Supporting Information

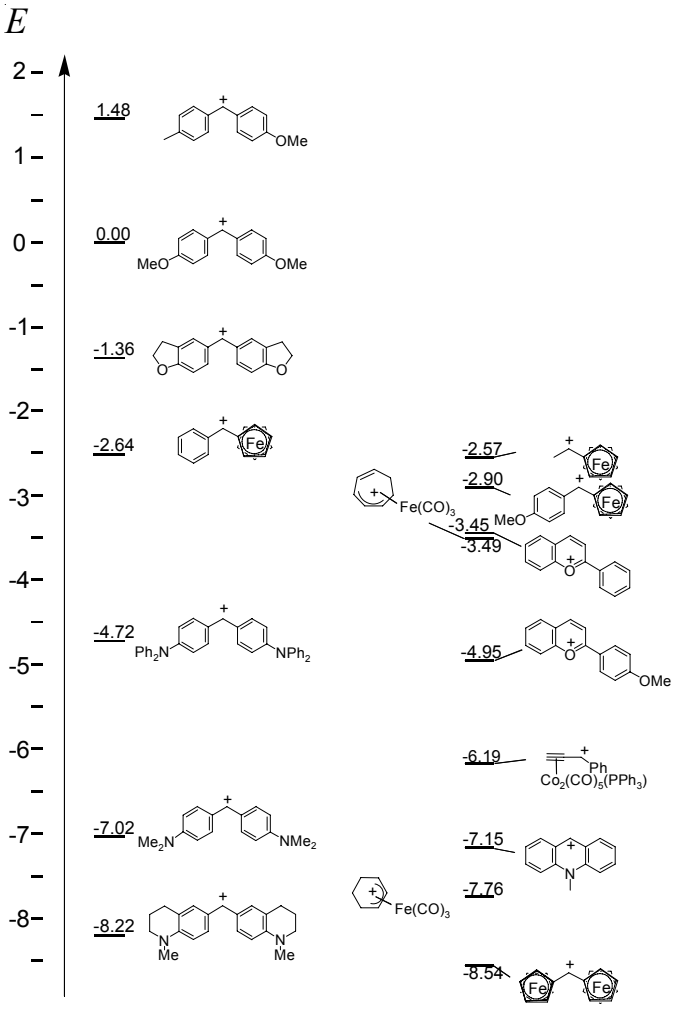
Catalytic Stereoselective Benzylic C-H Functionalizations by Oxidative C-H Activation and Organocatalysis

Fides Benfatti, Montse Guiteras Capdevila, Luca Zoli, Elena Benedetto, and Pier Giorgio Cozzi*

General: ^{1}H NMR spectra were recorded on Varian 200 MHz or Mercury 400 MHz spectrometers. chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.27 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian 50 MHz or Mercury 100 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0 ppm). Mass spectra were performed at an ionizing voltage of 70 eV. Chromatographic purification was done with 240-400 mesh silica gel. Analytical gas chromatography (GC) was performed on a Hewlett-Packard HP 6890 gas chromatograph with a flame ionization detector and split mode capillary injection system, using a 100% dimethylpolysiloxane (carrier gas helium) column or a Megadex5 chiral (25 m) column. Analytical high performance liquid chromatograph (HPLC) was performed on a HP 1090 liquid chromatograph equipped with a variable wavelength UV detector (deuterium lamp 190-600 nm), using Daicel Chiralcel^{TM} OD column (0.46 cm I.D. x 25 cm) (Daicel Inc.), Daicel Chiralcel^{TM} AD column (0.46 cm I.D. x 25 cm) (Daicel Inc.), Daicel Chiralcel^{TM} OF column (0.46 cm I.D. x 25 cm) (Daicel Inc.), Daicel Chiralcel^{TM} OJ column (0.46 cm I.D. x 25 cm) (Daicel Inc.), Daicel Chiralcel^{TM} IC column (0.46 cm I.D. x 25 cm) (Daicel Inc.); HPLC grade isopropanol and *n*hexane were used as the eluting solvents. Xanthene **1**, 1,3,5 cycloeptatriene **2** are commercially available, and were used as received. The flavone derivative **3** was prepared according literature.[1] The indole derivatives **4**-**7** were obtained by the reaction of the methyl indole with aldehydes in the presence of Et_3SiH and CF_3COOH, as reported in literature.[2] All the other reagents were commercially available (Fluka and Aldrich) and were used as received.

