Organocatalytic Asymmetric Friedel-Crafts Alkylation/Cyclization Cascade Reactions of 1-Naphthols and α,β-Unsaturated Aldehydes: An Enantioselective Synthesis of Chromenes and Benzopyranes

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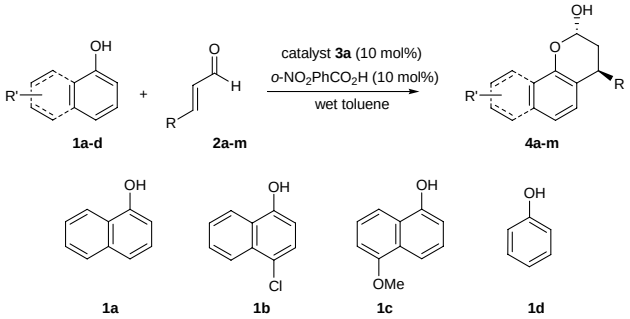
General Methods:

Unless stated otherwise, all reactions were carried out in flamedried glassware. All solvents were purified and dried according to standard methods prior to use.

^{1}H spectra were recorded on 300 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 75 MHz in $CDCl_3$ using TMS or residual protio solvent signals as internal standard. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm^{-1}. Highresolution mass spectra (HRMS) were obtained by the ESI ionization sources. The enantioselectivity was determined by chiral HPLC analysis after $NaBH_4$ reduction of both diastereomers using chiral HPLC with Daicel Chiracel OD-H, OJ-H or AD column on Waters with a 996 UV-detector.

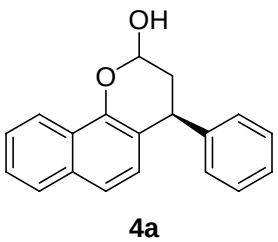
Experimental Procedures and Characterizations:

General procedure **A**: Enantioselective Synthesis of **4**.



To a solution of catalyst **3a** (0.03 mmol), *o*-NO_2PhCO_2H (0.03 mmol) and α,β-unsaturated aldehyde **2** (0.30 mmol) in toluene (1.0 mL) and H_2O (30 μL) was added 1-naphthol **1** (0.36 mmol) at the room temperature. The resulting solution was then stirred for 24-84h. After the complete consumption of the aldehyde (as monitored by TLC), the reaction mixture was poured into water, extracted with EtOAc, dried over Na_2SO_4, evaporated and then loaded onto silica gel and the products **4a-o** were obtained by column chromatography.

(*4S*)-4-phenyl-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4a).



4a

Following the general procedure **A**, **4a** was isolated by column chromatography using silica gel in 81% yield as a mixture of diastereomers (7:2).

Major diastereomer:

^{1}H NMR: δ 8.27-8.20 (m, 1H), 7.74-7.70 (m, 1H), 7.48-7.41 (m, 2H), 7.33-7.14 (m, 6H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.78 (s, 1H), 4.42 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.29 (s, 1H), 2.40-2.32 (m, 1H), 2.25- 2.17(m, 1H).

^{13}C NMR: δ 146.9, 144.6, 133.5, 128.8, 128.6, 127.5, 127.2, 126.7, 126.0, 125.4, 125.1, 121.6, 120.3, 118.5, 91.6, 37.5, 36.6.

Minor diastereomer (representative signals):

^{1}H NMR: δ 6.84 (d, *J* = 8.4 Hz, 1H), 5.63 (d, *J* = 6.6 Hz, 1H), 4.33 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.37 (s, 1H), 2.57-2.50 (m, 1H).

^{13}C NMR: δ 148.2, 144.3, 128.8, 128.4, 127.4, 127.0, 126.9, 126.2, 125.5, 125.0, 121.8, 120.4, 118.3, 94.7, 41.4, 39.0.

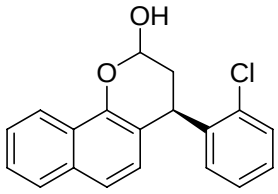
IR (film): 3404, 3056, 2934, 1709, 1575, 1497, 1451, 1395, 1261, 1189, 1049, 970, 894, 810, 752, 702.

HRMS: Calculated for $[C_{19}H_{16}O_2+H]^+$:277.1223; found: 277.1217.

$[\alpha]_D^{rt}$ = + 58 (c = 1.12, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (90:10)]; flow rate 1.0 mL/min; t_{major} = 13.6 min, t_{minor} = 11.8 min (92:8 e.r.).

(*4R*)-4-(2-chlorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4b).



4b

Following the general procedure **A**, **4b** was isolated by column chromatography using silica gel in 73% yield as a mixture of diastereomers (3:1).

Major diastereomer:

^{1}H NMR: δ 8.26-8.22 (m, 1H), 7.77-7.74 (m, 1H), 7.50-7.48 (m, 3H), 7.46 (dd, *J* = 5.4, 4.5 Hz, 1H), 7.43-7.10 (m, 2H), 6.96 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.75-5.73 (m, 1H), 4.97 (dd, *J* = 8.4, 6.6 Hz, 1H), 3.18 (d, *J* = 6.0 Hz, 1H), 2.45-2.37 (m, 1H), 2.30-2.23 (m, 1H).

^{13}C NMR: δ 147.6, 142.0, 134.2, 133.6, 130.5, 129.8, 128.0, 127.5, 127.2, 127.0, 126.2, 125.6, 125.2, 121.6, 120.6, 117.2, 91.8, 35.0, 34.6.

Minor diastereomer (representative signals):

^{1}H NMR: δ 6.86 (d, *J* = 8.7 Hz, 1H), 2.67-2.59 (m, 1H).

^{13}C NMR: δ 148.5, 141.9, 134.1, 133.5, 130.0, 129.6, 128.0, 127.5, 126.9, 126., 125.6, 121.7, 120.7, 117.3, 94.4, 36.3.

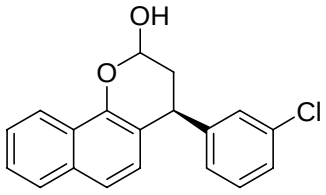
IR (film): 3386, 3056, 2929, 1574, 1469, 1396, 1347, 1263, 1190, 1131, 1097, 972, 907, 810, 753.

HRMS: Calculated for $[C_{19}H_{15}ClO_2+H]^+$:311.0833; found: 311.0841.

$[\alpha]_D^{rt}$ = + 45 (c = 1.04, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (95:5)]; flow rate 1.0 mL/min; t_{major} = 31.3 min, t_{minor} = 21.7 min (93:7 e.r.).

(*4S*)-4-(3-chlorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4c).



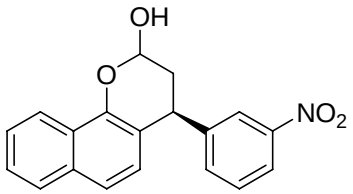
4c

Following the general procedure **A**, **4c** was isolated by column chromatography using silica gel in 85% yield as a mixture of diastereomers (3:1).

Major diastereomer:

^{1}H NMR: δ 8.23-8.18 (m, 1H), 7.74-7.71 (m, 1H), 7.47-7.42 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.23-7.15 (m, 3H), 7.05-6.97 (m, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 5.76 (t, *J* = 2.4 Hz, 1H), 4.38 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.50 (s, 1H), 2.37-3.29 (m, 1H), 2.18- 2.10 (m, 1H).
^{13}C NMR: δ 146.8, 146.7, 134.5, 133.5, 129.9, 128.9, 127.5, 127.0, 127.0, 126.9, 126.2, 125.5, 125.0, 121.5 120.5, 117.7, 91.4, 37.3, 36.4.
Minor diastereomer (representative signals):
^{1}H NMR: δ 7.28 (d, *J* = 7.8 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 5.58 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.26 (dd, *J* = 10.2, 6.3 Hz, 1H), 2.51-2.43 (m, 1H).
^{13}C NMR: δ 148.2, 146.4, 129.9, 128.6, 127.4, 127.0, 126.7, 126.6, 126.3, 125.6, 125.0, 121.7, 120.6, 117.4, 94.4, 41.1, 38.7.
IR (film): 3397, 3057, 2933, 1574, 1472, 1396, 1347, 1190, 1099, 976, 909, 811, 732.
HRMS: Calculated for $[C_{19}H_{15}ClO_2+Na]^+$:333.0653; found: 333.0661.
$[\alpha]_D^{rt}$ = + 54 (c = 1.21, $CHCl_3$).
The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (90:10)]; flow rate 0.8 mL/min; t_{major} = 13.1 min, t_{minor} = 12.2 min (95:5 e.r.).

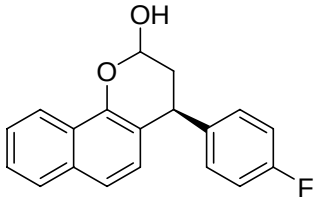
(*4S*)-4-(3-nitrophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4d).



4d

Following the general procedure **A**, **4d** was isolated by column chromatography using silica gel in 93% yield as a mixture of diastereomers (3:1).
Major diastereomer:
^{1}H NMR: δ 8.25-8.20 (m, 1H), 8.14-8.08 (m, 2H), 7.77-7.73 (m, 1H), 7.54-7.42 (m, 4H), 7.31 (d, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 5.85 (t, *J* = 3.0 Hz, 1H), 4.58 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.47 (s, 1H), 2.45-3.38 (m, 1H), 2.24-2.15 (m, 1H).
^{13}C NMR: δ 148.5, 146.9, 146.8, 135.0, 133.6, 129.6, 127.5, 126.4, 126.3, 125.7, 125.1, 123.6, 122.0, 121.6, 120.7, 117.0, 91.1, 37.2, 36.4.
Minor diastereomer (representative signals):
^{1}H NMR: δ 7.32 (d, *J* = 8.7 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.71 (dd, *J* = 7.5, 1.8 Hz, 1H), 4.46 (dd, *J* = 9.3, 6.9 Hz, 1H), 2.61-2.53 (m, 1H).
^{13}C NMR: δ 148.4, 148.3, 134.7, 129.5, 127.5, 126.5, 126.5, 125.8, 123.5, 121.9, 121.7, 120.9, 116.5, 93.9, 40.7, 38.1.
IR (film): 3426, 3060, 2932, 1576, 1529, 1350, 1190, 1107, 978, 910, 810, 734.
HRMS: Calculated for $[C_{19}H_{15}NO_4+NH_4]^+$:339.1339; found: 339.1345.
$[\alpha]_D^{rt}$ = + 40 (c = 1.31, $CHCl_3$).
The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/^{i}*Pr*OH (90:10)]; flow rate 0.5 mL/min; t_{major} = 47.9 min, t_{minor} = 44.6 min (93:7 e.r.).

(*4S*)-4-(4-fluorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4e).



4e

Following the general procedure **A**, **4e** was isolated by column chromatography using silica gel in 87% yield as a mixture of diastereomers (3:1).

Major diastereomer:

^{1}H NMR: δ 8.23-8.19 (m, 1H), 7.74-7.71 (m, 1H), 7.48-7.42 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.15-7.08 (m, 2H), 7.06-6.95 (m, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.78 (t, *J* = 2.4 Hz, 1H), 4.41 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.55 (s, 1H), 2.38-2.30 (m, 1H), 2.19-2.11 (m, 1H).

^{13}C NMR: δ 161.7 (J_{CF} = 243.0 Hz), 146.8, 140.3 (J_{CF} = 3.8 Hz), 133.5, 130.2 (J_{CF} = 7.5 Hz), 127.5, 127.0, 126.1, 125.5, 125.1, 121.5, 120.4, 118.3, 115.5 (J_{CF} = 21.0 Hz), 91.5, 36.7, 36.7.

Minor diastereomer (representative signals):

^{1}H NMR: δ 7.28 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.62 (dd, *J* = 8.4, 2.1 Hz, 1H), 4.32 (dd, *J* = 10.2, 6.3 Hz, 1H), 2.54-2.46 (m, 1H).

^{13}C NMR: δ 148.2, 139.9, 129.9 (J_{CF} = 8.3 Hz), 127.4, 126.8, 126.3, 125.6, 125.0, 121.7, 120.5, 118.1, 115.5 (J_{CF} = 21.0 Hz), 94.5, 40.7, 39.0.

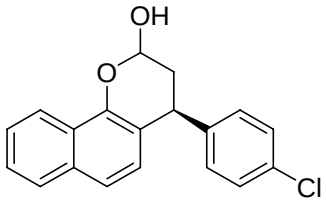
IR (film): 3387, 3056, 2929, 1699, 1602, 1575, 1507, 1395, 1348, 1225, 1077, 973, 906, 812, 732.

HRMS: Calculated for $[C_{19}H_{15}FO_2+H]^+$:295.1129; found: 295.1133.

$[\alpha]_D^{rt}$ = + 45 (c = 1.30, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/ EtOH (95:5)]; flow rate 1.0 mL/min; t_{major} = 18.3 min, t_{minor} = 16.6 min (92:8 e.r.).

(*4S*)-4-(4-chlorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4f).



4f

Following the general procedure **A**, **4f** was isolated by column chromatography using silica gel in 85% yield as a mixture of diastereomers (3:1).

Major diastereomer:

^{1}H NMR: δ 8.23-8.08 (m, 1H), 7.75-7.72 (m, 1H), 7.49-7.43 (m, 2H), 7.31-7.24 (m, 3H), 7.12 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 1H), 5.80 (dd, *J* = 3.6, 2.4 Hz, 1H), 4.41 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.43 (s, 1H), 2.40-2.32 (m, 1H), 2.21-2.11 (m, 1H).

^{13}C NMR: δ 146.8, 143.1, 133.5, 132.5, 130.1, 128.8, 127.5, 126.9, 126.1, 125.6, 125.1, 121.6, 120.5, 118.0, 91.4, 36.9, 36.5.

Minor diastereomer (representative signals):

^{1}H NMR: δ 7.11 (d, *J* = 9.0 Hz, 1H), 5.66 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.33 (dd, *J* = 10.2, 6.6 Hz, 1H), 2.57-2.50 (m, 1H).

^{13}C NMR: (100 MHz, CDCl3) δ 148.2, 142.9, 133.7, 132.6, 129.8, 128.8, 127.4, 126.8, 126.3, 125.7, 125.0, 121.7, 120.6, 117.7, 94.4, 40.8, 38.8.

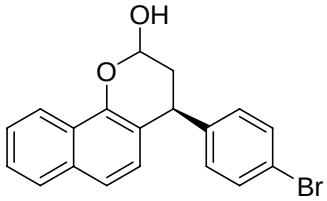
IR (film): 3390, 3056, 2932, 1702, 1576, 1490, 1397, 1348, 1190, 1093, 974, 907, 810, 732.

HRMS: Calculated for $[C_{19}H_{15}ClO_2+H]^+$:311.0833; found: 311.0825.

$[\alpha]_D^{rt}$ = + 58 (c = 1.30, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OJ column [hexane/EtOH (95:5)]; flow rate 1.0 mL/min; t_{major} = 64.4 min, t_{minor} = 40.7 min (93:7 e.r.).

(*4S*)-4-(4-bromophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4g).



4g

Following the general procedure **A**, **4g** was isolated by column chromatography using silica gel in 87% yield as a mixture of diastereomers (3:1).

Major diastereomer:

^{1}H NMR: δ 8.24-8.18 (m, 1H), 7.75-7.70 (m, 1H), 7.48-7.37 (m, 4H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 5.78 (s, 1H), 4.38 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.36 (s, 1H), 2.38-2.30 (m, 1H), 2.18-2.09 (m, 1H).

^{13}C NMR: δ 146.8, 143.6, 133.5, 131.8, 130.5, 127.5, 126.9, 126.1, 125.6, 125.1, 121.5, 120.6, 120.5, 117.9, 91.4, 36.9, 36.5.

Minor diastereomer (representative signals):

^{1}H NMR: δ 7.00 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 8.7 Hz, 1H), 5.62 (d, *J* = 7.2 Hz, 1H), 4.28 (dd, *J* = 10.2, 6.6 Hz, 1H), 3.44 (s, 1H), 2.53-2.46 (m, 1H).

^{13}C NMR: δ 148.2, 143.4, 131.8, 130.2, 127.4, 126.7, 126.3, 125.7, 125.0, 121.7, 120.5, 117.6, 94.4, 40.9, 36.9.

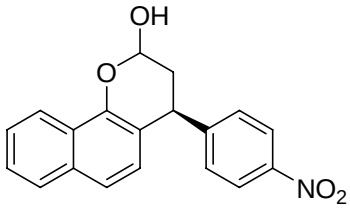
IR (film): 3389, 3055, 2931, 1703, 1576, 1486, 1399, 1262, 1190, 1094, 972, 895, 809, 751.

HRMS: Calculated for $[C_{19}H_{15}BrO_2+H]^+$:355.0328; found: 355.0321.

$[\alpha]_D^{rt}$ = +76 (c = 1.04, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OJ column [hexane/EtOH (90:10)]; flow rate 1.0 mL/min; t_{major} = 22.1 min, t_{minor} = 15.8 min (92:8 e.r.).

(*4S*)-4-(4-nitrophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4h).



4h

Following the general procedure **A**, **4h** was isolated by column chromatography using silica gel in 91% yield as a mixture of diastereomers (3:1).

Major diastereomer:

^{1}H NMR: δ 8.26-8.12 (m, 3H), 7.77-7.73 (m, 1H), 7.51-7.47 (m, 2H), 7.38-7.30 (m, 3H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.86 (t, *J* = 2.7 Hz, 1H), 4.58 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.39 (s, 1H), 2.45-2.37 (m, 1H), 2.24-2.13 (m, 1H).

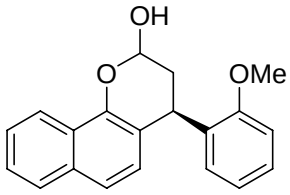
^{13}C NMR: δ 152.5, 146.9, 146.9, 133.6, 129.6, 127.5, 126.5, 126.4, 125.7, 125.1, 124.0, 121.6, 120.7, 116.9, 91.1, 37.4, 36.3.

Minor diastereomer (representative signals):

^{1}H NMR: δ 6.78 (d, *J* = 8.7 Hz, 1H), 5.72 (dd, *J* = 7.5, 2.1Hz, 1H), 4.48 (dd, *J* = 9.3, 6.9 Hz, 1H), 2.58-2.55 (m, 1H).

^{13}C NMR: δ 148.2, 146.8, 129.4, 127.5, 126.6, 125.8, 123.9, 121.7, 120.9, 116.4, 93.9, 40.8, 38.0.
IR (film): 3430, 3108, 2932, 1599, 1516, 1346, 1189, 1108, 973, 908, 856, 809, 731.
HRMS: Calculated for $[C_{19}H_{15}NO_4+NH_4]^+$:339.1339; found: 339.1341.
$[\alpha]_D^{rt}$ = + 68 (c = 1.23, $CHCl_3$).
The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OJ column [hexane/EtOH (90:10)]; flow rate 1.0 mL/min; t_{major} = 77.9 min, t_{minor} = 39.5 min (92:8 e.r.).

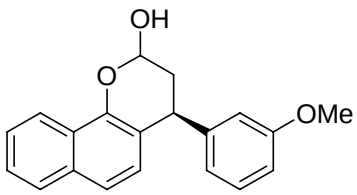
(*4S*)-4-(2-methoxyphenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4i).



4i

Following the general procedure **A**, **4i** was isolated by column chromatography using silica gel in 68% yield as a mixture of diastereomers (3:1).
Major diastereomer:
^{1}H NMR: δ 8.28-8.22 (m, 1H), 7.76-7.72 (m, 1H), 7.48-7.42 (m, 2H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.25-7.19 (m, 1H), 6.93 (dd, *J* = 8.7, 5.1 Hz, 2H), 6.89-6.79 (m, 2H), 5.68 (dd, *J* = 4.5, 3.6 Hz, 1H), 4.84 (t, *J* = 6.9 Hz, 1H), 3.84 (s, 3H), 2.32-2.29 (m, 2H).
^{13}C NMR: δ 157.2, 147.7, 133.4, 132.8, 130.0, 127.7, 127.4, 127.4, 125.9, 125.3, 125.1, 121.5, 120.5, 120.2, 118.0, 110.5, 92.2, 55.4, 34.6, 32.0.
Minor diastereomer (representative signals):
^{1}H NMR: δ 3.83 (s, 3H), 2.58-2.50 (m, 1H).
^{13}C NMR: δ 157.3, 148.3, 133.7, 132.3, 130.2, 129.0, 127.9, 127.1, 126.0, 125.4, 125.1, 121.7, 120.9, 120.3, 118.2, 110.7, 94.7, 55.4, 36.1, 33.9.
IR (film): 3397, 3056, 2931, 1685, 1579, 1491, 1462, 1396, 1244, 1110, 1028, 972, 907, 811, 754.
HRMS: Calculated for $[C_{20}H_{18}O_3+H]^+$:307.1329; found: 307.1335.
$[\alpha]_D^{rt}$ = + 42 (c = 1.36, $CHCl_3$).
The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (90:10)]; flow rate 1.0 mL/min; t_{major} = 22.1 min, t_{minor} = 11.0 min (90:10 e.r.).

(*4S*)-4-(3-methoxyphenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4j).



4j

Following the general procedure **A**, **4j** was isolated by column chromatography using silica gel in 79% yield as a mixture of diastereomers (3:1).
Major diastereomer:
^{1}H NMR: δ 8.23-8.20 (m, 1H), 7.75-7.71 (m, 1H), 7.48-7.42 (m, 2H), 7.31-7.19 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.81-6.73 (m, 3H), 5.80 (dd, *J* = 3.9, 2.4 Hz, 1H), 4.40 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.74 (s, 3H), 2.41-2.33 (m, 1H), 2.27-2.17 (m, 1H).
^{13}C NMR: δ 159.8, 146.8, 146.3, 133.5, 129.6, 127.5, 127.2, 126.0, 125.4, 125.0, 121.5, 121.2, 120.3, 118.3, 114.6, 112.0, 91.6, 55.2, 37.5, 36.5.

Minor diastereomer (representative signals):

^{1}H NMR: δ 6.87 (d, *J* = 8.4 Hz, 1H), 5.63 (dd, *J* = 8.4, 2.1 Hz, 1H), 4.32 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.73 (s, 3H), 2.58-2.50 (m, 1H).

^{13}C NMR: δ 159.9, 148.2, 145.9, 133.7, 129.7, 127.4, 127.0, 126.2, 125.5, 125.0, 121.7, 120.8, 120.4, 118.0, 114.2, 112.1, 94.6, 41.4, 38.8.

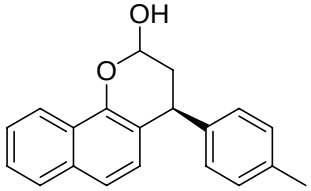
IR (film): 3420, 3054, 2935, 1699, 1601, 1488, 1396, 1346, 1262, 1153, 1048, 977, 910, 812, 732.

HRMS: Calculated for $[C_{20}H_{18}O_3+H]^+$:307.1329; found: 307.1323.

$[\alpha]_D^{rt}$ = + 53 (c = 1.19, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (90:10)]; flow rate 1.0 mL/min; t_{major} = 32.6 min, t_{minor} = 20.3 min (92:8 e.r.).

(*4S*)-4-p-tolyl-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4k).



4k

Following the general procedure **A**, **4k** was isolated by column chromatography using silica gel in 76% yield as a mixture of diastereomers (3:1).

Major diastereomer:

^{1}H NMR: δ 8.27-8.20 (m, 1H), 7.75-7.72 (m, 1H), 7.45 (t, *J* = 3.9 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 1H), 7.14-7.05 (m, 4H), 6.90 (d, *J* = 8.7 Hz, 1H), 5.80 (s, 1H), 4.40 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.22 (s, 1H), 2.40-2.38 (m, 1H), 2.34 (s, 3H), 2.27-2.22 (m, 1H).

^{13}C NMR: δ 146.8, 141.6, 136.3, 133.5, 129.3, 128.7, 127.5, 127.3, 126.0, 125.4, 125.1, 121.6, 120.3, 118.7, 91.6, 37.1, 36.7, 21.0.

Minor diastereomer (representative signals):

^{1}H NMR: δ 5.65 (d, *J* = 7.5 Hz, 1H), 3.29 (s, 1H), 2.58-2.51 (m, 1H).

^{13}C NMR: δ 141.2, 136.5, 129.5, 128.3, 127.4, 127.0, 126.1, 125.5, 121.8, 120.4, 118.4, 94.7, 40.9, 39.0.

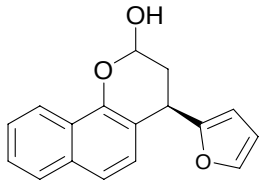
IR (film): 3394, 3052, 2926, 1575, 1510, 1395, 1348, 1188, 1055, 973, 906, 810, 732.

HRMS: Calculated for $[C_{20}H_{18}O_2+Na]^+$:313.1199; found: 313.1195.

$[\alpha]_D^{rt}$ = + 62 (c = 1.11, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (95:5)]; flow rate 1.0 mL/min; t major = 36.0 min, t minor = 28.1 min (91:9 e.r.).

(*4R*)-4-(furan-2-yl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4l).



4l

Following the general procedure **A**, **4l** was isolated by column chromatography using silica gel in 63% yield as a mixture of diastereomers (7:2).

Major diastereomer:

^{1}H NMR: δ 8.27-8.19 (m, 1H), 7.77-7.71 (m, 1H), 7.48-7.42 (m, 2H), 7.39-

7.33 (m, 2H), 7.08 (d, *J* = 8.7 Hz, 1H), 6.32 (d, *J* = 3.3 Hz, 1H), 6.08 (d, *J* = 3.3 Hz, 1H), 5.78 (d, *J* = 3.0 Hz, 1H), 4.50 (dd, *J* = 8.1, 5.7 Hz, 1H), 3.30 (s, 1 H), 2.54- 2.43 (m, 1H), 2.31-2.25 (m, 1H).

^{13}C NMR: δ 156.5, 146.9, 141.9, 133.6, 127.5, 126.4, 126.1, 125.4, 125.1, 121.6, 120.4, 115.8, 110.2, 107.3, 91.9, 33.0, 32.0.

Minor diastereomer (representative signals):

^{1}H NMR: δ 5.72 (s, 1H), 4.43 (t, *J* = 6.3 Hz, 1H), 3.61 (s, 1H).

^{13}C NMR: δ 156.6, 142.1, 133.8, 127.4, 126.6, 126.3, 125.6, 125.3, 121.9, 120.6, 114.8, 110.4, 106.7, 93.4, 33.5, 33.0.

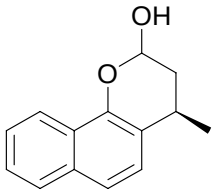
IR (film): 3376, 2927, 1673, 1625, 1468, 1392, 1265, 1125, 1074, 1018, 969, 811, 753.

HRMS: Calculated for $[C_{17}H_{14}O_3+H]^+$:267.1016; found: 267.1022.

$[\alpha]_D^{rt}$ = + 38 (c = 1.77, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (90:10)]; flow rate 1.0 mL/min; t major = 9.3 min, t minor = 8.2 min (87:13 e.r.).

(*4R*)-4-methyl-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4m).



4m

Following the general procedure **A**, **4m** was isolated by column chromatography using silica gel in 70% yield as a mixture of diastereomers (2:1).

Major diastereomer:

^{1}H NMR: δ 8.20-8.15 (m, 1H), 7.75-7.71 (m, 1H), 7.45-7.38 (m, 3H), 7.31-7.27 (m, 1H), 5.72 (dd, *J* = 4.8, 2.4 Hz, 1H), 3.35 (s, 1H), 3.25-3.15 (m, 1H), 2.16-2.08 (m, 1H), 1.88-1.80 (m, 1H), 1.38 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR: δ 146.0, 133.2, 127.3, 125.7, 125.3, 125.3, 125.0, 121.6, 120.7, 120.3, 91.7, 35.7, 25.2, 21.2.

Minor diastereomer (representative signals):

^{1}H NMR: δ 5.59 (dd, *J* = 7.8, 2.4 Hz, 1H), 2.29-2.67 (m, 1H), 1.84-1.76 (m, 1H), 1.41 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR: δ 146.9, 133.2, 127.4, 125.8, 125.4, 125.2, 125.0, 121.7, 120.5, 120.4, 94.4, 37.4, 28.4, 21.2.

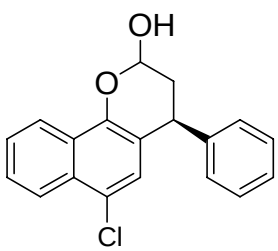
IR (film): 3379, 3055, 2959, 1574, 1394, 1198, 1086, 977, 807, 748.

HRMS: Calculated for $[C_{14}H_{14}O_2+H]^+$:215.1067; found: 215.1074.

