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Supporting Information

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Rhodium-Catalyzed Enantioselective 1,2-Addition of Aluminum Organyls to Cyclic Enones

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1. General Experimental Methods

^{1}H NMR spectra: Bruker AM 250 (250 MHz) or Varian Mercury 200 (200 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to $CHCl_3$ (δ = 7.26) as the internal reference unless stated otherwise. – ^{13}C NMR spectra: Bruker AW 250 (62.9 MHz) or Varian Mercury 200 (50.3 MHz). Chemical shifts in $CDCl_3$ are reported as δ values relative to $CDCl_3$ (δ = 77.0); the multiplicity of the signals was determined by the APT or DEPT technique and quoted as follows: APT: (+) for CH_3, CH, (–) for CH_2, quaternary carbons; DEPT: (+) for CH_3, CH, (–) for CH_2, and (C_{quat}) for quaternary carbons. – EI-MS: Finnigan MAT 95 spectrometer (70 eV). – ESI-HRMS: Bruker APEX-Q 7T IV spectrometer; preselected ion peak matching at R >> 10000 to be within ±2 ppm of the exact masses. – Optical rotation: Perkin-Elmer 241. – Melting points are uncorrected. – Solvents for extraction and chromatography were of technical grade and distilled prior to use. – All moisture sensitive reactions were carried out under dry nitrogen or argon in oven- and/or flame-dried glassware. – Column chromatography: silica gel 60 (0.040–0.063 mm/230–400 mesh ASTM, Machery&Nagel); prior to use the silica gel was treated with an aqueous solution of NaOAc (0.5% w/w), filtered and dried. – TLC: Macherey-Nagel precoated sheets, 0.25 mm SIL G/UV_{254}. – Tetrahydrofurane was distilled from sodium benzophenone ketyl and dichloromethane was distilled from CaH_2. – 5,5-Dimethylcyclohex-2-enone (**5**),[1] cyclohept-2-enone (**6**),[2] 4,4-dimethylcyclopent-2-enone (**8**),[3] (*E*)-1-phenylpent-1-en-3-one (**9**),[4] and $[Rh(cod)OMe]_2$[5] were prepared as described in the literature. All other enones are commercially available and were distilled prior to use.

General procedure for the 1,2-addition of $AlMe_3$ (GP 1, Table 3): A slurry of $[Rh(cod)OMe]_2$ (60.5 mg, 124 µmol) and (*S*)-BINAP (187 mg, 300 µmol) in THF (10 mL) was stirred for 0.5 h at RT. The reaction mixture was then cooled to 0 °C and $AlMe_3$ (2.50 mL, 5.00 mmol, 2.0 M in hexane) and the respective enone (5.00 mmol) were added. The mixture was stirred for the stated time at the given temperature and then quenched by addition of saturated NH_4Cl solution (20 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (5 × 30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to yield the crude product which was purified by Kugelrohr distillation or column chromatography on NaOAc treated silica gel.

(*R*)-1-Methylcyclohex-2-enol (Table 3, entry 1): Cyclohex-2-enone (**2**, 291 µL, 3.01 mmol) was treated with $[Rh(cod)OMe]_2$, (*S*)-BINAP and $AlMe_3$ for 2 h at 0 °C according to GP 1. The product was purified by column chromatography (55 g SiO_2, pentane:Et_2O 1:1) to furnish 284 mg (84%) of alcohol **3** (R_f = 0.37). The *ee* was determined by GC analysis on a heptakis-(2,3-di-*O*-acetyl-6-*O*-TBDMS)-ß-cyclodextrin column (50% in OV1701,

w/w, 25 m, 0.25 mm i.d.), 80 °C isothermal, 20 kPa flow. Retention times: 12.7 min [(*S*)-enantiomer], 13.4 min [(*R*)-enantiomer]. 98% *ee*. $[\alpha]^{20}_{D} = 76.5$ ($c = 1.0$ in Et_2O). The physical and spectroscopic data were consistent with the reported data.[6]

(*S*)-1,4,4-Trimethylcyclohex-2-enol (Table 3, entry 2): 4,4-Dimethylcyclohex-2-enone (**4**, 100 µL, 0.76 mmol) was treated with $[Rh(cod)OMe]_2$, (*R*)-BINAP and $AlMe_3$ for 3.5 h at 60 °C according to GP 1. The product was purified by column chromatography (20 g SiO_2, pentane:Et_2O 1:1) to yield 91 mg (86%) of the 1,2-adduct ($R_f = 0.45$). The *ee* was determined by GC analysis on a heptakis-(2,3-di-*O*-acetyl-6-*O*-TBDMS)-ß-cyclodextrin column (50% in OV1701, w/w, 25 m, 0.25 mm i.d.), 80 °C isothermal, 50 kPa flow. Retention times: 17.2 min (minor enantiomer), 18.1 min (major enantiomer). 99% *ee*. $[\alpha]^{20}_{D} = 3.1$ ($c = 0.49$ in $CHCl_3$). The absolute configuration was assigned in analogy with compound **3**. The physical and spectroscopic data were consistent with the reported data.[7]

(*S*)-1,5,5-Trimethylcyclohex-2-enol (Table 3, entry 3): 5,5-Dimethylcyclohex-2-enone (**5**, 62 mg, 0.50 mmol) was treated with $[Rh(cod)OMe]_2$, (*R*)-BINAP and $AlMe_3$ for 2.5 h at RT according to GP 1. The product was purified by Kugelrohr distillation (bp. 55-60 °C, 5 mbar) to furnish 22 mg (31%) of the 1,2-adduct. The *ee* was determined by GC analysis on a heptakis-(2,3-di-*O*-acetyl-6-*O*-TBDMS)-ß-cyclodextrin column (50% in OV1701, w/w, 25 m, 0.25 mm i.d.), 80 °C isothermal, 40 kPa flow. Retention times: 6.8 min (minor enantiomer), 7.3 min (major enantiomer). 99% *ee*. $[\alpha]^{20}_{D} = 18.8$ ($c = 0.67$ in $CHCl_3$). The absolute configuration was assigned in analogy with compound **3**. The physical and spectroscopic data were consistent with the reported data.[8]

(*R*)-1-Methylcyclohept-2-enol (Table 3, entry 4): Cyclohept-2-enone (**6**, 0.11 mL, 1.0 mmol) was treated with $[Rh(cod)OMe]_2$, (*S*)-BINAP and $AlMe_3$ for 2 h at 0 °C and then for 1 h at RT according to GP 1. The product was purified by column chromatography (10 g SiO_2, pentane:Et_2O 1:1) to yield 93 mg (74%) of the 1,2-adduct ($R_f = 0.37$). The *ee* was determined by GC analysis on a heptakis-(2,3-di-*O*-acetyl-6-*O*-TBDMS)-ß-cyclodextrin column (50% in OV1701, w/w, 25 m, 0.25 mm i.d.), 80 °C isothermal, 20 kPa flow. Retention times: 17.7 min (minor enantiomer), 18.6 min (major enantiomer). 98% *ee*. $[\alpha]^{20}_{D} = 24.7$ ($c = 0.48$ in $CHCl_3$). The absolute configuration was assigned in analogy with compound **3**. The physical and spectroscopic data were consistent with the reported data.[9]

1-Methylcyclopent-2-enol (Table 3, entry 5): Cyclopent-2-enone (**7**, 81 µL, 0.97 mmol) was treated with $[Rh(cod)OMe]_2$, (*R*)-BINAP and $AlMe_3$ for 1 h at 0 °C and then for 1 h at RT according to GP 1. The product was purified by column chromatography (20 g SiO_2, pentane:Et_2O 1:1) to yield 9.5 mg (10%) of the 1,2-adduct ($R_f = 0.45$). The physical and spectroscopic data were consistent with the reported data.[10]

(*R*)-1,4,4-Trimethylcyclopent-2-enol (Table 3, entry 6): 4,4-Dimethylcyclopent-2-enone (**8**, 110 mg, 0.999 mmol) was treated with $[Rh(cod)OMe]_2$, (*S*)-BINAP and $AlMe_3$ for 1 h at RT according to GP 1. The product was purified by Kugelrohr distillation (bp. 60-65 °C, 25 mbar) to furnish 35 mg (28%) of the 1,2-adduct as

a colorless oil. The *ee* was determined by GC analysis on a heptakis-(2,3-di-*O*-acetyl-6-*O*-TBDMS)-ß-cyclodextrin column (50% in OV1701, w/w, 25 m, 0.25 mm i.d.), 80 °C isothermal, 20 kPa flow. Retention times: 4.4 min (major enantiomer), 4.9 min (minor enantiomer). >95% *ee*. $[\alpha]^{20}_{D} = 50.2$ ($c = 0.5$, $CHCl_3$). The absolute configuration was assigned in analogy with compound **3**. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.08 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.65 (s, 1 H, OH), 1.83 (m_c, 2 H, 5-H), 5.54 (d, $J = 6.3$ Hz, 1 H, 2-H*), 5.61 (d, $J = 6.3$ Hz, 1 H, 3-H*). – ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): δ = 29.0 (+), 29.1 (+), 30.4 (+), 44.8 (C_{quat}), 54.8 (–), 83.7 (C_{quat}), 134.5 (+), 143.4 (+). – MS, *m/z* (%): 126 (1) [M^+], 111 (100) [M^+–CH_3], 93 (18), 77 (10), 55 (11) [$C_3H_3O^+$], 43 (20).

3-Methyl-1-phenylpent-(*E*)-1-en-3-ol (Table 3, entry 7): (*E*)-1-Phenylpent-1-en-3-one (**9**, 80 mg, 0.50 mmol) was treated with $[Rh(cod)OMe]_2$, (*S*)-BINAP and $AlMe_3$ for 3.5 h at RT according to GP 1. The product was purified by column chromatography (10 g SiO_2, hexane:EtOAc 5:1) to give 43 mg (49%) of the 1,2-adduct. The *ee* was determined by GC analysis on a heptakis-(2,3-di-*O*-acetyl-6-*O*-TBDMS)-ß-cyclodextrin column (50% in OV1701, w/w, 25 m, 0.25 mm i.d.), 110 °C isothermal, 20 kPa flow. Retention times: 94.1 min (minor enantiomer), 98.1 min (major enantiomer). 7% *ee*. The physical and spectroscopic data were consistent with the reported data.[11]

2-Phenylbutan-2-ol (Table 3, entry 8): Propiophenone (**10**, 67 µL, 0.50 mmol) was treated with $[Rh(cod)OMe]_2$, (*S*)-BINAP and $AlMe_3$ for 8 h at reflux according to GP 1. Due to the low conversion the product was not isolated. The *ee* was determined by GC analysis on a heptakis-(2,3-di-*O*-acetyl-6-*O*-TBDMS)-ß-cyclodextrin column (50% in OV1701, w/w, 25 m, 0.25 mm i.d.), 100 °C isothermal, 40 kPa flow. Retention times: 12.5 min (mayor enantiomer), 13.3 min (minor enantiomer). 54% *ee*.

General procedure for the sequence of 1,2-arylation and subsequent epoxidation (GP 2, Scheme 2): The respective arylmagnesium bromide (0.50 mmol, solution in THF) was added at 0 °C to a solution of $AlMe_2Cl$ (0.25 mL, 0.50 mmol, 2.0 M in hexane) in THF (1 mL) and the mixture was stirred for 0.5 h at 0 °C. In a second flask a slurry of $[Rh(cod)OMe]_2$ (6.0 mg, 12 µmol) and (*R*)-BINAP (18.7 mg, 30 µmol) in THF (1.5 mL) was stirred for 0.5 h at RT and then cooled to 0 °C. To this solution cyclohex-2-enone (**2**, 48.5 µL, 0.50 mmol) and the solution of the aryldimethylaluminum were added and the mixture was stirred for 1.5 h at 0 °C and was then quenched by addition of saturated NH_4Cl solution (0.5 mL). The mixture was poured onto Et_2O (10 mL) and water (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The thus obtained crude product was dissolved in CH_2Cl_2 (3 mL) and treated at 0 °C with *m*CPBA (0.16 g, 0.65 mmol, 70%). The mixture was stirred for 16 h and was allowed to warm up to RT during this time. It was then diluted with ethyl acetate (10 mL) and successively washed with saturated Na_2SO_3 solution (10 mL) and saturated $NaHCO_3$ solution (10 mL). The aqueous phases were extracted with ethyl acetate (5 mL) and the combined organic phases were washed with brine (5 mL), dried over $MgSO_4$ and concentrated in vacuo. The crude products were purified by column chromatography (20 g SiO_2, hexane:EtOAc 5:1).

(1*R*,2*R*,6*R*)-2-Phenyl-7-oxabicyclo[4.1.0]heptan-2-ol: Cyclohex-2-enone (**2**, 48.5 µL, 0.50 mmol) was treated with *in situ* prepared $PhAlMe_2$ and subsequently with *m*CPBA according to GP 2. Column chromatography furnished 62 mg (65%) of the desired product (R_f = 0.36, hexane:EtOAc 3:1) as colorless solid, m.p. 72 °C. The *ee* was determined by HPLC analysis on a Daicel CHIRALPAK IA column with hexane : *i*PrOH = 99 : 1, eluent flow: 0.6 mL/min. Retention times: 16.8 min (minor enantiomer), 18.4 min (major enantiomer). 99% *ee*. $[\alpha]^{20}_D$ = 3.5 (*c* = 1.0 in $CHCl_3$). The absolute configuration was assigned in analogy with compound **3**. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.17–1.88 (m, 5 H), 1.96–2.14 (m, 1 H), 2.78 (s, br, 1 H, OH), 3.27 (d, *J* = 4.0 Hz, 1 H, 1-H), 3.50 (m_c, 1 H, 6-H), 7.18–7.47 (m, 5 H, Ar-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): δ = 14.8 (–), 22.5 (–), 36.8 (–), 55.3 (+), 58.1 (+), 70.7 (–), 124.4 (+), 126.5 (+), 127.6 (+), 144.7 (–). – MS, *m/z* (%): 190 (18) [M^+], 159 (3), 133 (32), 121 (49), 105 (100), 91 (8), 77 (39), 55 (16), 43 (8). – Anal. calcd. for $C_{12}H_{14}O_2$: 213.08860 [*M*+Na]$^+$ (correct mass according to ESI-HRMS).