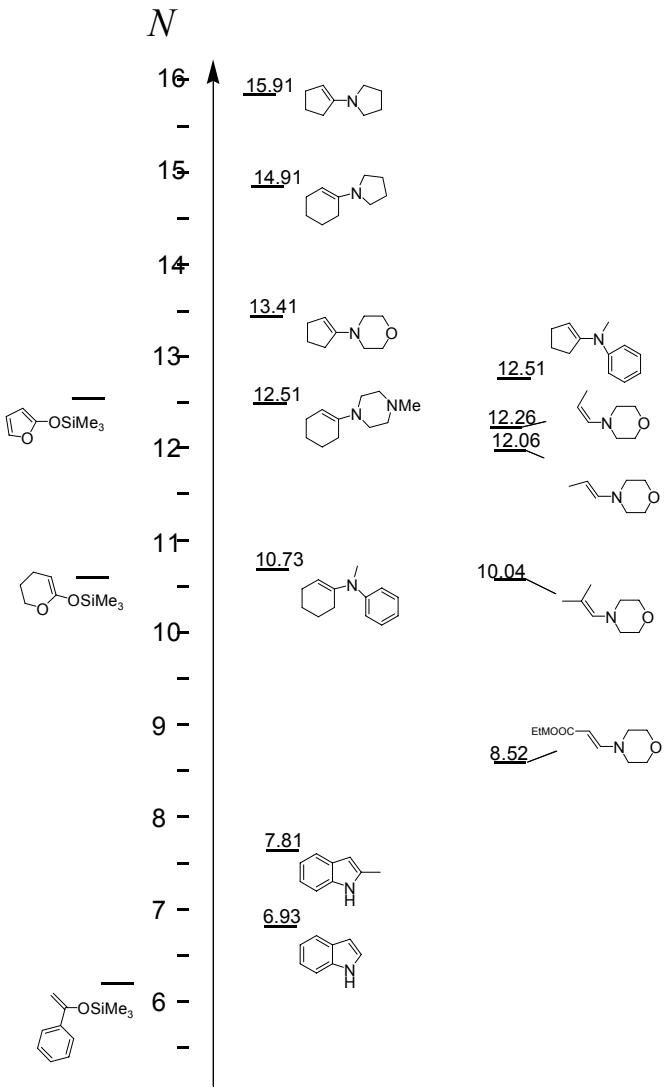
[1] C. Fichtner, G. Remennikov, H. Mayr, *Eur. J. Org. Chem.* **2001**, 4451.
[2] J. E. Appleton, K. N. Dack, A. D. Green, J. Steele, *Tetrahedron Lett.* **1993**, *34*, 1529.

Figure 1. Mayr's electrophilicity scale.[3]



[3] H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66, and ref. therein

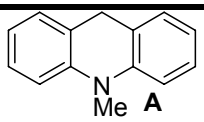
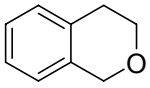
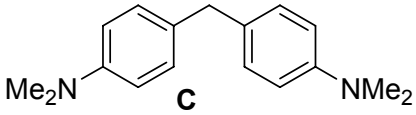
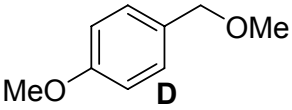
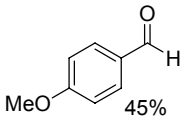
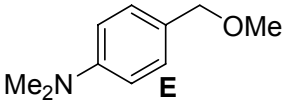
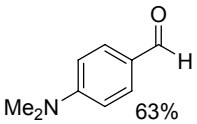
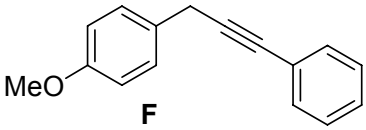
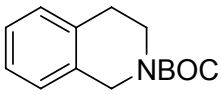
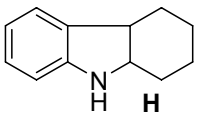
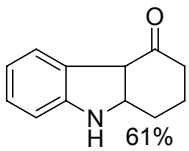
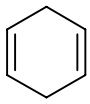
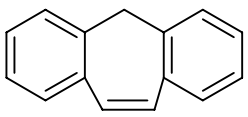
Figure 1. Mayr's Nucleophilicity scale[4]



[4] H. Mayr, B. Kempf, A. R. Ofial, *Acc. Chem. Res.* **2003**, *36*, 66, and ref. therein

Substrates **A-J** were tested in the direct organocatalytic C-H alkylation using the MacMillan catalyst in the presence of DDQ (1.3 equiv) at 0 °C following the general procedure 1. The outcome of the reaction are indicated in the Table 1. All the reactions were run for 4 hours.