$[\alpha]_D^{rt}$ = +4 (c = 1.36, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak AD column [hexane/EtOH (90:10)]; flow rate 0.7 mL/min; t major = 14.4 min, t minor = 13.8 min (86:14 e.r.).

(*4S*)-6-chloro-4-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-ol (4n).



4n

Following the general procedure **A**, **4n** was isolated by column chromatography using silica gel in 72% yield as a mixture of diastereomers (4:1).

Major diastereomer:

^{1}H NMR: δ 8.25 (d, *J* = 7.8 Hz, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 7.62-7.51 (m, 2H), 7.37-7.25 (m, 3H), 7.21-7.16 (m, 2H), 6.99 (s, 1H), 5.84 (dd, *J* = 6.0, 3.6 Hz, 1H), 4.40 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.26 (s, 1H), 2.42-2.34 (m, 1H), 2.31- 2.18 (m, 1H).

^{13}C NMR: δ 146.0, 143.8, 130.4, 128.8, 128.7, 127.0, 127.0, 126.8, 126.2, 126.1, 124.3, 123.4, 121.9, 119.1, 91.6, 37.2, 36.3.

Minor diastereomer (representative signals):

^{1}H NMR: δ 6.95 (s, 1H), 5.67 (t, *J* = 7.5 Hz, 1H), 4.33 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.35 (s, 1H), 2.60-2.53 (m, 1H).

^{13}C NMR: δ 147.4, 143.4, 128.9, 128.3, 127.2, 127.2, 126.6, 126.3, 126.0, 124.2, 123.5, 122.1, 118.7, 94.7, 41.2, 38.7.

IR (film): 3385, 2929, 1597, 1496, 1452, 1347, 1261, 1202, 1052, 979, 912, 762, 702.

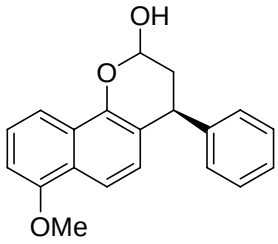
MS (EI) m/z (%): 310 (47) $[M]^+$, 265 (100), 202 (30).

MS (TOF ES$^+$): $[M+Na]^+$: 333.3.

$[\alpha]_D^{rt}$ = +39 (c = 1.06, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OJ column [hexane/EtOH (90:10)]; flow rate 1.0 mL/min; t_{major} = 12.8 min, t_{minor} = 11.0 min (88:12 e.r.).

(*4S*)-7-methoxy-4-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-ol (4o).



4o

Following the general procedure **A**, **4o** was isolated by column chromatography using silica gel in 83% yield as a mixture of diastereomers (5:1).

Major diastereomer:

^{1}H NMR: δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.42-7.26 (m, 4H), 7.24-7.17 (m, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 5.81 (dd, *J* = 6.6, 3.9 Hz, 1H), 4.45 (dd, *J* = 9.9, 6.0 Hz, 1H), 3.97 (s, 3H), 3.16 (dd, *J* = 4.2, 1.2 Hz, 1H), 2.43-2.35 (m, 1H), 2.28-2.18 (m, 1H).

^{13}C NMR: δ 155.3, 146.7, 144.7, 128.8, 128.6, 126.7, 126.5, 126.1, 125.5, 125.5, 119.2, 114.3, 113.8, 104.2, 91.6, 55.5, 37.5, 36.6.

Minor diastereomer (representative signals):

^{1}H NMR: δ 7.84 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.7 Hz, 1H), 5.68 (dt, *J* = 8.4, 2.4 Hz, 1H), 4.39 (dd, *J* = 10.2, 6.3 Hz, 1H), 3.99 (s, 3H), 3.24 (d, *J* = 7.2 Hz, 1H), 2.61-2.54 (m, 1H).

IR (film): 3400, 2932, 1599, 1505, 1448, 1395, 1351, 1258, 1073, 972, 912.

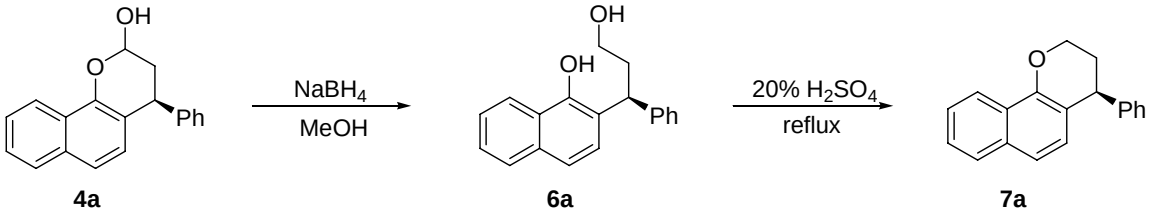
MS (EI) m/z (%): 306 (48) $[M]^+$, 261 (100), 246 (11), 218 (18), 202 (17), 189 (22), 174 (28).

MS (TOF ES$^+$): $[M+Na]^+$: 329.3.

$[\alpha]_D^{rt}$ = + 35 (c = 1.33, $CHCl_3$).

The product was converted to the corresponding alcohol with $NaBH_4$ and enantiomeric excess was determined by HPLC analysis using a Chiralpak OD-H column [hexane/EtOH (95:5)]; flow rate 1.0 mL/min; t_{major} = 28.2 min, t_{minor} = 31.0 min (92:8 e.r.).

General procedure **B**: Reduction and Cyclization of **4a**.



4a **6a** **7a**

To a solution of **4a** in methanol was added $NaBH_4$ (10 equiv). The mixture was heated under reflux for 1h. After cooling to room temperature, water was added and the resulting solution was acidified with diluted sulphuric acid and extracted with EtOAc, dried over Na_2SO_4 and evaporated. To the residue of **6a** was added aqueous sulphuric acid (20%). The resulting mixture was heated under reflux. After completion, the clear solution was cooled, diluted with water and extracted with EtOAc, dried over Na_2SO_4, evaporated and then loaded onto silica gel and the product **7a** was obtained by column chromatography.

Following the general procedure **B**, **6a** was isolated by column chromatography using silica gel in 78% yield.

^{1}H NMR: δ 8.25 (d, *J* = 7.8 Hz, 1H), 7.72-7.69 (m, 1H), 7.48-7.38 (m, 2H), 7.31-7.28 (m, 5H), 7.23-6.98 (m, 1H), 6.96 (d, *J* = 8.7 Hz, 1H), 4.80 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.87-3.81 (m, 1H), 3.45 (dt, *J* = 10.8, 3.6 Hz, 1H), 2.53-2.41 (m, 1H), 2.21-2.16 (m, 1H).

^{13}C NMR: δ 149.4, 143.8, 133.3, 128.5, 128.3, 127.4, 126.4, 126.2, 125.8, 125.5, 125.3, 123.8, 122.1, 120.7, 60.4, 38.3, 35.6.

IR (film): 3324, 3058, 2941, 1573, 1494, 1450, 1389, 1270, 1028, 907, 809, 745, 701.

HRMS: Calculated for $[C_{19}H_{18}O_2+H]^+$:279.1380; found: 279.1375.

Following the general procedure **B**, **7a** was isolated by column chromatography using silica gel in 69% yield (in two steps).

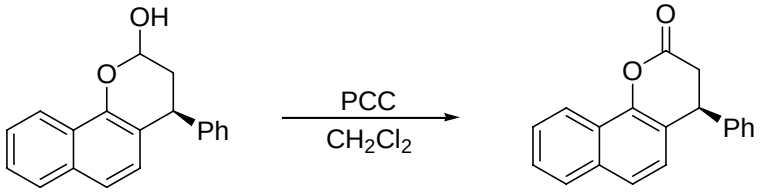
^{1}H NMR: δ 8.24-8.21 (m, 1H), 7.75-7.20 (m, 1H), 7.48-7.44 (m, 2H), 7.32-7.19 (m, 4H), 7.14 (d, *J* = 6.9 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 1H), 4.37-4.27 (m, 3H), 2.49-2.38 (m, 1H), 2.19-2.11 (m, 1H).

^{13}C NMR: δ 150.4, 145.9, 133.5, 128.8, 128.4, 128.3, 127.4, 126.4, 126.0, 125.3, 125.2, 121.7, 119.6, 117.6, 63.8, 40.9, 31.8.

IR (film): 3055, 2924, 1576, 1505, 1468, 1402, 1362, 1264, 1197, 1105, 801, 754, 702.

MS (EI) m/z (%): 260 (100) $[M]^+$, 231 (68), 202 (13), 183 (21), 169 (17), 115 (23).

General procedure **C**: Oxidation of **4a**.



4a **8a**

To a solution of **4a** in dichloromethane was added PCC (5 equiv). The resulting solution was stirred overnight at room temperature and filtered over celite. The solvent was removed in vacuo and the residue was subjected to column chromatography.

Following the general procedure **C**, **8a** was isolated by column chromatography using silica gel in 91% yield.

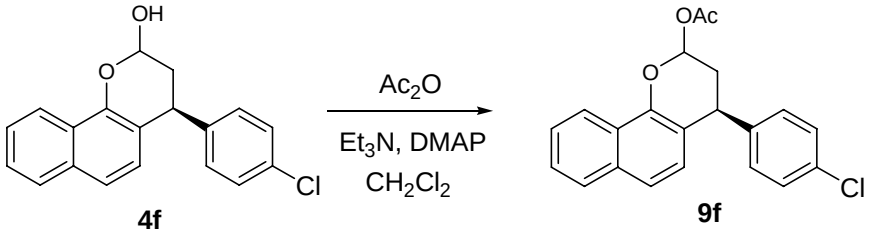
^{1}H NMR: δ 8.32 (d, *J* = 7.8 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.61-7.51 (m, 3H), 7.37-7.25 (m, 3H), 7.18 (dd, *J* = 6.9, 1.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 1H), 4.49 (t, *J* = 6.6 Hz, 1H), 3.21 (dd, *J* = 15.9, 6.3 Hz, 1H), 3.11 (dd, *J* = 15.6, 6.6 Hz, 1H).

^{13}C NMR: δ 167.4, 146.8, 140.7, 133.7, 129.2, 127.7, 127.6, 127.5, 126.9, 126.8, 125.3, 124.3, 123.7, 121.4, 119.9, 41.1, 37.3.

IR (film): 2955, 1770, 1499, 1377, 1215, 1130, 816, 750, 702.

HRMS: Calculated for $[C_{19}H_{14}O_2+NH_4]^+$:292.1332; found: 292.1336.

General procedure **D**: Acetylation of **4f**.



4f **9f**

To a solution of **4f** in dichloromethane, Ac2O (3 equiv), Et3N (3 equiv) and DMAP (0.2 equiv) were added and stirred at room temperature for about 2 h. The reaction mixture was poured into water, extracted with EtOAc, dried over Na_2SO4, evaporated and then loaded onto silica gel and the product **9f** was obtained by column chromatography.

Following the general procedure **D**, **9f** was isolated by column chromatography using silica gel in 95% yield.

^{1}H NMR: δ 8.25-8.22 (m, 1H), 7.79-7.72 (m, 1H), 7.52-7.49 (m, 2H), 7.48-7.24 (m, 4H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.75 (t, *J* = 2.7 Hz), 4.39 (dd, *J* = 10.2, 6.0 Hz, 1H), 2.47-2.36 (m, 1H), 2.31-2.27 (m, 1H), 2.09 (s, 3H).

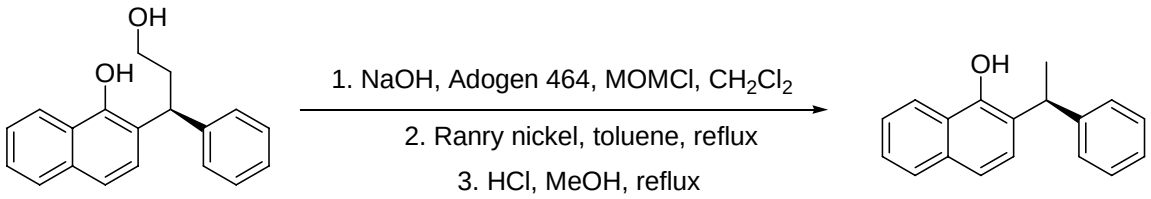
^{13}C NMR: δ 169.7, 146.4, 142.3, 133.4, 132.8, 130.1, 129.0, 127.4, 126.4, 126.4, 125.0, 124.8, 121.0, 118.1, 89.6, 36.6, 34.8, 21.2.

IR (film): 3056, 1754, 1576, 1490, 1402, 1369, 1183, 1120, 1037, 967, 809, 731.

HRMS: Calculated for $[C_{21}H_{17}ClO_3+H]^+$:353.0939; found: 353.0942.

$[\alpha]_D^{rt}$ = + 116 (c = 1.0, $CHCl_3$).

General procedure **E**: Dehydroxymethylation of **6a**.



6a **10a**

To a solution of **6a** in dichloromethane was added NaOH (1 equiv in water), and Adogen 464 (0.2 equiv), and stirred at room temperature for about 20 minutes. Then MOMCl (3 equiv) was added and stirred for about 30 minutes. After completion, the aqueous phase was separated and extracted with CH_2Cl_2, dried over Na_2SO_4, evaporated. To the above residue in toluene was added Raney nickel slurry (6 equiv weight), and refluxed for 3.5 h using Dean-Stark, cooled to room temperature, and filtered through a pad of Celite. The solvent was removed to leave yellow oil. To the above yellow residue was added MeOH and drops of HCl, and refluxed for 2h. After completion, the reaction mixture was poured into water, extracted with EtOAc, dried over Na_2SO4, evaporated and then loaded onto silica gel and the product **10a** was obtained by column chromatography.

Following the general procedure **E**, **10a** was isolated by column chromatography using silica gel in 53% yield in three steps.

^{1}H NMR: δ 8.09-8.04 (m, 1H), 7.81-7.76 (m, 1H), 7.49-7.40 (m, 4H), 7.33-7.28 (m, 4H), 7.26-7.22 (m, 1H), 5.09 (s, 1H), 4.46 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.73 (d, *J* = 7.2 Hz, 1H).

^{13}C NMR: δ 148.4, 144.7, 133.4, 129.0, 127.5, 127.5, 126.9, 125.8, 125.8, 125.3, 125.0, 124.9, 121.2, 120.4, 39.4, 21.0.

IR (film): 3514, 3058, 2967, 1572, 1493, 1452, 1388, 1237, 1196, 1059, 894, 811, 747, 701.

MS (EI) m/z (%): 248 (62) $[M]^+$, 233 (100), 203 (31), 170 (82), 115 (66).

$[\alpha]_D^{rt}$ = - 66 (c = 1.0, $CHCl_3$).

X-ray structure of 4o.

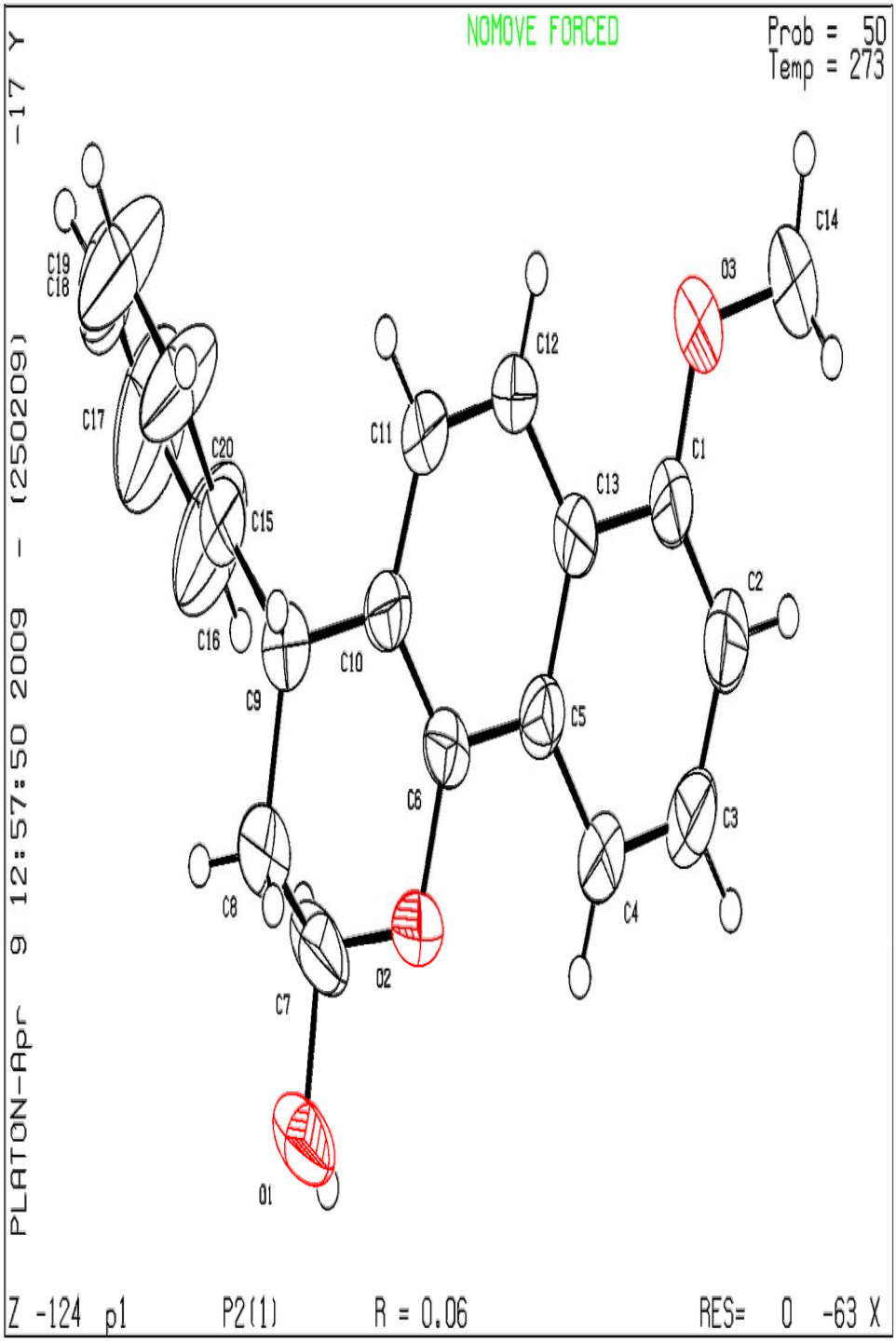


Table 1. Crystal data and structure refinement for p1.

Identification code	p1
Empirical formula	C20 H18 O3
Formula weight	306.34
Temperature	273(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2/1
Unit cell dimensions	a = 10.368(10) A alpha = 90 deg. b = 5.135(5) A beta = 99.164(17) deg. c = 14.763(14) A gamma = 90 deg.
Volume	775.9(13) A^3
Z, Calculated density	2, 1.311 Mg/m^3
Absorption coefficient	0.087 mm^-1
F(000)	324
Crystal size	0.52 x 0.27 x 0.22 mm
Theta range for data collection	1.40 to 26.50 deg.
Limiting indices	-13<=h<=10, -6<=k<=6, -16<=l<=18
Reflections collected / unique	4424 / 2789 [R(int) = 0.0279]
Completeness to theta = 26.50	99.3 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2789 / 1 / 210
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0612, wR2 = 0.1454
R indices (all data)	R1 = 0.0923, wR2 = 0.1660
Absolute structure parameter	1(2)
Largest diff. peak and hole	0.325 and -0.267 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for p1.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2084(3)	2476(8)	4649(2)	50(1)
C(2)	984(4)	1021(9)	4458(3)	59(1)
C(3)	133(4)	1398(9)	3646(3)	59(1)
C(4)	371(3)	3206(8)	3016(2)	51(1)
C(5)	1520(3)	4692(7)	3184(2)	42(1)
C(6)	1846(3)	6555(7)	2542(2)	41(1)
C(7)	1443(4)	8022(9)	1003(2)	74(1)
C(8)	2187(4)	10352(10)	1226(3)	68(1)
C(9)	3306(3)	10029(8)	2014(2)	51(1)
C(10)	2978(3)	7977(7)	2691(2)	43(1)
C(11)	3825(3)	7550(8)	3521(2)	52(1)
C(12)	3569(3)	5831(8)	4160(2)	53(1)
C(13)	2404(3)	4347(8)	4004(2)	46(1)
C(14)	2724(4)	459(13)	6103(3)	92(2)
C(15)	4639(3)	9527(8)	1735(2)	50(1)
C(16)	4890(5)	7511(13)	1196(4)	107(2)
C(17)	6131(7)	7193(17)	971(5)	138(3)
C(18)	7097(5)	8796(16)	1271(4)	103(2)
C(19)	6878(5)	10701(18)	1826(5)	136(3)

C(20)	5635(4)	11110(14)	2049(4)	103(2)
O(1)	343(3)	8436(6)	331(2)	73(1)
O(2)	940(2)	6827(5)	1752(1)	50(1)
O(3)	2977(3)	2315(7)	5434(2)	74(1)

Table 3. Bond lengths [A] and angles [deg] for p1.

C(1)-C(2)	1.355(5)
C(1)-O(3)	1.366(4)
C(1)-C(13)	1.428(5)
C(2)-C(3)	1.385(5)
C(2)-H(2)	0.9300
C(3)-C(4)	1.365(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.403(5)
C(4)-H(4)	0.9300
C(5)-C(13)	1.408(4)
C(5)-C(6)	1.425(4)
C(6)-C(10)	1.370(5)
C(6)-O(2)	1.383(3)
C(7)-O(1)	1.404(4)
C(7)-O(2)	1.433(5)
C(7)-C(8)	1.433(7)
C(7)-H(7)	0.9800
C(8)-C(9)	1.516(5)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(15)	1.525(5)
C(9)-C(10)	1.528(5)
C(9)-H(9)	0.9800
C(10)-C(11)	1.407(4)
C(11)-C(12)	1.349(5)
C(11)-H(11)	0.9300
C(12)-C(13)	1.416(5)
C(12)-H(12)	0.9300
C(14)-O(3)	1.426(5)
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-C(20)	1.338(6)
C(15)-C(16)	1.355(6)
C(16)-C(17)	1.389(7)
C(16)-H(16)	0.9300
C(17)-C(18)	1.317(9)
C(17)-H(17)	0.9300
C(18)-C(19)	1.319(9)
C(18)-H(18)	0.9300
C(19)-C(20)	1.397(7)
C(19)-H(19)	0.9300
C(20)-H(20)	0.9300
O(1)-H(1)	0.8200

C(2)-C(1)-O(3)	125.2(3)
C(2)-C(1)-C(13)	120.6(3)
O(3)-C(1)-C(13)	114.1(3)
C(1)-C(2)-C(3)	120.1(4)
C(1)-C(2)-H(2)	119.9
C(3)-C(2)-H(2)	119.9
C(4)-C(3)-C(2)	121.7(4)
C(4)-C(3)-H(3)	119.1
C(2)-C(3)-H(3)	119.1
C(3)-C(4)-C(5)	119.3(3)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
C(4)-C(5)-C(13)	120.1(3)
C(4)-C(5)-C(6)	122.1(3)
C(13)-C(5)-C(6)	117.8(3)
C(10)-C(6)-O(2)	122.1(3)
C(10)-C(6)-C(5)	122.6(3)
O(2)-C(6)-C(5)	115.4(3)
O(1)-C(7)-O(2)	104.8(3)
O(1)-C(7)-C(8)	112.5(4)
O(2)-C(7)-C(8)	115.4(3)
O(1)-C(7)-H(7)	107.9
O(2)-C(7)-H(7)	107.9
C(8)-C(7)-H(7)	107.9
C(7)-C(8)-C(9)	113.8(4)
C(7)-C(8)-H(8A)	108.8
C(9)-C(8)-H(8A)	108.8
C(7)-C(8)-H(8B)	108.8
C(9)-C(8)-H(8B)	108.8
H(8A)-C(8)-H(8B)	107.7
C(8)-C(9)-C(15)	115.2(3)
C(8)-C(9)-C(10)	110.8(3)
C(15)-C(9)-C(10)	111.5(3)
C(8)-C(9)-H(9)	106.2
C(15)-C(9)-H(9)	106.2
C(10)-C(9)-H(9)	106.2
C(6)-C(10)-C(11)	117.2(3)
C(6)-C(10)-C(9)	122.5(3)
C(11)-C(10)-C(9)	120.3(3)
C(12)-C(11)-C(10)	123.1(3)
C(12)-C(11)-H(11)	118.5
C(10)-C(11)-H(11)	118.5
C(11)-C(12)-C(13)	119.7(3)
C(11)-C(12)-H(12)	120.1
C(13)-C(12)-H(12)	120.1
C(5)-C(13)-C(12)	119.6(3)
C(5)-C(13)-C(1)	118.0(3)
C(12)-C(13)-C(1)	122.4(3)
O(3)-C(14)-H(14A)	109.5
O(3)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
O(3)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5

H(14B)-C(14)-H(14C)	109.5
C(20)-C(15)-C(16)	117.2(4)
C(20)-C(15)-C(9)	119.1(4)
C(16)-C(15)-C(9)	123.7(4)
C(15)-C(16)-C(17)	120.1(5)
C(15)-C(16)-H(16)	119.9
C(17)-C(16)-H(16)	119.9
C(18)-C(17)-C(16)	122.0(6)
C(18)-C(17)-H(17)	119.0
C(16)-C(17)-H(17)	119.0
C(17)-C(18)-C(19)	118.4(5)
C(17)-C(18)-H(18)	120.8
C(19)-C(18)-H(18)	120.8
C(18)-C(19)-C(20)	121.0(6)
C(18)-C(19)-H(19)	119.5
C(20)-C(19)-H(19)	119.5
C(15)-C(20)-C(19)	121.2(6)
C(15)-C(20)-H(20)	119.4
C(19)-C(20)-H(20)	119.4
C(7)-O(1)-H(1)	109.5
C(6)-O(2)-C(7)	114.3(3)
C(1)-O(3)-C(14)	117.0(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for p1.The anisotropic displacement factor exponent takes the form:-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	42(2)	58(3)	50(2)	14(2)	9(2)	3(2)
C(2)	52(2)	67(3)	62(2)	14(2)	17(2)	0(2)
C(3)	44(2)	60(3)	75(2)	0(2)	11(2)	-11(2)
C(4)	40(2)	58(3)	57(2)	4(2)	8(2)	-3(2)
C(5)	35(2)	47(2)	44(2)	-3(2)	8(1)	2(2)
C(6)	39(2)	47(2)	35(2)	-2(2)	3(1)	8(2)
C(7)	90(3)	71(3)	48(2)	13(2)	-24(2)	-12(3)
C(8)	60(2)	80(3)	61(2)	17(2)	-6(2)	-9(2)
C(9)	45(2)	57(3)	49(2)	3(2)	4(2)	-1(2)
C(10)	36(2)	52(2)	42(2)	-3(2)	4(1)	1(2)
C(11)	39(2)	65(3)	50(2)	4(2)	3(1)	-8(2)
C(12)	39(2)	73(3)	43(2)	9(2)	-2(1)	-7(2)
C(13)	40(2)	56(2)	40(2)	6(2)	6(1)	2(2)
C(14)	82(3)	121(5)	70(3)	47(3)	1(2)	-12(3)
C(15)	43(2)	60(3)	46(2)	4(2)	6(1)	-4(2)
C(16)	84(3)	117(5)	134(4)	-58(4)	55(3)	-22(3)
C(17)	128(5)	157(7)	153(6)	-53(5)	93(5)	-15(5)
C(18)	64(3)	140(6)	115(4)	24(4)	46(3)	9(4)
C(19)	55(3)	172(8)	182(7)	-44(7)	22(4)	-38(4)
C(20)	48(3)	131(5)	129(4)	-46(4)	13(3)	-26(3)
O(1)	88(2)	63(2)	55(2)	9(2)	-30(1)	-13(2)

O(2)	42(1)	61(2)	44(1)	0(1)	-7(1)	-4(1)
O(3)	62(2)	99(3)	58(2)	34(2)	-2(1)	-6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for p1.

	x	y	z	U(eq)
H(2)	800	-233	4874	71
H(3)	-621	392	3527	71
H(4)	-222	3451	2480	62
H(7)	2007	6753	762	88
H(8A)	1608	11706	1383	82
H(8B)	2536	10924	688	82
H(9)	3381	11687	2347	61
H(11)	4598	8498	3635	62
H(12)	4156	5622	4702	63
H(14A)	1900	841	6291	138
H(14B)	3405	544	6626	138
H(14C)	2698	-1257	5843	138
H(16)	4230	6338	977	129
H(17)	6284	5807	597	166
H(18)	7913	8588	1095	123
H(19)	7562	11788	2072	163
H(20)	5497	12507	2423	123
H(1)	36	7029	143	110

Table 6. Torsion angles [deg] for p1.