(1*R*,2*R*,6*R*)-2-(4-Fluorophenyl)-7-oxabicyclo[4.1.0]heptan-2-ol: Cyclohex-2-enone (**2**, 48.5 µL, 0.50 mmol) was treated with *in situ* prepared (*p*FC_6H_4)$AlMe_2$ and subsequently with *m*CPBA according to GP 2. Column chromatography furnished 49 mg (47%) of the desired product (R_f = 0.33, hexane:EtOAc 3:1) as colorless solid, m.p. 84 °C. The *ee* was determined by HPLC analysis on a Daicel CHIRALPAK IA column with hexane : *i*PrOH = 99 : 1, eluent flow: 0.6 mL/min. Retention times: 13.4 min (minor enantiomer), 14.4 min (major enantiomer). 92% *ee*. $[\alpha]^{20}_D$ = -4.6 (*c* = 1.0 in $CHCl_3$). The absolute configuration was assigned in analogy with compound **3**. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.18–1.59 (m, 3 H), 1.66–1.92 (m, 2 H), 2.01–2.17 (m, 1 H), 2.97 (s, br, 1 H, OH), 3.28 (d, *J* = 4.0 Hz, 1 H, 1-H), 3.54 (m_c, 1 H, 6-H), 7.02 (m_c, 2 H, Ar-H), 7.43 (m_c, 2 H, Ar-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): δ = 15.6 (–), 23.2 (–), 37.6 (–), 56.1 (+), 58.7 (+), 71.3 (–), 115.1 (+, d, $^2J_{C\text{-}F}$ = 21.3 Hz), 127.0 (+, d, $^3J_{C\text{-}F}$ = 8.0 Hz), 141.2 (–, d, $^4J_{C\text{-}F}$ = 2.5 Hz), 162.1 (–, d, $^1J_{C\text{-}F}$ = 246.2 Hz). – MS, *m/z* (%): 208 (14) [M^+], 190 (1) [M^+–H_2O], 177 (3), 151 (33), 139 (45), 123 (100), 109 (7), 95 (19) [$C_6H_4F^+$], 70 (17), 55 (5), 43 (3). – Anal. calcd. for $C_{12}H_{13}FO_2$: 231.07918 [*M*+Na]$^+$ (correct mass according to ESI-HRMS).

(1*R*,2*R*,6*R*)-2-(2-Methylphenyl)-7-oxabicyclo[4.1.0]heptan-2-ol: Cyclohex-2-enone (**2**, 48.5 µL, 0.50 mmol) was treated with *in situ* prepared (*o*Tolyl)$AlMe_2$ and subsequently with *m*CPBA according to GP 2. Column chromatography furnished 39 mg (38%) of the desired product (R_f = 0.41, hexane:EtOAc 3:1) as colorless solid, m.p. 41 °C. The *ee* was determined by HPLC analysis on a Daicel CHIRALPAK IA column with hexane : *i*PrOH = 99 : 1, eluent flow: 0.6 mL/min. Retention times: 38.4 min (minor enantiomer), 41.3 min (major enantiomer). 97% *ee*. $[\alpha]^{20}_D$ = 1.9 (*c* = 1.0 in $CHCl_3$). The absolute configuration was assigned in analogy with compound **3**. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20–1.86 (m, 5 H), 2.06–2.21 (m, 1 H), 2.39 (s, 3 H, CH_3), 3.02 (s, br, 1 H, OH), 3.36 (d, *J* = 4.0 Hz, 1 H, 1-H), 3.57 (m_c, 1 H, 6-H), 7.09–7.20 (m, 3 H, Ar-H), 7.64 (m_c, 1 H, Ar-H). – ^{13}C NMR (50.3 MHz, $CDCl_3$, APT): δ = 14.1 (–), 20.2 (+), 22.7 (–), 34.8 (–), 55.9 (+), 58.5 (+), 70.4 (–), 125.1 (+, 2 C), 126.5 (+), 131.3 (+), 133.2 (–), 142.5 (–). – MS, *m/z* (%): 204 (3) [M^+], 186 (24) [M^+–H_2O], 147

(13), 135 (13), 119 (100), 91 (33) [$C_7H_7^+$], 77 (6), 65 (8), 55 (10), 43 (4). – Anal. calcd. for $C_{13}H_{16}O_2$: 227.10425 [*M*+Na]$^+$ (correct mass according to ESI-HRMS).

2.Literature

[1] B. L. Shapiro, M. D. Johnston, T. W. Proulx, *J. Am. Chem. Soc.* **1973**, *95*, 520–526.

[2] H. O. House, T. V. Lee, *J. Org. Chem.* **1979**, *44*, 2819–2824.

[3] J. Yang, Y. O. Long, L. A. Paquette, *J. Am. Chem. Soc.* **2003**, *125*, 1567–1574.

[4] P. J. Smith, J. R. Dimmock, W. G. Taylor, *Can. J. Chem.* **1972**, *50*, 871–879.

[5] R. Uson, L. A. Oro, J. A. Cabeza, *Inorg. Synth.* **1985**, *23*, 126–130.

[6] K. Mori, B. G. Hazra, R. J. Pfeiffer, A. K. Gupta, B. S. Lindgren, *Tetrahedron* **1987**, *43*, 2249–2254.

[7] W. G. Dauben, D. M. Michno, *J. Org. Chem.* **1977**, *42*, 682–685.

[8] A. Takezawa, K. Yamaguchi, T. Ohmura, Y. Yamamoto, N. Miyaura, *Synlett* **2002**, 1733–1735.

[9] E. A. Mash, T. M. Gregg, M. A. Kaczynski, *J. Org. Chem.* **1996**, *61*, 2743–2752.

[10] I.-C. Chiu, H. Kohn, *J. Org. Chem.* **1983**, *48*, 2857–2866.

[11] D. J. Ramon, M. Yus, *Tetrahedron* **1998**, *54*, 5651–5666.

3. Spectral Data and Analyses:

(*R*)-1-Methylcyclohex-2-enol (Table 3, entry 1):

Area % Report

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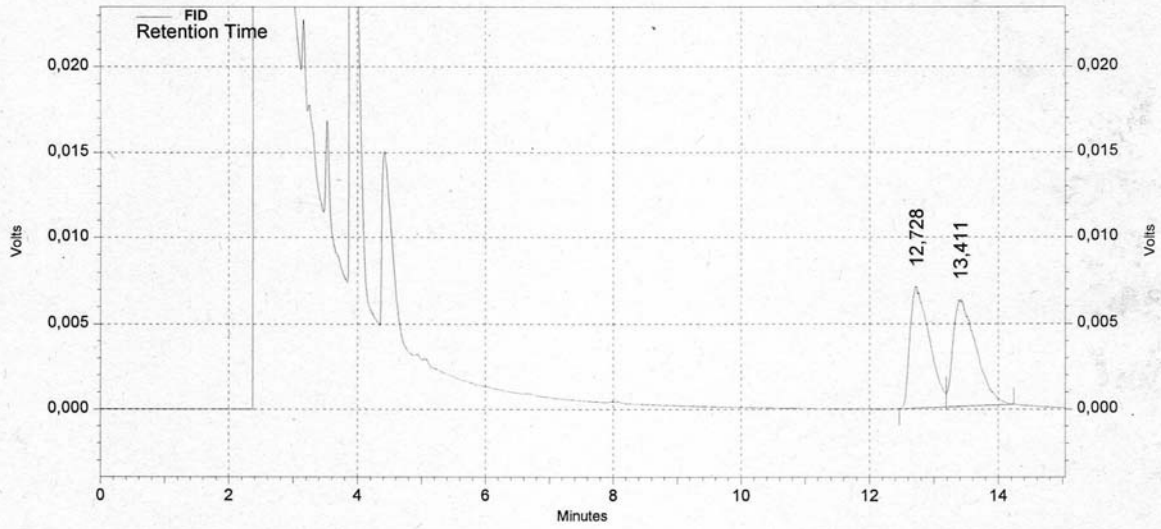

FID Results

Retention Time	Area	Area %	Height	Height %
12,728	148520	48,81	7105	53,17
13,411	155763	51,19	6259	46,83
Totals	304283	100,00	13364	100,00

Area % Report

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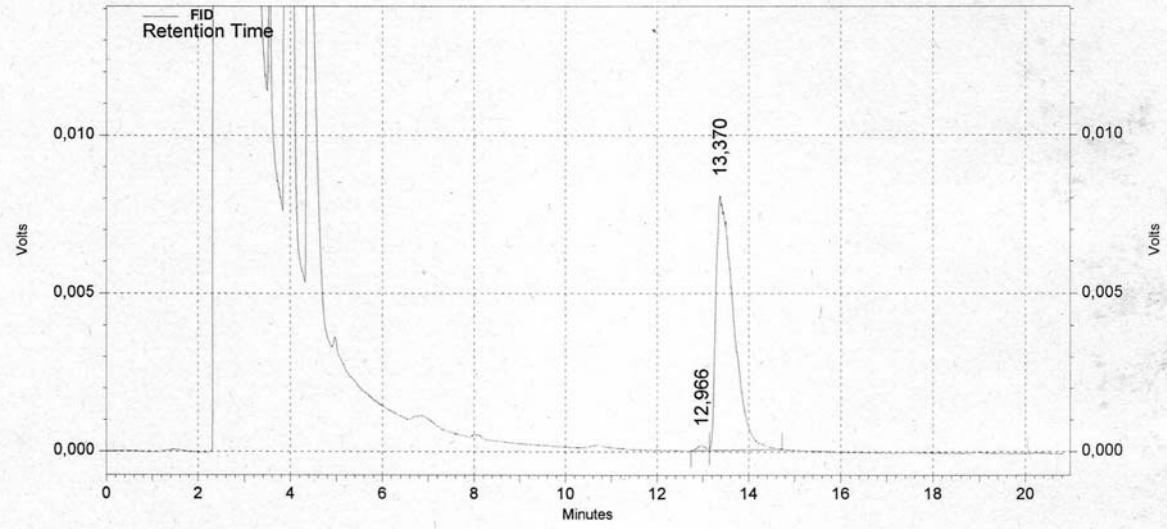

FID Results

Retention Time	Area	Area %	Height	Height %
12,966	1964	0,91	156	1,90
13,370	214060	99,09	8047	98,10
Totals	216024	100,00	8203	100,00

(*S*)-1,4,4-Trimethylcyclohex-2-enol (Table 3, entry 2):

CA150-3**Area % Report**

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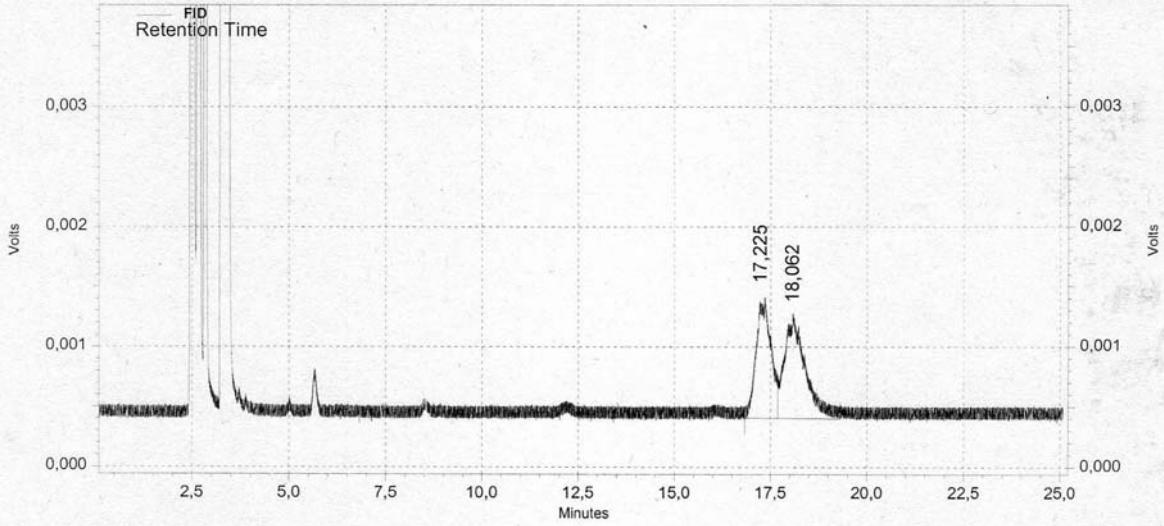

FID Results

Retention Time	Area	Area %	Height	Height %
17,225	26898	45,36	969	54,59
18,062	32406	54,64	806	45,41
Totals	59304	100,00	1775	100,00

CA150-3**Area % Report**

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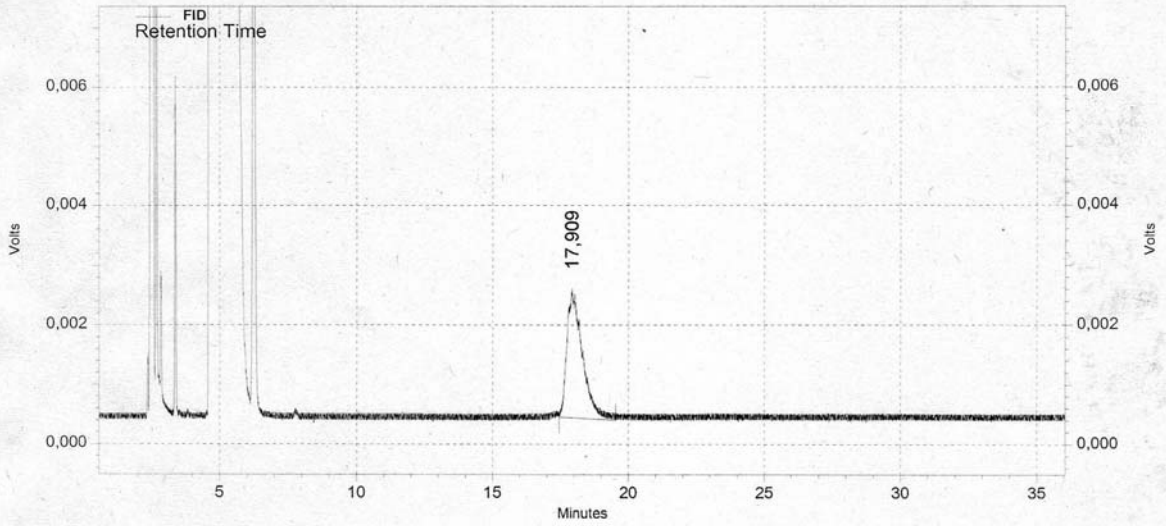

FID Results

Retention Time	Area	Area %	Height	Height %
17,909	86197	100,00	2169	100,00

Totals	86197	100,00	2169	100,00

(*S*)-1,5,5-Trimethylcyclohex-2-enol (Table 3, entry 3):