Table 3

Entry	Substrate	Isolated products
1	 **A**	Not characterized by-products
2	 **B**	Starting materials
3	 **C**	Not characterized by-products
4	 **D**	
5	 **E**	
6	 **F**	Not characterized by-products
7	 **G**	Starting materials
8	 **H**	
9	 **I**	Starting materials
10	 **J**	Starting materials

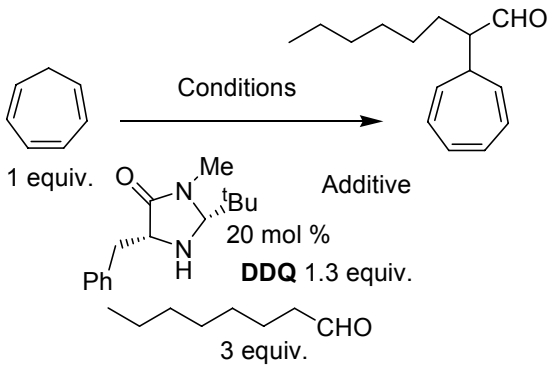


Table 4. Reaction of *n*-octanal with 1,3,5-cycloeptatriene performed in different solvents and conditions.

Entry[a]	T, °C	Additive, 20 mol%	Yield[%]	Ee[%]
1	RT	TFA	--	
2	-25	TFA	91	16
3	-25	$pNO_2PhCOOH$	90	46
4	-25	1,3,5-MeOPhCOOH	27	44
5	-25	--	82	40
6	-25	CF_3CH_2OH	32	20
7	-40	Mandelic acid		20
8	-25	N-BOC-Phe-OH		20
9[b]	-25	Proline		0

[a] All the reactions were conduced using the general procedure B, in the presence of different additives used in 20 mol% at the indicated temperature for 2.30 hours.. [b] Proline was used instead of the MacMillan catalyst

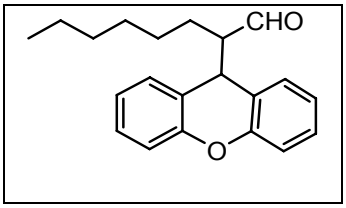
Synthetic procedures.

Procedure 1. Substrates 1 and 3.
In a two-necked flask containing degassed DCM (1 mL), the organocatalyst **8** (20 mol %), the aldehyde (3 eq., 0.3 mmol) and compound **1** or **3** (0.1mmol) are added under nitrogen at r.t. and the solution was stirred at r.t. for 5 min. After cooling to -25°C, DDQ (1.3 eq.) was added portion wise (3 portions) during 1 hour, and the solution was stirred at -25°C for 4 h. The reaction was quenched with water, and the organic phase was separated. The aqueous phase was extracted twice with DCM; the organic phases were dried over Na_2SO_4 and evaporated under reduced pressure to afford the crude reaction mixture, that was purified by FC (cyclohexane/Et_2O = 9/1 for **1a-f**, n-hexane/ Et_2O = 95/5 for **3a**).

Procedure 2. Substrate 2.
In a two-necked flask containing degassed DCM (1 mL), the organocatalyst **9** (20 mol %), the aldehyde (3 eq., 0.3 mmol) and compound **2** (0.1mmol) are added under nitrogen at r.t. and the solution was stirred at r.t. for 5 min. After cooling to -25°C, DDQ (1.3 eq.) was added portion wise (3 portions) during 1 hour, and the solution was stirred at -25°C for 4 h. The reaction was quenched with water, and the organic phase was separated. The aqueous phase was extracted twice with DCM; the organic phases were dried over Na_2SO_4 and evaporated under reduced pressure to afford the crude reaction mixture, that was purified by FC (cyclohexane/Et_2O = 9/1).

