Supporting Information

Relay Catalysis: Combined Metal Catalyzed Oxidation and Asymmetric Iminium Catalysis for the Synthesis of Bi- and Tricyclic Chromenes

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General information **S-2**

General procedures **S-3**

Description of the compounds **S-4**

Copies of NMR Spectra and analytical chiral HPLC traces **S-14**

General Information

Unless otherwise stated, all reagents were obtained from commercial suppliers. Organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon. Solvents for chromatography were technical grade and distilled prior to use. Thin layer chromatography (TLC) was carried out on Merck aluminium support plates Silicagel 60 F_{254}. Visualization was achieved under a UV mineral light. Column chromatography was performed using silicagel Merck 60 (particle size 0.2-0.063 mm). Proton NMR (^{1}H NMR) spectra were recorded at 400 MHz on an Inova 400 spectrometer or at 300 MHz on a Mercury 300 spectrometer. Carbon NMR (^{13}C) spectra were similarly recorded at 125 or 75 MHz, using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence. Proton and carbon NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual proton signals in $CDCl_3$ (δ = 7.26, 77.16) or in CD_2Cl_2 (δ = 5.32, 54.00). Coupling constants (*J*) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, qu: quintet, m: multiplet, br: broad. Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010 (column: Equity®-5, length × I.D. 30 m × 0.25 mm, df 0.25 µm, lot # 28089-U, Supelco). IR spectra were recorded on a Jasco FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Optical rotations were measured on a Perkin Elmer 241 polarimeter using 10 cm cells and the sodium D line (589 nm), in the solvent, at concentration and temperature indicated. The enantiomeric excesses were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralpak AS-H, AD-H, OJ-H or Chiralcel IC, eluent: *n*-hexane/2-propanol). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Chemical yields refer to pure isolated substances. Melting points (m.p.) were recorded using Büchi B-540 melting point apparatus and are uncorrected.

General procedures

Procedures for starting materials:

TPAP was prepared following a literature procedure.[1] The starting propargyl alcohols **2** were prepared either by Sonogashira coupling using the corresponding aryl iodide and propargyl alcohol or by hydroxymethylenation of the corresponding terminal alkynes via lithiation and subsequent reaction with paraformaldehyde.[2] The nitrostyrene derivatives **1** were prepared following a reported procedure.[3]

General procedure I for the oxidative iminium-enamine cascade: To a solution of propargyl alcohol **2** (0.60 mmol, 1.50 equiv) and NMO (0.64 mmol, 1.60 equiv) in CH_2Cl_2 (3.0 mL) were added TPAP (38 μmol, 7 mol%), nitrostyrene derivative **1** (0.40 mmol, 1.0 equiv) and diphenylprolinol TMS-ether organocatalyst **4** (80 μmol, 20 mol%). The resulting solution was stirred for 18h at room temperature under an argon atmosphere. The crude reaction mixture was directly charged on silica gel and purified by flash column chromatography (EtOAc/cyclohexane) to afford the pure desired products **3**.

Racemic products were synthesized according to the general procedure **I** by using pyrrolidine as catalyst.

General procedure II for the preparation of the tricyclic compounds: To a solution of (*R*)-4-(nitromethyl)-2-phenyl-4*H*-chromene-3-carbaldehyde **3a** (0.15 mmol) in CH_2Cl_2 (1.5 mL) were added the corresponding cinnamaldehyde **5** (0.23 mmol, 1.5 equiv) and diphenylprolinol TMS-ether **4** (30 μmol, 20 mol%). The resulting solution was stirred for 48h at room temperature under argon atmosphere. NEt_3 (0.30 mmol, 2.0 equiv) was then added and the resulting mixture was stirred for further 18h. The crude reaction mixture was directly purified by preparative thin layer chromatography (EtOAc/cyclohexane or toluene) to afford the desired tricyclic products.

[1] V. Farmer, T. Welton, *Green Chemistry* 2002, **4**, 97-102.
[2] F. Kleinbeck, F. D. Toste, *J. Am. Chem. Soc.* 2009, **131**, 9178-9179.
[3] a) J. McNulty, J. A. Steere, S.Wolf, *Tetrahedron Lett.* 1998, **39**, 8013-8016; b) J.-T. Liu, C.-F. Yao, *Tetrahedron Lett.* 2001, **42**, 6147-6150.

Description of the compounds

The absolute configuration of the tricyclic 4*H*-chromene compounds was unambiguously determined by X-ray crystallographic analysis of **6e** (Figure 1).[4] All three newly formed chiral centers possess the *R* configuration. It is worth pointing out that the nitro group lies *anti* to the aryl group, occupying the less sterically hindered position. This supports the proposed epimerization of the center α to the nitro group towards the thermodynamically more stable product.

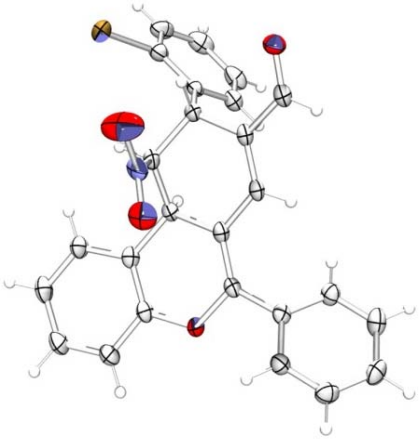
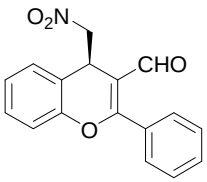


Figure. Molecular structure of compound **6e**.

(*R*)-4-(Nitromethyl)-2-phenyl-4*H*-chromene-3-carbaldehyde **3a**

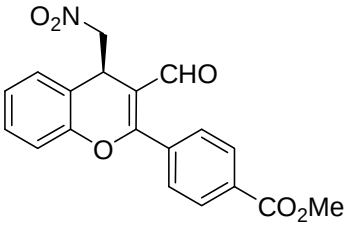


The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 81% yield.

m.p. 118-122 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.59-7.36 (m, 5H), 7.29-7.16 (m, 2H), 7.16-7.04 (m, 2H), 4.72-4.38 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.4, 170.0, 150.8, 131.9, 130.8, 130.5, 129.5, 128.8, 128.7, 126.1, 119.9, 117.3, 111.7, 79.8, 32.4. **IR** (KBr, cm^{-1}) ν 2919, 2862, 1724, 1635, 1580, 1548, 1489, 1364, 1290, 1259, 1218, 1181, 1112, 804, 761, 703. **MS** *m/z* (CI+) 296 ($[M+H]^+$). **HPLC** (Chiralpak AS-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 $mL.min^{-1}$) t_{major} = 27.63 min; t_{minor} = 38.2 min, *ee* = 95%. **$[\alpha]^{25}_D$** = +18.0 (*c* 0.5, $CHCl_3$).

[4] J. Dufor, M. S. Maji, M. Bolte *Acta Crystallographica*, *Section E: Structure Reports Online* 2011, E67(11), o2844.

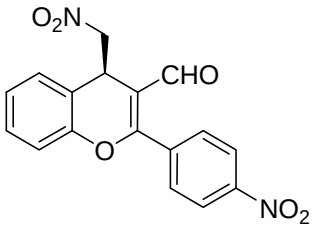
(*R*)-Methyl 4-(3-formyl-4-(nitromethyl)-4*H*-chromen-2-yl)benzoate **3b**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 86% yield.

m.p. 147-148 °C; **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.19 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.39-7.17 (m, 4H), 4.80-4.64 (m, 3H), 3.98 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.9, 168.6, 166.2, 150.7, 134.9, 133.1, 130.5, 129.9, 129.6, 128.6, 126.3, 119.6, 117.3, 112.5, 79.7, 52.7, 32.4. **MS** *m/z* (CI+) 354 ($[M+H]^+$); **IR** (KBr, cm^{-1}) ν 1723, 1650, 1629, 1608, 1578, 1549, 1489, 1365, 1281, 1258, 1216, 1188, 1109, 871, 761, 712. **HPLC** (Chiralpak AD-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.5 $mL.min^{-1}$) t_{major} = 22.98 min; t_{minor} = 25.01 min, *ee* = 96%. **$[\alpha]^{25}_D$** = –7.0 (*c* 1.0, $CHCl_3$).

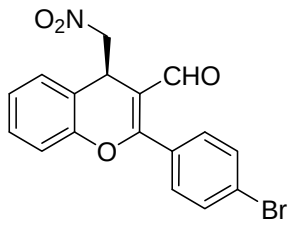
(*R*)-4-(Nitromethyl)-2-(4-nitrophenyl)-4*H*-chromene-3-carbaldehyde **3c**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 77% yield.

m.p. 51-54 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.39 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.41-7.26 (m, 3H), 7.19 (dd, *J* = 8.2, 1.2 Hz, 1H), 4.82 (dd, *J* = 13.2, 6.9 Hz, 1H), 4.74-4.65 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.2, 167.0, 150.6, 149.8, 136.8, 131.5, 129.8, 128.7, 126.6, 124.0, 119.2, 117.3, 113.3, 79.7, 32.4. **MS** *m/z* (CI+) 341 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 3108, 2860, 1736, 1657, 1545, 1521, 1489, 1348, 1291, 1259, 1217, 1179, 1108, 853, 759, 704. **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 50/50, flow rate = 0.6 $mL.min^{-1}$) t_{major} = 81.31 min; t_{minor} = 94.78 min, *ee* = 95%. **$[\alpha]^{25}_D$** = –15.2 (*c* 0.7, $CHCl_3$).

(*R*)-2-(4-Bromophenyl)-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3d**

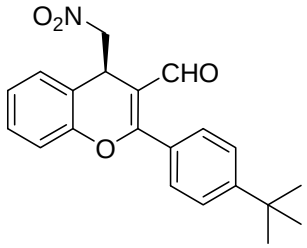


The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 80% yield.

m.p. 95-98 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.35 (ddd, *J* = 8.2, 7.2, 1.9 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.24 (ddd, *J* = 7.8, 7.2, 1.2 Hz, 1H), 7.18 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.75 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.70 (dd, *J* = 4.7, 3.0 Hz, 1H), 4.65 (dd, *J* = 9.5, 3.0 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.8, 168.7, 150.7, 132.2, 131.9, 129.7, 129.6, 128.6, 126.7, 126.3, 119.7, 117.3, 112.0, 79.8, 32.4. **MS** *m/z* (CI+)

376, 374 ([M+H]$^+$). **IR** (KBr, cm^{-1}) ν 3022, 2860, 1785, 1725, 1669, 1550, 1422, 1384, 1314, 1274, 1216, 1124, 1097, 1048, 990, 907, 757. **HPLC** (Chiralpak AS-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 31.47 min; t_{minor} = 52.36 min, *ee* = 97%. $[\alpha]^{25}_D$ = –7.4 (*c* 1.2, $CHCl_3$).

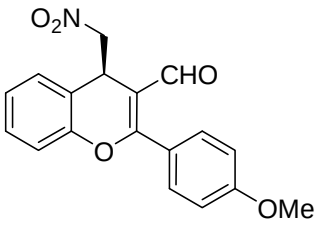
(*R*)-2-(4-*tert*-Butylphenyl)-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3e**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 80% yield.

m.p. 54-58 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.59-7.52 (m, 4H), 7.37-7.29 (m, 2H), 7.25-7.18 (m, 2H), 4.75-4.62 (m, 3H), 1.38 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.5, 170.1, 155.6, 150.9, 130.3, 129.4, 128.7, 127.9, 126.0, 125.8, 120.1, 117.3, 111.4, 79.8, 35.2, 32.4, 31.3. **IR** (KBr, cm–1) ν 2963, 2868, 1655, 1633, 1580, 1550, 1487, 1461, 1396, 1368, 1262, 1221, 1184, 1116, 843, 758. **MS** *m/z* (CI+) 352 ([M+H]$^+$). **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 22.66 min; t_{minor} = 55.73 min, *ee* = 95%. $[\alpha]^{25}_D$ = –20.1 (*c* 1.4, $CHCl_3$).

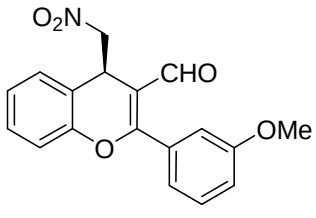
(*R*)-2-(4-Methoxyphenyl)-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3f**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 70% yield.

m.p. 103-106 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.37-7.29 (m, 2H), 7.24-7.19 (m, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 4.73-4.59 (m, 3H), 3.89 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.3, 169.9, 162.7, 150.8, 132.3, 129.4, 128.7, 126.0, 122.9, 120.2, 117.2, 114.2, 110.8, 79.8, 55.7, 32.4. **IR** (KBr, cm–1) ν 3286, 3070, 2861, 1649, 1605, 1536, 1507, 1456, 1395, 1365, 1308, 1247, 1170, 1112, 1019, 841. **MS** *m/z* (CI+) 326 ([M+H]$^+$). **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 41.36 min; t_{minor} = 107.26 min, *ee* = 96%. $[\alpha]^{25}_D$ = –20.1 (*c* 2.1, $CHCl_3$).

(*R*)-2-(3-Methoxyphenyl)-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3g**

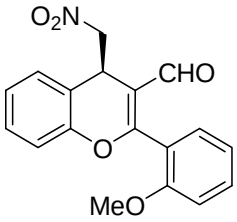


The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 84% yield.

m.p. 117-120 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.59 (s, 1H),

7.42-7.36 (m, 1H), 7.34-7.24 (m, 2H), 7.22-7.13 (m, 3H), 7.13-7.05 (m, 2H), 4.71-4.58 (m, 3H), 3.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.3, 169.6, 159.7, 150.7, 131.9, 129.8, 129.4, 128.6, 126.0, 123.0, 119.8, 117.5, 117.3, 115.5, 111.7, 79.8, 55.7, 32.5. **MS** *m/z* (CI+) 326 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 3024, 2914, 2860, 1782, 1725, 1659, 1578, 1550, 1488, 1425, 1365, 1311, 1271, 1230, 1096, 1045, 991, 879, 758. **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 31.47 min; t_{minor} = 72.87 min, *ee* = 96%. **$[\alpha]^{25}_D$** = +2.0 (*c* 0.5, $CHCl_3$).

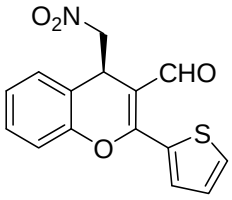
(*R*)-2-(2-Methoxyphenyl)-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3h**



The title compound was prepared following the general procedure **I** and isolated as a pale gummy solid in 49% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.55-7.49 (m, 1H), 7.45-7.42 (m, 1H), 7.35-7.28 (m, 2H), 7.23-7.17 (m, 1H), 7.14-7.01 (m, 3H), 4.74-4.61 (m, 3H), 3.83 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.7, 157.9, 151.1, 132.9, 131.8, 129.3, 128.6, 125.8, 120.7, 120.1, 120.0, 117.3, 112.5, 111.6, 79.6, 55.9, 32.3. **IR** (KBr, cm^{-1}) ν 2937, 2847, 1639, 1581, 1547, 1489, 1459, 1433, 1365, 1299, 1246, 1217, 1177, 1103, 1021, 755. **MS** *m/z* (CI+) 326 ($[M+H]^+$). **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 18.07 min; t_{minor} = 29.34 min, *ee* = 91%. **$[\alpha]^{25}_D$** = –26.1 (*c* 1.2, $CHCl_3$).

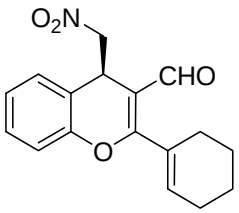
(*R*)-4-(Nitromethyl)-2-(thiophen-2-yl)-4*H*-chromene-3-carbaldehyde **3i**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 92% yield.

m.p. 138-140 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.60 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.46 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.30-7.08 (m, 5H), 4.67-4.61 (m, 1H), 4.57-4.51 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.3, 163.1, 150.5, 133.8, 132.3, 131.8, 129.5, 128.6, 127.9, 126.1, 120.1, 117.3, 111.7, 79.6, 32.5. **MS** *m/z* (CI+) 302 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2858, 1727, 1646, 1602, 1538, 1486, 1423, 1369, 1296, 1227, 1182, 1105, 879, 853, 794, 764, 719. **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 41.00 min; t_{minor} = 92.48 min, *ee* = 96%. **$[\alpha]^{25}_D$** = –11.1 (*c* 0.7, $CHCl_3$).

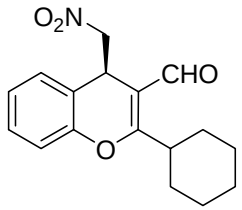
(*R*)-2-Cyclohexenyl-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3j**



The title compound was prepared following the general procedure **I** and isolated as a white solid in 90% yield.

m.p. 127-130 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.23 (ddd, *J* = 8.1, 7.1, 1.8 Hz, 2H), 7.18 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.10 (ddd, *J* = 7.7, 7.1, 1.2 Hz, 1H), 7.03 (dd, *J* = 8.1, 1.2 Hz, 1H), 6.27-6.08 (m, 1H), 4.57-4.45 (m, 3H), 2.58-2.39 (m, 1H), 2.28-2.16 (m, 2H), 2.11-1.97 (m, 1H), 1.76-1.53 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 189.5, 173.3, 150.6, 139.8, 129.9, 129.3, 128.6, 125.7, 119.9, 117.0, 111.4, 79.7, 32.3, 25.9, 25.8, 22.0, 21.7. **MS** *m/z* (CI+) 300 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2934, 2863, 1725, 1642, 1576, 1544, 1488, 1364, 1289, 1237, 1175, 1116, 922, 844, 793, 759, 710. **HPLC** (Chiralpak AS-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 18.18 min; t_{minor} = 25.88 min, *ee* = 99%. **$[\alpha]^{25}_D$** = –86.2 (*c* 0.7, $CHCl_3$).

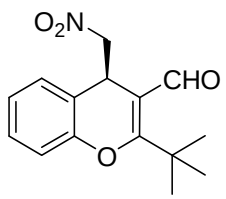
(*R*)-2-Cyclohexyl-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3k**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow oil in 95% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.09 (s, 1H), 7.37-7.25 (m, 2H), 7.22 (ddd, *J* = 8.0, 7.6, 1.0 Hz, 2H), 7.14 (dd, *J* = 8.1, 1.0 Hz, 1H), 4.59 (m, 3H), 3.33 – 3.21 (m, 1H), 1.98-1.74 (m, 6H), 1.52-1.25 (m, 4H).**^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.5, 176.1, 150.5, 129.2, 128.4, 125.7, 119.8, 116.8, 109.7, 79.7, 38.7, 31.9, 30.3, 29.9, 26.0, 25.8, 25.6. **MS** *m/z* (CI+) 302 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2930, 2854, 1715, 1653, 1631, 1579, 1542, 1452, 1364, 1232, 1172, 1008, 822, 759. **HPLC** (Chiralpak AS-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 23.90 min; t_{minor} = 18.44 min, *ee* = 97%. **$[\alpha]^{25}_D$** = –17.6 (*c* 0.5, $CHCl_3$).

(*R*)-2-*tert*-Butyl-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3l**

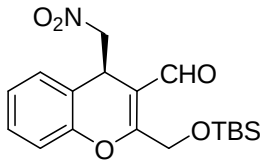


The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 96% yield.

m.p. 94-98 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 10.4 (s, 1H), 7.31-7.07 (m, 4H), 4.69 (dd, *J* = 6.3 Hz, 4.5 Hz, 1H), 4.50-4.40 (m, 2H), 1.50 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 188.7, 178.7, 150.7, 129.1, 128.2, 125.8, 120.2, 116.6, 110.5, 80.0, 39.0, 32.6, 31.2. **IR** (KBr, cm–1) ν 3046, 2970, 2894, 1642, 1573, 1538, 1481,

1458, 1396, 1360, 1223, 1182, 1142, 943, 863, 758. **MS** *m/z* (CI+) 276 ($[M+H]^+$). **HPLC** (Chiralpak AS-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 80/20, flow rate = 0.6 mL.min^{-1}) t_{major} = 14.69 min; t_{minor} = 17.18 min, *ee* = 98%. $[\alpha]^{25}_D$ = –55.5 (*c* 1.1, $CHCl_3$).

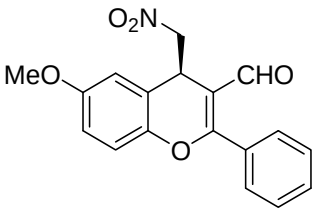
(*R*)-2-((*tert*-Butyldimethylsilyloxy)methyl)-4-(nitromethyl)-4*H*-chromene-3-carbaldehyde **3m**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow oil in 53% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.33-7.14 (m, 3H), 7.09 (d, *J* = 8.1 Hz, 1H), 4.78 (d, *J* = 13.9 Hz, 1H), 4.67 (d, *J* = 13.9 Hz, 1H), 4.68-4.53 (m, 3H), 0.92 (s, 9H), 0.16 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 188.7, 169.0, 150.3, 129.4, 128.6, 126,0, 119.8, 117.1, 112.2, 79.4, 60.5, 31.9, 25.9, 18.4, -5.1. **MS** *m/z* (CI+) 364 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2928, 2858, 1739, 1644, 1522, 1461, 1378, 1232, 1174, 1098, 1072, 966, 833, 759, 702. **HPLC** (Chiralpak OJ-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 96/4, flow rate = 0.6 mL.min^{-1}) t_{major} = 29.43 min; t_{minor} = 33.60 min, *ee* = 92%. $[\alpha]^{25}_D$ = +4.0 (*c* 0.3, $CHCl_3$).

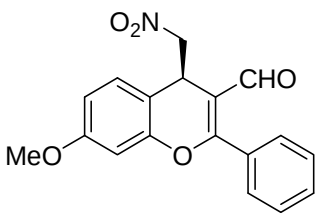
(*R*)-6-Methoxy-4-(nitromethyl)-2-phenyl-4*H*-chromene-3-carbaldehyde **3n**



The title compound was prepared following the general procedure **I** and isolated as a white solid in 74% yield.

m.p. 123-130 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.59 (s, *J* = 1.4 Hz, 1H), 7.66-7.45 (m, 5H), 7.13 (d, *J* = 8.9 Hz, 1H), 6.90-6.84 (m, 1H), 6.79 (d, *J* = 2.9 Hz, 1H), 4.78-4.59 (m, 3H), 3.81 (s, *J* = 1.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.4, 170.1, 157.4, 144.9, 131.8, 130.9, 130.4, 128.8, 120.7, 118.2, 115.3, 112.6, 110.8, 79.6, 55.9, 32.8. **MS** *m/z* (CI+) 326 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 3020, 2918, 2850, 1651, 1630, 1586, 1550, 1498, 1430, 1362, 1257, 1213, 1032, 756. **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 30.49 min; t_{minor} = 38.22 min, *ee* = 94%. $[\alpha]^{25}_D$ = +46.3 (*c* 0.3, $CHCl_3$).

(*R*)-7-Methoxy-4-(nitromethyl)-2-phenyl-*4H*-chromene-3-carbaldehyde **3o**

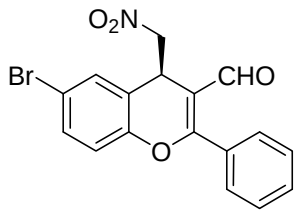


The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 74% yield.

m.p. 120-127 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.65-7.35 (m, 5H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.76 (dd, *J* = 8.5; 2.6 Hz, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 4.74-4.60 (m, 3H), 3.82 (s,

3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.5, 169.8, 160.4, 151.5, 131.9, 130.8, 130.4, 129.2, 128.8, 112.8, 112.1, 111.6, 102.3, 79.9, 55.7, 32.0. **MS** *m/z* (CI+) 326 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2924, 2859, 1725, 1639, 1577, 1542, 1505, 1441, 1361, 1331, 1167, 1106, 1025, 938, 829, 746, 695. **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 33.21 min; t_{minor} = 67.23 min, *ee* = 97%. **$[\alpha]^{25}_D$** = +60.0 (*c* 0.6, $CHCl_3$).

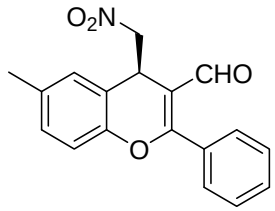
(*R*)-6-Bromo-4-(nitromethyl)-2-phenyl-4H-chromene-3-carbaldehyde **3p**



The title compound was prepared following the general procedure **I** and isolated as a yellow solid in 76% yield.

m.p. 188-190 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.62-7.41 (m, 7H), 7.12-7.03 (m, 1H), 4.81-4.73 (m, 1H), 4.67-4.61 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.2, 169.6, 150.0, 132.5, 132.1, 131.3, 130.4, 128.9, 122.1, 119.0, 118.4, 111.2, 79.5, 32.2. **MS** *m/z* (CI+) 374, 376 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2879, 1738, 1649, 1628, 1573, 1537, 1480, 1424, 1358, 1255, 1217, 1178, 1126, 891, 807, 726, 695. **HPLC** (Chiralpak AS-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 31.12 min; t_{minor} = 57.55 min, *ee* = 95%. **$[\alpha]^{25}_D$** = +87.8 (*c* 0.7, $CHCl_3$).

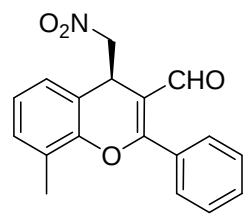
(*R*)-6-Methyl-4-(nitromethyl)-2-phenyl-4*H*-chromene-3-carbaldehyde **3q**



The title compound was prepared following the general procedure **I** and isolated as a white solid in 84% yield.

m.p. 153-155 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 7.66-7.45 (m, 5H), 7.19-7.03 (m, 3H), 4.78-4.59 (m, 3H), 2.36 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.5, 170.1, 148.8, 135.9, 131.8, 130.9, 130.5, 130.1, 128.8, 119.6, 117.0, 111.6, 79.8, 32.4, 21.0. **MS** *m/z* (CI+) 310 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2863, 2070, 1732, 1643, 1621, 1583, 1547, 1494, 1423, 1358, 1259, 1196, 1124, 815, 759, 701. **HPLC** (Chiralcel IC, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 mL.min^{-1}) t_{major} = 29.57 min; t_{minor} = 47.34 min, *ee* = 96%. **$[\alpha]^{25}_D$** = +43.0 (*c* 0.6, $CHCl_3$).

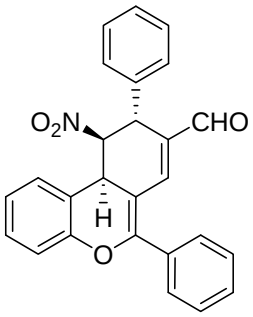
(*R*)-8-Methyl-4-(nitromethyl)-2-phenyl-4*H*-chromene-3-carbaldehyde **3r**



The title compound was prepared following the general procedure **I** and isolated as a pale yellow solid in 71% yield. **m.p.** 117-120 °C. **^{1}H NMR**

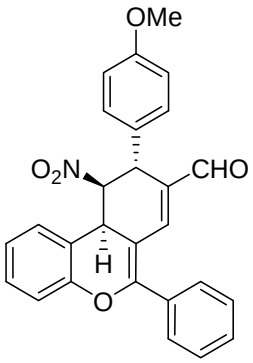
(300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.68-7.46 (m, 5H), 7.22-7.08 (m, 3H), 4.75-4.60 (m, 3H), 2.38 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.4, 169.9, 149.2, 132.0, 131.0, 130.9, 130.6, 129.0, 126.7, 126.2, 125.6, 119.7, 111.7, 80.0, 32.6, 16.0. **MS** *m/z* (CI+) 310 ($[M+H]^+$). **IR** (KBr, cm^{-1}) ν 2920, 2854, 1735, 1653, 1588, 1549, 1468, 1445, 1371, 1271, 1188, 1078, 910, 780, 734, 701. **HPLC** (Chiralpak AS-H, 0.46 x 25 cm, *n*-hexane/2-propanol = 70/30, flow rate = 0.6 $mL.min^{-1}$) t_{major} = 21.69 min; t_{minor} = 27.15 min, *ee* = 77%. **$[\alpha]^{25}_D$** = +75.0 (*c* 0.6, $CHCl_3$).

(9*R*,10*R*,10aR)-10-Nitro-6,9-diphenyl-10,10a-dihydro-9*H*-benzo[*c*]chromene-8-carbaldehyde **6a**



The title compound was prepared following the general procedure **II** and isolated as a pale yellow solid in 77% yield. **m.p.** 132-136 °C. **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 9.44 (s, 1H), 7.71-7.65 (m, 2H), 7.63 (s, 1H), 7.61-7.54 (m, 3H), 7.48-7.20 (m, 6H), 7.20-7.02 (m, 3H), 5.46 (dd, *J* = 3.1, 1.6 Hz, 1H), 4.75 (brs, 1H), 4.33 (d, *J* = 3.1 Hz, 1H). **^{13}C NMR** (75 MHz, CD_2Cl_2) δ 191.5, 157.1, 151.4, 145.5, 139.8, 133.2, 133.0, 131.1, 130.1, 129.8, 129.5, 129.2, 128.7, 128.6, 126.2, 125.2, 118.7, 117.8, 105.2, 86.1, 43.3, 32.6. **MS** *m/z* (EI+) 410 ($[M+H]^+$). **HRMS** *m/z* (ES+) calcd for $C_{26}H_{20}NO_4$ ($[M+H]^+$) 410.13868, found 410.13870. **IR** (KBr, cm^{-1}) ν 2919, 2851, 1734, 1676, 1548, 1454, 1376, 1238, 1163, 1115, 1075, 950, 765, 704. **$[\alpha]^{25}_D$** = –90.3 (*c* 1.4, $CHCl_3$).

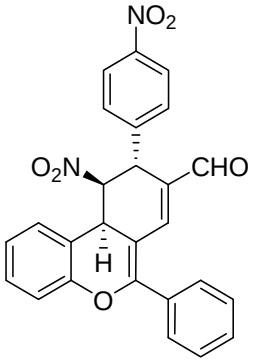
(9*R*,10*R*,10a*R*)-9-(4-Methoxyphenyl)-10-nitro-6-phenyl-10,10a-dihydro-9*H*-benzo[*c*]chromene-8-carbaldehyde **6b**



The title compound was prepared following general procedure **II** and isolated as a yellow solid in 83% yield. **m.p.** 119-123 °C. **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 9.43 (s, *J* = 10.2 Hz, 1H), 7.74-7.65 (m, 2H), 7.63-7.51 (m, 4H), 7.33-7.03 (m, 6H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.42 (dd, *J* = 3.4, 1.7 Hz, 1H), 4.69 (brs, 1H), 4.34 (d, *J* = 3.1 Hz, 1H), 3.80 (s, *J* = 2.3 Hz, 3H).**^{13}C NMR** (75 MHz, CD_2Cl_2) δ 191.5, 160.0, 156.9, 151.4, 145.2, 133.5, 133.0, 131.7, 131.1, 130.1, 129.8, 129.4, 129.2, 126.2, 125.2, 118.8, 117.8, 115.1, 105.2, 86.3, 55.9, 42.6, 32.5. **MS** *m/z*

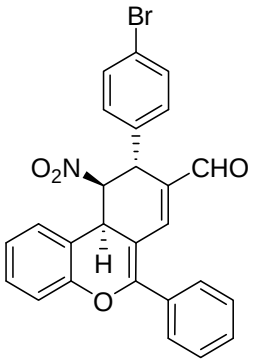
(EI+) 440 ($[M+H]^+$). **HRMS** *m/z* (EI+) calcd for $C_{27}H_{22}NO_5$ ($[M+H]^+$) 440.14925, found 440.14932. **IR** (KBr, cm^{-1}) ν 2194, 2121, 1732, 1673, 1607, 1545, 1506, 1452, 1364, 1303, 1245, 1161, 1118, 1074, 1028, 949, 825, 759, 697. $[\alpha]^{25}_D$ = –125.2 (*c* 1.6, $CHCl_3$).

(9*R*,10*R*,10a*R*)-10-Nitro-9-(4-nitrophenyl)-6-phenyl-10,10a-dihydro-9*H*-benzo[*c*]chromene-8-carbaldehyde **6c**



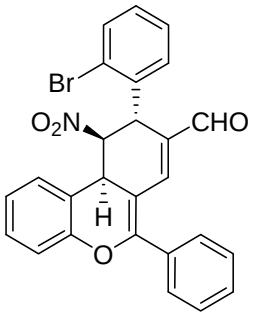
The title compound was prepared following general procedure **II** and isolated as a yellow solid in 81% yield. **m.p.** 175-178 °C. **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 9.45 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 2H), 7.70 (s, 1H), 7.70-7.64 (m, 2H), 7.62-7.56 (m, 3H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.36-7.25 (m, 1H), 7.14 (dd, *J* = 6.6, 1.3 Hz, 2H), 7.13- 7.07 (m, 1H), 5.44 (dd, *J* = 3.2, 1.5 Hz, 1H), 4.85 (brs, 1H), 4.29 (d, J = 3.2 Hz, 1H). **^{13}C NMR** (75 MHz, CD_2Cl_2) δ 191.2, 157.9, 151.3, 148.2, 146.9, 146.2, 132.8, 132.1, 131.3, 130.7, 130.1, 129.9, 129.7, 129.3, 126.2, 125.4, 124.9, 118.0, 104.4, 85.4, 43.0, 32.8. **MS** *m/z* (EI+) 454 (M). **HRMS** *m/z* (EI+) calcd for $C_{26}H_{18}NO_4$ ($[M–NO_2]^+$) 408.12303, found 408.12392. **IR** (KBr, cm^{-1}) ν 2920, 2851, 1672, 1627, 1604, 1577, 1548, 1518, 1346, 1261, 1230, 1163, 1113, 1076, 907, 858, 828, 762, 728. $[\alpha]^{25}_D$ = –191.3 (*c* 1.5, $CHCl_3$).

