Asymmetric Brønsted Acid Catalysis in Aqueous Solution

Magnus Rueping[*] *and Thomas Theissmann*

Supporting information

General: Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm). Solvent mixtures are understood as volume/volume.

^{1}H-NMR and ^{13}C-NMR were recorded on a Bruker AM 250 spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br s (broadened singlet), s (singlet), d (doublet), t (triplet), m (multiplet)); coupling constants (*J*) are in Hertz (Hz). Mass spectra (MS-EI, 70 eV) were conducted on GC-MS Shimadzu QP2010 (column: Equity®-5, length × I.D. 30 m × 0.25 mm, d_f 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. The enantiomeric excesses were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. CHIRALCEL OD-H; eluent: hexane/2-propanol). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Chemical yields refer to pure isolated substances. The yields and enantiomeric excesses are given in the respective tables.

[*] E-mail: Magnus.Rueping@rwth-aachen.de

CPK views of catalyst 1c and 1e

The following CPK views are based on our recently obtained X-ray crystal structures of catalyst **1c** and **1e**. As can be deduced from figure 1 and 2, the active center of the catalysts is located in a hydrophobic pocket. Due to the sterically more demanding 2,4,6-trisopropylphenyl residues, the phosphoric acid **1c** is more shielded and hence intrusion of water is more difficult to occur as compared to the phenanthryl-substituted Brønsted acid **1e**.

Figure 1. X-ray crystal structure of catalyst **1c**

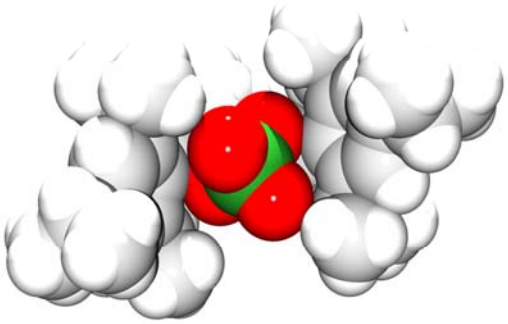
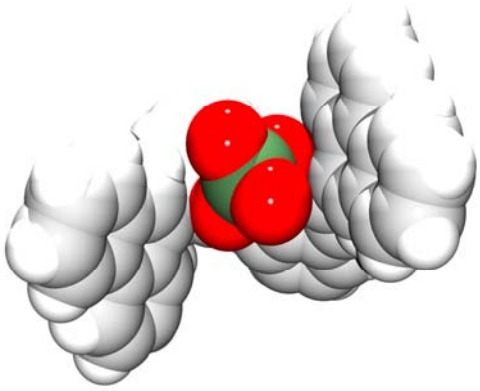


Figure 2. X-ray crystal structure of catalyst **1e**



General procedure: Quinoline **2** (0.1 mmol), catalyst **1c** (2 mol%) and Hantzsch dihydropyridine **4c** (2.4 equiv.) were added to brine solution (0.14 M) in a screw-capped vial. The resulting reaction was allowed to stir at 50°C for 36-45 h. After cooling to room temperature the aqueous reaction mixture was extracted several times with dichloromethane. The combined organic phases were dried over $MgSO_4$, the solvent was removed under reduced pressure and purification of the crude product by column chromatography on silica gel (toluene) afforded the pure 1,2,3,4-tetrahydroquinoline **3**.

In case of 3-Phenyl-3,4-dihydro-2*H*-1,4-benzoxazine **5** water was directly evaporated (*no work up with organic solvents!*) and the residue was directly purified by column chromatography on silica gel using toluene as eluent.

Physical data:

(*S*)-2-Phenyl-1,2,3,4-tetrahydroquinoline [Table 4, entry 1]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.51-7.27 (m, 5H), 7.13-6.97 (m, 2H), 6.69 (t, J(H,H)=7.4 Hz, 1H), 6.57 (d, J(H,H)= 7.9 Hz, 1H), 4.47 (dd, J(H,H)=9.2, 3.4 Hz, 1H), 4.07 (br s, 1H), 3.07-2.87 (m, 1H), 2.77 (dt, J(H,H)=16.4, 4.8 Hz, 1H), 2.25-1.93 ppm (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ= 144.79, 144.68, 129.25, 128.53, 127.38, 126.86, 126.50, 120.85, 117.13, 113.95, 56.23, 30.94, 26.33 ppm; $[\alpha]_D^{RT}$=-30.4 (c=1.0 in $CHCl_3$); HPLC conditions: n-

hexane/2-propanol = 95/5, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=18.90 min; minor enantiomer: t_R=26.18 min.

(*S*)-2-(3-Fluorophenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 2]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.28-6.80 (m, 6H), 6.57 (t, J(H,H)=7.3, 1H), 6.45 (d, J(H,H)=7.8 Hz, 1H), 4.33 (dd, J(H,H)=8.9, 3.4 Hz, 1H), 3.92 (br s, 1H), 2.90-2.71 (m, 1H), 2.61 (dt, J(H,H)=16.4, 5.0 Hz, 1H), 2.11-1.76 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=163.03 (d, J(C,F)=245.9 Hz), 147.62 (d, J(C,F)=6.6 Hz), 144.31, 129.98 (d, J(C,F)=8.2 Hz), 129.25, 126.93, 122.04 (d, J(C,F)=2.8 Hz), 120.76, 117.38, 114.16 (d, J(C,F)=21.2 Hz), 114.05, 113.37 (d, J(C,F)=21.8 Hz), 55.70 (d, J(C,F)=1.7 Hz) 30.83, 26.02 ppm; $[\alpha]_D^{RT}$=-46.9 (c=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=17.17 min; minor enantiomer: t_R=26.14 min.

(*S*)-2-(3-Methylphenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 3]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.21-6.85 (m, 6H), 6.55 (t, J(H,H)=7.4 Hz 1H), 6.43 (d, J(H,H)=7.9 Hz, 1H), 4.29 (dd, J(H,H)=9.3, 3.4 Hz, 1H), 3.90 (br s, 1H), 2.93-2.74 (m, 1H), 2.64 (dt, J(H,H)=16.3, 4.7 Hz, 1H), 2.27 (s, 3H), 2.10-1.78 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=144.74, 138.16, 129.22, 128.43, 128.13, 127.18, 126.83, 123.58, 120.86, 117.08, 113.93, 56.27, 30.99,

26.49, 21.41 ppm; $[\alpha]_D^{RT}$=-31.1 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=12.03 min; minor enantiomer: t_R=15.33 min.

(*S*)-2-(4-Ethylphenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 4]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.21 (d, J(H,H)=8.0 Hz, 2H), 7.09 (d, J(H,H)=8.0 Hz, 2H), 6.97-6.85 (m, 2H), 6.55 (t, J(H,H)=7.4 Hz, 1H), 6.42 (d, J(H,H)=7.9 Hz, 1H), 4.30 (dd, J(H,H)=9.3, 3.4 Hz), 1H), 3.90 (br s, 1H), 2.91-2.74 (m, 1H), 2.73-2.48 (m, 3H), 2.09-1.78 (m, 2H), 1.15 (t, J(H,H)=7.6 Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=144.77, 143.42, 142.02, 129.22, 127.98, 126.81, 126.48, 120.83, 117.03, 113.90, 56.02, 30.95, 28.48, 26.46, 15.56 ppm; $[\alpha]_D^{RT}$=-15.8 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=11.13 min; minor enantiomer: t_R=16,89 min.

(*S*)-2-(2-Naphthyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 5]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.94-7.76 (m, 4H), 7.58-7.42 (m, 3H), 7.13-6.98 (m, 2H), 6.69 (t, J(H,H)=7.4 Hz, 1H), 6.60 (d, J(H,H)=7.8 Hz, 1H), 4.62 (dd, J(H,H)=9.0, 3.6 Hz, 1H), 4.15 (br s, 1H), 3.11-2.88 (m, 1H), 2.78 (dt, J(H,H)=16.3, 4.8 Hz, 1H), 2.29-2.00 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=144.67, 142.19, 133.41, 132.95, 129.28, 128.31, 127.82, 127.64, 126.92, 126.12, 125.73, 125.07, 124.83, 120.95, 117.22, 114.01, 56.35,

30.93, 26.40 ppm; $[\alpha]_D^{RT}$=-28.7 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=21.27 min; minor enantiomer: t_R=40.31 min.

(*S*)-2-(3-Bromophenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 6]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.50-7.43 (m, 1H), 7.32 (d, *J*(H,H)=7.8 Hz, 1H), 7.22 (d, *J*(H,H)=7.7 Hz, 1H), 7.17-7.06 (m, 1H), 6.99-6.86 (m, 2H), 6.58 (t, *J*(H,H)=7.3 Hz, 1H), 6.46 (d, *J*(H,H)=7.9 Hz, 1H), 4.31 (dd, *J*(H,H)=9.1, 3.4 Hz, 1H), 3.92 (br s, 1H), 2.92-2.72 (m, 1H), 2.62 (dt, *J*(H,H)=16.4, 4.9 Hz, 1H), 2.11-1.76 ppm (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=147.23, 144.25, 130.45, 130.11, 129.61, 129.24, 126.94, 125.17, 122.64, 120.75, 117.43, 114.07, 55.70, 30.92, 26.09 ppm; $[\alpha]_D^{RT}$=-42.0 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=17.67 min; minor enantiomer: t_R=28.14 min.

(*S*)-2-[4-(Trifluoromethyl)phenyl]-1,2,3,4-tetrahydroquinoline

[Table 4, entry 7]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.69-7.56 (m, 2H), 7.55-7.47 (m, 2H), 7.11-6.96 (m, 2H), 6.68 (t, *J*(H,H)=7.4 Hz, 1H), 6.58 (d, *J*(H,H)=7.9 Hz, 1H), 4.53 (dd, *J*(H,H)=8.8, 3.4 Hz, 1H), 4.06 (br s, 1H), 3.02-2.83 (m, 1H), 2.71 (dt, *J*(H,H)=16.4, 5.1 Hz, 1H), 2.24-1.88 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): 148.92 (d, *J*(C,F)=1.2 Hz), 144.21, 129.68 (d, *J*(C,F)=32.4 Hz), 129.33, 127.03, 126.32,

125.52 (q, J(C,F)=3.8 Hz), 124,16 (d, J(C,F)=272.0 Hz) 120.76, 117.57, 114.12, 55.78, 30.84, 25.92 ppm; $[\alpha]_D^{RT}$=-41.6 (c=1 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=18.21 min; minor enantiomer: t_R=32.53 min.

(*S*)-2-(1,1'-Biphenyl-4-yl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 8]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.67-7.54 (m, 4H), 7.52-7.31 (m, 5H), 7.09-6.97 (m, 2H), 6.68 (t, J(H,H)=7.4 Hz, 1H), 6.58 (d, J(H,H)=7.8 Hz, 1H), 4.51 (dd, J(H,H)=9.1, 3.4 Hz, 1H), 4.06 (br s, 1H), 3.09-2.87 (m, 1H), 2.78 (dt, J(H,H)=16.4, 4.8 Hz, 1H), 2.29-1.93 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ= 144.66, 143.86, 140.85, 140.42, 129.29, 128.76, 127.29, 127.24, 127.05, 126.96, 126.91, 120.89, 117.22, 114.01, 55.97, 30.94, 26.35 ppm; $[\alpha]_D^{RT}$=-18.5 (c=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 80/20, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=20.76 min; minor enantiomer: t_R=34.58 min.

(*S*)-2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 9]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.32 (d, J(H,H)=8.6 Hz, 2H), 7.09-6.96 (m, 2H), 6.90 (d, J(H,H)=8.6 Hz, 2H), 6.66 (t, J(H,H)=7.3 Hz, 1H), 6.45 (d, J(H,H)=8.1 Hz, 1H), 4.39 (dd, J(H,H)=9.3, 3.2 Hz, 1H), 4.01 (br s, 1H), 3.82 (s, 3H), 3.06-2.85 (m, 1H), 2.75 (dt, J(H,H)=16.4, 4.5 Hz, 1H), 2.20-1.86 ppm (m, 2H); ^{13}C NMR (62.5

MHz, $CDCl_3$): δ= 158.97, 144.79, 136.88, 129.25, 127.60, 126.83, 120.87, 117.10, 113.92, 55.72, 55.29, 31.07, 26.52, ppm; $[\alpha]_D^{RT}$=-22.1 (c=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=15.37 min; minor enantiomer: t_R=25.09 min.

(*S*)-2-(2-Furyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 10]

^1H NMR (250 MHz, $CDCl_3$): δ=7.20-7.08 (m, 1H), 7.01-6.83 (m, 4H), 6.59 (t, J(H,H)=7.4 Hz, 1H), 6.45 (d, J(H,H)= 7.5 Hz, 1H), 4.67 (dd, J(H,H)=8.9, 3.4 Hz, 1H), 4.09 (br s, 1H), 2.95-2.77 (m, 1H), 2.69 (dt, J(H,H)=16.5, 5.0 Hz, 1H), 2.23-1.89 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=148.87, 143.95, 129.24, 126.87, 126.61, 124.01, 123.50, 120.88, 117.66, 114.26, 51.97, 31.77, 26.12 ppm; $[\alpha]_D^{RT}$=-16.2 (c=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=17.44 min; minor enantiomer: t_R=22.91 min.

(*S*)-2-(4-Chlorophenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 11]

^1H NMR (250 MHz, $CDCl_3$): δ=7.31-7.17 (m, 4H), 7.02-6.89 (m, 2H), 6.61 (t, J(H,H)=7.0 Hz, 1H), 6.49 (d, J(H,H)=7.8 Hz, 1H), 4.37 (dd, J(H,H)=9.0, 3.4 Hz, 1H), 3.96 (br s, 1H), 2.95-2.75 (m, 1H), 2.65 (dt, J(H,H)=16.4, 4.9 Hz, 1H), 2.16-1.77 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=144.38, 143.33, 133.01, 129.30, 128.68, 127.89, 126.95, 120.80, 117.42, 114.06, 55.59, 30.95, 26.11 ppm;

$[\alpha]_D^{RT}$=-40.9 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=13,35 min; minor enantiomer: t_R=15,50 min.

(*S*)-2-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 12]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.43-7.30 (m, 2H), 7.11-6.96 (m, 4H), 6.67(t, *J*(H,H)=7.4 Hz, 1H), 6.55 (d, *J*(H,H)=7.7 Hz, 1H), 4.43 (dd, *J*(H,H)=9.2, 3.3 Hz, 1H), 4.01 (br s, 1H), 3.03-2.84 (m, 1H), 2.73 (dt, *J*(H,H)=16.4, 4.8 Hz, 1H), 2.21-1.84 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$, 25 °C, TMS): δ=162.12 (d, *J*(C,F)=245.2 Hz), 144.45, 140.50 (d, *J*(C,F)=3.1 Hz), 129.29, 128.05 (d, *J*(C,F)=8.0 Hz), 126.92, 120.82, 117.35, 115.32 (d, *J*(C,F)=21.3 Hz), 114.04, 55.60, 31.11 (d, *J*(C,F)=0.67 Hz), 26.28 ppm; $[\alpha]_D^{RT}$=-42.8 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=14.56 min; minor enantiomer: t_R=23.87 min.

2-(3,4,5-Trimethoxyphenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 13]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.09-6.95 (m, 2H), 6.71-6.61 (m, 3H), 6.56 (d, *J*(H,H)=7.9 Hz, 1H), 4.36 (dd, *J*(H,H)=9.7, 3.2 Hz, 1H), 4.02 (br s, 1H), 3.95-3.77 (m, 9H), 3.07-2.87 (m, 1H), 2.77 (dt, *J*(H,H)=16.4, 4.3 Hz, 1H), 2.23-1.87 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=153.34, 144.63, 140.51, 137.20, 129.27, 126.88, 120.84, 117.35, 114.04, 103.40, 60.80, 56.74, 56.12, 31.41,

26.71 ppm; $[\alpha]_D^{RT}$=-30.6 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 65/35, flow rate = 1.0 mL min^{-1}, major enantiomer: t_R=10.38 min; minor enantiomer: t_R=17.16 min.

(*S*)-2-(3-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline

[Table 4, entry 14]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.21 (d, *J*(H,H)=7.7 Hz, 1H), 7.03-6.88 (m, 4H), 6.84-6.75 (m, 1H), 6.61 (t, *J*(H,H)=7.4 Hz, 1H), 6.50 (d, *J*(H,H)=7.9 Hz, 1H), 4.37 (dd, *J*(H,H)=9.3, 3.4 Hz, 1H), 4.01 (br s, 1H), 3.77 (s, 3H), 2.99-2.80 (m, 1H), 2.70 (dt, *J*(H,H)=16.4, 4.7 Hz, 1H), 2.19-1.82 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=159.70, 146.37, 144.46, 129.37, 129.08, 126.70, 120.70, 118.70, 117.01, 113.82, 112.62, 111.91, 56.08, 55.04, 30.80, 26.23, ppm; $[\alpha]_D^{RT}$=-31.9 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-propanol = 95/5, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=36.30 min; minor enantiomer: t_R=39.34 min.

(*R*)-3-Phenyl-3,4-dihydro-2*H*-1,4-benzoxazine

[Scheme 1, compound 6]

^{1}H NMR (250 MHz, $CDCl_3$): δ=7.43-7.21 (m, 5H), 6.82-6.69 (m, 2H), 6.68-6.56 (m, 2H), 4.44 (dd, *J*(H,H)=8.6, 3.0 Hz, 1H), 4.22 (dd, *J*(H,H)=10.6, 3.0 Hz, 1H), 3.93 (dd, *J*(H,H)=10.6, 8.6 Hz, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$): δ=143.52, 139.14, 133.87, 128.81, 128.32, 127.16, 121.46, 118.91, 116.58, 115.34, 70.96, 54.22 ppm; $[\alpha]_D^{RT}$=-133.1 (*c*=1.0 in $CHCl_3$); HPLC conditions: n-hexane/2-

propanol = 90/10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R=19.26 min; minor enantiomer: t_R=27.13 min.

Determination of configuration

The absolute (*S*)-configuration of the 2-aryl tetrahydroquinolines are based on the X-ray crystal structure of 2-(4-chlorophenyl)-1,2,3,4-tetrahydroquinoline (see figure 3). All other compounds were assigned accordingly. The result and the optical rotation data are in agreement with our previously reported findings (M. Rueping, A. P. Antonchick, T. Theissmann, *Angew. Chem. Int. Ed.* **2006**, *45*, 3683-3686, *Angew. Chem.* **2006**, *118*, 3765-3768; M. Rueping, A. P. Antonchick, T. Theissmann, *Angew. Chem. Int. Ed.* **2006**, *45*, 6751-6755, *Angew. Chem.* **2006**, *118*, 6903-6907).

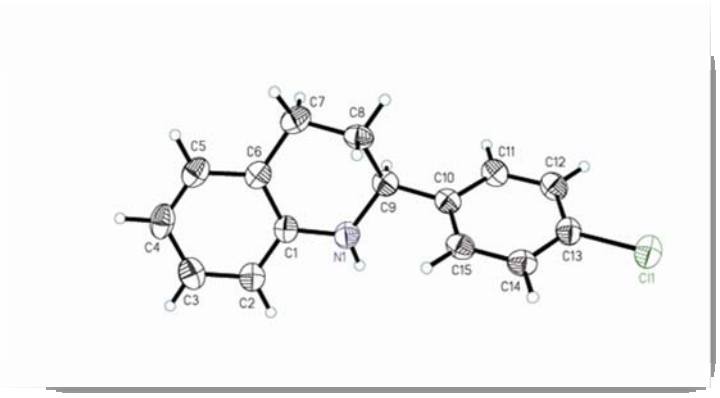
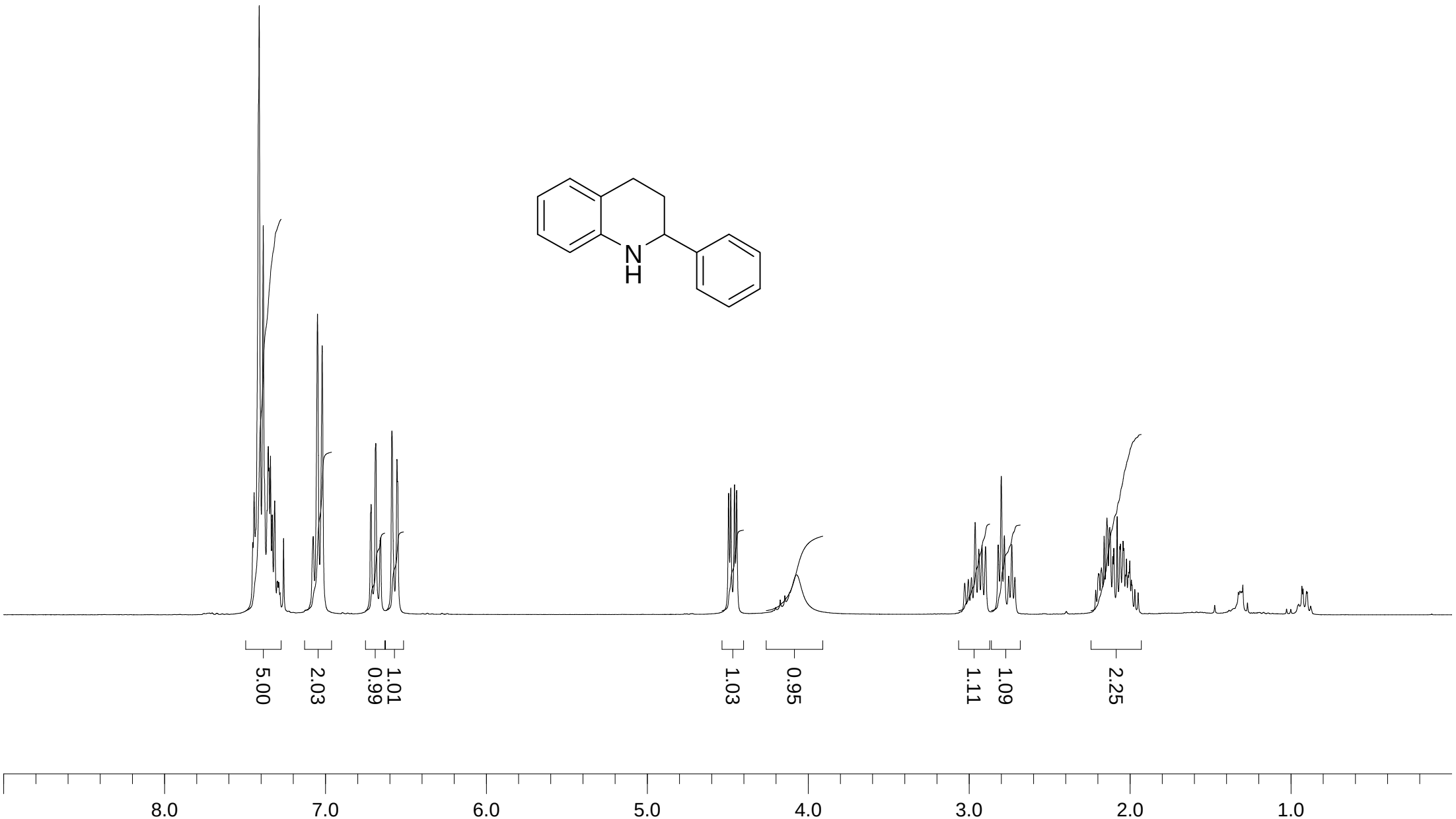
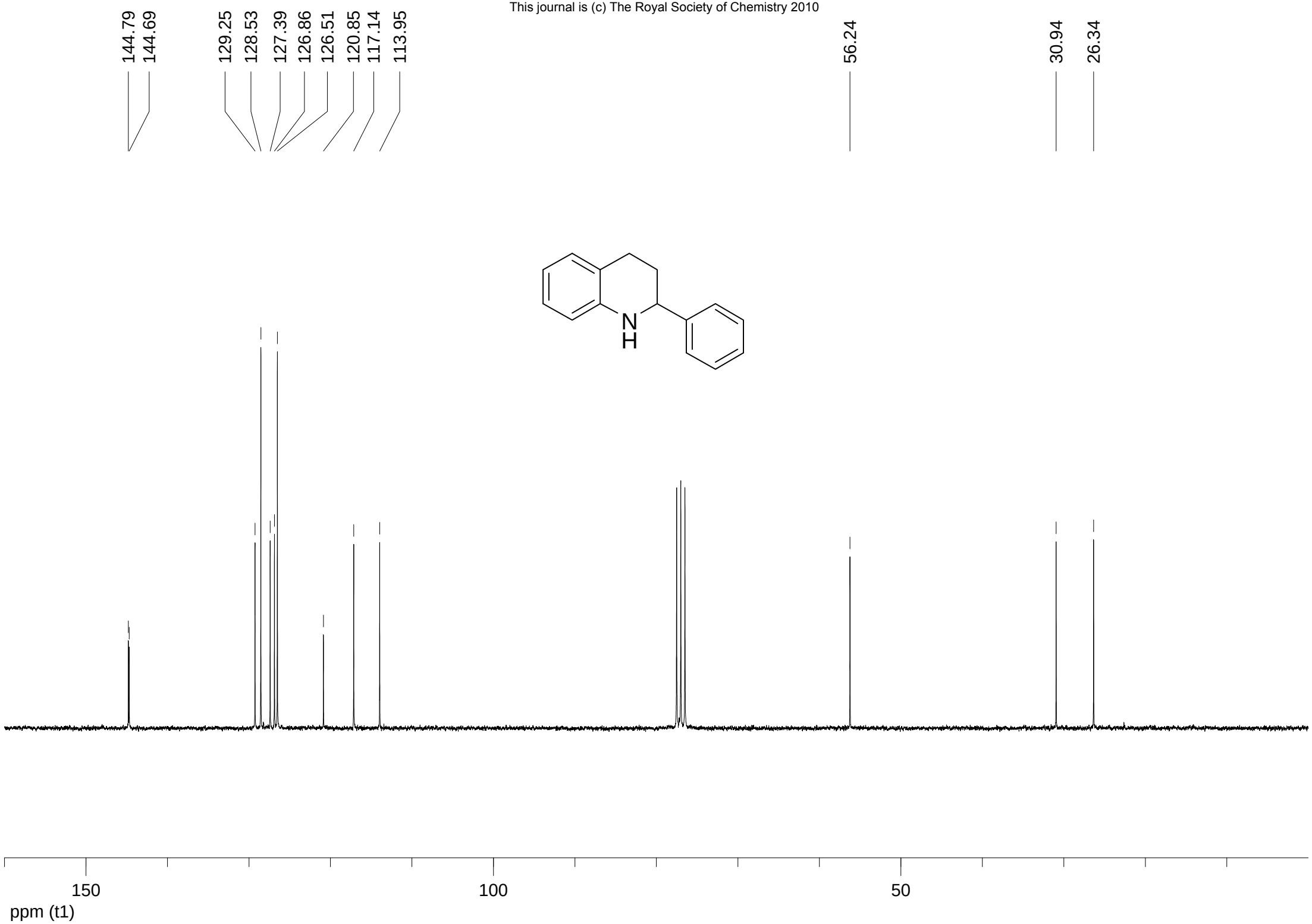


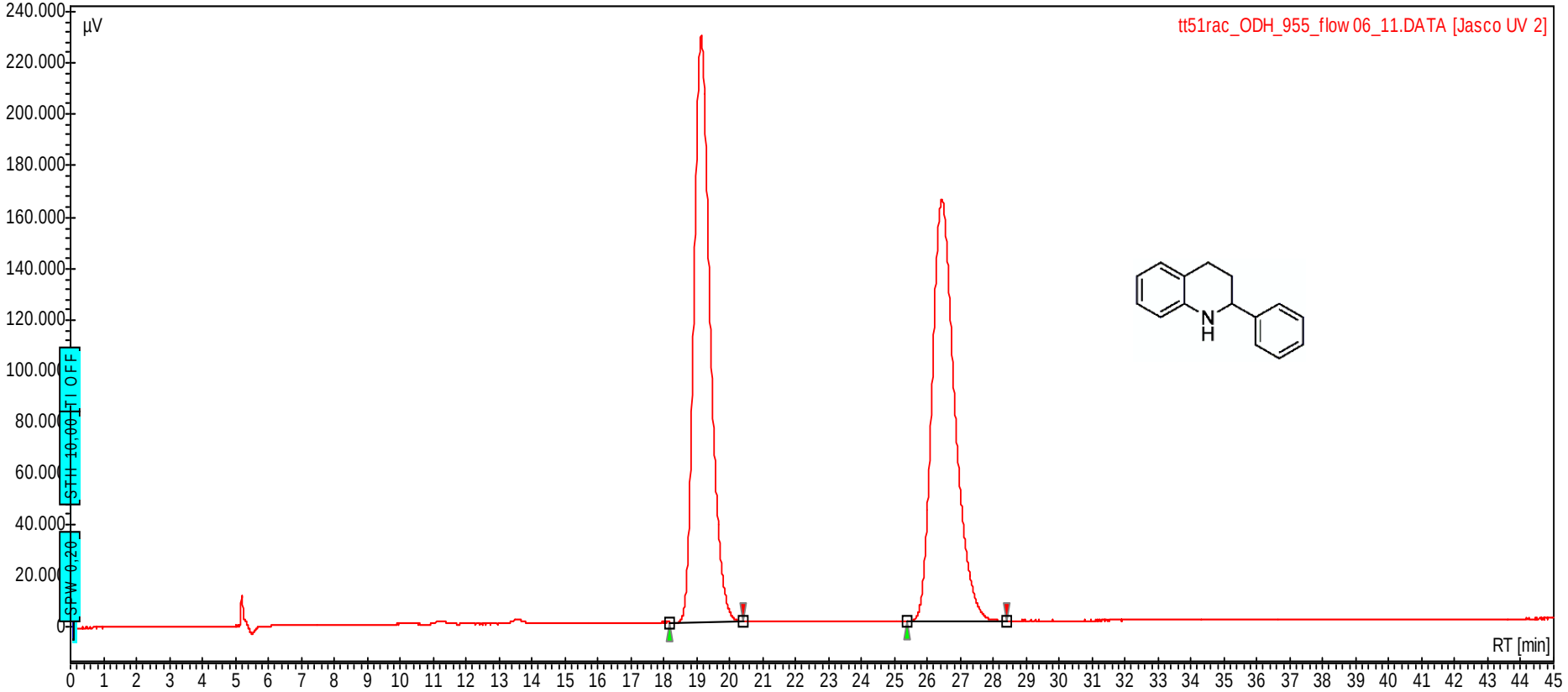
Figure 3: X-ray crystal structure of 2-(4-Chlorophenyl)-tetrahydroquinoline.