O(3)-C(1)-C(2)-C(3)	178.5(4)
C(13)-C(1)-C(2)-C(3)	-2.2(6)
C(1)-C(2)-C(3)-C(4)	0.4(6)
C(2)-C(3)-C(4)-C(5)	1.3(6)
C(3)-C(4)-C(5)-C(13)	-1.2(5)
C(3)-C(4)-C(5)-C(6)	178.1(3)
C(4)-C(5)-C(6)-C(10)	-178.6(3)
C(13)-C(5)-C(6)-C(10)	0.6(4)
C(4)-C(5)-C(6)-O(2)	1.2(4)
C(13)-C(5)-C(6)-O(2)	-179.6(3)
O(1)-C(7)-C(8)-C(9)	174.4(3)
O(2)-C(7)-C(8)-C(9)	54.2(6)
C(7)-C(8)-C(9)-C(15)	97.1(4)
C(7)-C(8)-C(9)-C(10)	-30.6(5)
O(2)-C(6)-C(10)-C(11)	179.7(3)
C(5)-C(6)-C(10)-C(11)	-0.5(5)
O(2)-C(6)-C(10)-C(9)	2.0(5)
C(5)-C(6)-C(10)-C(9)	-178.2(3)
C(8)-C(9)-C(10)-C(6)	3.9(5)
C(15)-C(9)-C(10)-C(6)	-125.8(3)

C(8)-C(9)-C(10)-C(11)	-173.6(3)
C(15)-C(9)-C(10)-C(11)	56.6(4)
C(6)-C(10)-C(11)-C(12)	0.0(5)
C(9)-C(10)-C(11)-C(12)	177.7(3)
C(10)-C(11)-C(12)-C(13)	0.4(6)
C(4)-C(5)-C(13)-C(12)	179.1(3)
C(6)-C(5)-C(13)-C(12)	-0.2(5)
C(4)-C(5)-C(13)-C(1)	-0.5(5)
C(6)-C(5)-C(13)-C(1)	-179.8(3)
C(11)-C(12)-C(13)-C(5)	-0.3(5)
C(11)-C(12)-C(13)-C(1)	179.3(4)
C(2)-C(1)-C(13)-C(5)	2.2(5)
O(3)-C(1)-C(13)-C(5)	-178.4(3)
C(2)-C(1)-C(13)-C(12)	-177.4(4)
O(3)-C(1)-C(13)-C(12)	2.0(5)
C(8)-C(9)-C(15)-C(20)	124.4(5)
C(10)-C(9)-C(15)-C(20)	-108.2(5)
C(8)-C(9)-C(15)-C(16)	-57.2(6)
C(10)-C(9)-C(15)-C(16)	70.2(5)
C(20)-C(15)-C(16)-C(17)	-1.7(9)
C(9)-C(15)-C(16)-C(17)	179.8(5)
C(15)-C(16)-C(17)-C(18)	0.5(11)
C(16)-C(17)-C(18)-C(19)	2.3(12)
C(17)-C(18)-C(19)-C(20)	-3.7(11)
C(16)-C(15)-C(20)-C(19)	0.3(9)
C(9)-C(15)-C(20)-C(19)	178.8(5)
C(18)-C(19)-C(20)-C(15)	2.5(11)
C(10)-C(6)-O(2)-C(7)	18.9(5)
C(5)-C(6)-O(2)-C(7)	-160.9(3)
O(1)-C(7)-O(2)-C(6)	-172.0(3)
C(8)-C(7)-O(2)-C(6)	-47.7(5)
C(2)-C(1)-O(3)-C(14)	0.1(6)
C(13)-C(1)-O(3)-C(14)	-179.3(4)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for p1 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

X-ray structure of 6a

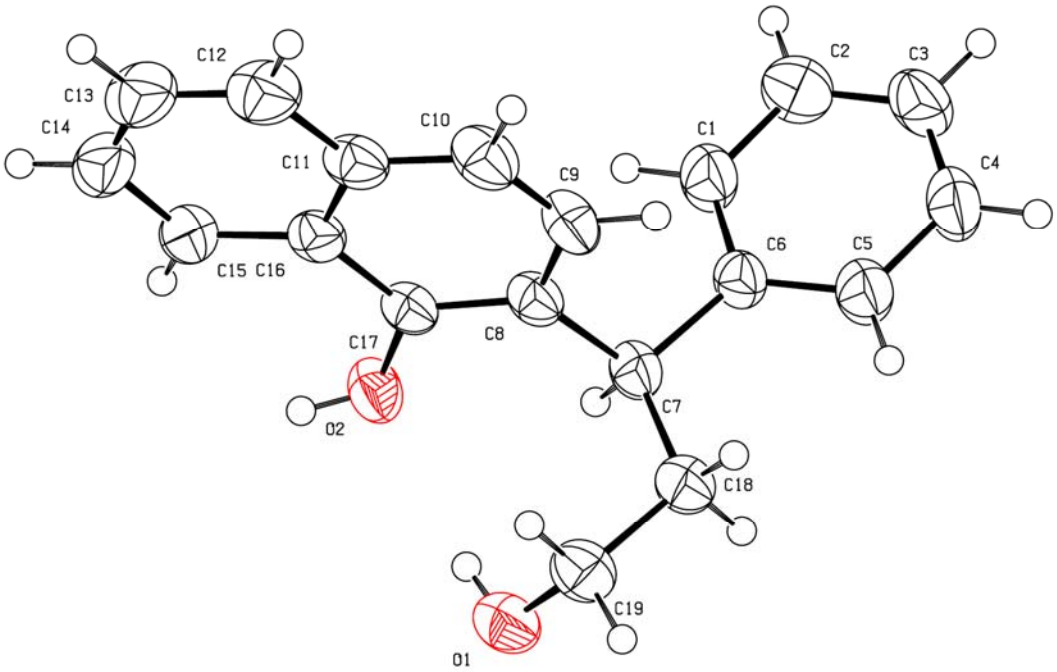


Table 1. Crystal data and structure refinement for p212121.

Identification code	p212121
Empirical formula	C19 H18 O2
Formula weight	278.33
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 5.788(2) A alpha = 90 deg.
	b = 10.571(4) A beta = 90 deg.
	c = 23.447(10) A gamma = 90 deg.
Volume	1434.8(10) A^3
Z, Calculated density	4, 1.288 Mg/m^3
Absorption coefficient	0.082 mm^-1
F(000)	592
Crystal size	? x ? x ? mm
Theta range for data collection	2.11 to 26.46 deg.
Limiting indices	-7<=h<=7, -13<=k<=13, -29<=l<=19
Reflections collected / unique	8123 / 2910 [R(int) = 0.0246]

Completeness to theta = 26.46	98.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2910 / 0 / 192
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0365, wR2 = 0.0842
R indices (all data)	R1 = 0.0455, wR2 = 0.0897
Absolute structure parameter	1.5(14)
Largest diff. peak and hole	0.129 and -0.135 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for p212121. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	y	z	U(eq)
C(1)	6570(3)	2540(2)	8850(1)	51(1)
C(2)	6572(4)	1346(2)	8616(1)	62(1)
C(3)	8417(4)	558(2)	8706(1)	57(1)
C(4)	10211(4)	965(2)	9029(1)	59(1)
C(5)	10206(3)	2169(2)	9263(1)	51(1)
C(6)	8387(3)	2979(1)	9173(1)	38(1)
C(7)	8290(3)	4332(1)	9398(1)	37(1)
C(8)	8083(3)	5254(1)	8904(1)	37(1)
C(9)	9641(3)	5178(2)	8443(1)	45(1)
C(10)	9526(3)	5980(2)	7994(1)	49(1)
C(11)	7783(3)	6902(2)	7963(1)	43(1)
C(12)	7567(4)	7732(2)	7494(1)	57(1)
C(13)	5818(4)	8581(2)	7467(1)	60(1)
C(14)	4182(4)	8636(2)	7899(1)	55(1)
C(15)	4353(3)	7875(2)	8363(1)	45(1)
C(16)	6172(3)	6999(2)	8412(1)	37(1)
C(17)	6442(3)	6185(1)	8891(1)	35(1)
C(18)	10315(3)	4655(1)	9789(1)	44(1)
C(19)	10320(3)	6005(2)	9992(1)	49(1)
O(1)	8338(2)	6356(1)	10309(1)	52(1)
O(2)	5040(2)	6306(1)	9359(1)	44(1)

Table 3. Bond lengths [A] and angles [deg] for p212121.

C(1)-C(2)	1.376(3)
C(1)-C(6)	1.377(2)
C(1)-H(1A)	0.9300
C(2)-C(3)	1.371(3)
C(2)-H(2A)	0.9300
C(3)-C(4)	1.355(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.387(2)
C(4)-H(4)	0.9300
C(5)-C(6)	1.373(2)
C(5)-H(5)	0.9300
C(6)-C(7)	1.525(2)
C(7)-C(8)	1.519(2)
C(7)-C(18)	1.526(2)
C(7)-H(7)	0.9800
C(8)-C(17)	1.368(2)
C(8)-C(9)	1.410(2)
C(9)-C(10)	1.354(2)
C(9)-H(9)	0.9300
C(10)-C(11)	1.404(2)
C(10)-H(10)	0.9300
C(11)-C(16)	1.410(2)
C(11)-C(12)	1.412(2)
C(12)-C(13)	1.354(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.389(3)
C(13)-H(13)	0.9300
C(14)-C(15)	1.355(2)
C(14)-H(14)	0.9300
C(15)-C(16)	1.407(2)
C(15)-H(15)	0.9300
C(16)-C(17)	1.424(2)
C(17)-O(2)	1.3709(18)
C(18)-C(19)	1.505(2)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(19)-O(1)	1.416(2)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
O(1)-H(1)	0.8200
O(2)-H(2)	0.8200

C(2)-C(1)-C(6)	121.88(18)
C(2)-C(1)-H(1A)	119.1
C(6)-C(1)-H(1A)	119.1
C(3)-C(2)-C(1)	119.76(18)
C(3)-C(2)-H(2A)	120.1
C(1)-C(2)-H(2A)	120.1
C(4)-C(3)-C(2)	119.35(17)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(3)-C(4)-C(5)	120.74(19)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(6)-C(5)-C(4)	120.88(18)
C(6)-C(5)-H(5)	119.6
C(4)-C(5)-H(5)	119.6
C(5)-C(6)-C(1)	117.36(15)
C(5)-C(6)-C(7)	124.02(16)
C(1)-C(6)-C(7)	118.60(15)
C(8)-C(7)-C(6)	109.91(13)
C(8)-C(7)-C(18)	112.00(13)
C(6)-C(7)-C(18)	112.92(13)
C(8)-C(7)-H(7)	107.2
C(6)-C(7)-H(7)	107.2
C(18)-C(7)-H(7)	107.2
C(17)-C(8)-C(9)	117.93(14)
C(17)-C(8)-C(7)	122.23(14)
C(9)-C(8)-C(7)	119.83(14)
C(10)-C(9)-C(8)	121.94(16)
C(10)-C(9)-H(9)	119.0
C(8)-C(9)-H(9)	119.0
C(9)-C(10)-C(11)	120.65(16)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-H(10)	119.7
C(10)-C(11)-C(16)	119.18(15)
C(10)-C(11)-C(12)	122.34(17)
C(16)-C(11)-C(12)	118.48(18)
C(13)-C(12)-C(11)	121.00(19)
C(13)-C(12)-H(12)	119.5
C(11)-C(12)-H(12)	119.5
C(12)-C(13)-C(14)	120.20(18)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	120.69(19)

C(15)-C(14)-H(14)	119.7
C(13)-C(14)-H(14)	119.7
C(14)-C(15)-C(16)	120.74(18)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(15)-C(16)-C(11)	118.80(15)
C(15)-C(16)-C(17)	122.99(15)
C(11)-C(16)-C(17)	118.20(15)
C(8)-C(17)-O(2)	117.44(13)
C(8)-C(17)-C(16)	121.86(14)
O(2)-C(17)-C(16)	120.69(13)
C(19)-C(18)-C(7)	113.83(15)
C(19)-C(18)-H(18A)	108.8
C(7)-C(18)-H(18A)	108.8
C(19)-C(18)-H(18B)	108.8
C(7)-C(18)-H(18B)	108.8
H(18A)-C(18)-H(18B)	107.7
O(1)-C(19)-C(18)	114.42(16)
O(1)-C(19)-H(19A)	108.7
C(18)-C(19)-H(19A)	108.7
O(1)-C(19)-H(19B)	108.7
C(18)-C(19)-H(19B)	108.7
H(19A)-C(19)-H(19B)	107.6
C(19)-O(1)-H(1)	109.5
C(17)-O(2)-H(2)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for p212121. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	51(1)	37(1)	66(1)	-5(1)	-12(1)	3(1)
C(2)	70(1)	46(1)	70(1)	-10(1)	-18(1)	-8(1)
C(3)	77(1)	33(1)	60(1)	-7(1)	-1(1)	0(1)
C(4)	64(1)	37(1)	74(1)	-2(1)	-8(1)	12(1)
C(5)	51(1)	39(1)	61(1)	-5(1)	-10(1)	4(1)
C(6)	45(1)	30(1)	40(1)	2(1)	1(1)	1(1)
C(7)	41(1)	30(1)	40(1)	0(1)	3(1)	1(1)
C(8)	44(1)	29(1)	37(1)	-3(1)	3(1)	-3(1)
C(9)	51(1)	36(1)	49(1)	-5(1)	11(1)	5(1)
C(10)	58(1)	44(1)	45(1)	-3(1)	16(1)	-2(1)

C(11)	58(1)	35(1)	36(1)	-3(1)	3(1)	-9(1)
C(12)	79(1)	51(1)	41(1)	6(1)	5(1)	-9(1)
C(13)	88(2)	49(1)	45(1)	12(1)	-9(1)	-6(1)
C(14)	67(1)	41(1)	56(1)	4(1)	-18(1)	-1(1)
C(15)	52(1)	38(1)	45(1)	0(1)	-5(1)	1(1)
C(16)	46(1)	28(1)	37(1)	-2(1)	-3(1)	-7(1)
C(17)	40(1)	30(1)	35(1)	-4(1)	3(1)	-3(1)
C(18)	48(1)	38(1)	48(1)	-5(1)	-4(1)	-1(1)
C(19)	51(1)	42(1)	53(1)	-6(1)	-1(1)	-5(1)
O(1)	59(1)	45(1)	52(1)	-11(1)	-2(1)	-2(1)
O(2)	51(1)	38(1)	43(1)	2(1)	11(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for p212121.

x	y	z	U(eq)
H(1A)	5306	3065	8788	62
H(2A)	5325	1074	8398	74
H(3)	8438	-248	8546	68
H(4)	11459	430	9094	70
H(5)	11451	2432	9483	61
H(7)	6877	4408	9626	44
H(9)	10782	4559	8448	55
H(10)	10613	5921	7703	59
H(12)	8643	7696	7200	68
H(13)	5711	9128	7157	72
H(14)	2956	9202	7871	66
H(15)	3256	7933	8651	54
H(18A)	10272	4099	10118	53
H(18B)	11746	4492	9586	53
H(19A)	11677	6139	10227	58
H(19B)	10447	6558	9664	58
H(1)	7199	6333	10101	78
H(2)	4506	7024	9370	66

Table 6. Torsion angles [deg] for p212121.

C(6)-C(1)-C(2)-C(3)	0.3(3)
C(1)-C(2)-C(3)-C(4)	0.5(3)
C(2)-C(3)-C(4)-C(5)	-0.7(3)
C(3)-C(4)-C(5)-C(6)	0.0(3)
C(4)-C(5)-C(6)-C(1)	0.9(3)
C(4)-C(5)-C(6)-C(7)	-177.80(17)
C(2)-C(1)-C(6)-C(5)	-1.0(3)
C(2)-C(1)-C(6)-C(7)	177.73(17)
C(5)-C(6)-C(7)-C(8)	119.79(18)
C(1)-C(6)-C(7)-C(8)	-58.9(2)
C(5)-C(6)-C(7)-C(18)	-6.1(2)
C(1)-C(6)-C(7)-C(18)	175.27(15)
C(6)-C(7)-C(8)-C(17)	129.97(15)
C(18)-C(7)-C(8)-C(17)	-103.65(18)
C(6)-C(7)-C(8)-C(9)	-51.2(2)
C(18)-C(7)-C(8)-C(9)	75.23(18)
C(17)-C(8)-C(9)-C(10)	-1.0(2)
C(7)-C(8)-C(9)-C(10)	-179.89(16)
C(8)-C(9)-C(10)-C(11)	-2.0(3)
C(9)-C(10)-C(11)-C(16)	1.2(3)
C(9)-C(10)-C(11)-C(12)	-178.23(18)
C(10)-C(11)-C(12)-C(13)	177.56(18)
C(16)-C(11)-C(12)-C(13)	-1.9(3)
C(11)-C(12)-C(13)-C(14)	-0.7(3)
C(12)-C(13)-C(14)-C(15)	2.2(3)
C(13)-C(14)-C(15)-C(16)	-0.9(3)
C(14)-C(15)-C(16)-C(11)	-1.7(2)
C(14)-C(15)-C(16)-C(17)	179.47(16)
C(10)-C(11)-C(16)-C(15)	-176.40(16)
C(12)-C(11)-C(16)-C(15)	3.1(2)
C(10)-C(11)-C(16)-C(17)	2.5(2)
C(12)-C(11)-C(16)-C(17)	-178.06(16)
C(9)-C(8)-C(17)-O(2)	-175.59(14)
C(7)-C(8)-C(17)-O(2)	3.3(2)
C(9)-C(8)-C(17)-C(16)	4.8(2)
C(7)-C(8)-C(17)-C(16)	-176.26(14)
C(15)-C(16)-C(17)-C(8)	173.21(15)
C(11)-C(16)-C(17)-C(8)	-5.6(2)
C(15)-C(16)-C(17)-O(2)	-6.3(2)
C(11)-C(16)-C(17)-O(2)	174.83(14)
C(8)-C(7)-C(18)-C(19)	52.34(19)

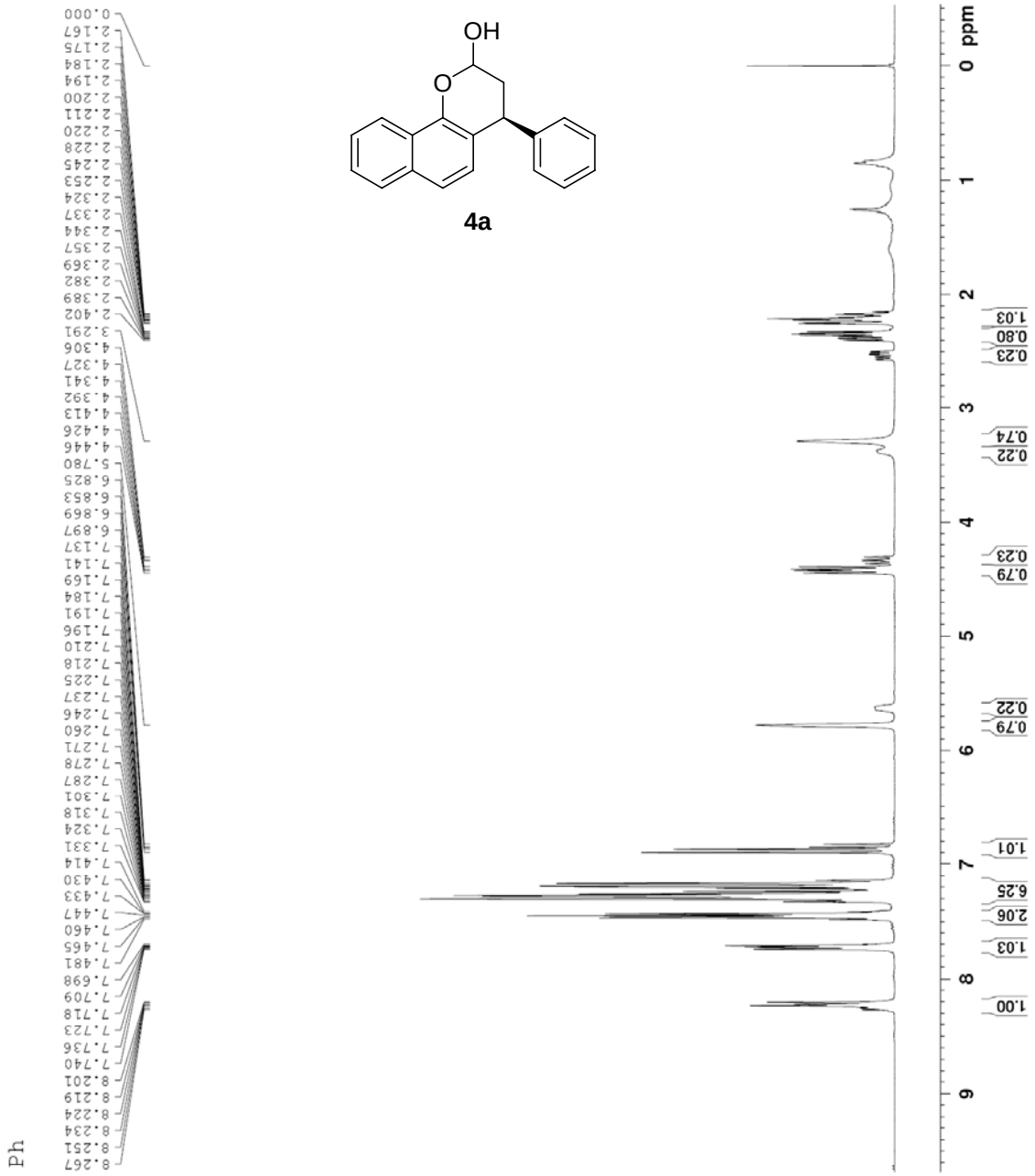
C(6)-C(7)-C(18)-C(19)	177.07(15)
C(7)-C(18)-C(19)-O(1)	60.0(2)

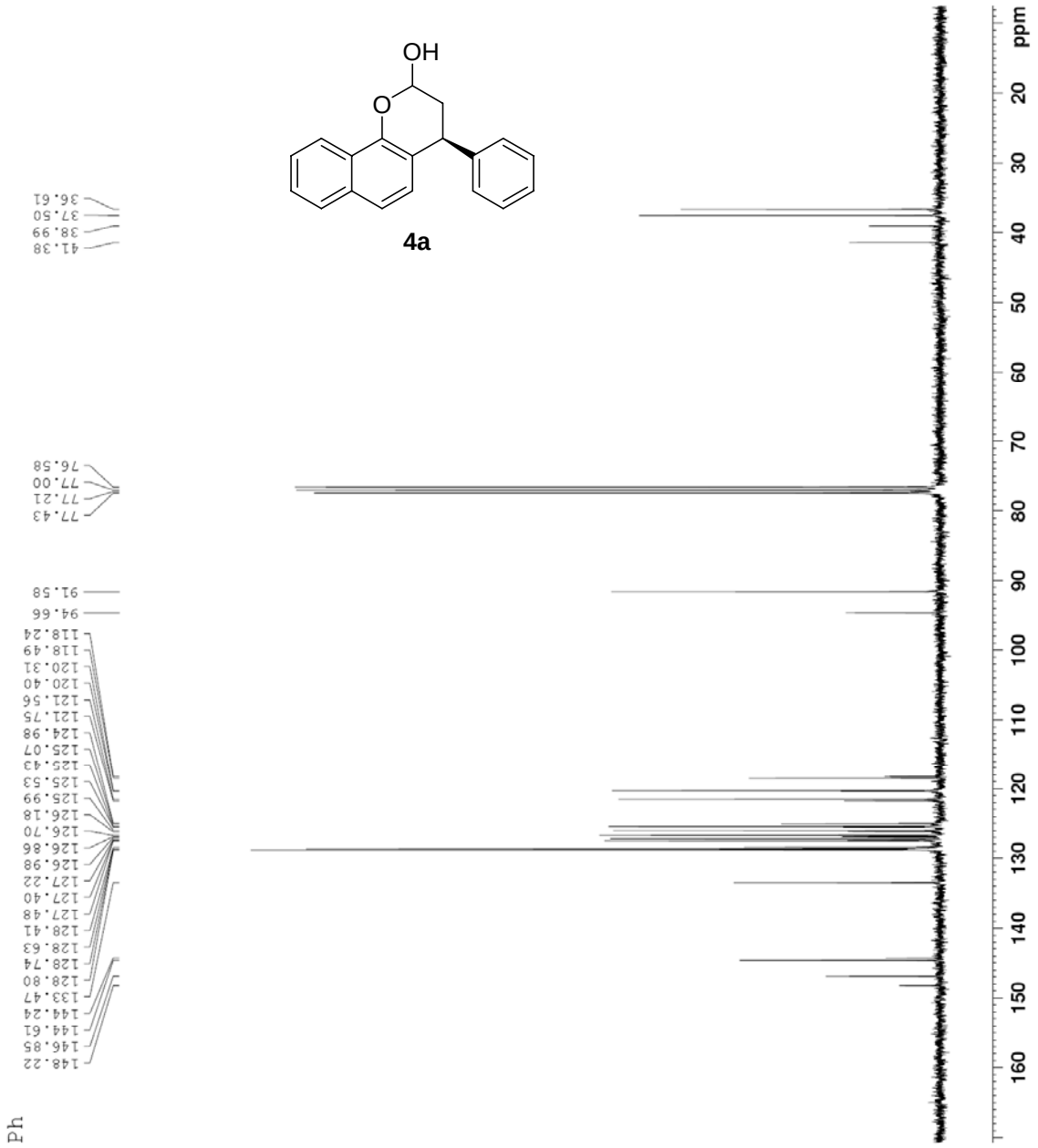
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for p212121 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

^{1}H NMR and ^{13}C NMR:

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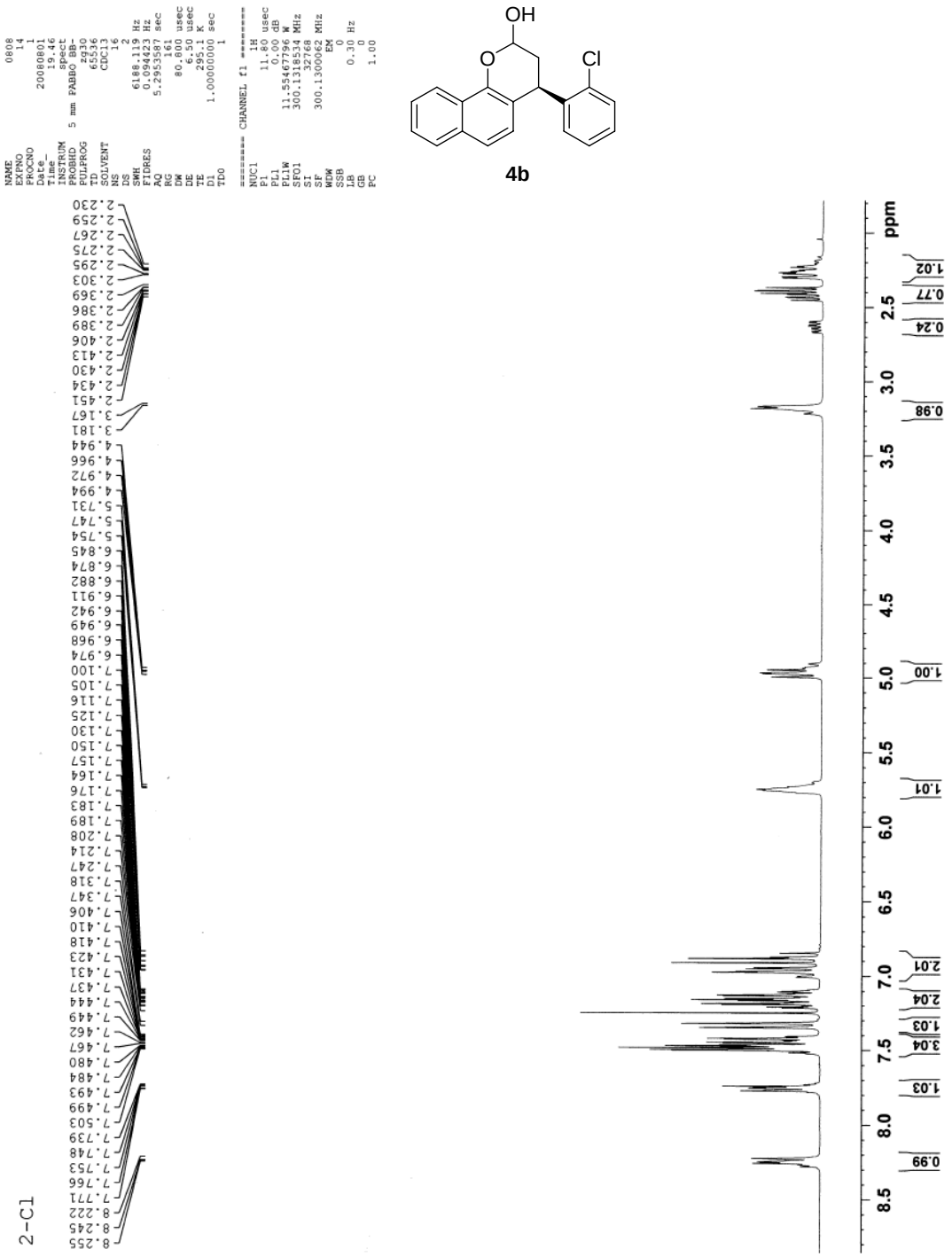
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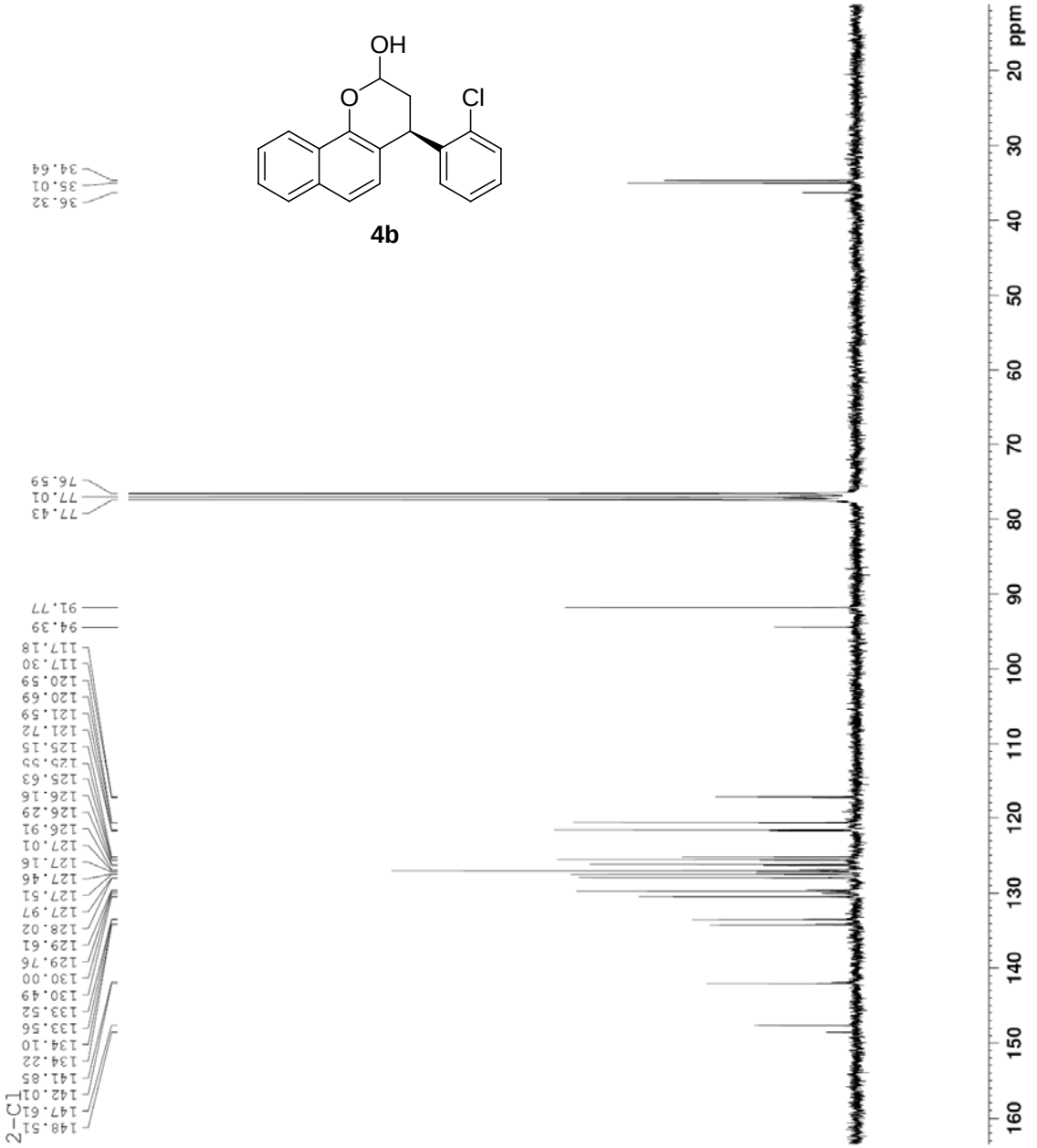
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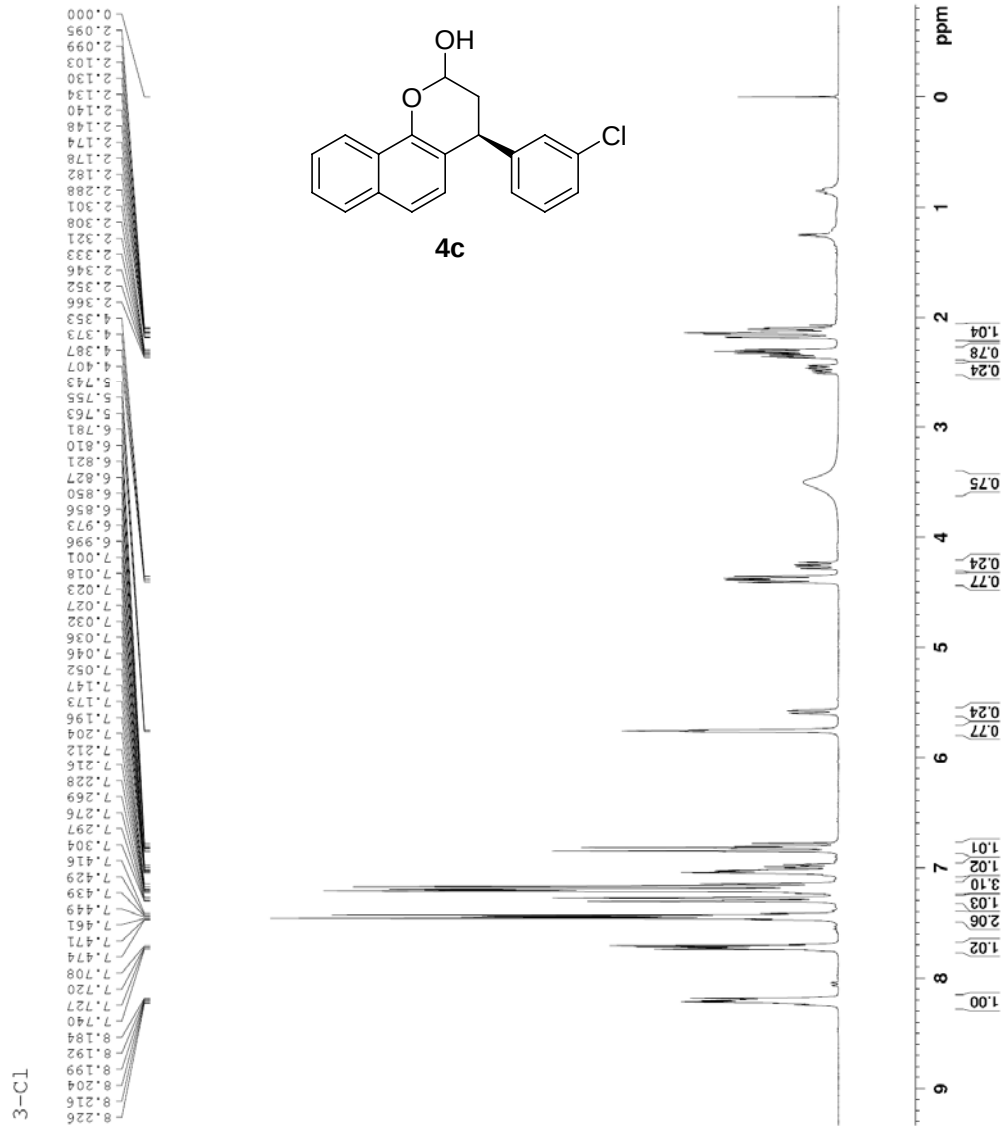
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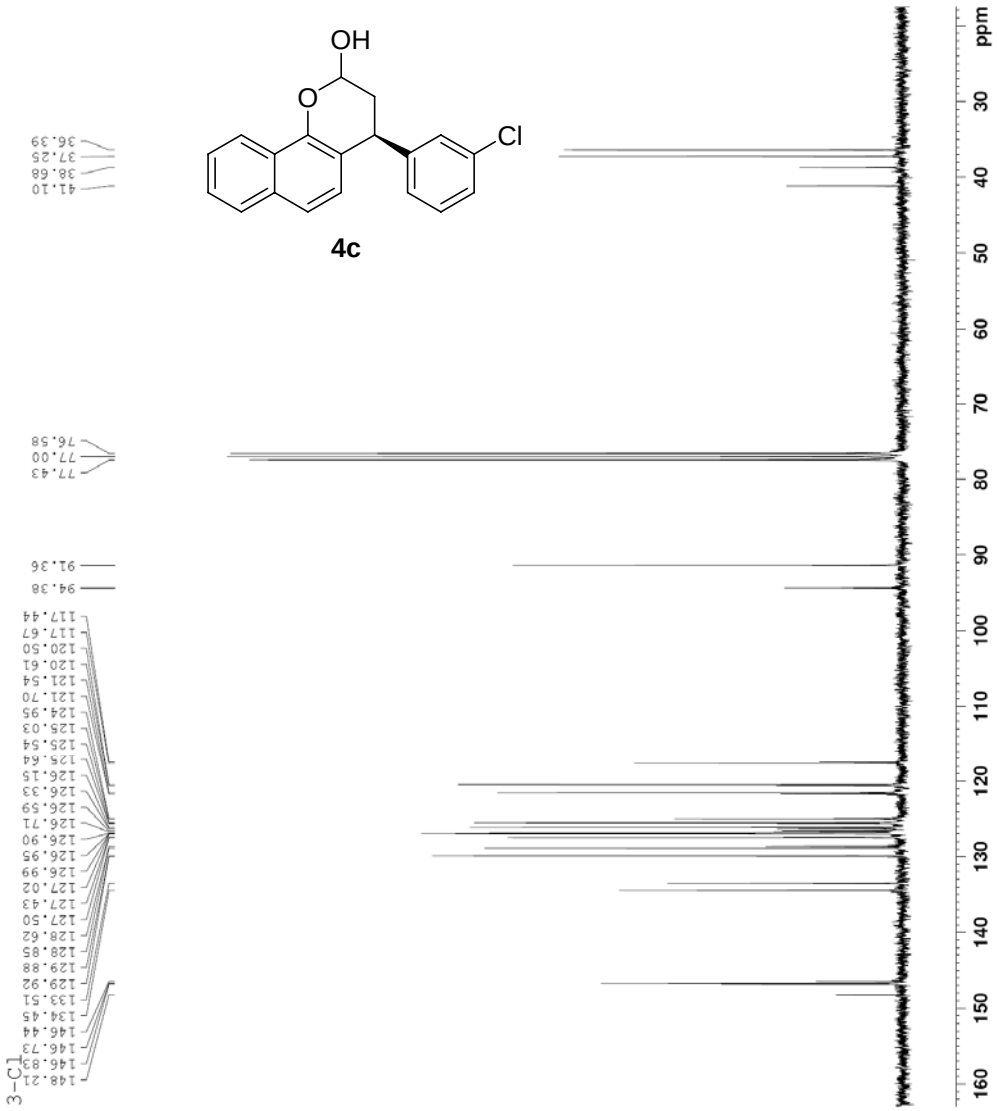
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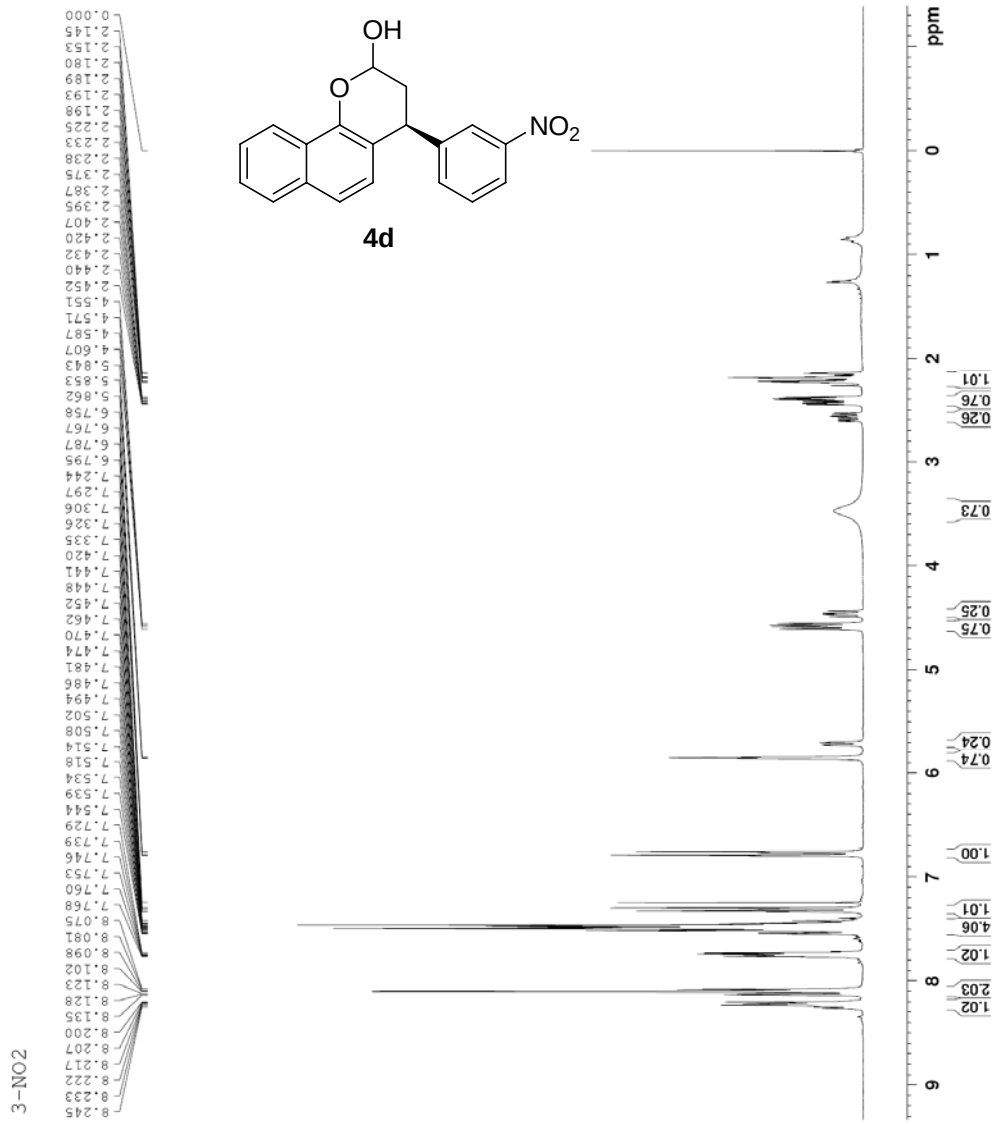
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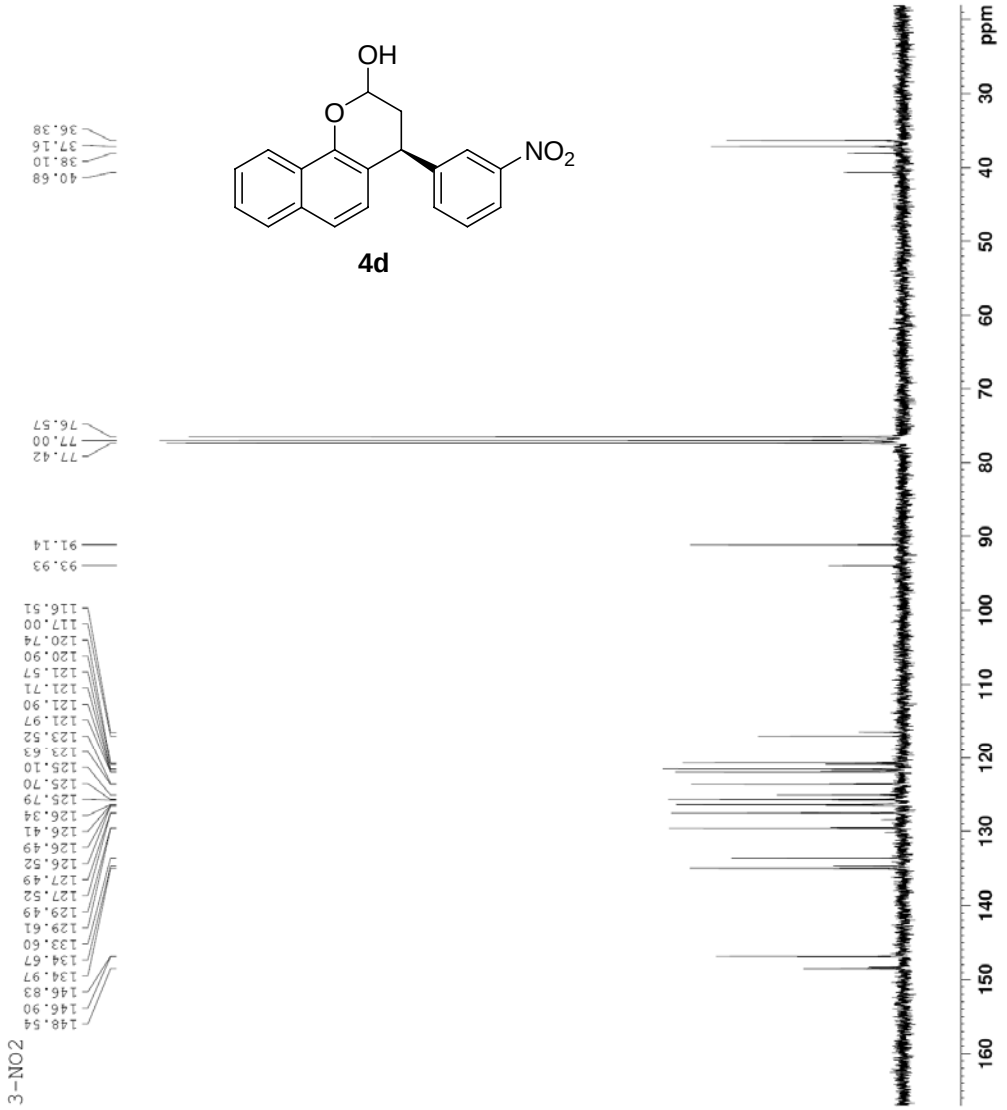
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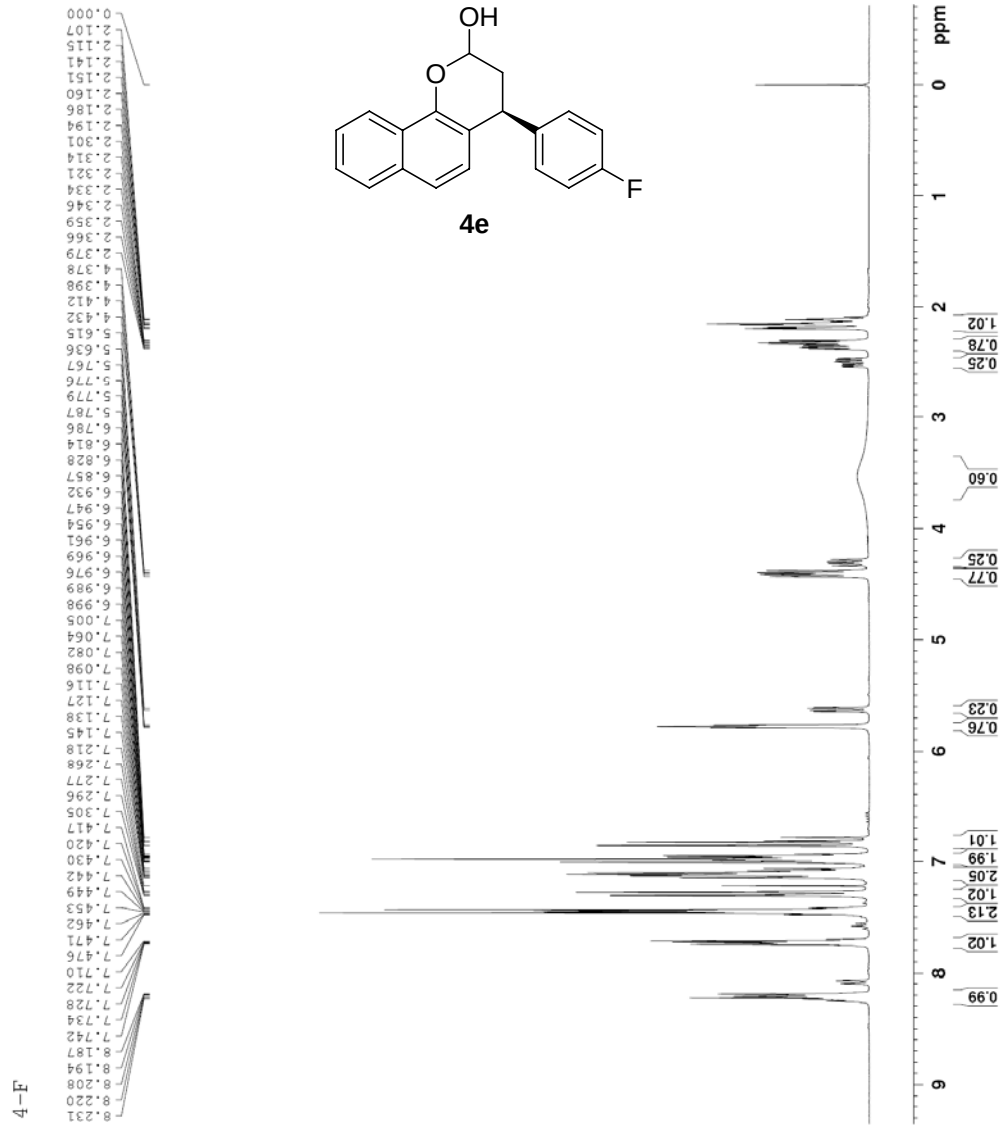
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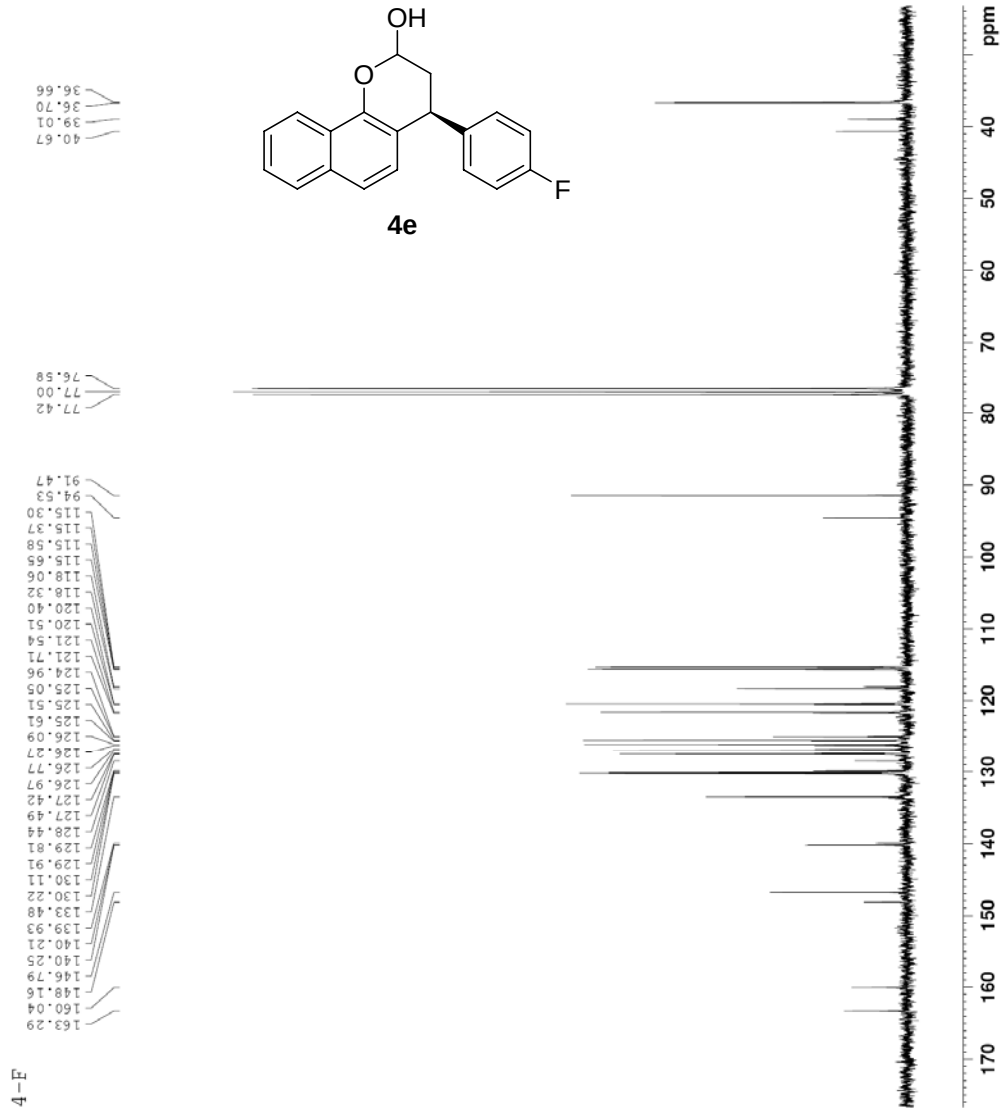
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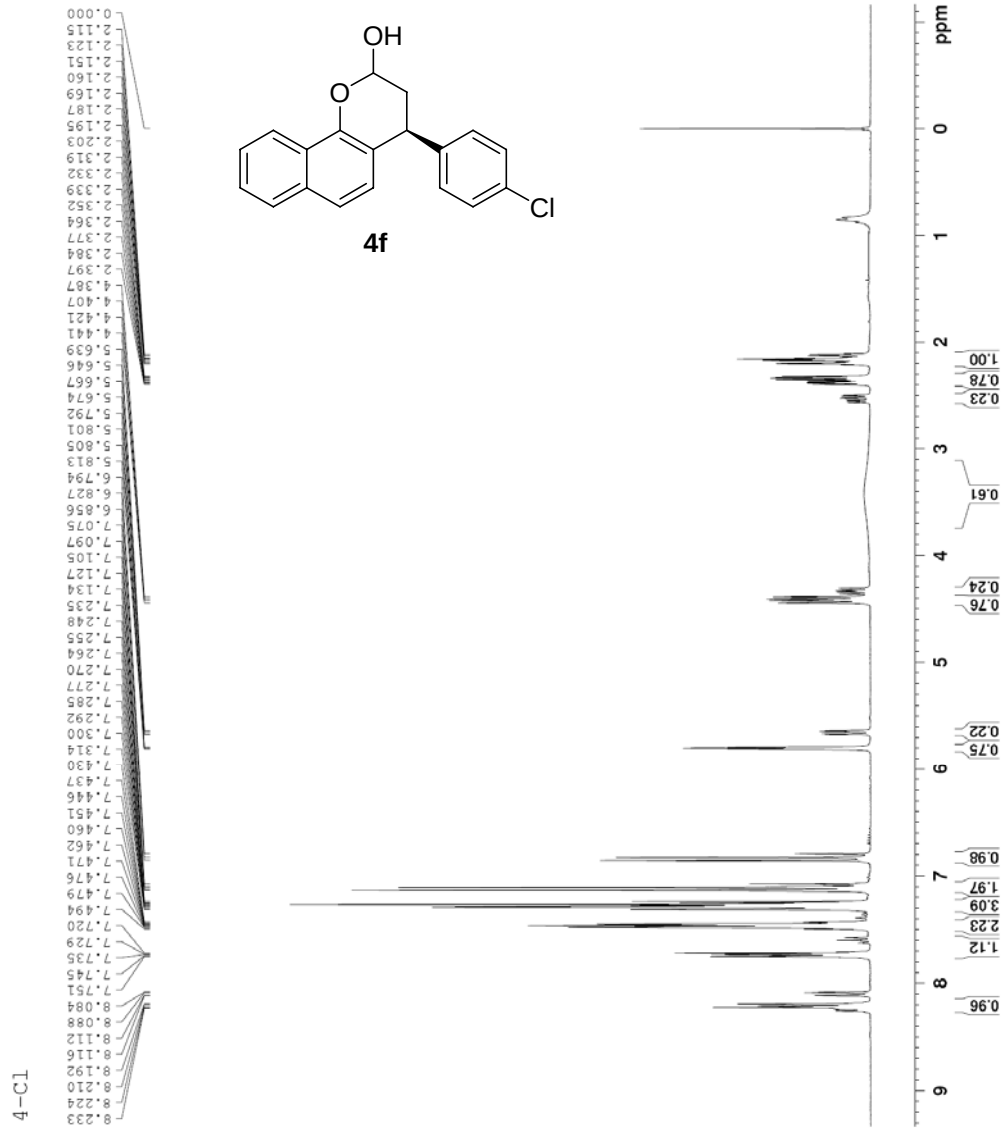
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1.00