(9*R*,10*R*,10a*R*)-9-(4-Bromophenyl)-10-nitro-6-phenyl-10,10a-dihydro-9*H*-benzo[*c*]chromene-8-carbaldehyde **6d**



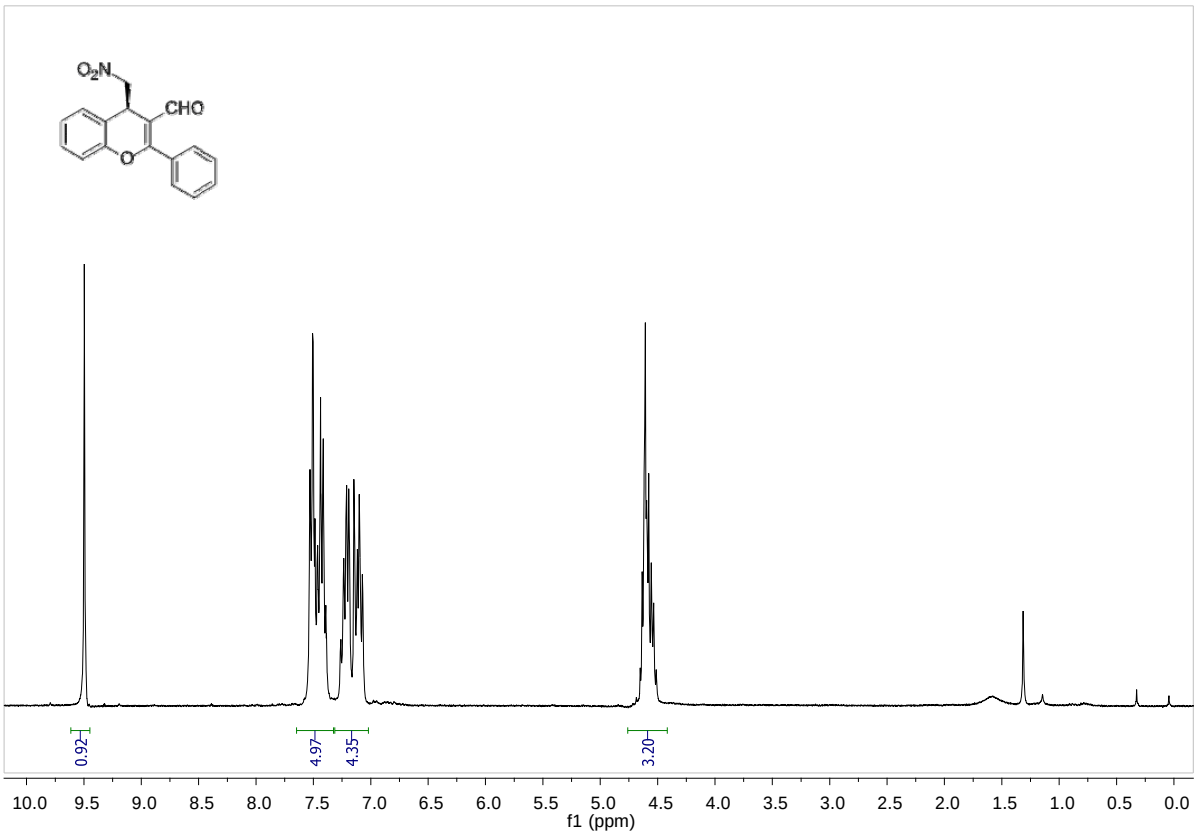
The title compound was prepared following general procedure **II** and isolated as a pale yellow solid in 78% yield. **m.p.** 110-113 °C. **^{1}H NMR** (300 MHz, CD_2Cl_2) δ 9.40 (s, 1H), 7.69-7.64 (m, 2H), 7.63 (s, 1H), 7.61-7.47 (m, 5H), 7.31-7.24 (m, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.19-7.06 (m, 3H), 5.40 (dd, *J* = 3.4, 1.5 Hz, 1H), 4.70 (brs, 1H), 4.29 (d, *J* = 3.1 Hz, 1H).**^{13}C NMR** (75 MHz, CD_2Cl_2) δ 191.3, 157.35, 151.4, 145.7, 139.0, 132.9, 132.7, 131.2, 130.5, 130.4, 130.1, 129.6, 129.3, 126.2, 125.3, 122.6, 118.4, 117.9, 104.9, 85.8, 42.7, 32.6 **MS** *m/z* (EI+) 487; 489 (M). **HRMS** *m/z* (EI+) calcd for $C_{26}H_{18}NO_4{}^{79}Br$ ([M) 487.04137, found 487.04178. **IR** (KBr, cm^{-1}) ν 2919, 2851, 1907, 1733, 1676, 1628, 1545, 1457, 1373, 1236, 1161, 1165, 1117, 1074, 1012, 951, 821, 762, 706. $[\alpha]^{25}_D$ = –284.0 (*c* 0.5, $CHCl_3$).

(9*R*,10*R*,10a*R*)-9-(2-Bromophenyl)-10-nitro-6-phenyl-10,10a-dihydro-9*H*-benzo[*c*]chromene-8-carbaldehyde **6e**



The title compound was prepared following general procedure **II** and isolated as a pale yellow solid in 85% yield. **m.p.** 196-199 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.72 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.68 (s, 1H), 7.67-7.63 (m, 2H), 7.59-7.54 (m, 3H), 7.28-7.16 (m, 5H), 7.11 (td, *J* = 7.5, 1.2 Hz, 1H), 7.06 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.02 (dd, *J* = 7.5, 1.7 Hz, 1H), 5.49 (dd, *J* = 3.3, 1.4 Hz, 1H), 5.10 (brs, 1H), 4.24 (d, *J* = 3.3 Hz, 1H)..**^{13}C NMR** (75 MHz, $CDCl_3$) δ 190.8, 157.0, 150.9, 145.8, 137.9, 134.2, 132.8, 132.4, 130.8, 129.8, 129.7, 129.7, 129.2, 128.8, 128.0, 126.2, 125.0, 124.8, 117.5, 117.3, 104.3, 83.5, 42.3, 32.7. **MS** *m/z* (EI+) 487; 489 (M). **HRMS** *m/z* (EI+) calcd for $C_{26}H_{18}NO_4{}^{79}Br$ ([M]) 487.04137, found 487.04142. **IR** (KBr, cm^{-1}) ν 2327, 2070, 1733, 1675, 1609, 1574, 1544, 1489, 1455, 1366, 1258, 1230, 1165, 1117, 1072, 1020, 947, 830, 761, 696. **$[\alpha]^{25}_D$** = +58.0 (*c* 2.9, $CHCl_3$).

Compound **3a**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O
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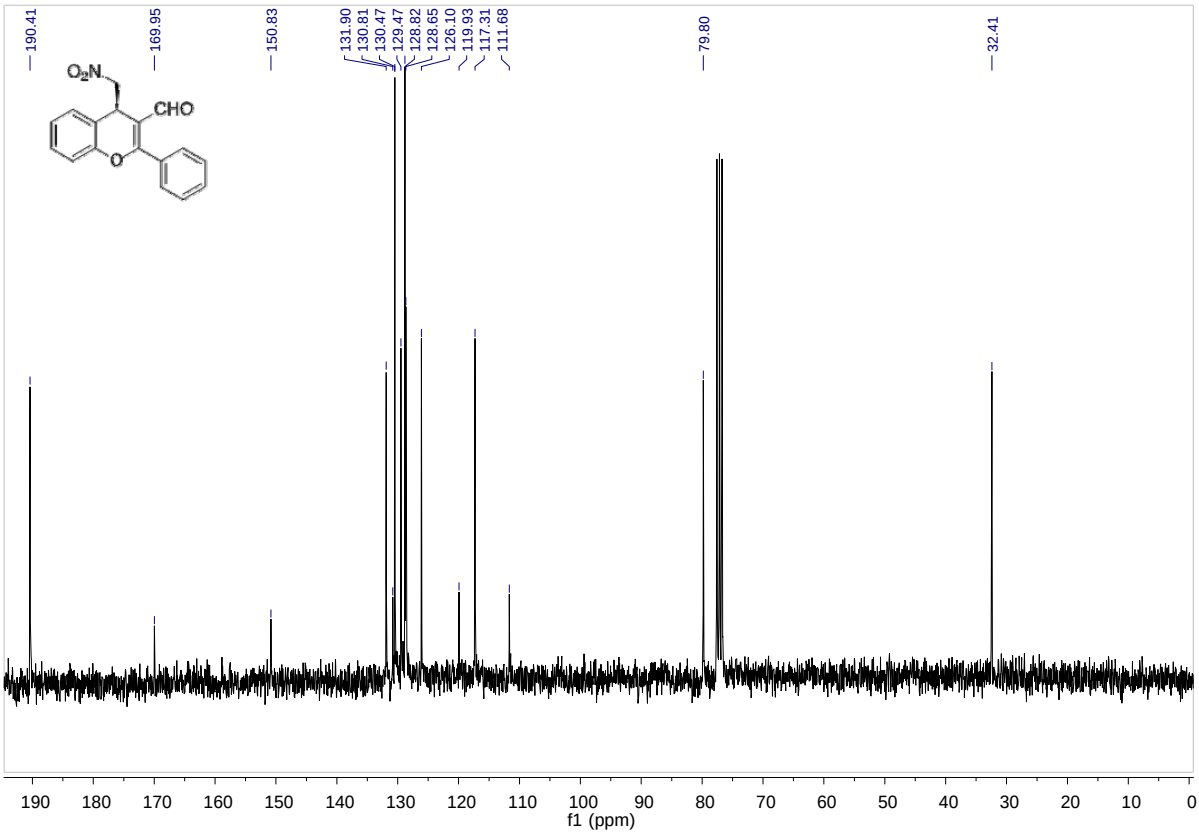
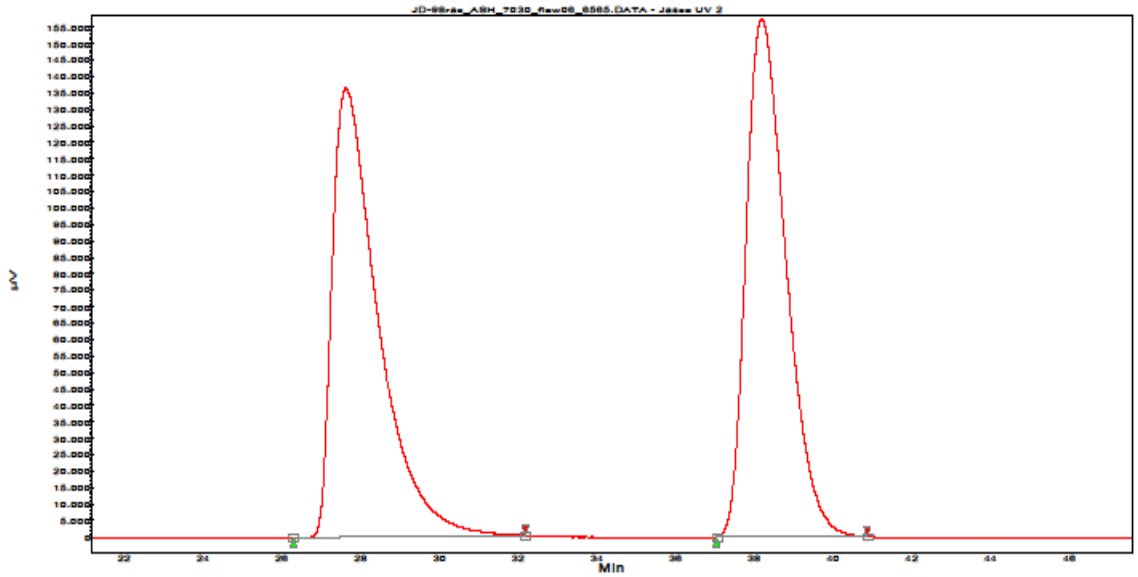
4.97
4.35
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.41
169.95
150.83
131.90
130.81
130.47
129.47
128.82
128.65
126.10
119.93
117.31
111.68
79.80
32.41
O2N
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

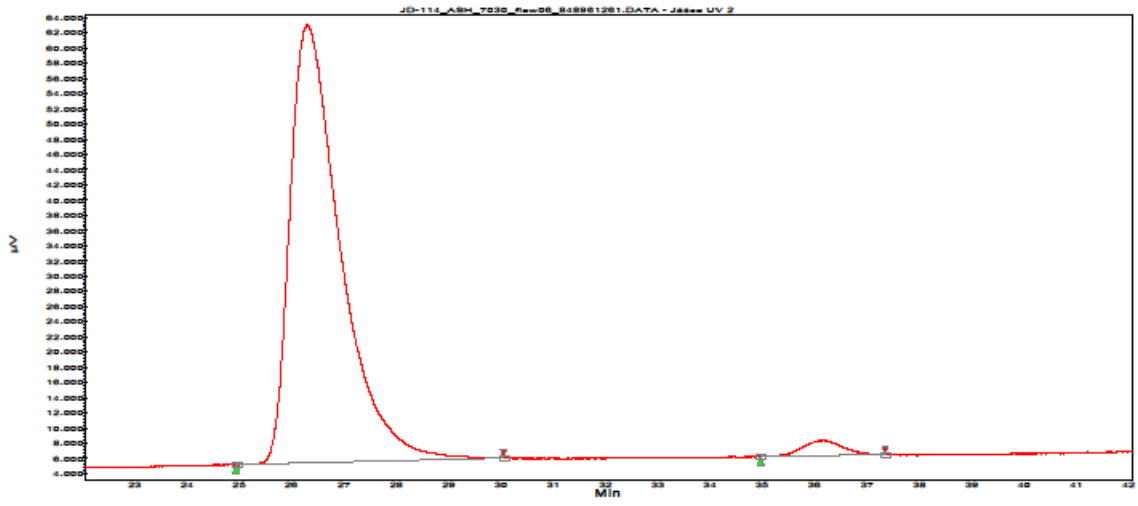
Compound **3a**

Data file: JD-98rac_ASH_7030_flow06_6565.DATA
Method: HPLC1_ASH_7030_flow06_acq_50
Date: 18.06.2010 20:11:48



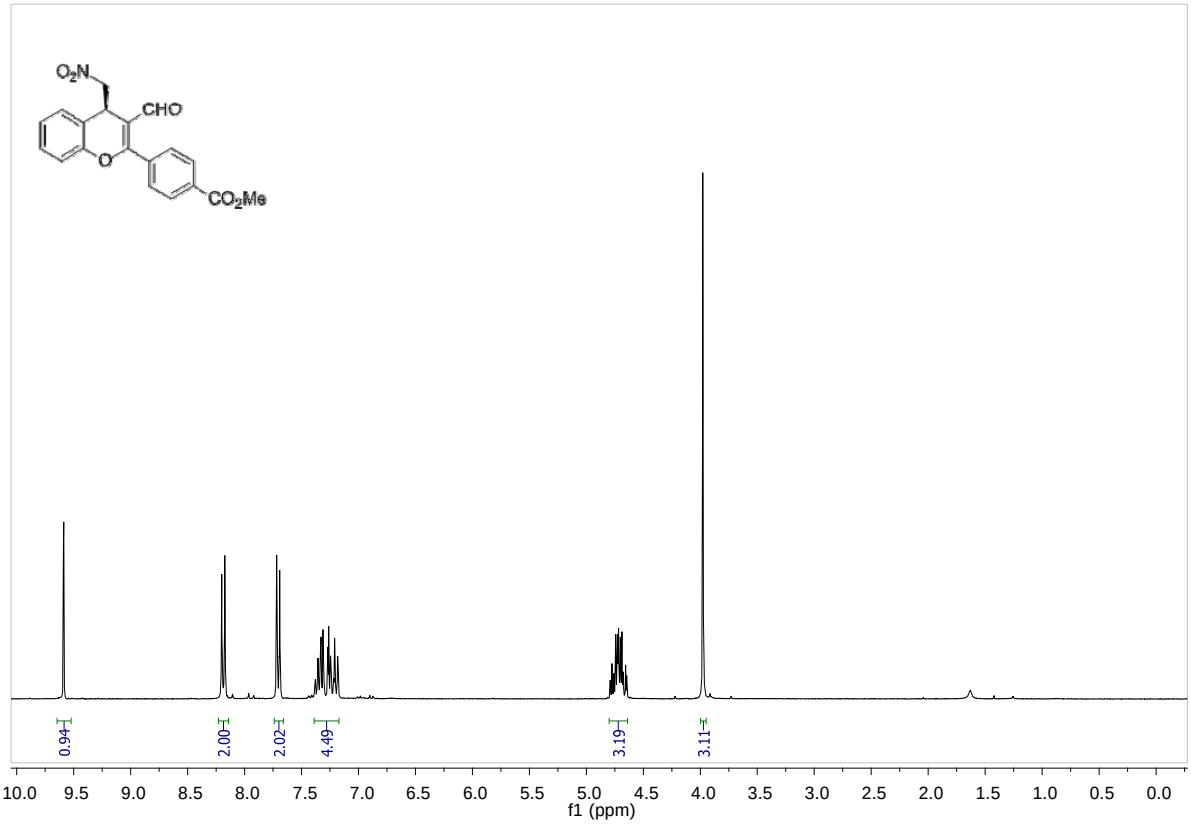
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	26,291	27,633	32,180	49,804
2	37,035	38,200	40,857	50,196
Total				100,000

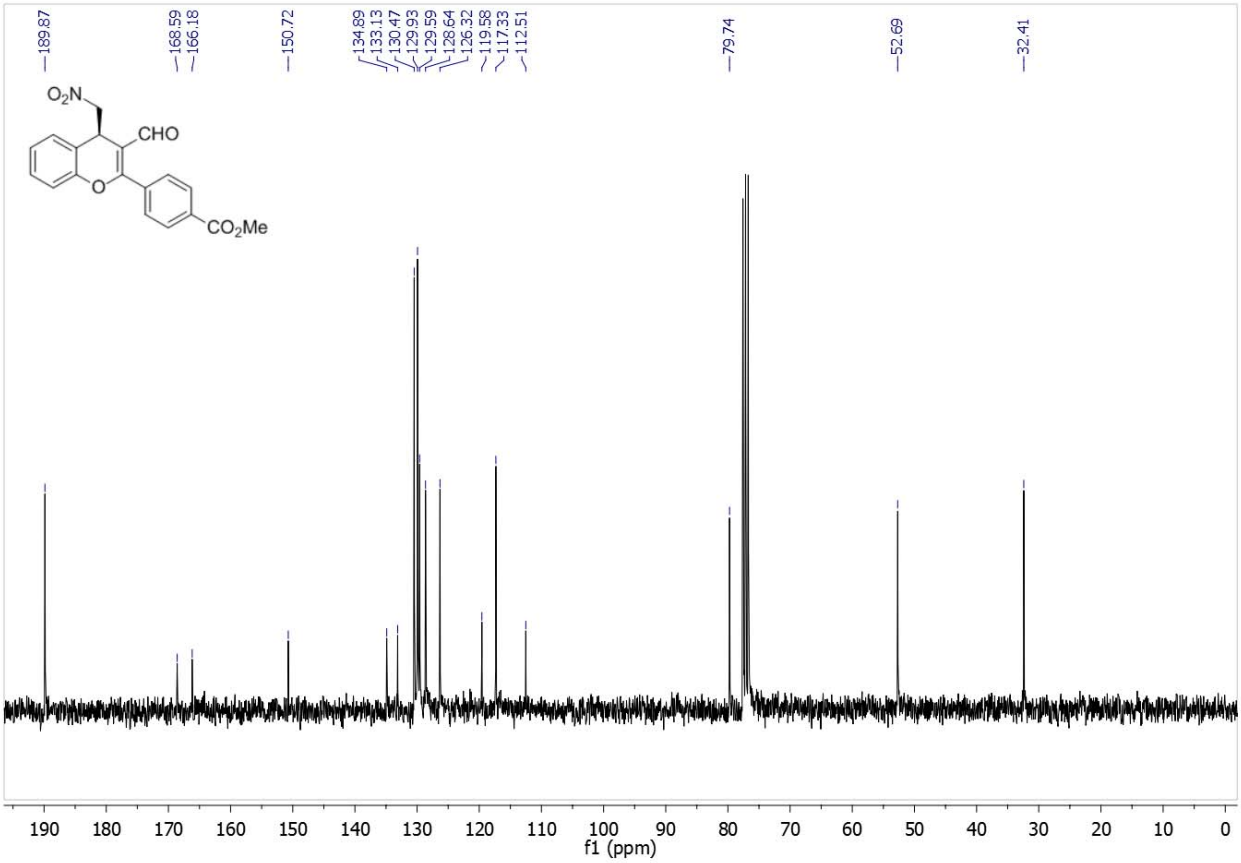
Data file: JD-114_ASH_7030_flow06_848961261.DATA
Method: HPLC1_ASH_7030_flow06_acq_50
Date: 05.07.2010 21:31:59



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	24,947	26,300	30,048	97,335
2	34,962	36,167	37,337	2,665
Total				100,000

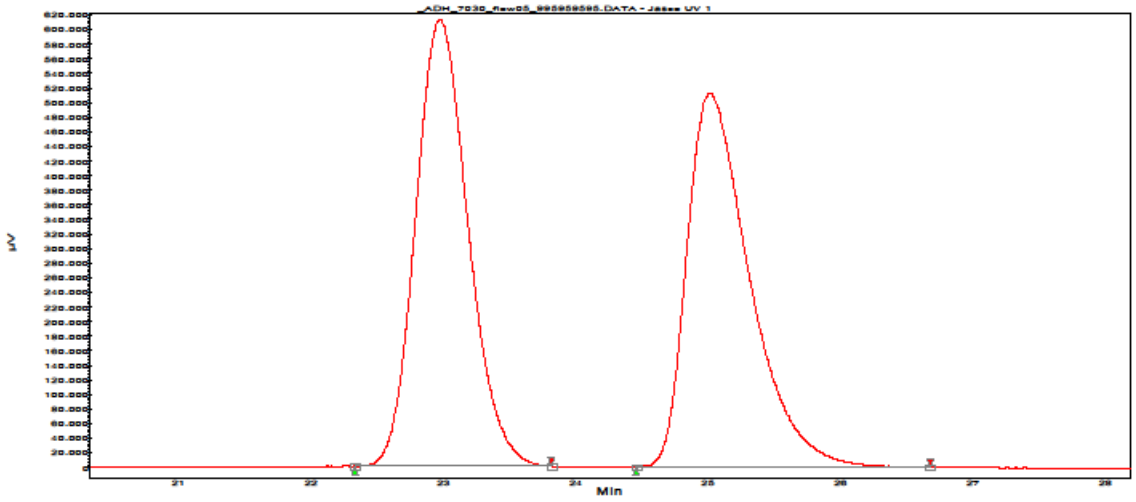
Compound **3b**


O2N
CHO
O
CO2Me
0.94
2.00
2.02
4.49
3.19
3.11
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


189.87
168.59
166.18
150.72
134.89
133.13
130.47
129.93
129.59
128.64
126.32
119.58
117.33
112.51
79.74
52.69
32.41
O2N
CHO
O
CO2Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

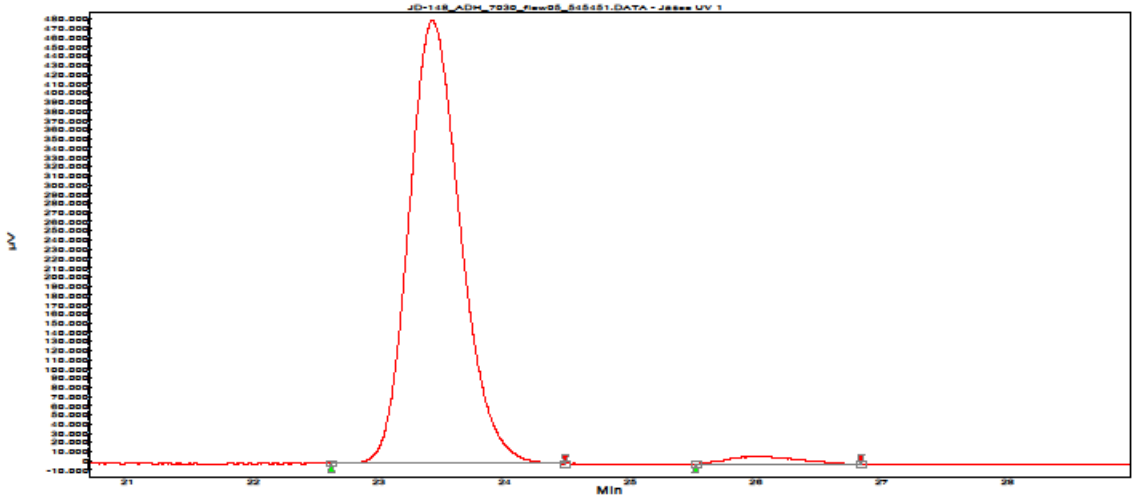
Compound **3b**

Data file: _ADH_7030_flow05_995959595.DATA
Method: HPLC1_ADH_7030_flow05_acq_90
Date: 16.07.2010 00:16:15



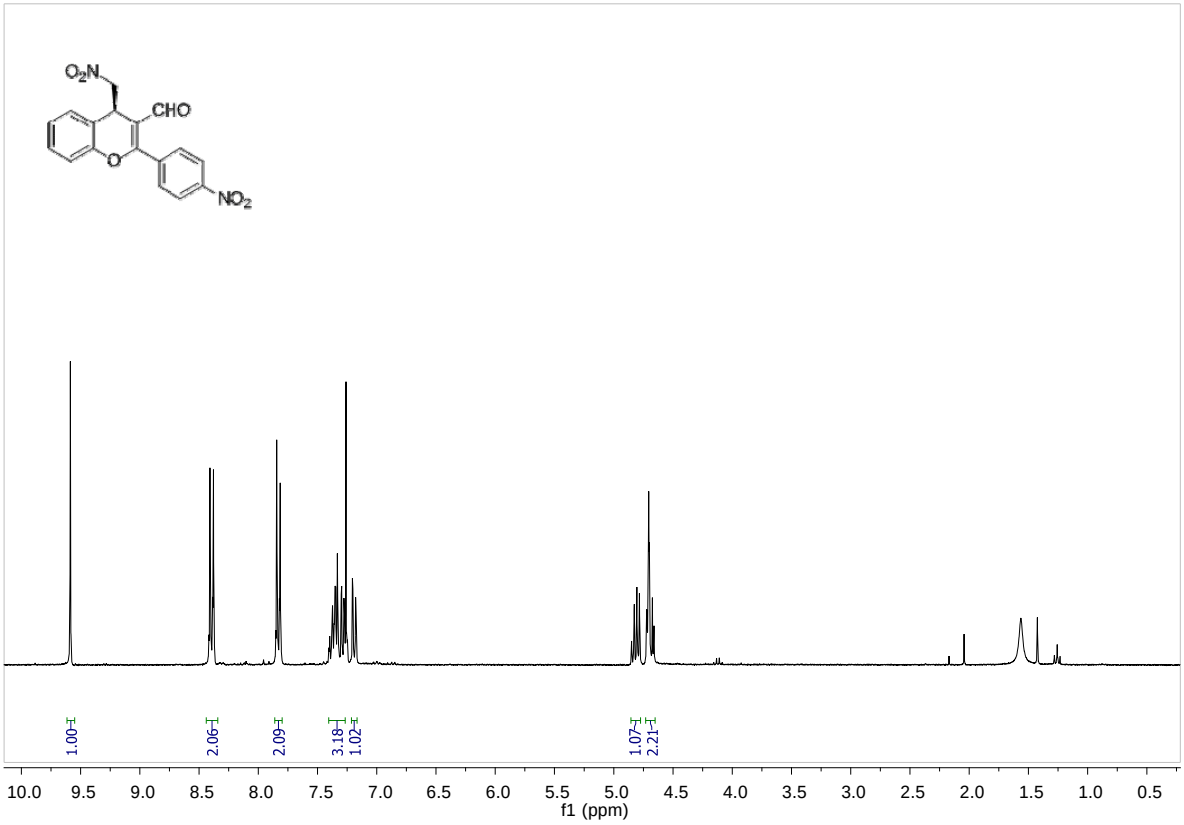
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	22,332	22,975	23,817	50,099
2	24,456	25,008	26,678	49,901
Total				100,000

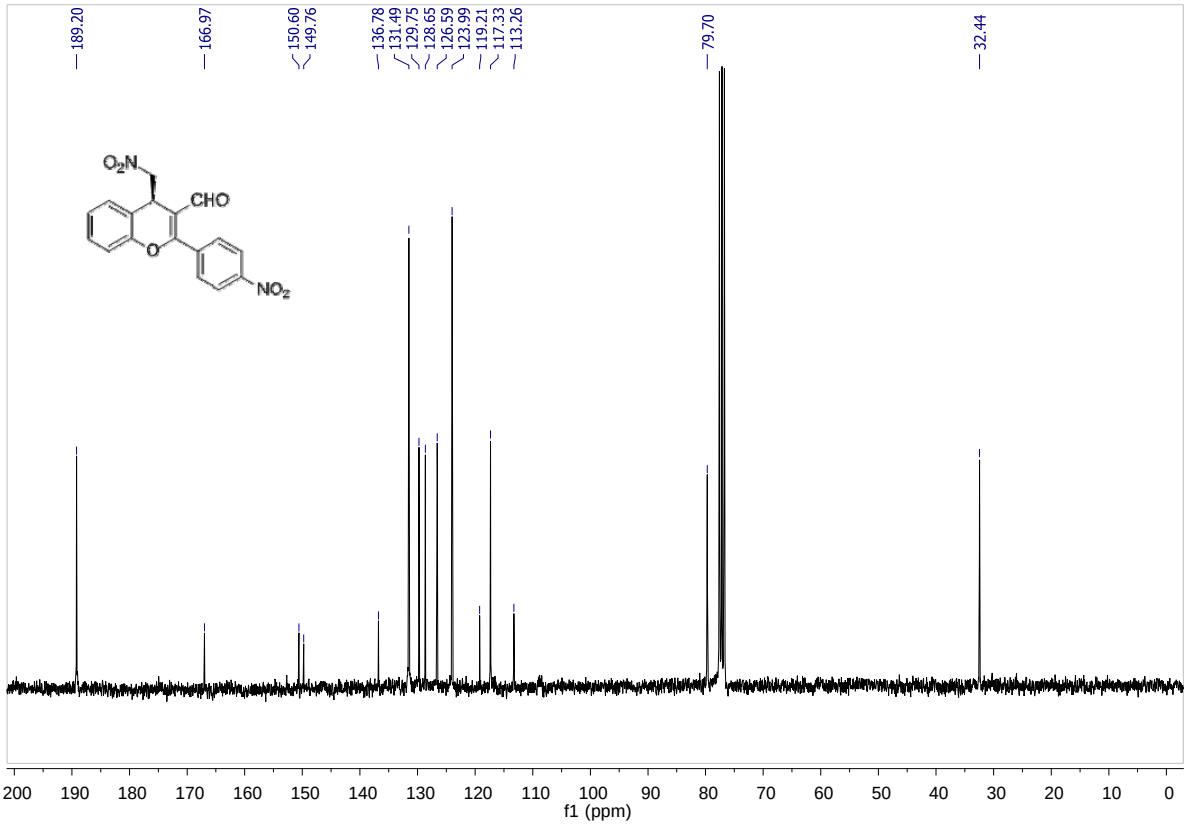
Data file: JD-148_ADH_7030_flow05_545451.DATA
Method: HPLC1_ADH_7030_flow05_acq_90
Date: 27.07.2010 11:48:47



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	22,621	23,425	24,479	97,829
2	25,518	25,975	26,833	2,171
Total				100,000