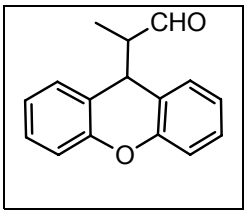
Procedure 3. Substrates 4-7.
In a two-necked flask containing degassed DCM (1 mL), the organocatalyst **8** (20 mol %), the aldehyde (3 eq., 0.3 mmol), MeOH (2eq., 0.2 mmol) and compound **4-7** (0.1 mmol) are added under nitrogen at r.t. and the solution was stirred at r.t. for 5 min. After cooling to -25°C, DDQ (1.3 eq.) was added and the solution was stirred at -25°C for 4 h. The reaction was quenched with water, and the organic phase was separated. The aqueous phase was extracted twice with DCM; the organic phases were dried over Na_2SO_4 and evaporated under reduced pressure to afford the crude reaction mixture, that was purified by FC (cyclohexane/AcOEt, gradient from 9/1 to 8/2).

2-(*9H*-xanthen-9-yl)octanal, 1a.



Analytical data for compound **1a** are reported in ref. 5.

2-(*9H*-xanthen-9-yl)propanal, 1b.



$C_{16}H_{14}O_2$ Fw = 238.28

$[\alpha]_D$ = +7.6 (c 1.1, $CHCl_3$).

Colorless oil.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.93 (3H, d, J = 7.4 Hz), 2.67-2.76 (1H, m), 4.64 (1H, d, J = 4.0 Hz), 7.02-7.32 (8H, m); 9.78 (1H, s).

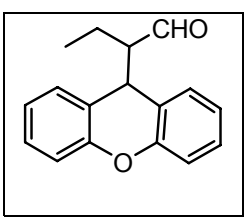
^{13}C NMR ($CDCl_3$, 50 MHz) δ: 9.4, 39.7, 55.8, 116.6, 118.0, 121.5, 123.3, 123.4, 123.6, 128.2, 128.3, 128.6, 129.0, 152.9, 153.1, 203.7.

GC-MS: rt: 19.2 min; *m/z*: 238(5), 183(12), 182(146), 181(1000), 180(12), 165(13), 153(15), 152(112), 151(39), 150(14), 127(15), 126(15), 77(10), 76(11), 63(7) .

HPLC analysis: Chiracel IC: 99:1 (hexane: *i*-PrOH), flow 0.7mL/min. tm:12.2 min; TM: 11.7 min.

HRMS Calcd for $C_{17}H_{16}O_2$: 238.09938, $[M]^+$, found: 238.0991.

2-(*9H*-xanthen-9-yl)butanal, 1c.



$C_{17}H_{16}O_2$ Fw = 252.31

$[\alpha]_D$ = +19.5 (c 1.2, $CHCl_3$).

Colorless oil.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.84 (3H, t, J = 7.5 Hz), 1.45-1.65 (2H, m), 2.42-2.53 (1H, m), 4.49 (1H, d, J = 4.4 Hz); 7.04-7.32 (8H, m); 9.67 (1H, d, J = 2.6 Hz).

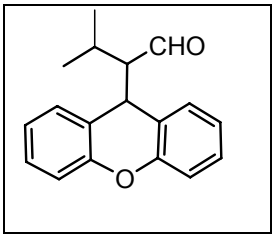
^{13}C NMR ($CDCl_3$, 50 MHz) δ: 12.0, 18.7, 40.0, 62.3, 116.7, 116.8, 122.2, 123.2, 123.4, 123.5, 128.2, 128.3, 128.7, 128.9, 152.9, 153.0, 204.5.

GC-MS: rt: 22.7 min; *m/z*: 252(5), 207(9), 205(7), 196(5), 183(17), 182(18), 181(1000), 180(13), 165(10), 153(18), 152(116), 151(38), 150(14), 139(6), 91(9), 77(9), 76(15), 75(9),70(9), 69(9), 63(10).

HPLC analysis (derivatized to alcohol): Chiracel OF: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:23.3 min; TM: 21.4 min.

HRMS Calcd for $C_{17}H_{16}O_2$: 252.11503, $[M]^+$, found: 252.1151.

3-methyl-2-(*9H*-xanthen-9-yl)butanal, 1d.