144.79
144.69
129.25
128.53
127.39
126.86
126.51
120.85
117.14
113.95
56.24
30.94
26.34
N
H
150
100
50
ppm (t1)

Chromatogram : tt51rac_ODH_955_flow06_11

Data file: tt51rac_ODH_955_flow06_11.DATA
Method: HPLC1_ODH_955_flow06_acq_45
Date: 23.05.2009 10:40:53

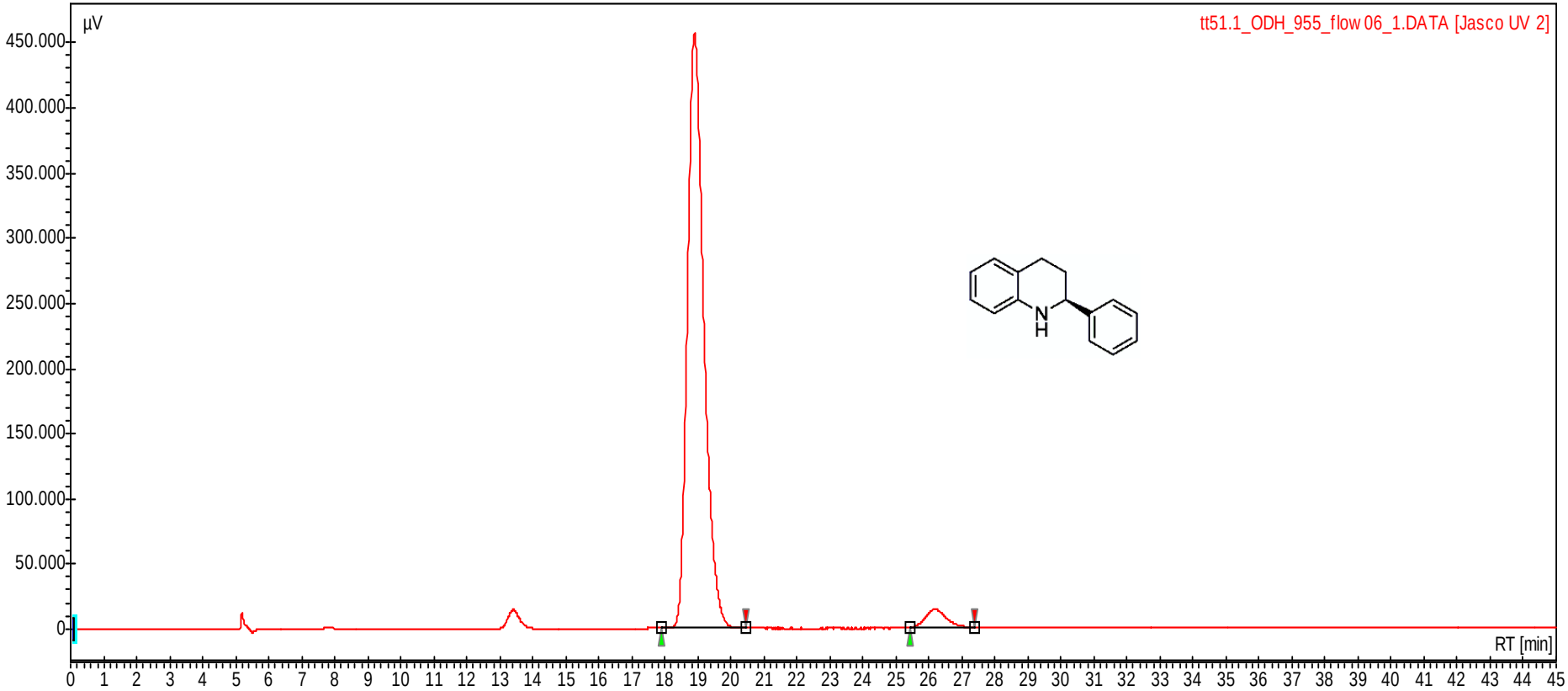


tt51rac_ODH_955_flow06_11.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	18,177	19,133	20,408	49,923
1	25,382	26,433	28,404	50,077
Total				100,000

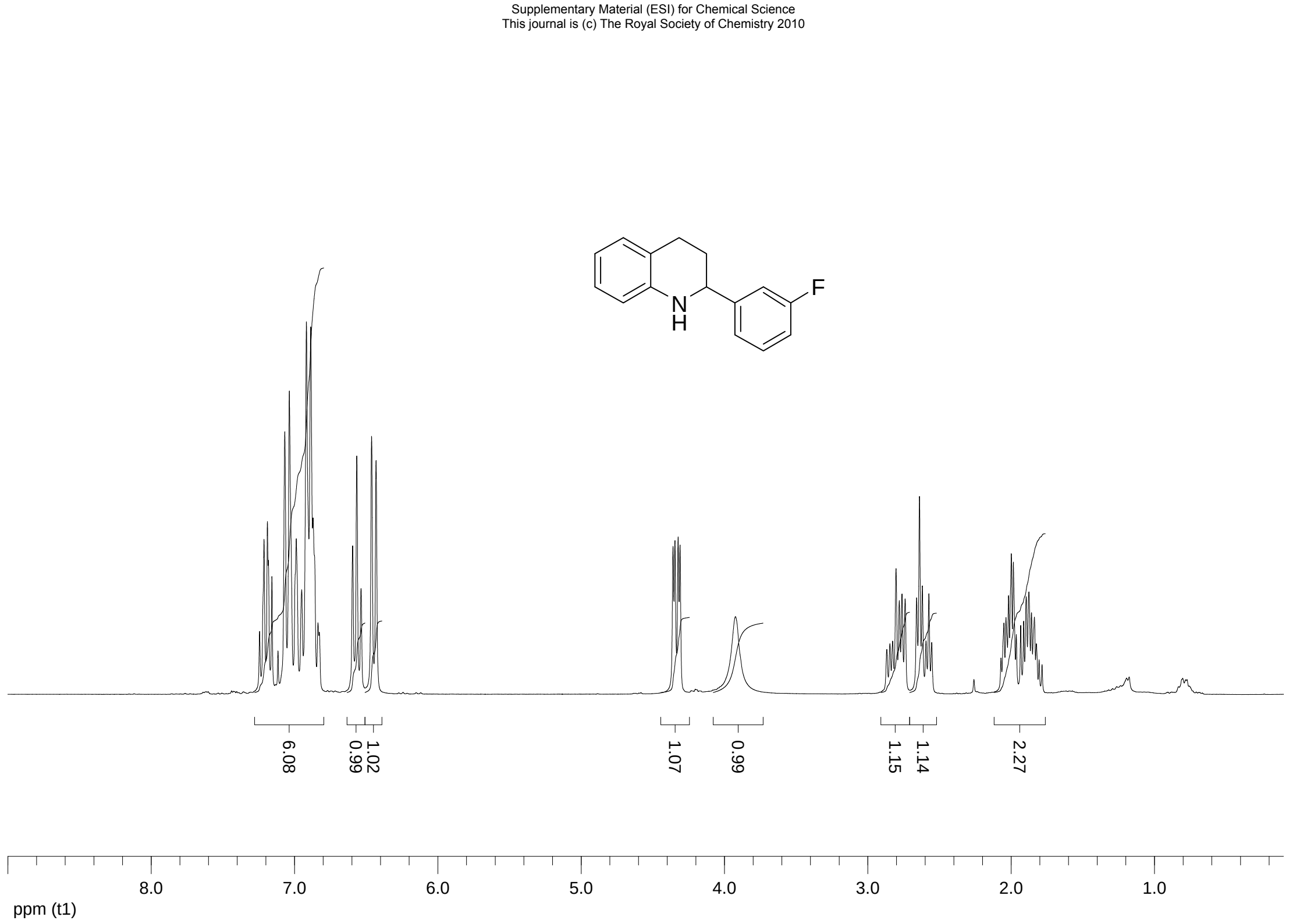
Chromatogram : tt51.1_ODH_955_flow06_1

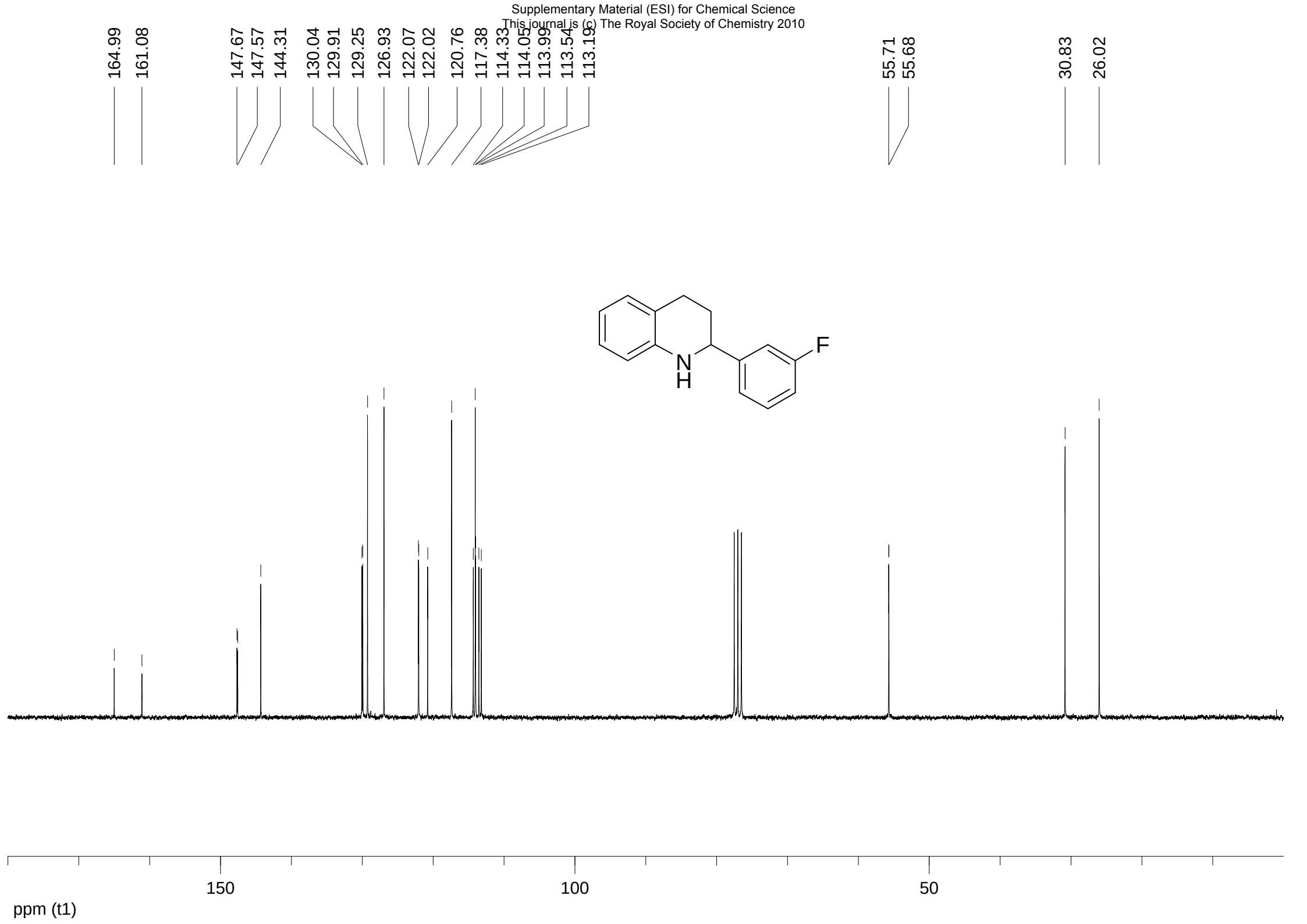
Data file: tt51.1_ODH_955_flow06_1.DATA
Method: HPLC1_ODH_955_flow06_acq_45
Date: 23.05.2009 11:28:36



tt51.1_ODH_955_flow06_1.DATA [Jasco UV 2]

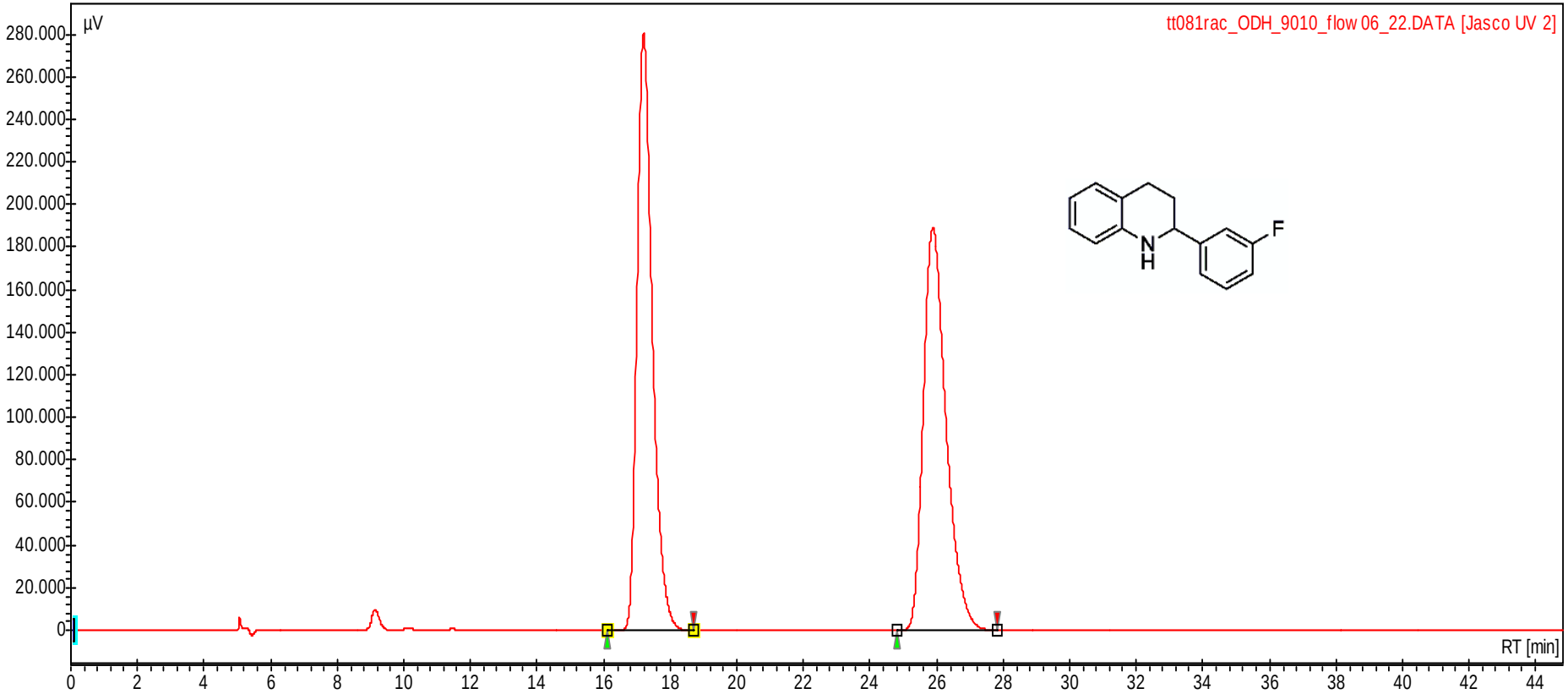
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17,898	18,900	20,455	96,038
2	25,440	26,175	27,364	3,962
Total				100,000





Chromatogram : tt081rac_ODH_9010_flow06_22

Data file: tt081rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_60
Date: 20.05.2009 01:56:55

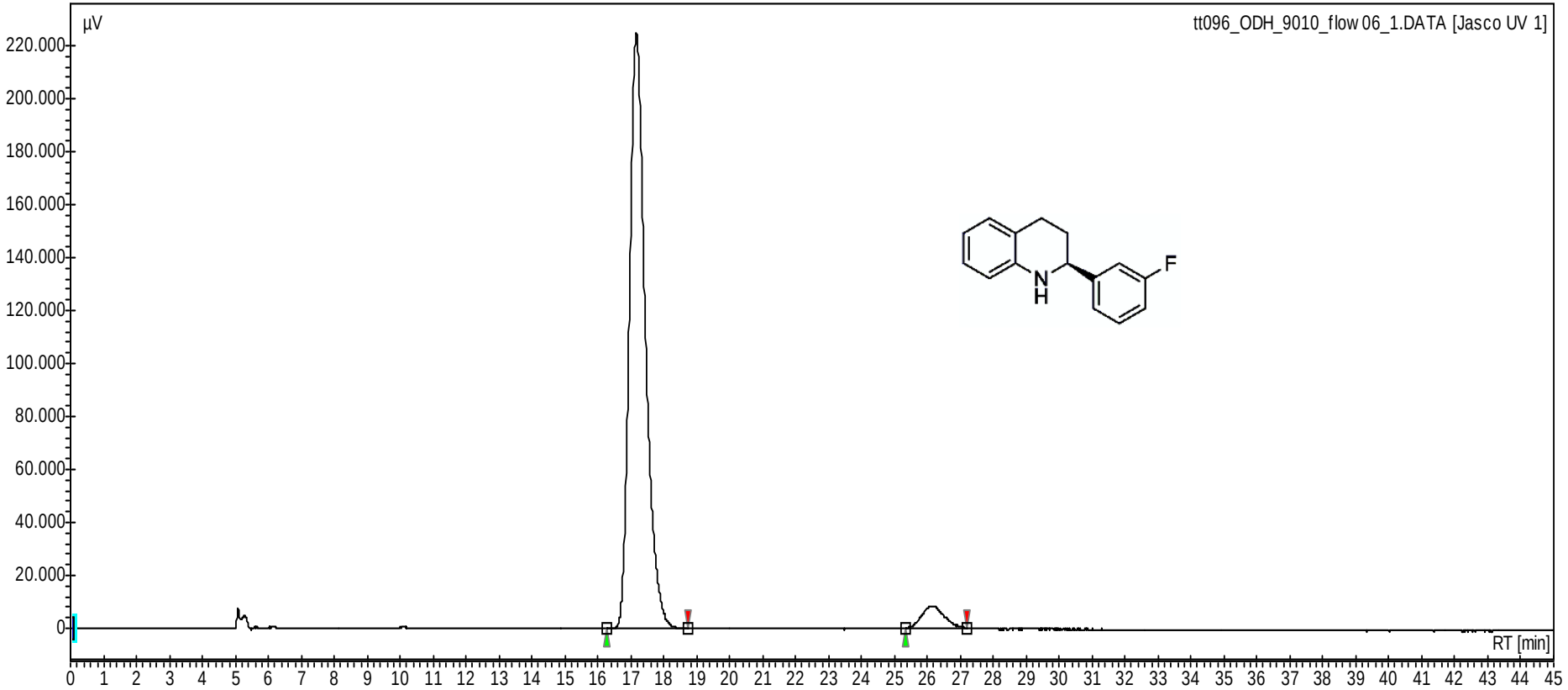


tt081rac_ODH_9010_flow06_22.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16,116	17,200	18,719	49,967
2	24,793	25,892	27,831	50,033
Total				100,000

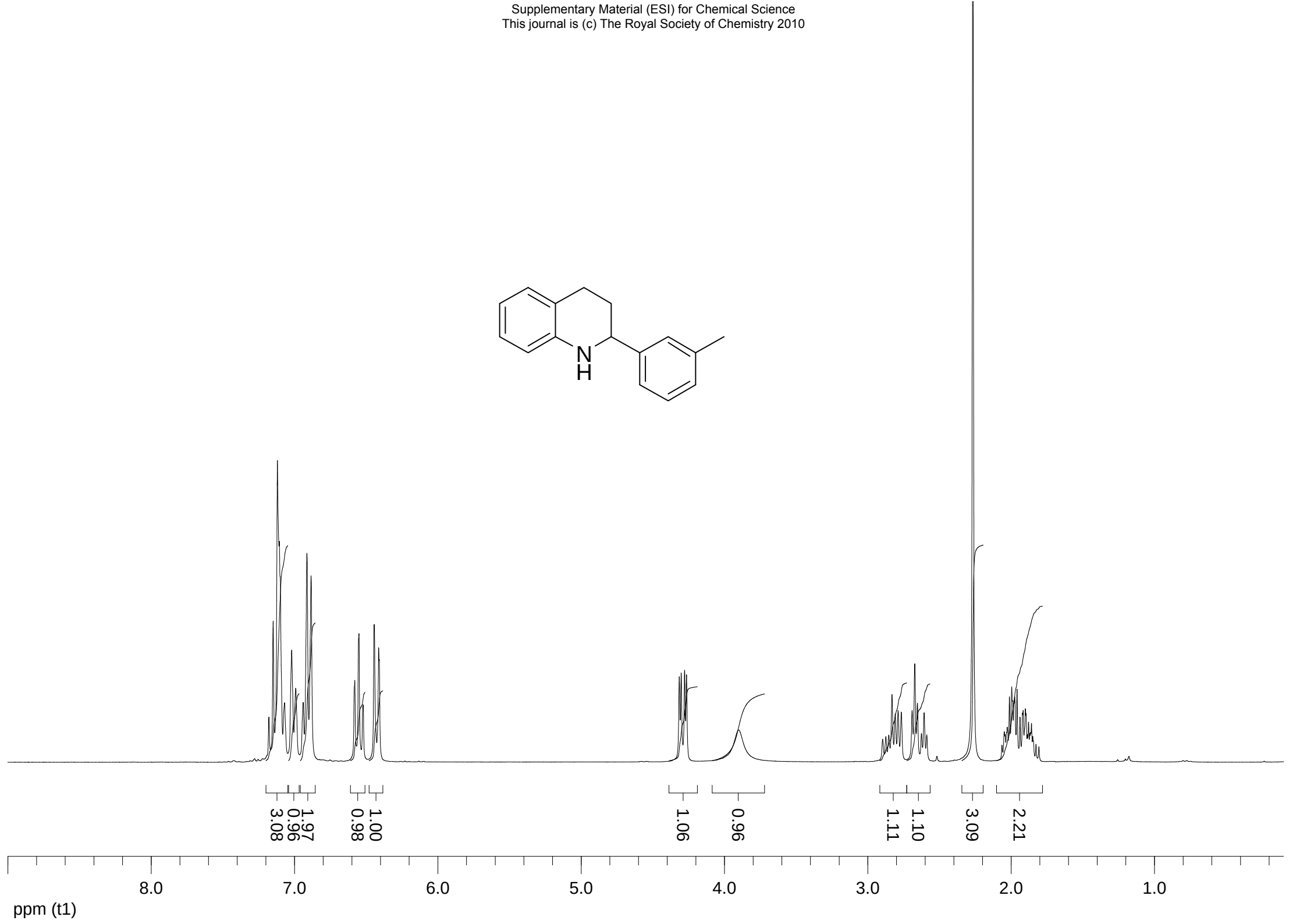
Chromatogram : tt096_ODH_9010_flow06_1

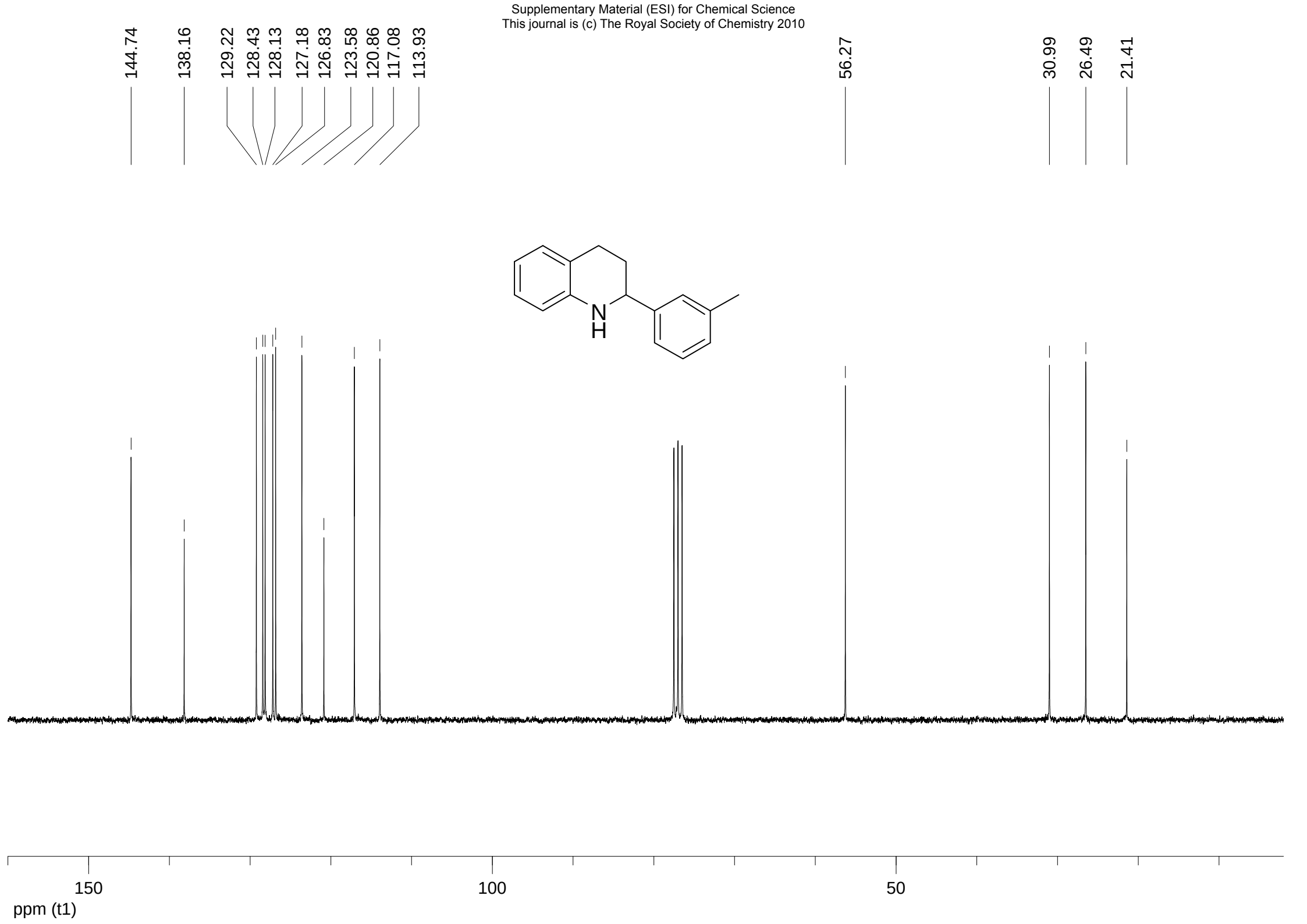
Data file: tt096_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 22.05.2009 18:46:49



tt096_ODH_9010_flow06_1.DATA [Jasco UV 1]

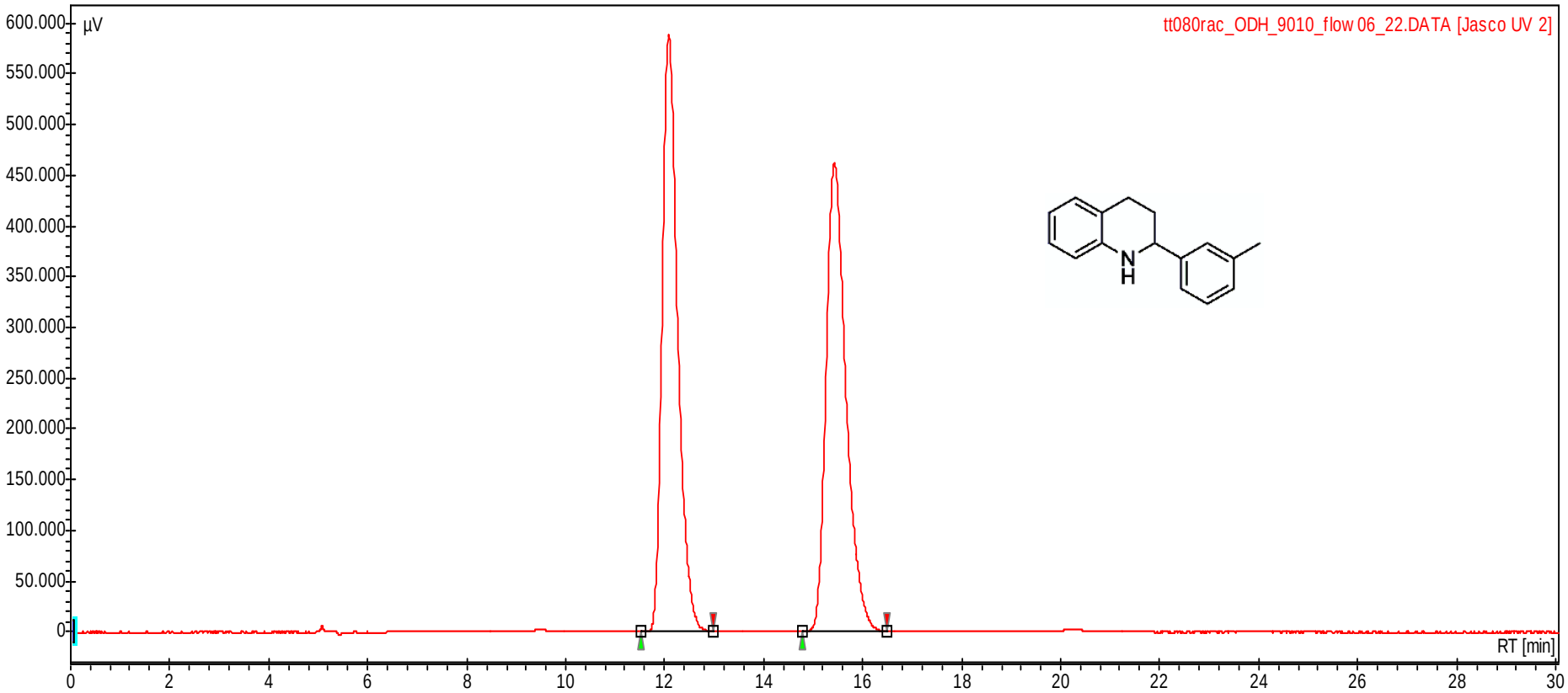
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16,271	17,167	18,735	94,903
2	25,336	26,142	27,195	5,097
Total				100,000




144.74
138.16
129.22
128.43
128.13
127.18
126.83
123.58
120.86
117.08
113.93
56.27
30.99
26.49
21.41
N
H
150
100
50
ppm (t1)

Chromatogram : tt080rac_ODH_9010_flow06_22

Data file: tt080rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_60
Date: 20.05.2009 00:54:12