Area % Report

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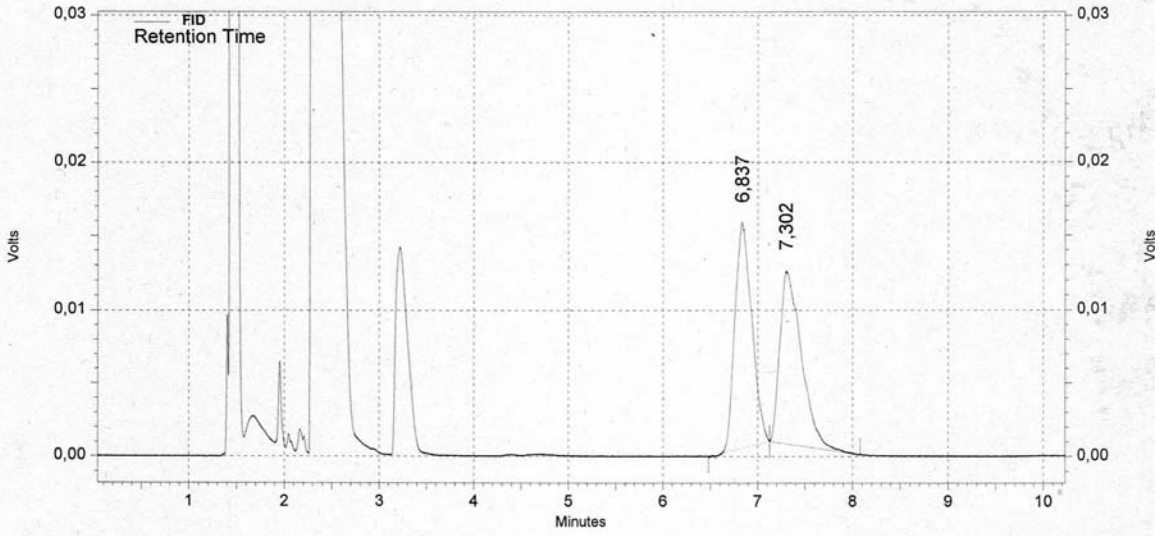

FID Results

Retention Time	Area	Area %	Height	Height %
6,837	189330	50,39	15365	56,56
7,302	186382	49,61	11803	43,44
Totals	375712	100,00	27168	100,00

Area % Report

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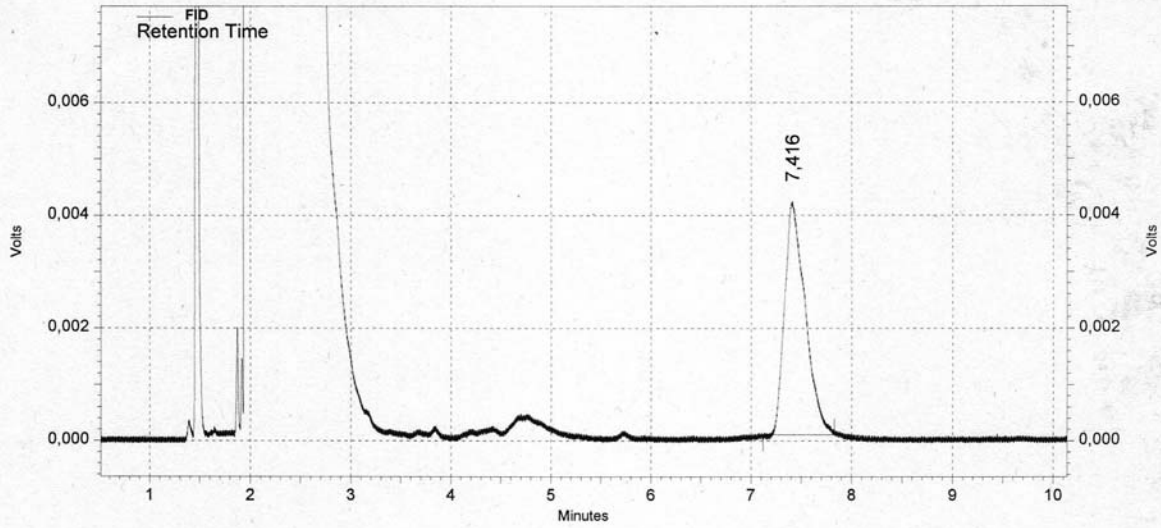
4



FID Results

Retention Time	Area	Area %	Height	Height %
7,416	59029	100,00	4141	100,00

Totals	59029	100,00	4141	100,00

(*R*)-1-Methylcyclohept-2-enol (Table 3, entry 4):

Area % Report

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Acquired: 03.03.06 20:00:21
Printed: 20.04.07 17:24:52
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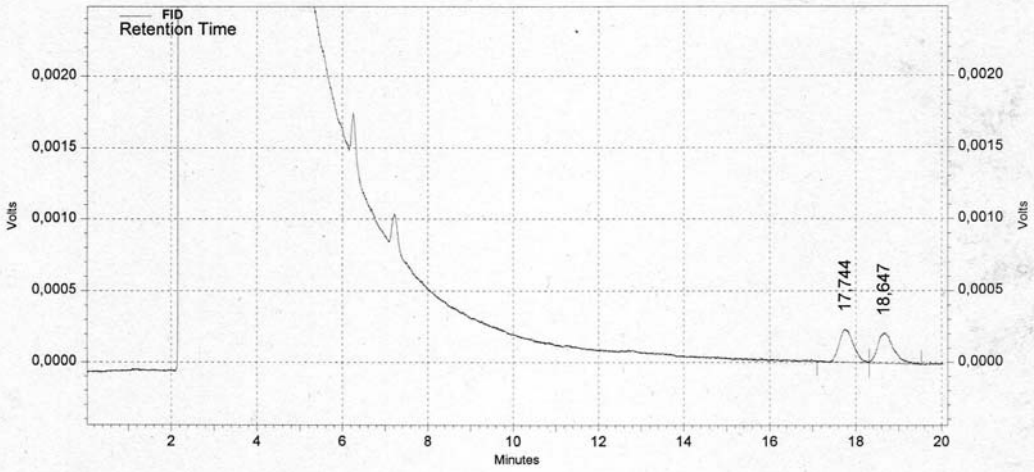
4



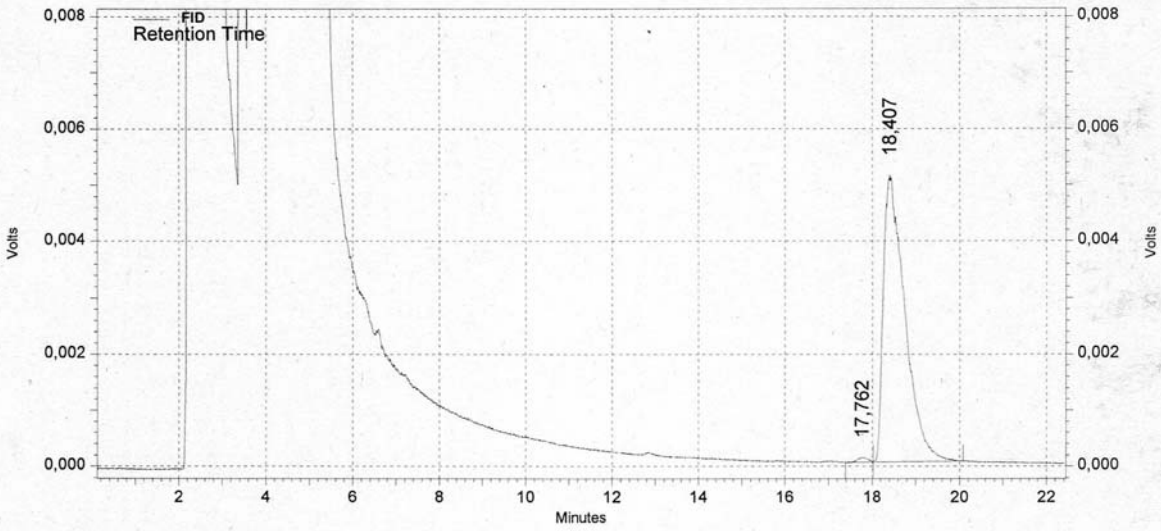
FID Results

Retention Time	Area	Area %	Height	Height %
17,744	5252	49,53	233	52,24
18,647	5352	50,47	213	47,76
Totals	10604	100,00	446	100,00

Area % Report

Data File: C:\Programme\CP-Maitre Elite\Projects\Default\Data\Ca149-1
Method: C:\Programme\CP-Maitre Elite\Projects\Default\Methods\standard1.met
Acquired: 03.03.06 21:13:30
Printed: 20.04.07 17:49:08
1 Threshold 0 0 50

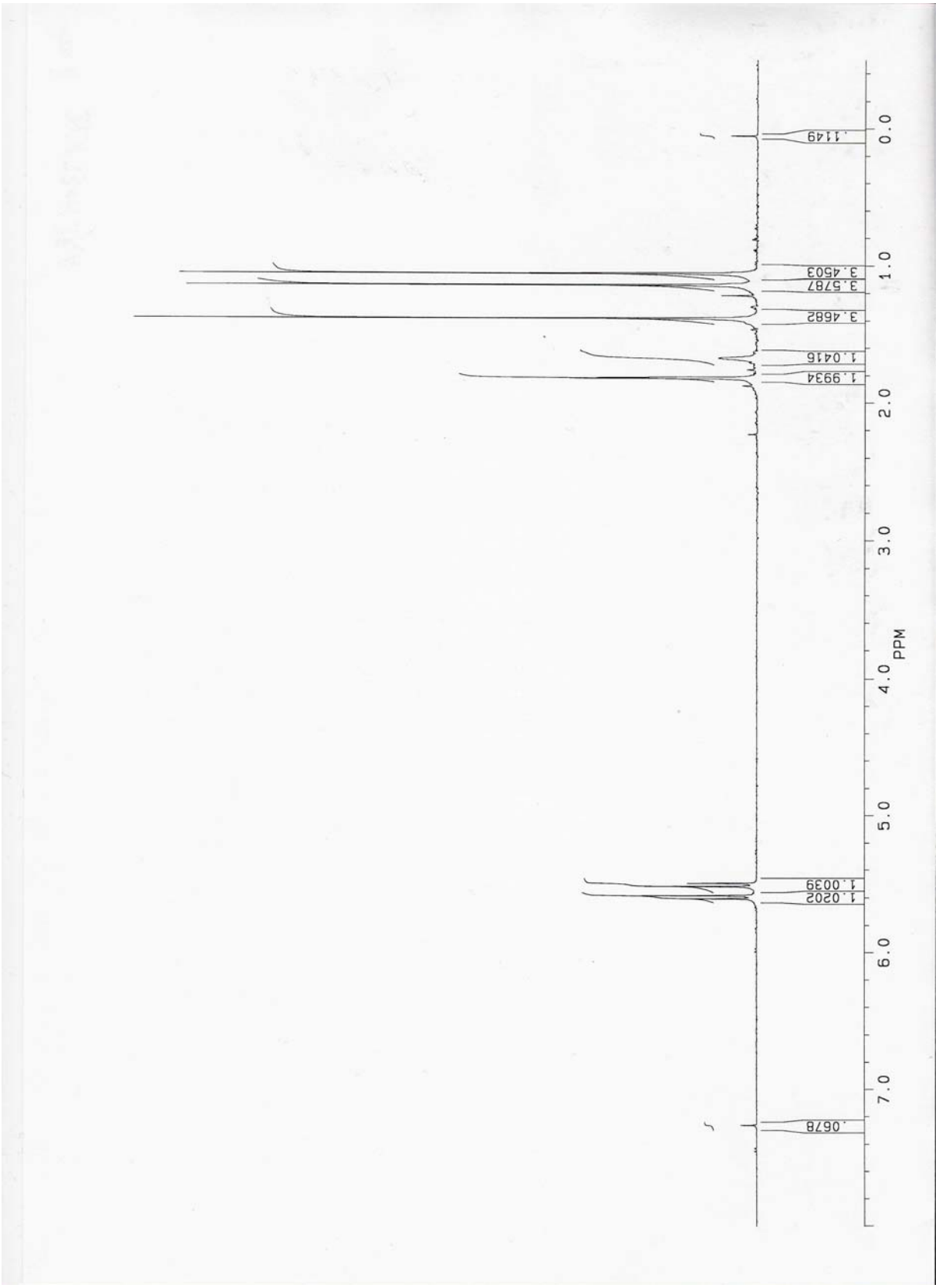
4

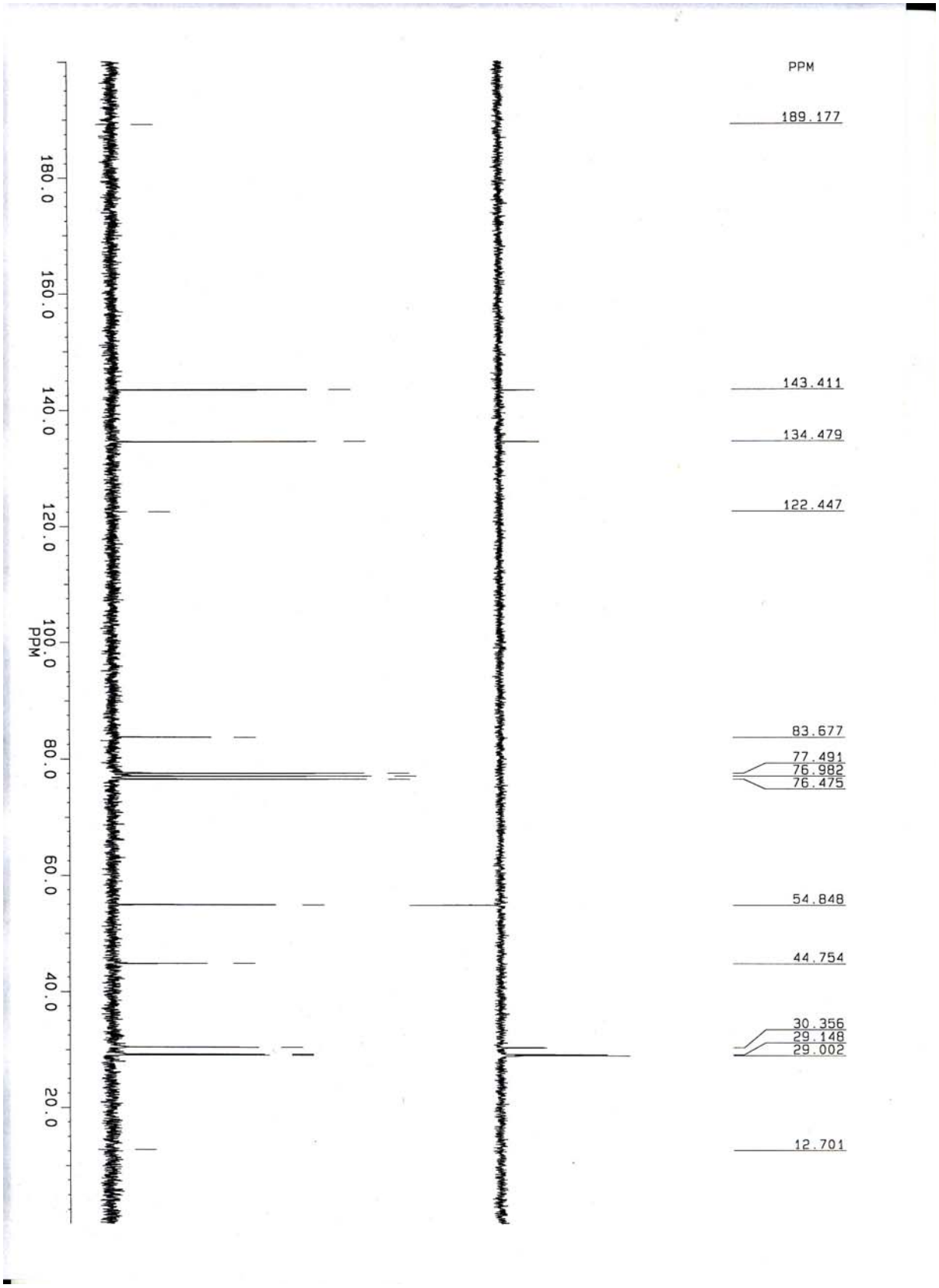


FID Results

Retention Time	Area	Area %	Height	Height %
17,762	1414	0,81	88	1,70
18,407	173472	99,19	5096	98,30
Totals	174886	100,00	5184	100,00