$C_{18}H_{18}O_2$ Fw = 266.33

$[\alpha]_D$ = + 10.5 (c 0.38, $CHCl_3$).

White solid. Mp=46.2-48.5°C

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.90 (3H, d, J = 6.8 Hz), 1.11 (3H, d, J=6.8Hz), 1.94-2.03 (1H,m), 2.31 (1H, ddd, J= 4.0, 6.0, 6.8Hz), 4.50 (1H, d, J = 6.0 Hz), 7.07-7.13 (4H, m), 7.24-7.28 (4H, m), 9.52 (1H, d, J =4.0 Hz).

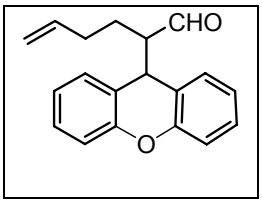
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 19.3, 21.7, 26.1, 38.2, 66.2, 116.7, 116.8, 123.1, 123.3, 123.5, 124.0, 128.1, 128.2, 128.7, 128.8, 152.9, 153.2, 204.4.

GC-MS: rt: 26.4 min; *m/z*: 266(2), 223(8), 205(8), 183(16), 182(166), 181(1000), 180(11), 165(12), 153(13), 152(100), 151(31), 150(12), 127(12), 126(10), 76(8), 63(7).

HPLC analysis: Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:14.8 min; TM: 15.9 min.

HRMS Calcd for $C_{18}H_{18}O_2$: 266.13068, $[M]^+$, found: 266.1307.

2-(*9H*-xanthen-9-yl)hex-5-enal, 1e.



$C_{19}H_{18}O_2$ Fw = 278.35

$[\alpha]_D$ = + 2.3 (c 0.48, $CHCl_3$).

Colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.43-1.49 (1H,m), 160-1.69 (1H, m), 1.85-1.91 (1H, m), 1.96-2.02 (1H, m), 2.60 (1H, ddt, J= 2.4, 4.4, 9.6 Hz), 4.50 (1H, d, J= 4.4 Hz), 4.84 (1H, d, J=17.2 Hz), 4.89 (1H, d, J=10.4 Hz), 5.57 (1H, ddt, J= 3.2, 10.4, 17.2 Hz), 7.04-7.12 (4H, m), 7.21-7.28 (4H, m), 9.67 (1H, d, J=2.4 Hz).

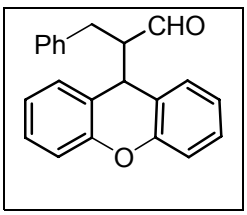
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.4, 31.3, 39.9, 59.9, 115.5, 116.7, 116.8, 122.9 (2C), 123.4, 123.6, 128.3, 128.4, 128.7, 128.9, 137.3, 152.8 (2C), 204.2.

GC-MS: rt: 30.2 min; *m/z*: 278(4), 207(14), 183(11), 182(138), 181(1000), 180(10), 153(14), 152(86), 151(23), 127(10), 126(9), 77(7).

HPLC analysis (derivatized to alcohol) Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:27.8 min; TM: 29.0 min.

HRMS Calcd for $C_{19}H_{18}O_2$: 278.13068, $[M]^+$, found: 268.1308.

3-phenyl-2-(*9H*-xanthen-9-yl)propanal, 1f.



$C_{22}H_{18}O_2$ Fw =314.38

$[\alpha]_D$ = + 100.0 (c 0.30, $CHCl_3$).

White solid.Mp= 84-89 °C

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.68-2.90(2H, m), 2.98-3.08 (1H,m), 4.63 (1H, d, J = 7.2 Hz), 7.01 (2H, d, J=8.0Hz), 7.11-7.36 (11H, m), 9.68 (1H, d, J = 3.6 Hz).

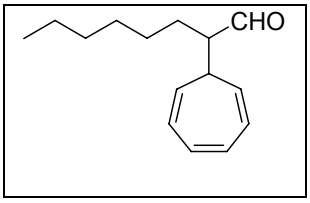
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 31.2, 39.5, 62.4, 116.7, 116.8, 121.7, 122.6, 123.5, 123.6, 126.3 (2C), 128.2, 128.4, 128.5, 128.6 (2C), 128.8, 128.9, 138.7, 152.8, 152.9, 203.4.

ESI-MS: rt: 12.7 min; *m/z*: 313 (M-H_2+1), 335 (M-H_2+Na^+).