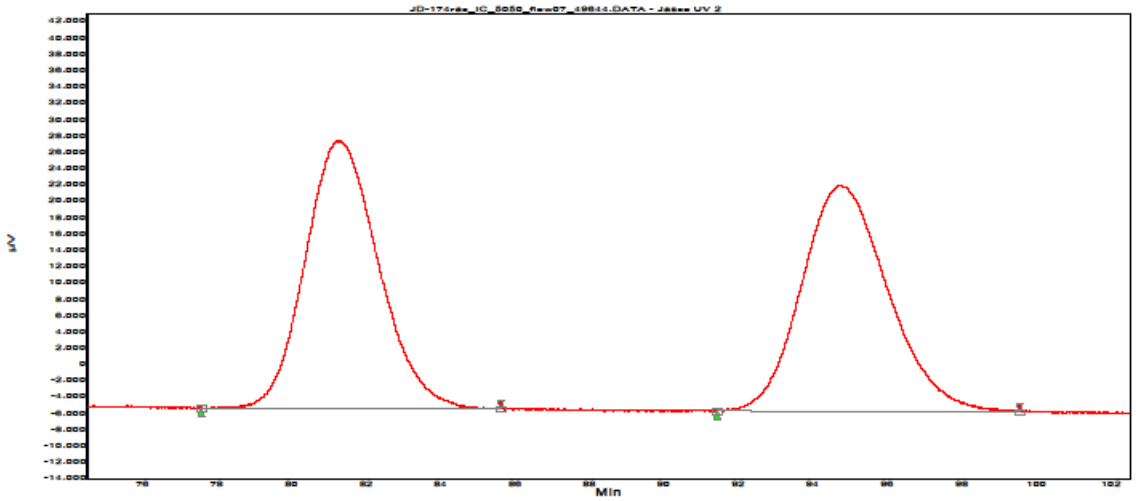
Compound **3c**


O2N
CHO
O
NO2
1.00
2.06
2.09
3.18
1.02
1.07
2.21
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)


189.20
166.97
150.60
149.76
136.78
131.49
129.75
128.65
126.59
123.99
119.21
117.33
113.26
79.70
32.44
O2N
CHO
O
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

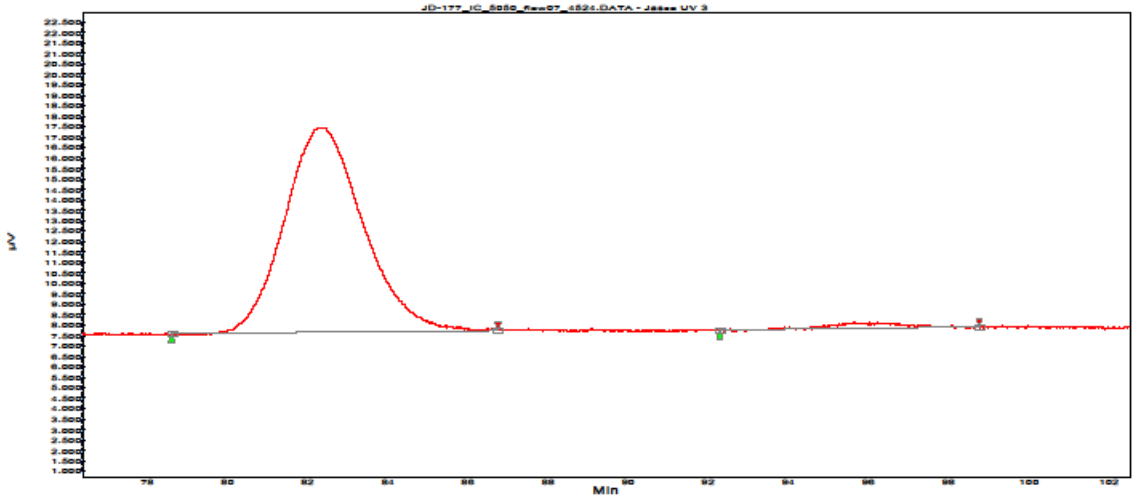
Compound **3c**

Data file: JD-174rac_IC_5050_flow07_49644.DATA
Method: HPLC1_IC_5050_flow0.7_acq_130
Date: 12.08.2010 17:22:46



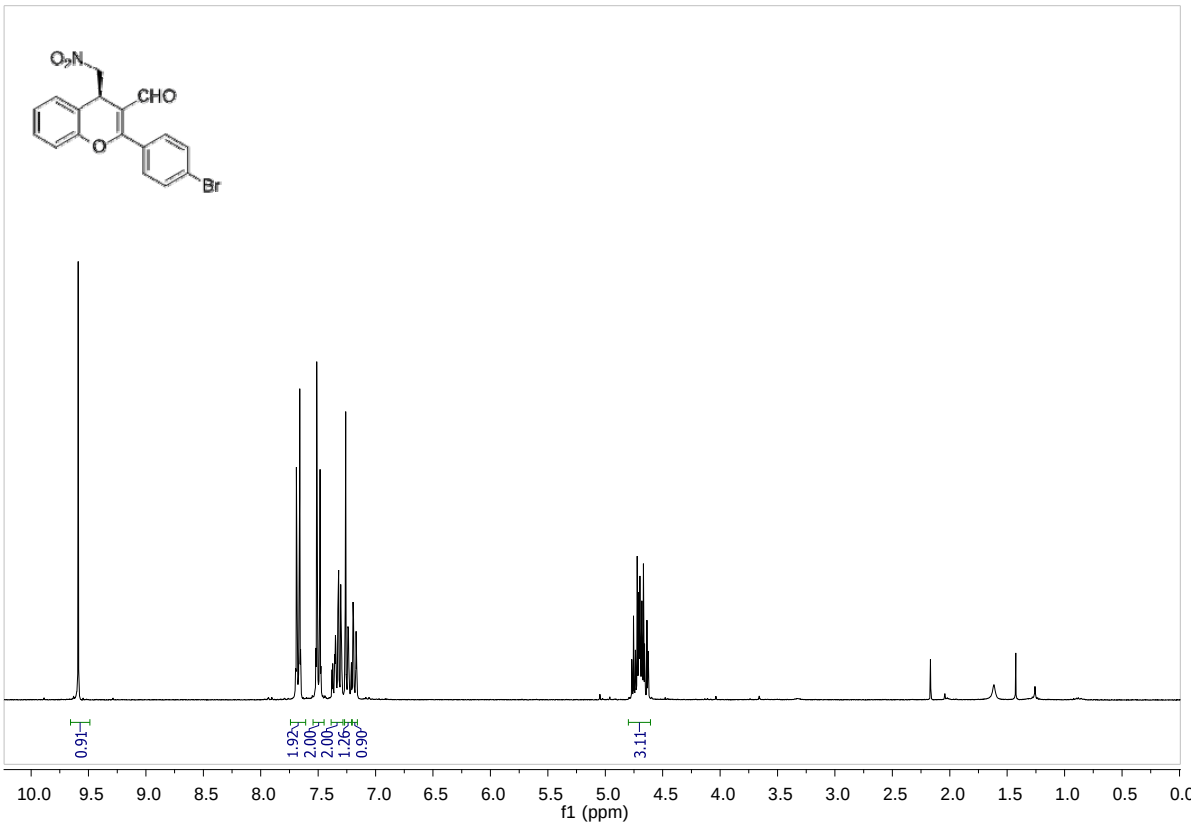
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	77,588	81,308	85,621	50,107
2	91,429	94,783	99,549	49,893
Total				100,000

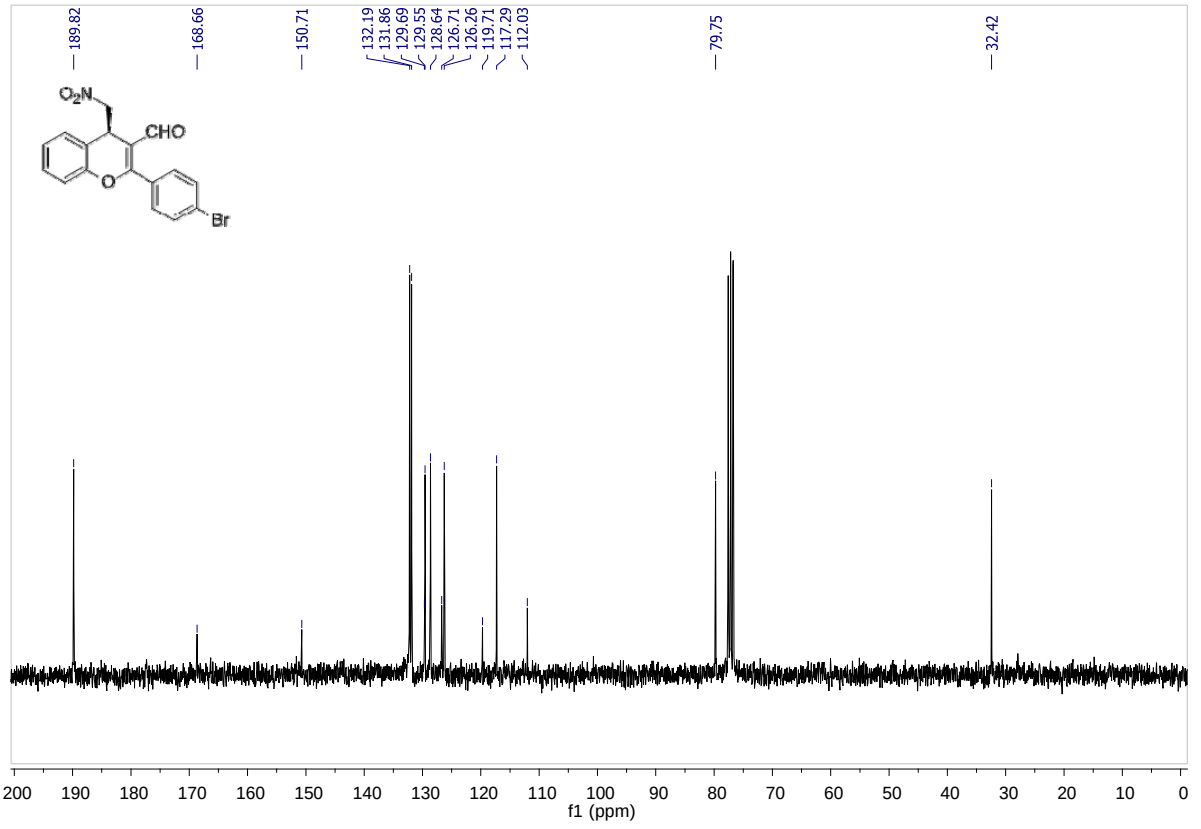
Data file: JD-177_IC_5050_flow07_4524.DATA
Method: HPLC1_IC_5050_flow0.7_acq_130
Date: 13.08.2010 10:08:06



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	78,611	82,367	86,756	0,000	97,58	9811,6	22171,0	97,578
2	UNKNOWN	92,284	96,308	98,757	0,000	2,42	242,3	550,4	2,422
Total						100,00	10053,9	22721,4	100,000

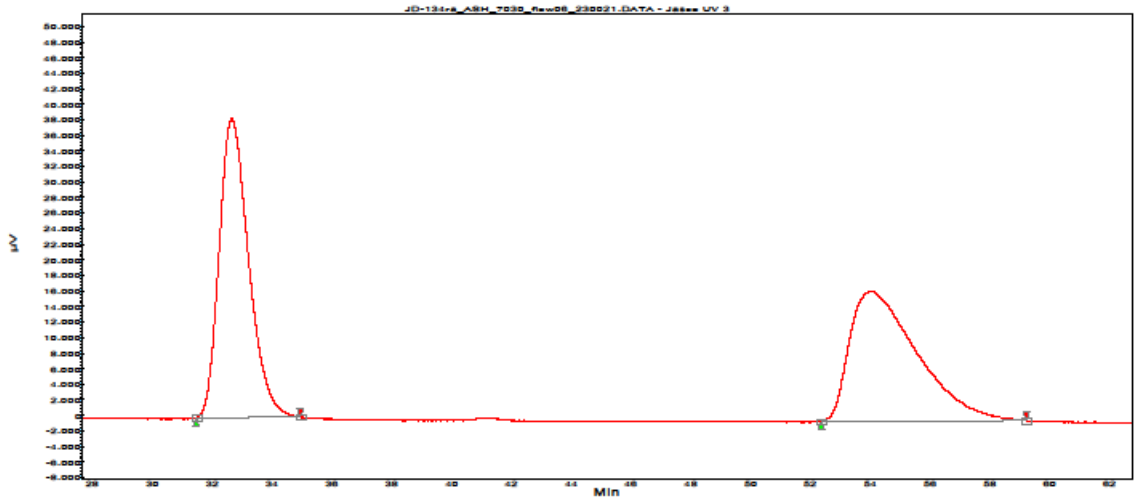
Compound **3d**


O2N
CHO
O
Br
0.91
1.92
2.00
2.00
1.26
0.90
3.11
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)


189.82
168.66
150.71
132.19
131.86
129.69
129.55
128.64
126.71
126.26
119.71
117.29
112.03
79.75
32.42
O2N
CHO
O
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

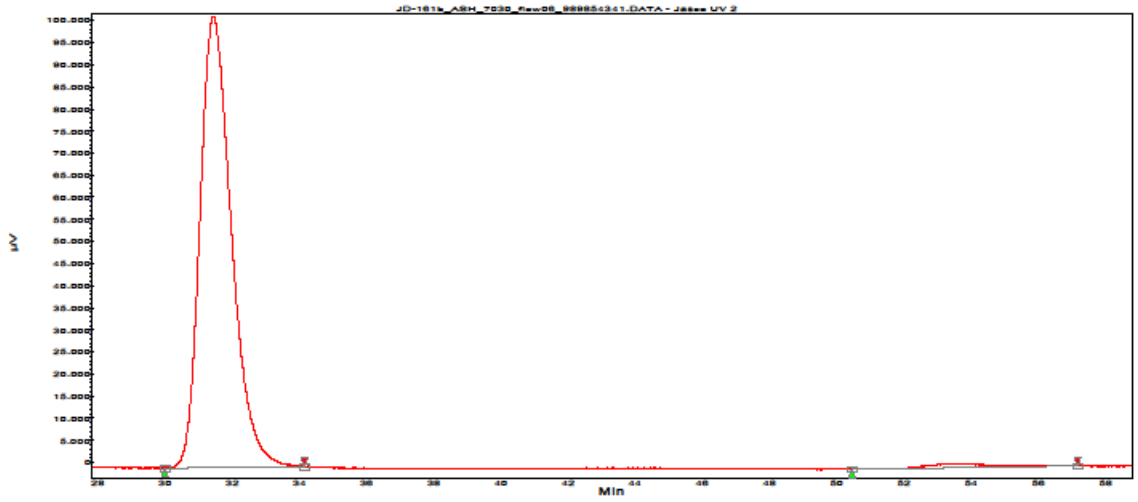
Compound **3d**

Data file: JD-134ra_ASH_7030_flow06_230021.DATA
Method: HPLC1_ASH_7030_flow06_acq_90
Date: 06.08.2010 20:59:21



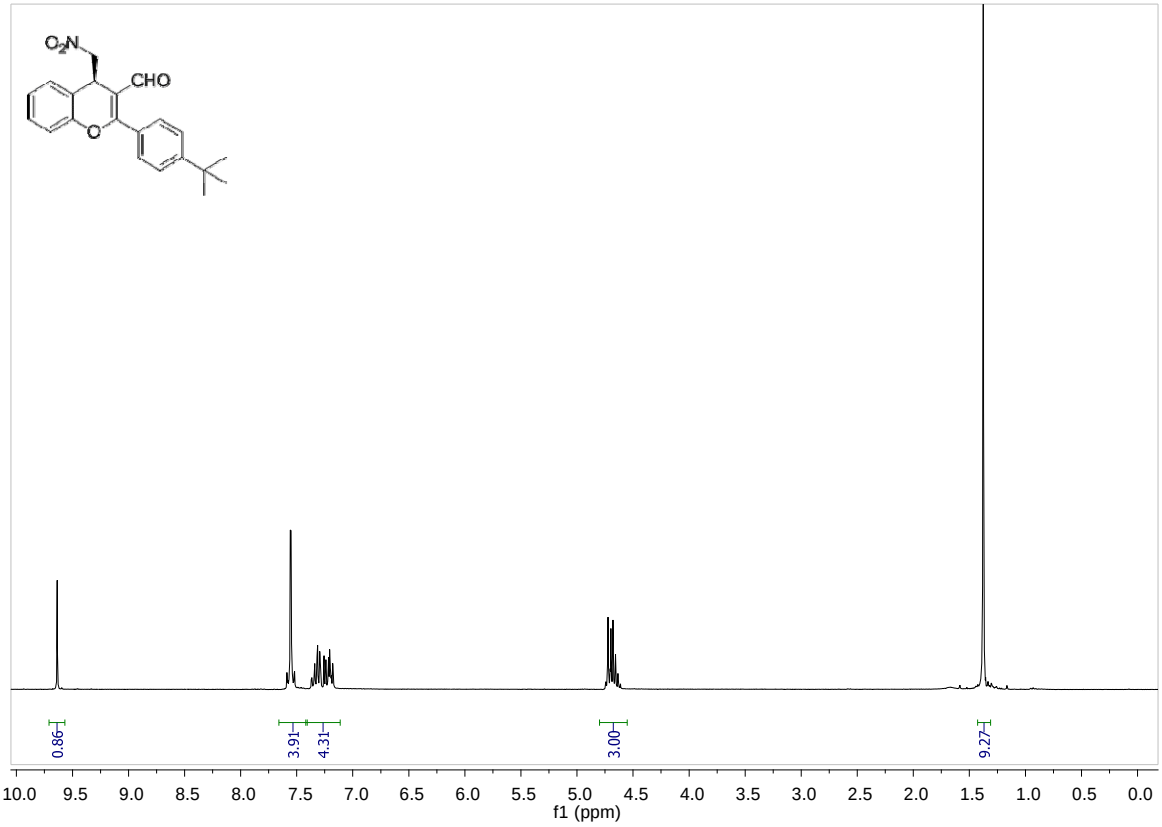
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	31,467	32,658	34,944	0,000	50,15	38434,2	43686,9	50,147
1	UNKNOWN	52,361	54,000	59,205	0,000	49,85	16731,0	43430,2	49,853
Total						100,00	55165,2	87117,0	100,000

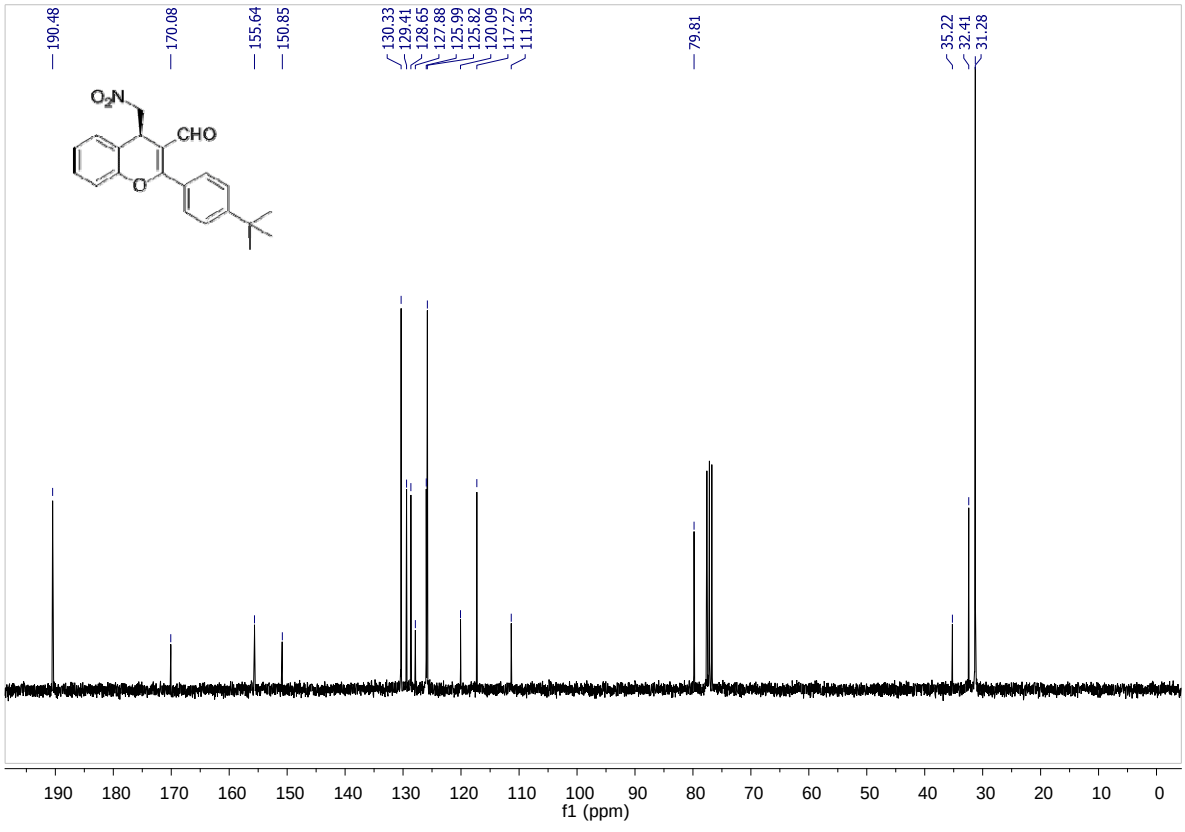
Data file: JD-161b_ASH_7030_flow06_989854341.DATA
Method: HPLC1_ASH_7030_flow06_acq_90
Date: 06.08.2010 15:31:37



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	30,003	31,442	34,157	98,370
2	50,450	53,450	57,156	1,630
Total				100,000

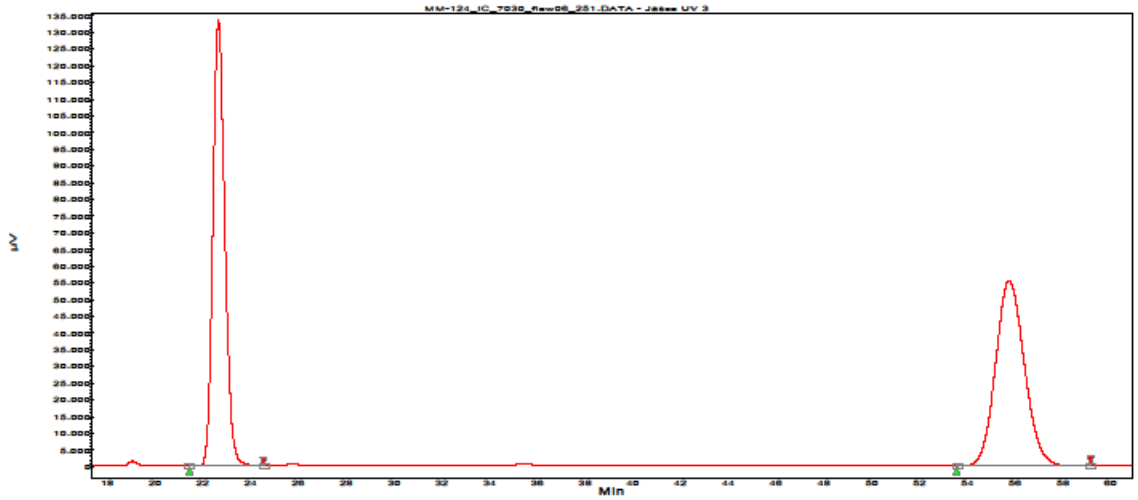
Compound **3e**


O2N
CHO
O
0.86
3.91
4.31
3.00
9.27
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.48
170.08
155.64
150.85
130.33
129.41
128.65
127.88
125.99
125.82
120.09
117.27
111.35
79.81
35.22
32.41
31.28
O2N
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

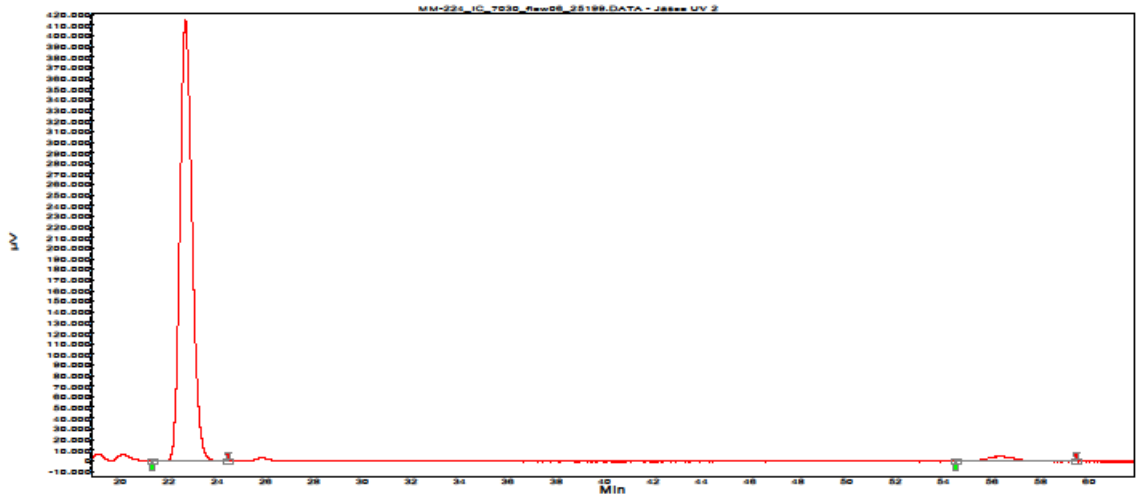
Compound **3e**

Data file: MM-124_IC_7030_flow06_251.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 28.08.2010 15:32:27



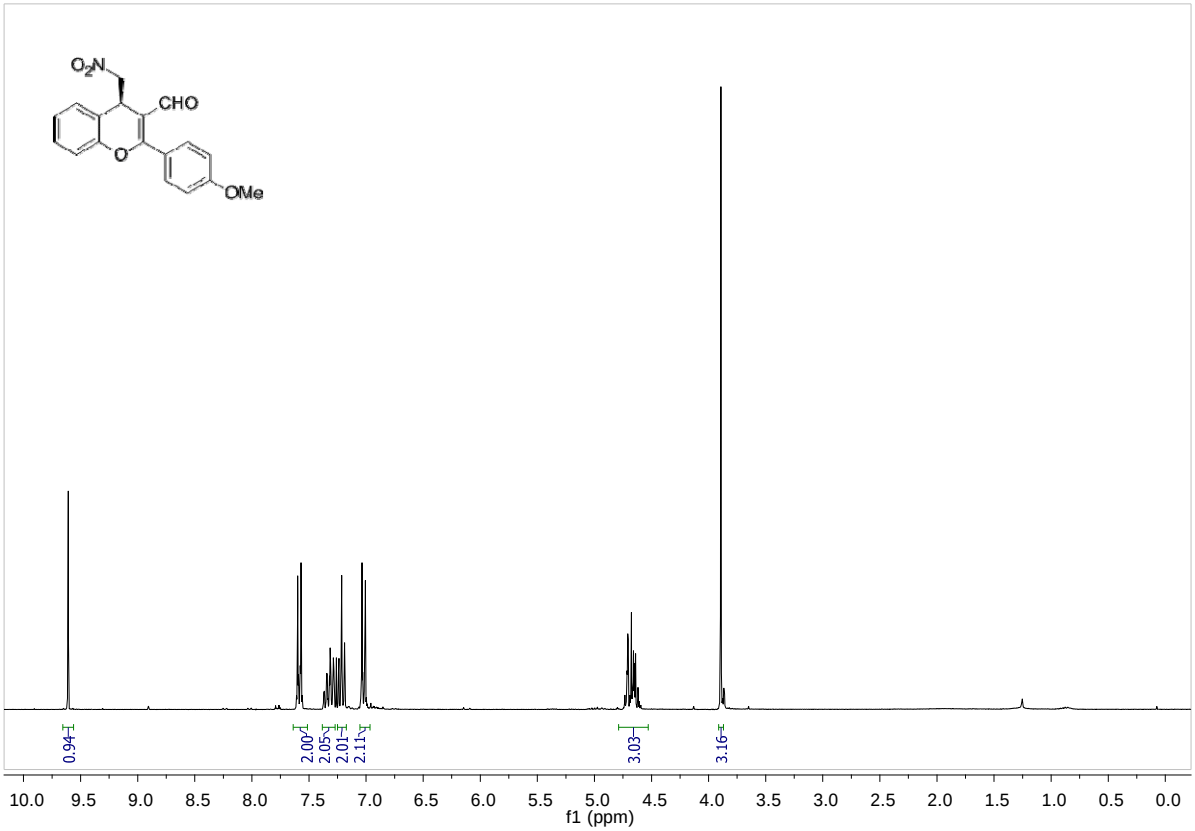
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	21,456	22,658	24,555	0,000	50,13	133395,1	77389,2	50,129
1	UNKNOWN	53,529	55,733	59,144	0,000	49,87	55439,1	76991,5	49,871
Total						100,00	188834,2	154380,7	100,000

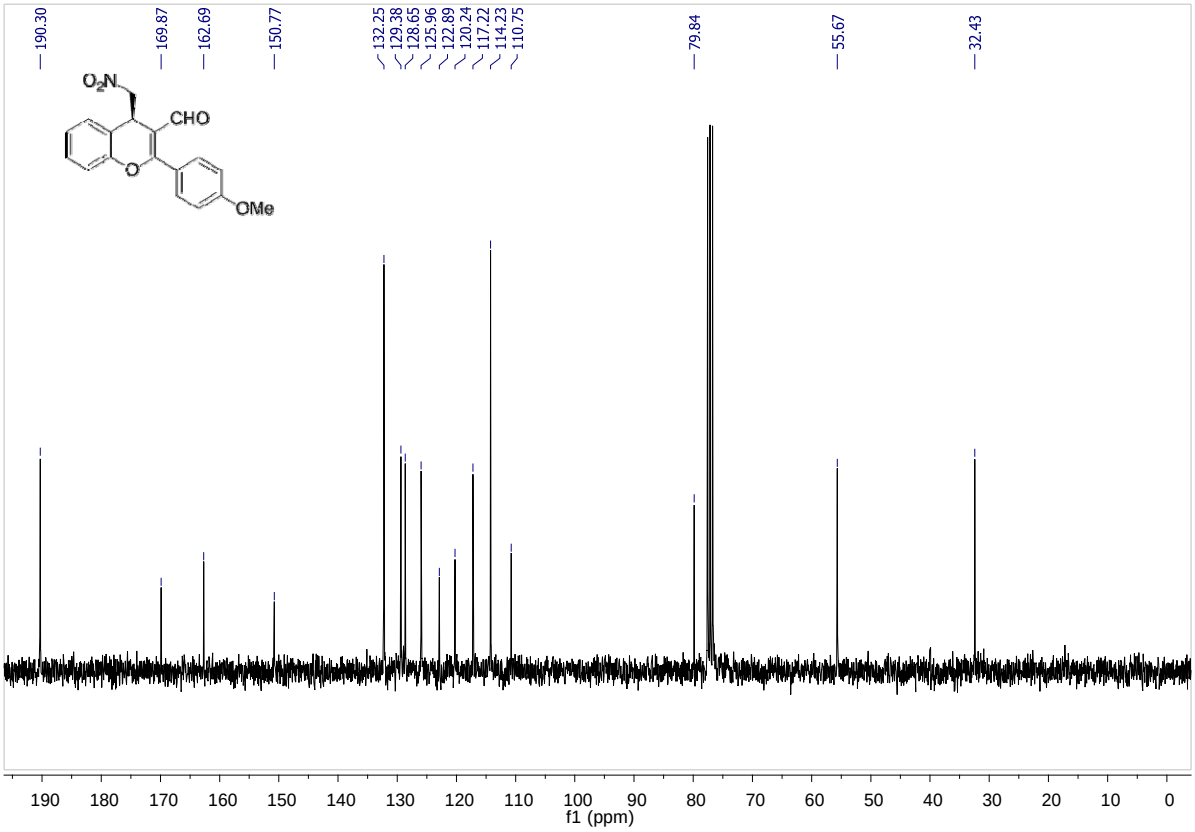
Data file: MM-224_IC_7030_flow06_25199.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 30.08.2010 17:30:25



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	21,319	22,692	24,452	97,449
2	54,480	56,292	59,441	2,551
Total				100,000

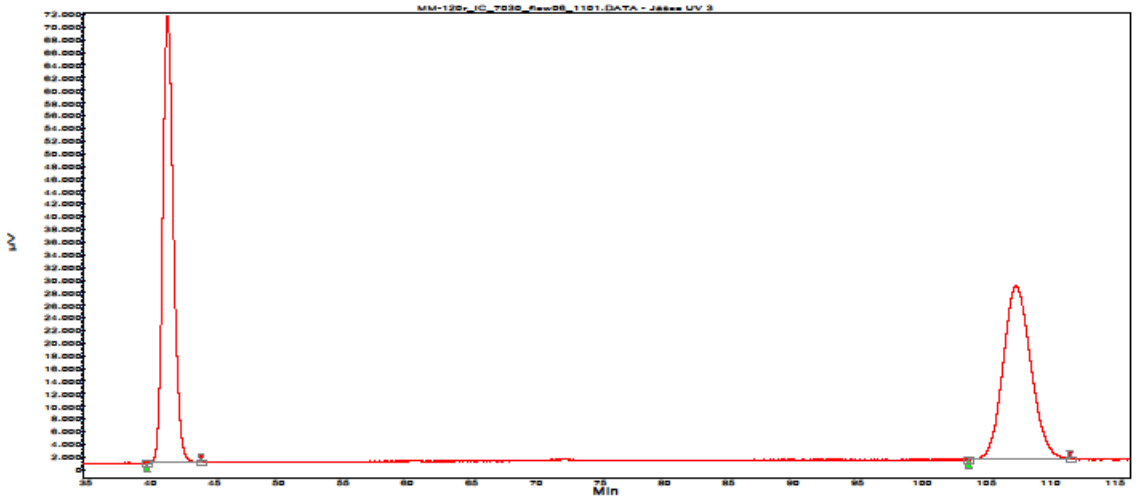
Compound **3f**


O2N
CHO
O
OMe
0.94
2.00
2.05
2.01
2.11
3.03
3.16
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.30
169.87
162.69
150.77
132.25
129.38
128.65
125.96
122.89
120.24
117.22
114.23
110.75
79.84
55.67
32.43
O2N
CHO
O
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