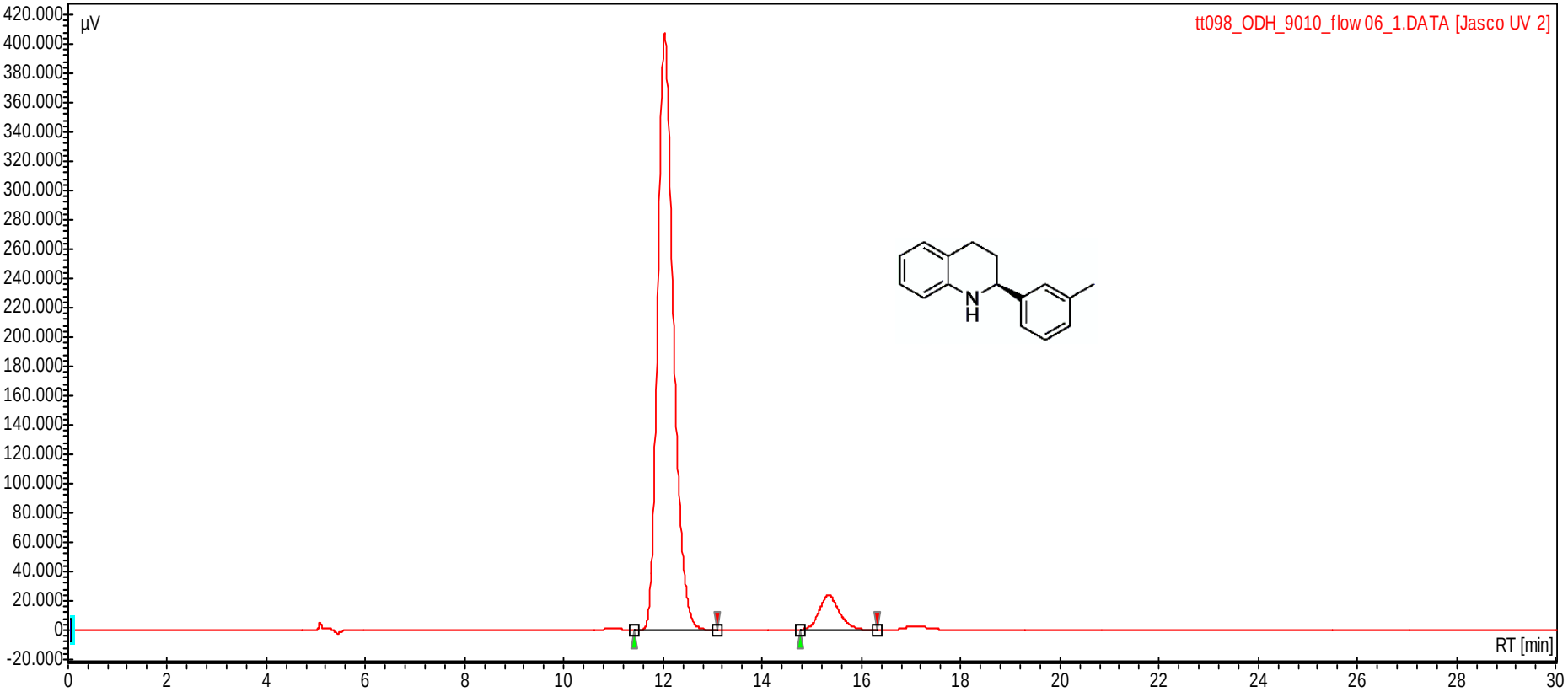


tt080rac_ODH_9010_flow06_22.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	11,523	12,083	12,987	49,732
2	14,797	15,433	16,479	50,268
Total				100,000

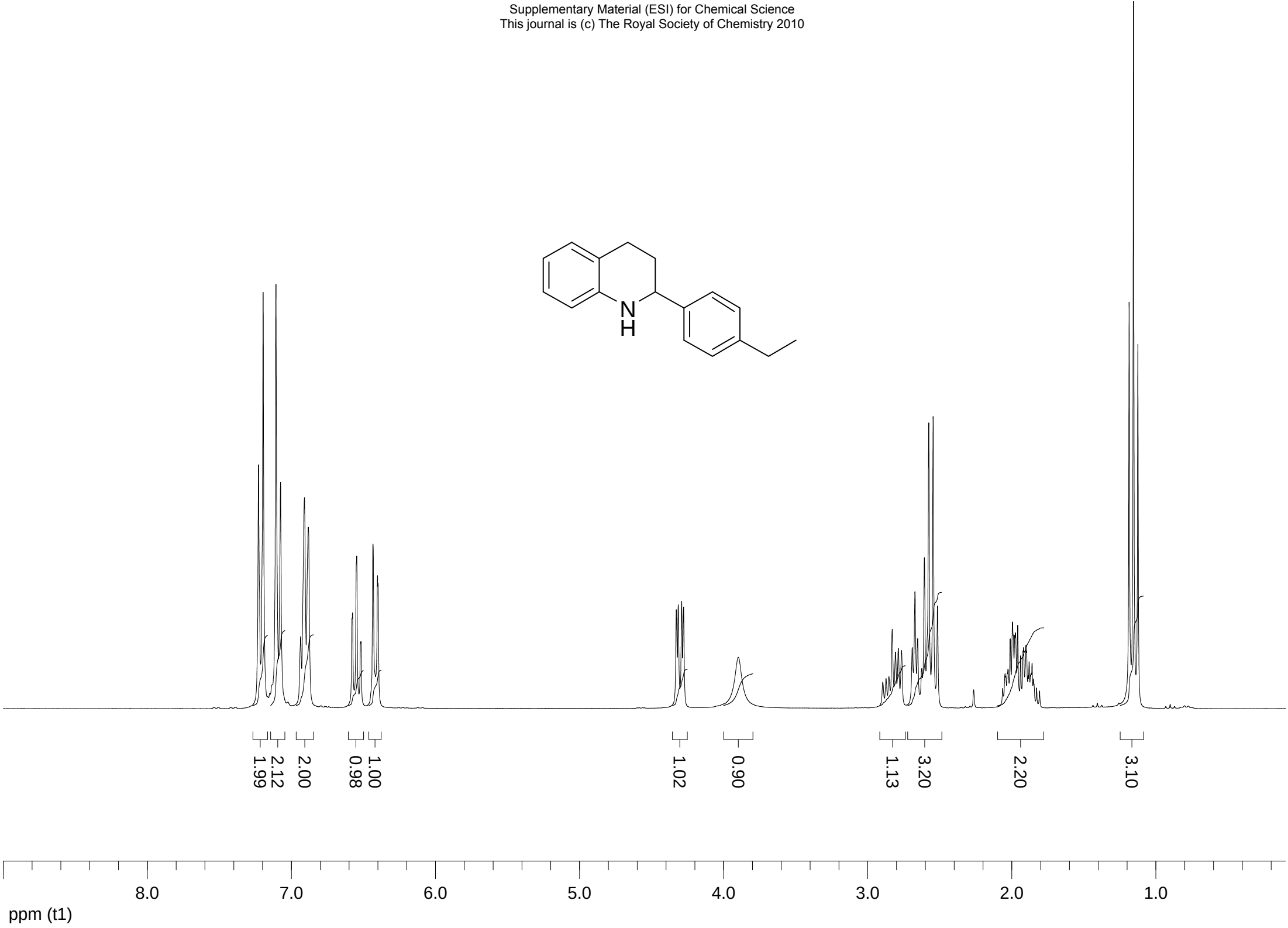
Chromatogram : tt098_ODH_9010_flow06_1

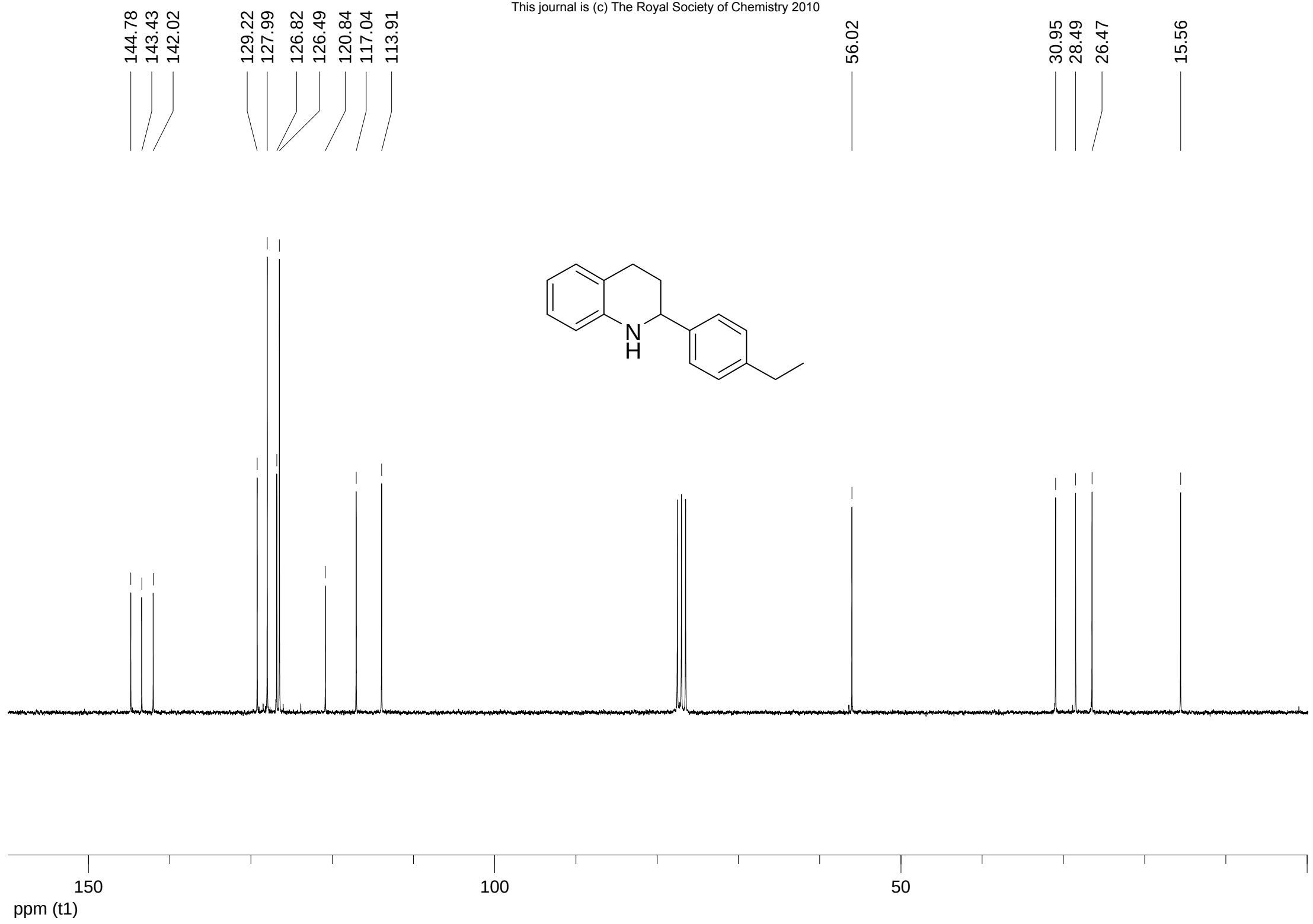
Data file: tt098_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 22.05.2009 20:22:14



tt098_ODH_9010_flow06_1.DATA [Jasco UV 2]

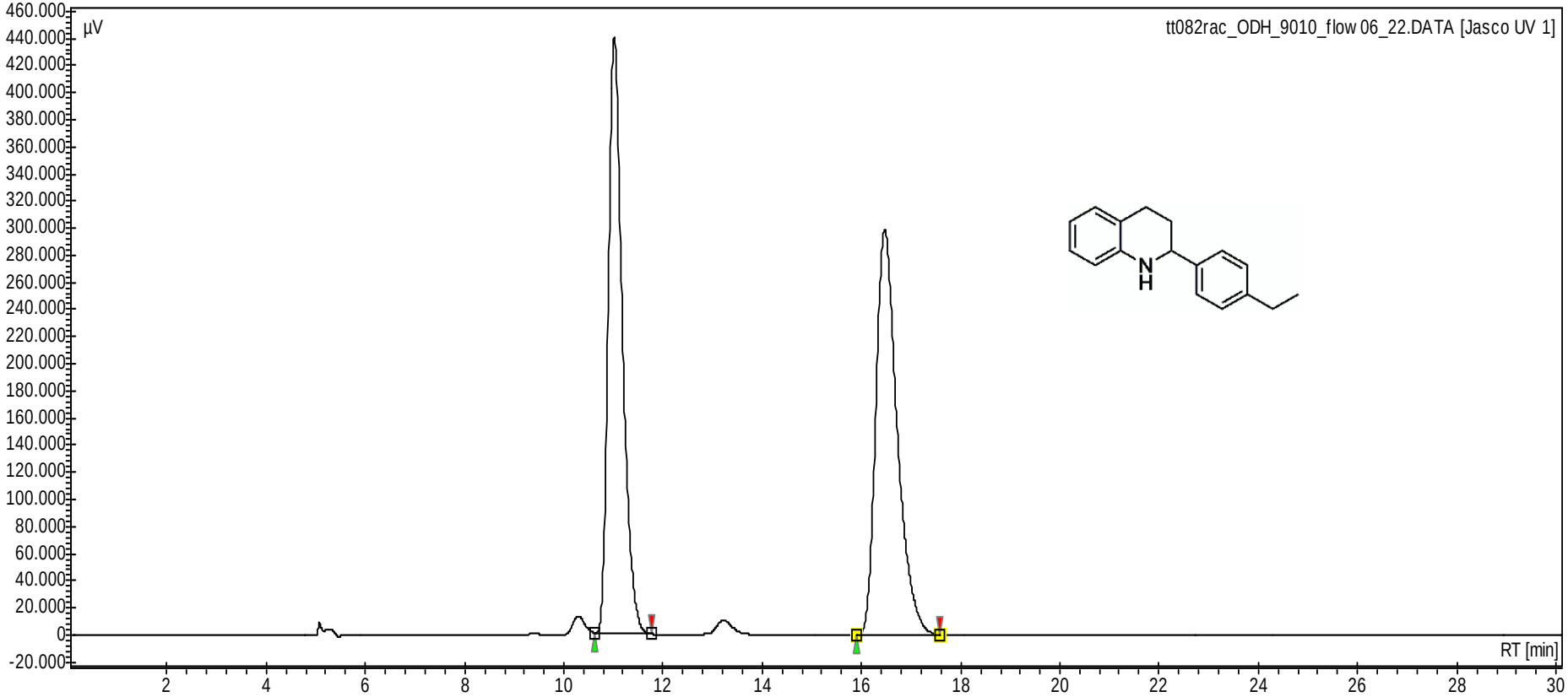
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	11,405	12,025	13,104	93,016
2	14,765	15,333	16,325	6,984
Total				100,000




144.78
143.43
142.02
129.22
127.99
126.82
126.49
120.84
117.04
113.91
56.02
30.95
28.49
26.47
15.56
N
H
150
100
50
ppm (t1)

Chromatogram : tt082rac_ODH_9010_flow06_22

Data file: tt082rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_60
Date: 20.05.2009 02:59:37

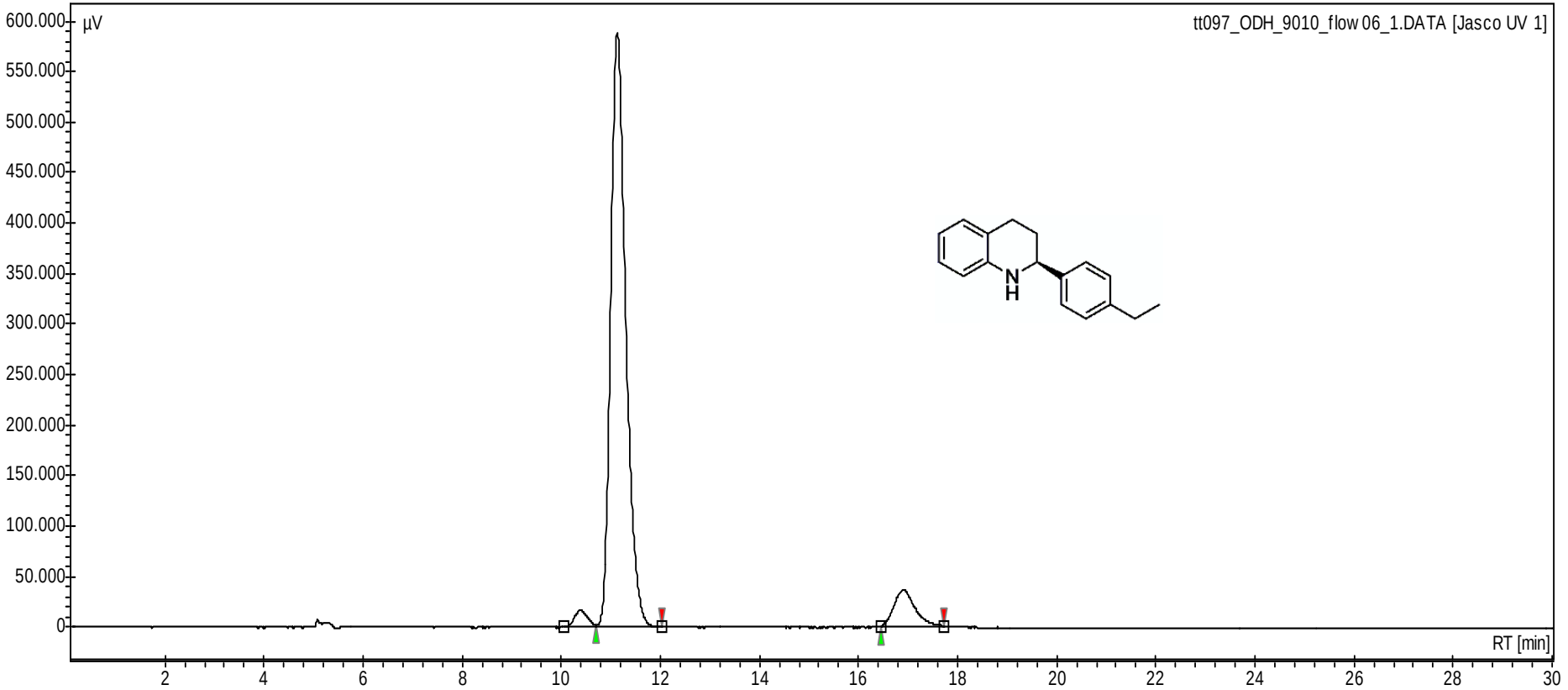


tt082rac_ODH_9010_flow06_22.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	10,629	11,017	11,772	49,446
1	15,903	16,467	17,587	50,554
Total				100,000

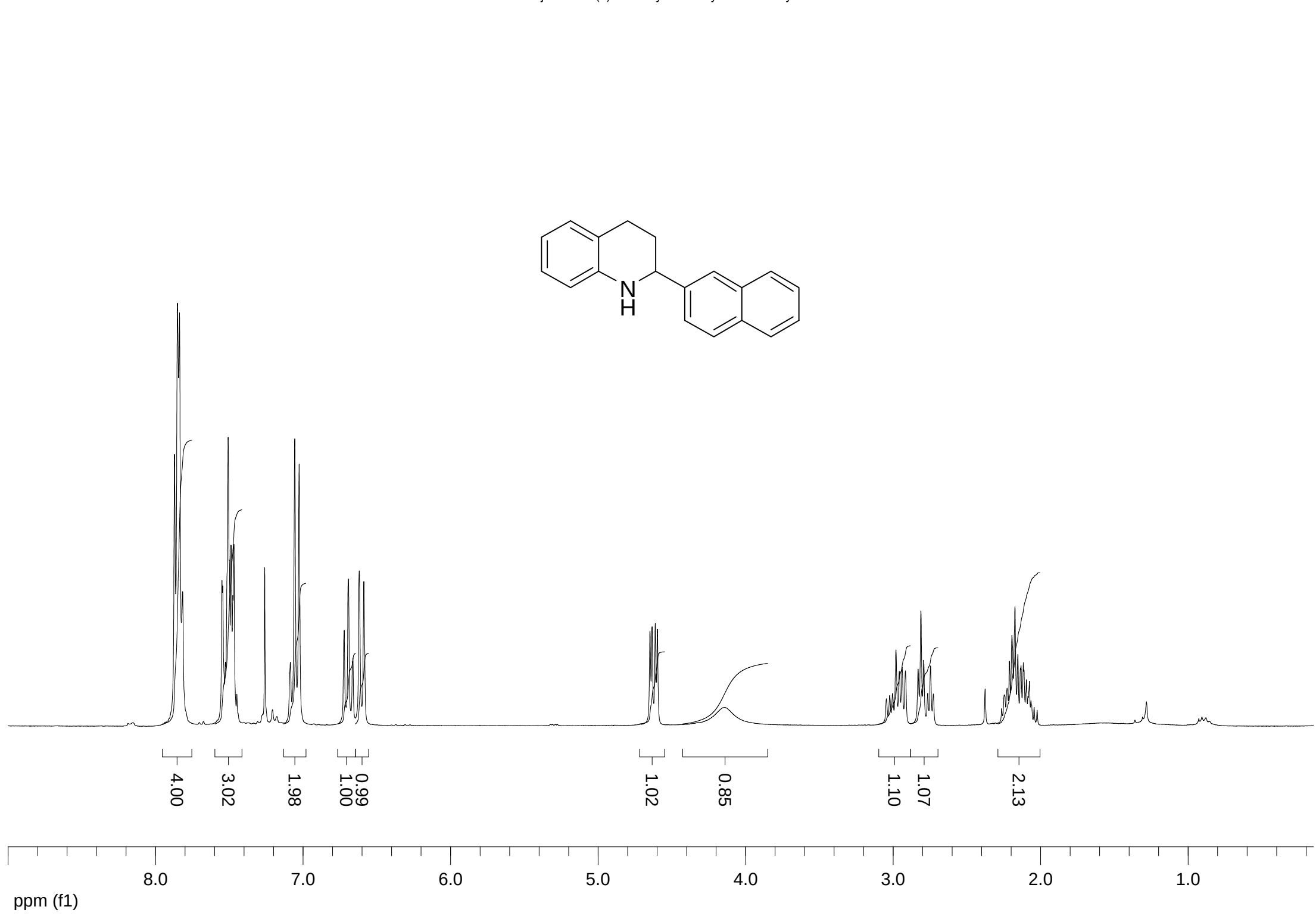
Chromatogram : tt097_ODH_9010_flow06_1

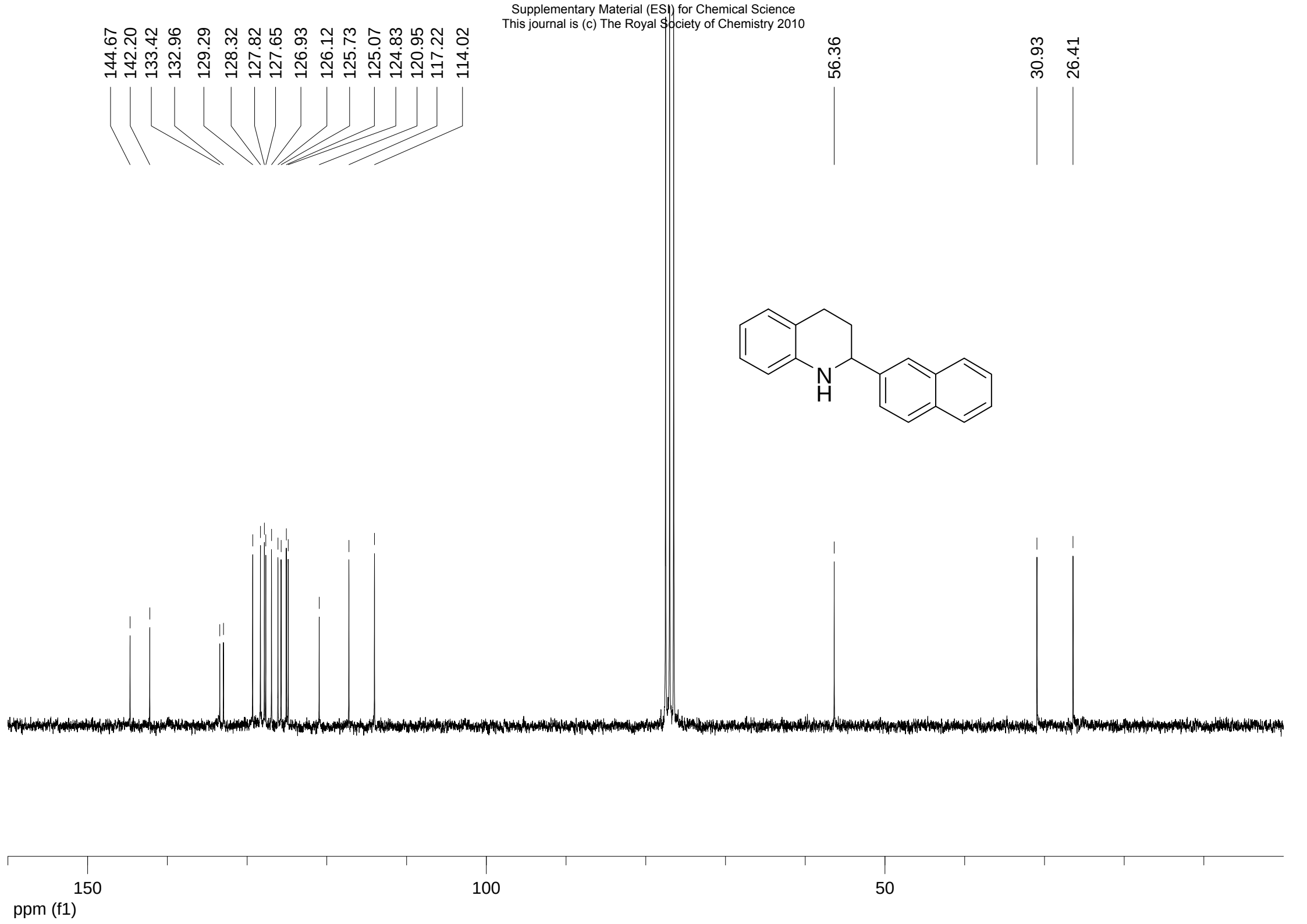
Data file: tt097_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 22.05.2009 19:34:31



tt097_ODH_9010_flow06_1.DATA [Jasco UV 1]

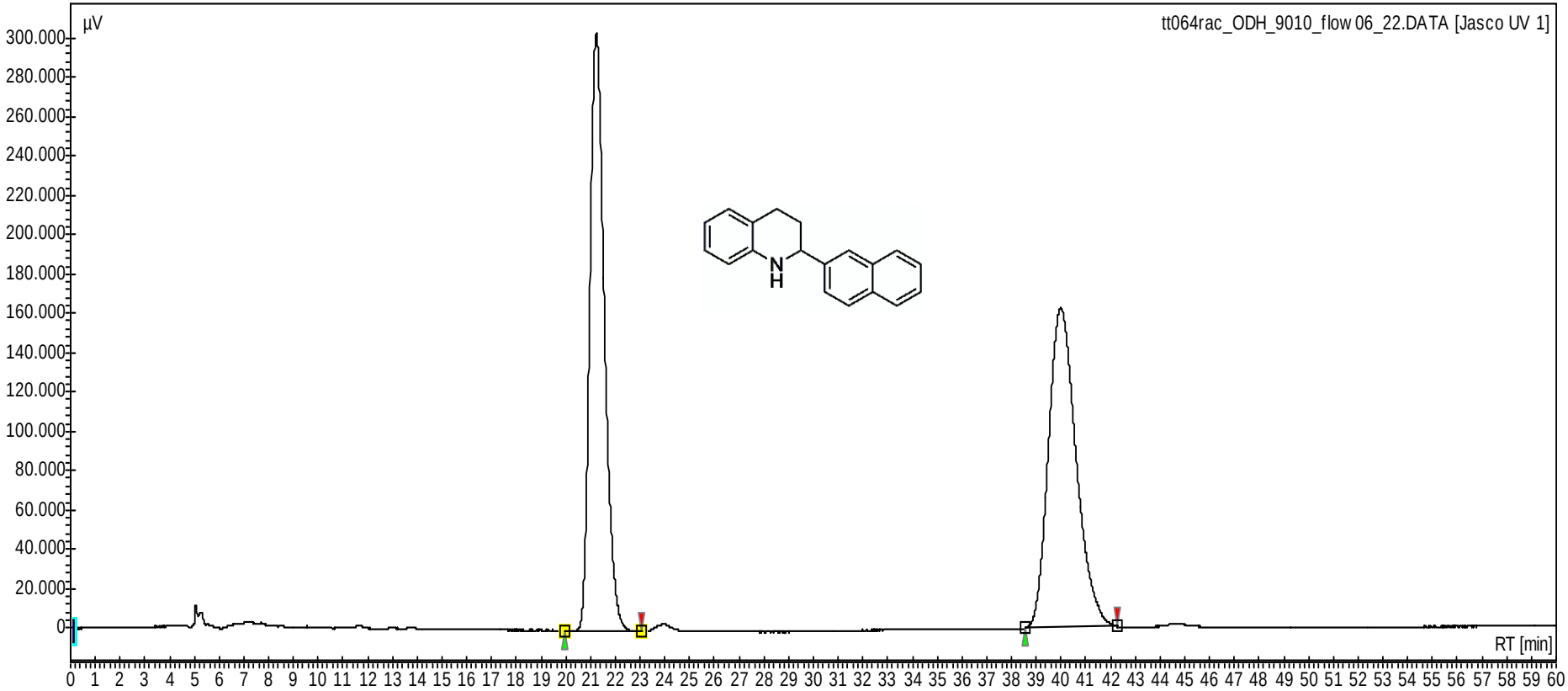
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	10,692	11,125	12,017	92,247
2	16,454	16,892	17,722	7,753
Total				100,000





Chromatogram : tt064rac_ODH_9010_flow06_22

Data file: tt064rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_60
Date: 19.05.2009 15:09:05

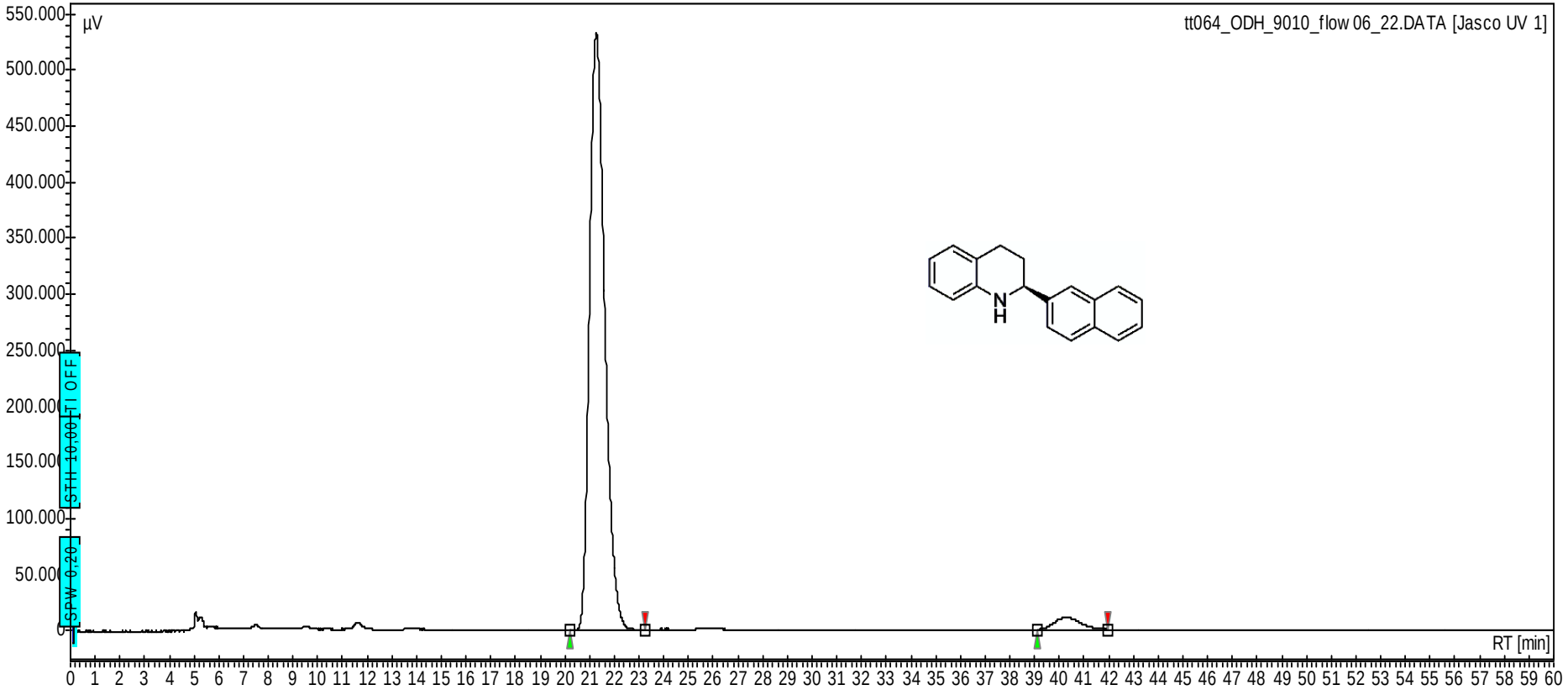


tt064rac_ODH_9010_flow06_22.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	19,959	21,233	23,058	49,464
2	38,554	39,992	42,273	50,536
Total				100,000