HPLC analysis: Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:17.1 min; TM: 16.3 min.

HRMS Calcd for $C_{22}H_{18}O_2$: 314.13068, $[M]^+$, found: 314.1307.

2-((2Z,4Z,6Z)-cyclohepta-2,4,6-trienyl) octanal, 2a.



$C_{15}H_{22}O$ Fw = 218.33

$[\alpha]_D$ = + 8.4 (c 0.90, $CHCl_3$).

Colorless oil.

^{1}H NMR ($CDCl_3$, 200 MHz) δ: 0.88 (3H, t, J = 6.6 Hz), 1.09-1.44 (8H, m), 1.53-1.81 (2H, m), 1.81-2.07 (1H, m), 2.52-2.69 (1H, m), 5.23 (2H, pseudo t, J = 7.2 Hz), 6.24 (2H, m), 6.69 (2H, pseudo t, J = 2.8 Hz), 9.64 (1H, d, J = 3.4Hz).

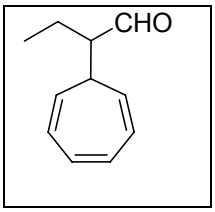
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1, 23.6, 29.1, 29.3, 31.8, 34.4, 38.8, 54.0, 122.2, 123.1, 125.6, 125.7, 131.0, 131.1, 204.7.

GC-MS: rt: 14.7 min; *m/z*: 218(5), 147(7), 133(45), 129(19), 128(10), 118(6), 117(28), 116(9), 115(32), 105(40), 104(12), 103(17), 92(92), 91(1000), 90(6), 79(17), 78(29), 77(34), 69(6), 65(46), 55(22), 51(11).

HPLC analysis: Chiracel OD-H: 99:1 (hexane: *i*-PrOH), flow 0.6mL/min. tm:21.1 min; TM: 19.2 min.

HRMS Calcd for $C_{15}H_{22}O_2$: 218.16706, $[M]^+$, found: 218.1672.

2-((2Z,4Z,6Z)-cyclohepta-2,4,6-trienyl) butanal, 2c.



$C_{11}H_{14}O$ Fw = 162.23

$[\alpha]_D$ = + 2.7 (c 0.67, $CHCl_3$).

Colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.94 (3H, t, J = 7.2 Hz), 1.74-1.84 (2H, m), 1.97-2.02 (1H, m), 2.54-2.60 (1H, m), 5.24 (2H, dt, J = 5.6, 10.0 Hz), 6.25 (2H, tt, J = 2.8, 10.0 Hz), 6.69 (2H, pseudo t, J = 2.8 Hz), 9.65 (1H, d, J = 3.6Hz).

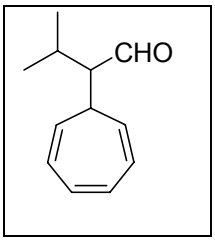
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 11.5, 20.2, 38.5, 55.1, 122.1, 123.1, 125.6, 125.8, 131.0, 131.1, 204.5.

GC-MS: rt: 9.3 min; *m/z*: 162(3), 133(16), 131(7), 128(7), 117(14), 115(29), 105(40), 104(10), 103(20), 92(85), 91(1000), 89(20), 79(18), 78(57), 77(55), 65(77), 63(28), 62(9),55(24), 51(29).

HPLC analysis: Chiracel OD-H: 99:1 (hexane: *i*-PrOH), flow 0.6mL/min. tm:28.6min; TM: 26.9min.

HRMS Calcd for $C_{11}H_{14}O$: 162.10447, $[M]^+$, found: 162.1045.

2-((2Z,4Z,6Z)-cyclohepta-2,4,6-trienyl)-3-methylbutanal, 2d.



$C_{12}H_{16}O$ Fw = 176.25

$[\alpha]_D$ = + 8.8 (c 0.51, $CHCl_3$).

Colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.95 (3H, d, J = 7.2 Hz), 1.06 (3H, d, J=7.2Hz), 2.05-2.12 (1H, m), 2.25-2.33 (1H, m), 2.50 (1H, m), 5.21 (2H, dd, J=6.0, 9.2 Hz), 6.24 (2H, pseudo tt, J=2.8, 9.2 Hz), 6.70 (2H, dd, J=2.8 Hz), 9.78 (1H, d, J = 4.4 Hz).