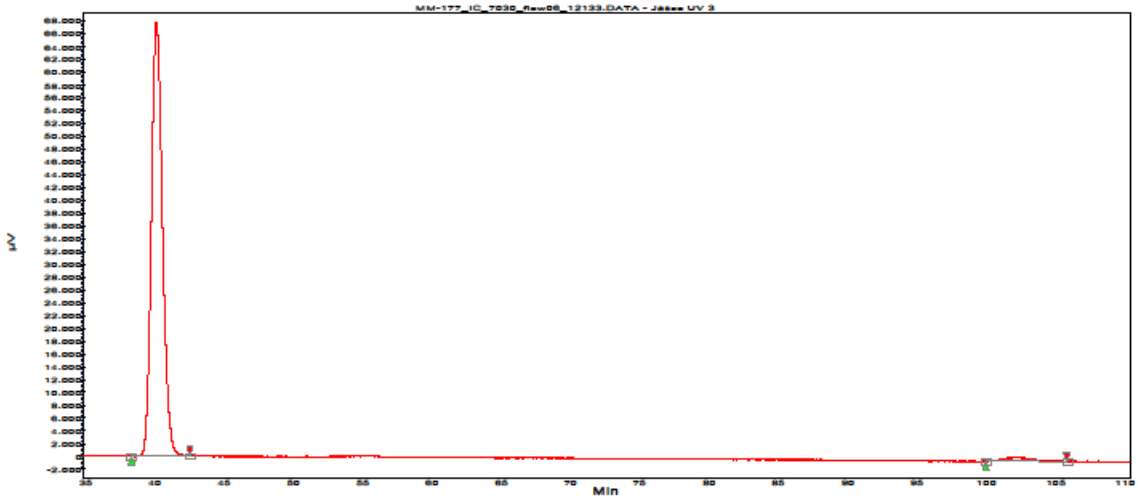
Compound **3f**

Data file: MM-120r_IC_7030_flow06_1101.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 12.08.2010 02:52:33



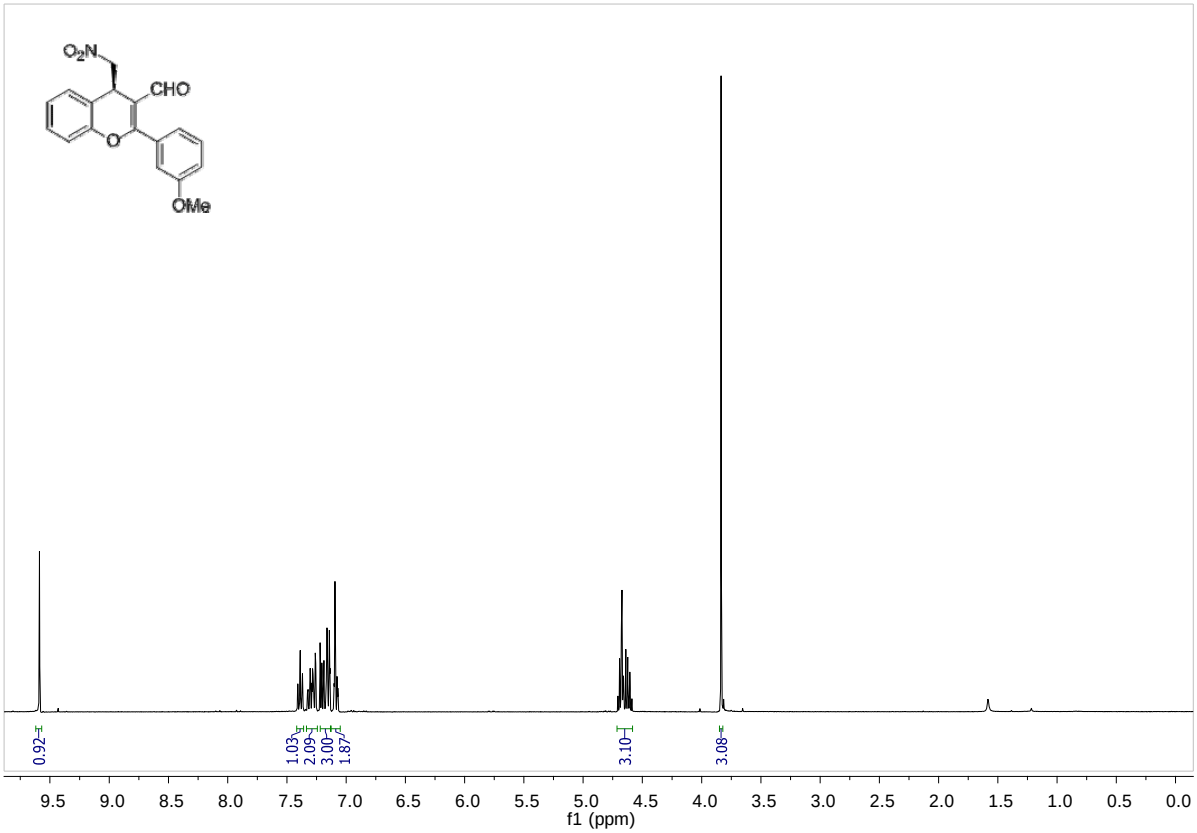
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	39,742	41,358	43,943	0,000	49,94	70679,0	68579,0	49,942
2	UNKNOWN	103,590	107,258	111,487	0,000	50,06	27411,3	68739,4	50,058
Total						100,00	98090,3	137318,4	100,000

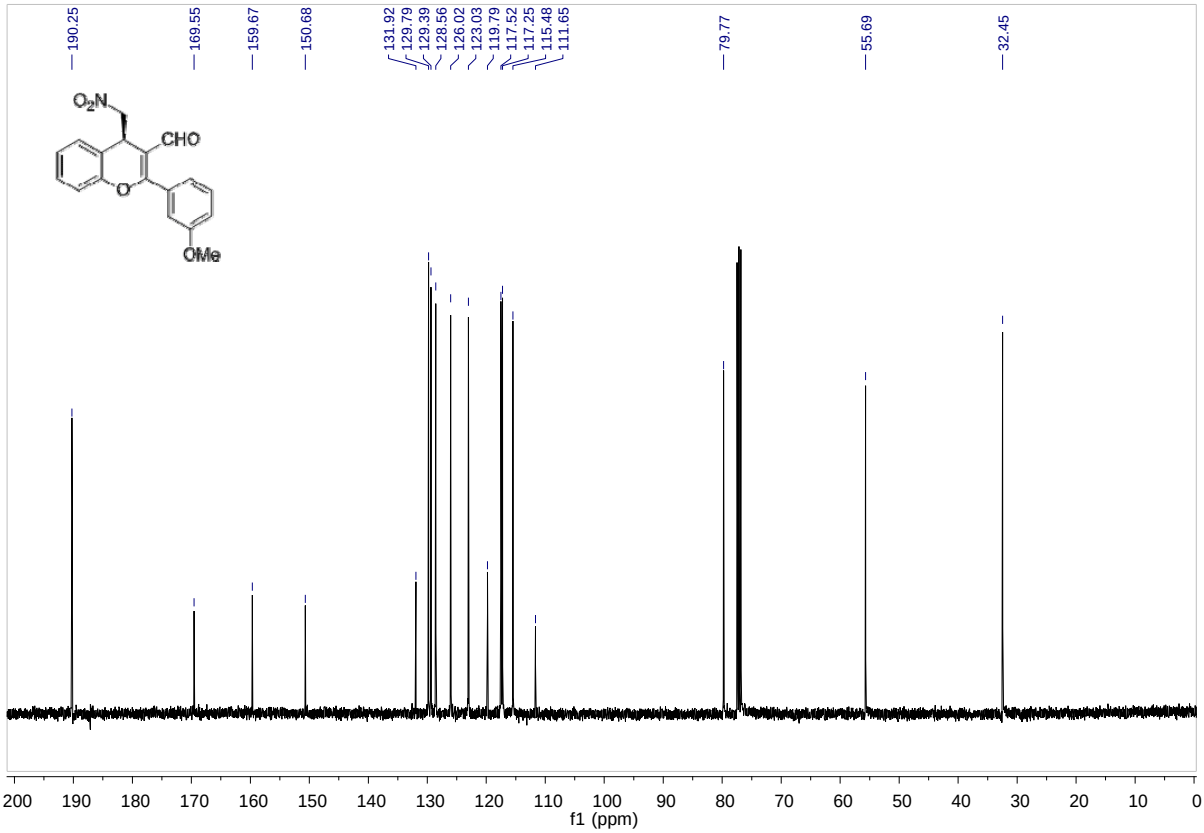
Data file: MM-177_IC_7030_flow06_12133.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 10.08.2010 20:19:57



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	38,314	40,117	42,527	0,000	97,84	67733,4	62756,6	97,840
2	UNKNOWN	99,936	102,433	105,789	0,000	2,16	583,0	1385,4	2,160
Total						100,00	68316,4	64142,0	100,000

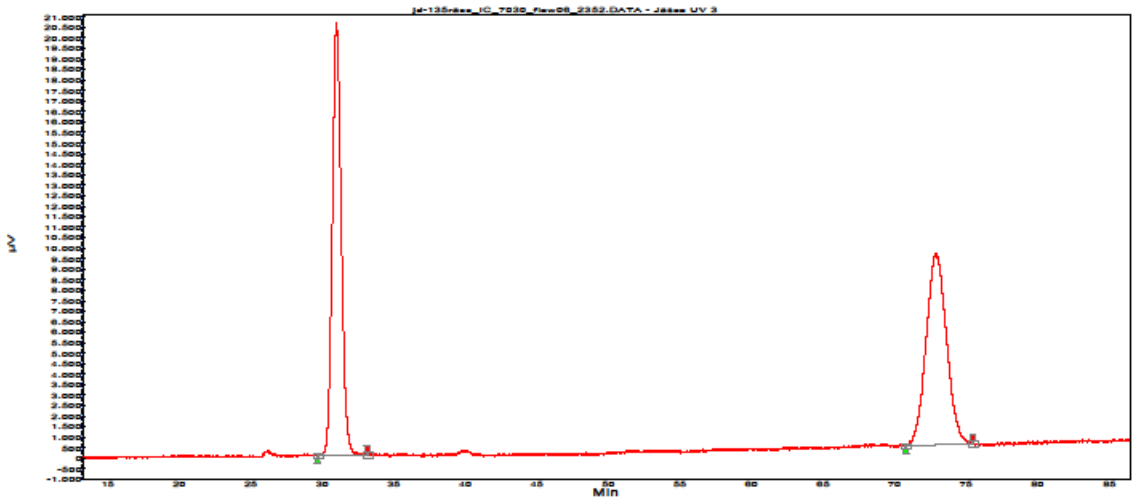
Compound **3g**


O2N
CHO
O
OMe
0.92
1.03
2.09
3.00
1.87
3.10
3.08
9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.25
169.55
159.67
150.68
131.92
129.79
129.39
128.56
126.02
123.03
119.79
117.52
117.25
115.48
111.65
79.77
55.69
32.45
O2N
CHO
O
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

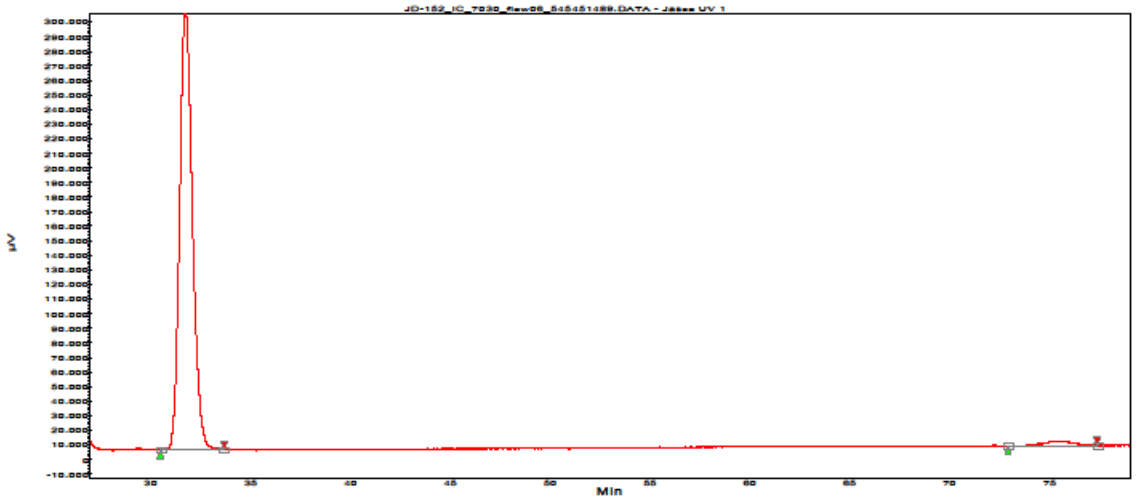
Compound **3g**

Data file: jd-135racc_IC_7030_flow06_2352.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 28.07.2010 12:50:55



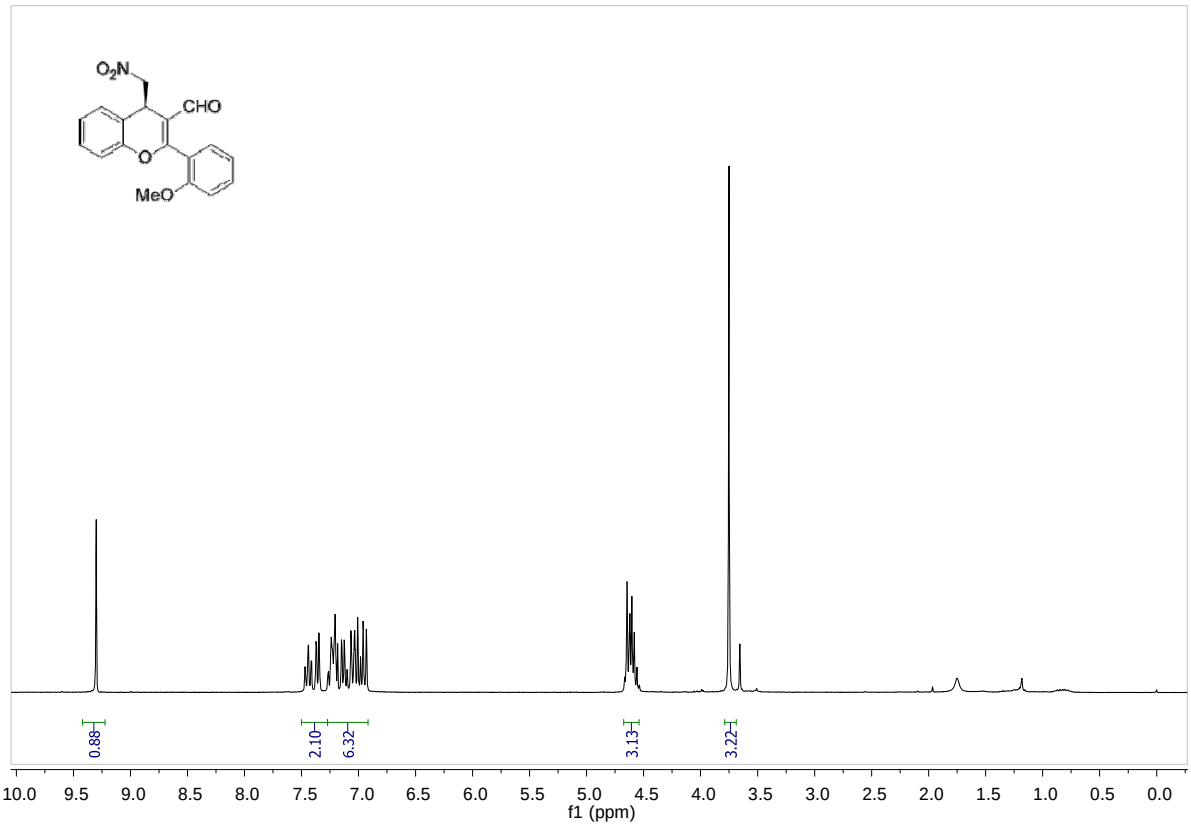
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	29,678	30,992	33,150	0,000	49,86	20557,9	14922,3	49,857
1	UNKNOWN	70,747	72,867	75,427	0,000	50,14	9095,8	15008,1	50,143
Total						100,00	29653,7	29930,4	100,000

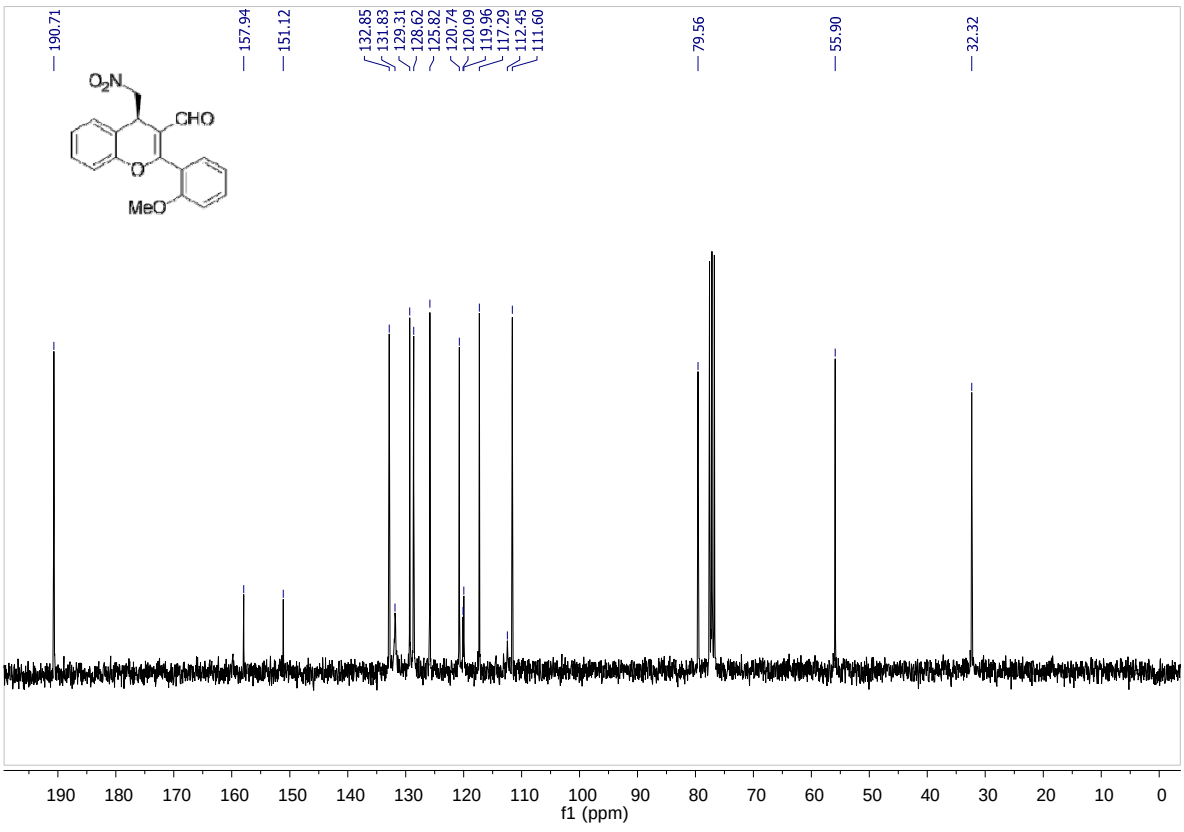
Data file: JD-152_IC_7030_flow06_545451489.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 28.07.2010 09:53:59



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	30,509	31,750	33,679	97,860
2	72,900	75,442	77,359	2,140
Total				100,000

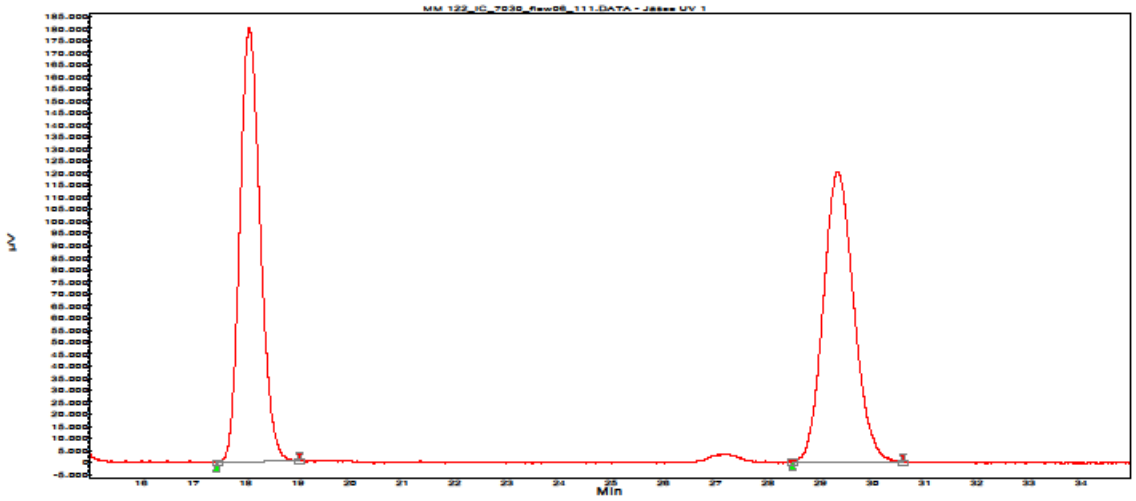
Compound **3h**


O2N
CHO
O
MeO
0.88
2.10
6.32
3.13
3.22
f1 (ppm)


190.71
157.94
151.12
132.85
131.83
129.31
128.62
125.82
120.74
120.09
119.96
117.29
112.45
111.60
79.56
55.90
32.32
O2N
CHO
O
MeO
f1 (ppm)

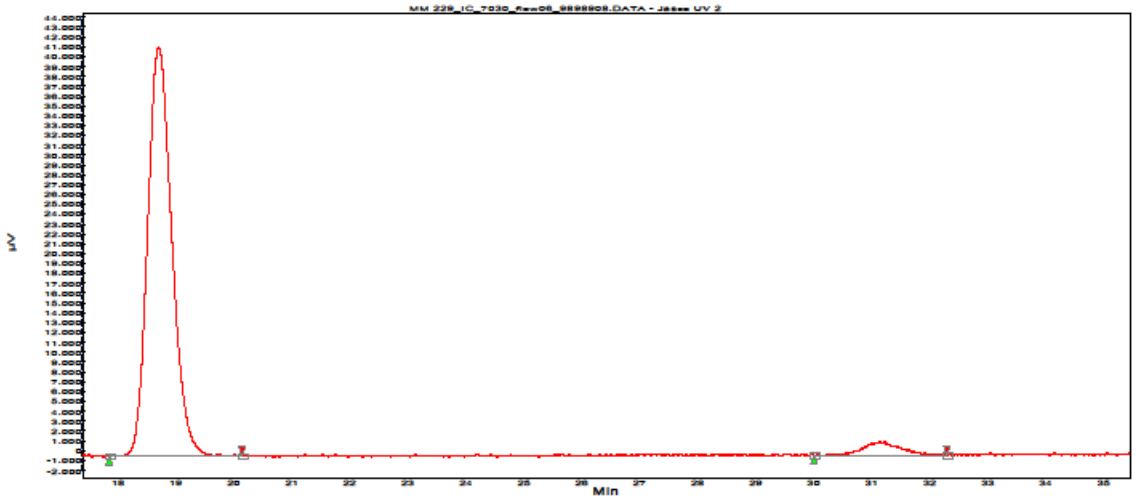
Compound **3h**

Data file: MM 122_IC_7030_flow06_111.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 11.08.2010 00:25:17



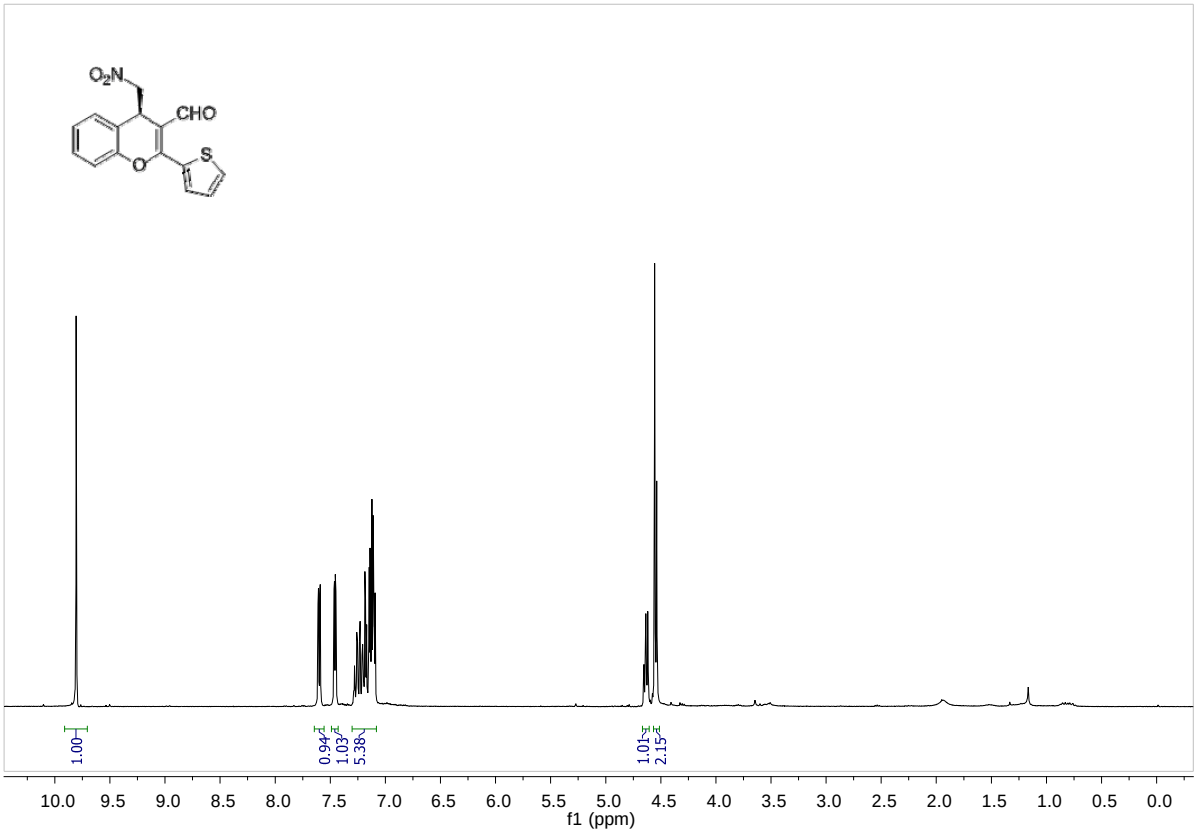
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	17,445	18,067	19,028	49,936
1	28,463	29,342	30,580	50,064
Total				100,000

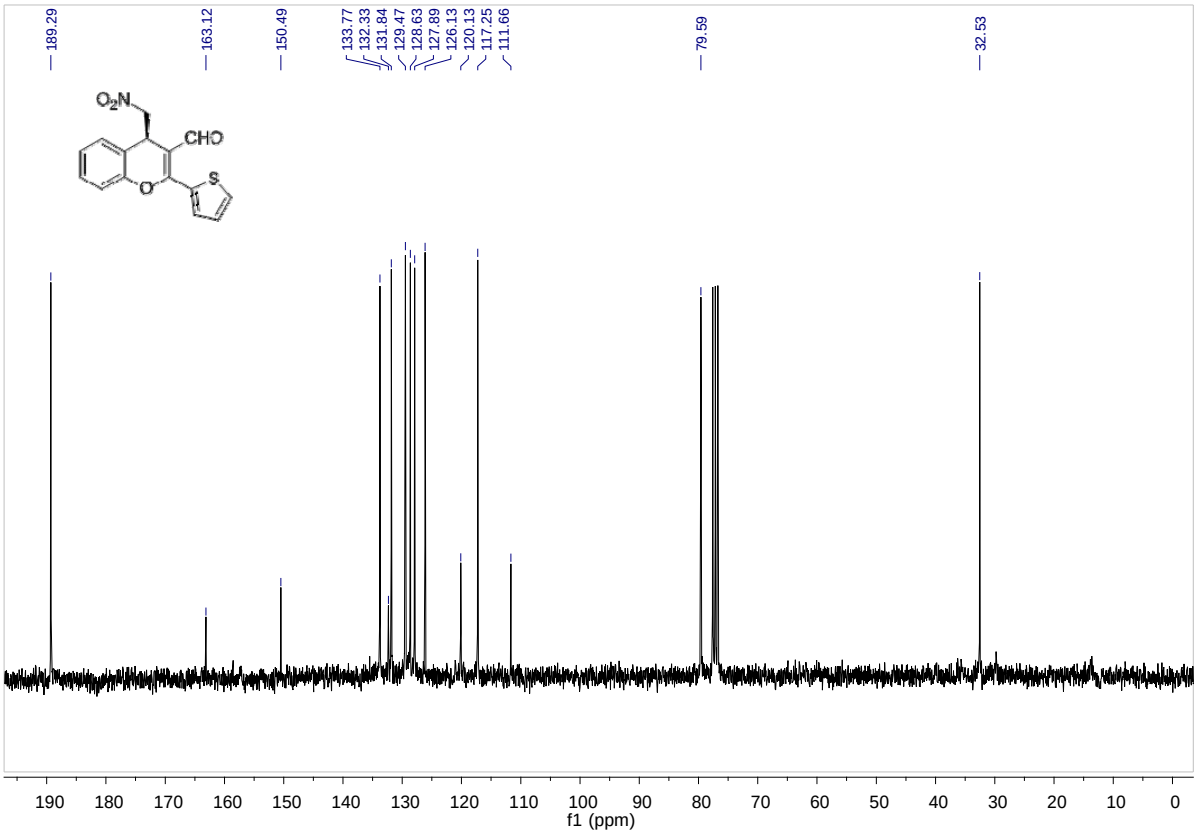
Data file: MM 229_IC_7030_flow06_9898908.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 30.08.2010 18:47:16



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17,854	18,708	20,145	95,361
2	29,996	31,217	32,287	4,639
Total				100,000

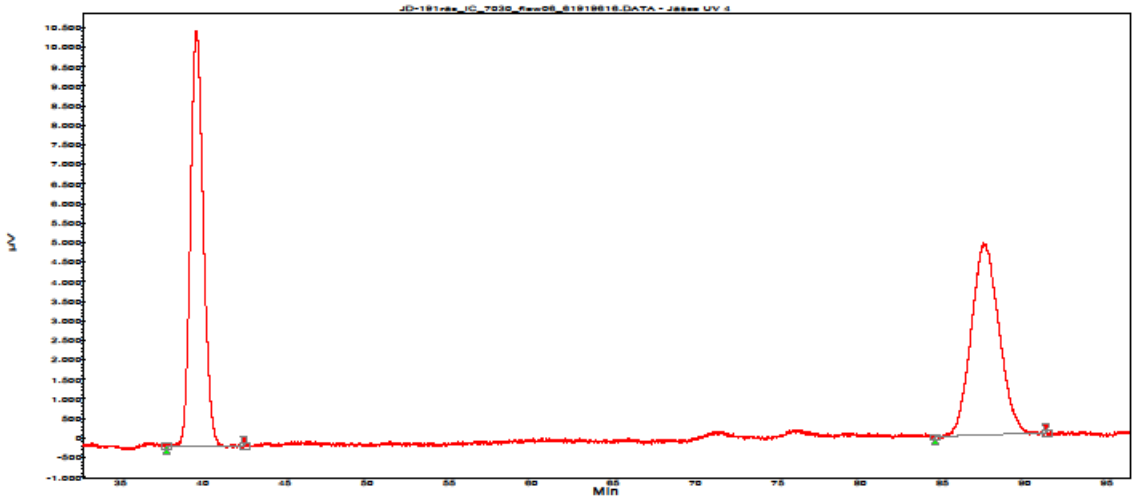
Compound **3i**


O2N
CHO
O
S
1.00
0.94
1.03
5.38
1.01
2.15
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


189.29
163.12
150.49
133.77
132.33
131.84
129.47
128.63
127.89
126.13
120.13
117.25
111.66
79.59
32.53
O2N
CHO
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