(*R*)-1,4,4-Trimethylcyclopent-2-enol (Table 3, entry 6):

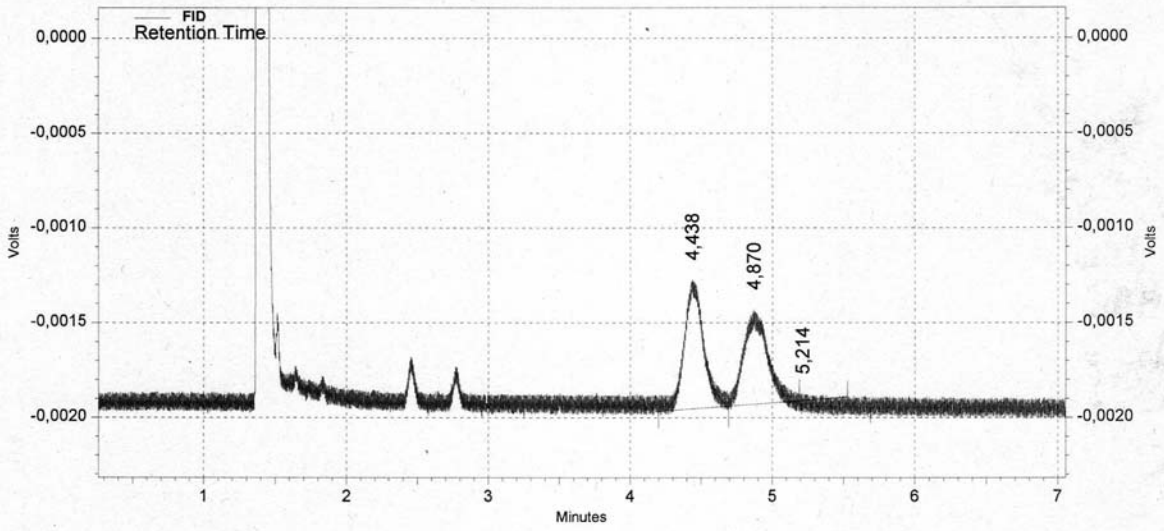



PPM
189.177
143.411
134.479
122.447
83.677
77.491
76.982
76.475
54.848
44.754
30.356
29.148
29.002
12.701
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
PPM

Area % Report

Data File: C:\Programme\CP-Maitre Elite\Projects\Default\Data\Jsca3081
Method: C:\Programme\CP-Maitre Elite\Projects\Default\Methods\standard1.met
Acquired: 06.03.07 10:22:29
Printed: 20.04.07 18:13:53
1 Threshold 0 0 50

4



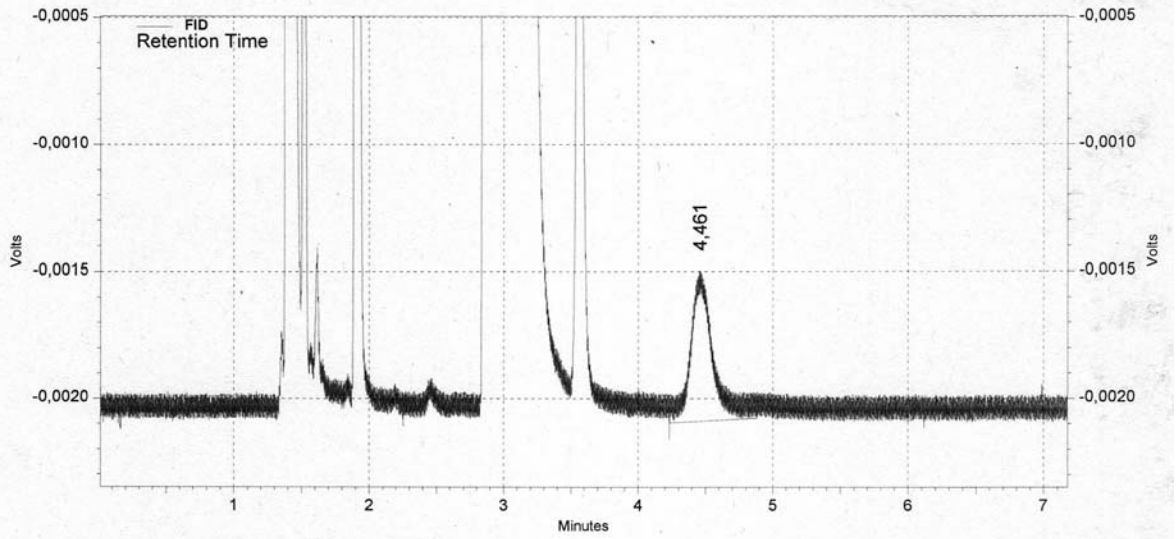
FID Results

Retention Time	Area	Area %	Height	Height %
4,438	5321	46,41	681	55,96
4,870	5471	47,72	500	41,08
5,214	673	5,87	36	2,96
Totals	11465	100,00	1217	100,00

Area % Report

Data File: C:\Programme\CP-Maitre Elite\Projects\Default\Data\Ca308-3
Method: C:\Programme\CP-Maitre Elite\Projects\Default\Methods\standard1.met
Acquired: 06.03.07 18:04:29
Printed: 20.04.07 18:02:32
1 Threshold 0 0 50

4



FID Results

Retention Time	Area	Area %	Height	Height %
4,461	6900	100,00	594	100,00

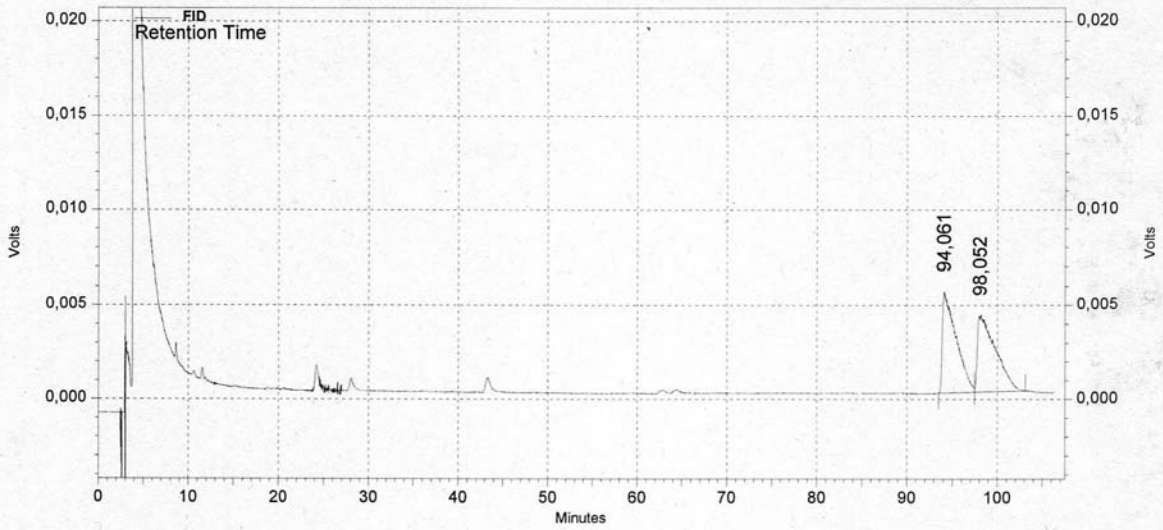
Totals	6900	100,00	594	100,00

3-Methyl-1-phenylpent-(*E*)-1-en-3-ol (Table 3, entry 7):

Area % Report

Data File: C:\Programme\CP-Maitre Elite\Projects\Default\Data\CA195rac
Method: C:\Programme\CP-Maitre Elite\Projects\Default\Methods\standard1.met
Acquired: 03.05.06 11:07:17
Printed: 20.04.07 17:28:15
1 Threshold 0 0 50

4



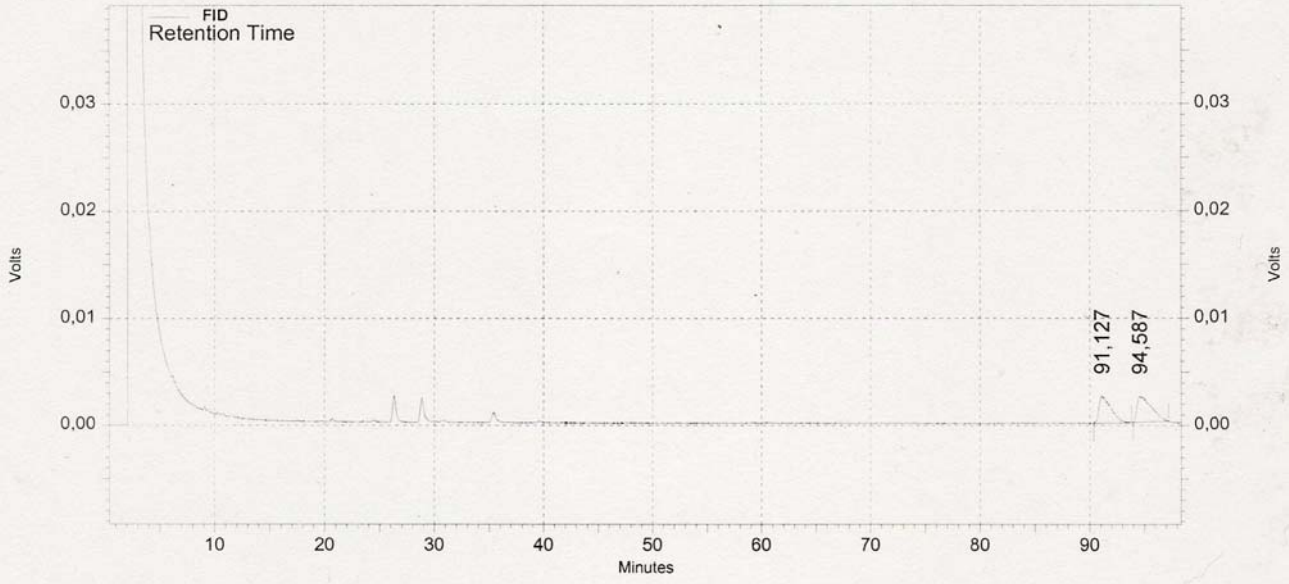
FID Results

Retention Time	Area	Area %	Height	Height %
94,061	569235	49,86	5392	56,85
98,052	572528	50,14	4092	43,15
Totals	1141763	100,00	9484	100,00

CA150-3**Area % Report**

Data File: C:\Programme\CP-Maitre Elite\Projects\Default\Data\Ca202-1
Method: C:\Programme\CP-Maitre Elite\Projects\Default\Methods\standard1.met
Acquired: 05.05.06 14:40:53
Printed: 18.05.07 15:57:04
1 Threshold 0 0 50

4



FID Results

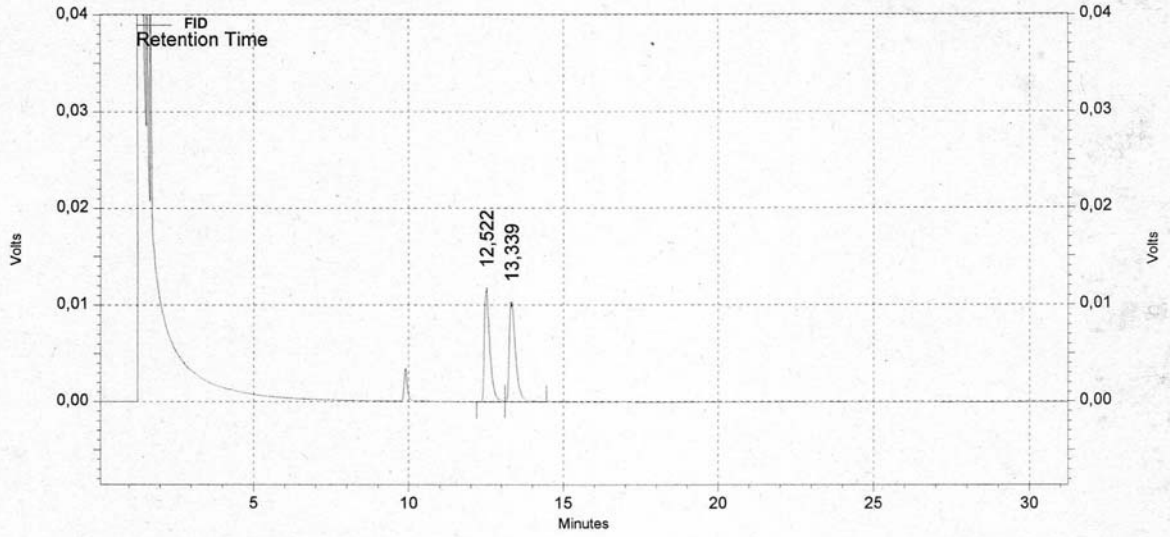
Retention Time	Area	Area %	Height	Height %
91,127	192471	46,42	2566	51,16
94,587	222122	53,58	2450	48,84
Totals	414593	100,00	5016	100,00

2-Phenylbutan-2-ol (Table 3, entry 8):

Area % Report

Data File: C:\Programme\CP-Maitre Elite\Projects\Default\Data\CA150rac
Method: C:\Programme\CP-Maitre Elite\Projects\Default\Methods\standard1.met
Acquired: 08.03.06 14:39:53
Printed: 20.04.07 17:34:10
1 Threshold 0 0 50