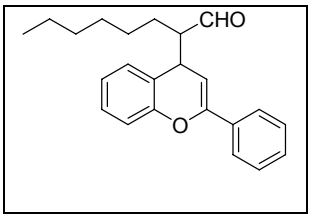
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 18.6, 21.2, 21.5, 37.3, 59.0, 122.0, 122.7, 125.4, 125.5, 130.9, 131.0, 205.7.

GC-MS: rt: 10.2 min; *m/z*: 176(5), 174(6), 134(10), 133(94), 131(20), 129(11), 128(17), 117(18), 116(11), 115(50), 105(59), 104(12), 92(114), 91(1000), 90(9), 89(21), 79(39), 78(59), 77(70), 65(80), 63(24), 55(38), 53(17), 52(14), 51(38), 50(12).

HPLC analysis: Chiracel OD-H: 99:1 (hexane: i-PrOH), flow 0.6mL/min. tm:29.0min; TM: 24.9min.

HRMS Calcd for $C_{12}H_{16}O$: 176.12012, $[M]^+$, found: 176.1200.

2-(2-phenyl-4*H*-chromen-4-yl) octanal, 3a.



$C_{23}H_{26}O_2$ Fw = 334.45

Colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 0.82 (3H M, t, J = 7.2 Hz), 0.88 (3H m, t, J = 7.2 Hz), 0.91-1.45 (16H, m), 1.61-1.73 (2H m, m), 1.73-1.80 (2H M, m), 2.58-2.62 (1H m, m), 2.62-2.66 (1H M, m), 4.06 (1H m,

t, J=4.4Hz), 4.22 (1H M, t, J=4.4Hz), 5.38 (1H M, d, J= 4.8Hz), 5.55 (1H m, d, J= 4.8Hz), 7.07-7.26 (6H, m), 7.24 (1H M + 1H m, t, J=5.8Hz), 7.33-7.40 (6H, m), 7.69 (4H, d, J=6.8Hz), 9.72 (1H m, d, J=2.4Hz), 9.84 (1H M, d, J=2.4Hz).

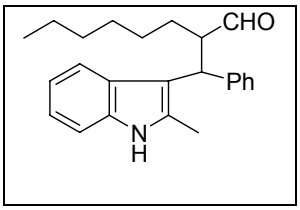
^{13}C NMR ($CDCl_3$, 100 MHz) δ (major): 13.9, 24.9(2C), 27.8, 29.1, 31.4, 35.0, 59.5, 96.6, 116.7, 116.8, 121.3, 123.7, 124.7, 124.8, 127.9, 128.3, 128.4, 128.7, 133.8, 150.6, 152.5, 204.4.

ESI-MS: rt: 17.3 min; *m/z*: 335 (M+1), 357 ($M+Na^+$).

HPLC analysis: Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm (major):12.8 min; TM (major): 14.6 min. tm (minor):15.7 min; TM (minor): 13.8 min.

HRMS Calcd for $C_{24}H_{26}O_2$: 334.19328, $[M]^+$, found: 334.1935.

2-((2-methyl-1*H*-indol-3-yl)(phenyl)methyl)octanal, 4a.



$C_{24}H_{29}NO$ Fw = 347.49

Colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.79 (3Hanti, t, J=7.2Hz), 0.86 (3Hsyn, t, J=7.2Hz), 1.09-1.28 (16H, m), 1.48-1.54 (2H, m), 1.54-1.62 (2H, m), 2.42 (3Hsyn, s), 2.44 (3Hanti, s), 3.50-3.61 (2H,m), 4.34 (1Hsyn, d, J = 11.6 Hz), 4.46 (1Hanti, d, J = 11.6 Hz), 7.05-7.41 (18H, m), 7.74 (1Hsyn, bs), 7.80 (1Hanti, bs), 9.42 (1Hsyn, d, J = 4.4 Hz), 9.63 (1Hanti, d, J = 4.0 Hz).