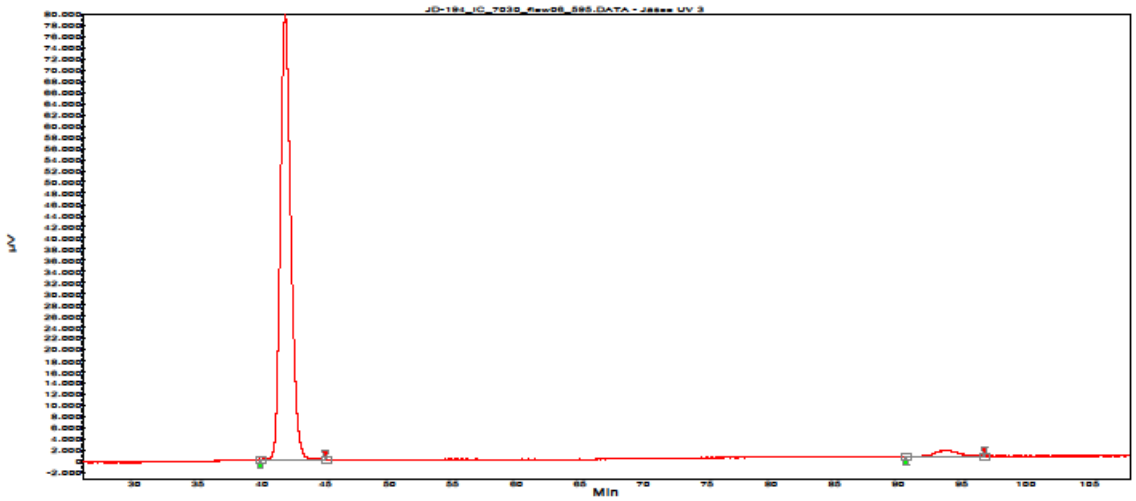
Compound **3i**

Data file: JD-191rac_IC_7030_flow06_61919616.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 26.08.2010 14:36:27



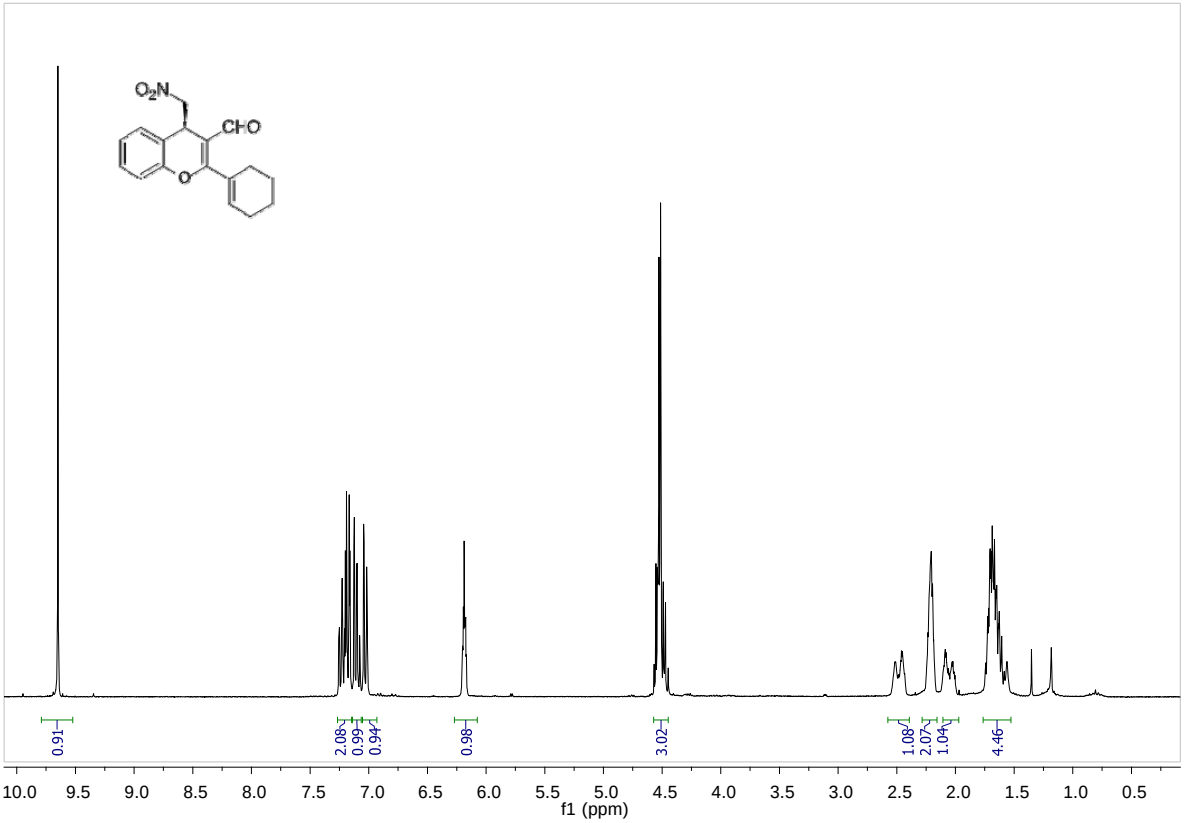
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	37,789	39,625	42,523	0,000	50,09	10591,5	9579,6	50,093
1	UNKNOWN	84,530	87,508	91,302	0,000	49,91	4905,0	9544,2	49,907
Total						100,00	15496,5	19123,8	100,000

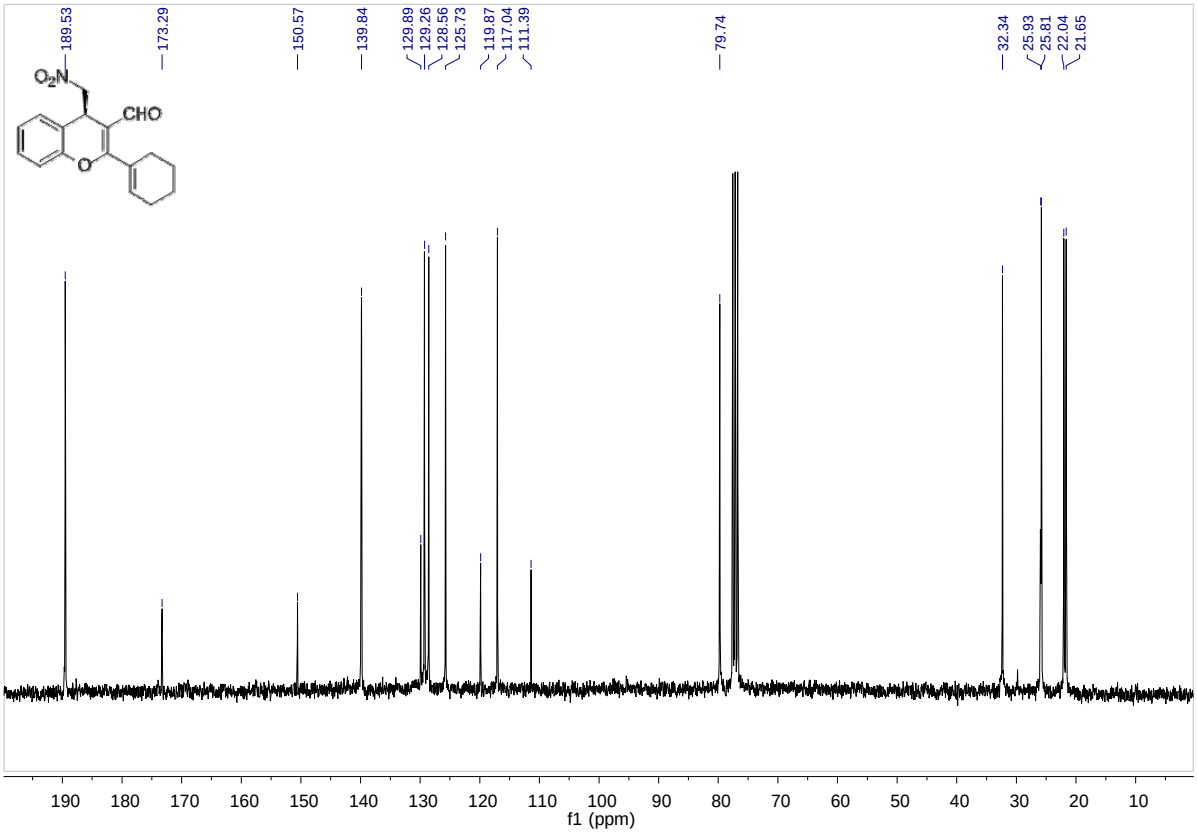
Data file: JD-194_IC_7030_flow06_595.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 31.08.2010 18:04:03



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	39,886	41,833	45,000	0,000	97,25	79537,9	75955,6	97,249
2	UNKNOWN	90,568	93,742	96,705	0,000	2,75	1065,7	2148,6	2,751
Total						100,00	80603,6	78104,3	100,000

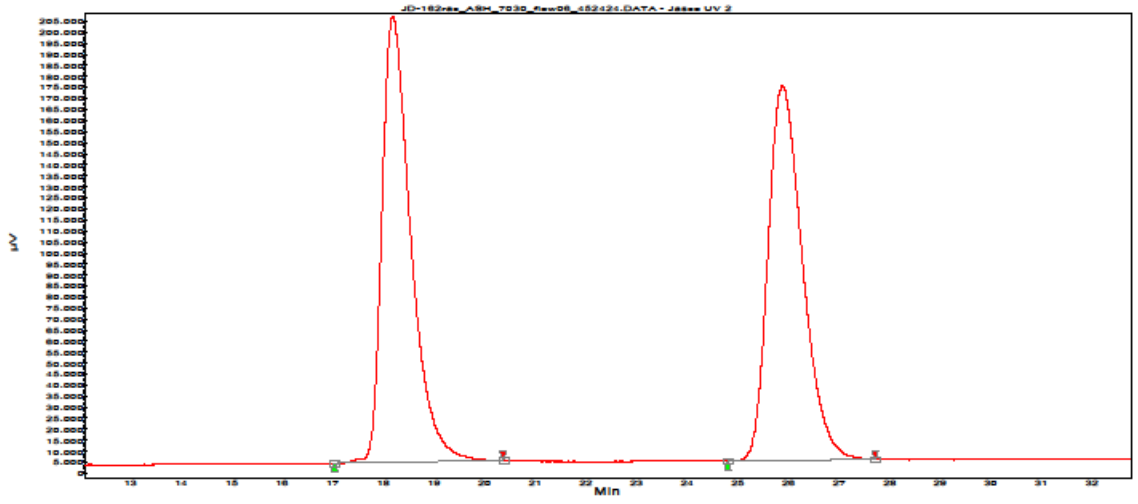
Compound **3j**


O2N
CHO
O
0.91
2.08
0.99
0.94
0.98
3.02
1.08
2.07
1.04
4.46
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)


189.53
173.29
150.57
139.84
129.89
129.26
128.56
125.73
119.87
117.04
111.39
79.74
32.34
25.93
25.81
22.04
21.65
O2N
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

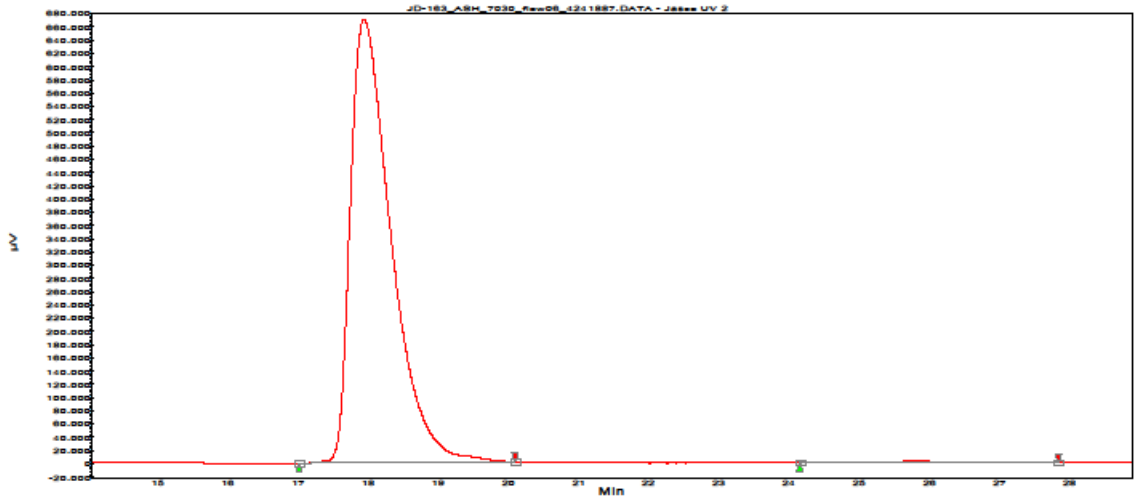
Compound **3j**

Data file: JD-162rac_ASH_7030_flow06_452424.DATA
Method: HPLC1_ASH_7030_flow06_acq_60
Date: 04.08.2010 17:43:57



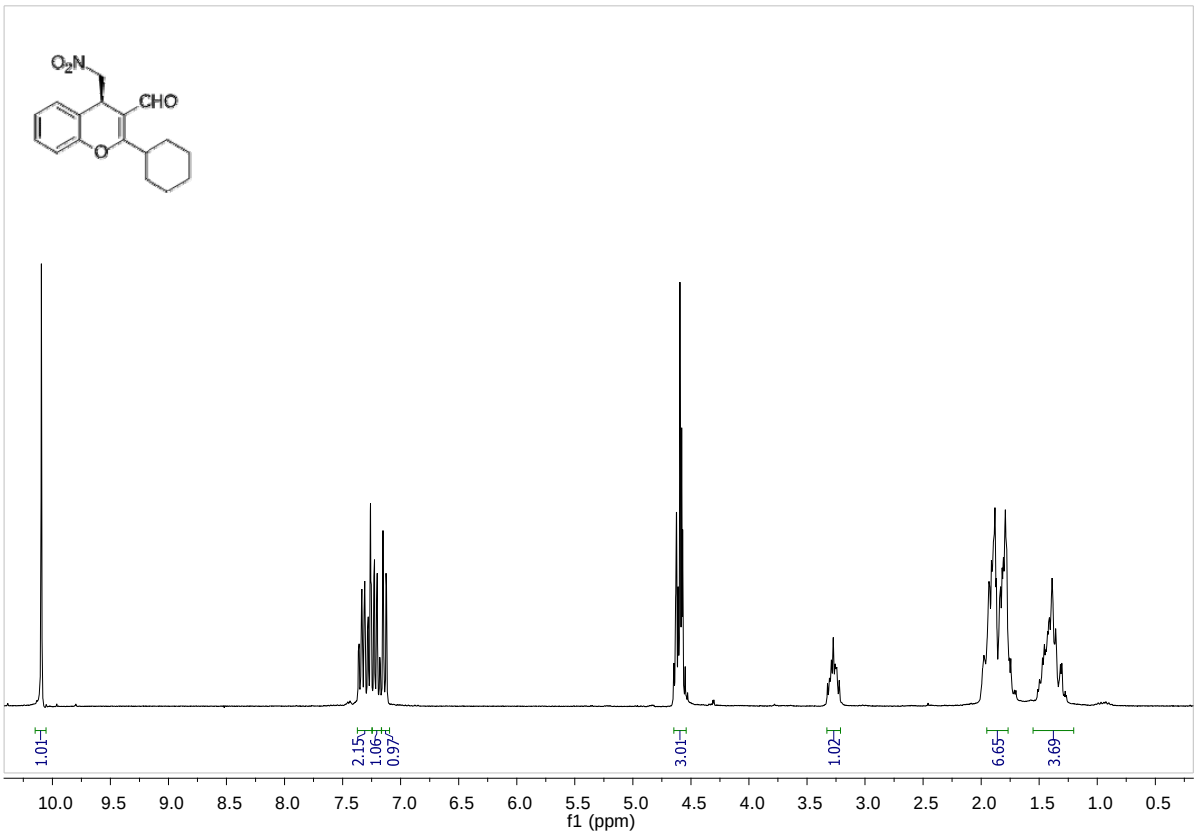
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	17,034	18,183	20,360	49,932
1	24,793	25,883	27,707	50,068
Total				100,000

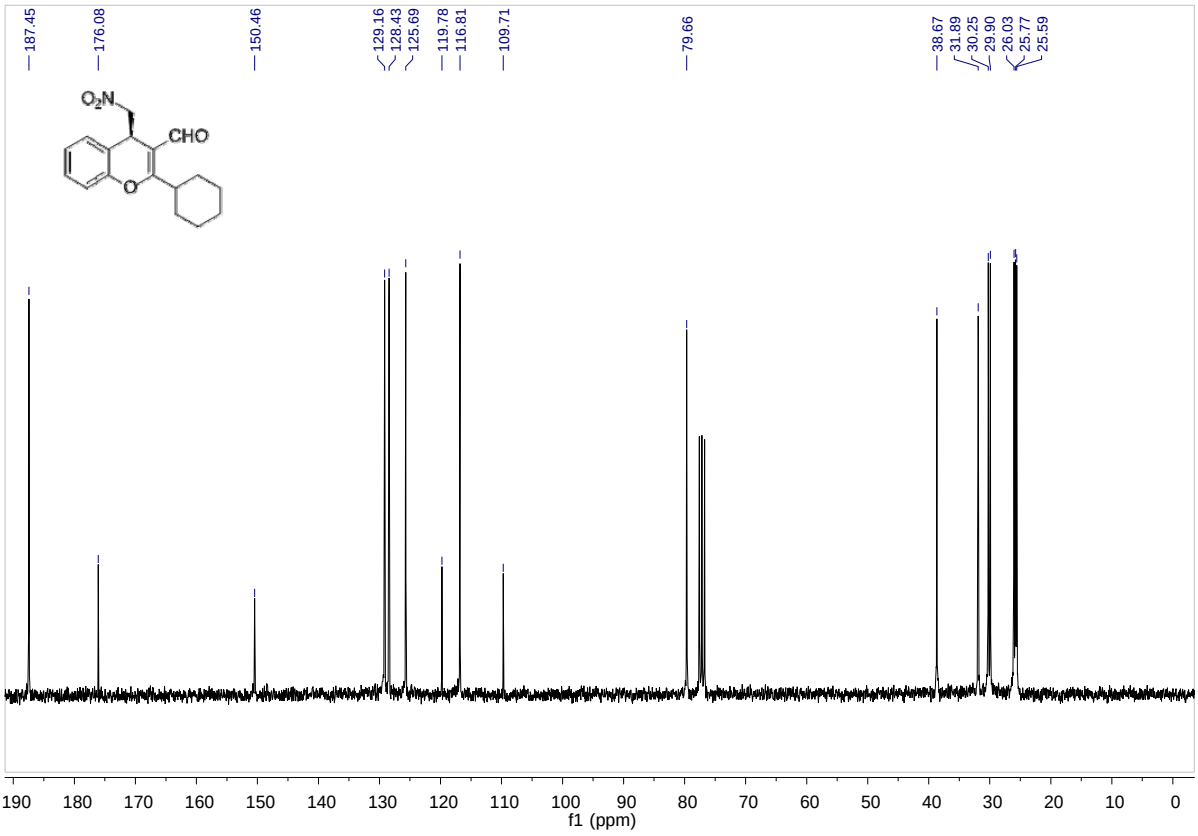
Data file: JD-163_ASH_7030_flow06_4241887.DATA
Method: HPLC1_ASH_7030_flow06_acq_60
Date: 05.08.2010 10:27:40



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17,018	17,942	20,093	99,553
2	24,148	25,783	27,836	0,447
Total				100,000

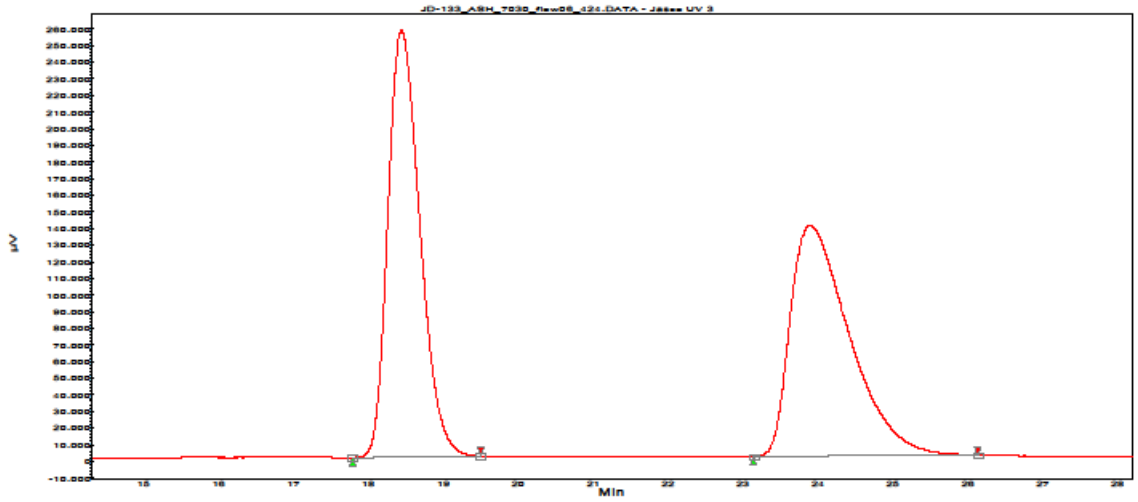
Compound **3k**


O2N
CHO
O
1.01
2.15
1.06
0.97
3.01
1.02
6.65
3.69
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)


187.45
176.08
150.46
129.16
128.43
125.69
119.78
116.81
109.71
79.66
38.67
31.89
30.25
29.90
26.03
25.77
25.59
O2N
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

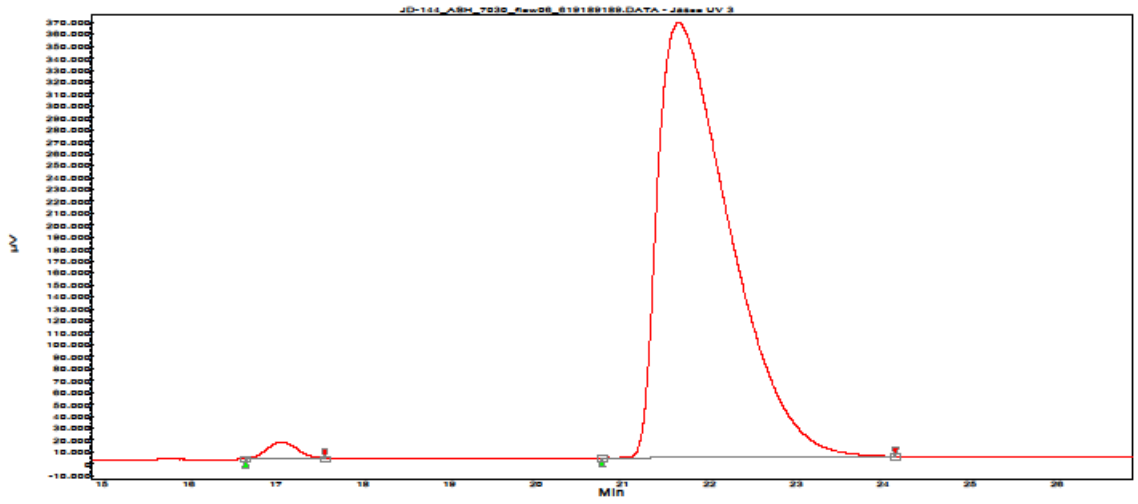
Compound **3k**

Data file: JD-133_ASH_7030_flow06_424.DATA
Method: HPLC1_ASH_7030_flow06_acq_50
Date: 19.07.2010 09:48:06



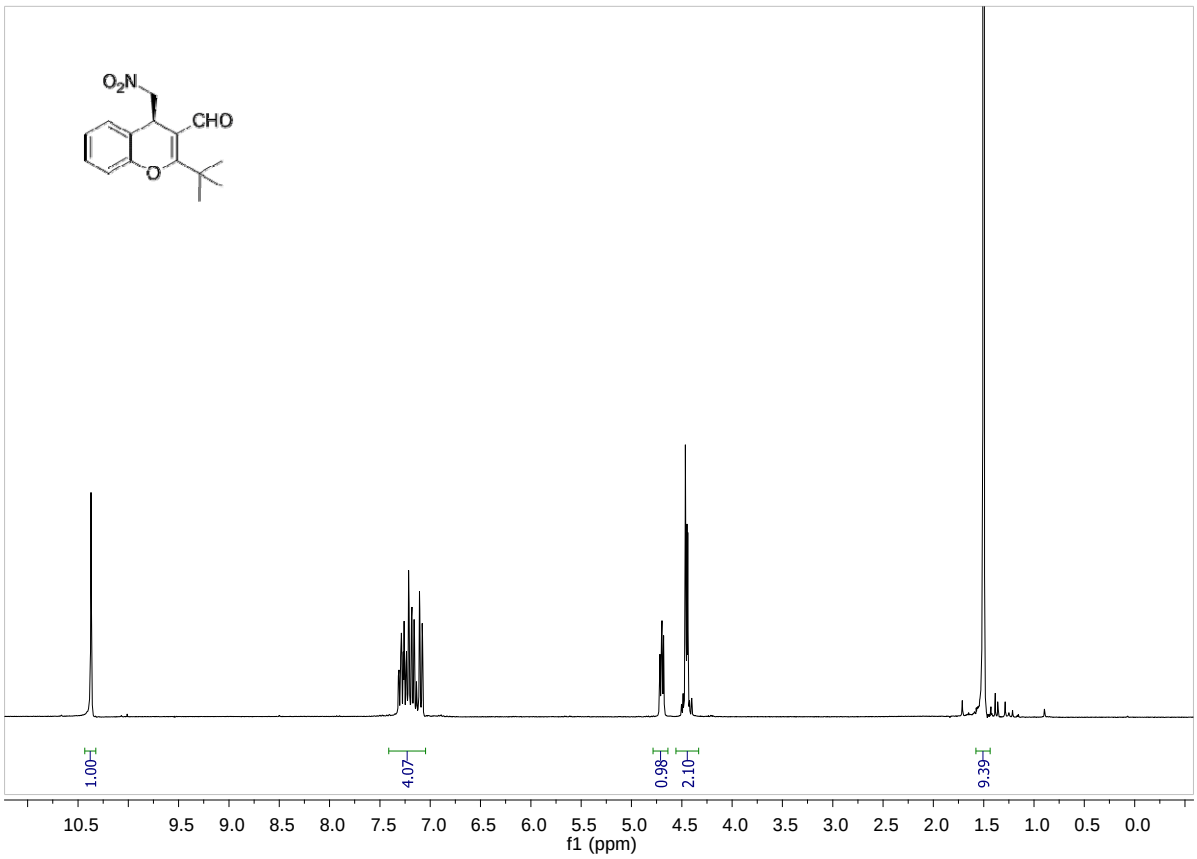
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	17,793	18,442	19,498	0,000	50,08	256407,5	126812,1	50,075
2	UNKNOWN	23,137	23,900	26,131	0,000	49,92	138472,1	126432,0	49,925
Total						100,00	394879,6	253244,1	100,000

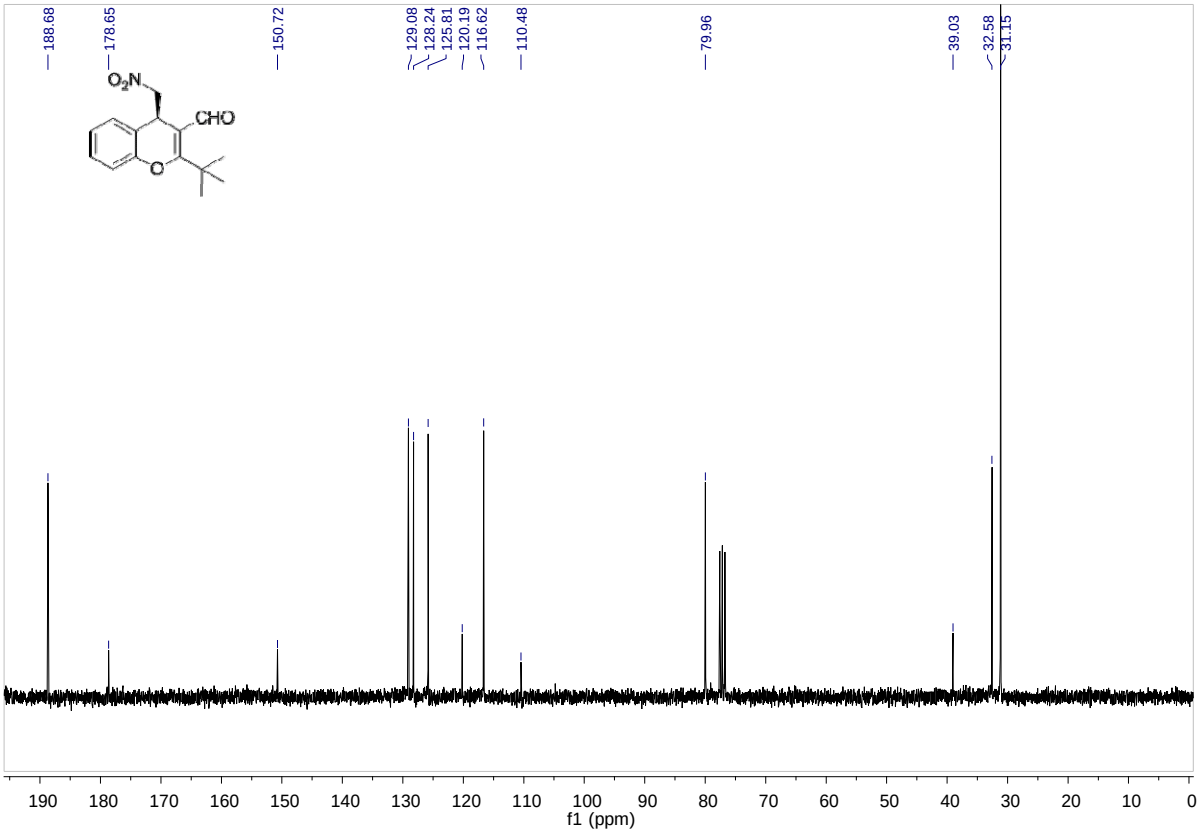
Data file: JD-144_ASH_7030_flow06_619189189.DATA
Method: HPLC1_ASH_7030_flow06_acq_50
Date: 22.07.2010 17:19:07



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	16,653	17,067	17,568	0,000	1,62	14119,9	5742,7	1,623
1	UNKNOWN	20,758	21,642	24,134	0,000	98,38	364178,3	348106,8	98,377
Total						100,00	378298,1	353849,5	100,000

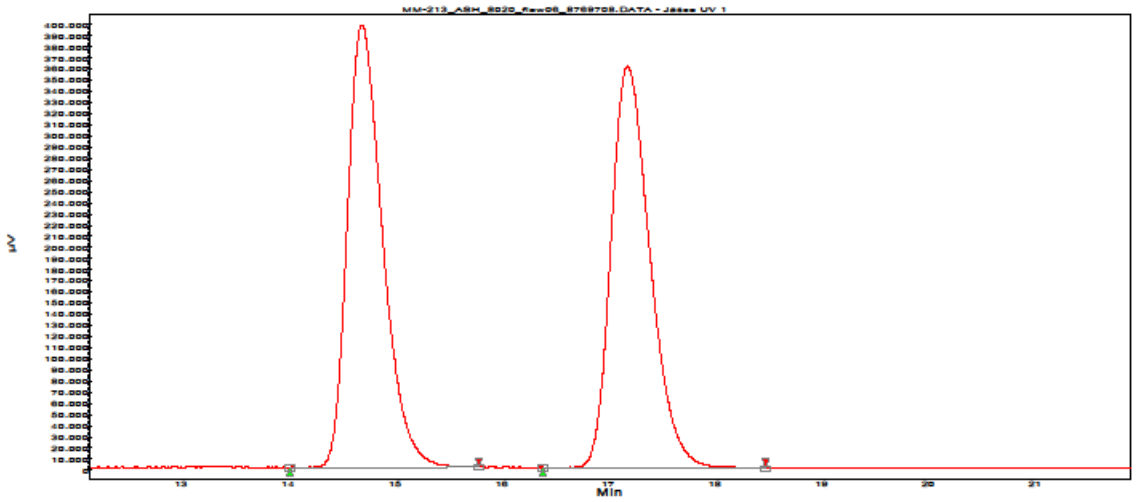
Compound **3l**


O2N
CHO
O
1.00
4.07
0.98
2.10
9.39
10.5
9.5
9.0
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


188.68
178.65
150.72
129.08
128.24
125.81
120.19
116.62
110.48
79.96
39.03
32.58
31.15
O2N
CHO
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

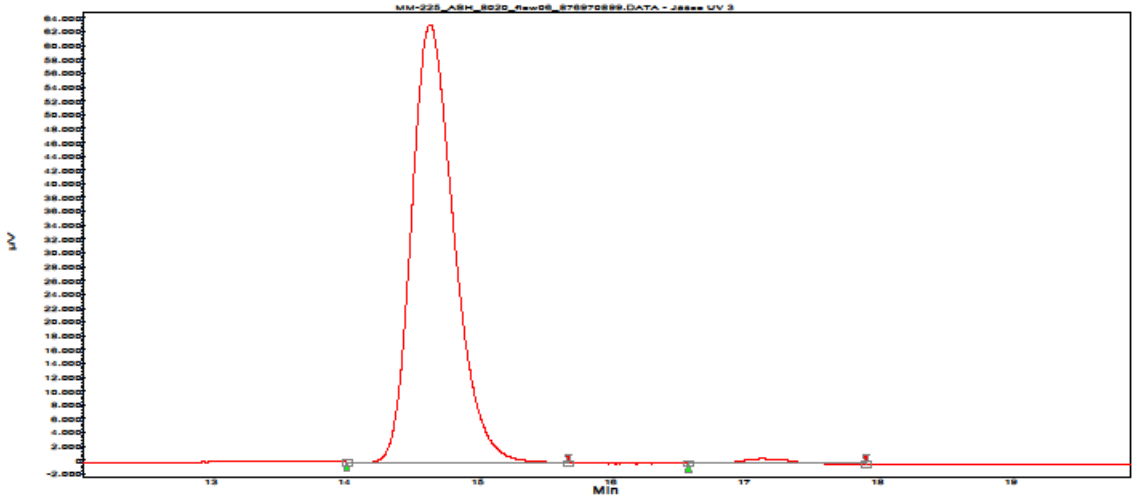
Compound **3l**

Data file: MM-213_ASH_8020_flow06_8769708.DATA
Method: HPLC1_ASH_8020_flow06_acq_60
Date: 28.08.2010 13:57:08