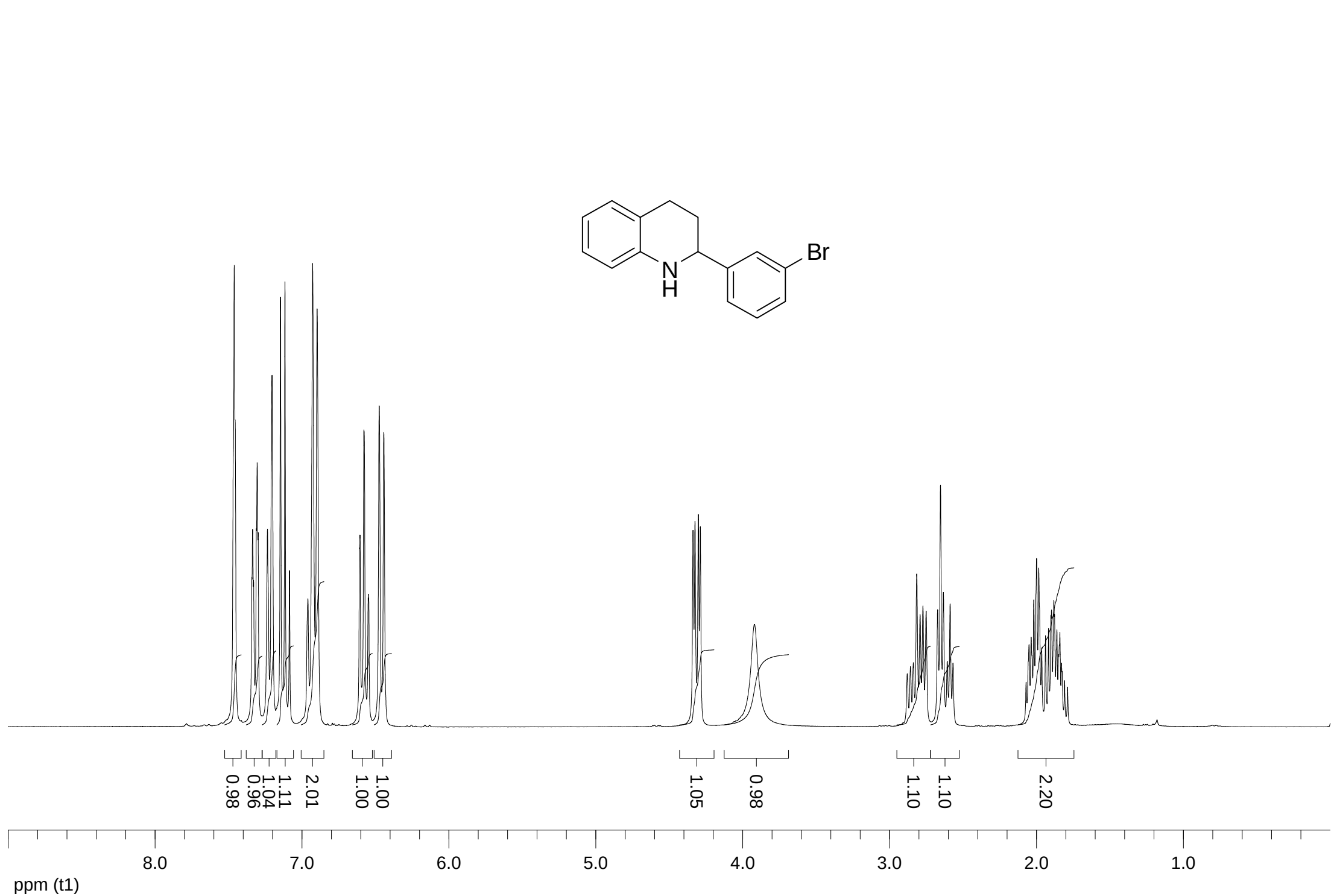
Chromatogram : tt064_ODH_9010_flow06_22

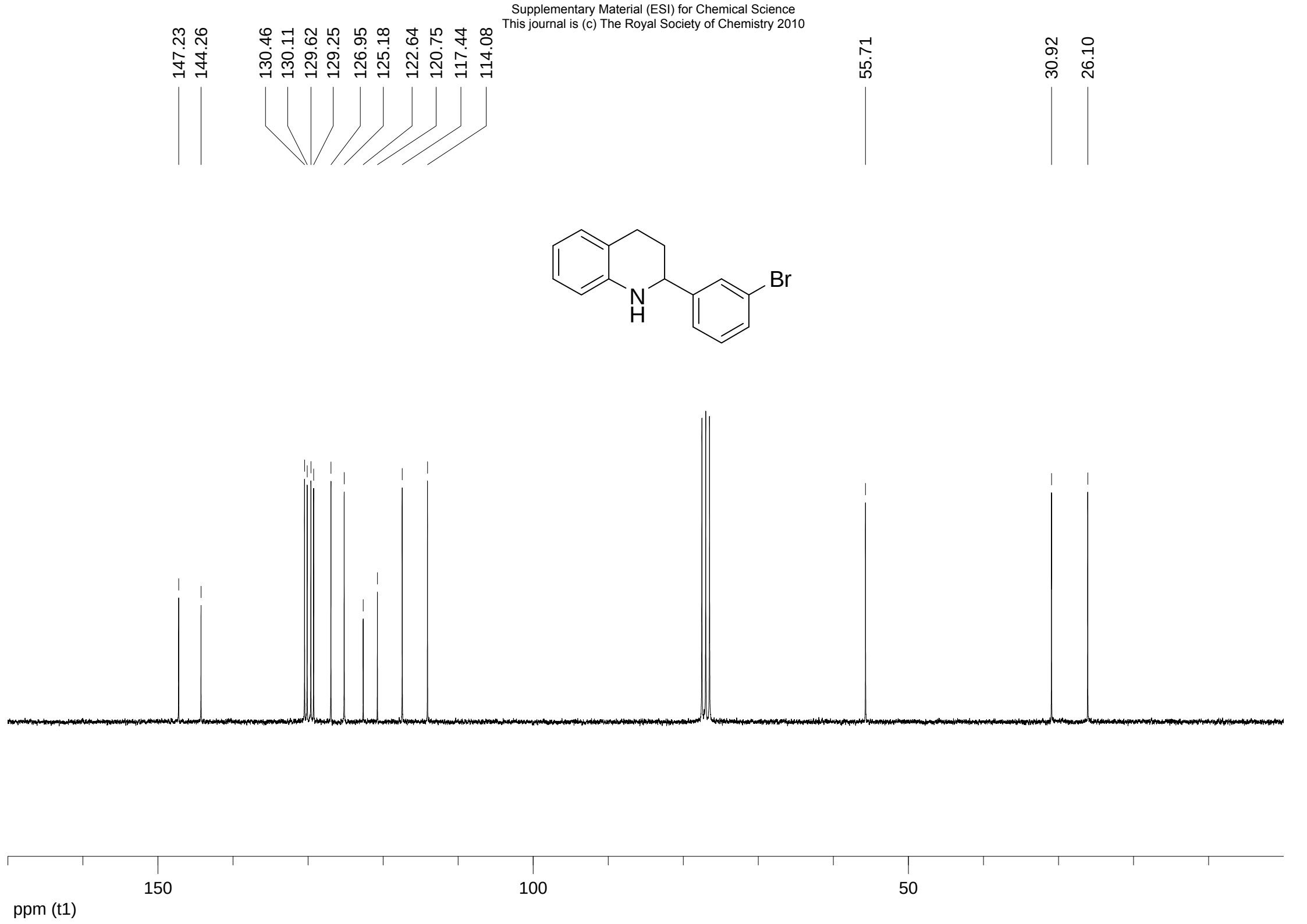
Data file: tt064_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_60
Date: 19.05.2009 16:11:50



tt064_ODH_9010_flow06_22.DATA [Jasco UV 1]

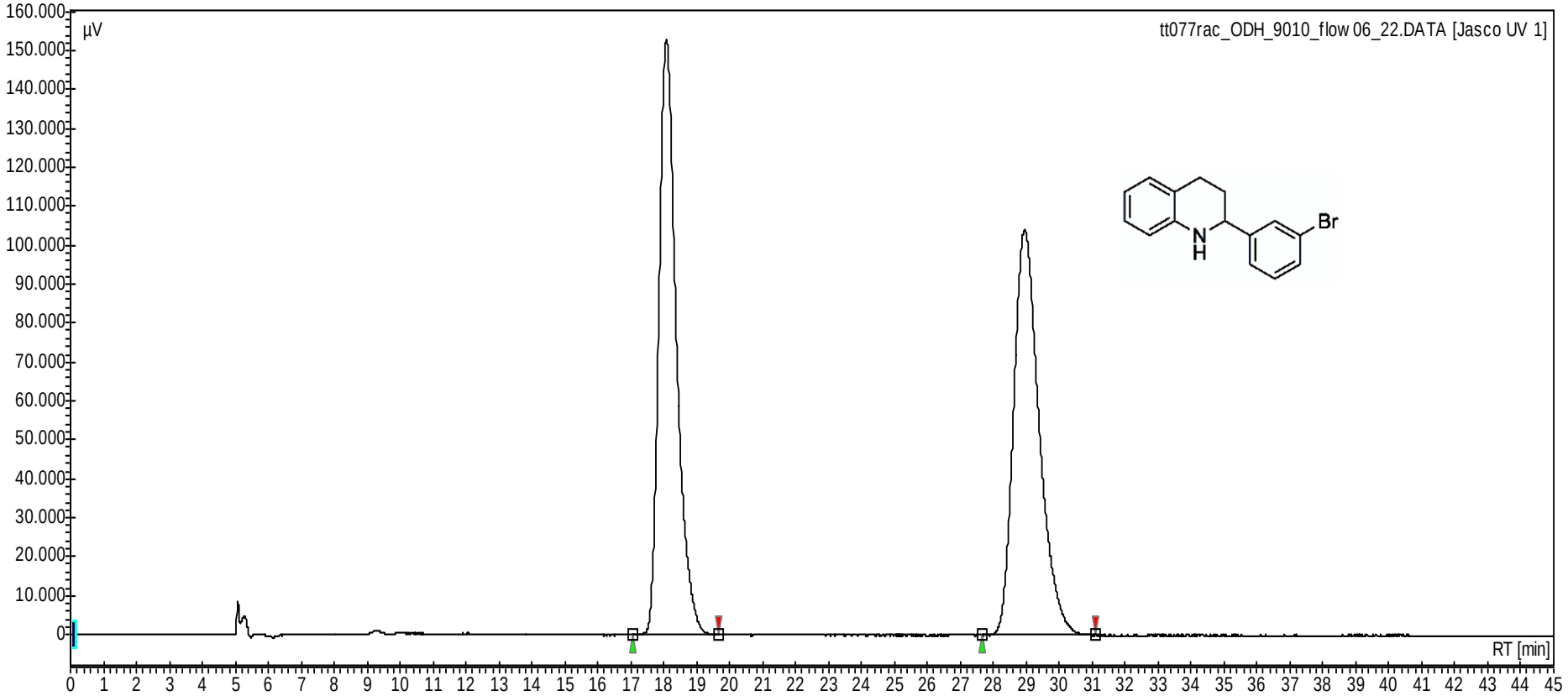
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	20,196	21,267	23,264	96,610
2	39,124	40,308	41,987	3,390
Total				100,000




147.23
144.26
130.46
130.11
129.62
129.25
126.95
125.18
122.64
120.75
117.44
114.08
55.71
30.92
26.10
N
H
Br
150
100
50
ppm (t1)

Chromatogram : tt077rac_ODH_9010_flow06_22

Data file: tt077rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 19.05.2009 22:31:04

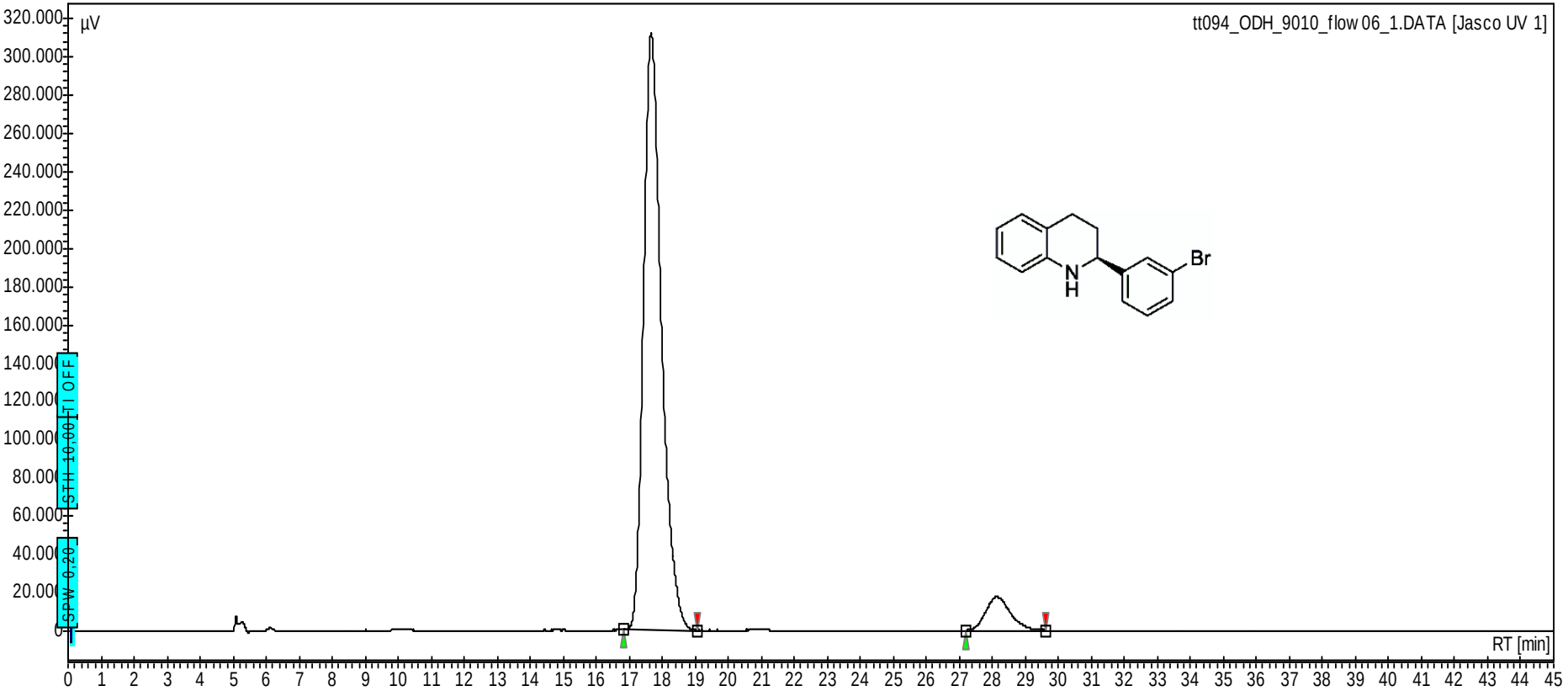


tt077rac_ODH_9010_flow06_22.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17,061	18,075	19,664	49,974
2	27,660	28,958	31,100	50,026
Total				100,000

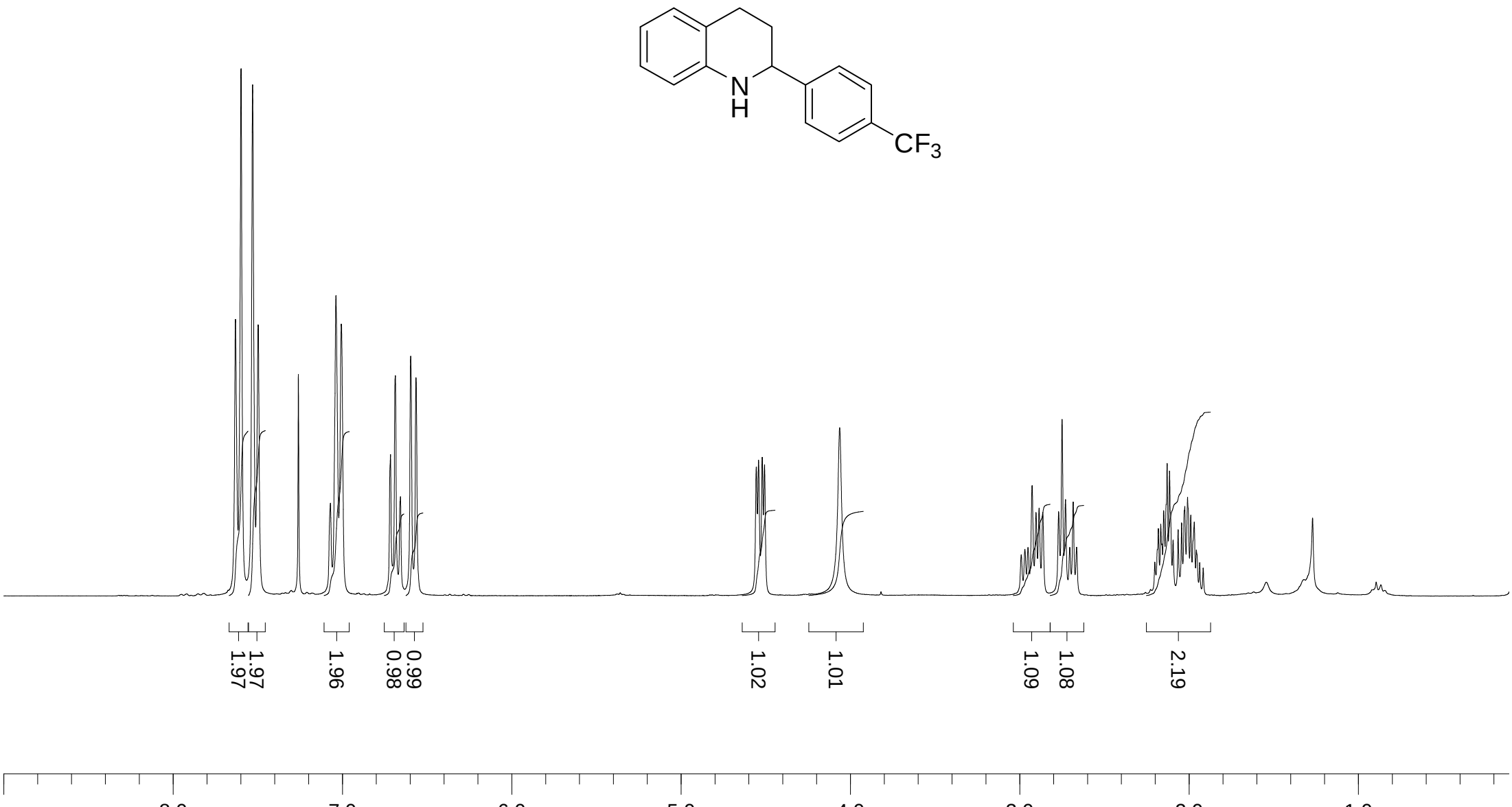
Chromatogram : tt094_ODH_9010_flow06_1

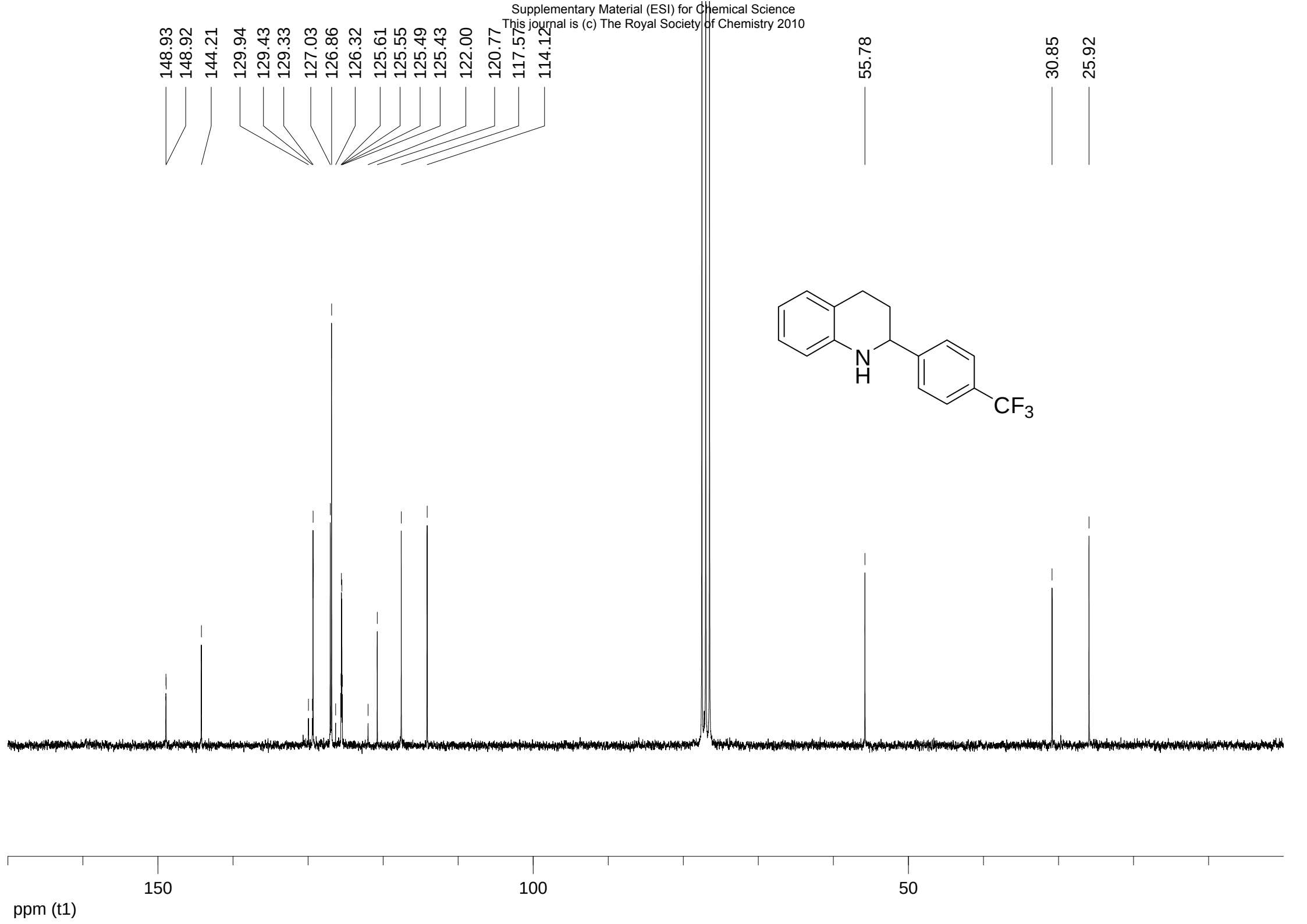
Data file: tt094_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 22.05.2009 17:19:30



tt094_ODH_9010_flow06_1.DATA [Jasco UV 1]

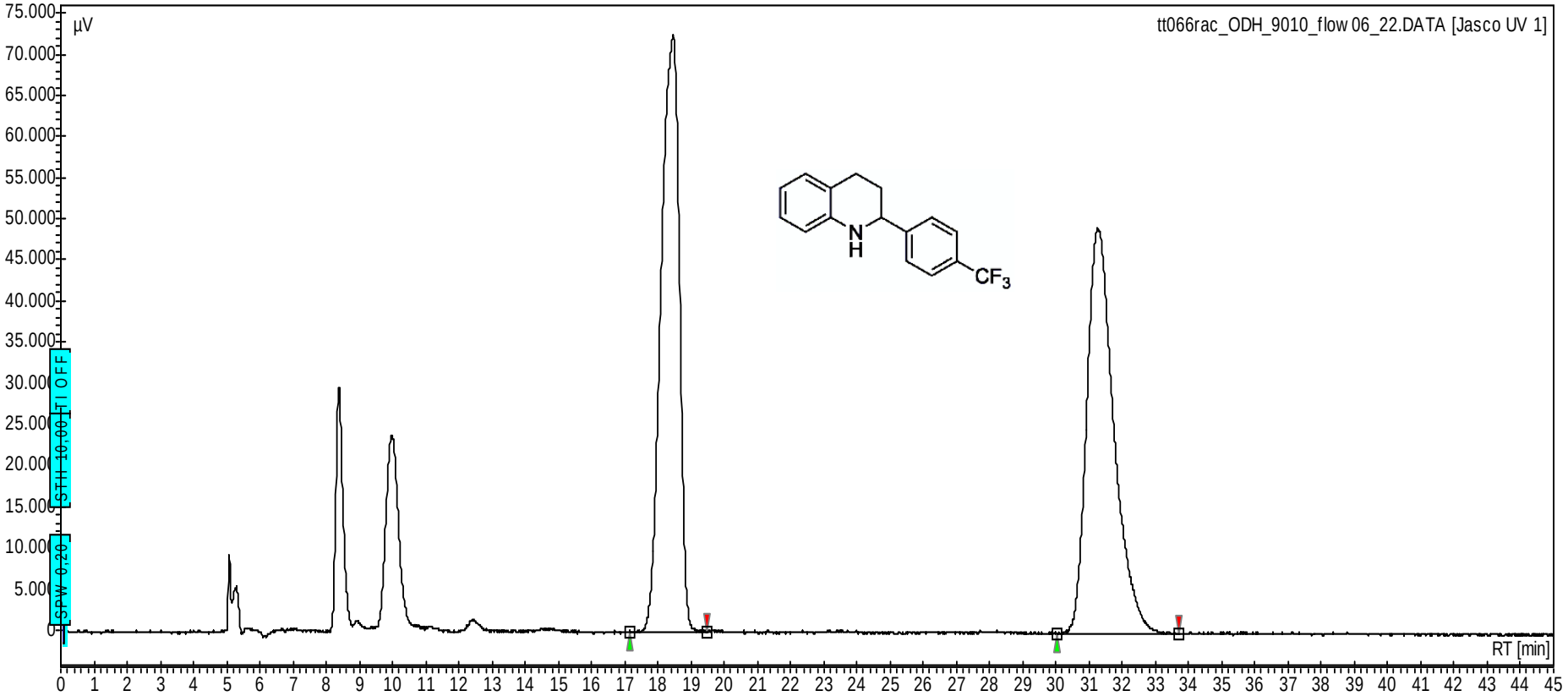
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	16,808	17,667	19,051	92,832
1	27,205	28,142	29,610	7,168
Total				100,000





Chromatogram : tt066rac_ODH_9010_flow06_22

Data file: tt066rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 19.05.2009 18:50:05

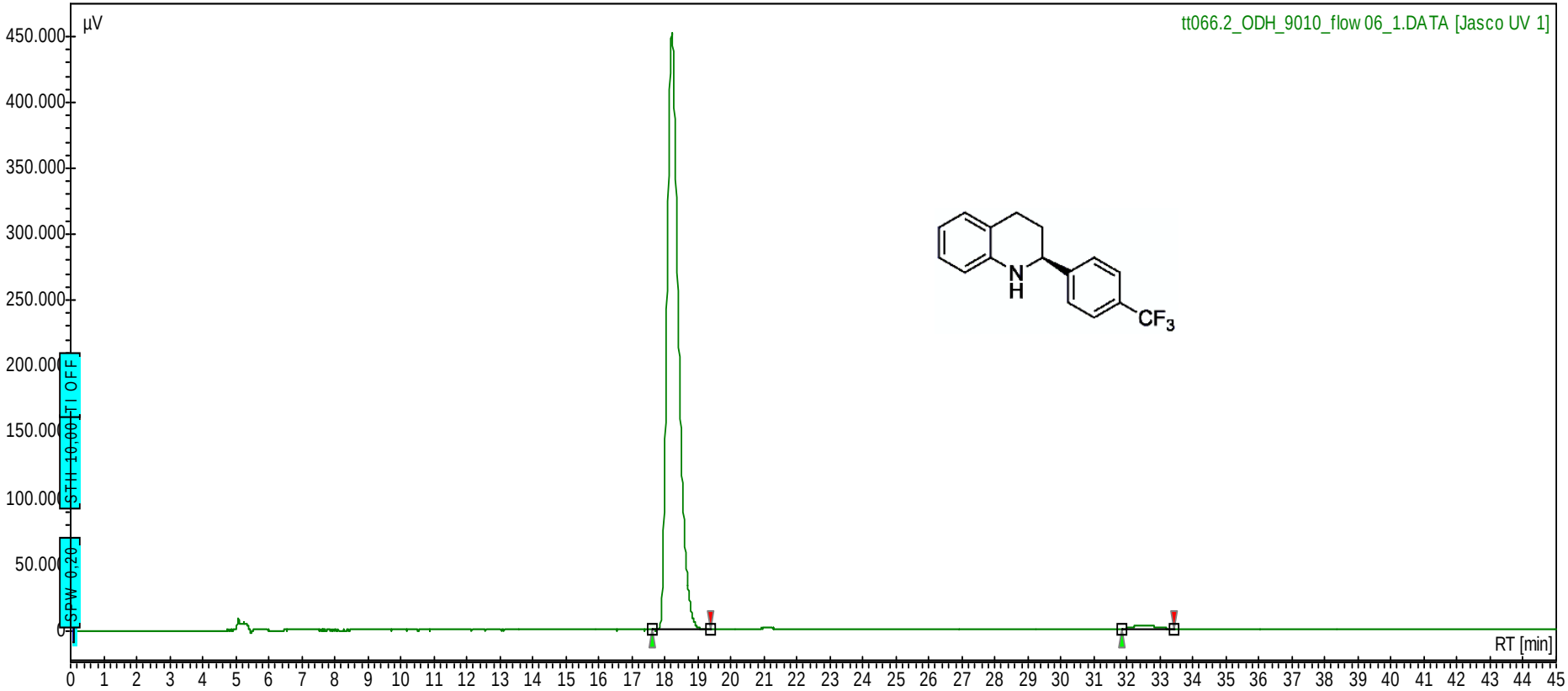


tt066rac_ODH_9010_flow06_22.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17,154	18,458	19,478	49,664
2	30,031	31,258	33,704	50,336
Total				100,000

