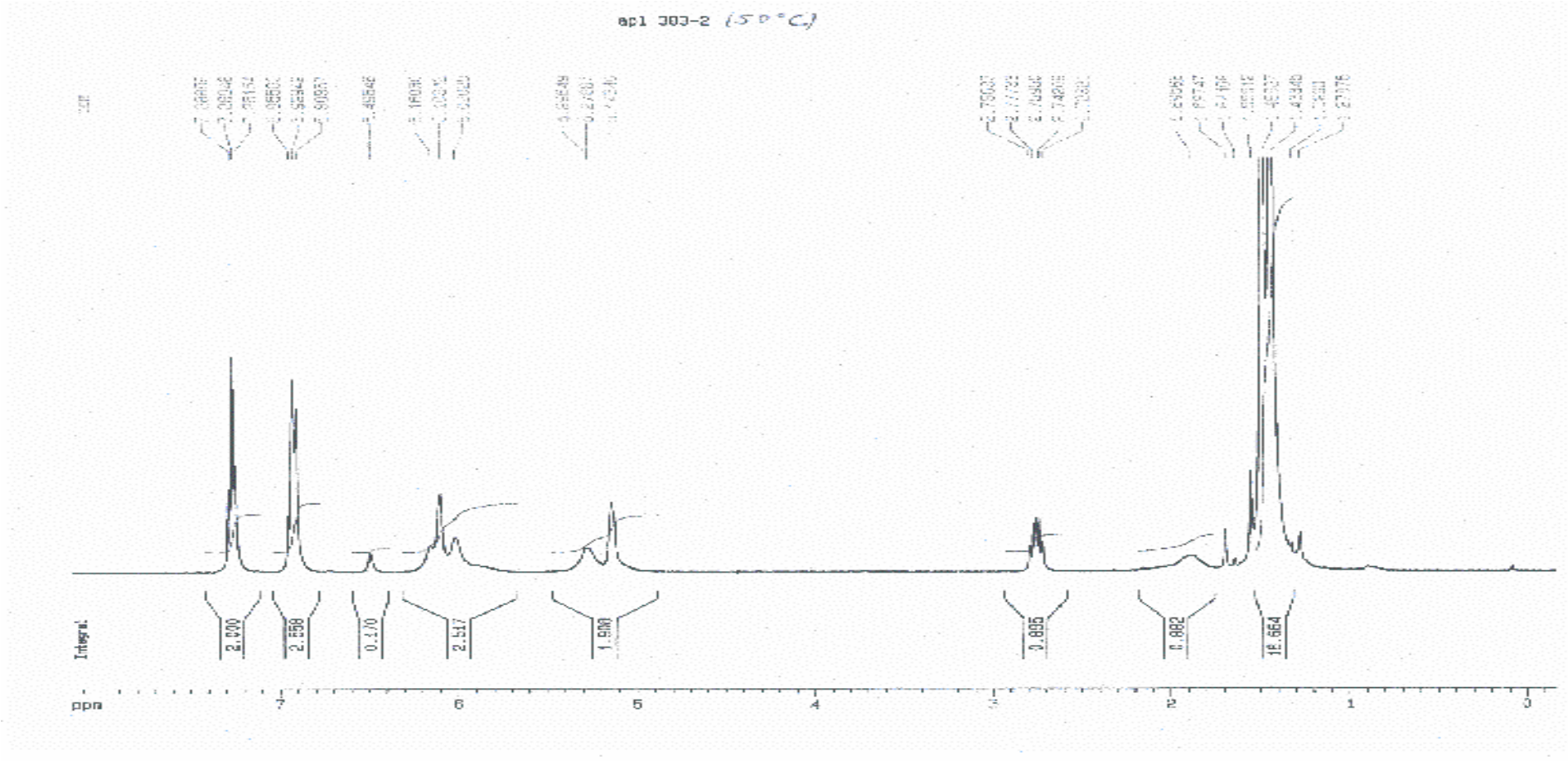
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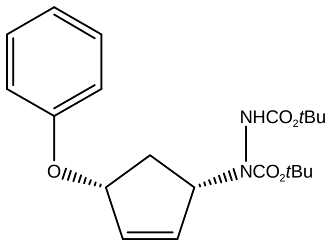