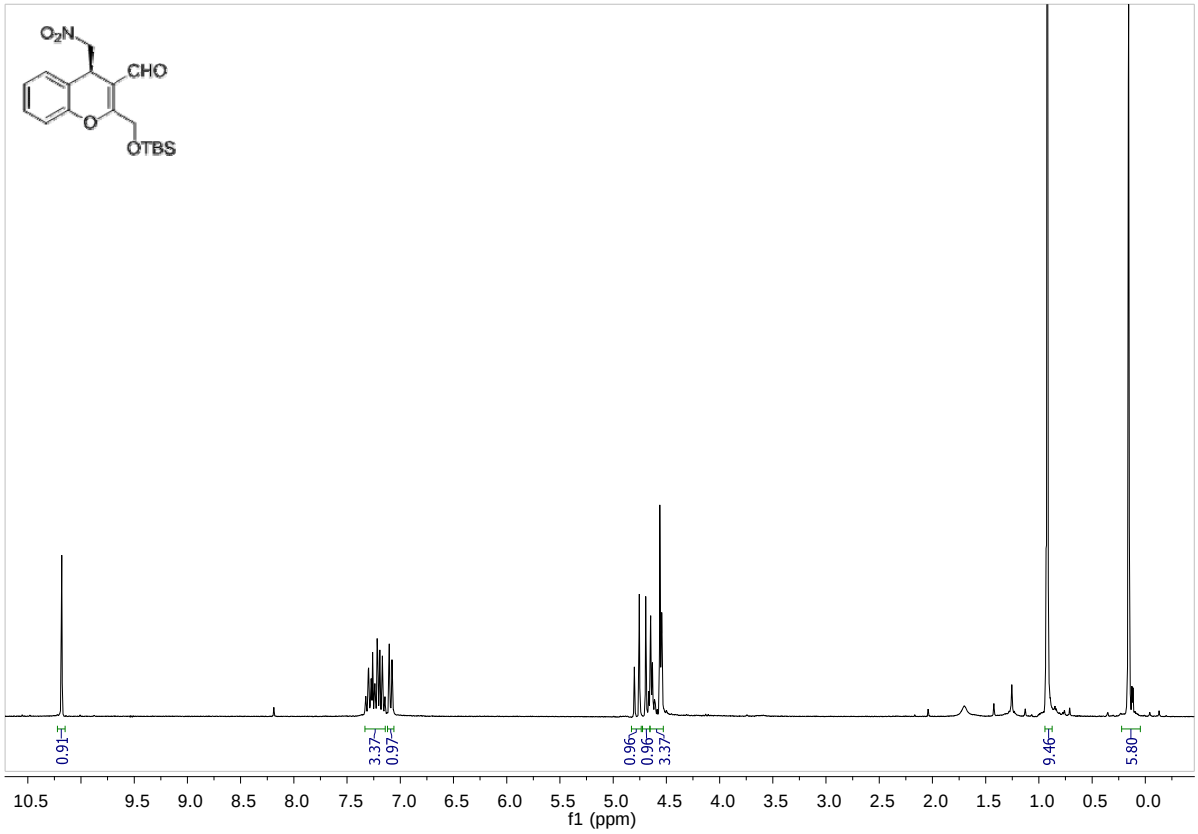
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	14,019	14,692	15,788	49,941
2	16,391	17,183	18,472	50,059
Total				100,000

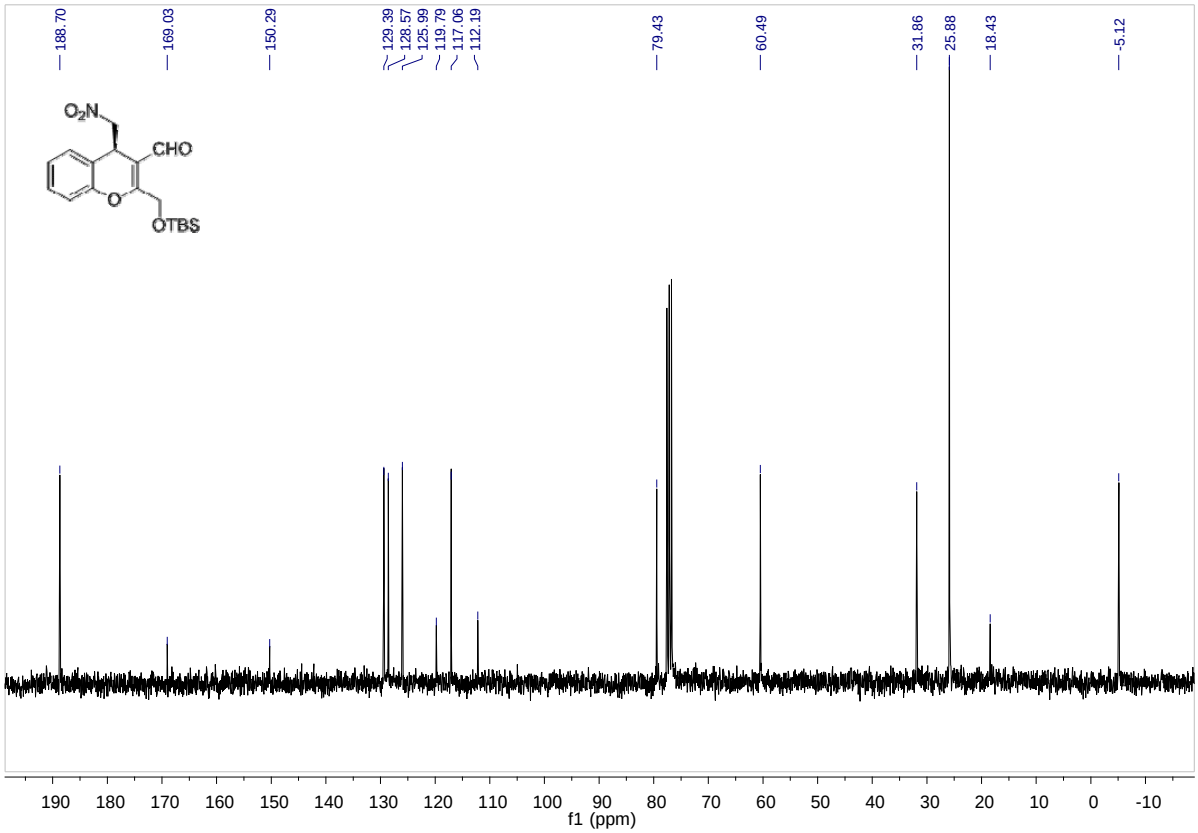
Data file: MM-225_ASH_8020_flow06_876970899.DATA
Method: HPLC1_ASH_8020_flow06_acq_60
Date: 30.08.2010 15:55:18



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	14,018	14,642	15,680	0,000	98,95	63338,6	23305,6	98,949
2	UNKNOWN	16,579	17,133	17,909	0,000	1,05	679,7	247,6	1,051
Total						100,00	64018,3	23553,2	100,000

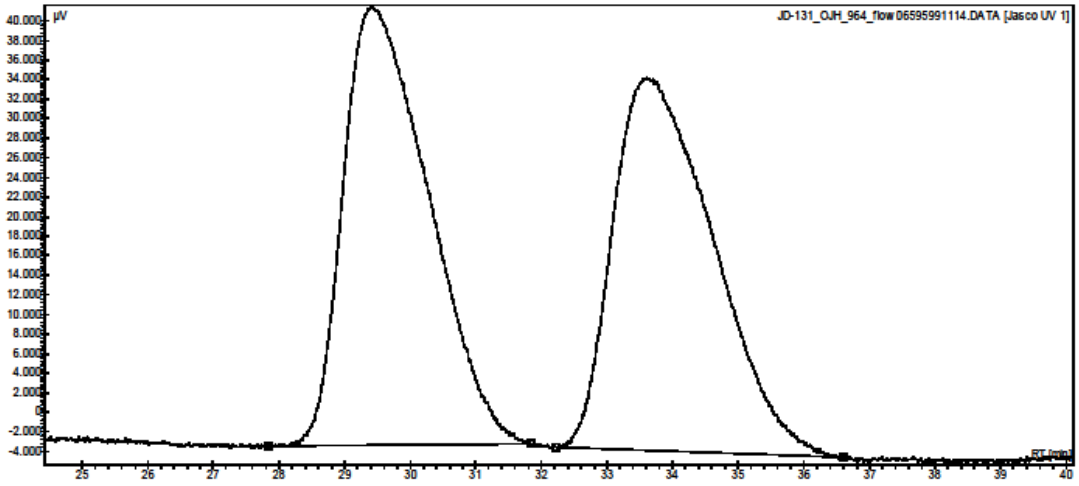
Compound **3m**


O2N
CHO
O
OTBS
0.91
3.37
0.97
0.96
0.96
3.37
9.46
5.80
f1 (ppm)


188.70
169.03
150.29
129.39
128.57
125.99
119.79
117.06
112.19
79.43
60.49
31.86
25.88
18.43
-5.12
O2N
CHO
O
OTBS
f1 (ppm)

Compound **3m**

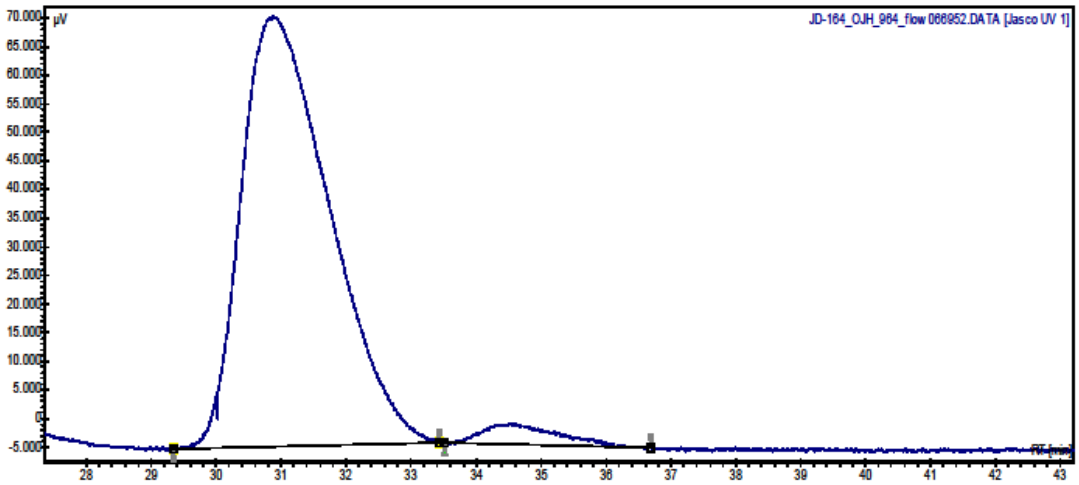
Method: HPLC1_OJH_964_flow06_acq90
Date: 18.07.2010 18:29:48



JD-131_OJH_964_flow06595991114.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	27,830	29,425	31,841	50,071
2	32,225	33,600	36,605	49,929
Total				100,000

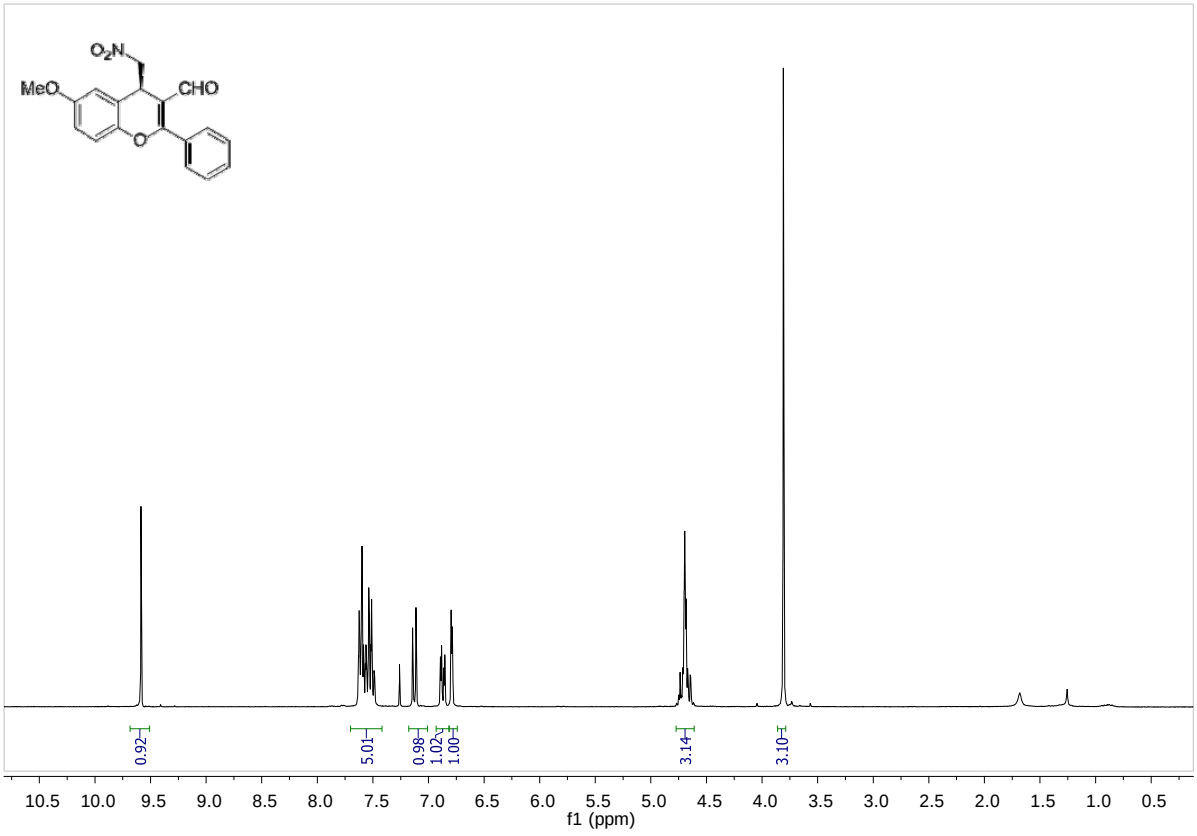
Method: HPLC1_OJH_964_flow06_acq90
Date: 06.08.2010 13:02:51

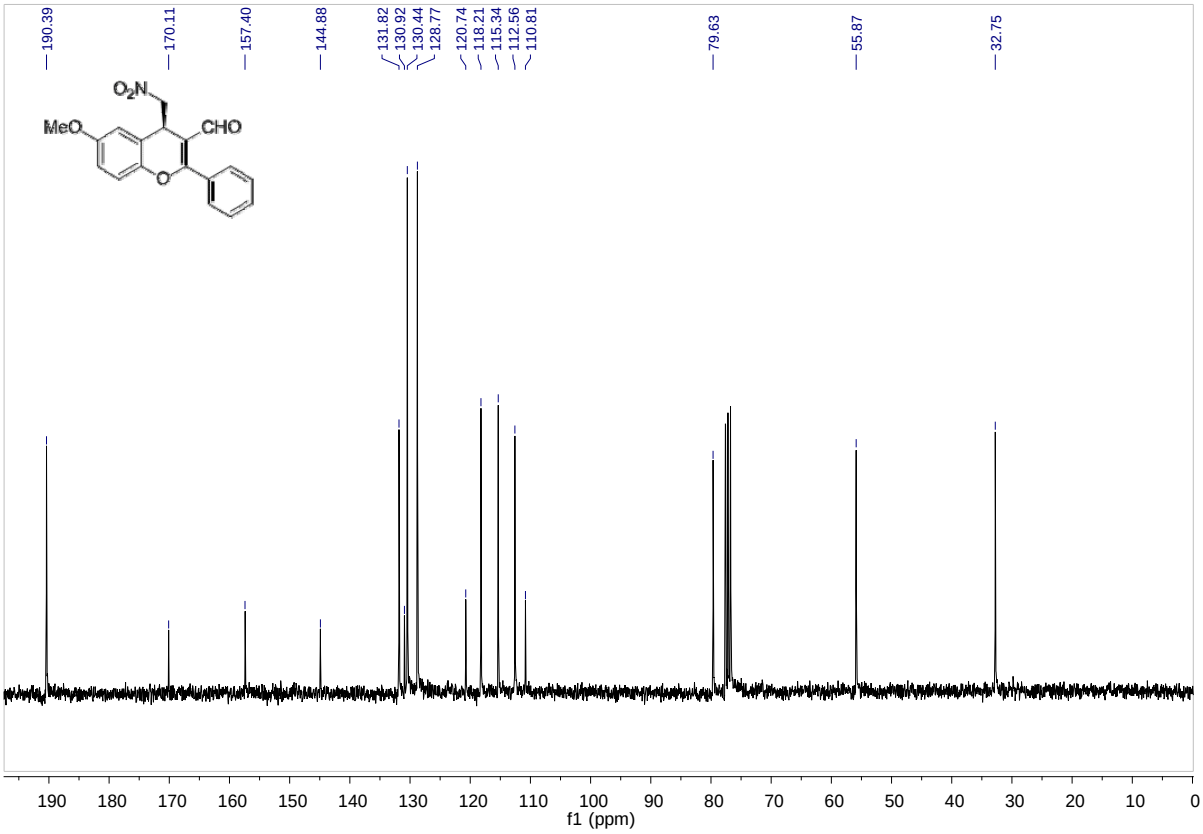


JD-164_OJH_964_flow066952.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	29,339	30,883	33,435	96,028
2	33,517	34,542	36,695	3,972
Total				100,000

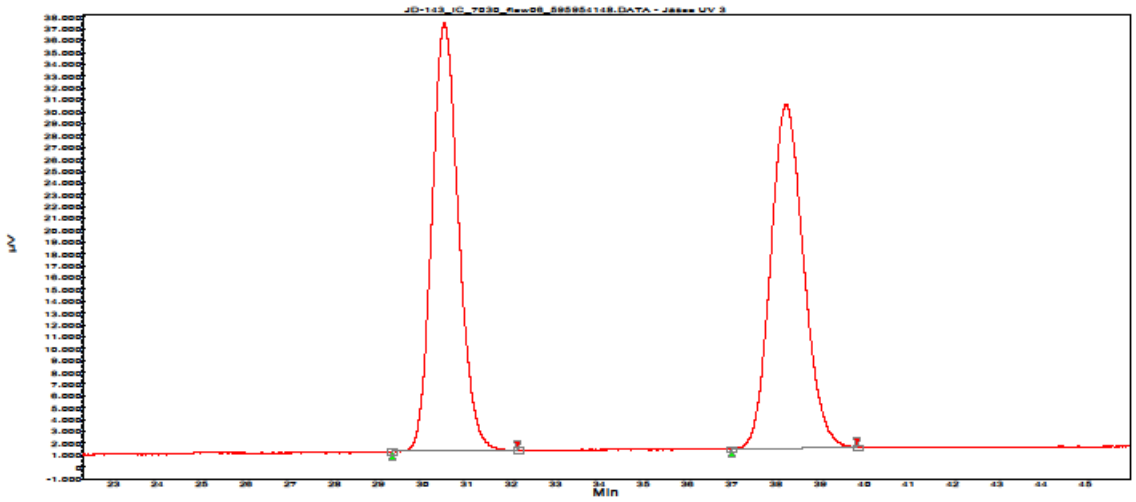
Compound **3n**


O2N
MeO
CHO
O
0.92
5.01
0.98
1.02
1.00
3.14
3.10
10.5 10.0 9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)


190.39
170.11
157.40
144.88
131.82
130.92
130.44
128.77
120.74
118.21
115.34
112.56
110.81
79.63
55.87
32.75
O2N
MeO
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

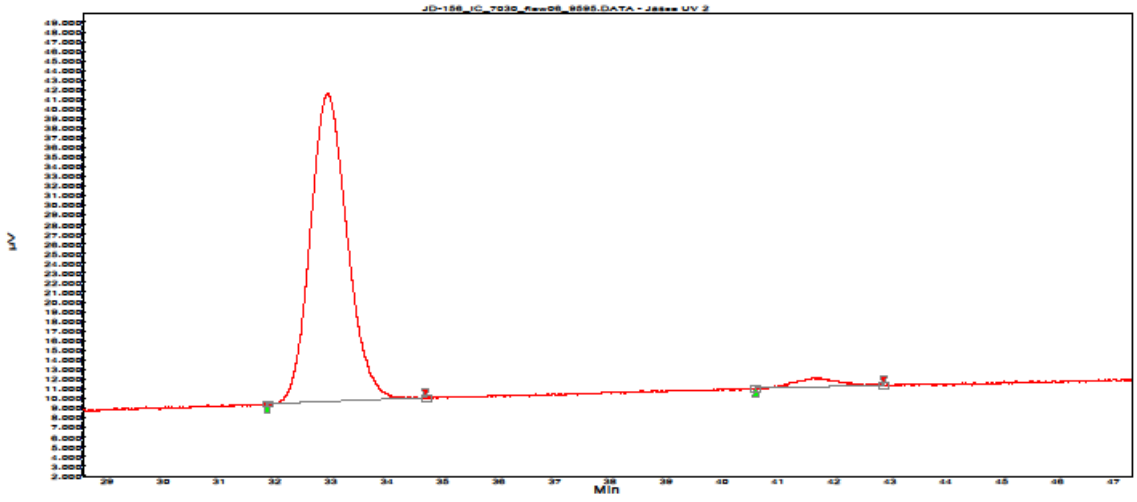
Compound **3n**

Data file: JD-143_IC_7030_flow06_595954148.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 23.07.2010 12:38:35



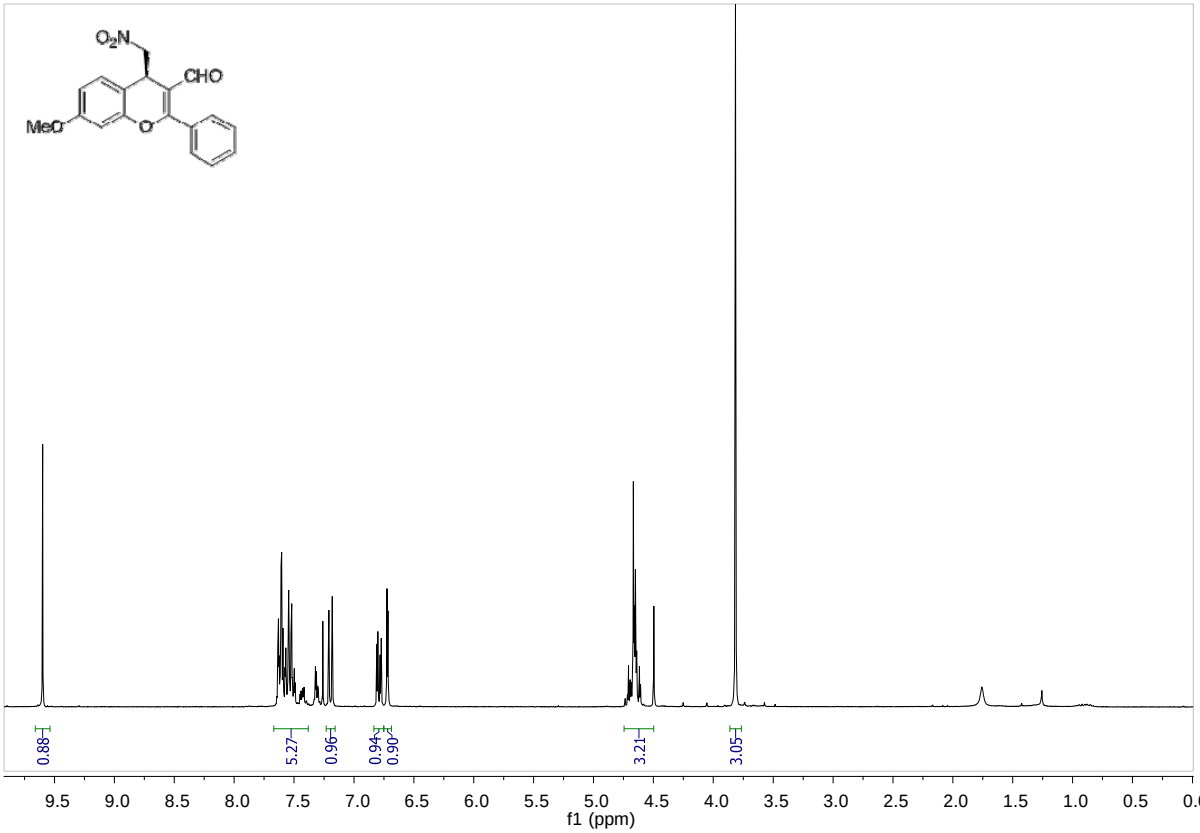
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	29,310	30,492	32,147	0,000	50,11	36147,7	25239,9	50,107
2	UNKNOWN	36,990	38,217	39,828	0,000	49,89	29010,5	25132,4	49,893
Total						100,00	65158,2	50372,3	100,000

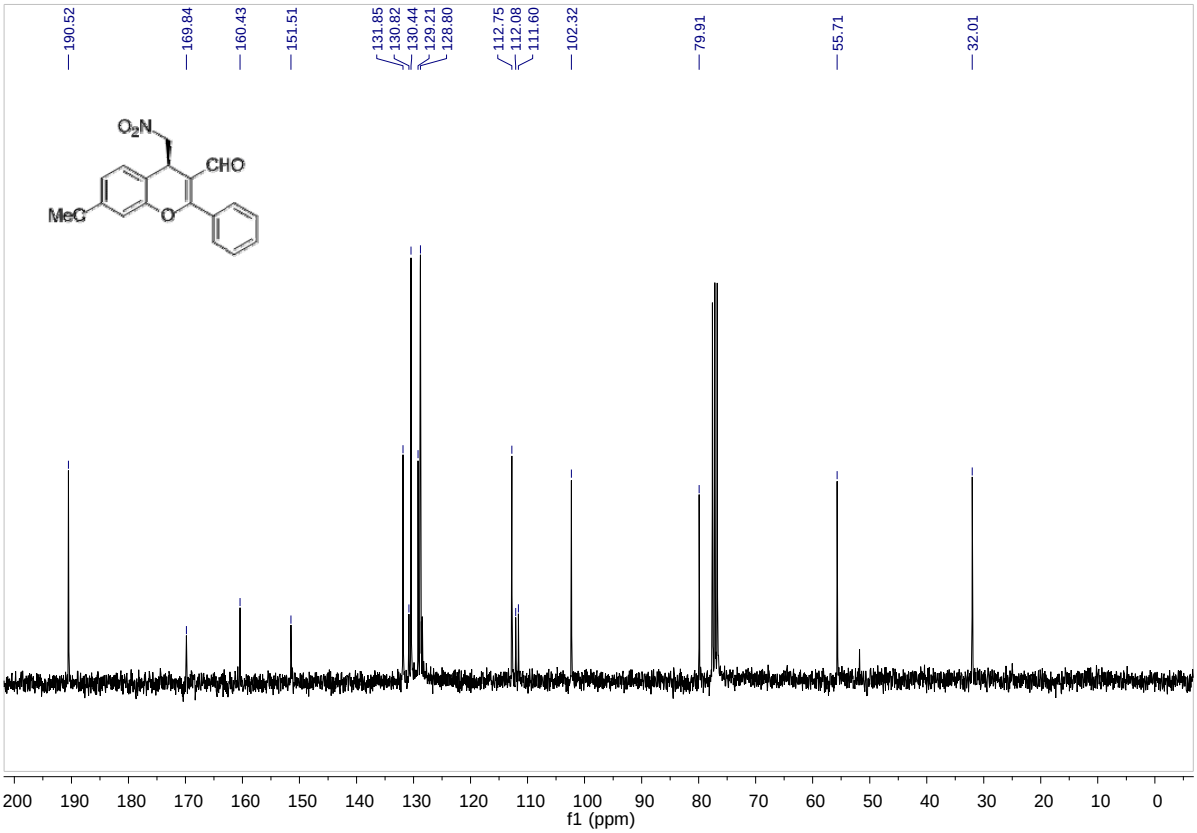
Data file: JD-156_IC_7030_flow06_9595.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 29.07.2010 17:02:33



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	31,862	32,950	34,689	96,926
1	40,594	41,692	42,878	3,074
Total				100,000

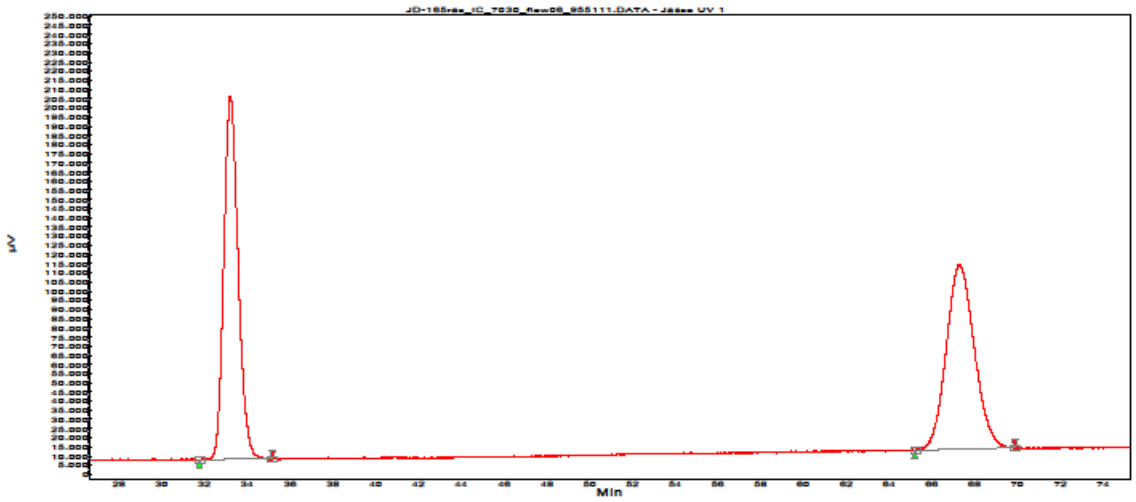
Compound **3o**


O2N
CHO
MeO
O
0.88
5.27
0.96
0.94
0.90
3.21
3.05
f1 (ppm)


190.52
169.84
160.43
151.51
131.85
130.82
130.44
129.21
128.80
112.75
112.08
111.60
102.32
79.91
55.71
32.01
O2N
CHO
MeO
O
f1 (ppm)

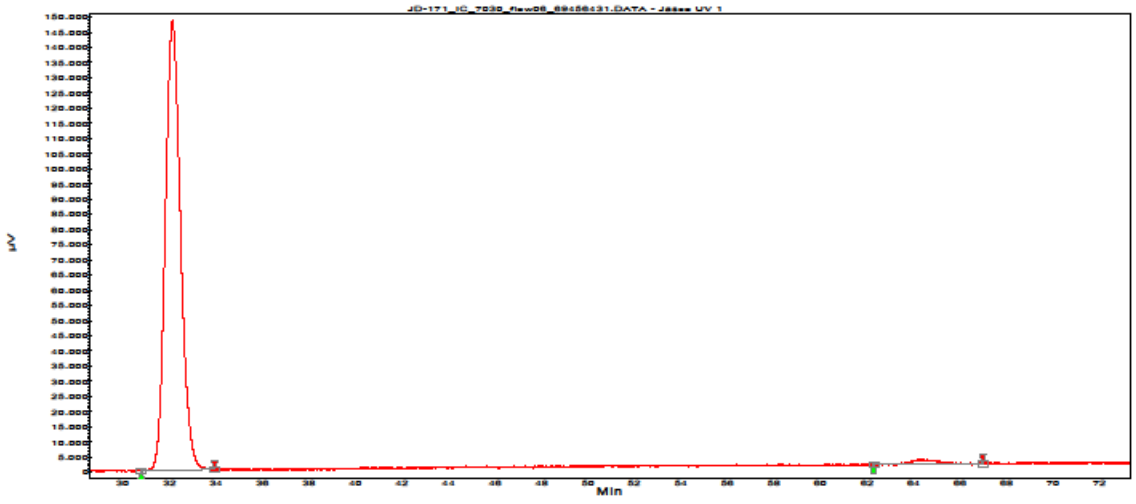
Compound **3o**

Data file: JD-165rac_IC_7030_flow06_955111.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 07.08.2010 16:09:12