OH
O
Cl
4f
ppm
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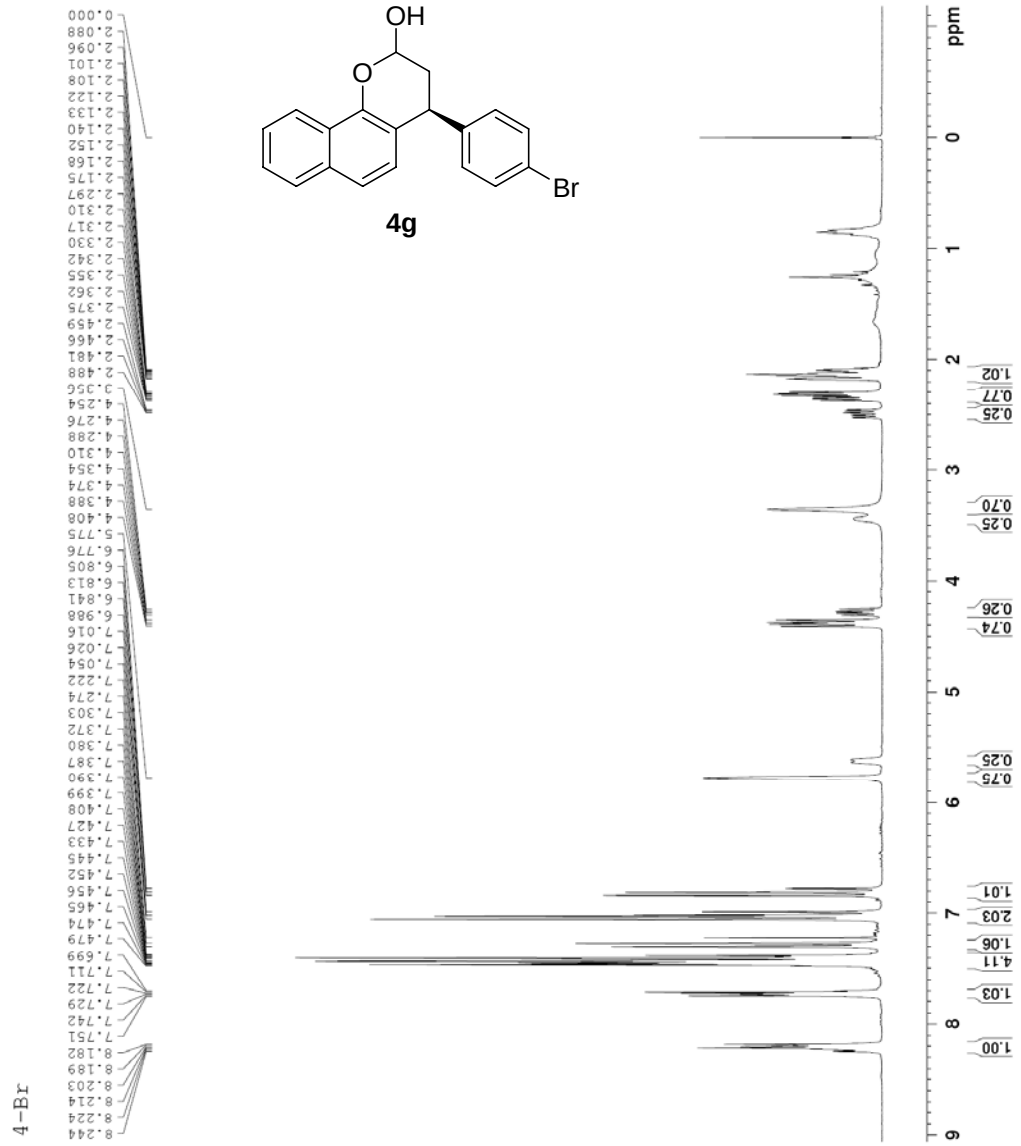
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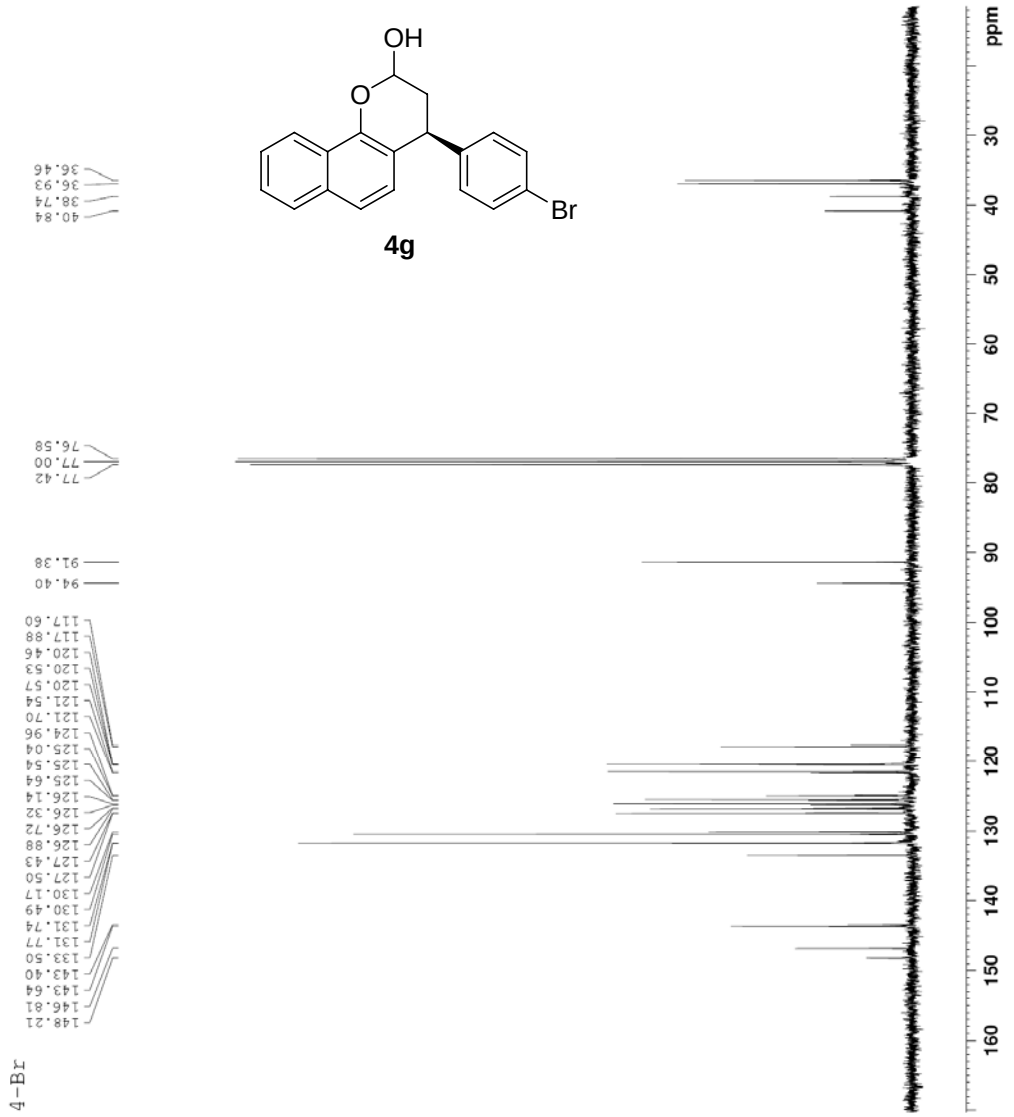
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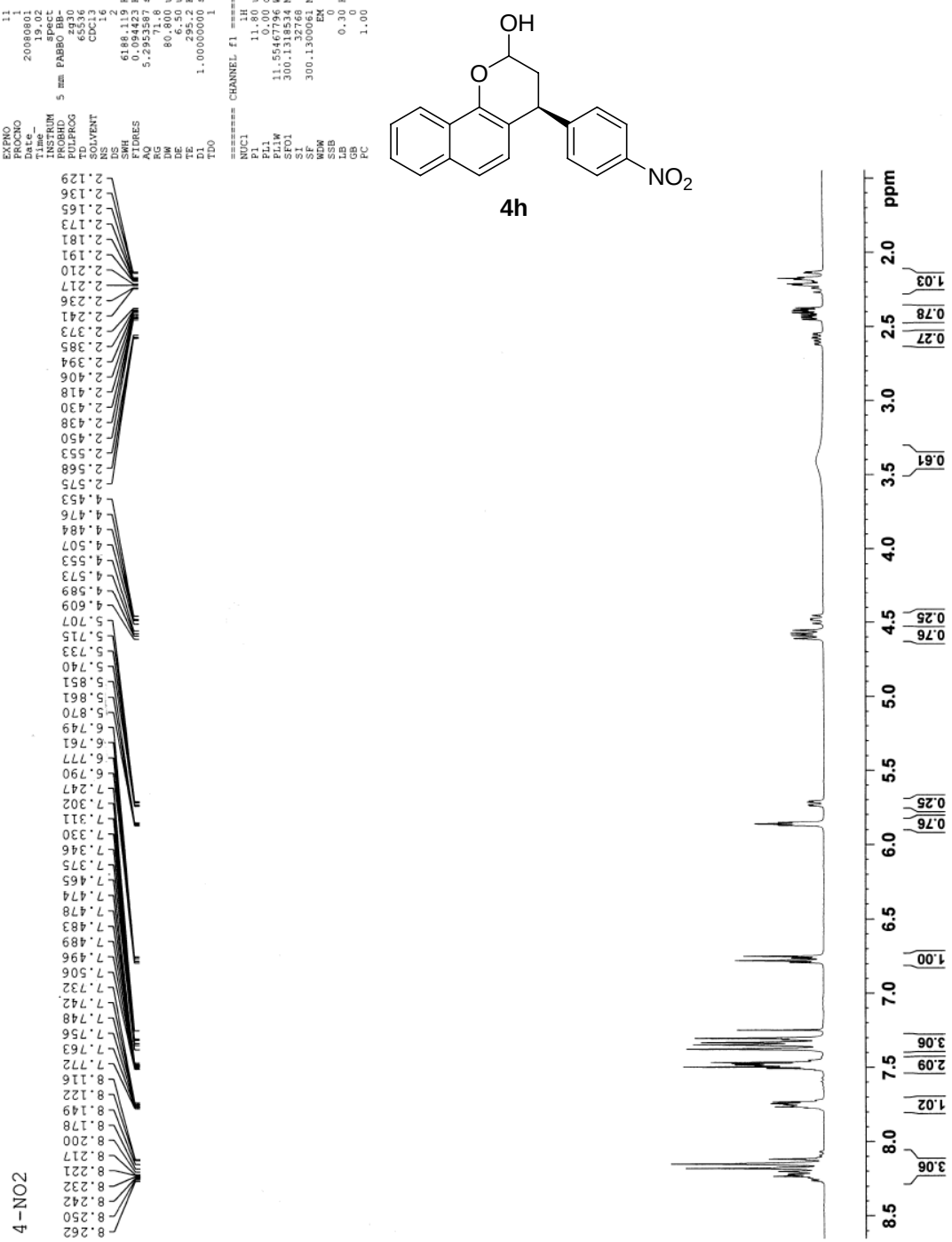
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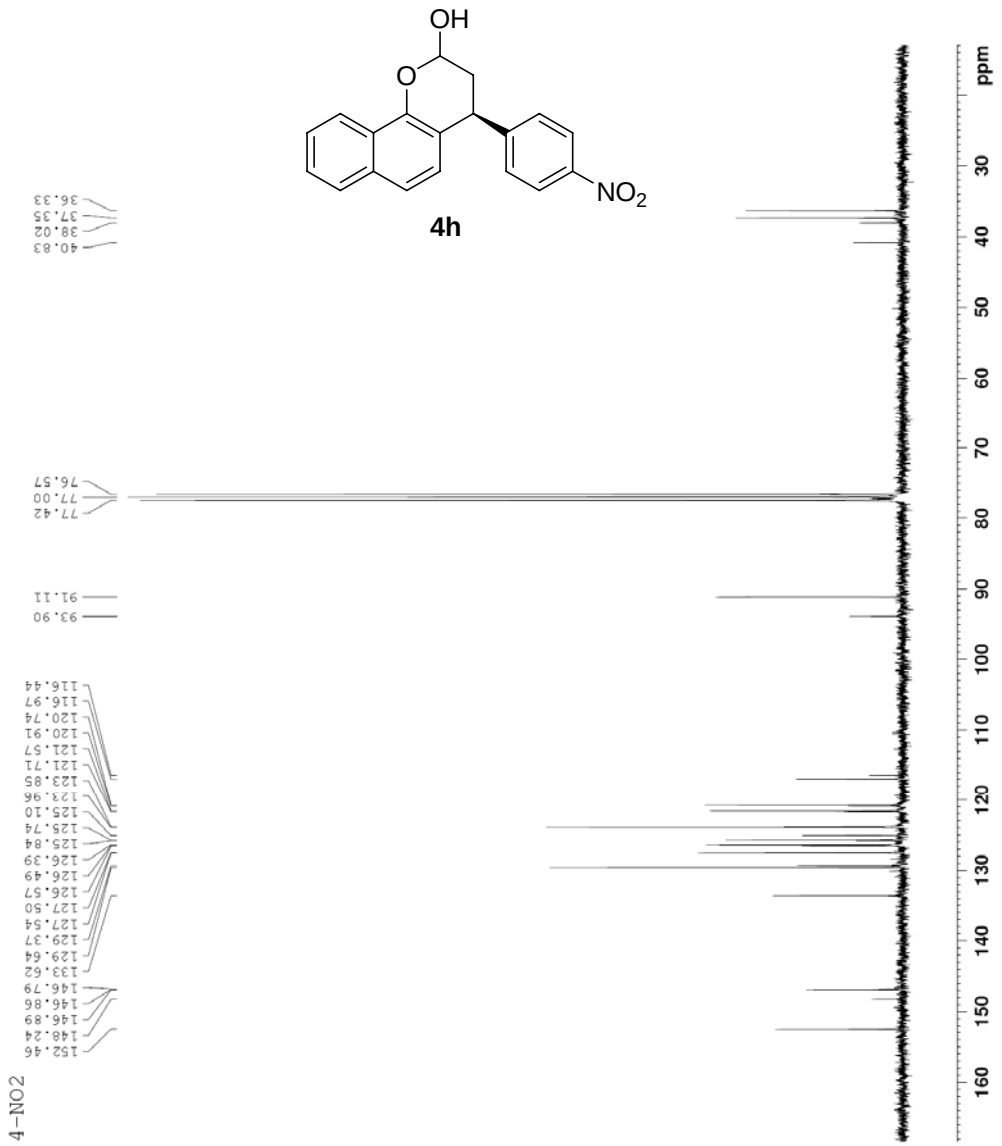
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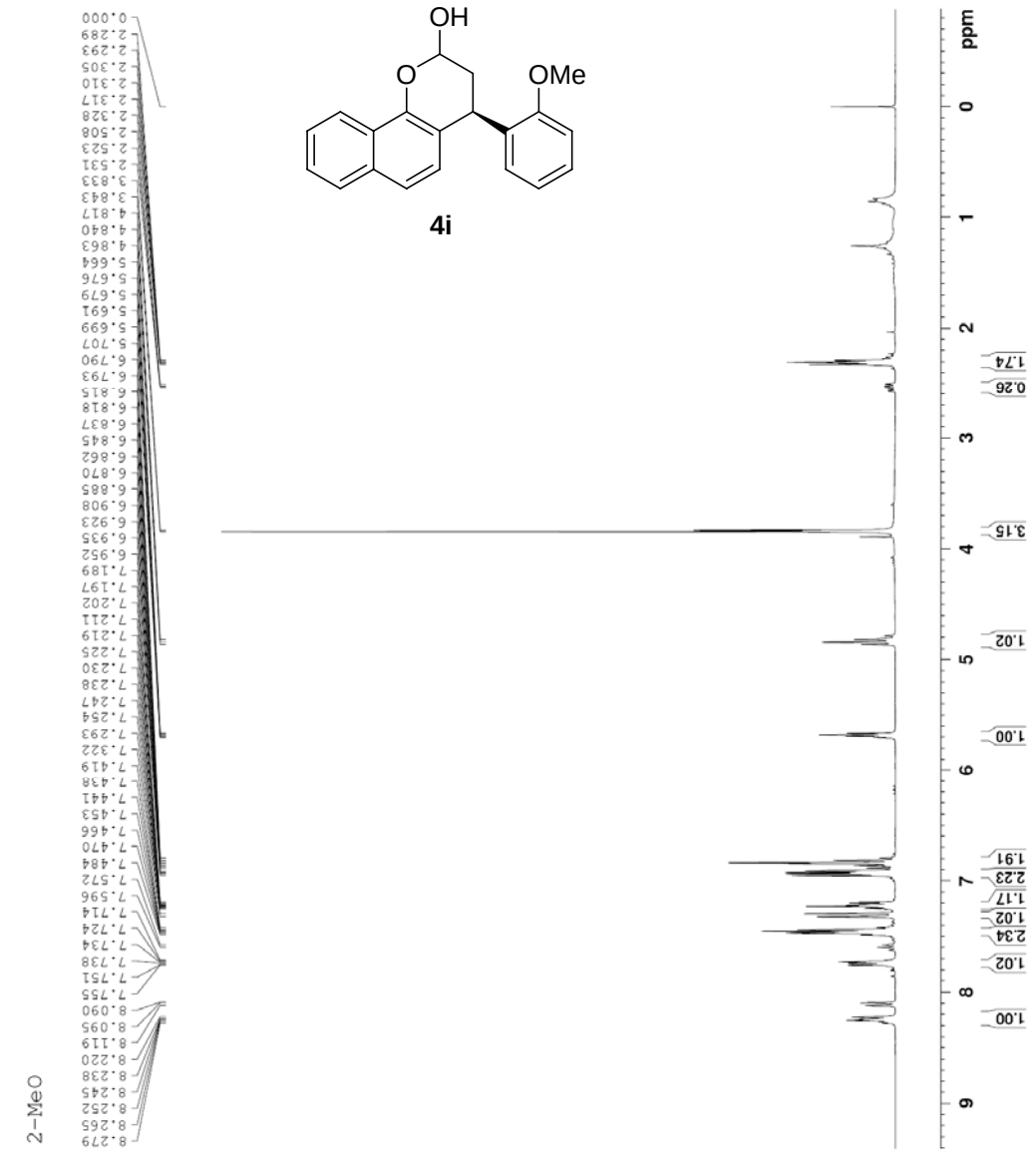
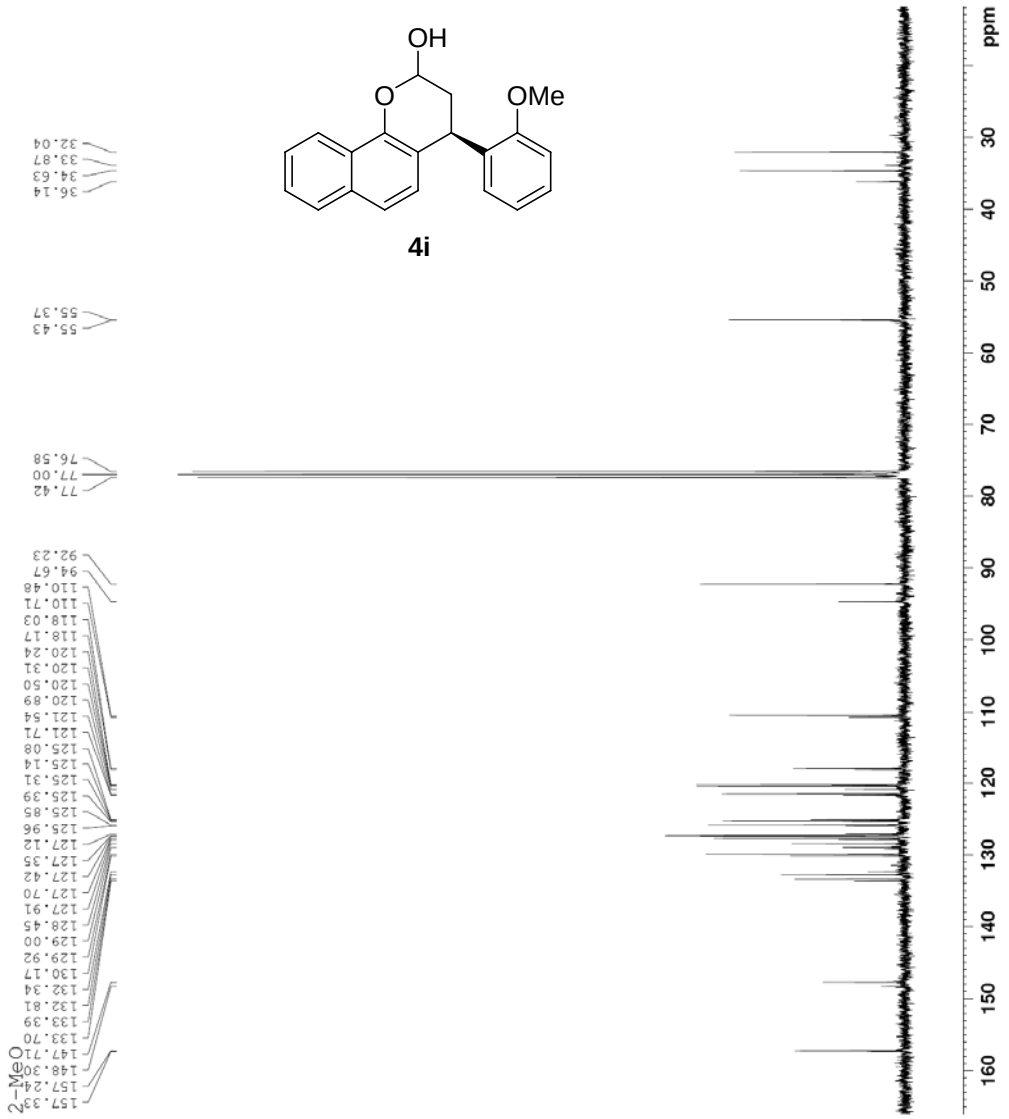
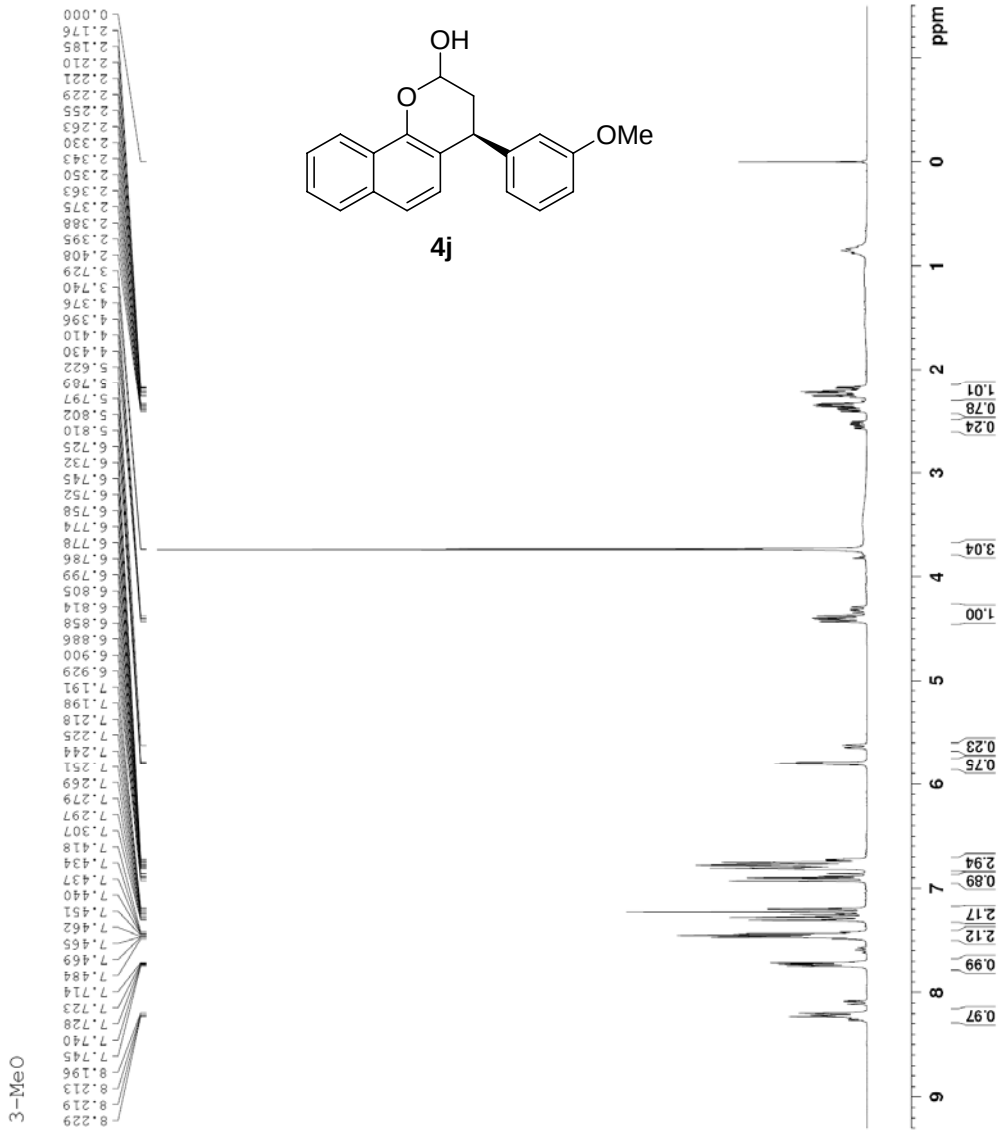
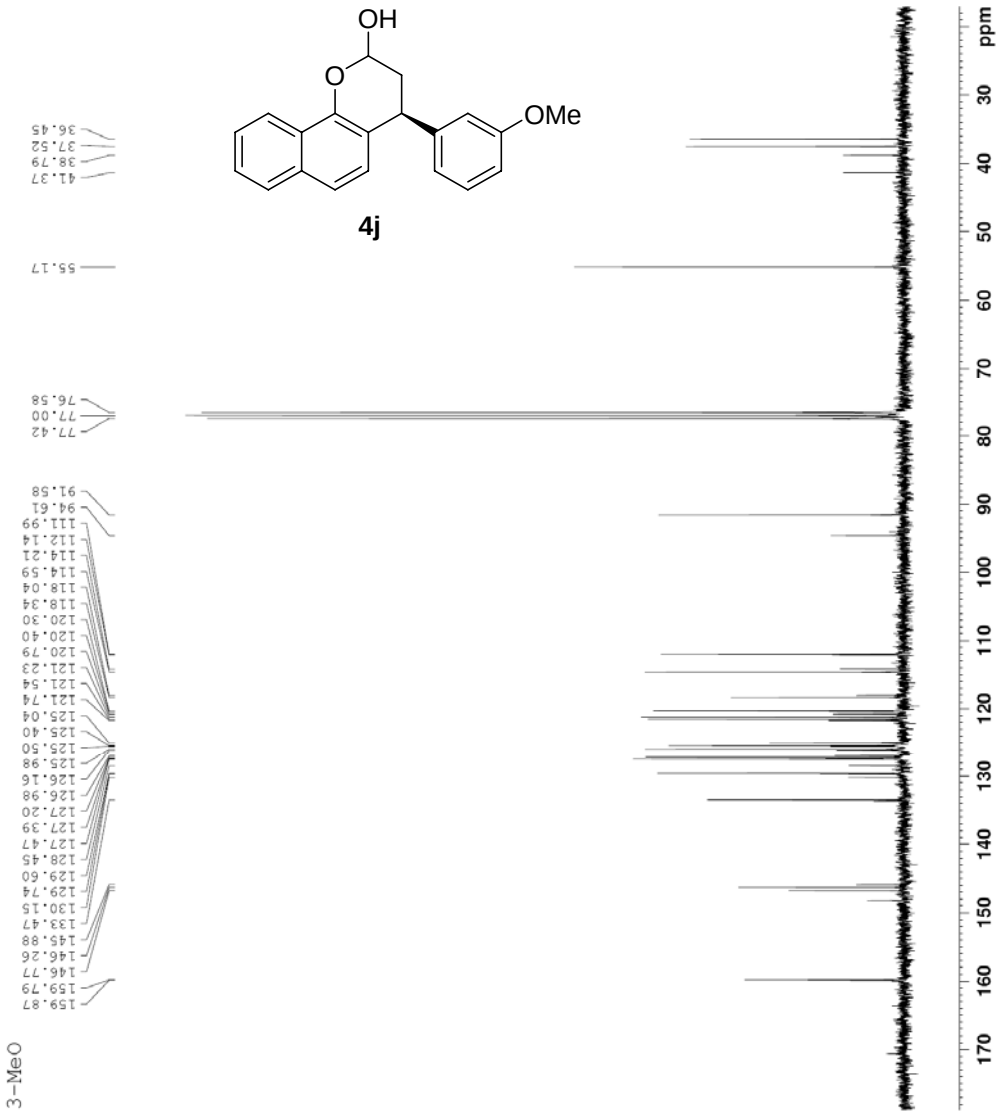
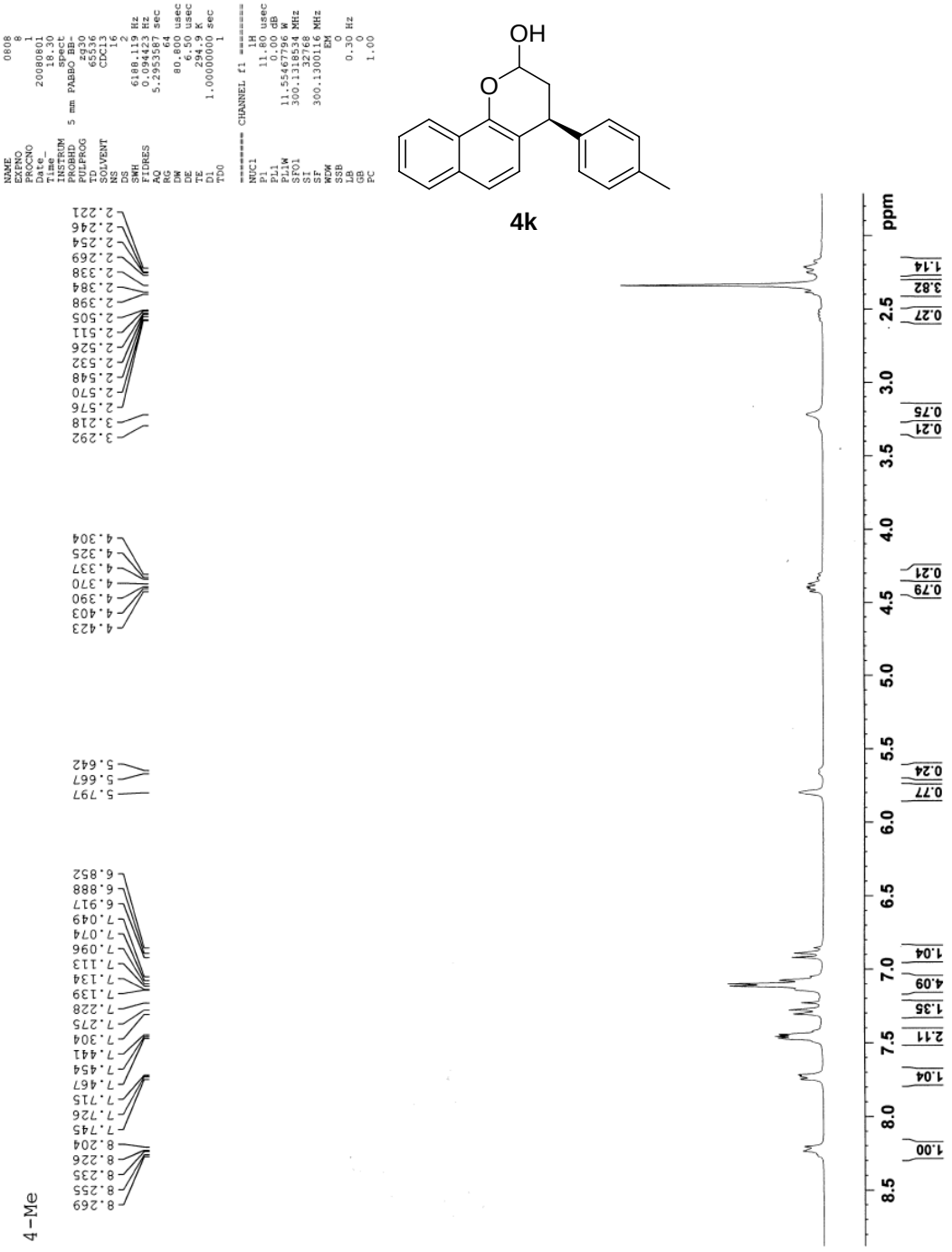
NO2
4h
4-NO2
ppm