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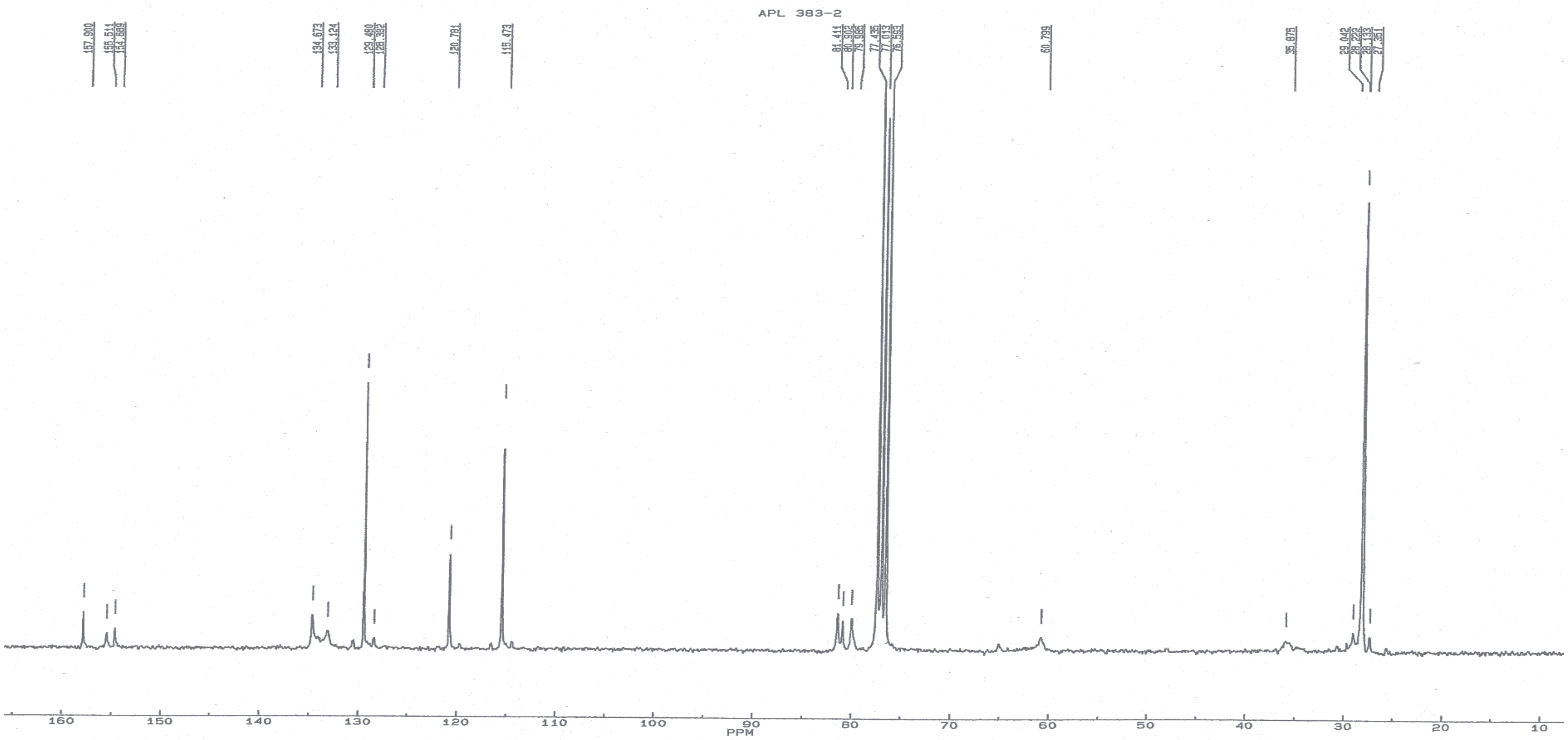
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