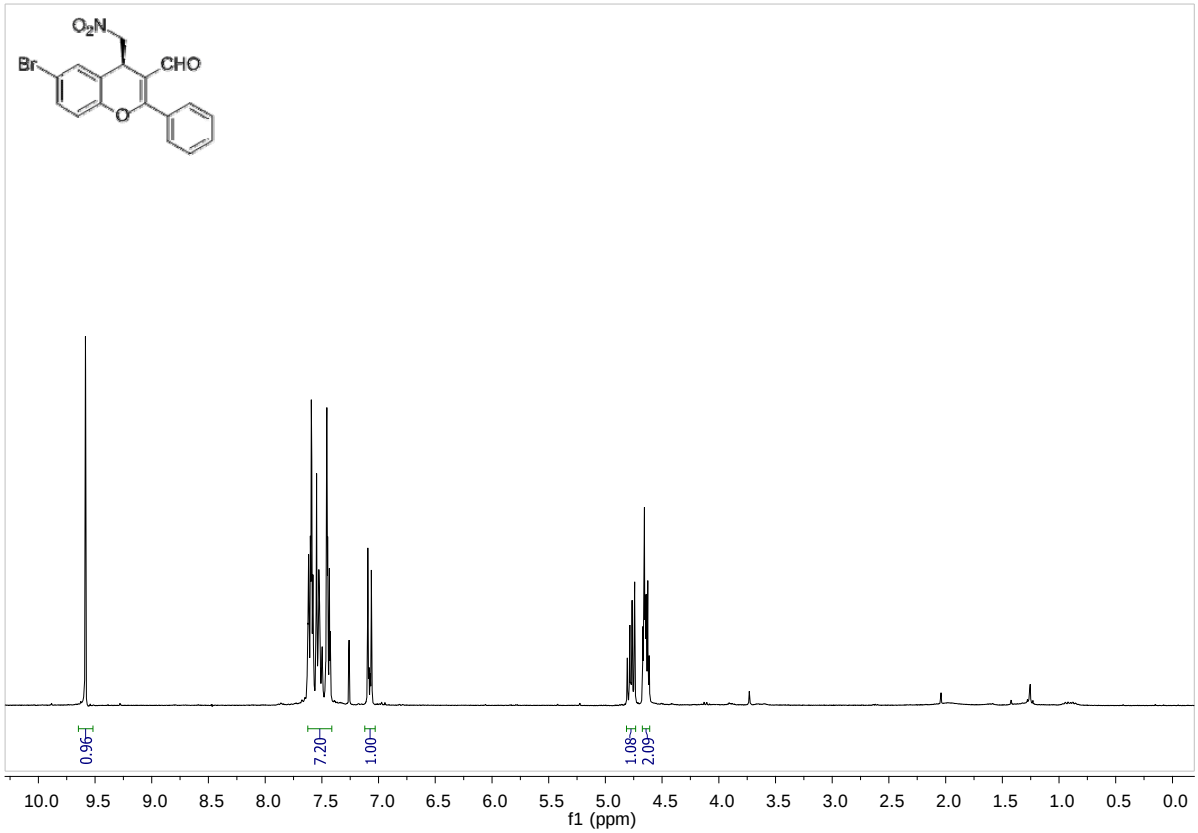
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	31,771	33,208	35,182	50,219
1	65,183	67,233	69,848	49,781
Total				100,000

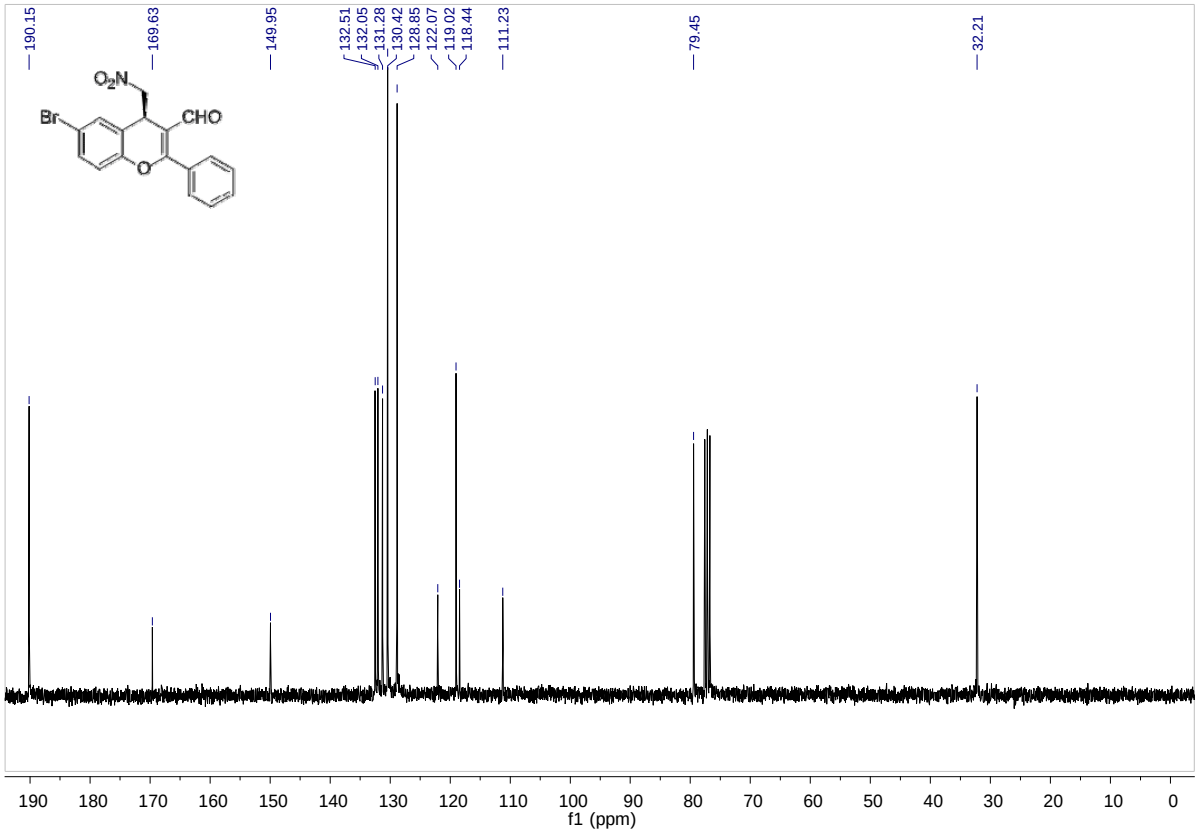
Data file: JD-171_IC_7030_flow06_69456431.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 10.08.2010 13:50:22



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	30,791	32,150	33,952	98,362
2	62,275	64,383	66,962	1,638
Total				100,000

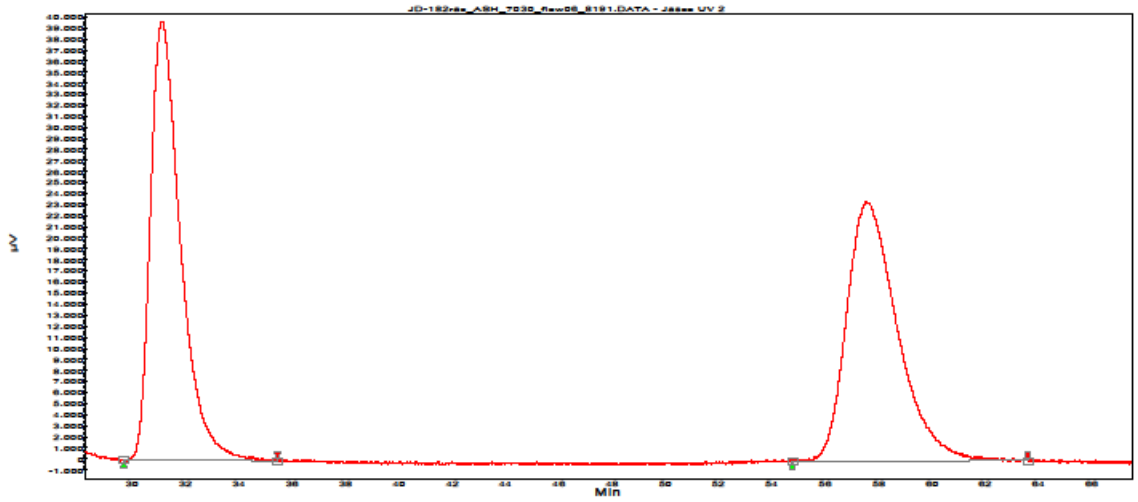
Compound **3p**


O2N
Br
CHO
O
0.96
7.20
1.00
1.08
2.09
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.15
169.63
149.95
132.51
132.05
131.28
130.42
128.85
122.07
119.02
118.44
111.23
79.45
32.21
O2N
Br
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

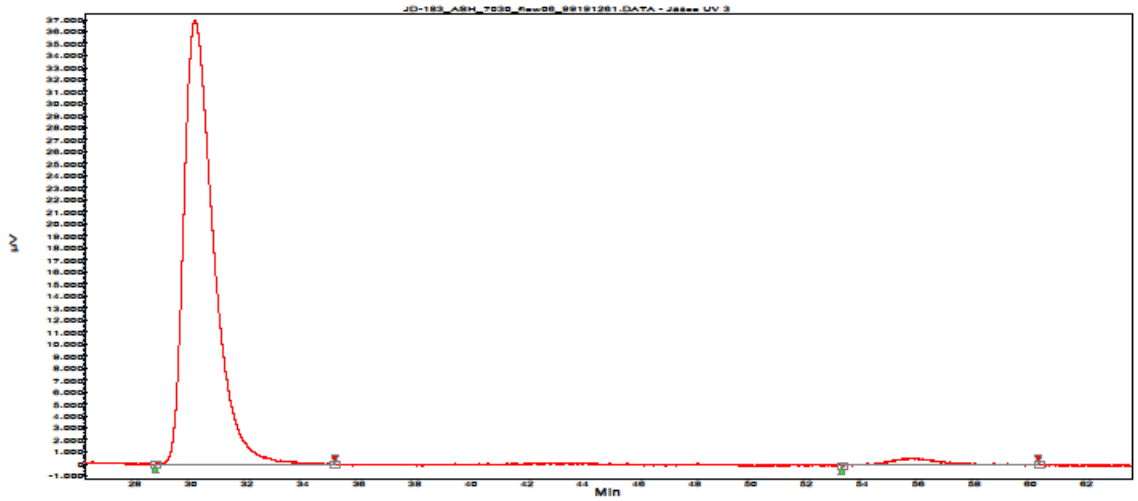
Compound **3p**

Data file: JD-182rac_ASH_7030_flow06_8191.DATA
Method: HPLC1_ASH_7030_flow06_acq_90
Date: 18.08.2010 14:35:43



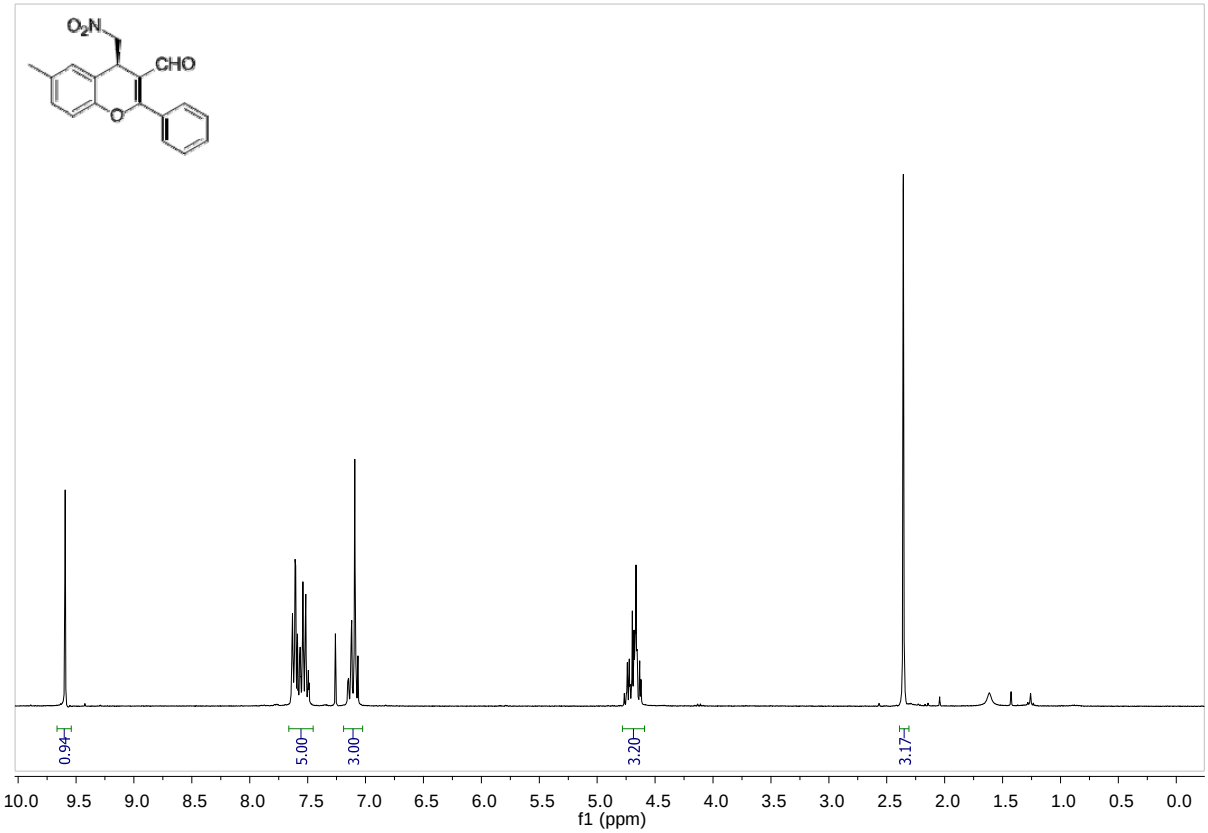
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	29,688	31,117	35,445	50,131
1	54,742	57,550	63,580	49,869
Total				100,000

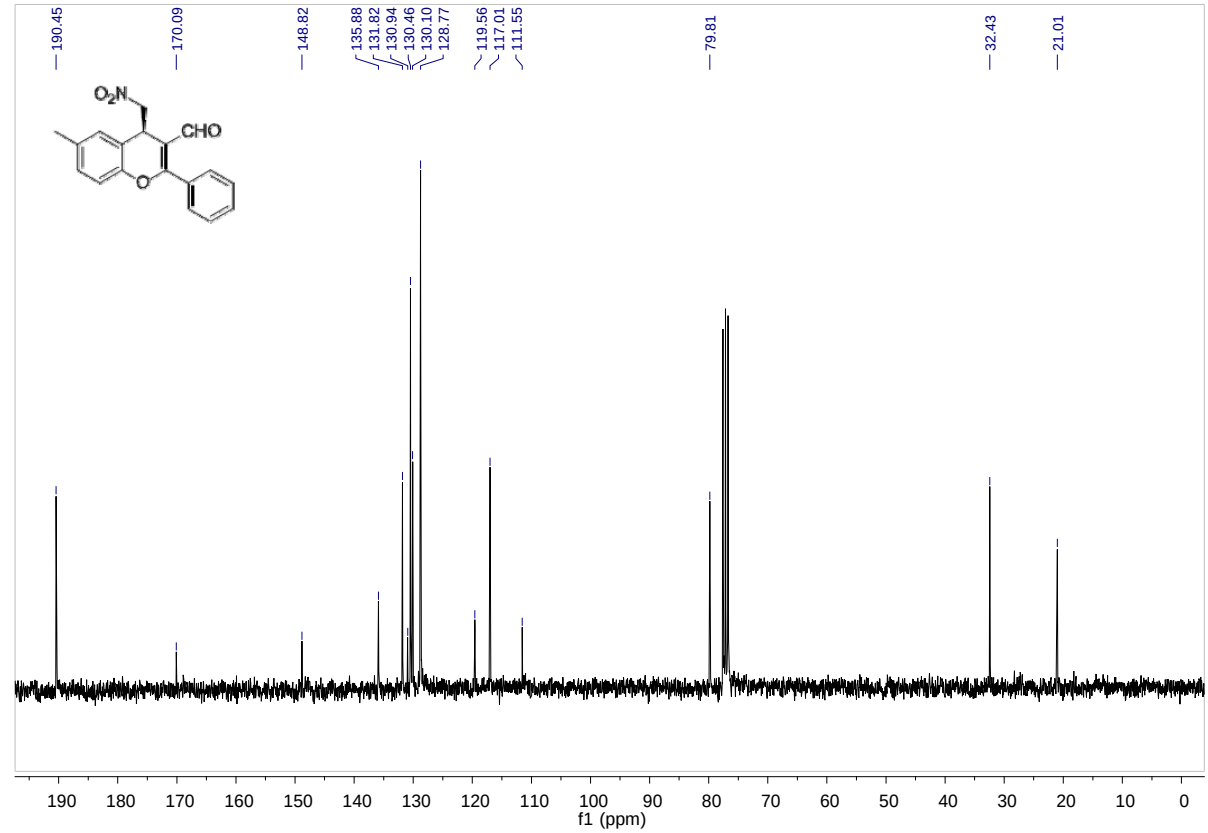
Data file: JD-183_ASH_7030_flow06_99191261.DATA
Method: HPLC1_ASH_7030_flow06_acq_90
Date: 20.08.2010 23:25:59



Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	28,729	30,150	35,138	0,000	97,66	36913,8	45040,0	97,661
1	UNKNOWN	53,247	55,683	60,274	0,000	2,34	544,7	1078,7	2,339
Total						100,00	37458,6	46118,6	100,000

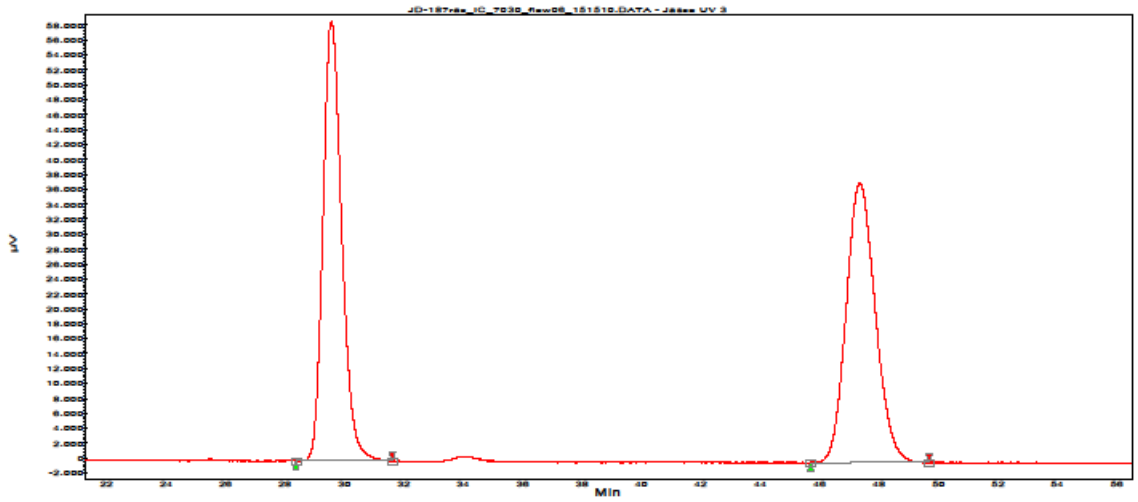
Compound **3q**


O2N
CHO
O
0.94
5.00
3.00
3.20
3.17
10.0 9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.45
170.09
148.82
135.88
131.82
130.94
130.46
130.10
128.77
119.56
117.01
111.55
79.81
32.43
21.01
O2N
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

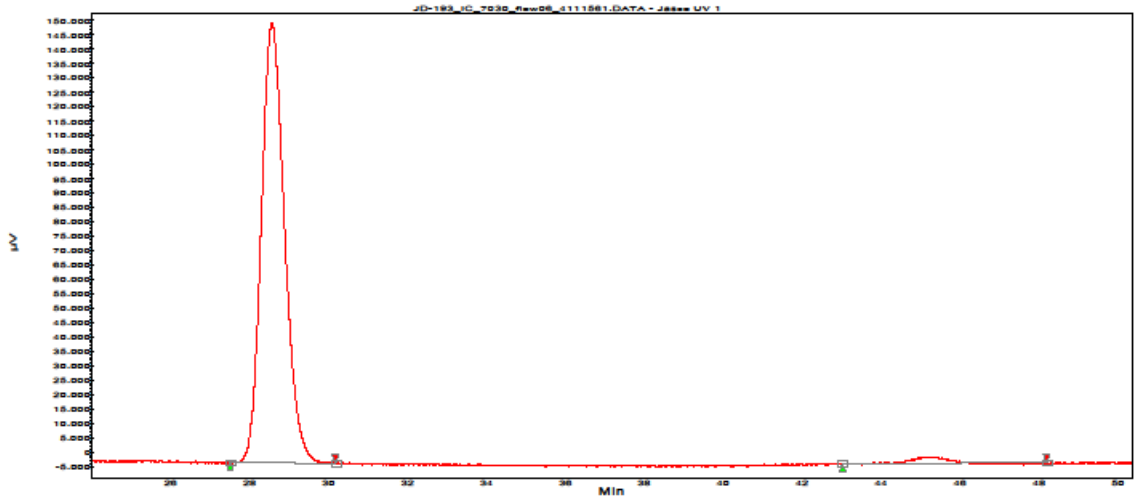
Compound **3q**

Data file: JD-187rac_IC_7030_flow06_151510.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 19.08.2010 23:06:59



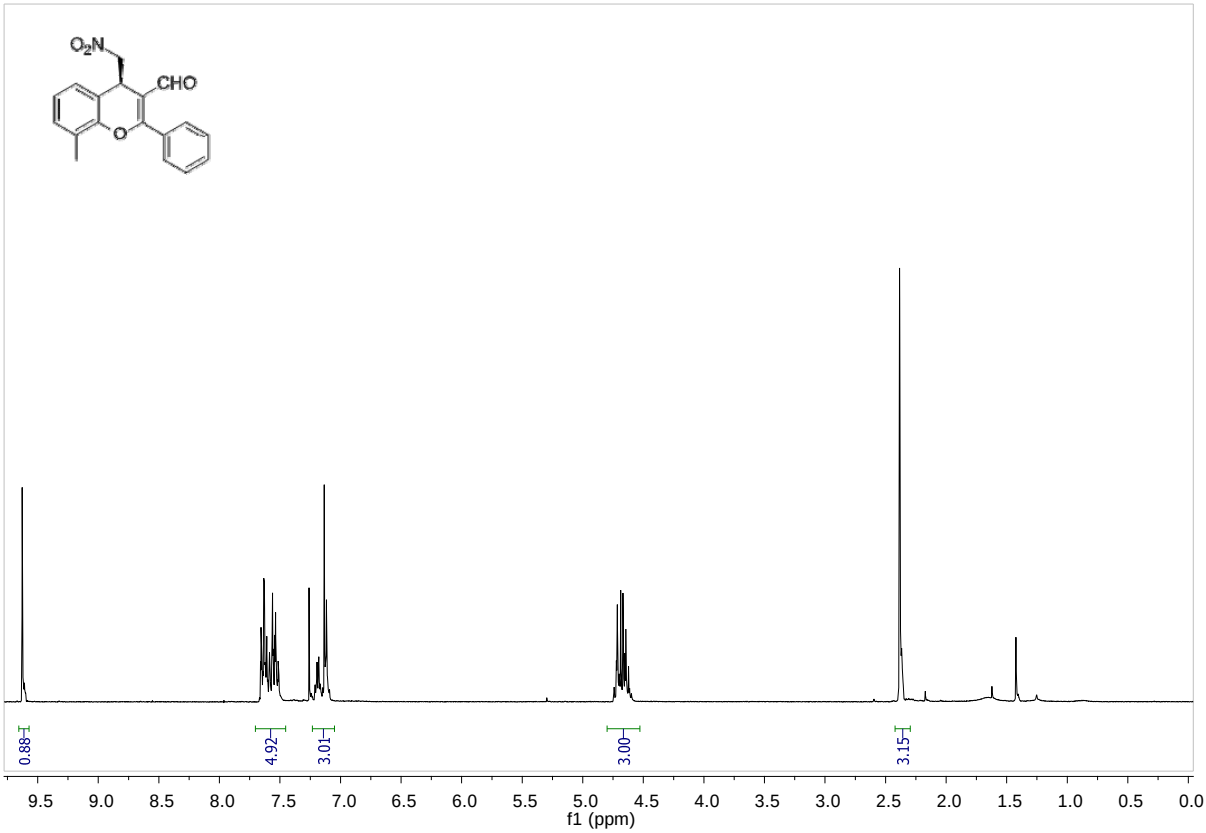
Index	Name	Start	Time	End	Ret. time Offset	Quantity	Height	Area	Area %
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	28,364	29,567	31,601	0,000	50,25	58799,8	42964,9	50,254
1	UNKNOWN	45,675	47,342	49,676	0,000	49,75	37429,9	42530,2	49,746
Total						100,00	96229,7	85495,1	100,000

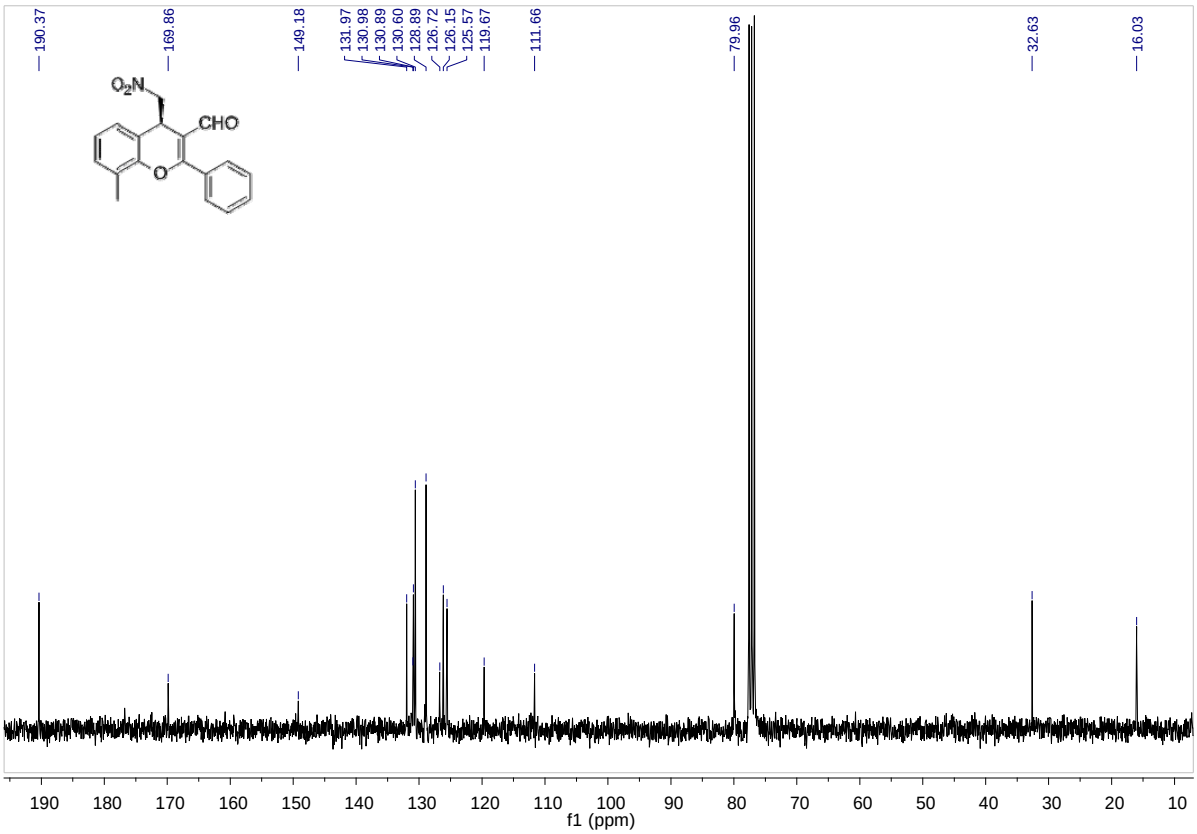
Data file: JD-193_IC_7030_flow06_4111561.DATA
Method: HPLC1_IC_7030_flow06_acq_120
Date: 26.08.2010 18:41:21



Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	27,516	28,567	30,181	98,169
2	43,016	45,300	48,182	1,831
Total				100,000

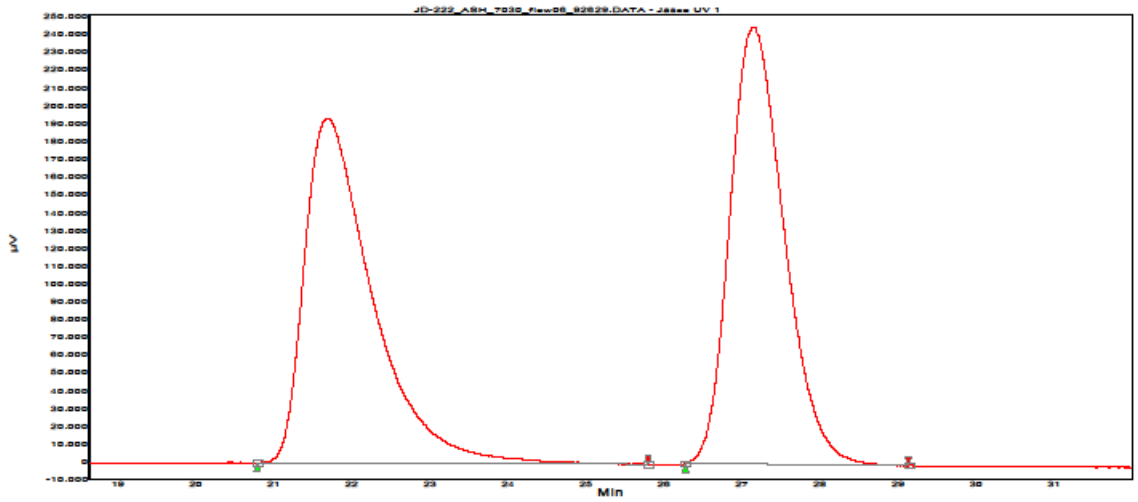
Compound **3r**


O2N
CHO
O
0.88
4.92
3.01
3.00
3.15
9.5 9.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.37
169.86
149.18
131.97
130.98
130.89
130.60
128.89
126.72
126.15
125.57
119.67
111.66
79.96
32.63
16.03
O2N
CHO
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

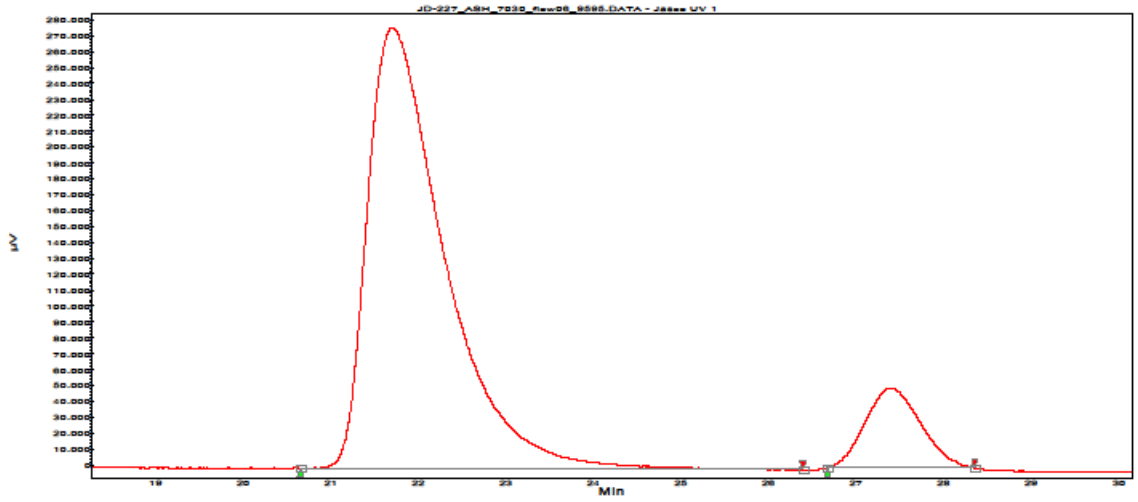
Compound **3r**

Data file: JD-222_ASH_7030_flow06_92629.DATA
Method: HPLC1_ASH_7030_flow06_acq_90
Date: 20.09.2010 19:06:22