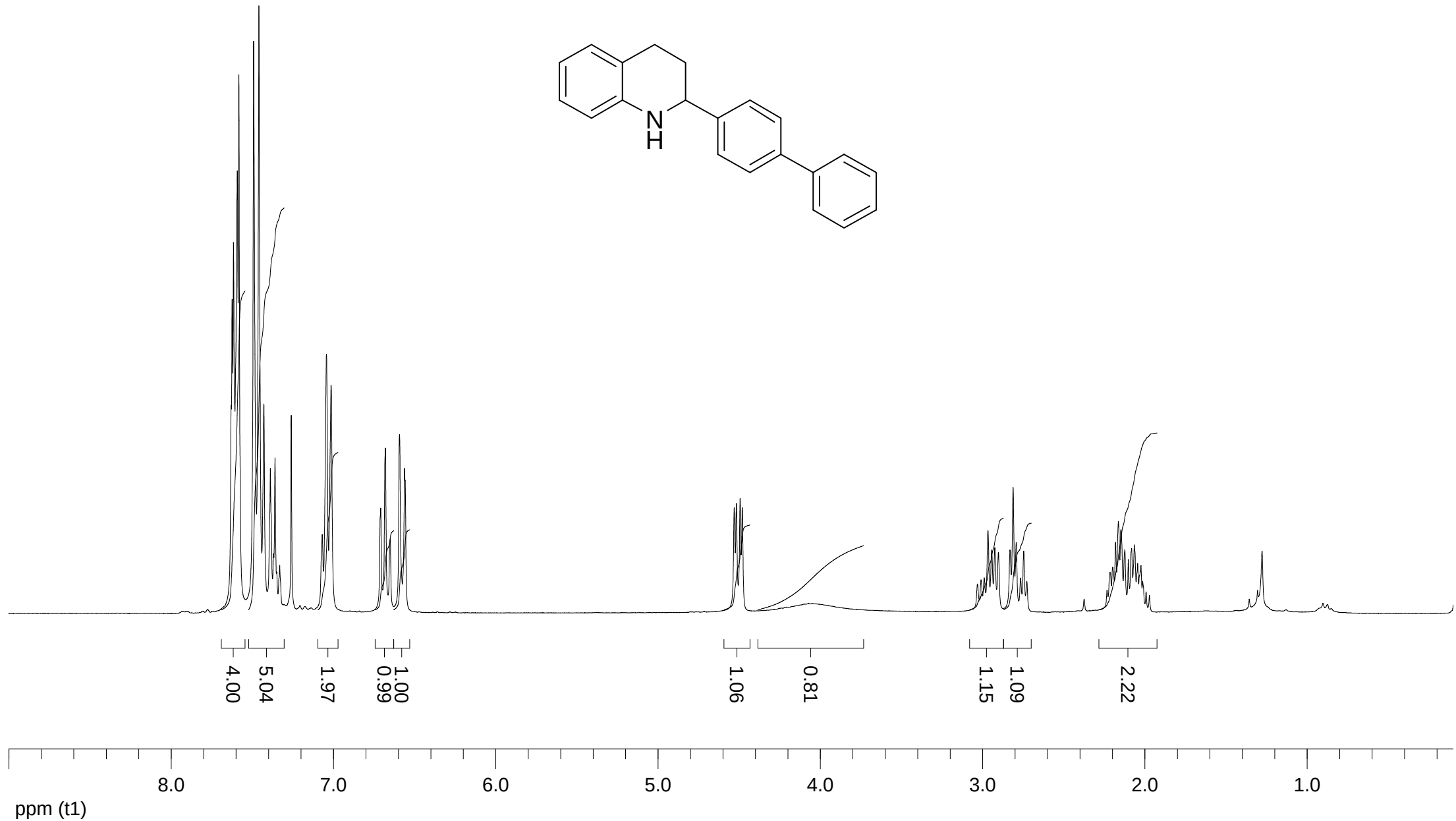
Chromatogram : tt066.2_ODH_9010_flow06_1

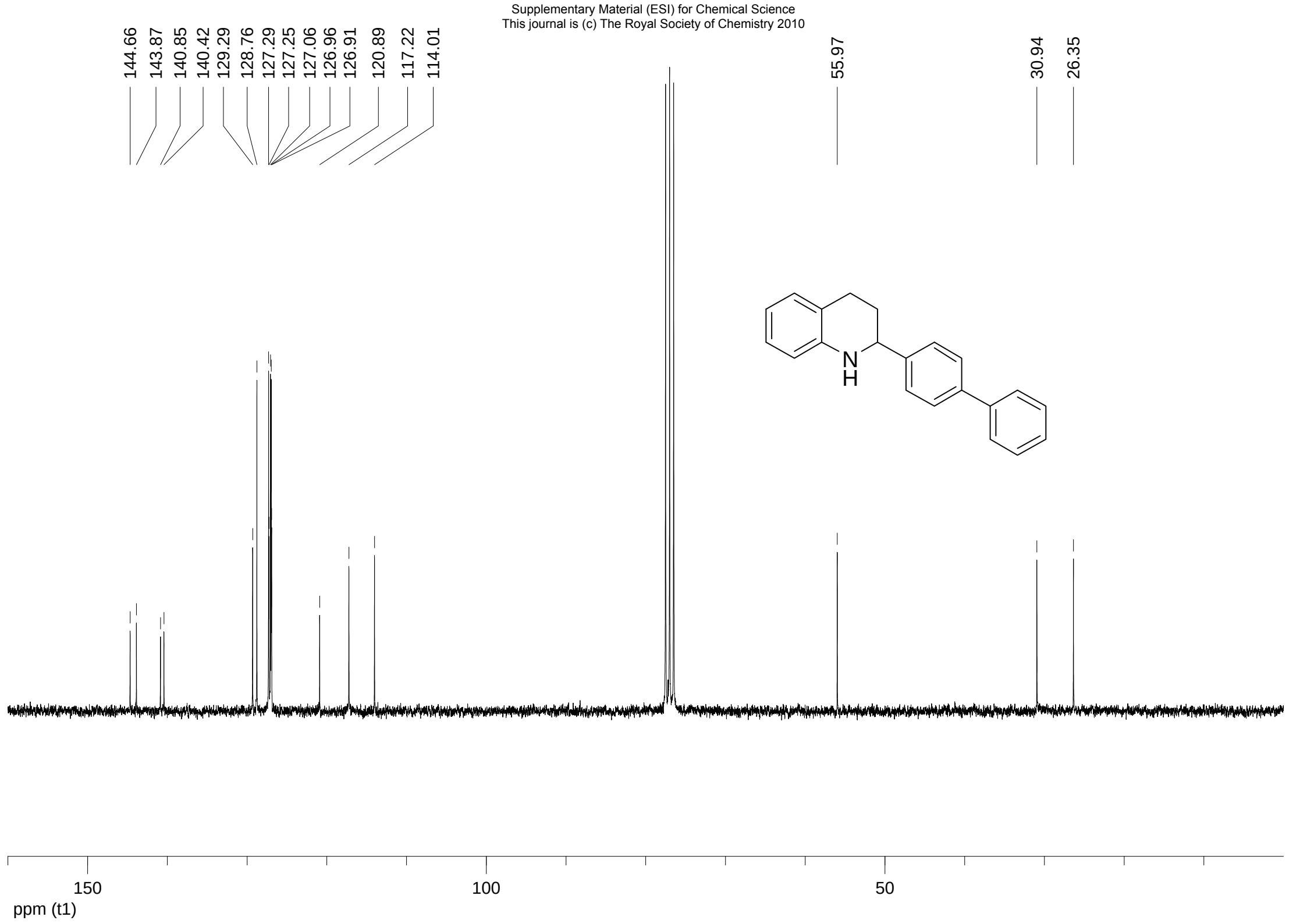
Data file: tt066.2_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 05.06.2009 14:32:31



tt066.2_ODH_9010_flow06_1.DATA [Jasco UV 1]

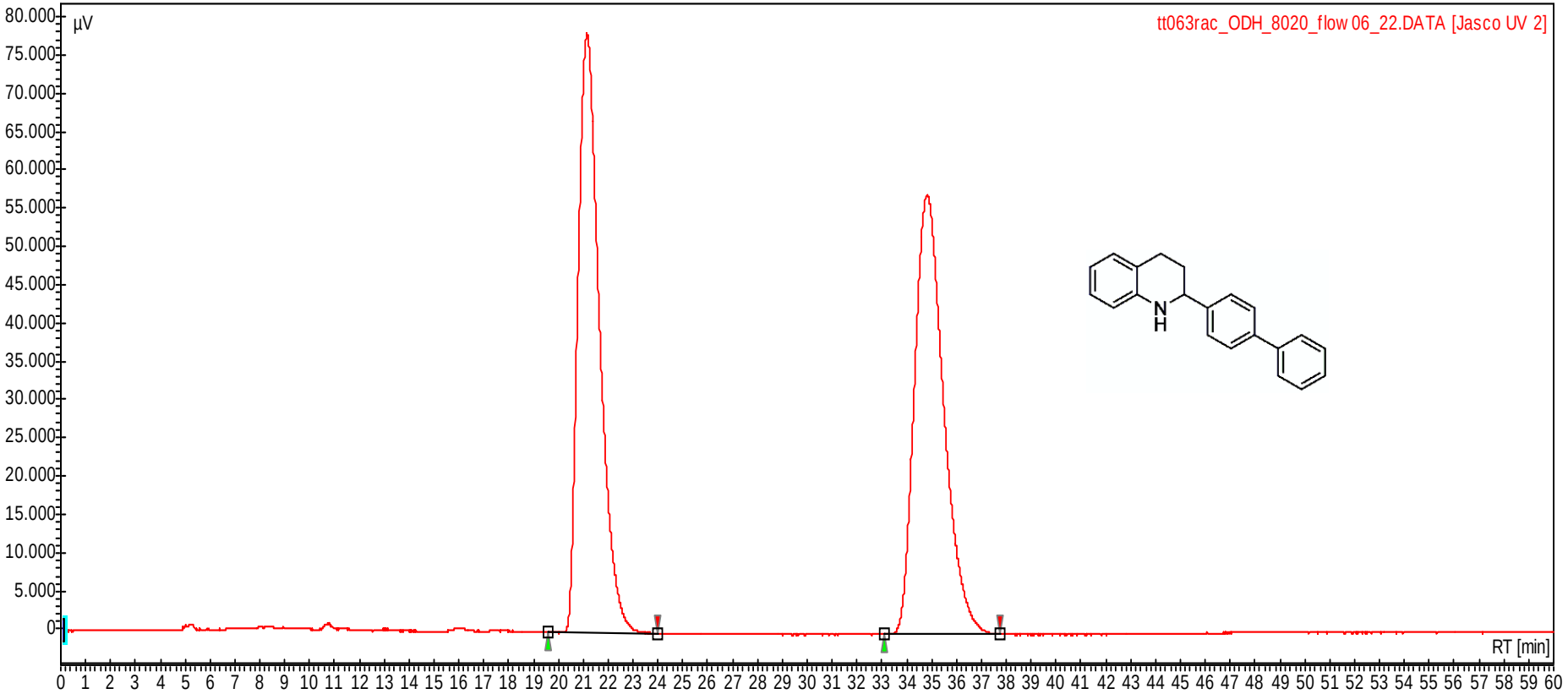
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	17,597	18,208	19,402	98,646
2	31,836	32,533	33,440	1,354
Total				100,000




144.66
143.87
140.85
140.42
129.29
128.76
127.29
127.25
127.06
126.96
126.91
120.89
117.22
114.01
55.97
30.94
26.35
N
H
150
100
50
ppm (t1)

Chromatogram : tt063rac_ODH_8020_flow06_22

Data file: tt063rac_ODH_8020_flow06_22.DATA
Method: HPLC1_ODH_8020_flow06_acq_60
Date: 20.05.2009 10:33:11

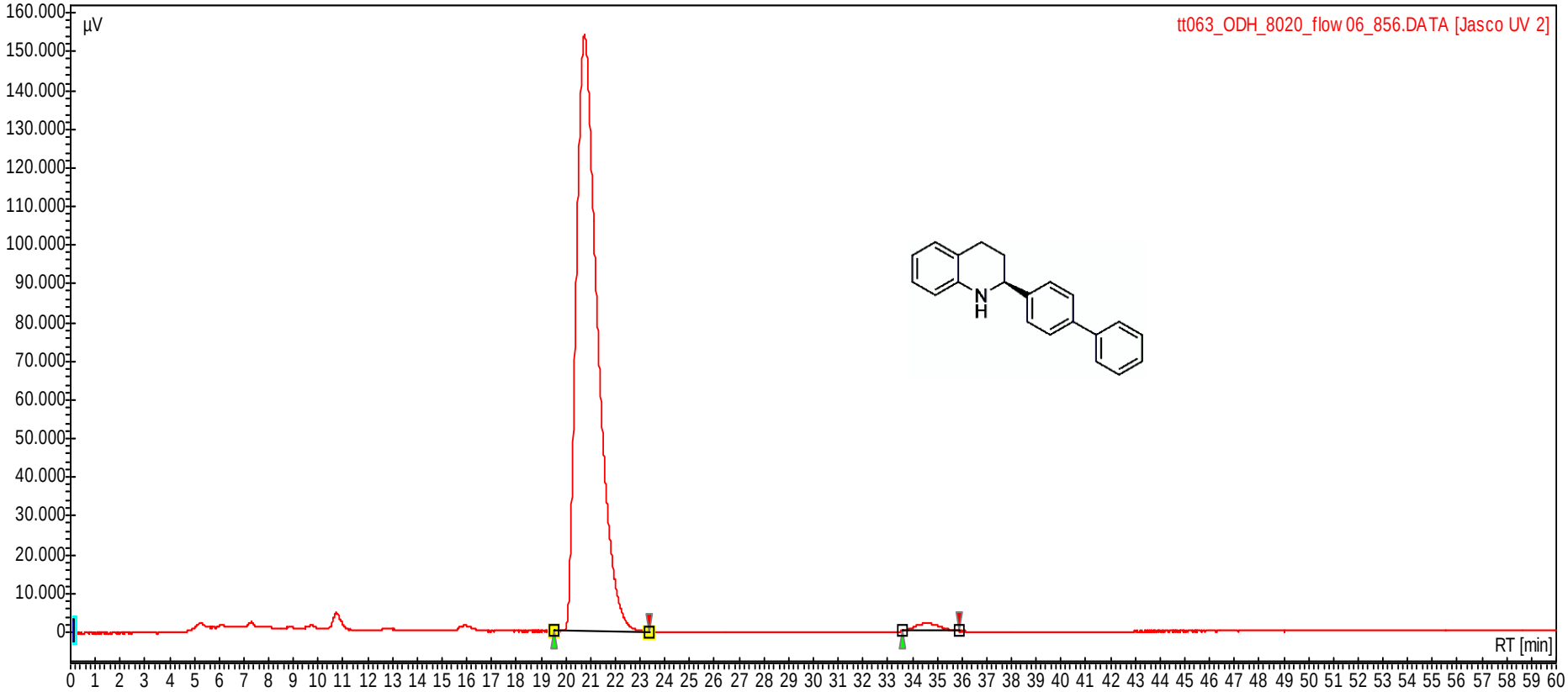


tt063rac_ODH_8020_flow06_22.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	19,587	21,150	23,988	49,980
2	33,099	34,825	37,748	50,020
Total				100,000

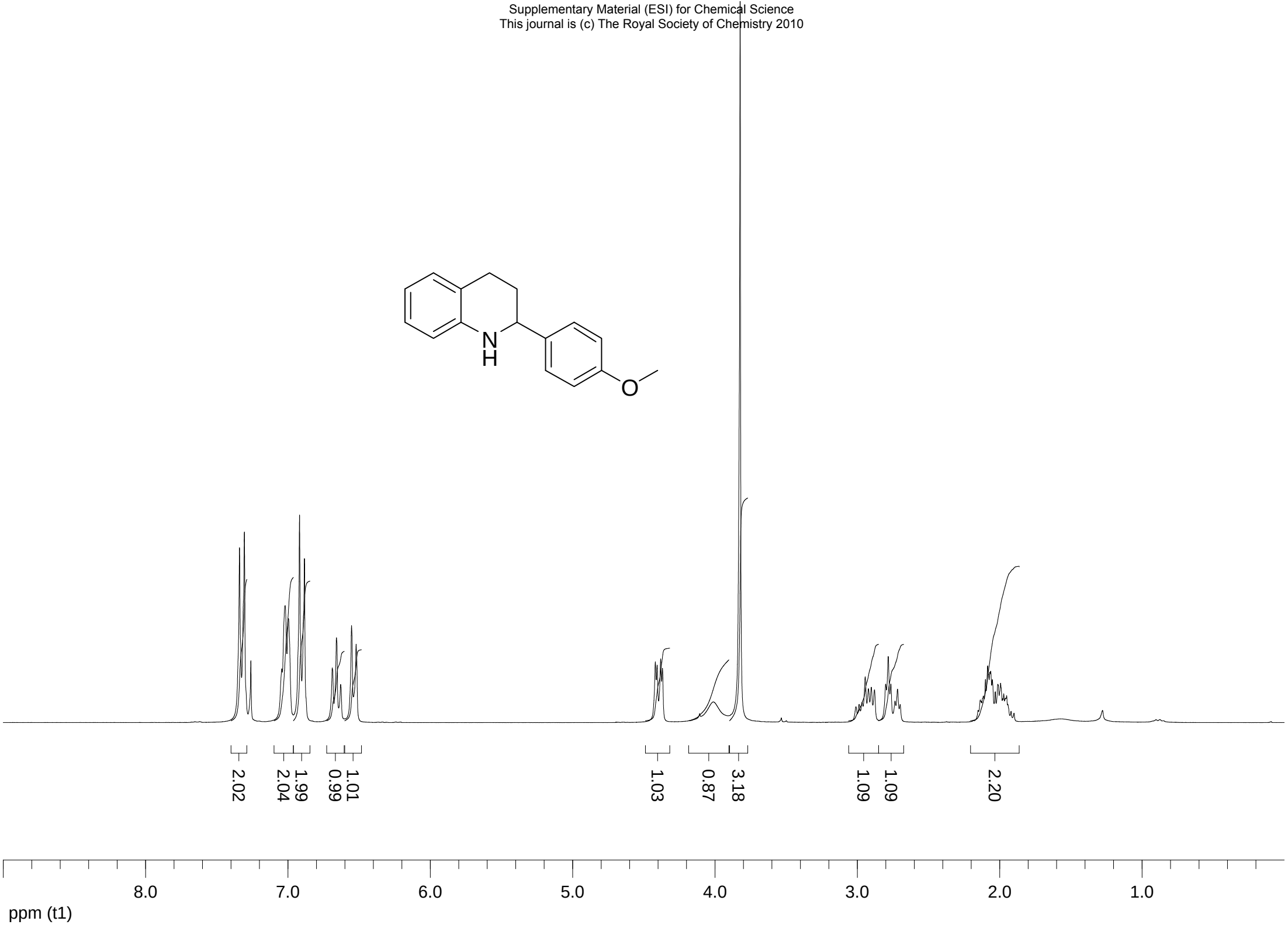
Chromatogram : tt063_ODH_8020_flow06_856

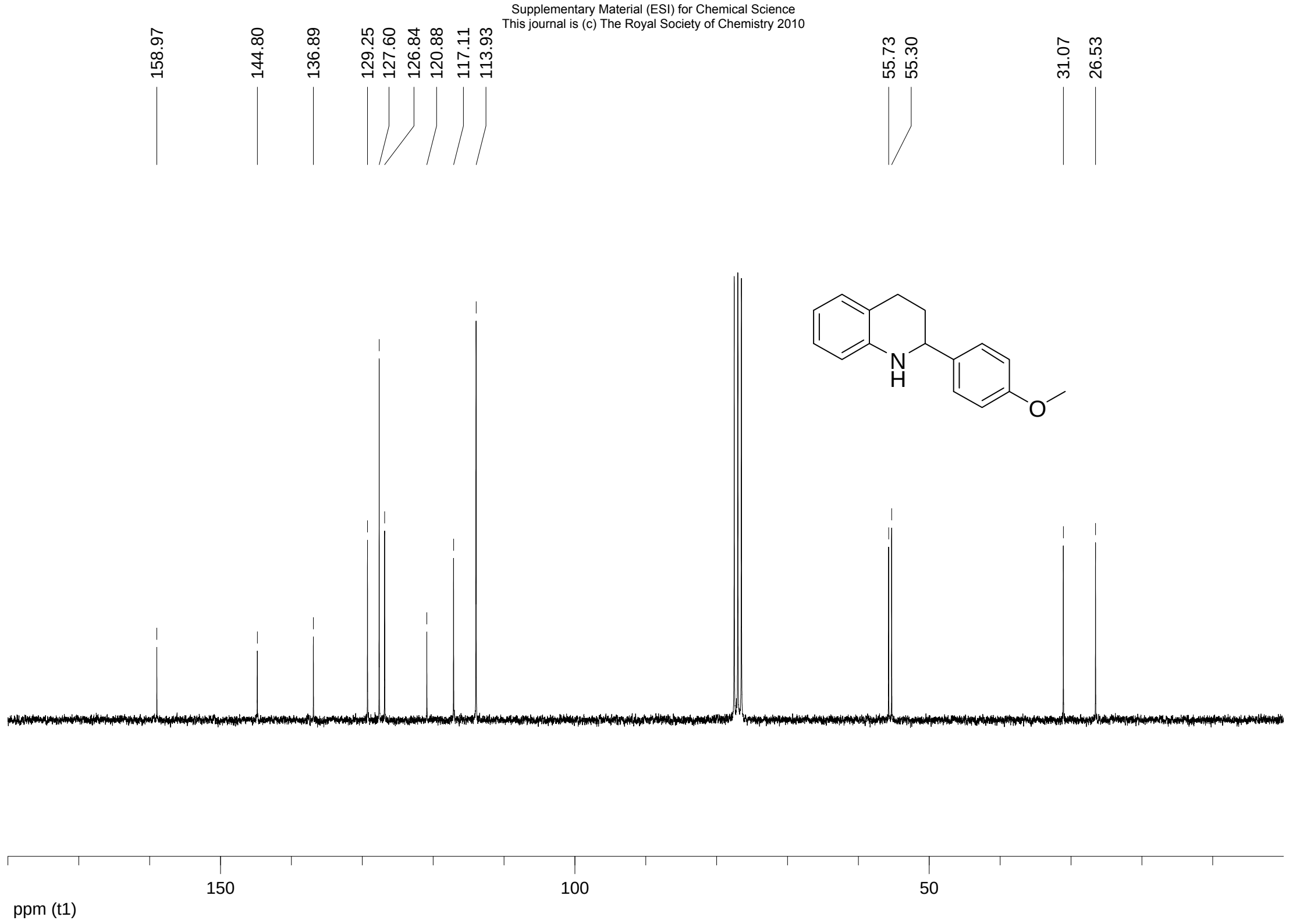
Data file: tt063_ODH_8020_flow06_856.DATA
Method: HPLC1_ODH_8020_flow06_acq_60
Date: 20.05.2009 12:23:55



tt063_ODH_8020_flow06_856.DATA [Jasco UV 2]

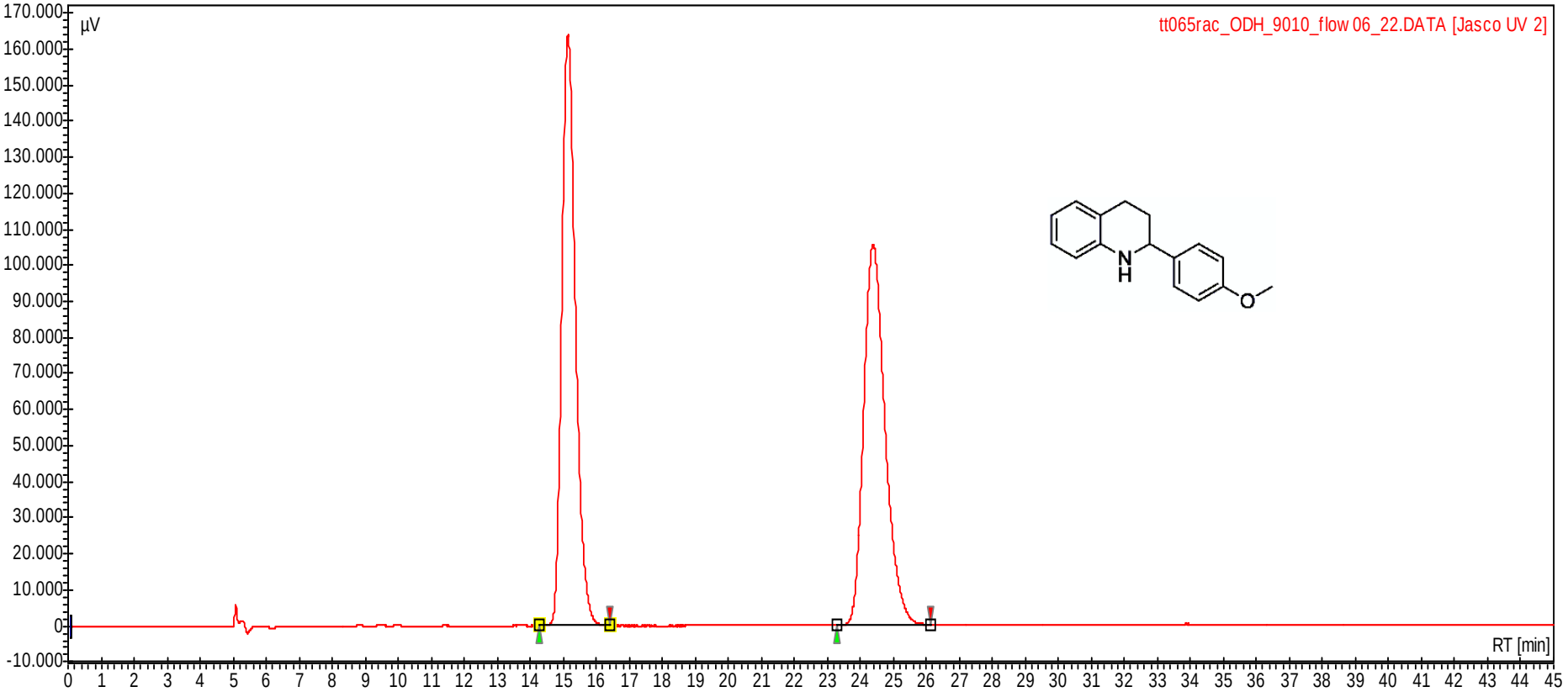
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	19,551	20,758	23,361	98,578
2	33,616	34,575	35,880	1,422
Total				100,000





Chromatogram : tt065rac_ODH_9010_flow06_22

Data file: tt065rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 19.05.2009 17:14:35

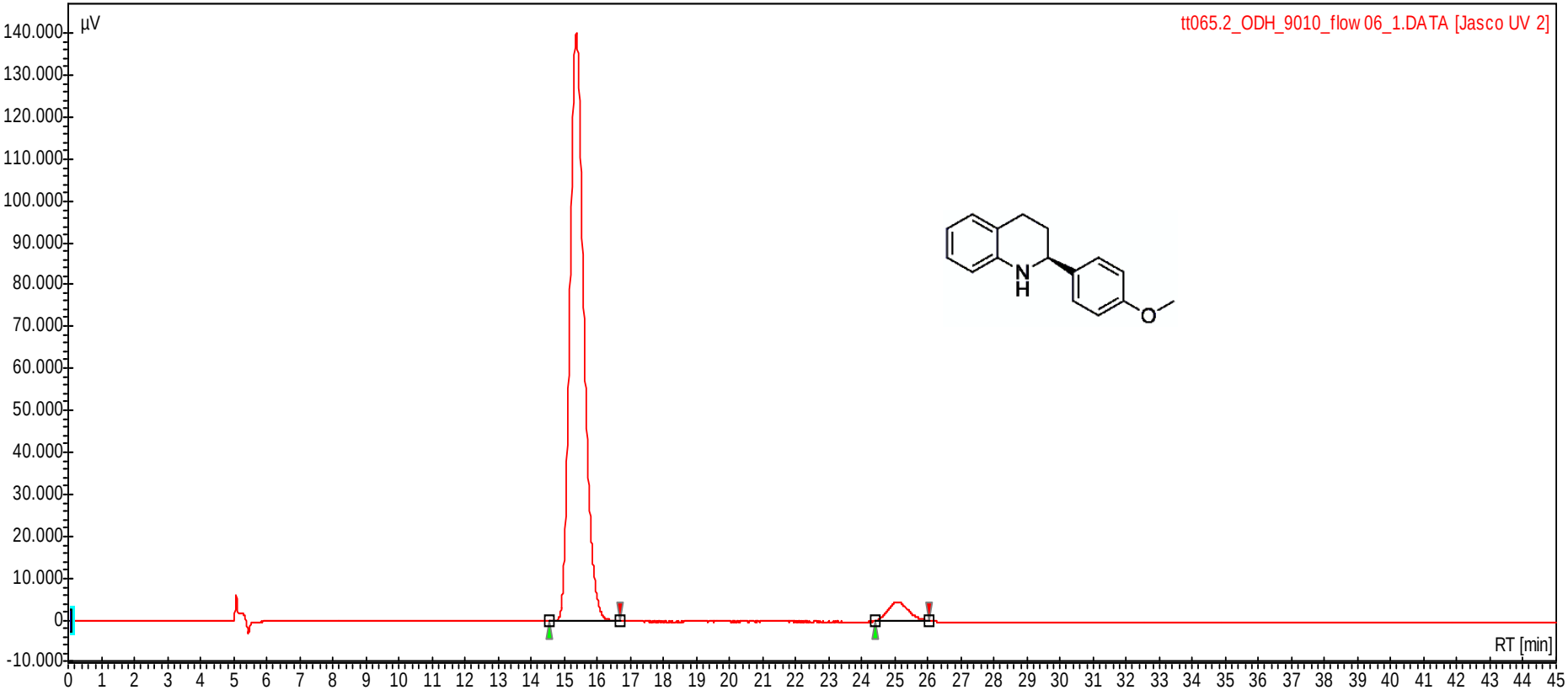


tt065rac_ODH_9010_flow06_22.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	14,272	15,142	16,410	49,884
2	23,290	24,383	26,126	50,116
Total				100,000