4



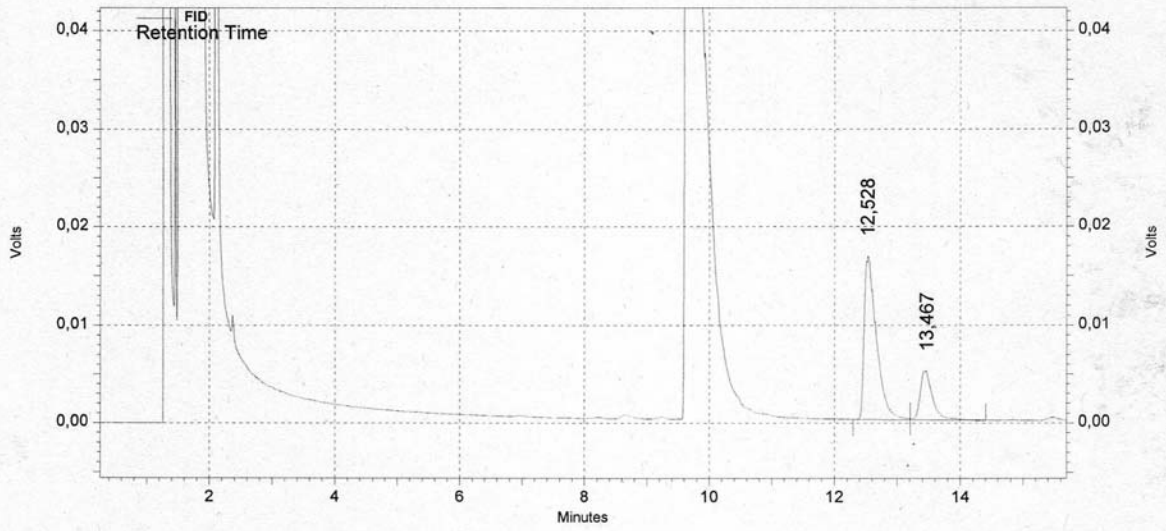
FID Results

Retention Time	Area	Area %	Height	Height %
12,522	145130	49,69	11829	53,25
13,339	146923	50,31	10387	46,75
Totals	292053	100,00	22216	100,00

Area % Report

Data File: C:\Programme\CP-Maitre Elite\Projects\Default\Data\Ca150-2
Method: C:\Programme\CP-Maitre Elite\Projects\Default\Methods\standard1.met
Acquired: 09.03.06 15:21:39
Printed: 20.04.07 17:37:06
1 Threshold 0 0 50

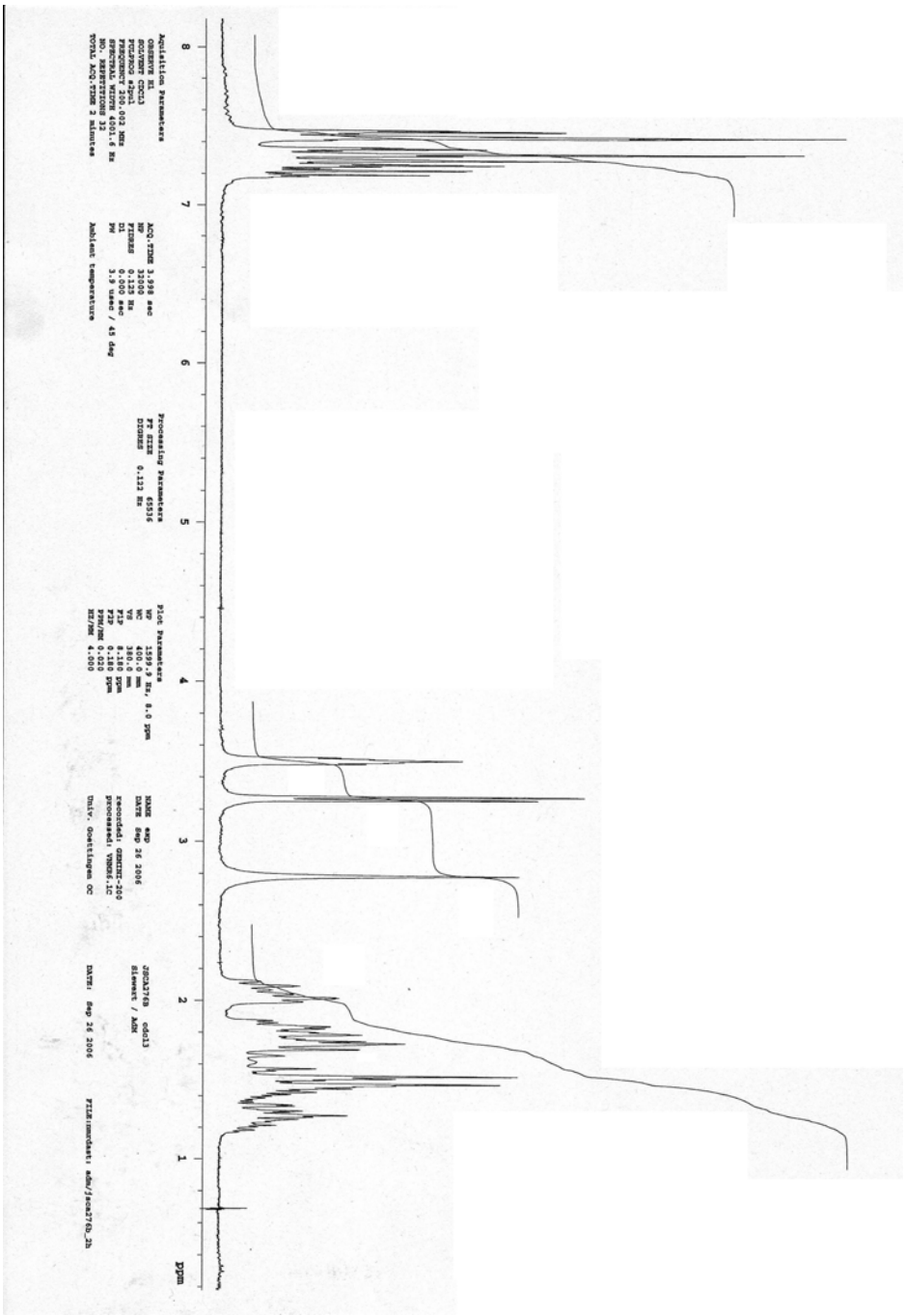
4

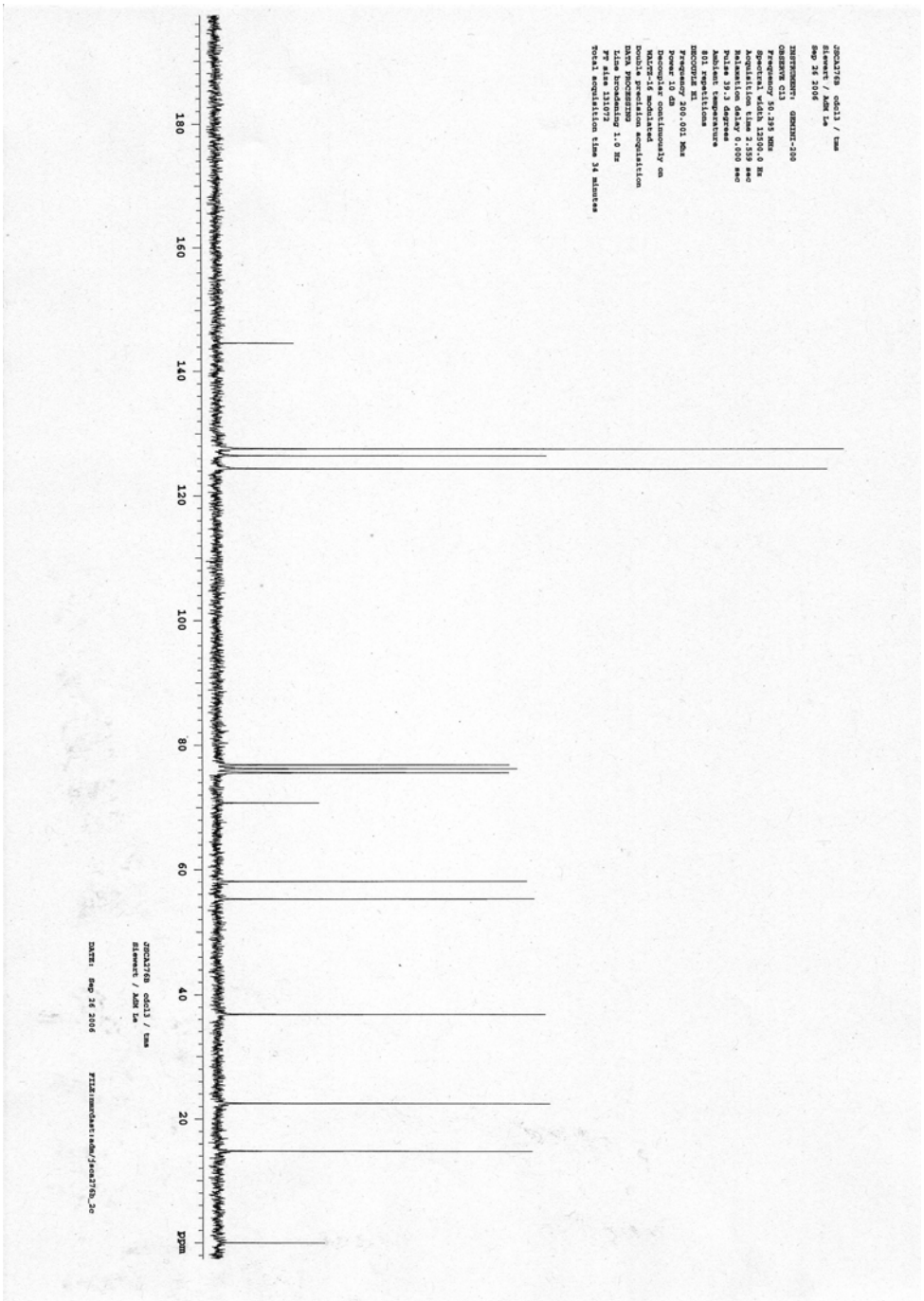


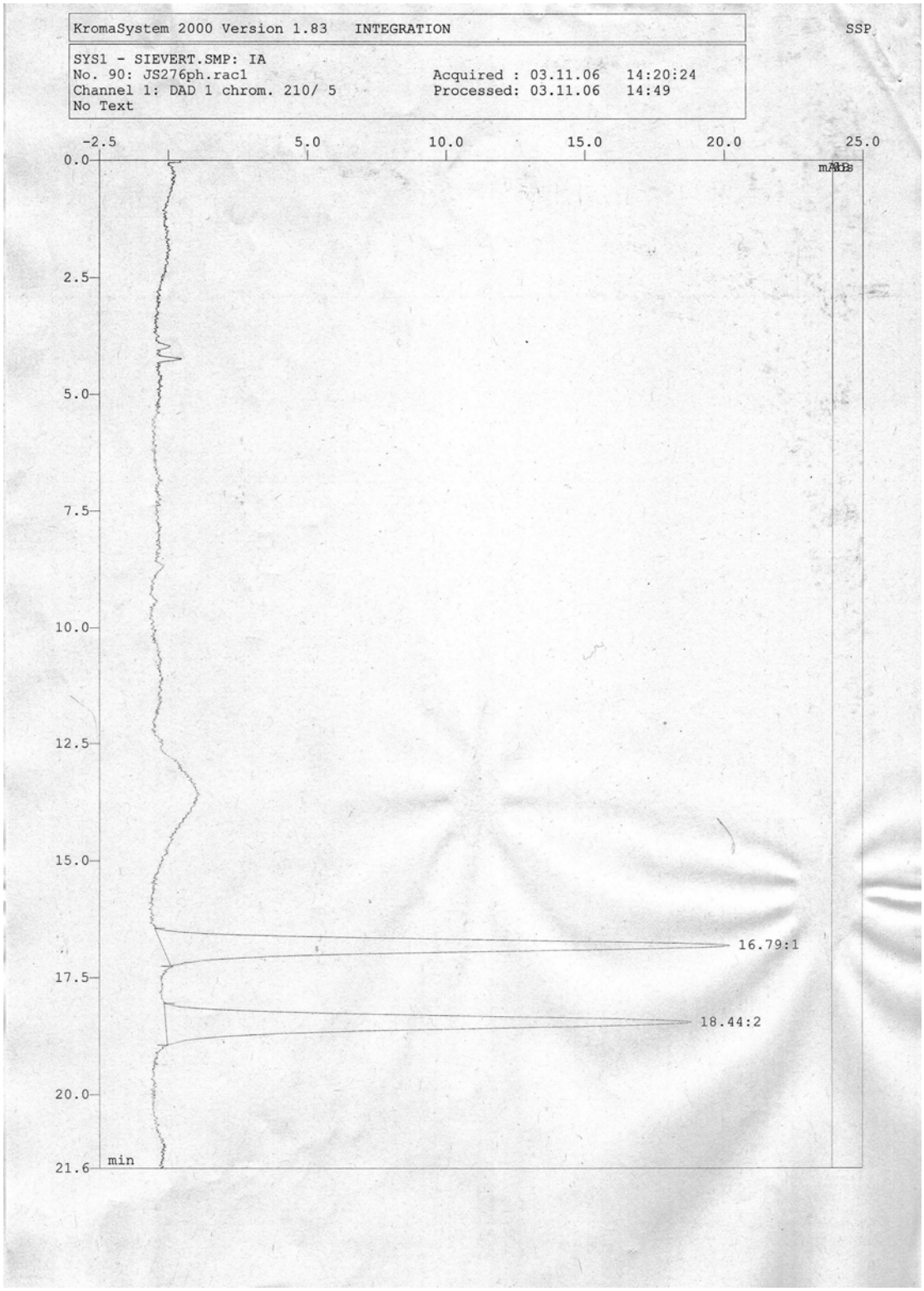
FID Results

Retention Time	Area	Area %	Height	Height %
12,528	226775	76,83	16703	76,61
13,467	68393	23,17	5100	23,39
Totals	295168	100,00	21803	100,00

(*1R,2R,6R*)-2-Phenyl-7-oxabicyclo[4.1.0]heptan-2-ol:




JSCA376b cdcl3 / tms
Elewest / ADM La
Sep 26 2006
INSTRUMENT: GEMINI-200
OBSERVE C13
Frequency 50.289 MHz
Spectral width 12050.0 Hz
Acquisition time 1.3599 sec
Relaxation delay 0.050 sec
Pulse 39.3 degrees
Ambient temperature
801 repetitions
DECOUPLE H1
Frequency 200.001 MHz
Power 10 dB
Decoupler continuously on
WALTZ-16 modulated
Double precision acquisition
Digital resolution
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 34 minutes
180
160
140
120
100
80
60
40
20
ppm
JSCA376b cdcl3 / tms
Elewest / ADM La
DATE: Sep 26 2006
PIAM:nmrdata:adm/jsca376b_2c