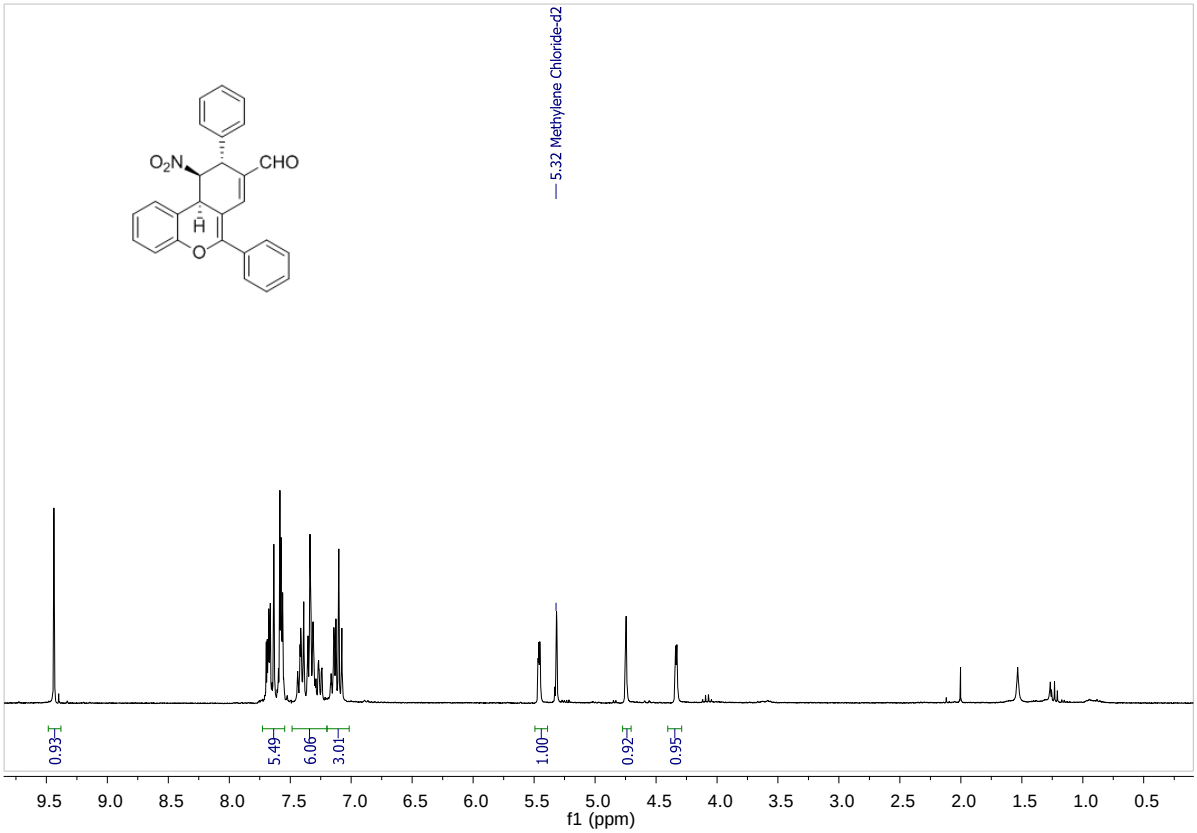
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	20,788	21,692	25,796	49,872
2	26,279	27,150	29,135	50,128
Total				100,000

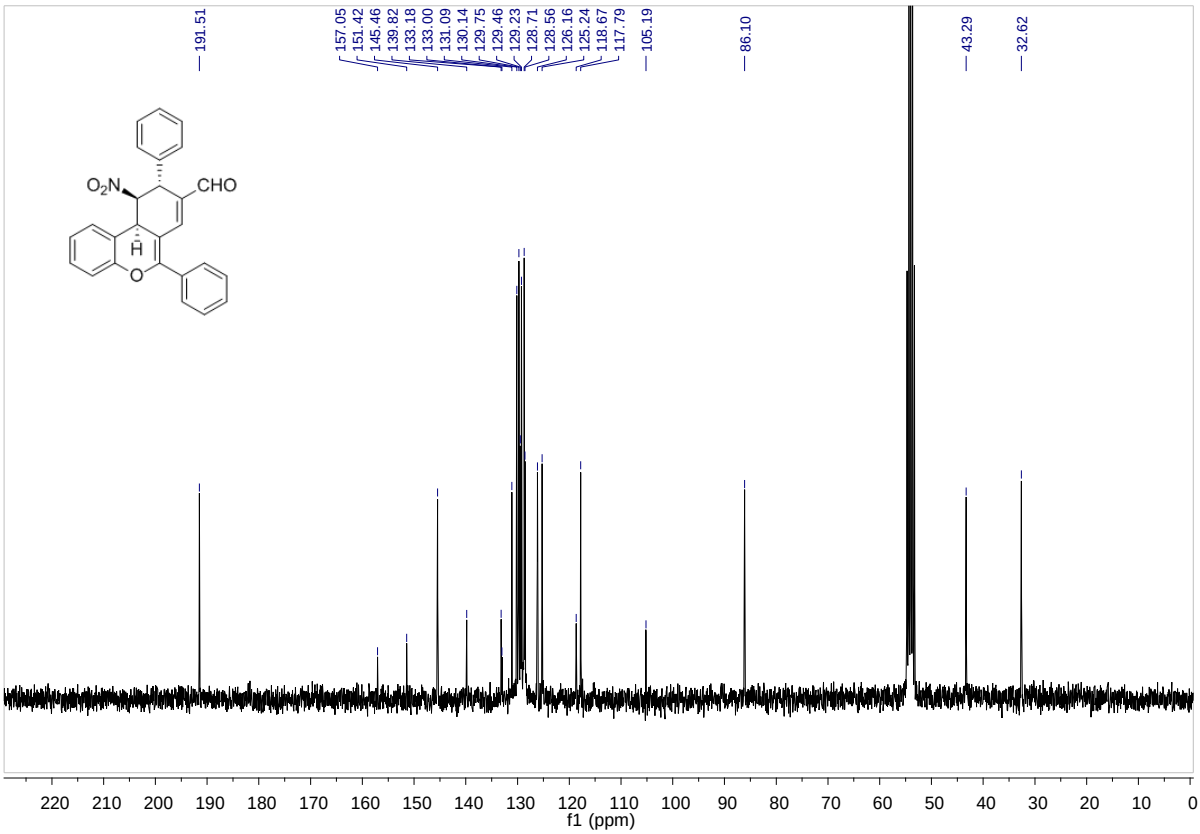
Data file: JD-227_ASH_7030_flow06_9595.DATA
Method: HPLC1_ASH_7030_flow06_acq_50
Date: 21.09.2010 17:07:33



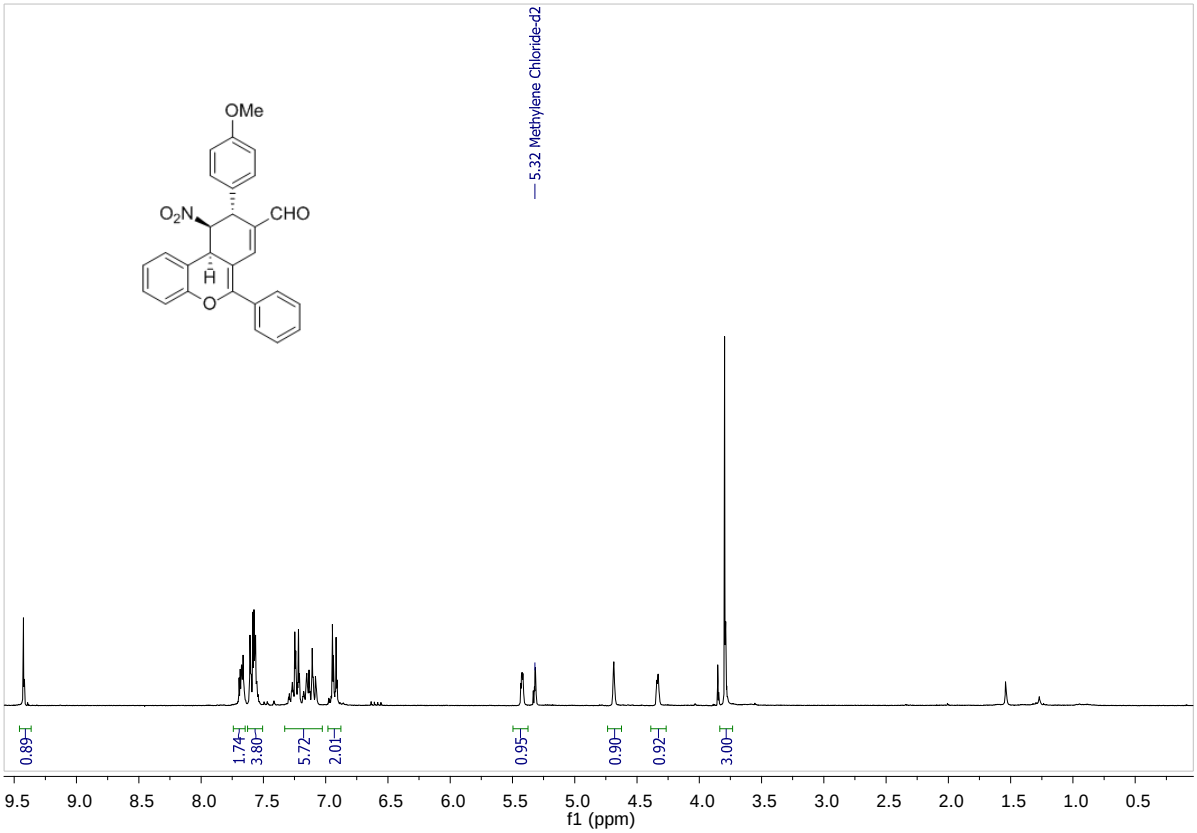
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	20,656	21,708	26,391	88,477
2	26,673	27,408	28,352	11,523
Total				100,000

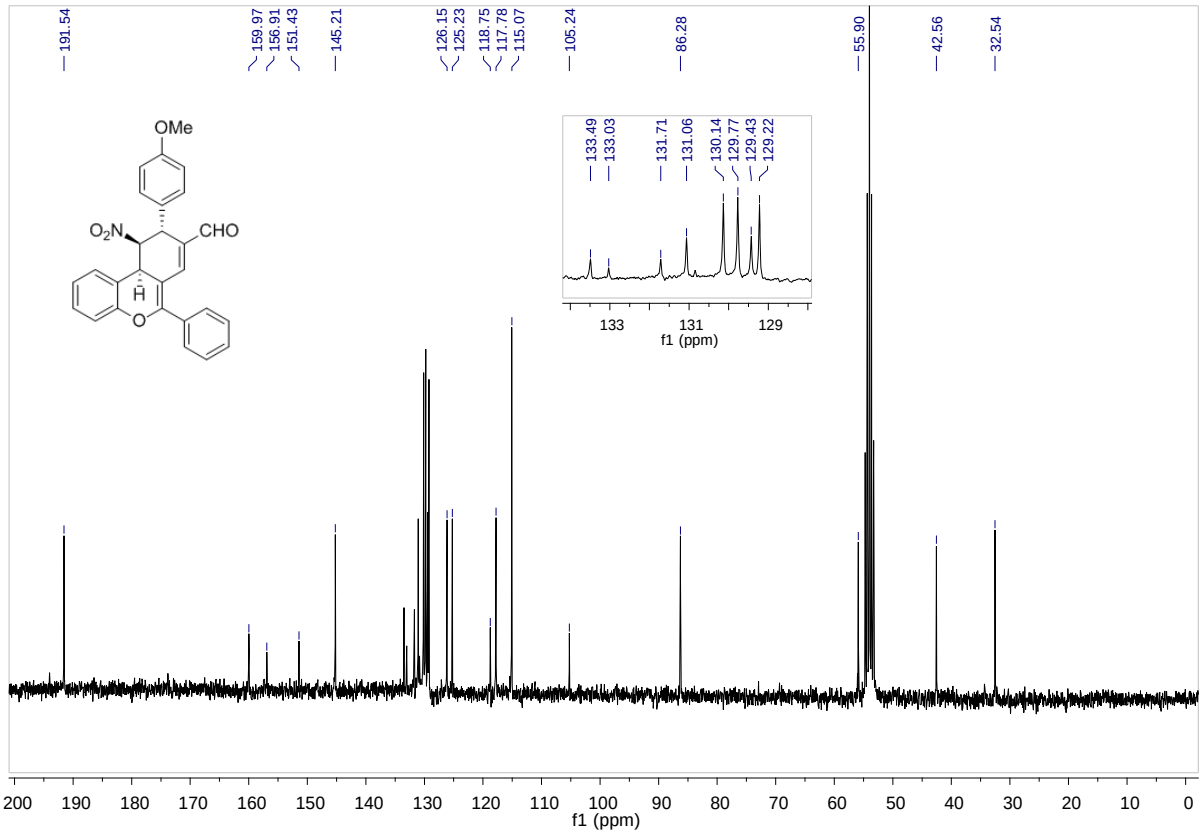
Compound **6a**


5.32 Methylene Chloride-d2
O2N
CHO
H
O
0.93
5.49
6.06
3.01
1.00
0.92
0.95
9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)

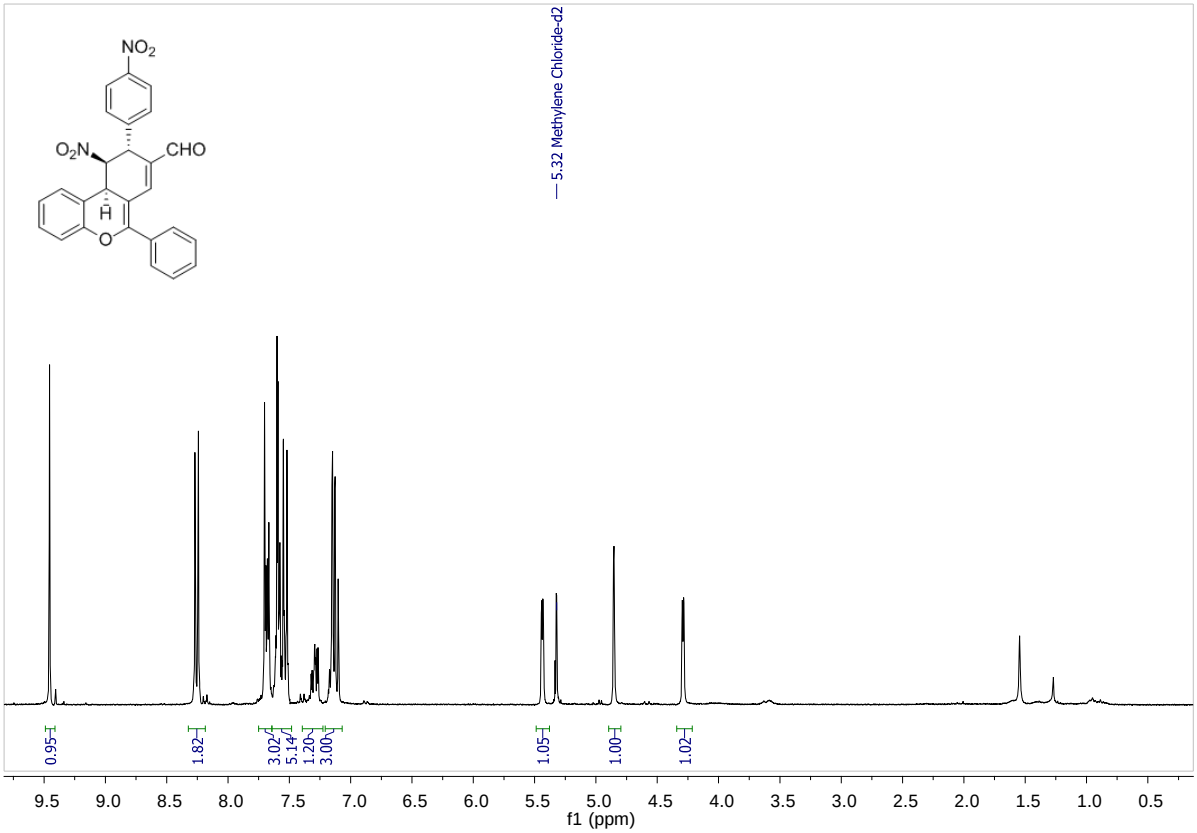

191.51
157.05
151.42
145.46
139.82
133.18
133.00
131.09
130.14
129.75
129.46
129.23
128.71
128.56
126.16
125.24
118.67
117.79
105.19
86.10
43.29
32.62
O2N
CHO
H
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

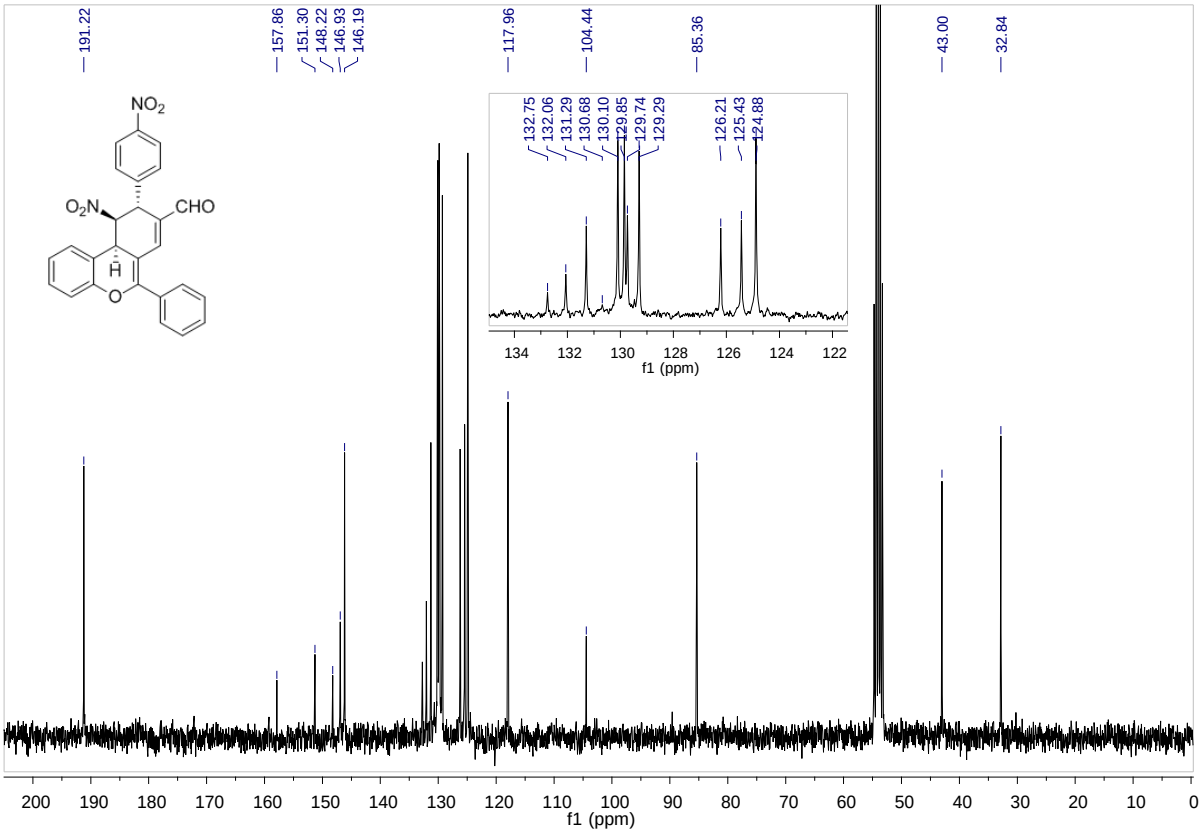
Compound **6b**


OMe
O_2N
CHO
H
O
5.32 Methylene Chloride-d2
0.89
1.74
3.80
5.72
2.01
0.95
0.90
0.92
3.00
9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)

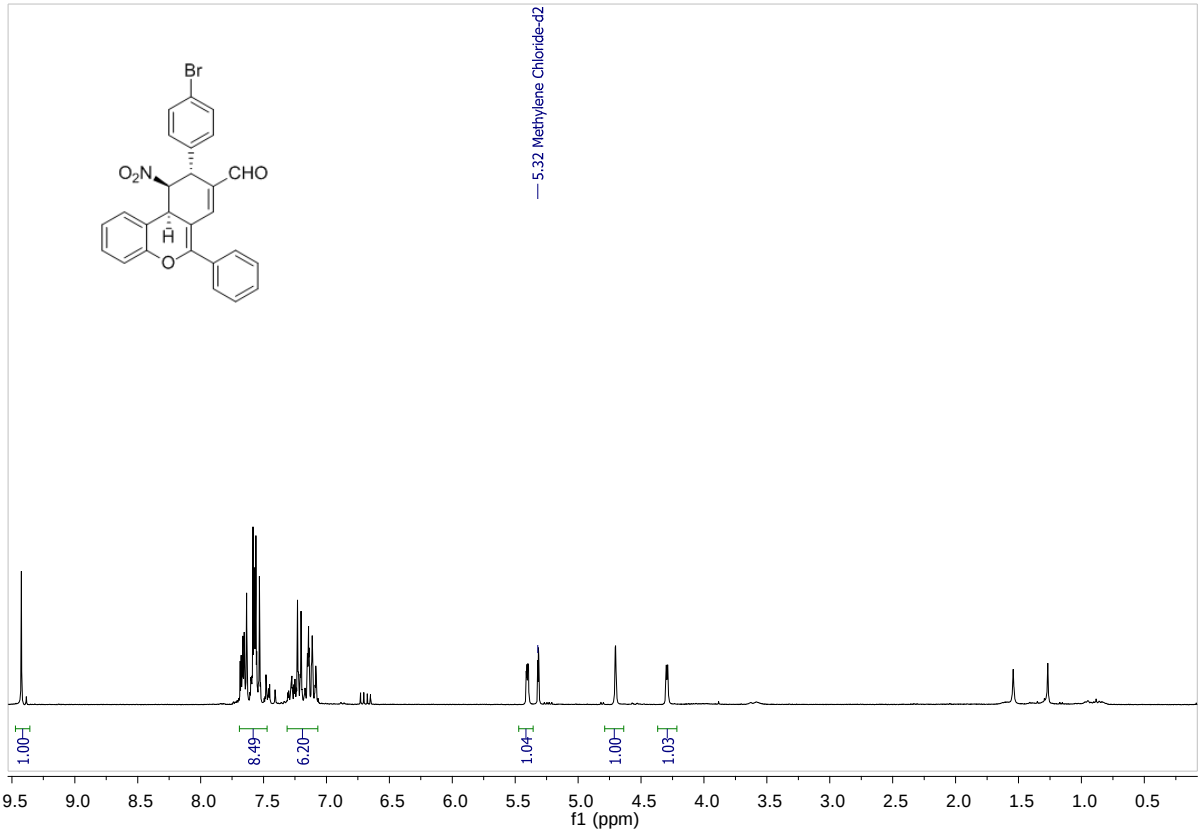

191.54
159.97
156.91
151.43
145.21
126.15
125.23
118.75
117.78
115.07
105.24
86.28
55.90
42.56
32.54
OMe
O_2N
CHO
H
O
133.49
133.03
131.71
131.06
130.14
129.77
129.43
129.22
133 131 129
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

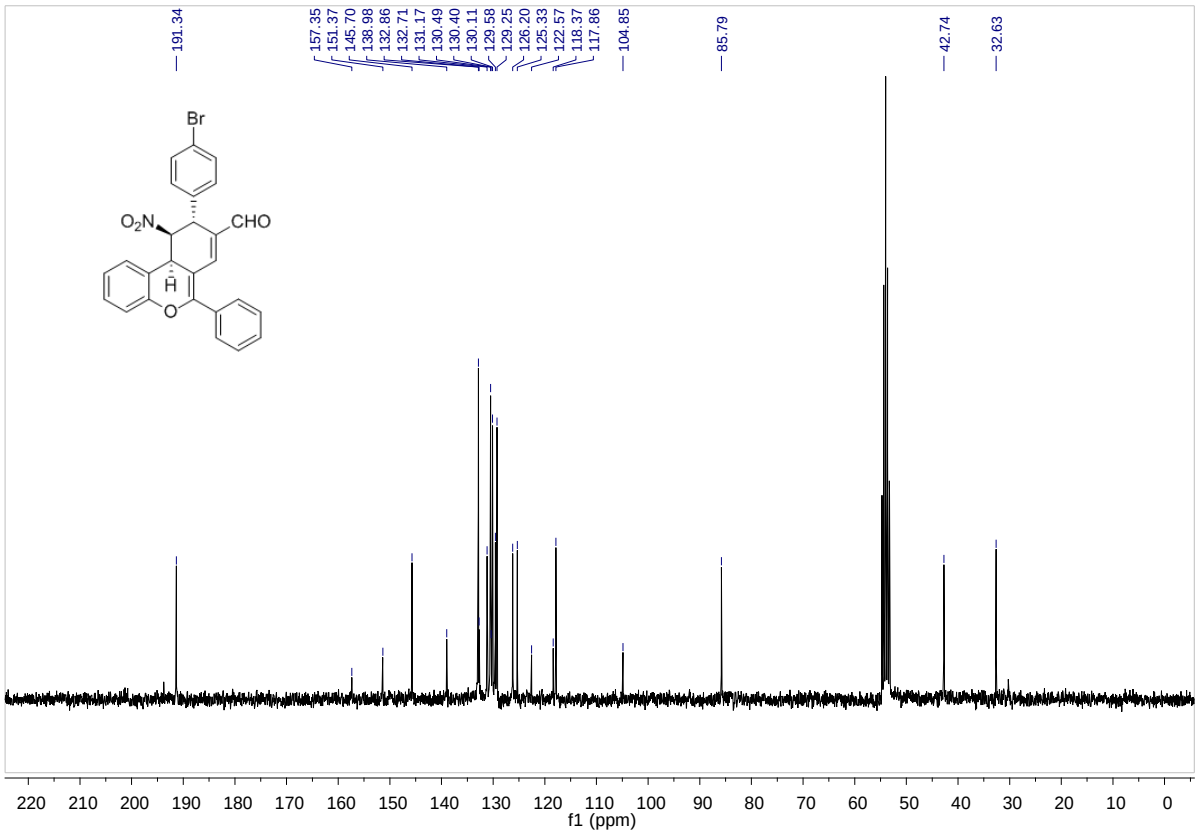
Compound **6c**


NO2
O2N
CHO
H
O
5.32 Methylene Chloride-d2
0.95
1.82
3.02
5.14
1.20
3.00
1.05
1.00
1.02
9.5 9.0 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 2.0 1.5 1.0 0.5
f1 (ppm)

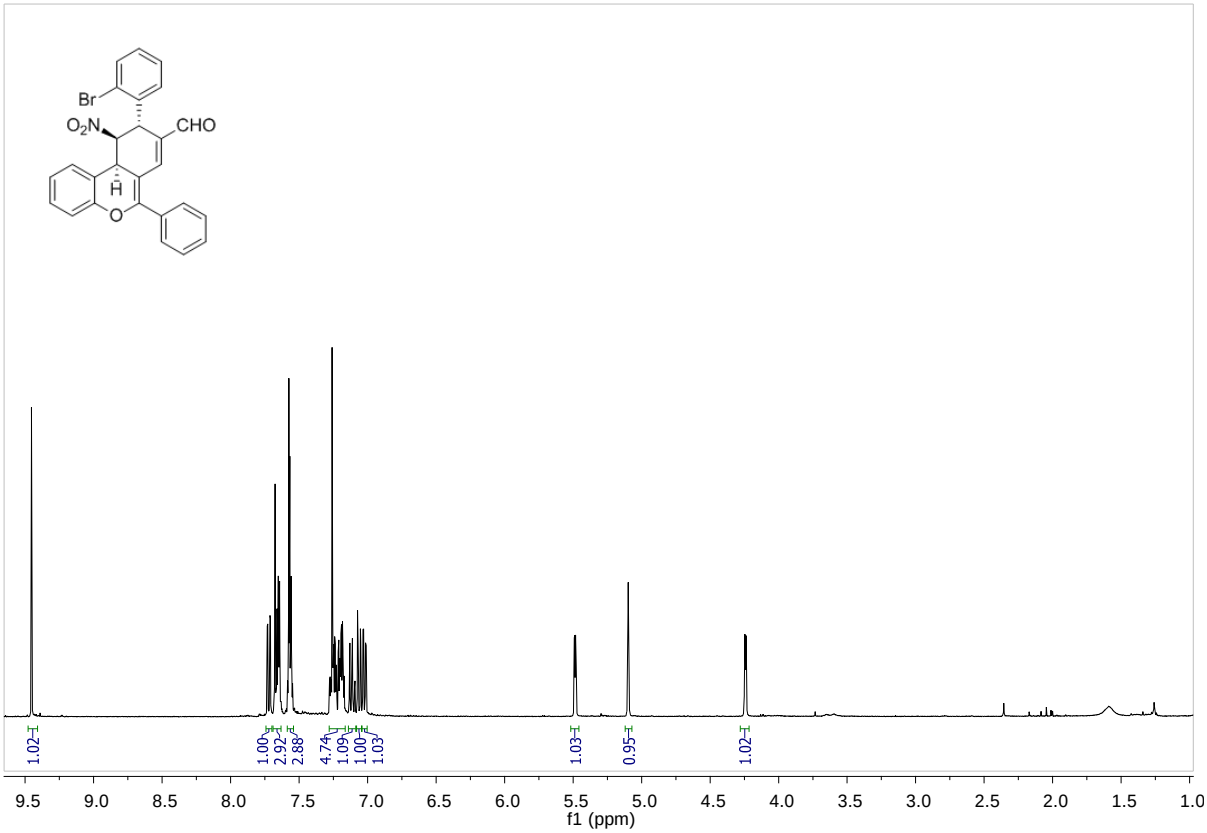

191.22
157.86
151.30
148.22
146.93
146.19
117.96
104.44
85.36
43.00
32.84
132.75
132.06
131.29
130.68
130.10
129.85
129.74
129.29
126.21
125.43
124.88
NO2
O2N
CHO
H
O
134 132 130 128 126 124 122
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

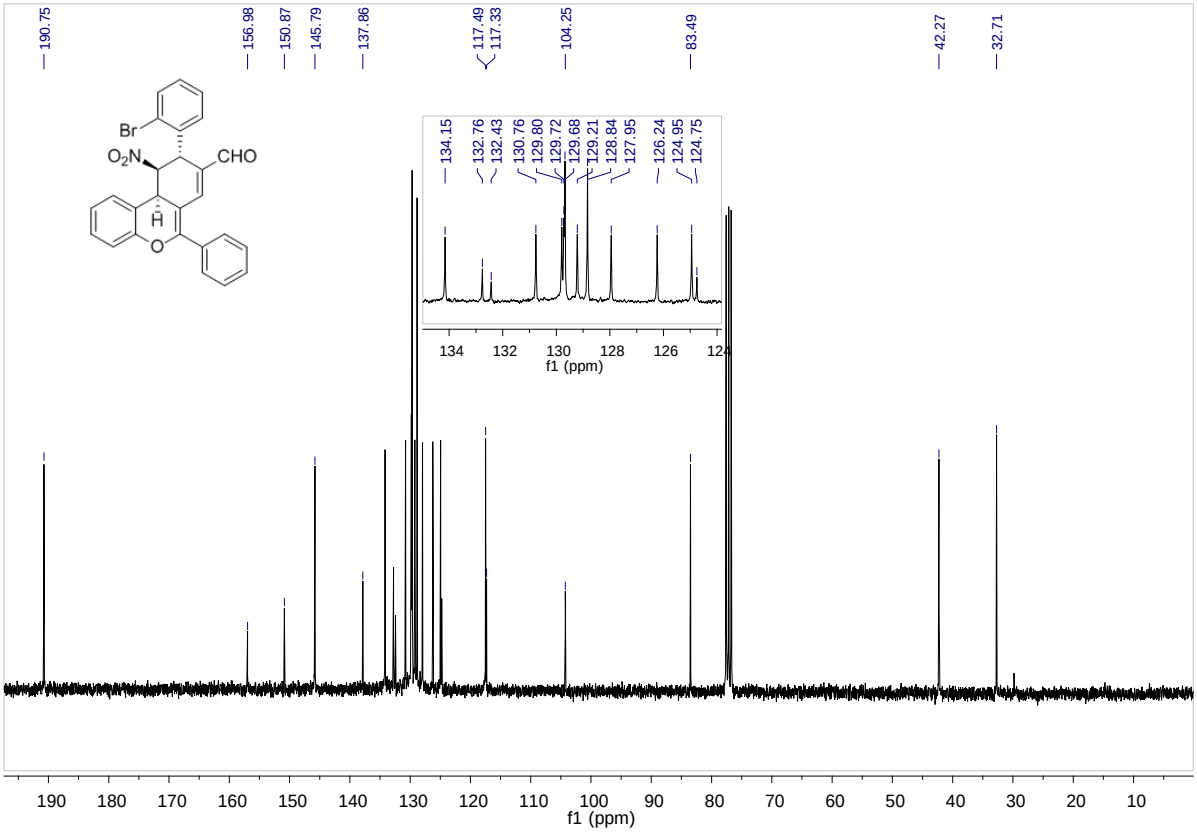
Compound **6d**


Br
O2N
CHO
H
O
5.32 Methylene Chloride-d2
1.00
8.49
6.20
1.04
1.00
1.03
f1 (ppm)


191.34
157.35
151.37
145.70
138.98
132.86
132.71
131.17
130.49
130.40
130.11
129.58
129.25
126.20
125.33
122.57
118.37
117.86
104.85
85.79
42.74
32.63
Br
O2N
CHO
H
O
f1 (ppm)

Compound **6e**


Br
O2N
CHO
H
O
1.02
1.00
2.92
2.88
4.74
1.09
1.00
1.03
1.03
0.95
1.02
9.5 9.0 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 2.0 1.5 1.0
f1 (ppm)


190.75
156.98
150.87
145.79
137.86
117.49
117.33
104.25
83.49
42.27
32.71
Br
O2N
CHO
H
O
134.15
132.76
132.43
130.76
129.80
129.72
129.68
129.21
128.84
127.95
126.24
124.95
124.75
134 132 130 128 126
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)