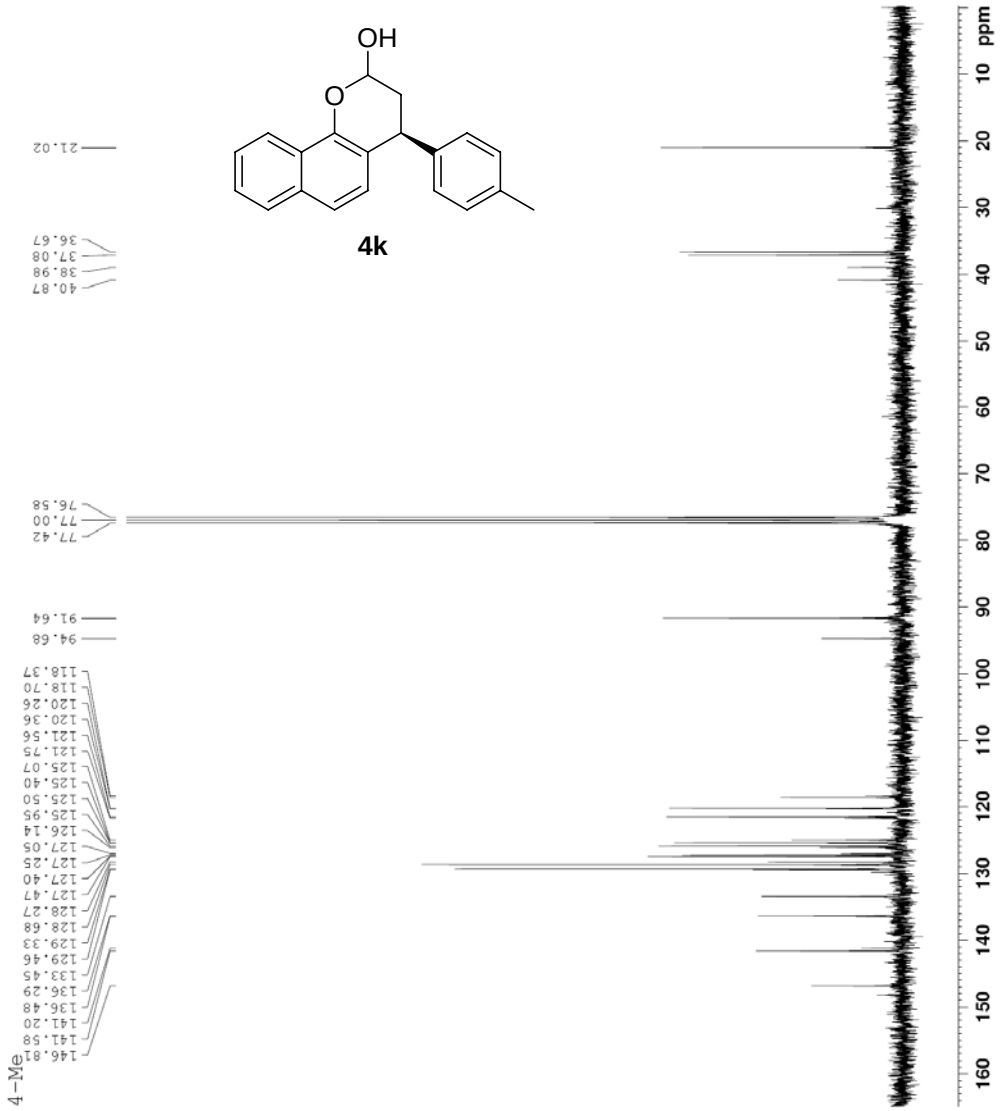

OH
O
OMe
4i
2-MeO
ppm
1.74
0.26
3.15
1.02
1.00
1.91
2.23
1.17
1.02
2.34
1.02
1.00

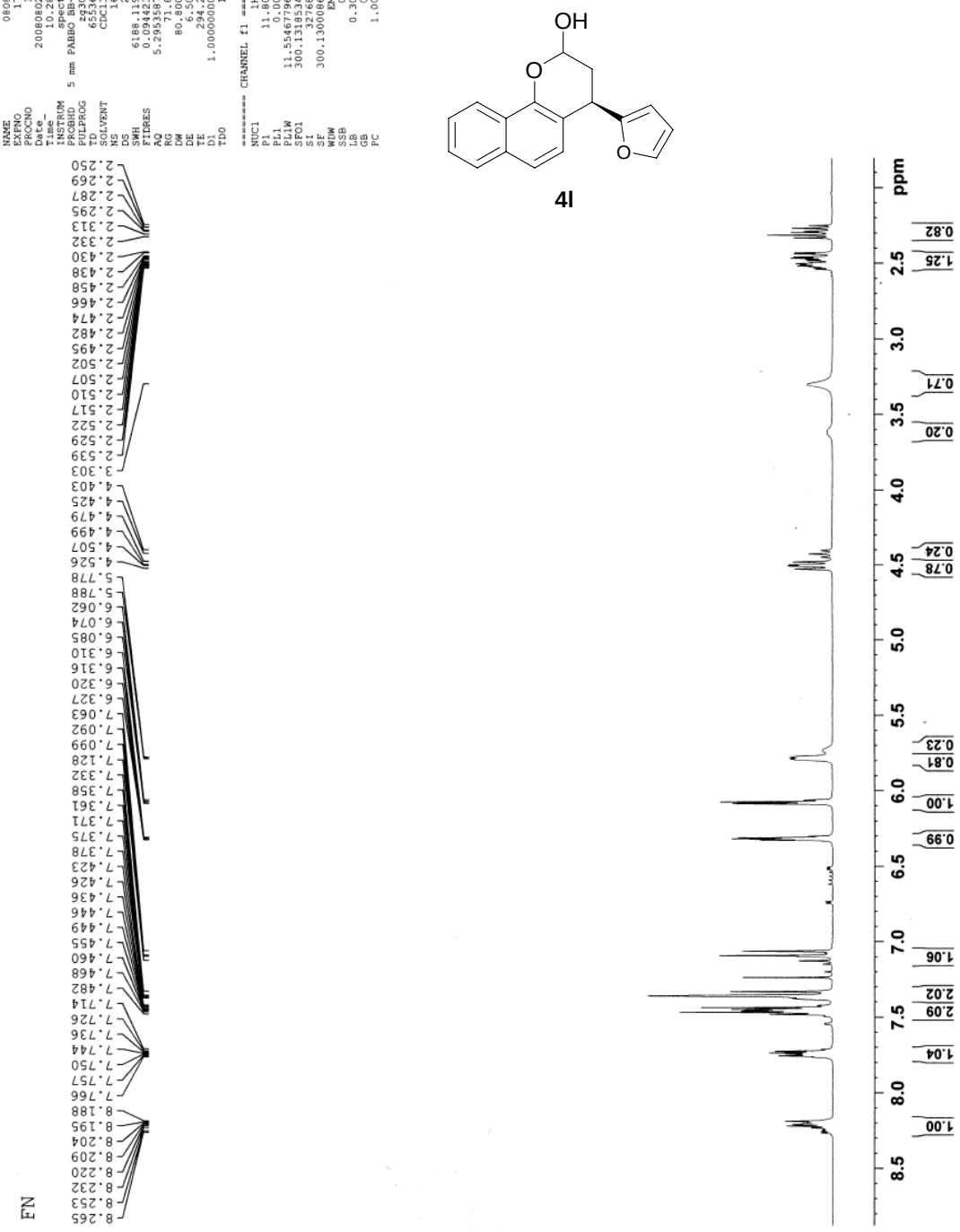

OH
O
OMe
4i
32.04
33.87
34.63
36.14
55.37
55.43
76.58
77.00
77.42
92.23
94.67
110.48
110.71
118.03
118.17
120.24
120.31
120.50
120.89
121.54
121.71
125.08
125.14
125.31
125.39
125.85
125.96
127.12
127.35
127.42
127.70
127.91
128.45
129.00
129.92
130.17
132.34
132.81
133.39
133.70
147.71
148.30
157.24
157.33
2-MeO
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160

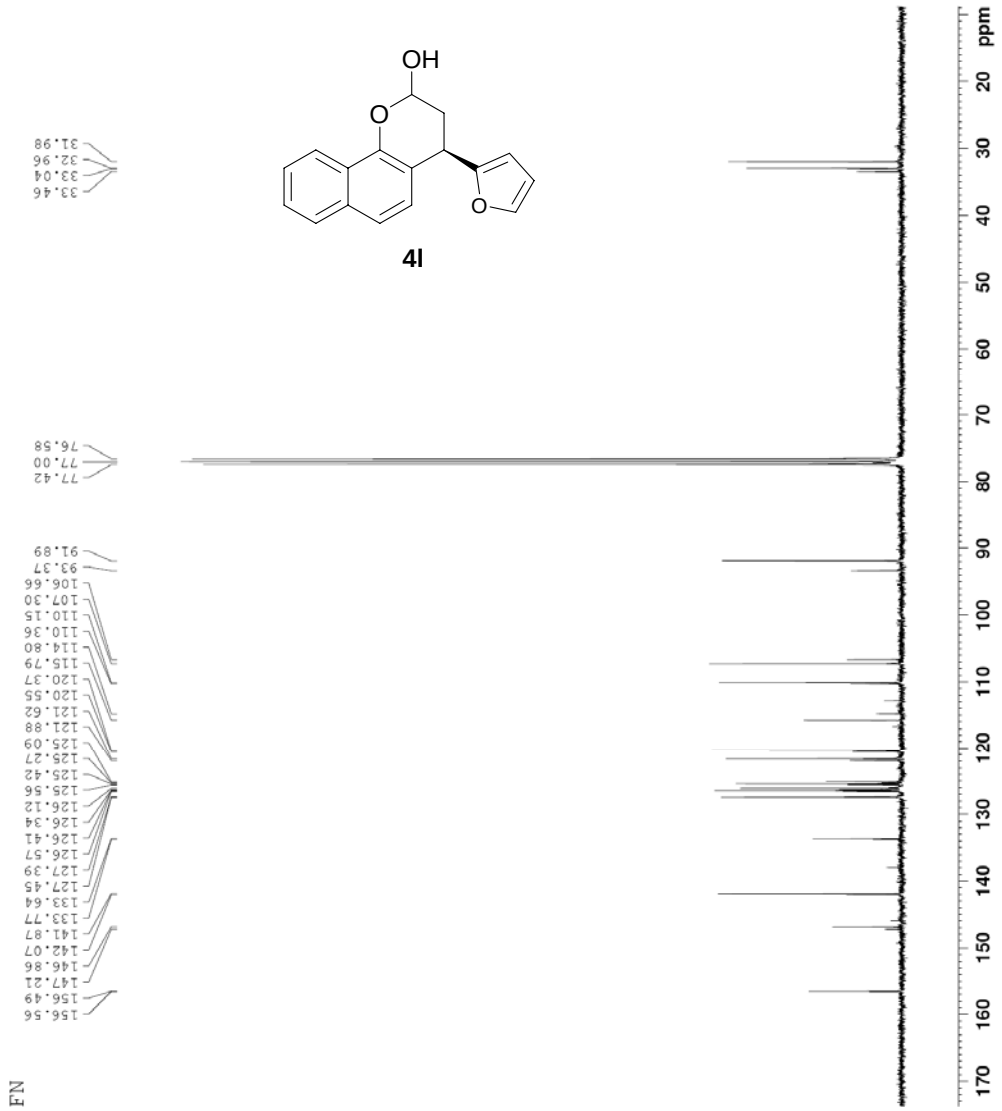

OH
O
OMe
4j
3-MeO
ppm
0.97
0.99
2.12
2.17
0.89
2.94
0.75
0.23
1.00
3.04
0.24
0.78
1.01

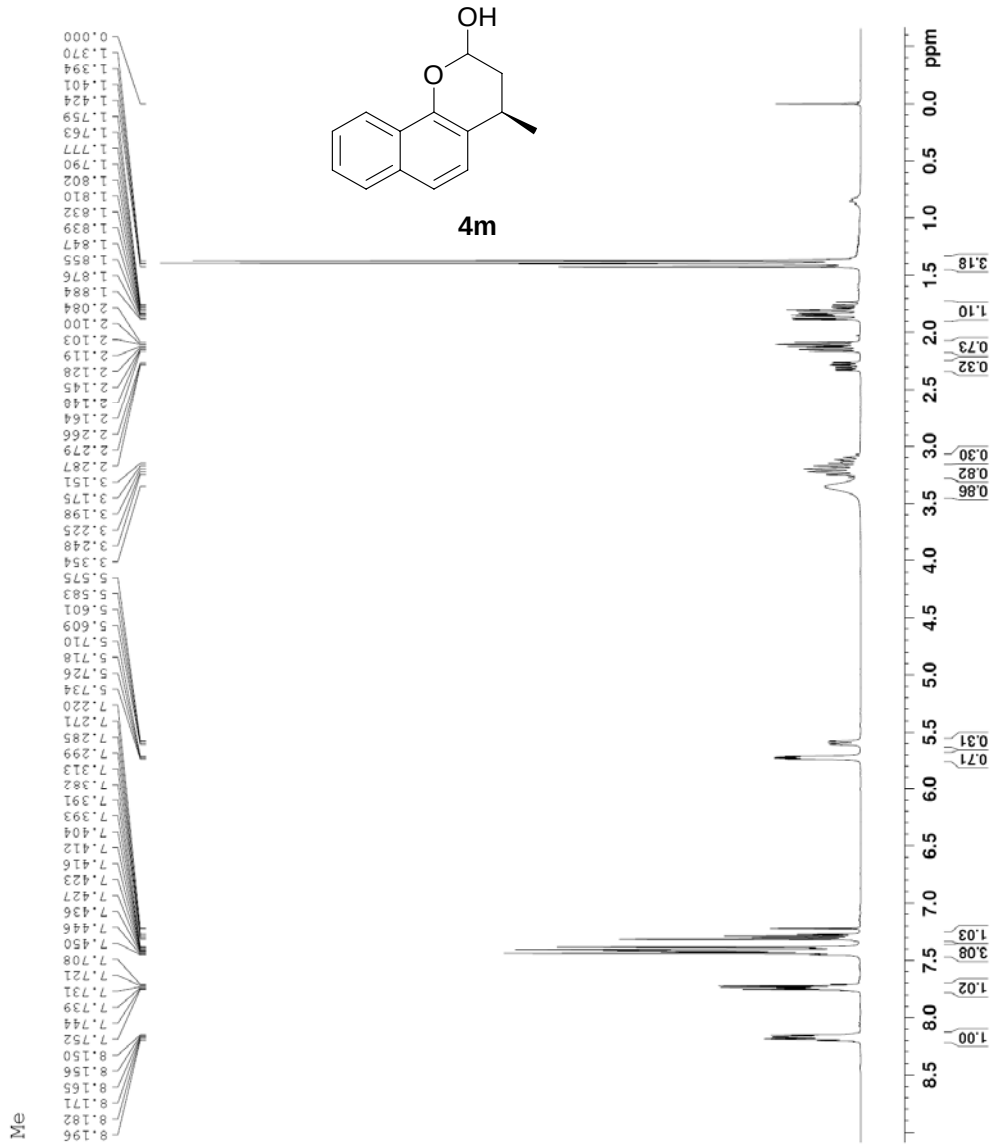

OH
O
OMe
4j
36.45
37.52
38.79
41.37
55.17
76.58
77.00
77.42
91.58
94.61
111.99
112.14
114.21
114.59
118.04
118.34
120.30
120.40
120.79
121.23
121.54
121.74
125.04
125.40
125.50
125.98
126.16
126.98
127.20
127.39
127.47
128.45
129.60
129.74
130.15
133.47
145.88
146.26
146.77
159.79
159.87
3-MeO
ppm
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

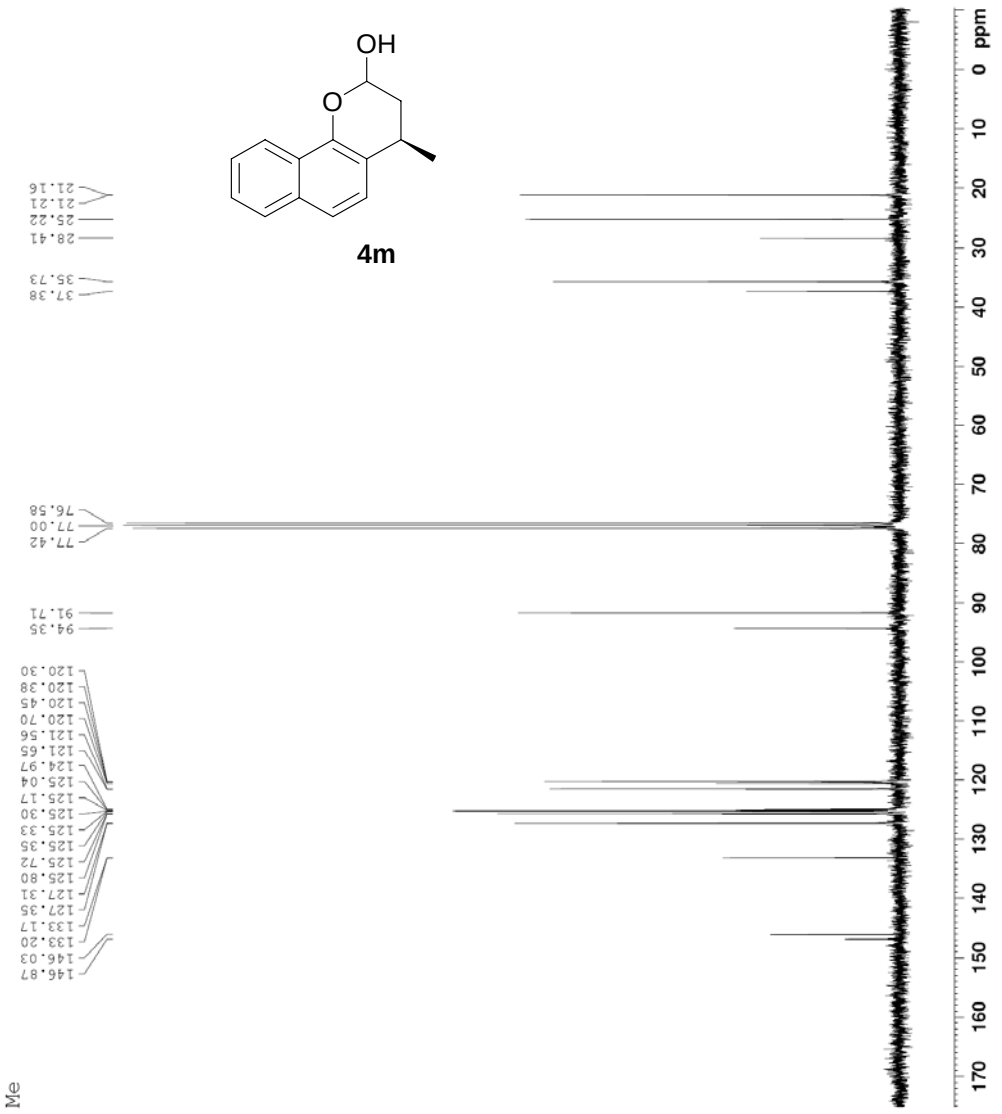

NAME 0808
EXPNO 8
PROCNO 1
Date_ 20080801
Time 18.30
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 64
DW 80.800 usec
DE 6.50 usec
TE 294.0 K
D1 1.0000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.80 usec
PL1 0.00 dB
PL1W 11.55467796 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300116 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
O
4k
4-Me
2.221
2.246
2.254
2.269
2.338
2.384
2.398
2.505
2.511
2.526
2.532
2.548
2.570
2.576
3.218
3.292
4.303
4.325
4.337
4.370
4.390
4.403
4.423
5.642
5.667
5.797
6.852
6.888
6.917
7.049
7.074
7.096
7.113
7.134
7.139
7.228
7.275
7.304
7.441
7.454
7.467
7.715
7.726
7.745
8.204
8.226
8.235
8.255
8.269
ppm
1.00
1.04
2.11
1.35
4.09
1.04
0.24
0.77
0.21
0.79
0.75
0.21
0.27
3.82
1.14

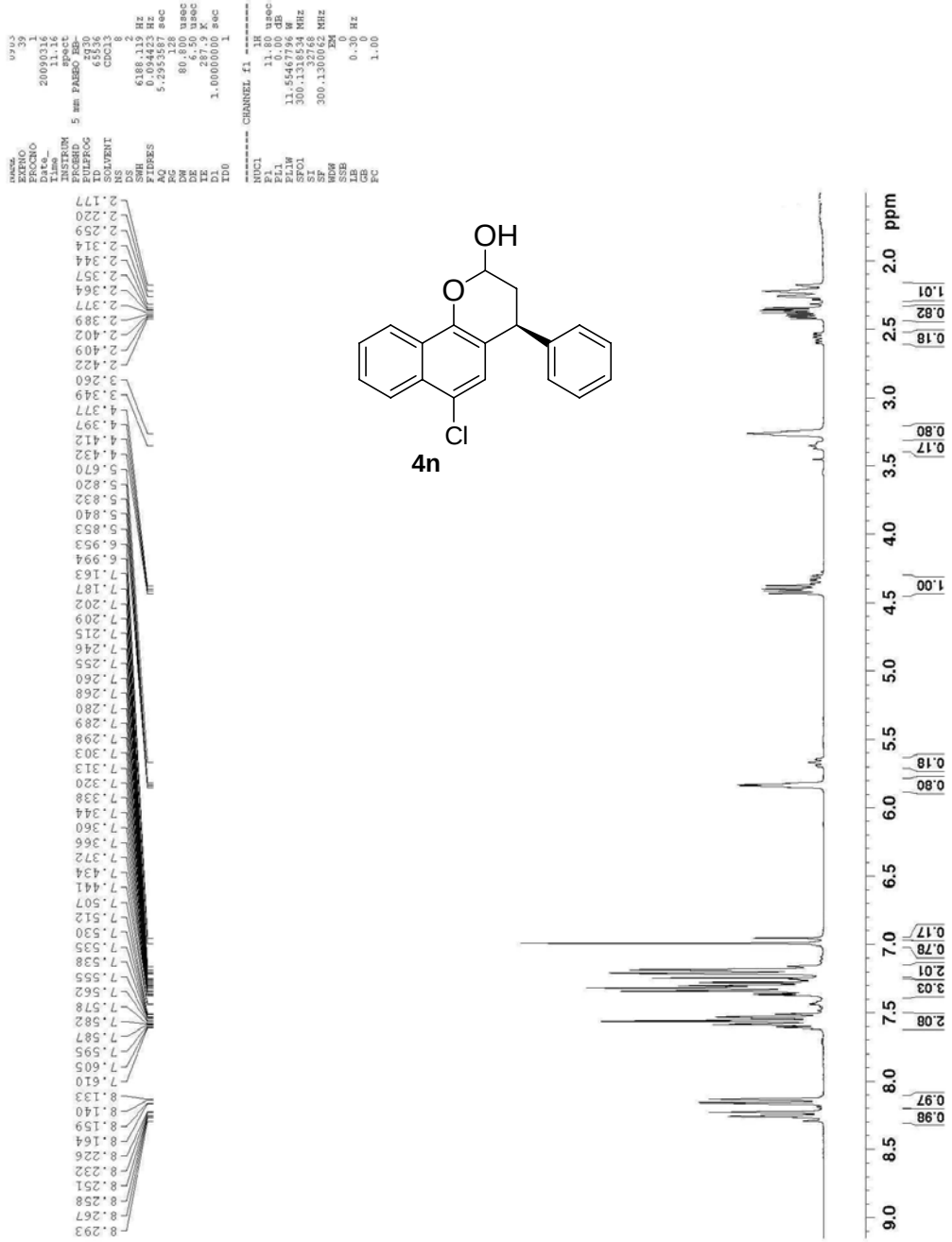

OH
O
4k
21.02
36.67
37.08
38.98
40.87
76.58
77.00
77.42
91.64
94.68
118.37
118.70
120.26
120.36
121.56
121.75
125.07
125.40
125.50
125.95
126.14
127.05
127.25
127.40
127.47
128.27
128.68
129.33
129.46
133.45
136.29
136.48
141.20
141.58
146.81
4-Me
ppm