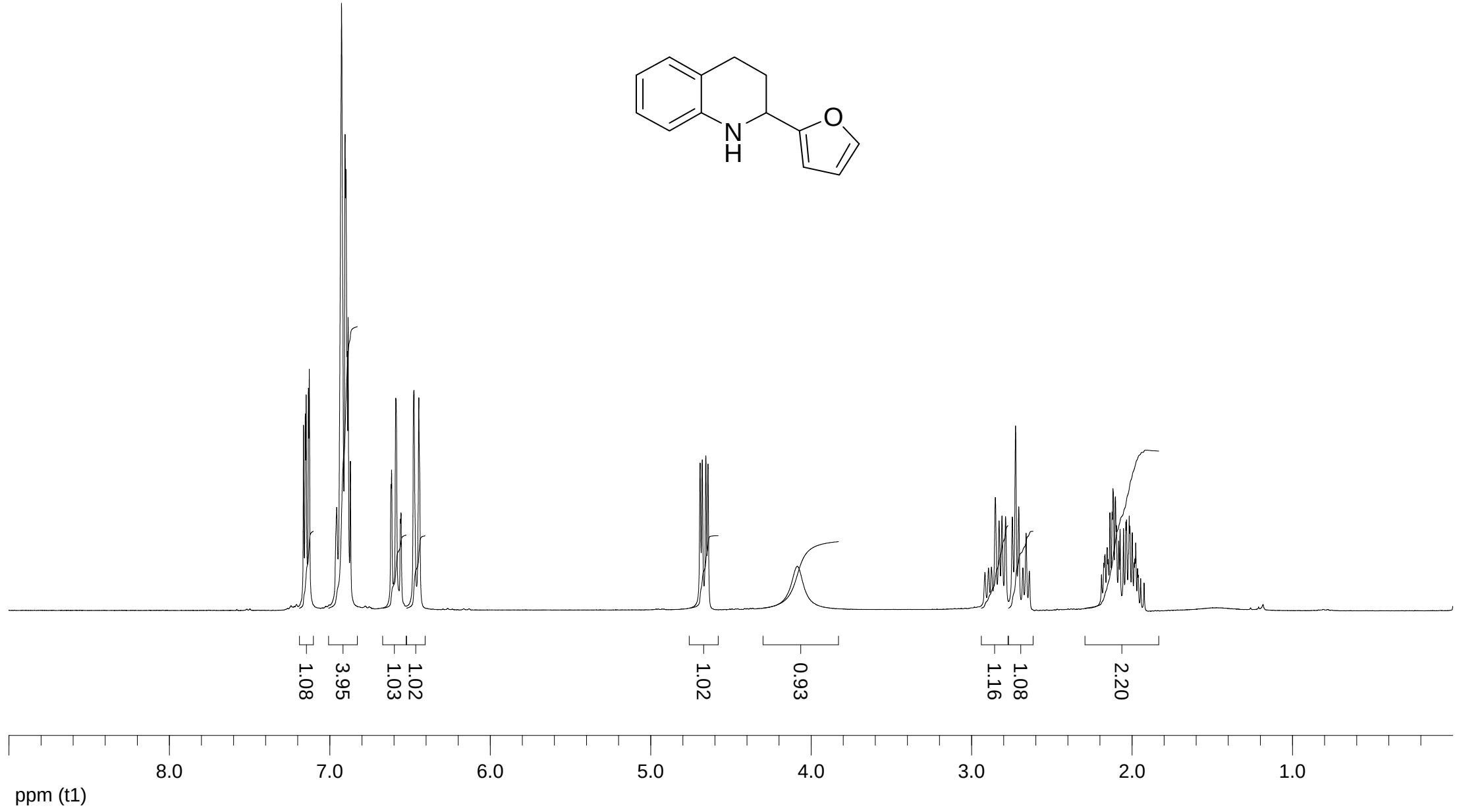
Chromatogram : tt065.2_ODH_9010_flow06_1

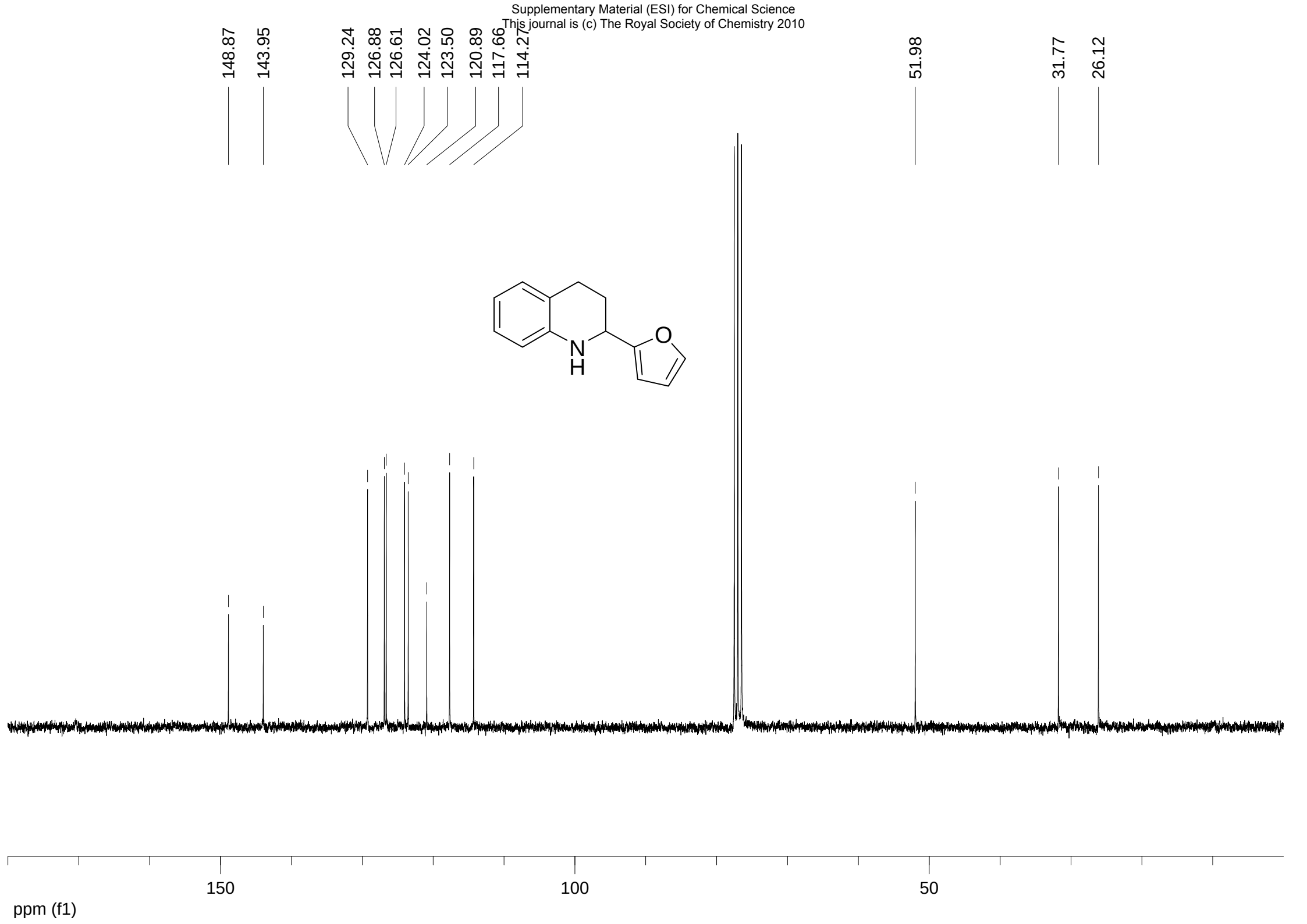
Data file: tt065.2_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 05.06.2009 13:44:46



tt065.2_ODH_9010_flow06_1.DATA [Jasco UV 2]

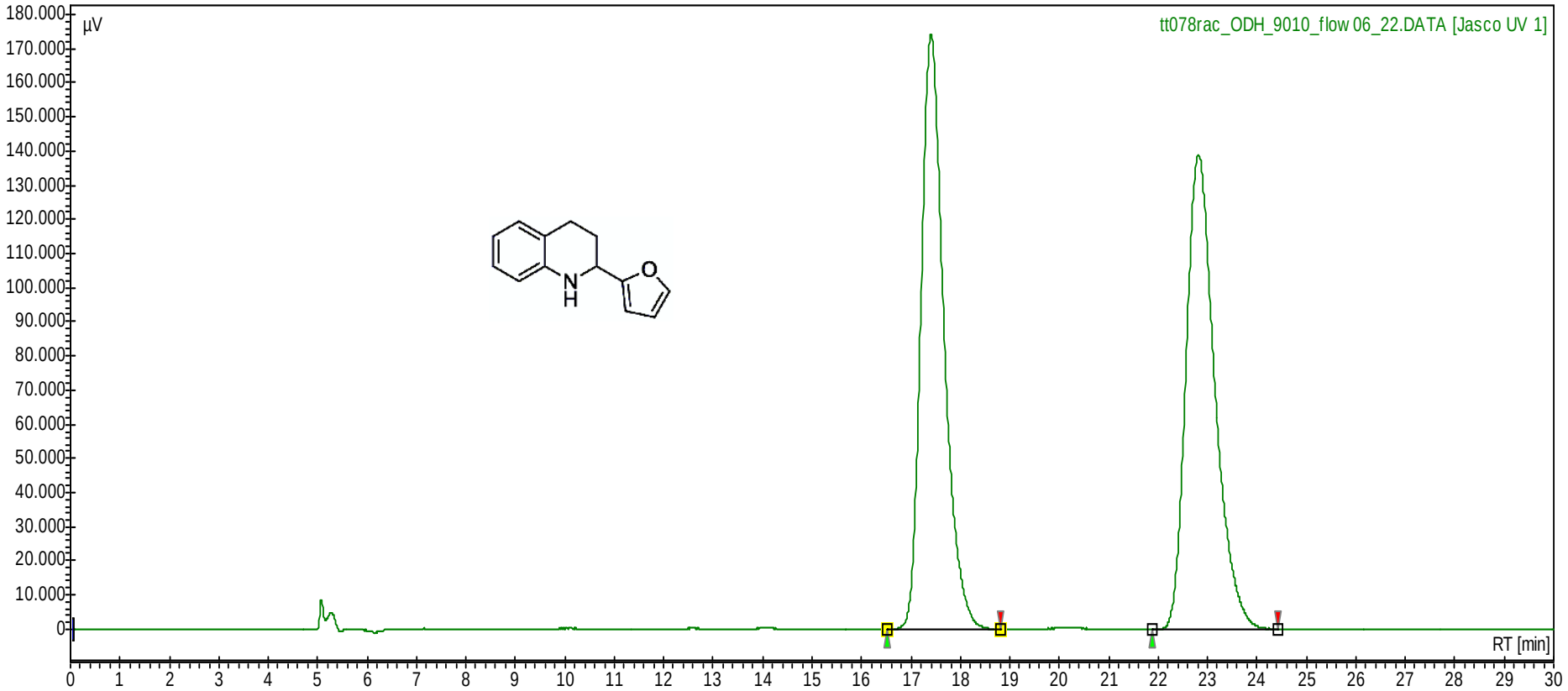
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	14,549	15,367	16,677	95,538
2	24,424	25,092	26,022	4,462
Total				100,000




148.87
143.95
129.24
126.88
126.61
124.02
123.50
120.89
117.66
114.27
51.98
31.77
26.12
N
H
O
150
100
50
ppm (f1)

Chromatogram : tt078rac_ODH_9010_flow06_22

Data file: tt078rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_30
Date: 19.05.2009 23:18:47

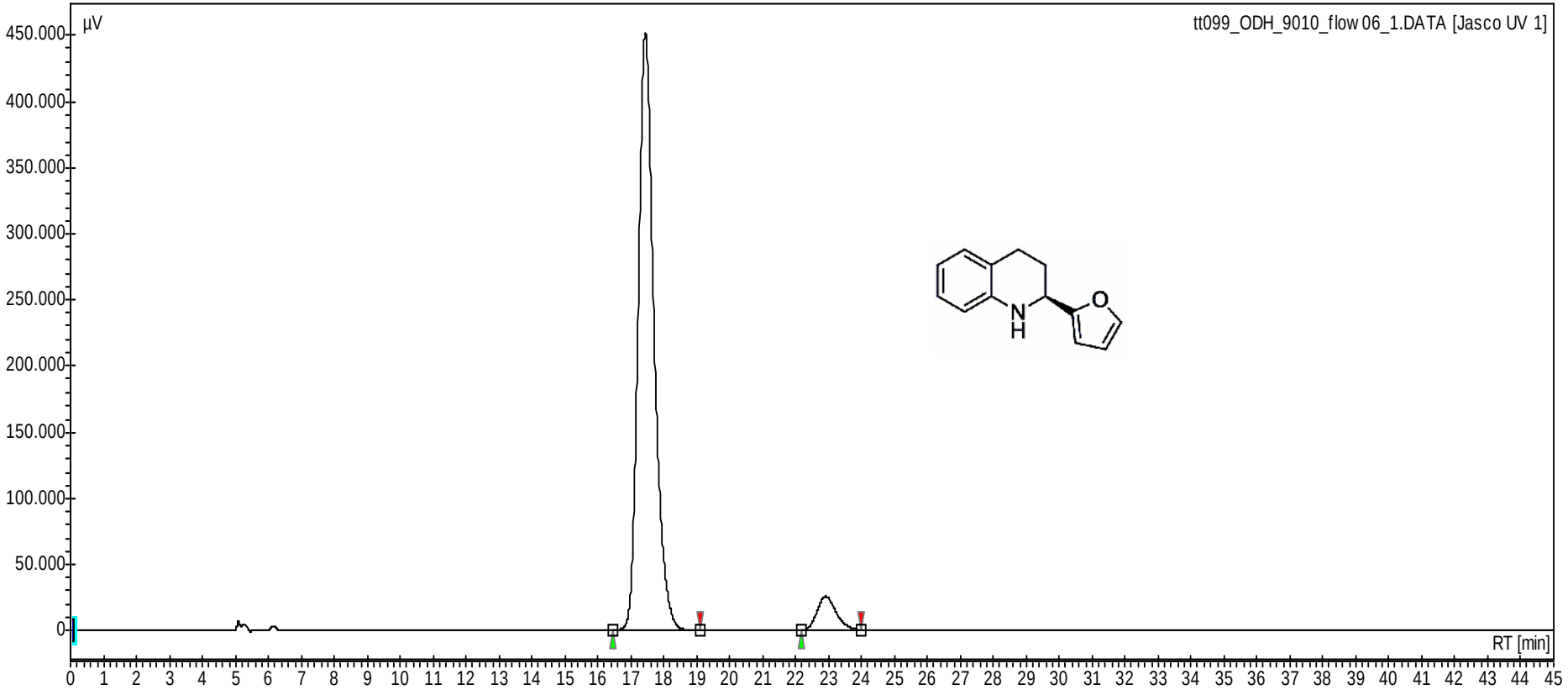


tt078rac_ODH_9010_flow06_22.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16,519	17,408	18,812	49,955
2	21,880	22,817	24,421	50,045
Total				100,000

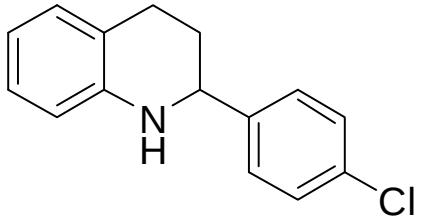
Chromatogram : tt099_ODH_9010_flow06_1

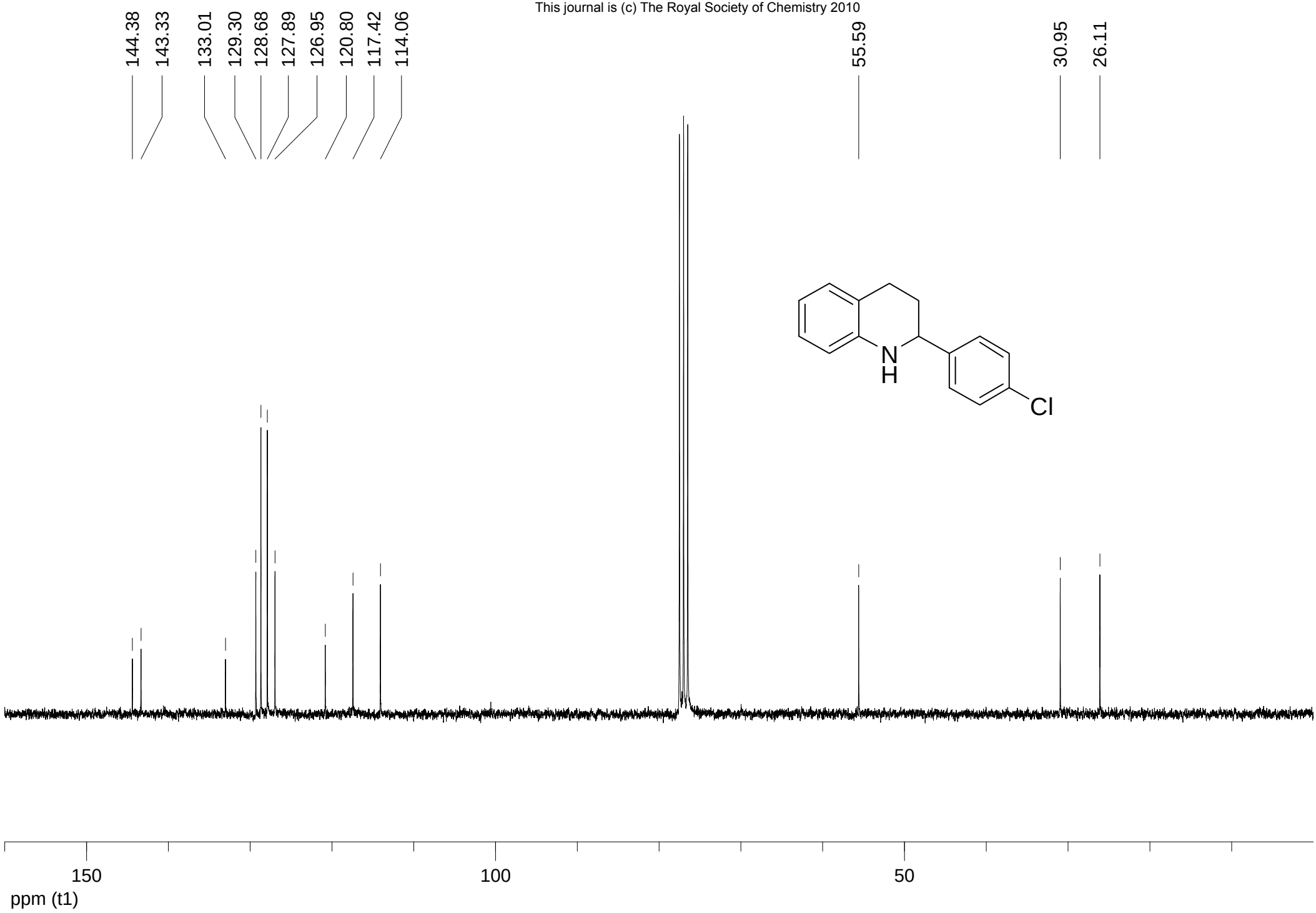
Data file: tt099_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 22.05.2009 21:09:56



tt099_ODH_9010_flow06_1.DATA [Jasco UV 1]

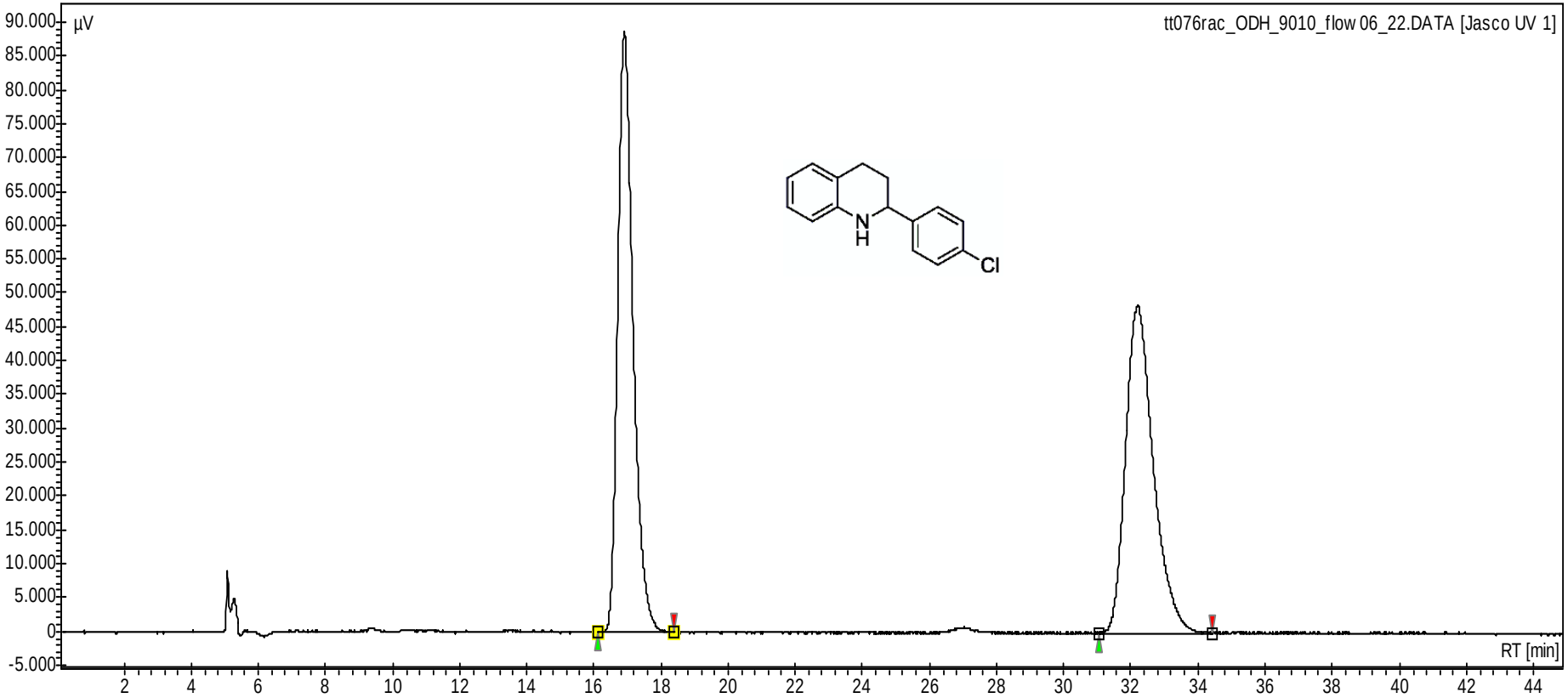
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16,443	17,442	19,114	93,505
2	22,184	22,908	24,008	6,495
Total				100,000





Chromatogram : tt076rac_ODH_9010_flow06_22

Data file: tt076rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_60
Date: 19.05.2009 21:28:19

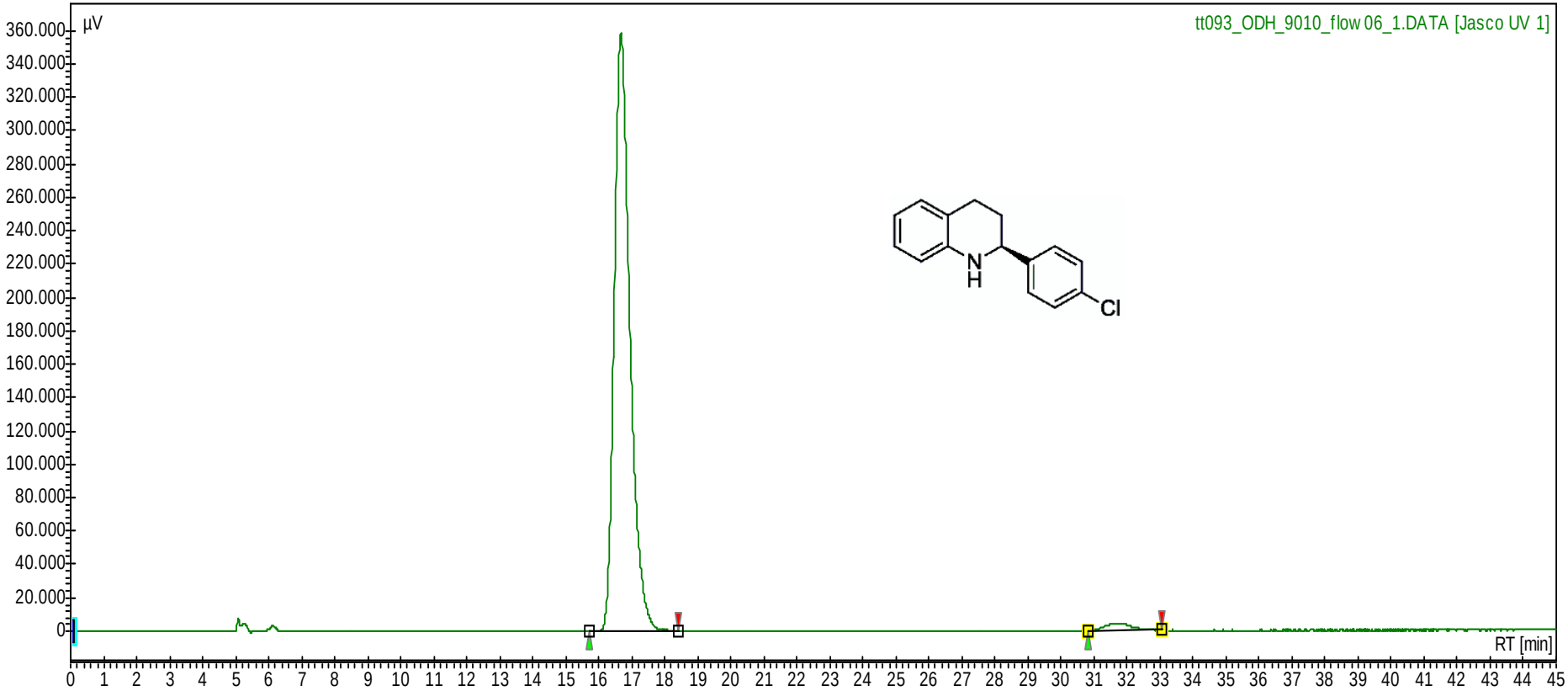


tt076rac_ODH_9010_flow06_22.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	16,123	16,908	18,391	50,297
2	31,035	32,217	34,405	49,703
Total				100,000

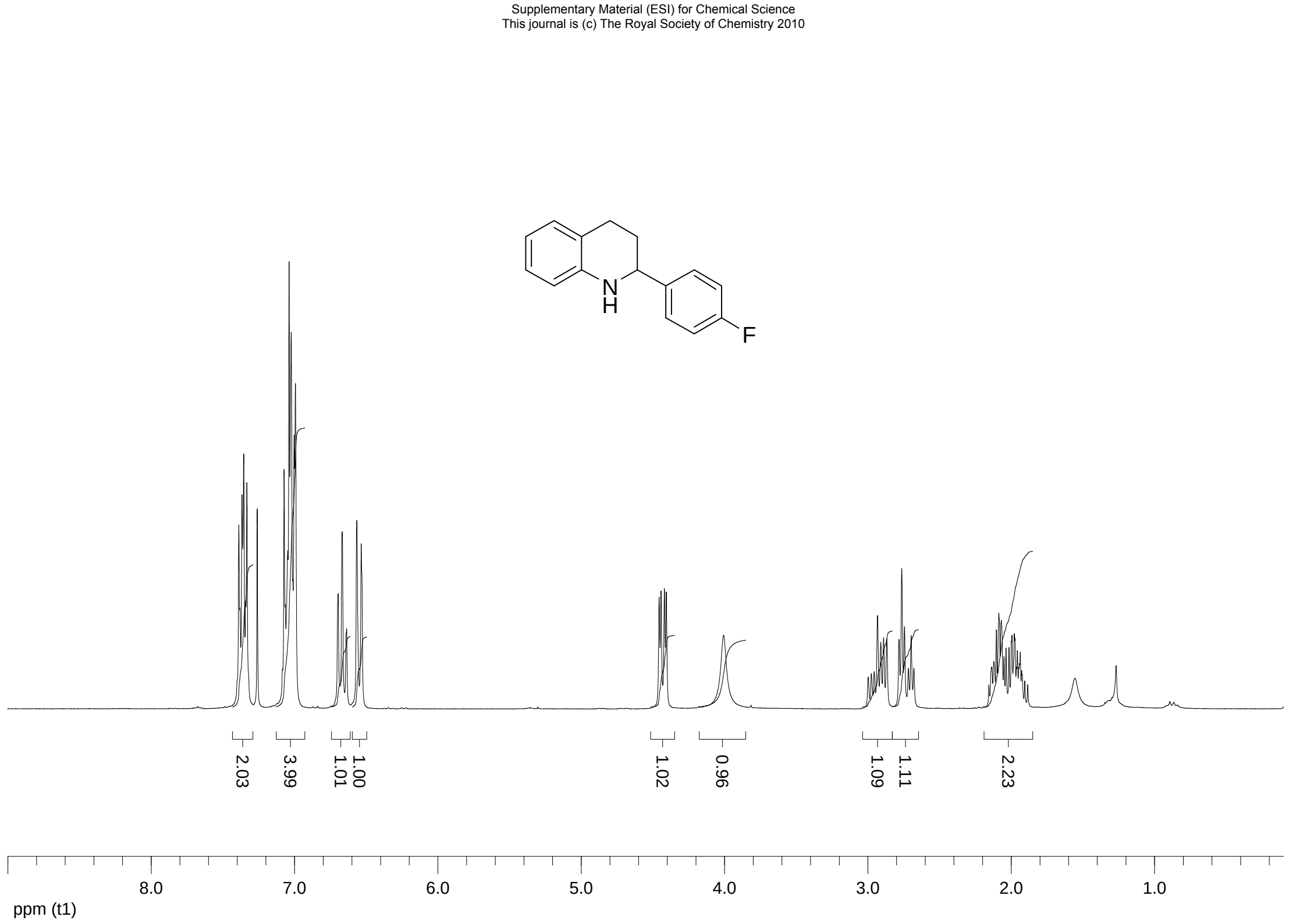
Chromatogram : tt093_ODH_9010_flow06_1

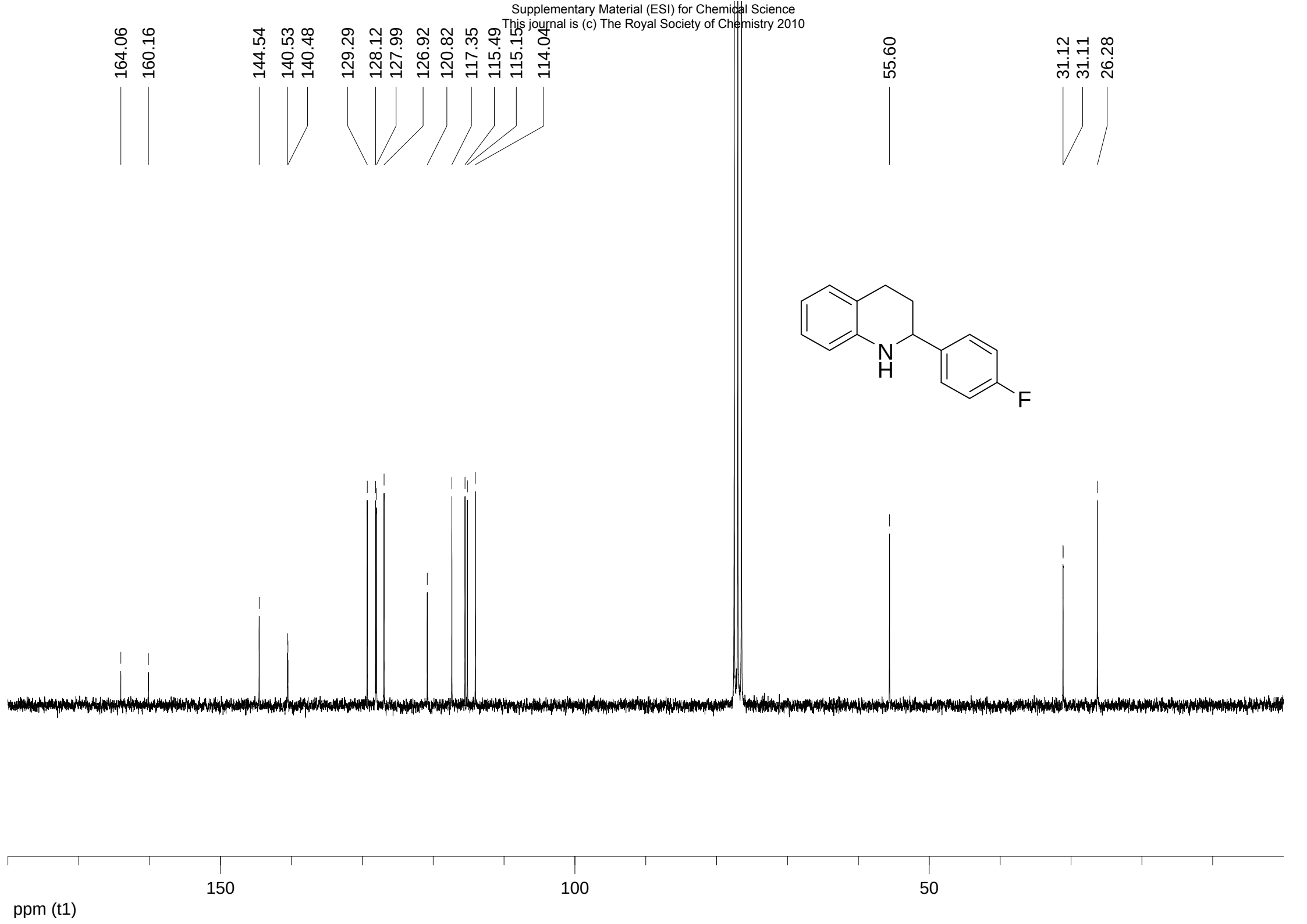
Data file: tt093_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 22.05.2009 16:31:47



tt093_ODH_9010_flow06_1.DATA [Jasco UV 1]