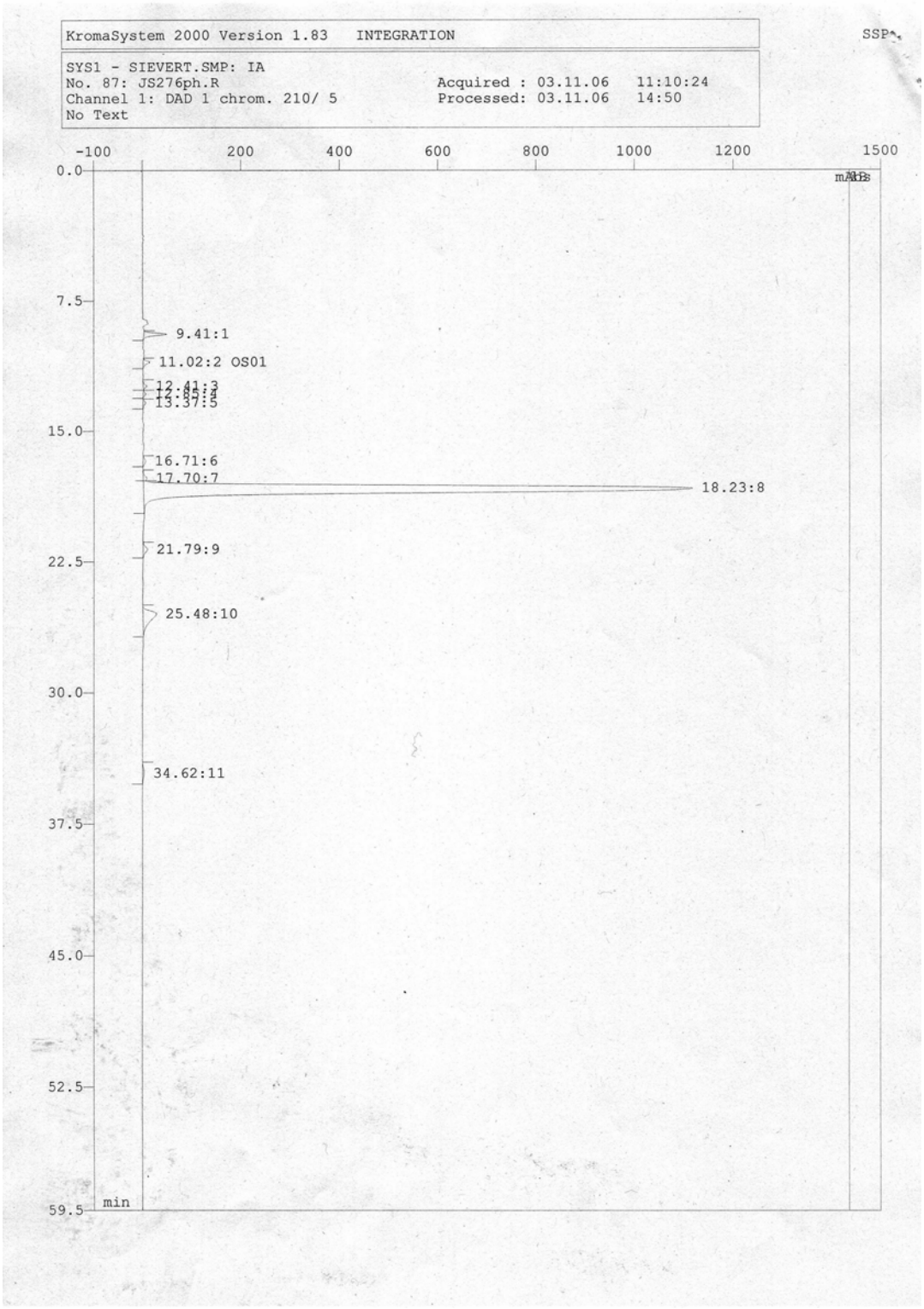

KromaSystem 2000 Version 1.83 INTEGRATION
SSP
SYS1 - SIEVERT.SMP: IA
No. 90: JS276ph.rac1
Channel 1: DAD 1 chrom. 210/ 5
No Text
Acquired : 03.11.06 14:20:24
Processed: 03.11.06 14:49
-2.5
5.0
10.0
15.0
20.0
25.0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
21.6
min
16.79:1
18.44:2

KromaSystem 2000 Version 1.83 RESULT REPORT: INTEGRATION

SYS1 - SIEVERT.SMP: IA
No. 90: JS276ph.rac1 Acquired : 03.11.06 14:20:24
Channel 1: DAD 1 chrom. 210/ 5 Processed: 03.11.06 14:49
No Text

Program File ..... SIEVER21 .....
Worksheet ..... OS01 ..... Standard
Peak Table ..... OS01 ..... Auto-generated
Parameter Table .. STANDARD .....
Report File ....
Document File .... OS01 .....

No.	PNo	Ret.Time min	Type	Name	Area mAbs*min	Amount	Rel.Ar %
1	?	16.79	MLR	?	6.2312e+000	?	49.71
2	?	18.44	MLR	?	6.3036e+000	?	50.29
					1.2535e+001	0.0000e+000	100.00


KromaSystem 2000 Version 1.83 INTEGRATION
SSP
SYS1 - SIEVERT.SMP: IA
No. 87: JS276ph.R
Channel 1: DAD 1 chrom. 210/ 5
No Text
Acquired : 03.11.06 11:10:24
Processed: 03.11.06 14:50
-100
200
400
600
800
1000
1200
1500
0.0
7.5
15.0
22.5
30.0
37.5
45.0
52.5
59.5
min
mAU
9.41:1
11.02:2 OS01
12.41:3
13.37:5
16.71:6
17.70:7
18.23:8
21.79:9
25.48:10
34.62:11

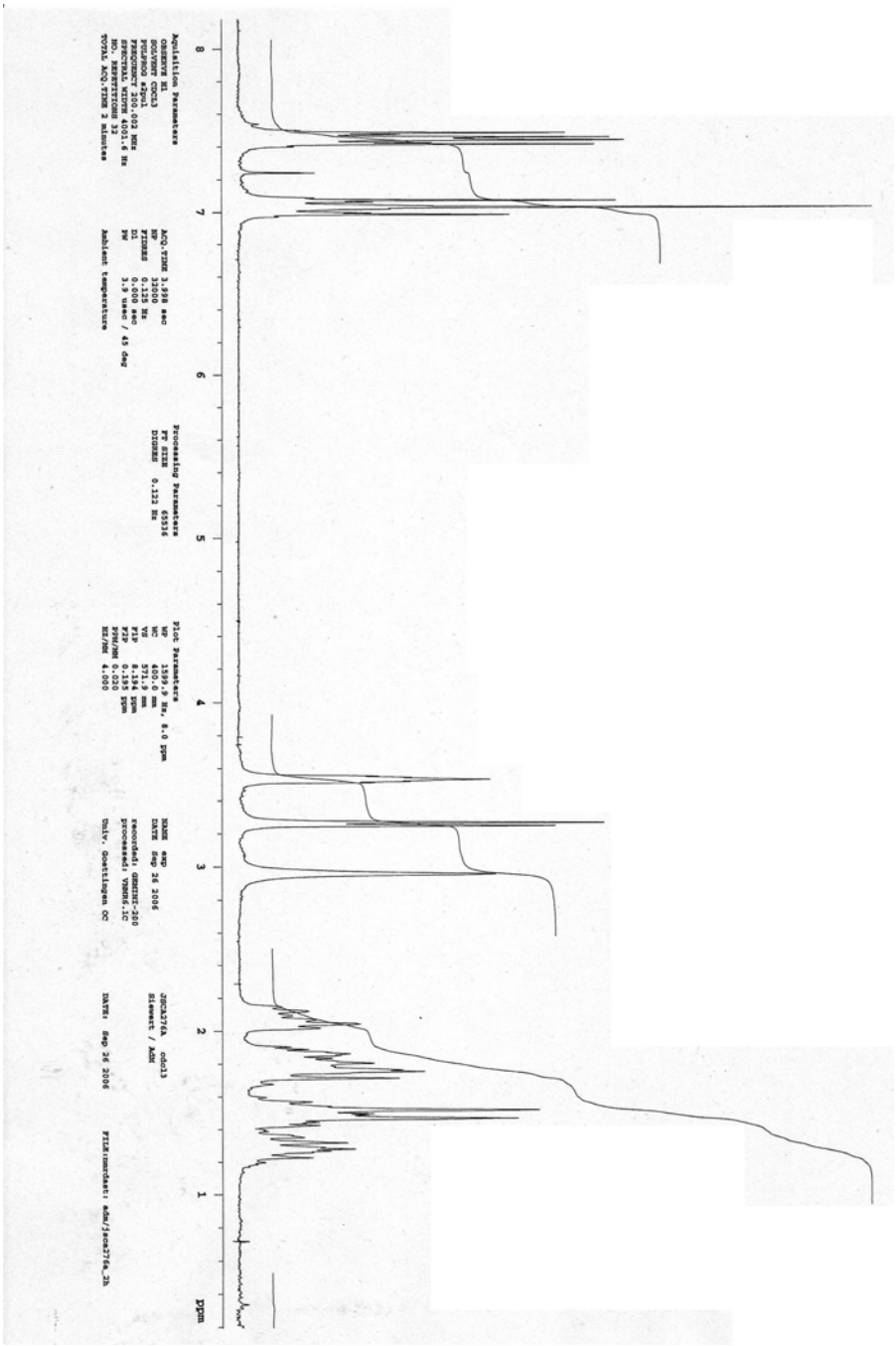
KromaSystem 2000 Version 1.83 RESULT REPORT: INTEGRATION

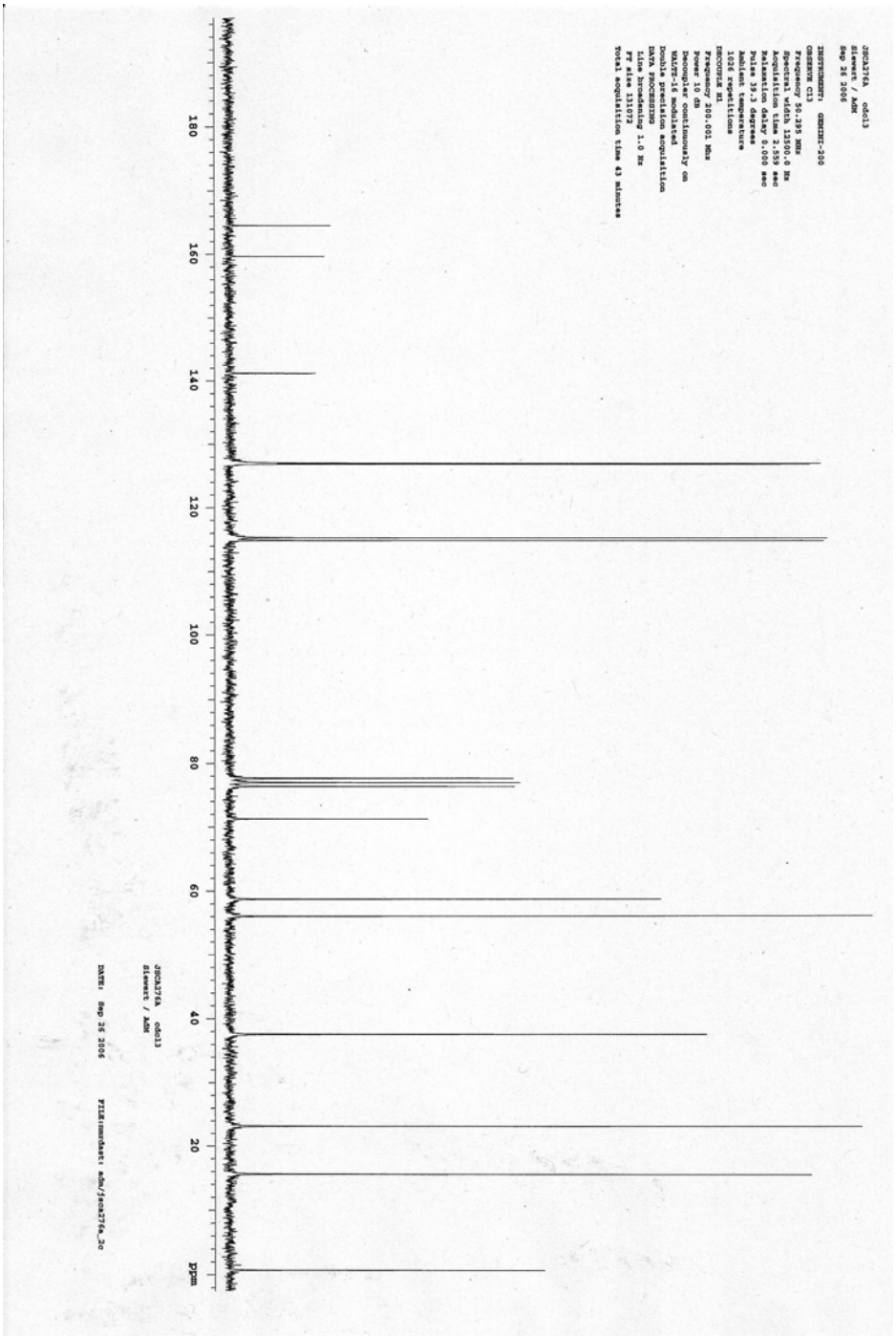
SYS1 - SIEVERT.SMP: IA
No. 87: JS276ph.R Acquired : 03.11.06 11:10:24
Channel 1: DAD 1 chrom. 210/ 5 Processed: 03.11.06 14:50
No Text