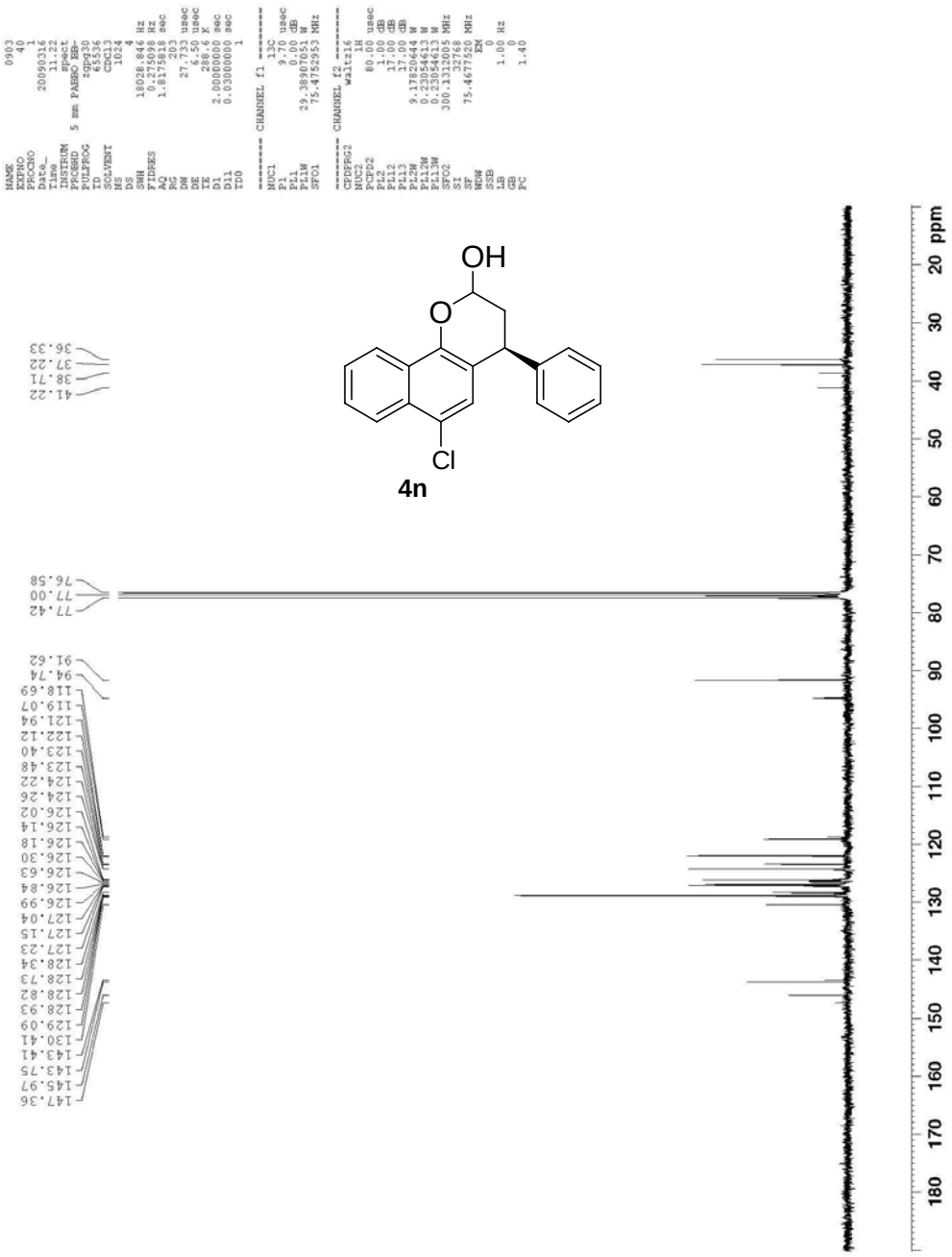

NAME 0808
EXPNO 17
PROCNO 1
Date_ 20080802
Time_ 10.28
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953587 sec
RG 71.8
DW 80.800 usec
DE 6.50 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 11.80 usec
PL1 0.00 dB
PL1W 11.55467796 W
SFO1 300.1318534 MHz
SI 32768
SF 300.1300086 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
FN
OH
O
O
4l
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
1.00
1.04
2.09
2.02
1.06
0.99
1.00
0.81
0.23
0.78
0.24
0.20
0.71
1.25
0.82

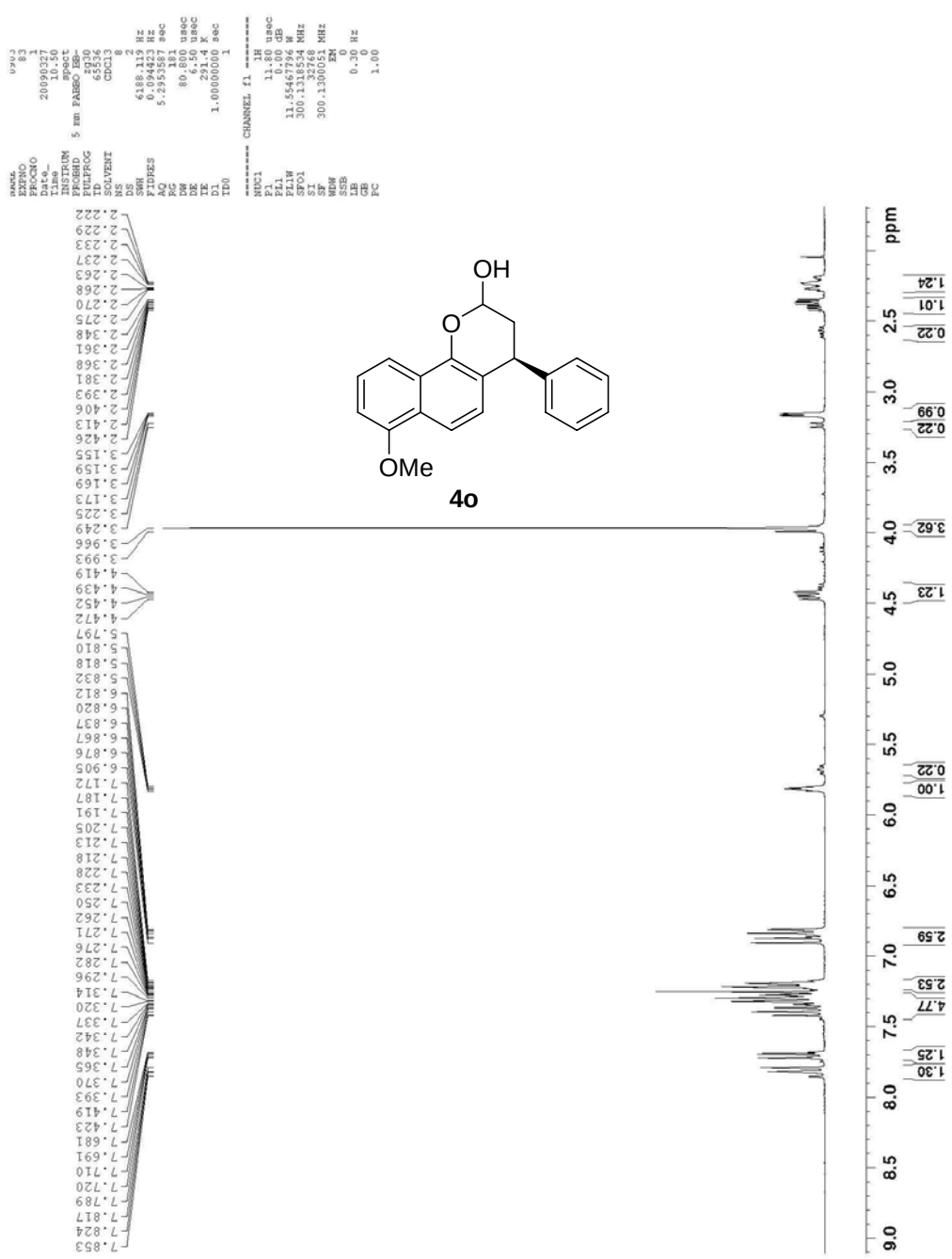

OH
O
O
4l
31.98
32.96
33.04
33.46
77.42
77.00
76.58
91.89
93.37
106.66
107.30
110.15
110.36
114.80
115.79
120.37
120.55
121.62
121.88
125.09
125.27
125.42
125.56
126.12
126.34
126.41
126.57
127.39
127.45
133.64
133.77
141.87
142.07
146.86
147.21
156.49
156.56
FN
ppm
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

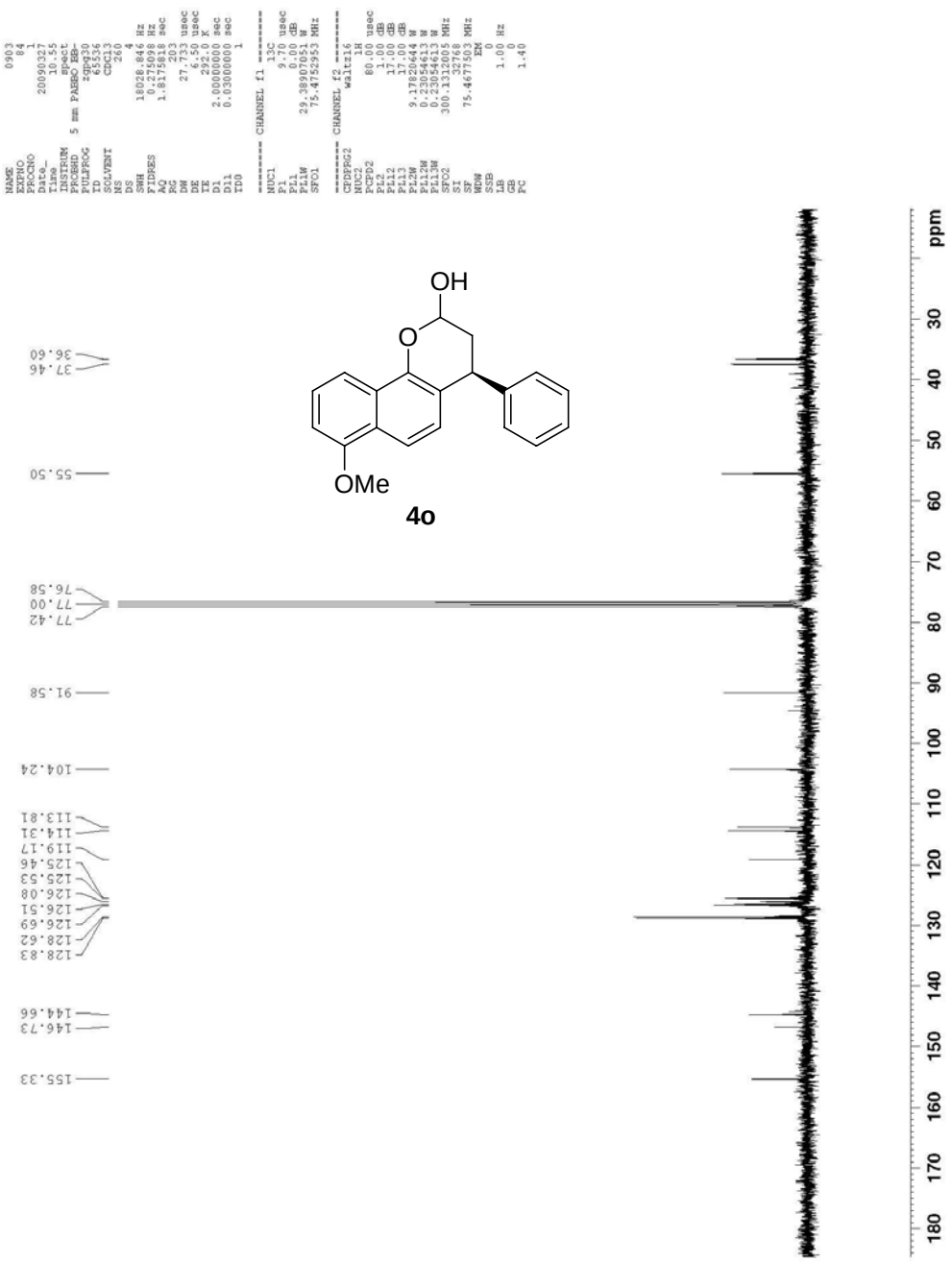

OH
O
4m
Me
ppm

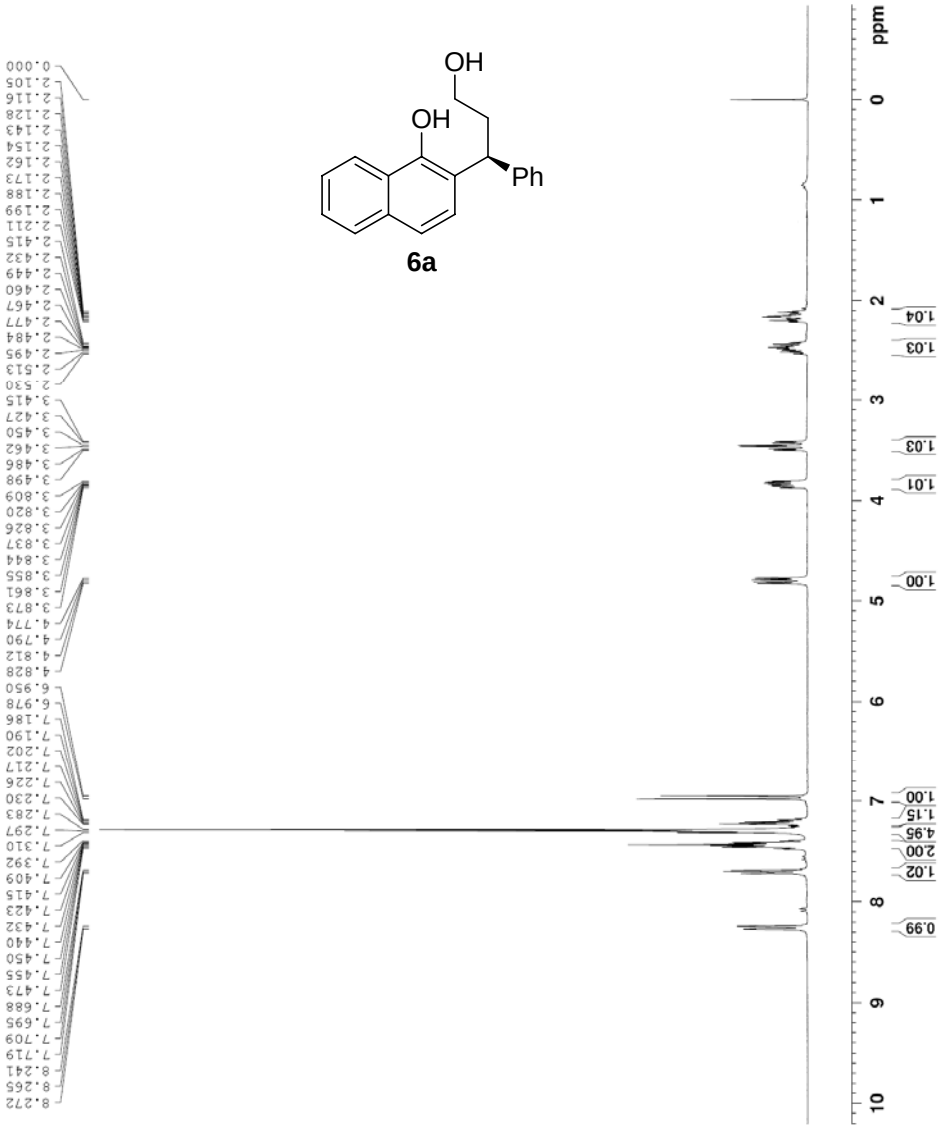

OH
O
4m
21.16
21.21
25.22
28.41
35.73
37.38
76.58
77.00
77.42
91.71
94.35
120.30
120.38
120.45
120.70
121.56
121.65
124.97
125.04
125.17
125.30
125.33
125.35
125.72
125.80
127.31
127.35
133.17
133.20
146.03
146.87
Me
0 ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170


OH
O
Cl
4n
ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
1.01
0.82
0.18
0.80
0.17
1.00
0.18
0.80
0.17
0.78
2.01
3.03
2.08
0.97
0.98

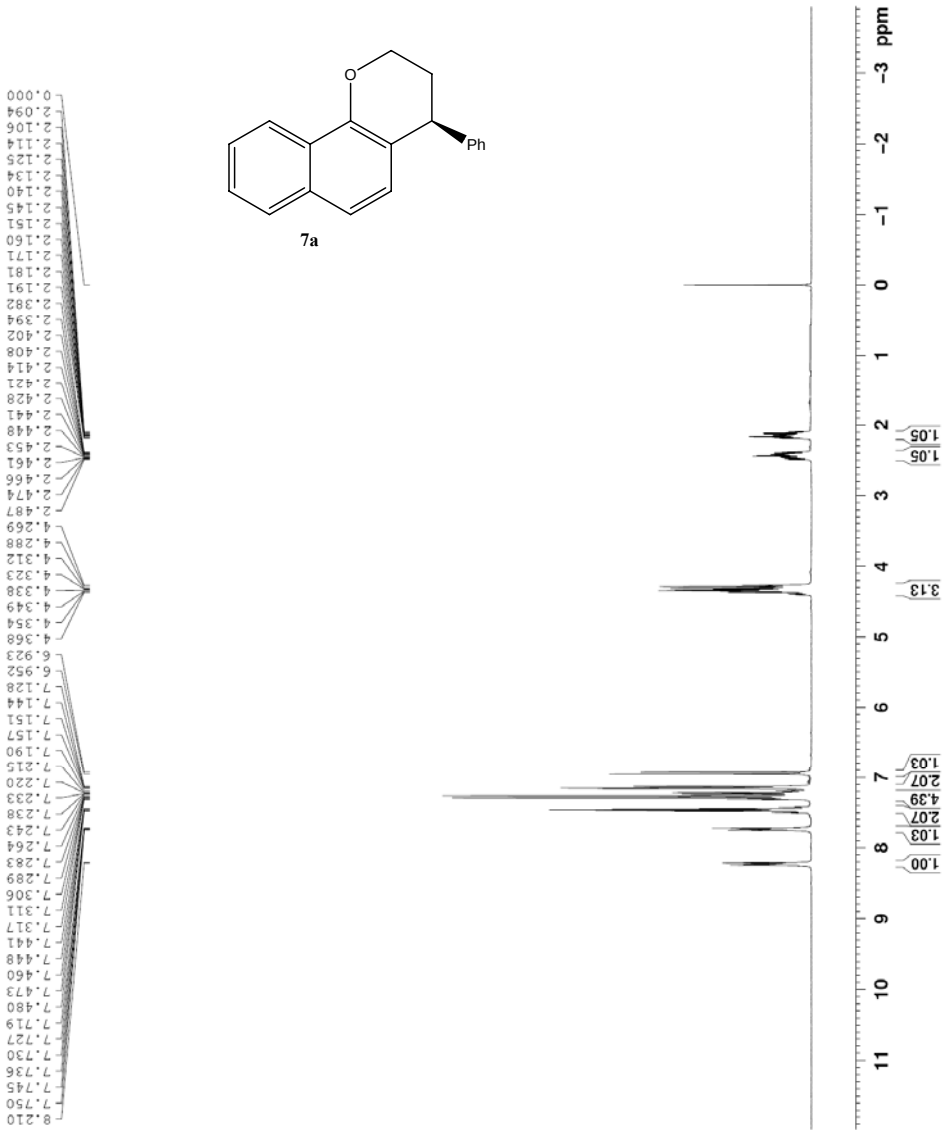

OH
O
Cl
4n
ppm

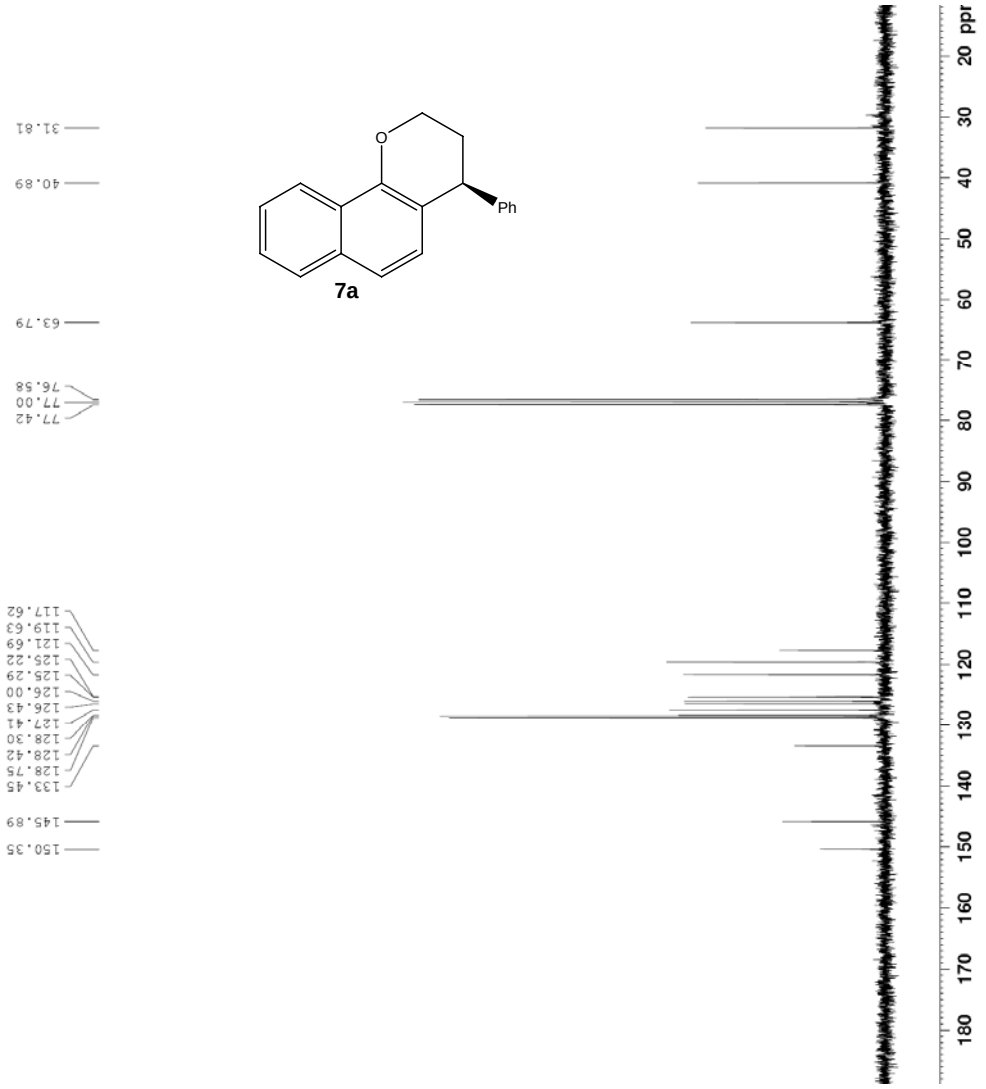

OH
O
OMe
4o
ppm

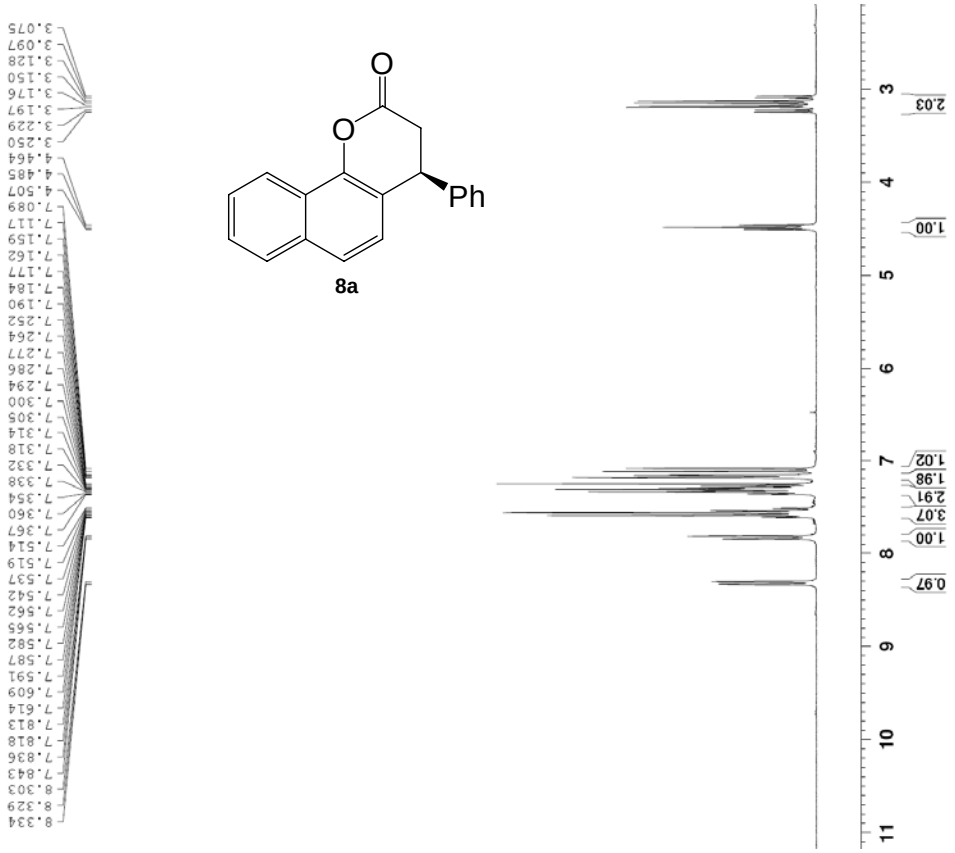

OH
O
OMe
4o
36.60
37.46
55.50
76.58
77.00
77.42
91.58
104.24
113.81
114.31
119.17
125.46
125.53
126.08
126.51
126.69
128.62
128.83
144.66
146.73
155.33
ppm


OH
OH
Ph
6a
ppm

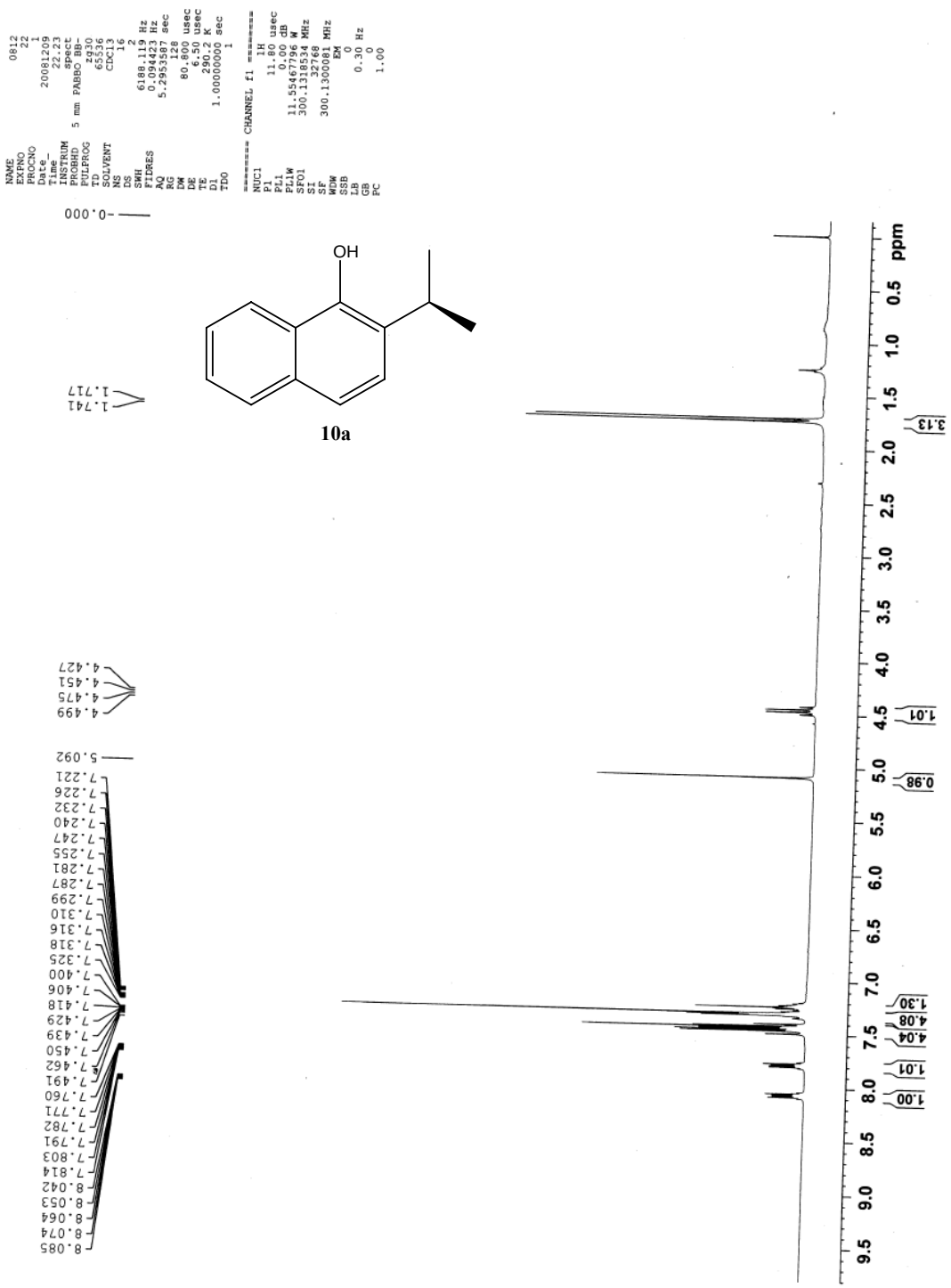

OH
OH
Ph
6a
35.62
38.31
60.44
76.57
77.00
77.42
120.70
122.14
123.81
125.28
125.49
125.82
126.22
126.40
127.36
128.25
128.46
133.25
143.84
149.37
ppm