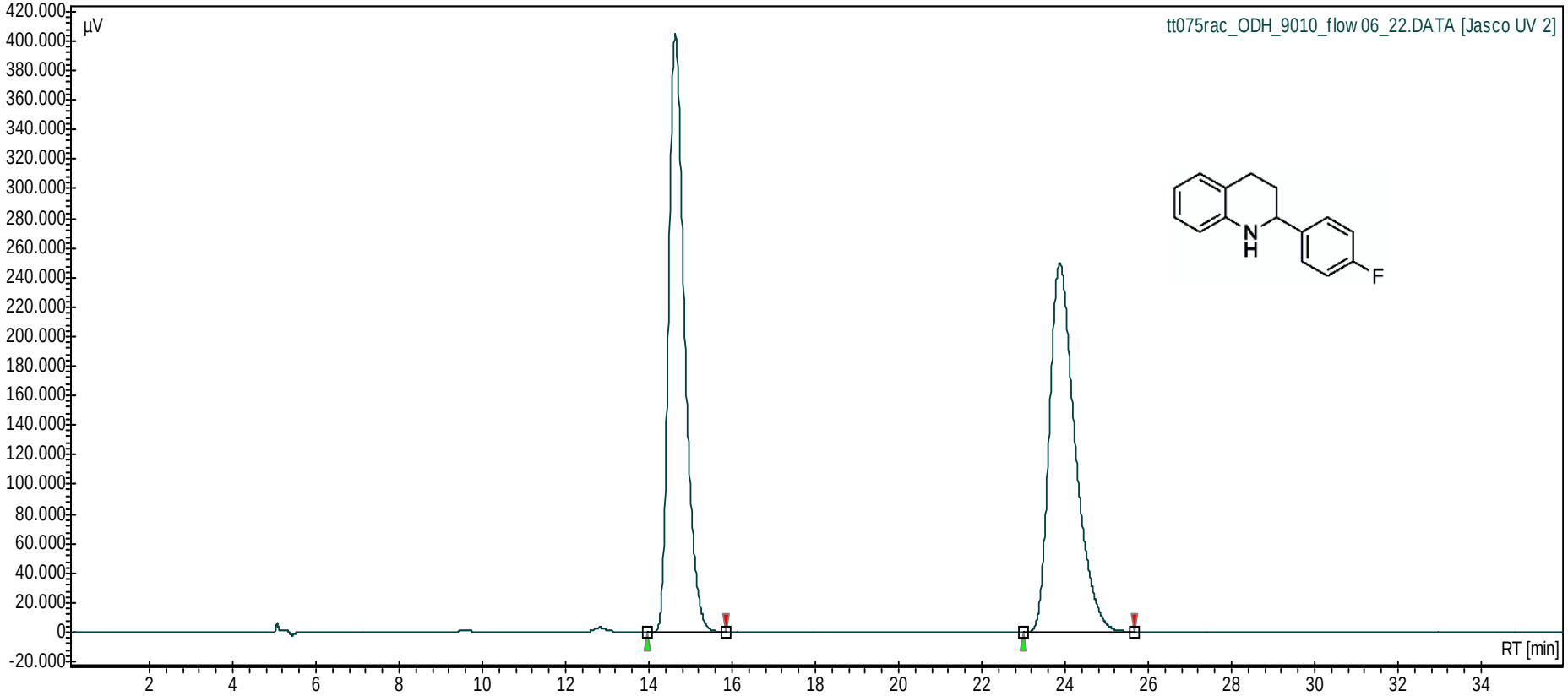
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	15,713	16,667	18,409	98,119
1	30,829	31,700	33,070	1,881
Total				100,000





Chromatogram : tt075rac_ODH_9010_flow06_22

Data file: tt075rac_ODH_9010_flow06_22.DATA
Method: HPLC1_ODH_9010_flow06_acq_60
Date: 19.05.2009 20:25:36

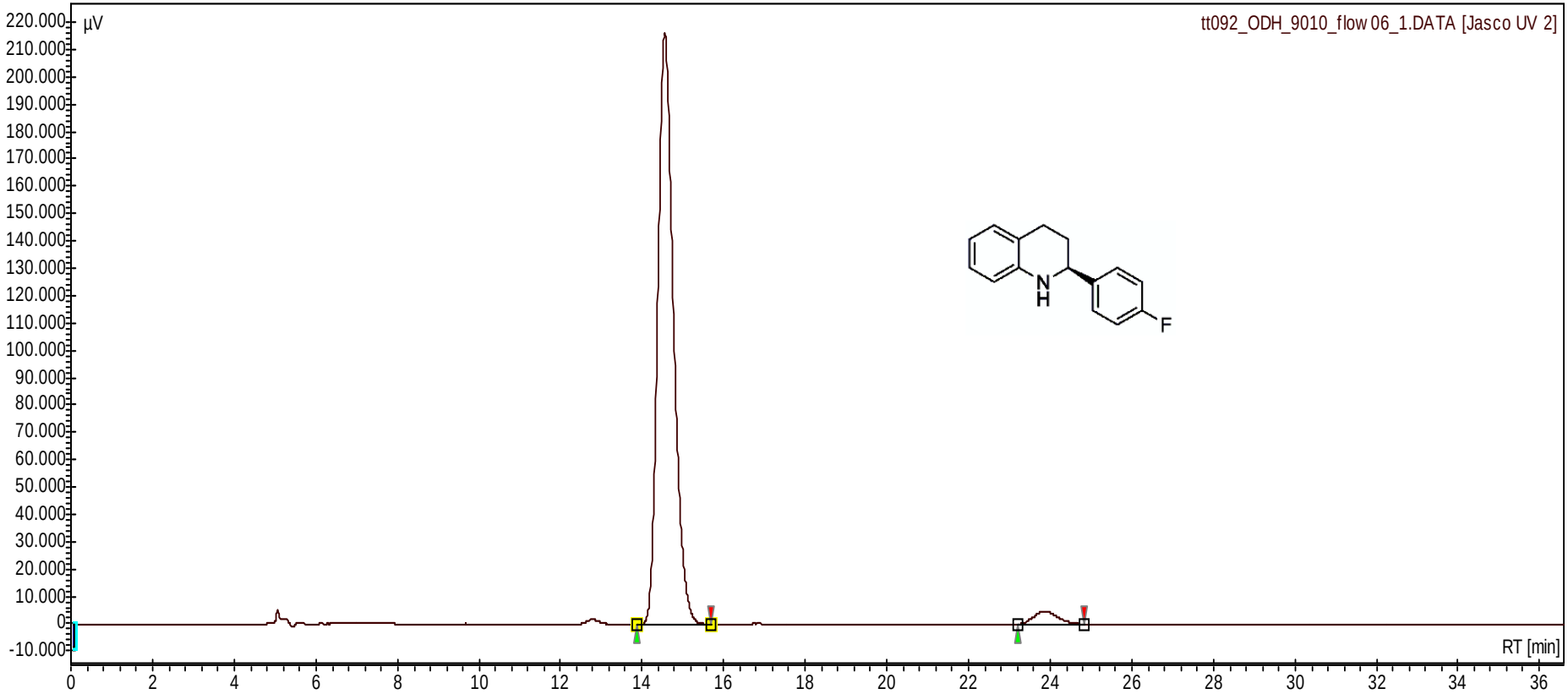


tt075rac_ODH_9010_flow06_22.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	13,974	14,633	15,860	50,061
2	22,999	23,875	25,662	49,939
Total				100,000

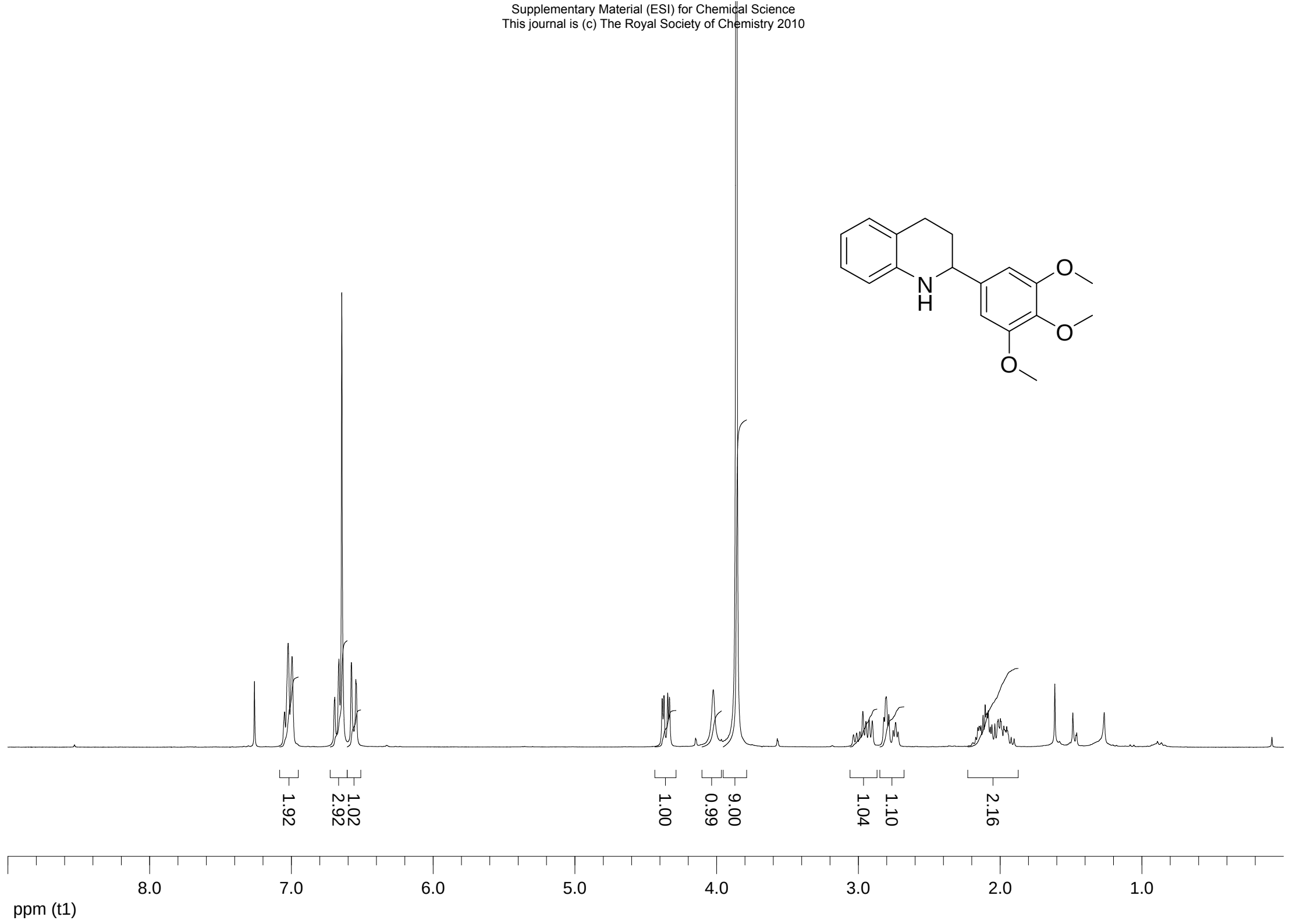
Chromatogram : tt092_ODH_9010_flow06_1

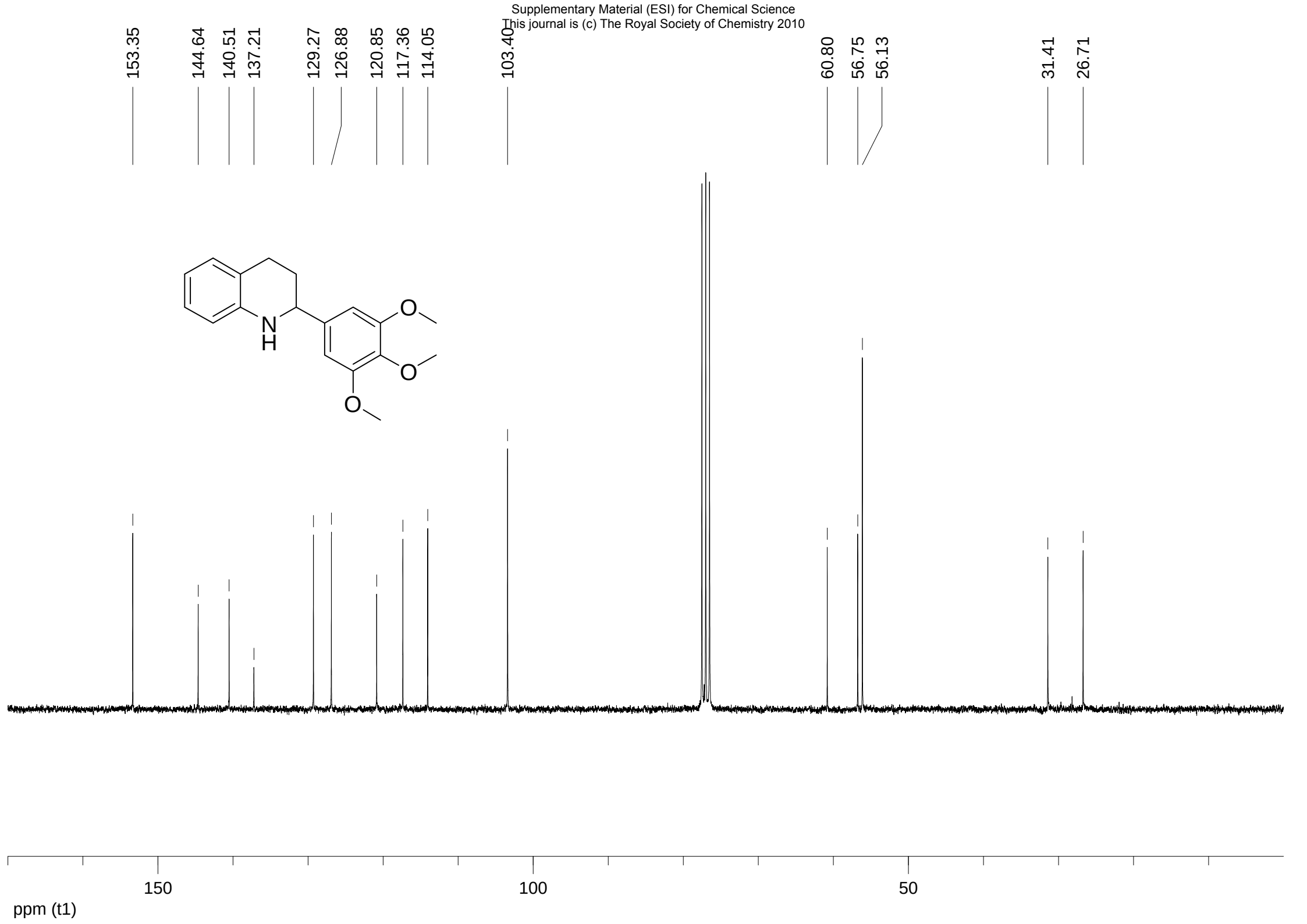
Data file: tt092_ODH_9010_flow06_1.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 22.05.2009 15:52:42



tt092_ODH_9010_flow06_1.DATA [Jasco UV 2]

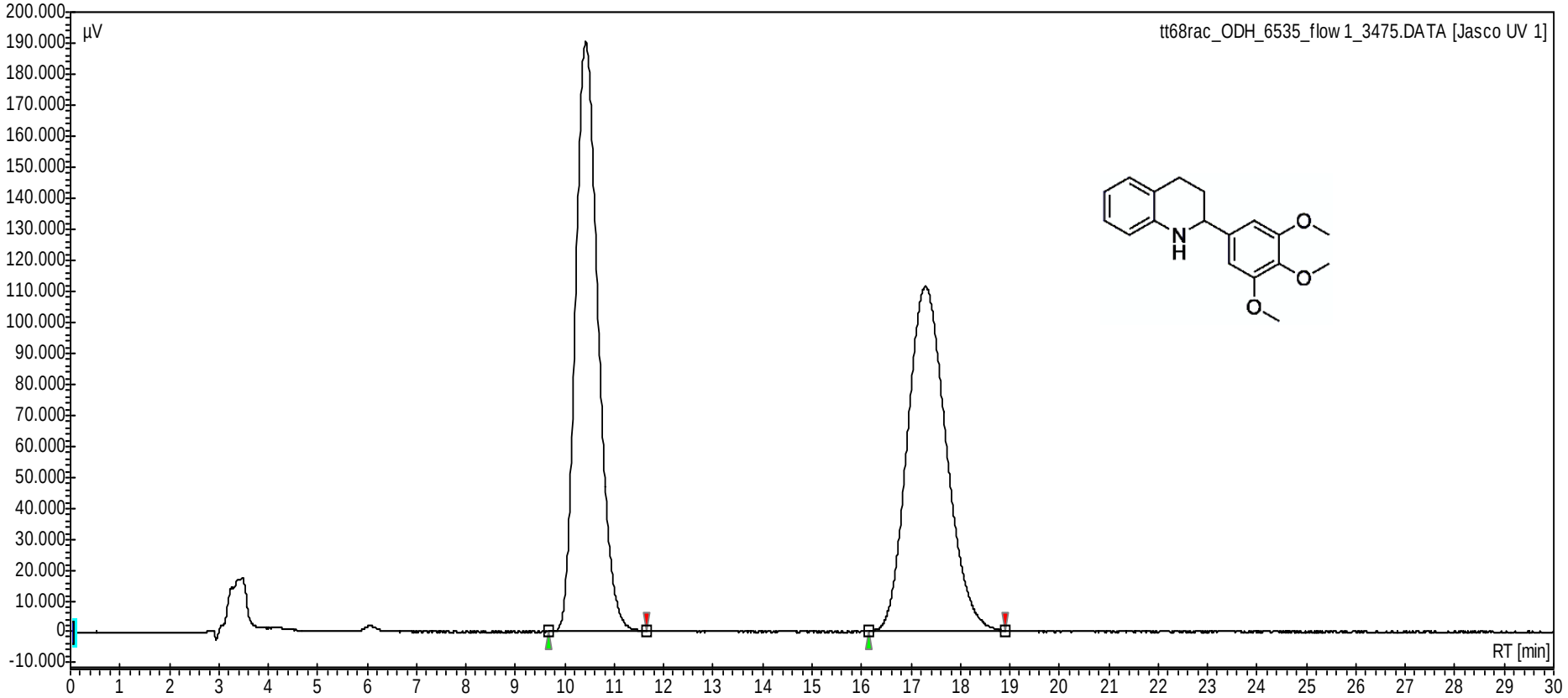
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	13,867	14,558	15,679	96,717
2	23,204	23,867	24,820	3,283
Total				100,000





Chromatogram : tt68rac_ODH_6535_flow1_3475

Data file: tt68rac_ODH_6535_flow1_3475.DATA
Method: HPLC1_ODH_6535_flow1_acq_30
Date: 05.06.2009 22:00:31

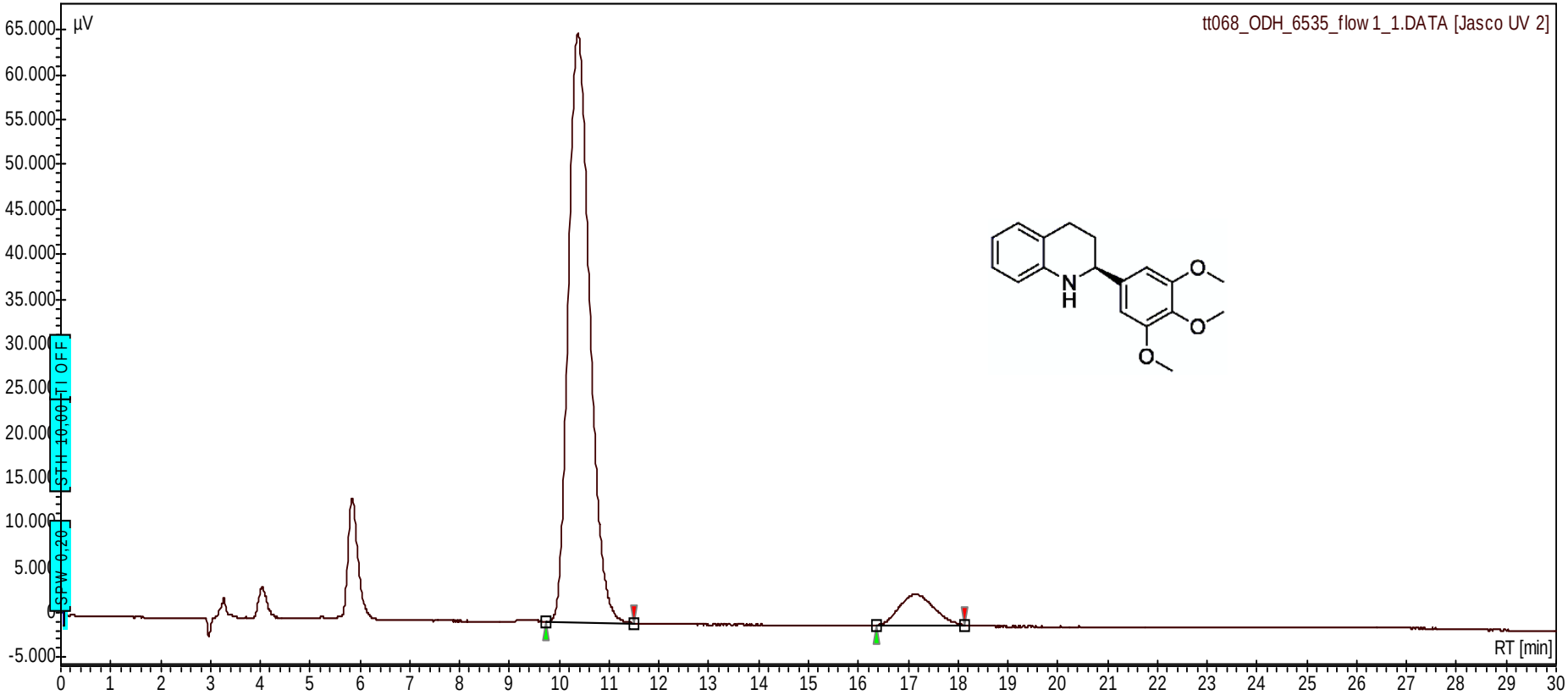


tt68rac_ODH_6535_flow1_3475.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	9,669	10,425	11,653	49,997
2	16,147	17,300	18,905	50,003
Total				100,000

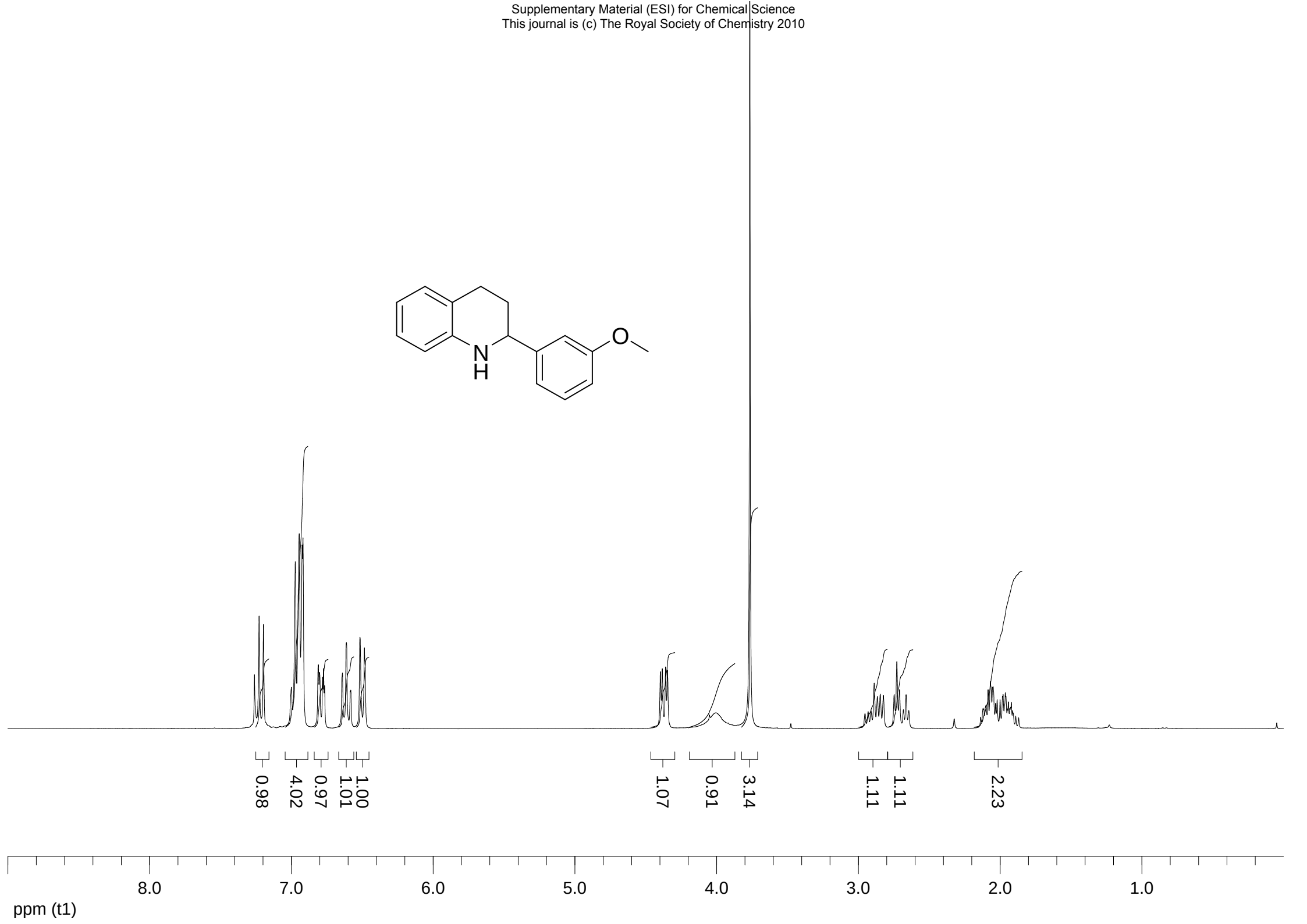
Chromatogram : tt068_ODH_6535_flow1_1

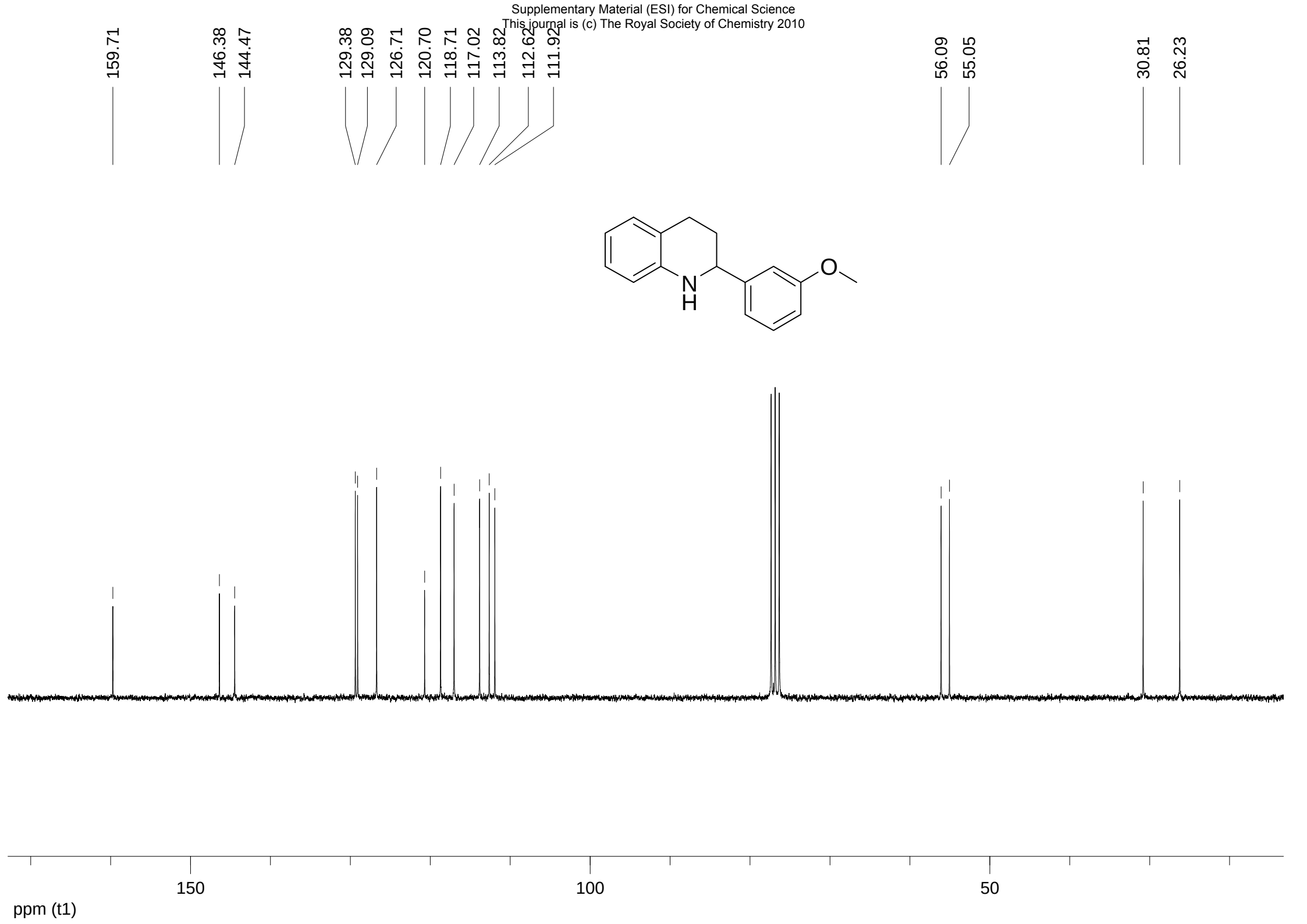
Data file: tt068_ODH_6535_flow1_1.DATA
Method: HPLC1_ODH_6535_flow1_acq_30
Date: 24.04.2009 17:25:46



tt068_ODH_6535_flow1_1.DATA [Jasco UV 2]