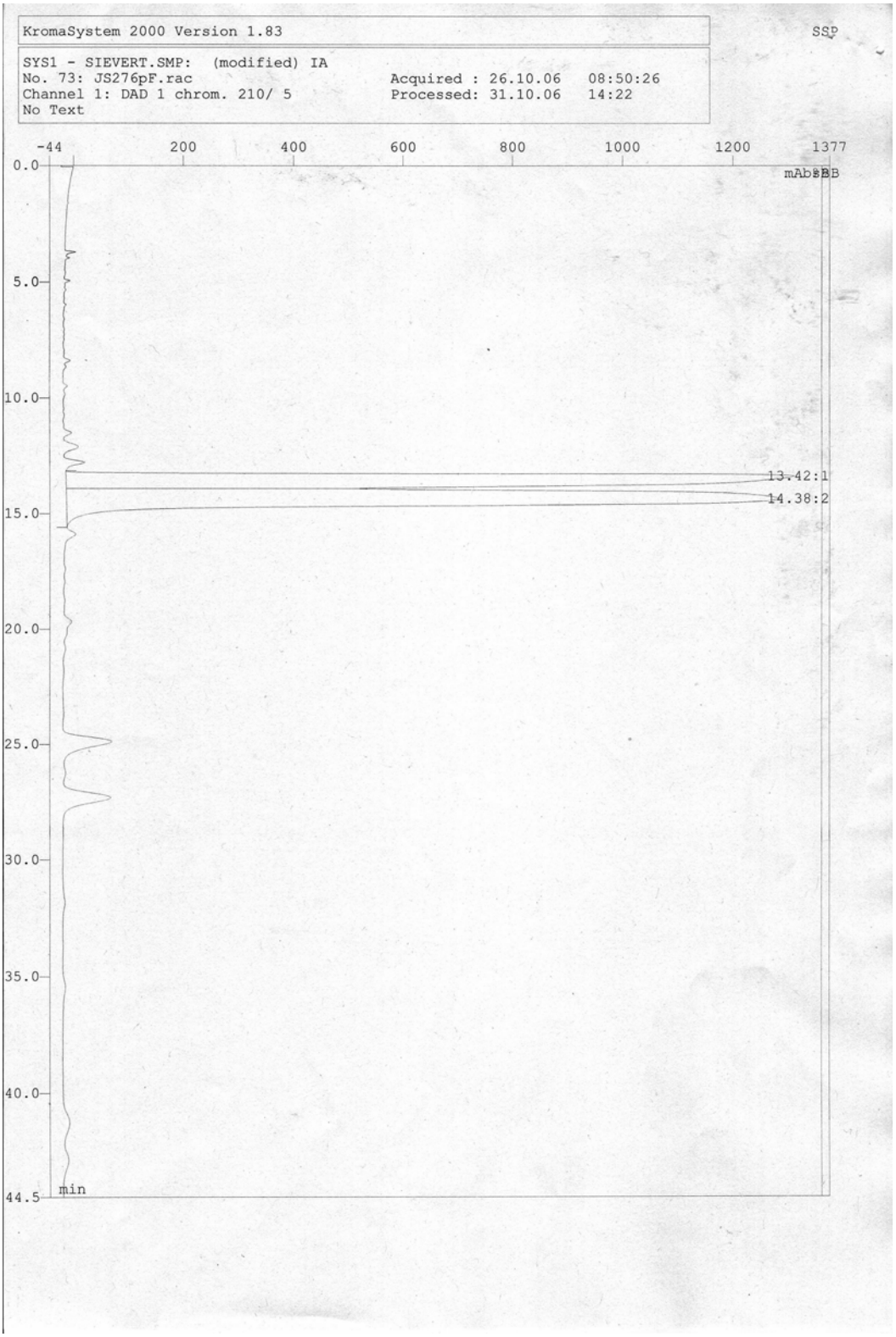
Program File ..... SIEVER21 .....
Worksheet ..... OS01 ..... Standard
Peak Table ..... OS01 ..... Auto-generated
Parameter Table .. STANDARD .....
Report File ....
Document File .... OS01 .....

No.	PNo	Ret.Time min	Type	Name	Area mAbs*min	Amount	Rel.Ar %
1	?	9.41	MLR	?	7.9128e+000	?	1.39
2	8	11.02	MLR	OS01-8	2.9360e+000	1.8953e+002	0.51
3	?	12.41	MLr	?	1.4978e+000	?	0.26
4	?	12.85	MlR	?	1.0441e+000	?	0.18
5	?	13.37	MLR	?	1.2874e+000	?	0.23
6	?	16.71	MLR	?	1.5989e+000	?	0.28
7	?	17.70	ML	?	2.0616e+000	?	0.36
8	?	18.23	M R	?	5.2823e+002	?	92.51
9	?	21.79	MLR	?	3.4289e+000	?	0.60
10	?	25.48	MLR	?	1.9111e+001	?	3.35
11	?	34.62	MLR	?	1.9153e+000	?	0.34
					5.7103e+002	1.8953e+002	100.00

(*1R,2R,6R*)-2-(4-Fluorophenyl)-7-oxabicyclo[4.1.0]heptan-2-ol:




JBDA276A odcl3
dlewart / ADM
Sep 26 2006
INSTRUMENT 1 GEMINI-300
CHANNEL f1 CH1
Frequency 50.295 MHz
Spectral width 12500.0 Hz
Acquisition time 2.559 sec
Relaxation delay 0.000 sec
Pulse 39.3 degrees
1024 repetitions
OBSERVE H1
Frequency 200.001 MHz
Power 10 db
Decoupler continuously on
WALTZ16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 43 minutes
180
160
140
120
100
80
60
40
20
ppm
JBDA276A odcl3
dlewart / ADM
DATE: Sep 26 2006
File:/nmrdata: adm/jbda276a_2c

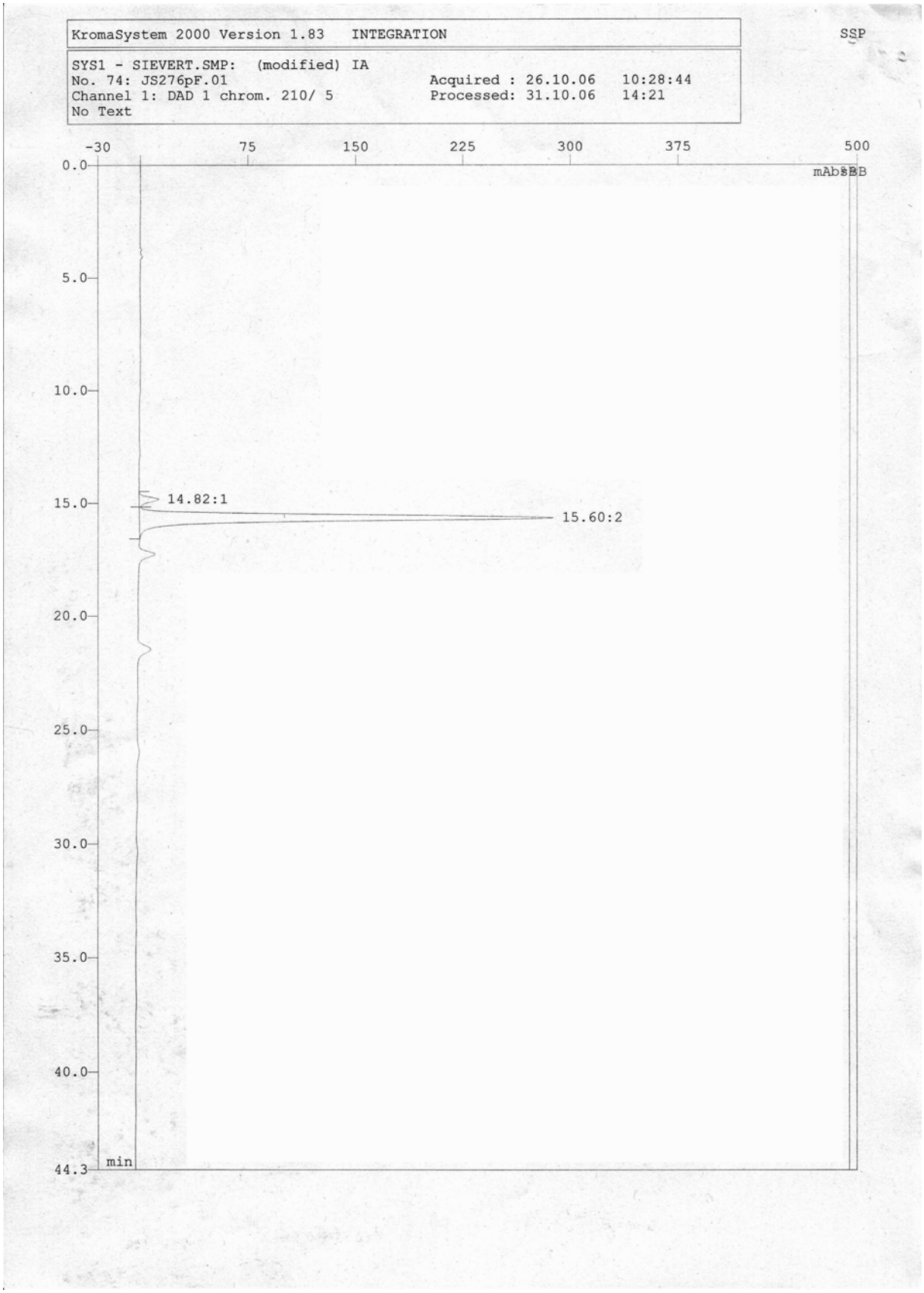

KromaSystem 2000 Version 1.83
SSP
SYS1 - SIEVERT.SMP: (modified) IA
No. 73: JS276pF.rac
Acquired : 26.10.06 08:50:26
Channel 1: DAD 1 chrom. 210/ 5
Processed: 31.10.06 14:22
No Text
-44
200
400
600
800
1000
1200
1377
0.0
mAbs
BB
5.0
10.0
13.42:1
14.38:2
15.0
20.0
25.0
30.0
35.0
40.0
min
44.5

KromaSystem 2000 Version 1.83 RESULT REPORT: INTEGRATION

SYS1 - SIEVERT.SMP (modified): IA
No. 73: JS276pF.rac Acquired : 26.10.06 08:50:26
Channel 1: DAD 1 chrom. 210/ 5 Processed: 31.10.06 14:22
No Text

Program File ..... SIEVER18 .....
Worksheet ..... OS01 ..... Standard
Peak Table ..... OS01 ..... Auto-generated
Parameter Table .. STANDARD .....
Report File ....
Document File .... OS01 .....

No.	PNo	Ret.Time min	Type	Name	Area mAbs*min	Amount	Rel.Ar %
1	?	13.42	ML	?	7.3262e+002	?	44.79
2	?	14.38	M R	?	9.0291e+002	?	55.21
					1.6355e+003	0.0000e+000	100.00


KromaSystem 2000 Version 1.83 INTEGRATION
SSP
SYS1 - SIEVERT.SMP: (modified) IA
No. 74: JS276pF.01
Acquired : 26.10.06 10:28:44
Channel 1: DAD 1 chrom. 210/ 5
Processed: 31.10.06 14:21
No Text
-30
75
150
225
300
375
500
0.0
mAbs
5.0
10.0
15.0
14.82:1
15.60:2
20.0
25.0
30.0
35.0
40.0
44.3
min

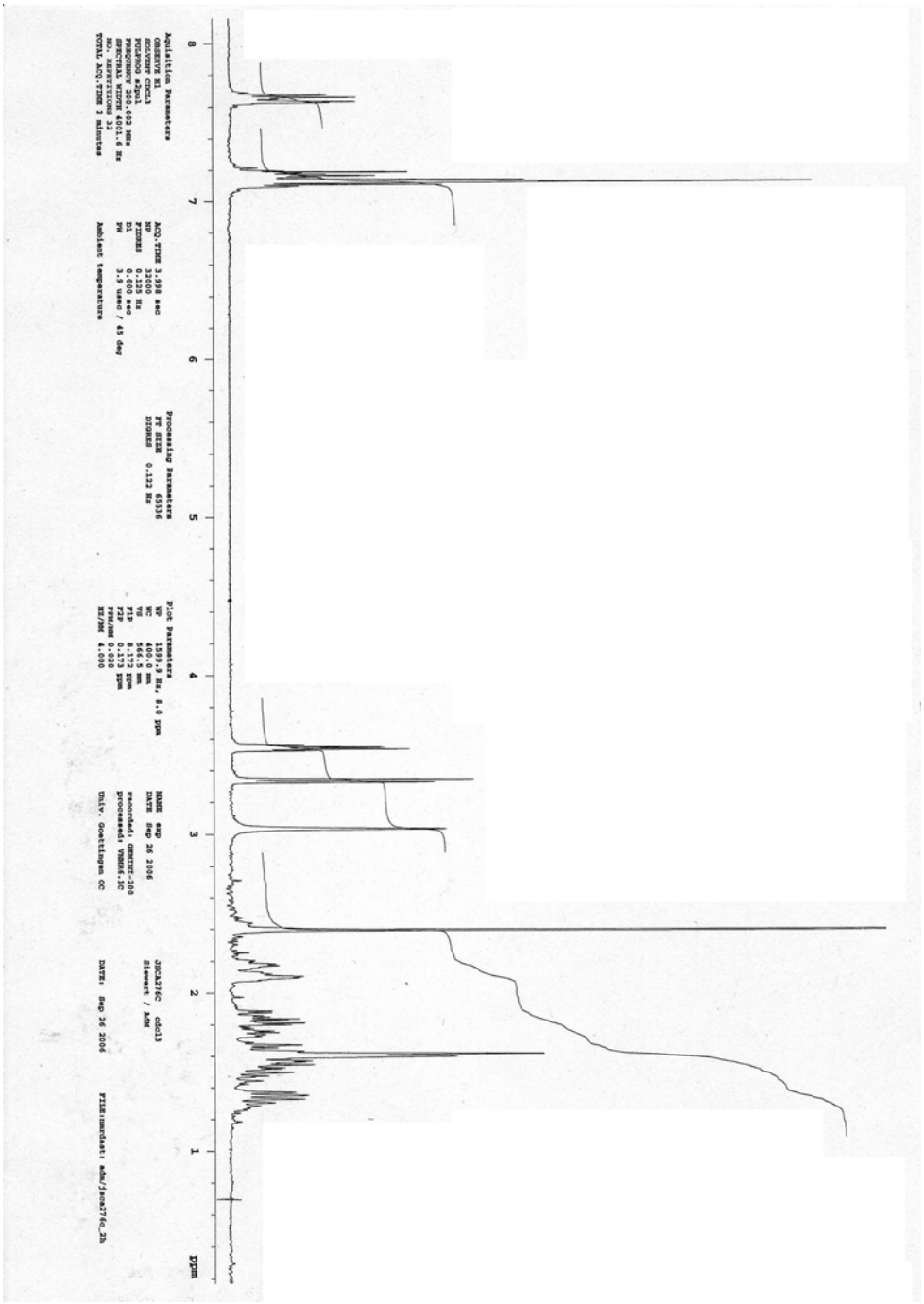
KromaSystem 2000 Version 1.83 RESULT REPORT: INTEGRATION