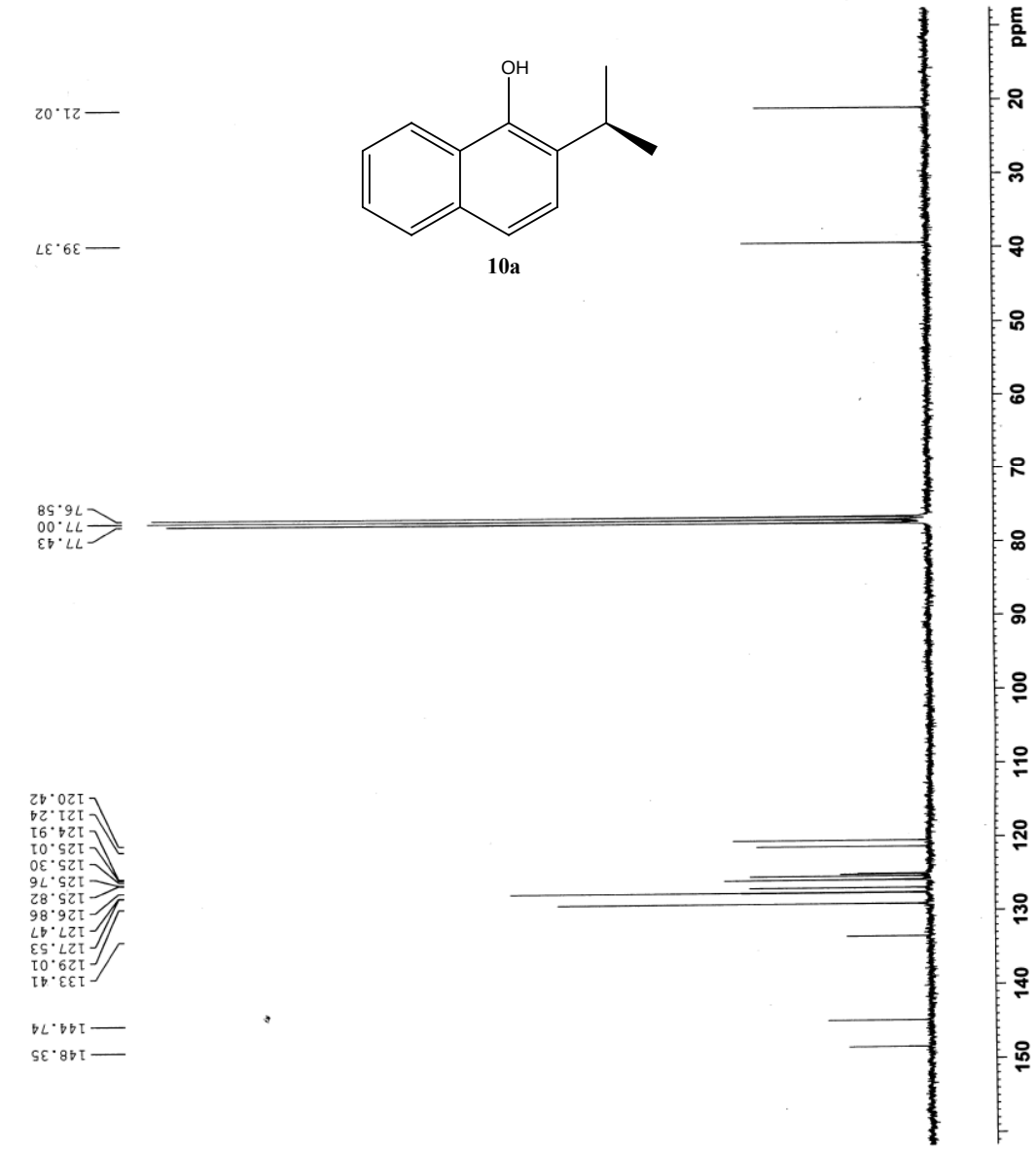

O
Ph
7a
ppm
1.00
1.03
2.07
4.39
2.07
1.03
1.05
1.05
3.13


31.81
40.89
63.79
76.58
77.00
77.42
117.62
119.63
121.69
125.22
125.29
126.00
126.43
127.41
128.30
128.42
128.75
133.45
145.89
150.35
O
Ph
7a
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
ppm


3.075
3.097
3.128
3.150
3.176
3.197
3.229
3.250
4.464
4.485
4.507
7.089
7.117
7.159
7.162
7.177
7.184
7.190
7.252
7.264
7.277
7.286
7.294
7.300
7.305
7.314
7.318
7.332
7.338
7.354
7.360
7.367
7.514
7.519
7.537
7.542
7.562
7.565
7.582
7.587
7.591
7.609
7.614
7.813
7.818
7.836
7.843
8.303
8.329
8.334
O
O
Ph
8a
2.03
1.00
1.02
1.98
2.91
3.07
1.00
0.97
3
4
5
6
7
8
9
10
11


NAME 0808
EXPNO 33
PROCNO 1
Date_ 20080827
Time_ 12.04
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677484 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
O
O
Ph
8a
37.30
41.11
76.59
77.02
77.44
119.90
121.36
123.74
124.28
125.32
126.75
126.86
127.53
127.59
127.67
129.18
133.72
140.66
146.77
167.37
ppm


OH
10a
ppm

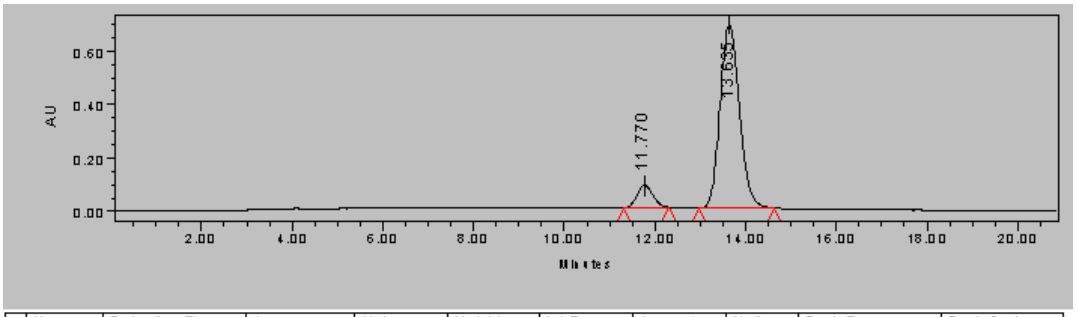

OH
21.02
39.37
76.58
77.00
77.43
120.42
121.24
124.91
125.01
125.30
125.76
125.82
126.86
127.47
127.53
129.01
133.41
144.74
148.35
ppm

10a

HPLC Data:

(*4S*)-4-phenyl-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4a).

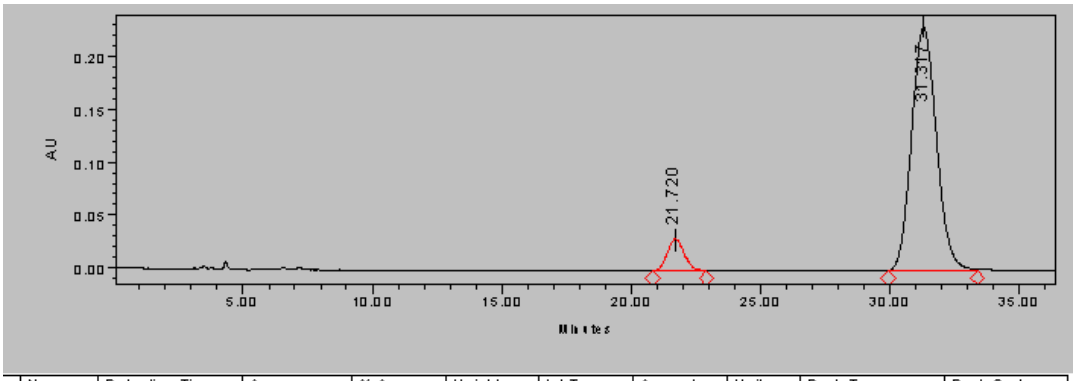
Chiralpak OD-H column, hexane/EtOH (90:10), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		11.770	1733412	7.88	77326	bb			Unknown	
2		13.635	20270055	92.12	687057	bb			Unknown	

(*4R*)-4-(2-chlorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4b).

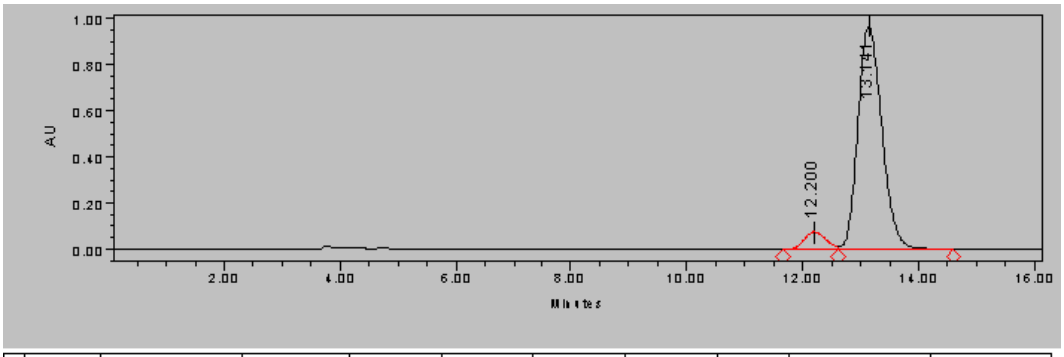
Chiralpak OD-H column, hexane/EtOH (95:5), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		21.728	1145543	7.14	27196	bb			Unknown	
2		31.321	14894444	92.86	222352	bb			Unknown	

(*4S*)-4-(3-chlorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4c).

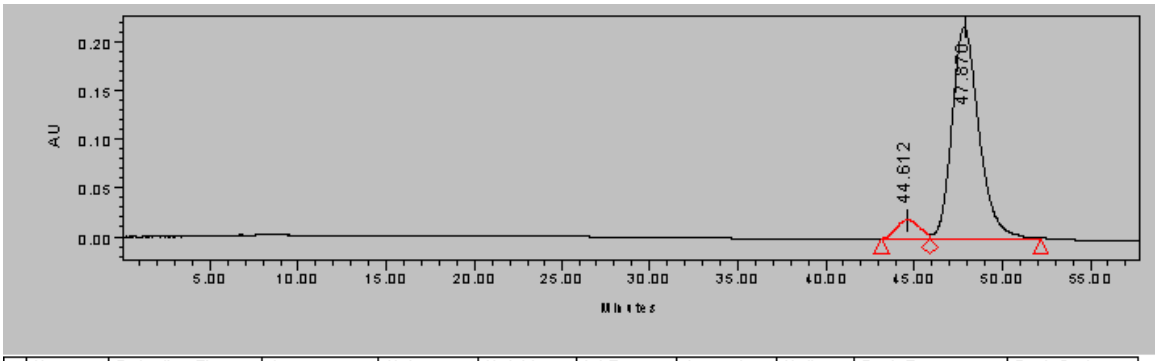
Chiralpak OD-H column, hexane/EtOH (90:10), flow rate 0.8 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		12.200	1592501	5.56	68585	bb			Unknown	
2		13.141	27070730	94.44	959064	bb			Unknown	

(*4S*)-4-(3-nitrophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4d).

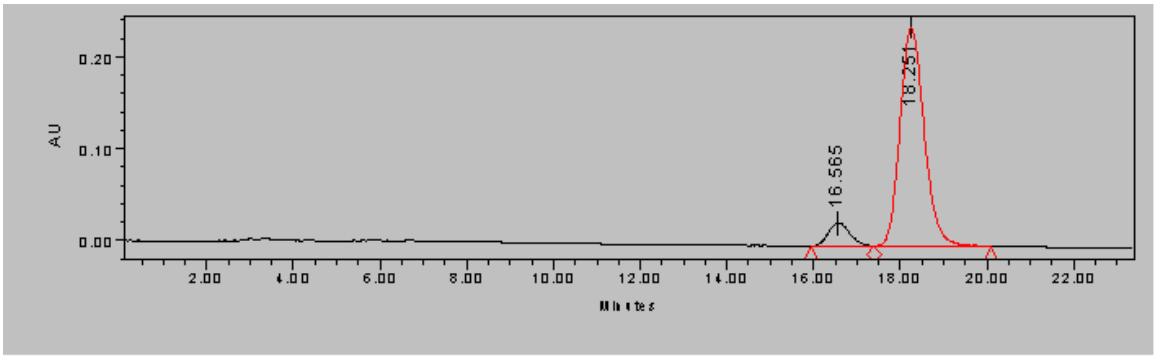
Chiralpak OD-H column, hexane/^{i}*Pr*OH (90:10), flow rate 0.5 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		44.612	1776176	7.13	19863	BV			Unknown	
2		47.870	23133747	92.87	216776	VB			Unknown	

(*4S*)-4-(4-fluorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4e).

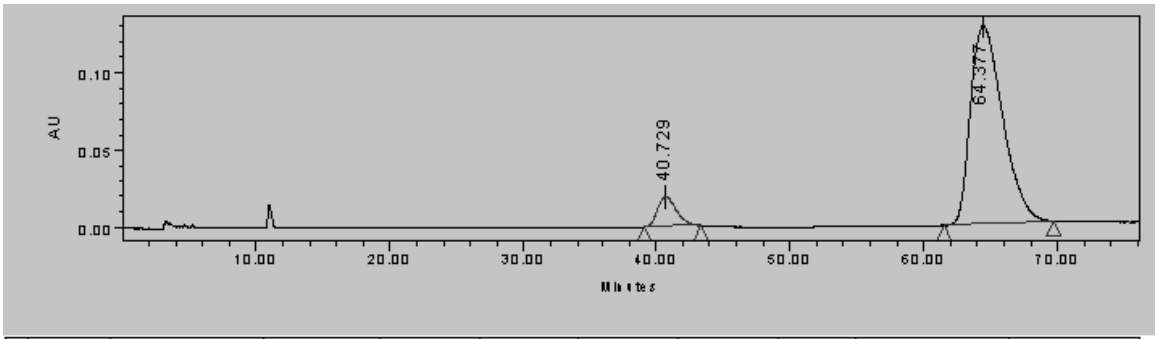
Chiralpak OD-H column, hexane/ EtOH (95:5), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		16.565	825695	8.31	24738	bb			Unknown	
2		18.251	9113895	91.69	237355	bb			Unknown	

(*4S*)-4-(4-chlorophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4f).

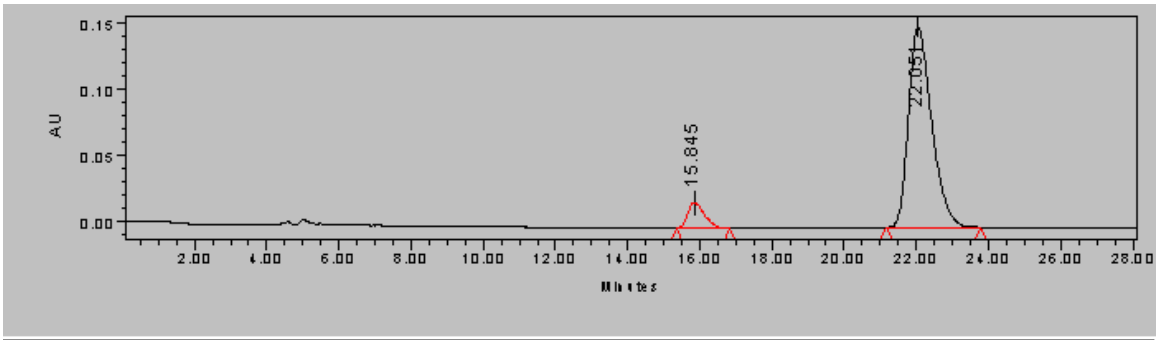
Chiralpak OJ column, hexane/EtOH (95:5), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		40.729	1705556	7.33	18509	bb			Unknown	
2		64.377	21570952	92.67	127607	bb			Unknown	

(*4S*)-4-(4-bromophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4g).

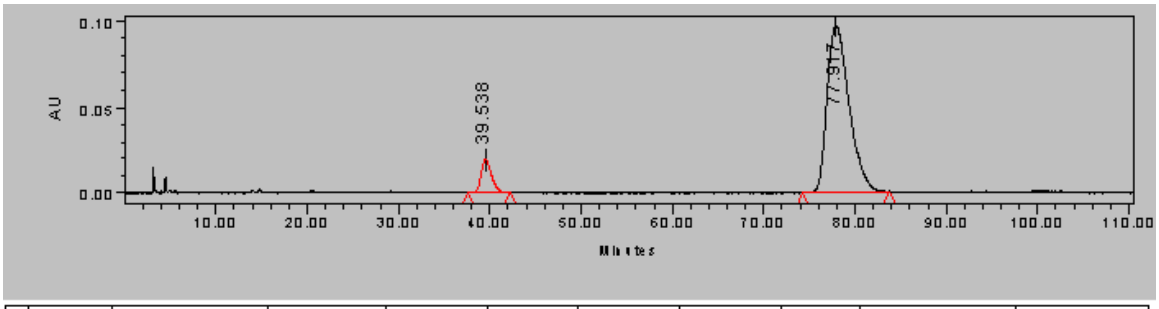
Chiralpak OJ column, hexane/EtOH (90:10), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		15.845	570862	7.72	18931	bb			Unknown	
2		22.051	6827603	92.28	152553	bb			Unknown	

(*4S*)-4-(4-nitrophenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4h).

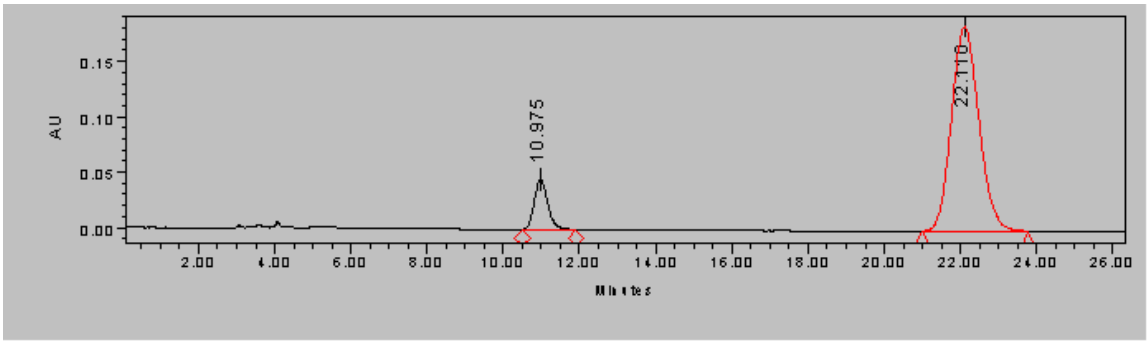
Chiralpak OJ column, hexane/EtOH (90:10), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		39.538	1478983	8.26	19202	bb			Unknown	
2		77.917	16420103	91.74	97406	bb			Unknown	

(*4S*)-4-(2-methoxyphenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4i).

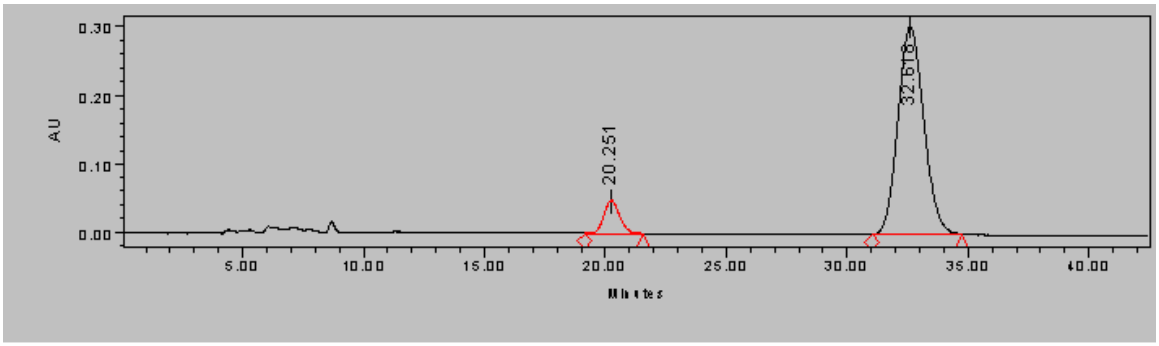
Chiralpak OD-H column, hexane/EtOH (90:10), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.975	1045271	10.09	44940	bb			Unknown	
2		22.109	9315258	89.91	184352	bb			Unknown	

(*4S*)-4-(3-methoxyphenyl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4j).

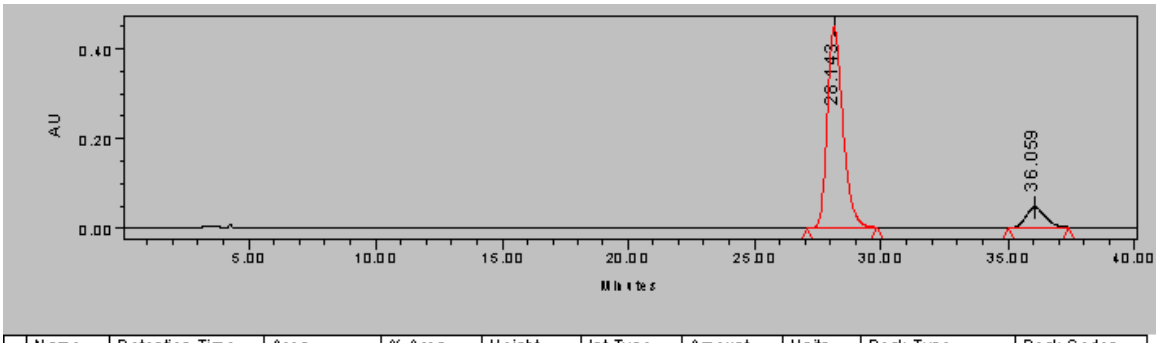
Chiralpak OD-H column, hexane/EtOH (90:10), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		20.251	1968078	7.99	45760	bb			Unknown	
2		32.618	22650404	92.01	303080	bb			Unknown	

(*4S*)-4-p-tolyl-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4k).

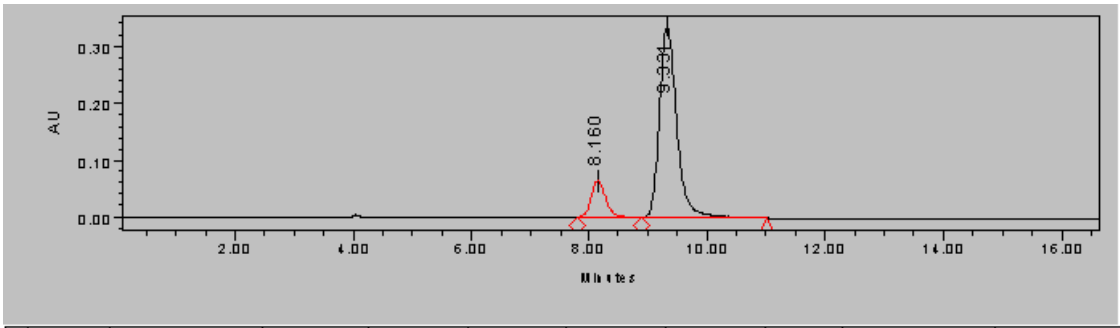
Chiralpak OD-H column, hexane/EtOH (95:5), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		28.143	19213583	90.59	448480	bb			Unknown	
2		36.059	1995770	9.41	41918	bb			Unknown	

(*4R*)-4-(furan-2-yl)-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4l).

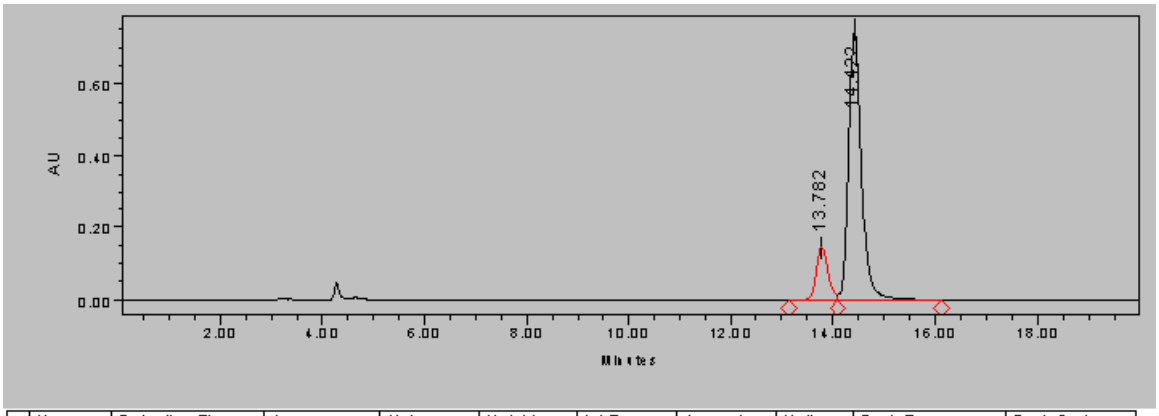
Chiralpak OD-H column, hexane/EtOH (90:10), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		8.160	1023587	13.04	62171	bb			Unknown	
2		9.331	6826442	86.96	337139	bb			Unknown	

(*4R*)-4-methyl-3,4-dihydro-*2H*-benzo[*h*]chromen-2-ol (4m).

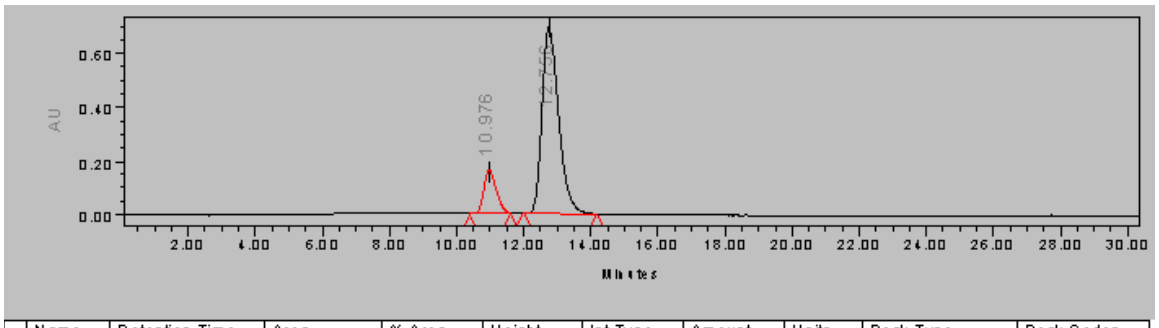
Chiralpak AD column, hexane/EtOH (90:10), flow rate 0.7 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		13.782	2038987	14.32	138397	bb			Unknown	
2		14.422	12200970	85.68	738063	bb			Unknown	

(*4S*)-6-chloro-4-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-ol (4n).

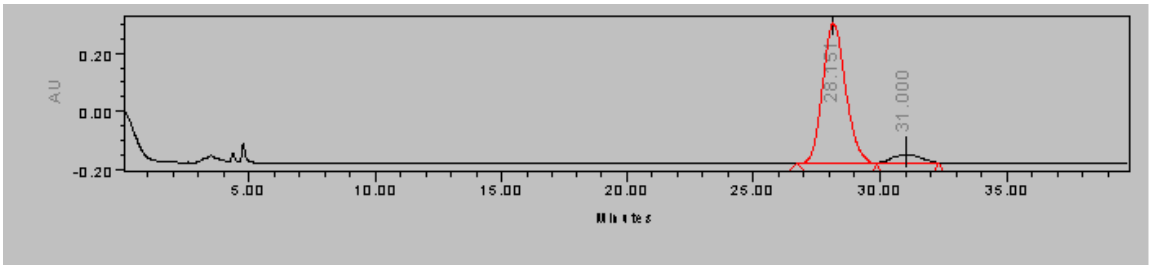
Chiralpak OJ column, hexane/EtOH (90:10), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		10.976	3353721	12.35	142345	bb			Unknown	
2		12.756	23790993	87.65	692958	bb			Unknown	

(*4S*)-7-methoxy-4-phenyl-3,4-dihydro-2*H*-benzo[*h*]chromen-2-ol (4o).

Chiralpak OD column, hexane/EtOH (95:5), flow rate 1.0 mL/min.



	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Peak Codes
1		28.151	30909883	91.86	484829	VV			Unknown	
2		30.999	2738408	8.14	51682	bb			Unknown	