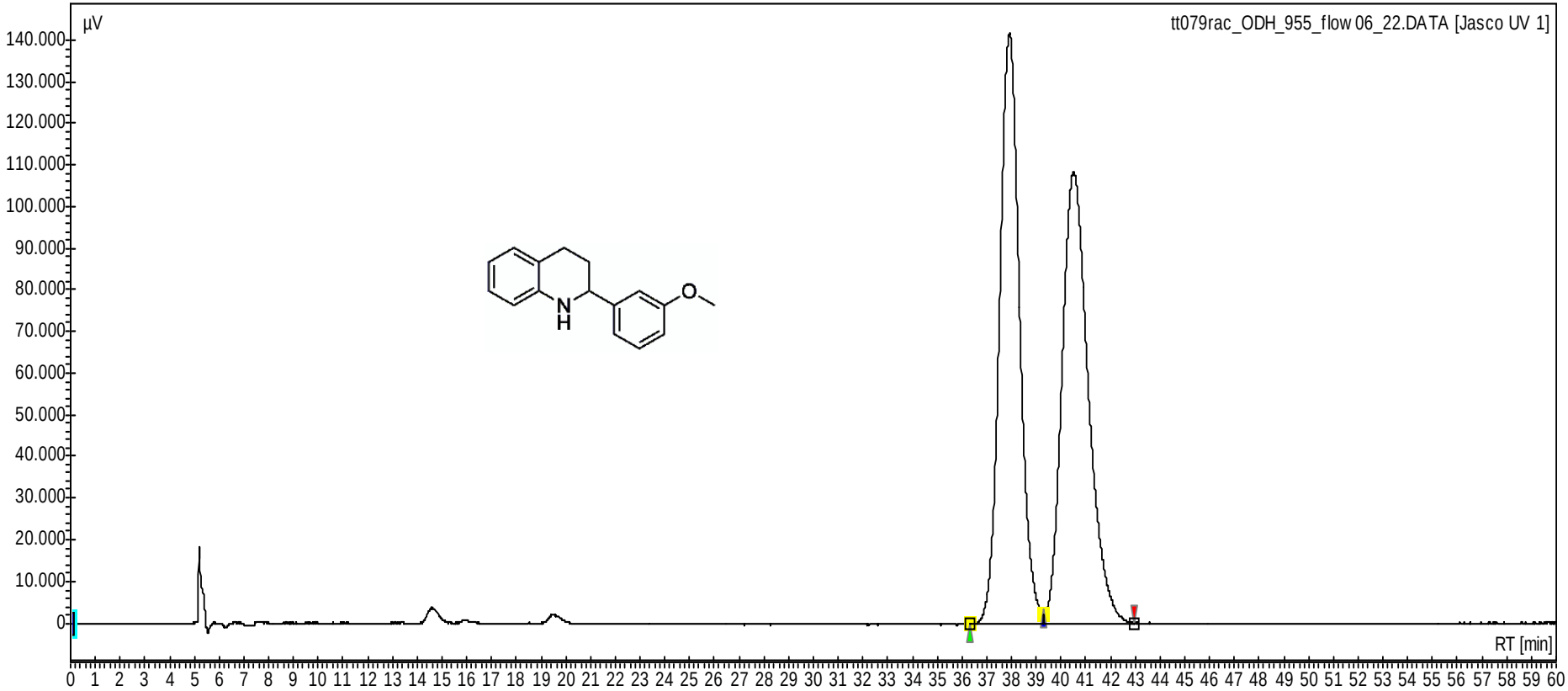
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	9,726	10,375	11,509	92,302
1	16,363	17,158	18,118	7,698
Total				100,000





Chromatogram : tt079rac_ODH_955_flow06_22

Data file: tt079rac_ODH_955_flow06_22.DATA
Method: HPLC1_ODH_955_flow06_acq_60
Date: 20.05.2009 08:57:50

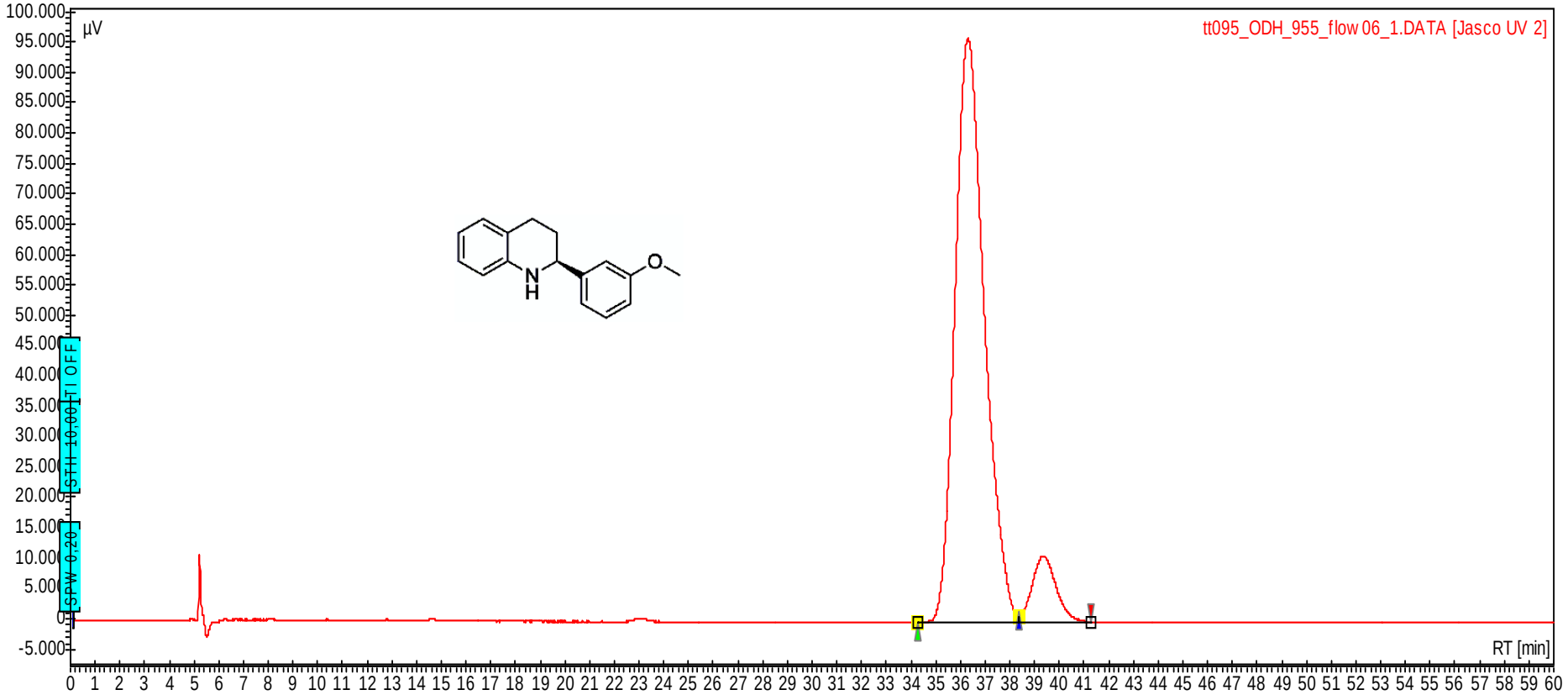


tt079rac_ODH_955_flow06_22.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	36,330	37,917	39,299	49,858
2	39,299	40,500	42,984	50,142
Total				100,000

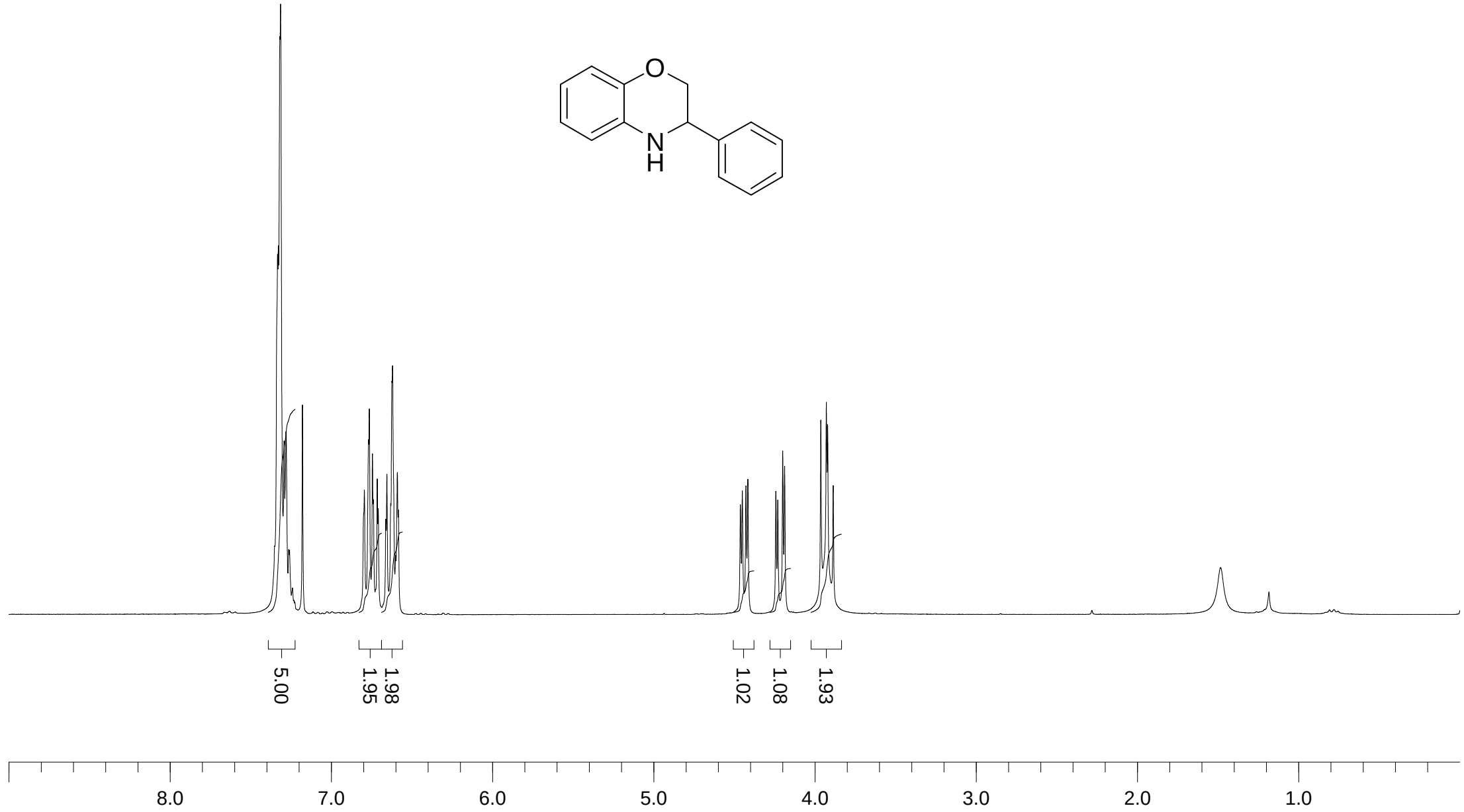
Chromatogram : tt095_ODH_955_flow06_1

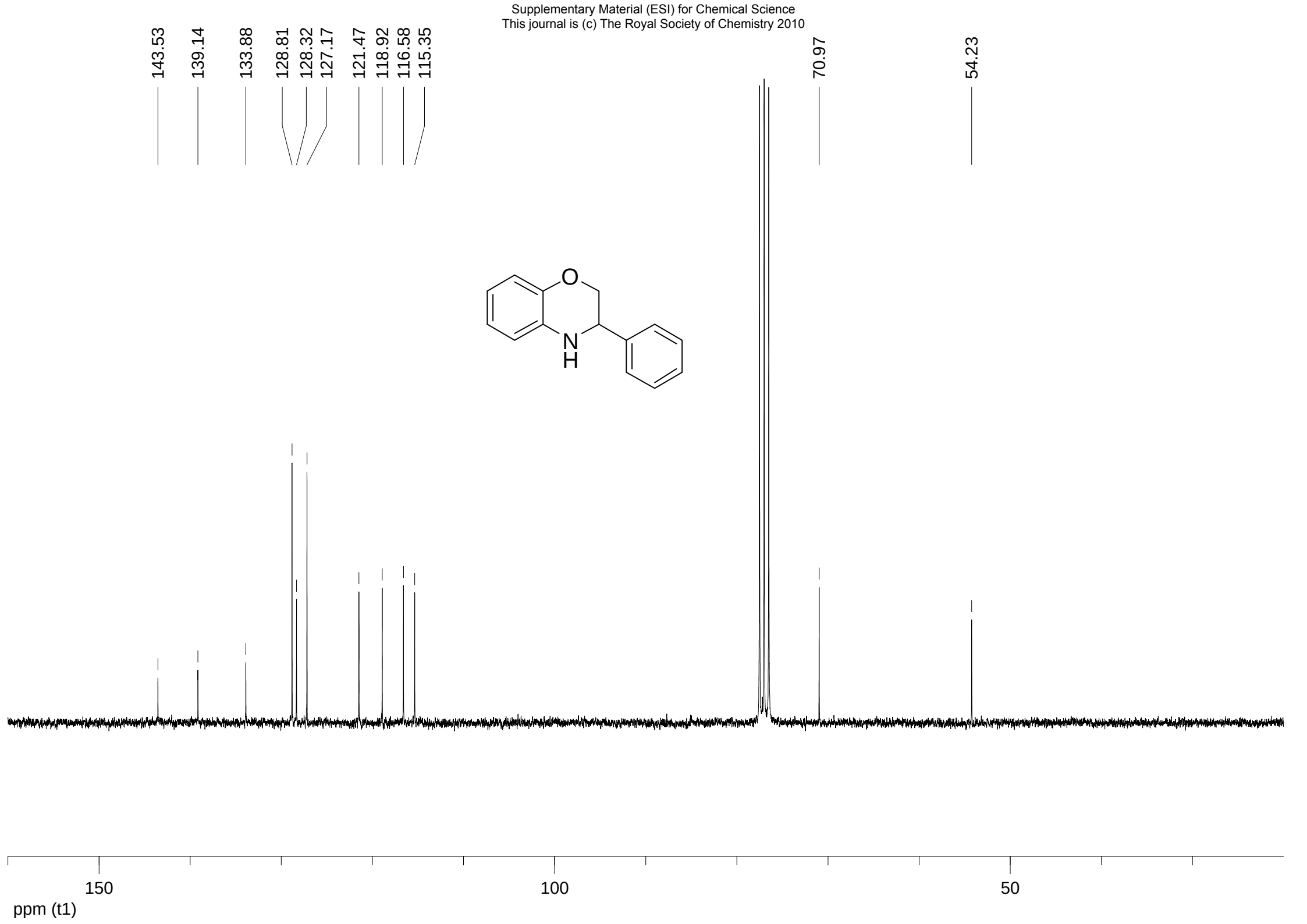
Data file: tt095_ODH_955_flow06_1.DATA
Method: HPLC1_ODH_955_flow06_acq_60
Date: 22.05.2009 22:30:17



tt095_ODH_955_flow06_1.DATA [Jasco UV 2]

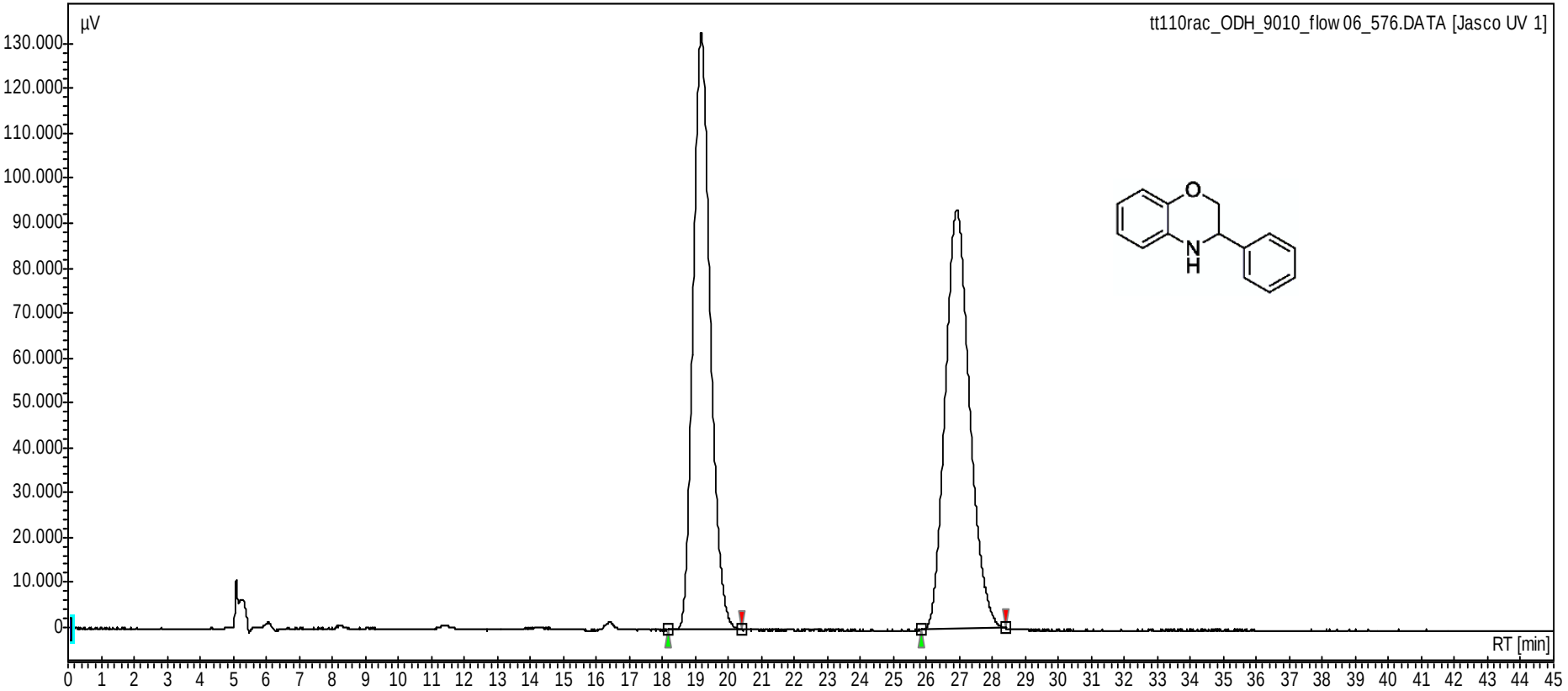
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	34,285	36,300	38,353	91,493
2	38,353	39,342	41,299	8,507
Total				100,000




143.53
139.14
133.88
128.81
128.32
127.17
121.47
118.92
116.58
115.35
70.97
54.23
O
N
H
150
100
50
ppm (t1)

Chromatogram : tt110rac_ODH_9010_flow06_576

Data file: tt110rac_ODH_9010_flow06_576.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 29.06.2009 18:02:55

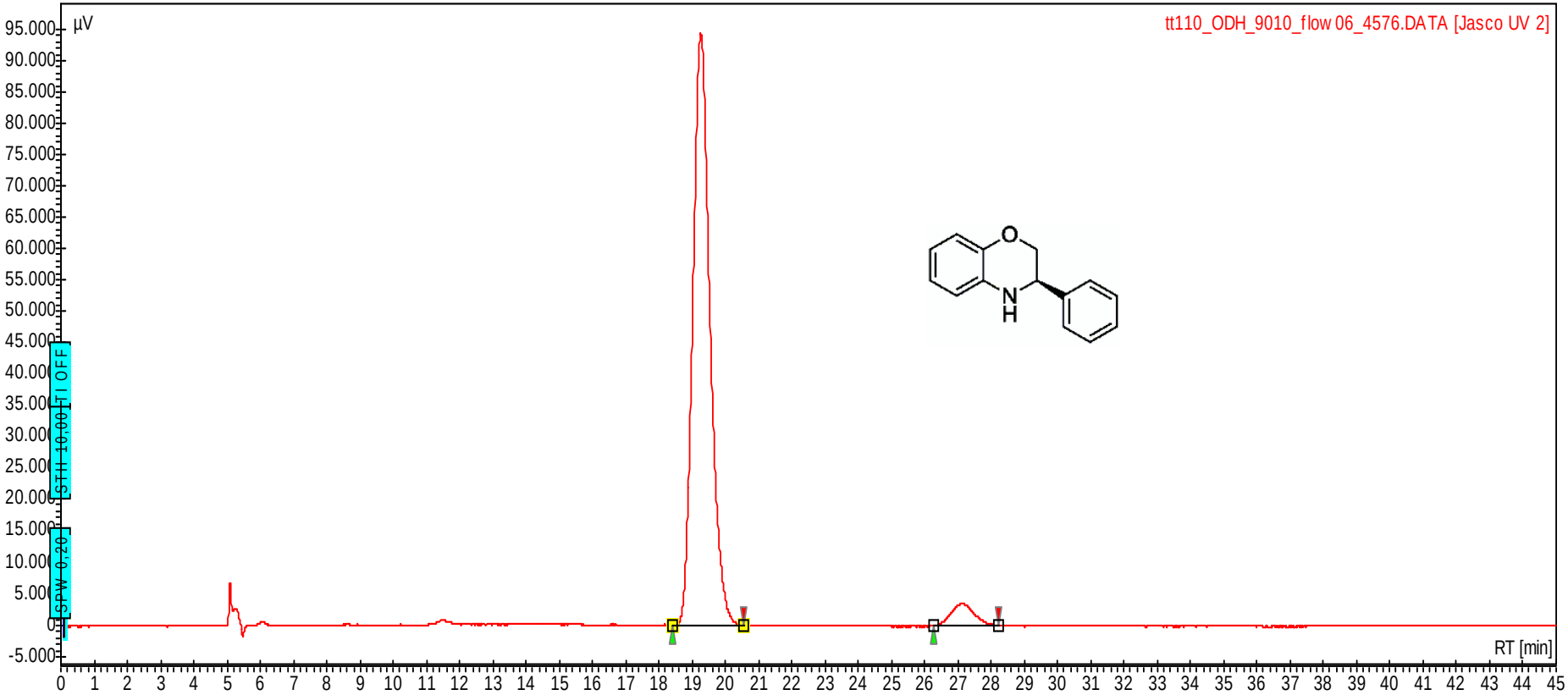


tt110rac_ODH_9010_flow06_576.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	18,180	19,175	20,428	49,889
1	25,831	26,917	28,418	50,111
Total				100,000

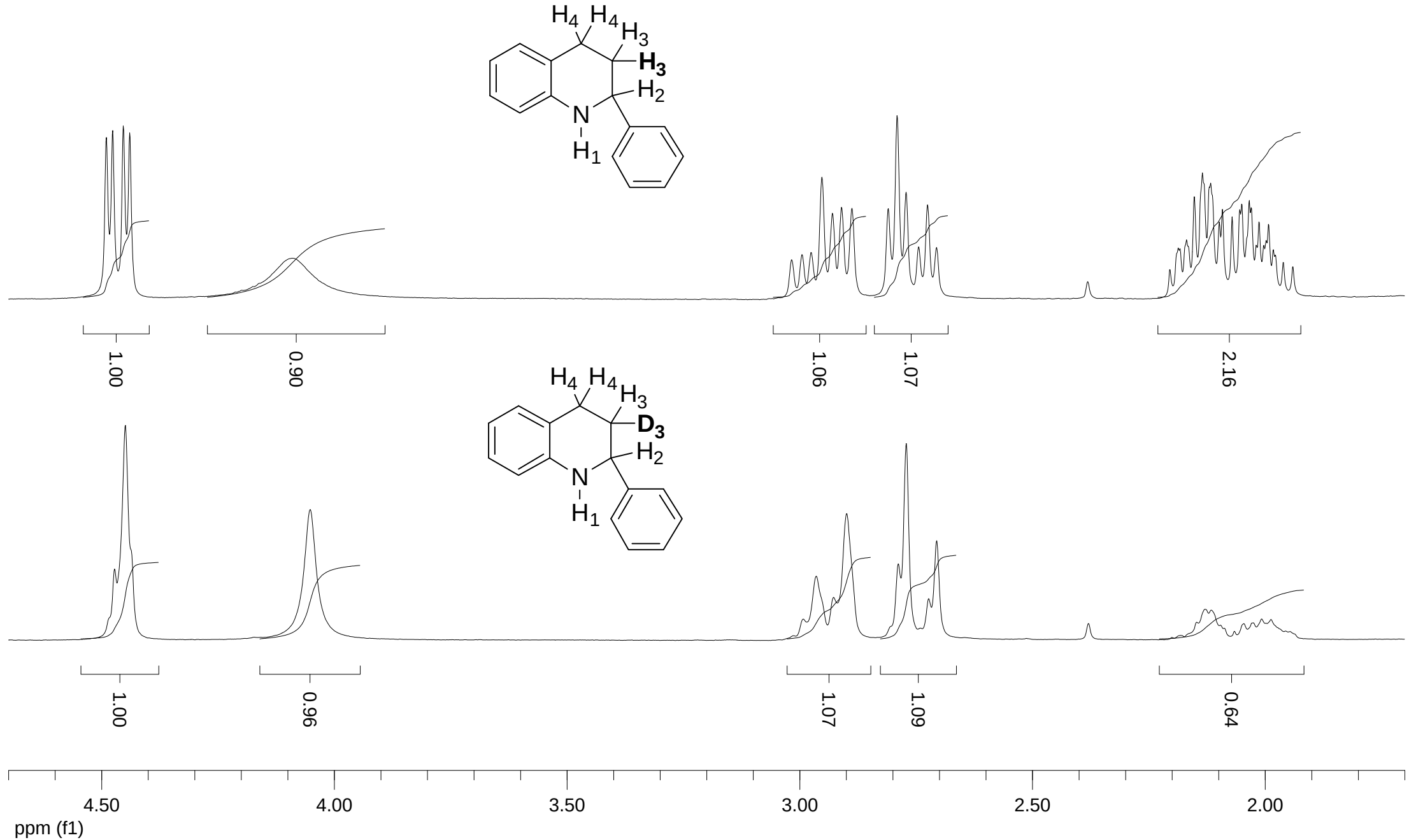
Chromatogram : tt110_ODH_9010_flow06_4576

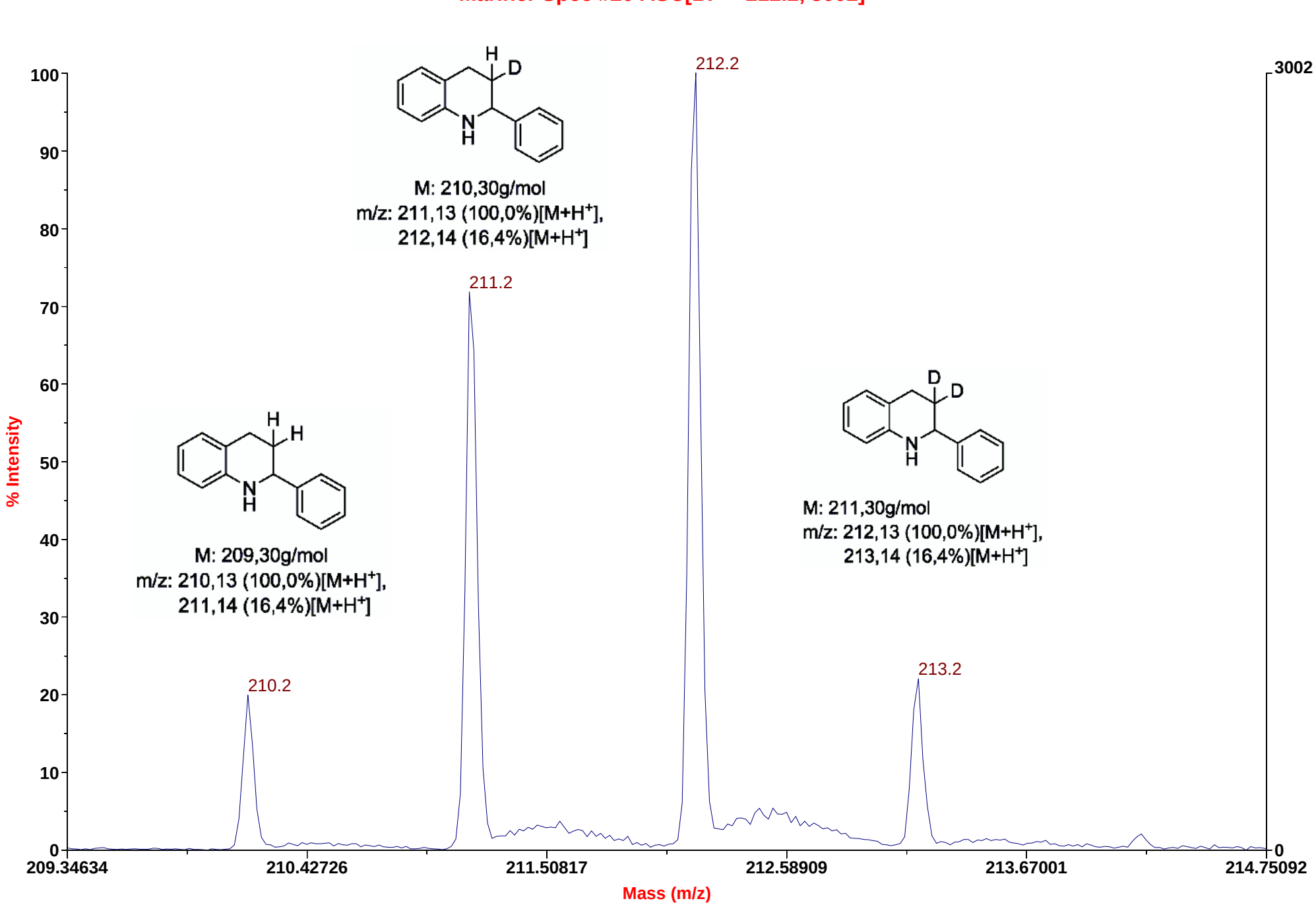
Data file: tt110_ODH_9010_flow06_4576.DATA
Method: HPLC1_ODH_9010_flow06_acq_45
Date: 29.06.2009 18:50:40



tt110_ODH_9010_flow06_4576.DATA [Jasco UV 2]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	18,395	19,258	20,567	95,079
2	26,268	27,133	28,226	4,921
Total				100,000





Mariner Mass Spectrum
H:\...\H_116003.dat
Acquired: Jun 30 16:30:00 2009