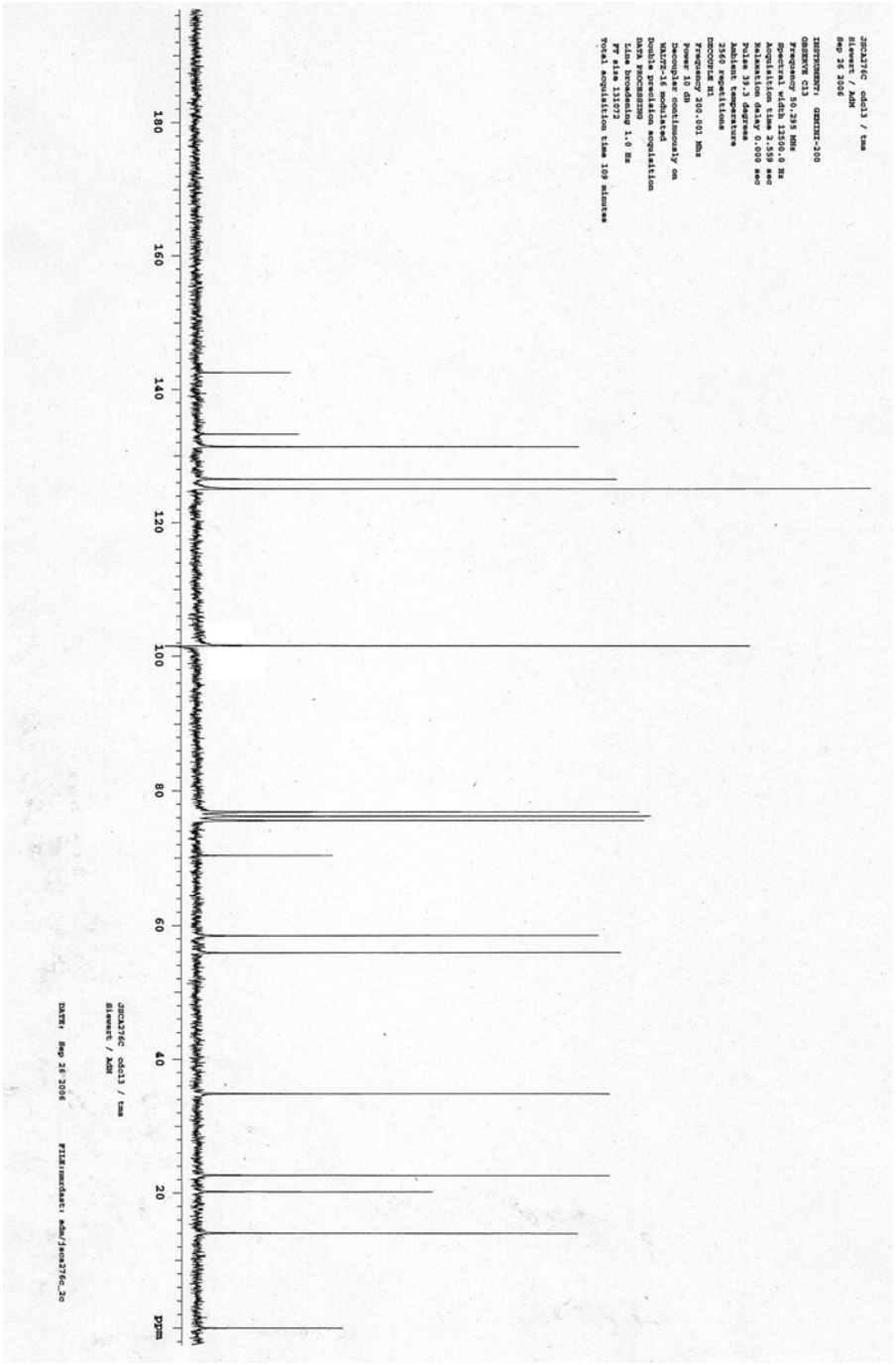
SYS1 - SIEVERT.SMP (modified): IA
No. 74: JS276pF.01 Acquired : 26.10.06 10:28:44
Channel 1: DAD 1 chrom. 210/ 5 Processed: 31.10.06 14:21
No Text

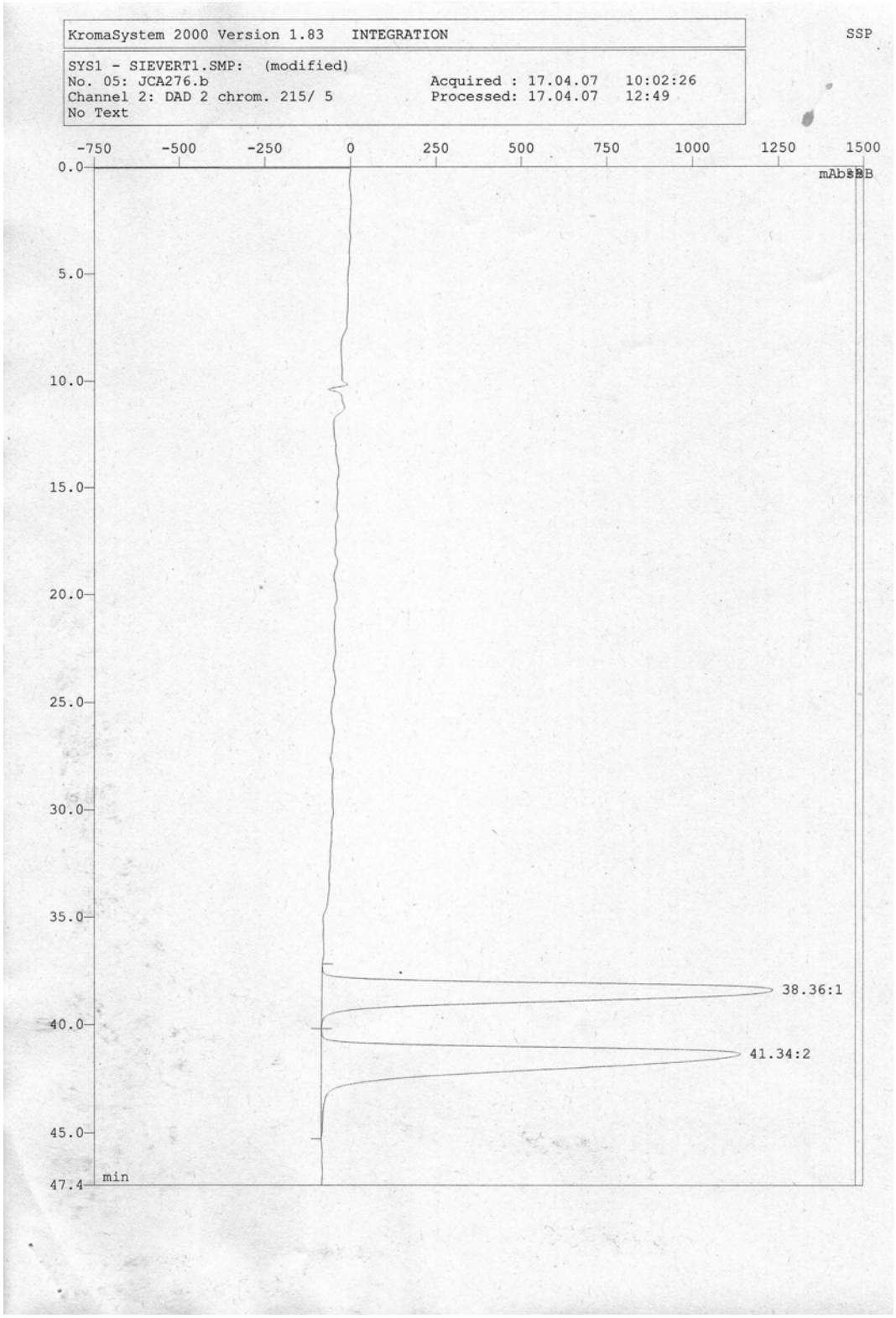
Program File ..... SIEVER18 .....
Worksheet ..... OS01 ..... Standard
Peak Table ..... OS01 ..... Auto-generated
Parameter Table .. STANDARD .....
Report File ....
Document File .... OS01 .....

No.	PNo	Ret.Time min	Type	Name	Area mAbs*min	Amount	Rel.Ar %
1	?	14.82	ML	?	3.7389e+000	?	3.86
2	?	15.60	M R	?	9.3051e+001	?	96.14
					9.6789e+001	0.0000e+000	100.00

(*1R,2R,6R*)-2-(2-Methylphenyl)-7-oxabicyclo[4.1.0]heptan-2-ol:




JSCA376C cdcl3 / tms
Stewart / ADM
Sep 26 2006
INSTRUMENT: GEMINI-200
OBSERVE C13
Frequency 50.295 MHz
Spectral width 12500.0 Hz
Acquisition time 2.559 sec
Acquisition delay 0.000 sec
Pulse 30.3 degrees
Ambient temperature
2560 repetitions
DECOUPLE H1
Frequency 200.001 MHz
Power 35 dB continuously on
WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total acquisition time 109 minutes
180
160
140
120
100
80
60
40
20
ppm
JSCA376C cdcl3 / tms
Stewart / ADM
INSTR: Sep 26 2006
PIR:nmrdata: adm/jsca376c_2c

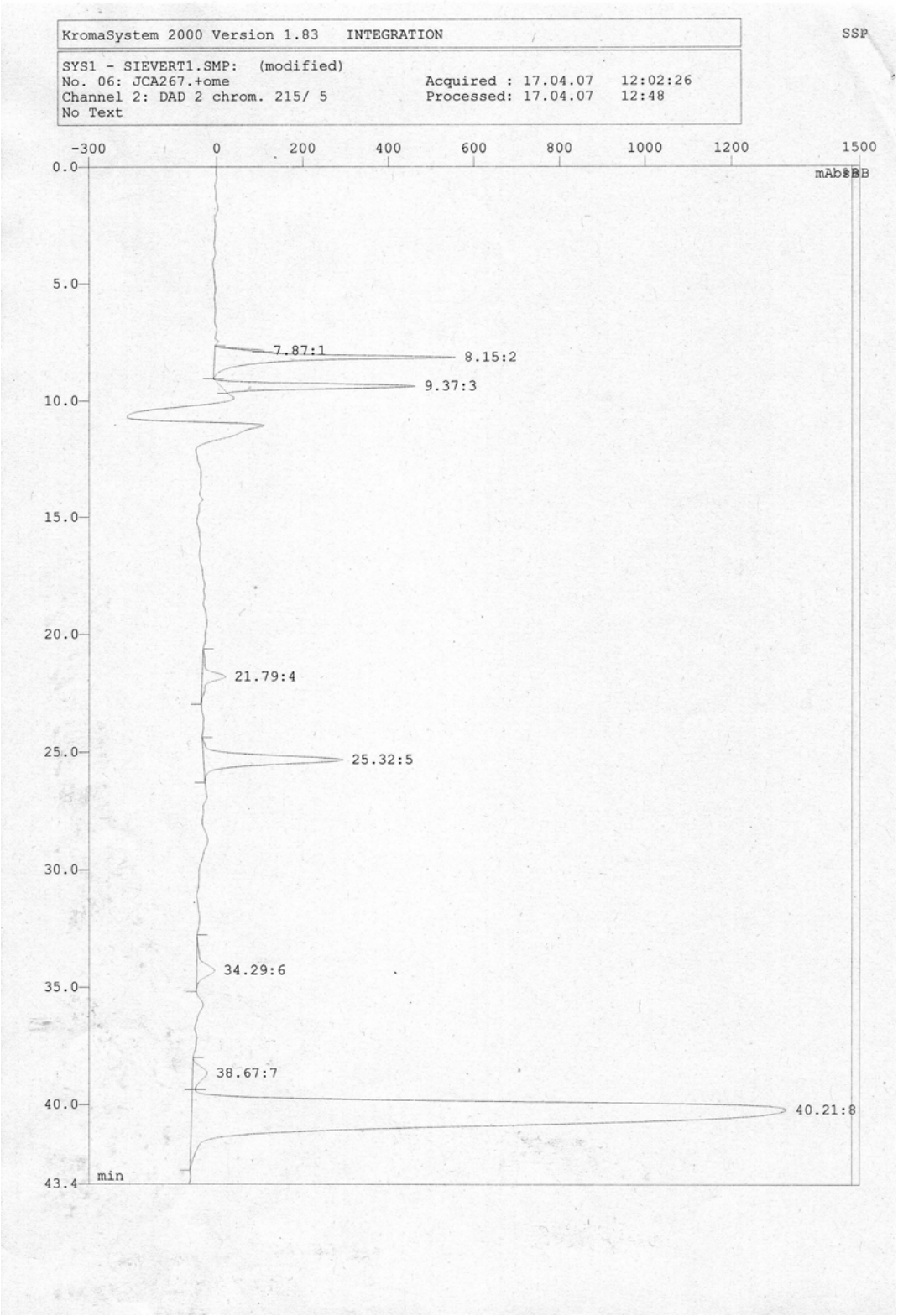

KromaSystem 2000 Version 1.83 INTEGRATION
SSP
SYS1 - SIEVERT1.SMP: (modified)
No. 05: JCA276.b
Acquired : 17.04.07 10:02:26
Channel 2: DAD 2 chrom. 215/ 5
Processed: 17.04.07 12:49
No Text
-750 -500 -250 0 250 500 750 1000 1250 1500
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
47.4
min
mAbs
38.36:1
41.34:2

KromaSystem 2000 Version 1.83 RESULT REPORT: INTEGRATION

SYS1 - SIEVERT1.SMP (modified):
No. 05: JCA276.b Acquired : 17.04.07 10:02:26
Channel 2: DAD 2 chrom. 215/ 5 Processed: 17.04.07 12:49
No Text

Program File ..... SIEVER3 .....
Worksheet ..... OS01 ..... Standard
Peak Table ..... OS01 ..... Auto-generated
Parameter Table .. OS01 .....
Report File ....
Document File .... OS01 .....

No.	PNo	Ret.Time min	Type	Name	Area mAbs*min	Amount	Rel.Ar %
1	?	38.36	MLr	?	1.2038e+003	?	46.32
2	?	41.34	MlR	?	1.3950e+003	?	53.68
					2.5988e+003	0.0000e+000	100.00


KromaSystem 2000 Version 1.83 INTEGRATION
SSP
SYS1 - SIEVERT1.SMP: (modified)
No. 06: JCA267.+ome
Acquired : 17.04.07 12:02:26
Channel 2: DAD 2 chrom. 215/ 5
Processed: 17.04.07 12:48
No Text
-300
0
200
400
600
800
1000
1200
1500
0.0
mAbs
5.0
7.87:1
8.15:2
9.37:3
10.0
15.0
20.0
21.79:4
25.0
25.32:5
30.0
34.29:6
35.0
38.67:7
40.0
40.21:8
43.4
min

KromaSystem 2000 Version 1.83 RESULT REPORT: INTEGRATION

SYS1 - SIEVERT1.SMP (modified):
No. 06: JCA267.+ome Acquired : 17.04.07 12:02:26
Channel 2: DAD 2 chrom. 215/ 5 Processed: 17.04.07 12:49
No Text

Program File ..... SIEVER3 .....
Worksheet ..... OS01 ..... Standard
Peak Table ..... OS01 ..... Auto-generated
Parameter Table .. OS01 .....
Report File ....
Document File .... OS01 .....

No.	PNo	Ret.Time min	Type	Name	Area mAbs*min	Amount	Rel.Ar %
1	?	7.87	RuL	?	3.7674e+000	?	0.19
2	?	8.15	M R	?	1.6810e+002	?	8.46
3	?	9.37	MLR	?	1.0745e+002	?	5.41
4	?	21.79	MLR	?	2.6384e+001	?	1.33
5	?	25.32	MLR	?	1.4382e+002	?	7.24
6	?	34.29	MLR	?	2.7725e+001	?	1.40
7	?	38.67	ML	?	2.3277e+001	?	1.17
8	?	40.21	M R	?	1.4865e+003	?	74.81
					1.9870e+003	0.0000e+000	100.00