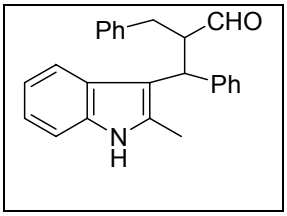
^{13}C NMR ($CDCl_3$, 100 MHz) δ (anti+syn): 13.9(2C), 14.0(2C), 22.4, 22.5, 26.7, 27.0, 28.7, 29.2, 29.3, 29.7, 31.4, 31.5, 43.1, 43.9, 54.3, 54.4, 110.3, 110.4, 112.1 (2C), 118.8, 119.0, 119.5, 119.6, 121.0, 121.1, 126.3 (2C), 127.9, 128.0 (2C), 128.1, 128.2, 128.5, 128.6 (2C), 131.2 (2C), 131.6 (2C), 135.3 (2C), 142.5, 142.6, 204.2, 205.5.

ESI MS: rt: 13.7 min; *m/z*: 348 ($M+H^+$); 370 ($M+Na^+$).

HPLC analysis Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. TM (anti): 31.6 min; tm (anti): 23.8 min; TM (syn): 21.0 min; tm (syn): 24.5 min;

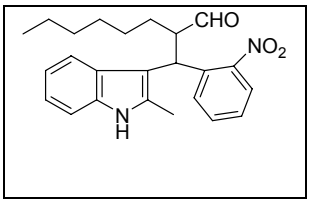
HRMS Calcd for $C_{17}H_{16}O_2$: 347.22491, $[M]^+$, found: 347.2247.

2-benzyl-3-(2-methyl-1*H*-indol-3-yl)-3-phenylpropanal, 4f.



Analytical data are reported in ref. 5.

2-((2-methyl-1*H*-indol-3-yl)(2-nitrophenyl)methyl)octanal, 5a.



$C_{24}H_{28}N_2O_3$ Fw = 392.49

$[\alpha]_D$ = +113.0 (c 0.60, $CHCl_3$).

Yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (syn): 0.86 (3H, t, J=7.2Hz),1.17-1.32 (8H, m), 1.49-1.57 (1H, m), 1.73-1.80 (1H,m), 2.38 (3H, s), 3.45-3.52 (1H,m), 5.22 (1H, d, J = 10.8 Hz), 7.00-7.09 (2H, m), 7.18 (1H, d, J=7.2Hz), 7.30 (1H, t, J=8.0Hz), 7.49-7.59 (2H,m), 7.63 (1H, dd, J=1.2, 8.0Hz), 7.85 (1Hsyn, bs), 7.87 (1H, d, J=8.0Hz), 9.38 (1H, d, J = 4.4 Hz).

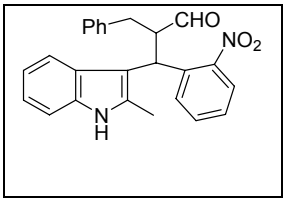
^{13}C NMR ($CDCl_3$, 100 MHz) δ (syn): 12.4, 14.0, 22.5, 26.9, 28.8, 29.1, 31.5, 37.3, 54.6, 110.0, 110.6, 118.7, 119.8, 121.3, 124.4, 127.1, 127.2, 129.3, 132.3, 132.7, 135.3, 136.5, 150.3, 203.2.

ESI MS: rt: 12.9 min (syn); *m/z*: 393 ($M+H^+$); 415 ($M+Na^+$).

HPLC analysis: Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 1.0mL/min. TM (syn): 24.1 min; tm (syn): 17.7min.

HRMS Calcd for $C_{24}H_{28}N_2O_3$: 392.20999, $[M]^+$, found: 392.2098.

2-benzyl-3-(2-methyl-1*H*-indol-3-yl)-3-(2-nitrophenyl)propanal, 5f.



$C_{25}H_{22}N_2O_3$ Fw = 398.45

$[\alpha]_D$ = +131.0 (c 0.27, $CHCl_3$).

Yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ (syn): 2.36 (3H, s), 2.87 (1H, dd, J=3.6, 14.0 Hz), 3.18 (1H, dd, J=10.4, 14.0 Hz), 3.99 (1H, ddd, J= 3.6, 10.4, 10.8 Hz), 5.27 (1H, d, J= 10.8 Hz), 6.97-7.26 (9H, m), 7.34 (1H, t, J=8.0Hz), 7.56 (1H, t, J=8.0 Hz), 7.66 (1H, d, J=8.0 Hz), 7.82 (1H, bs), 7.99 (1H, d, J= 8.0Hz), 9.43 (1H, d, J= 3.6Hz).

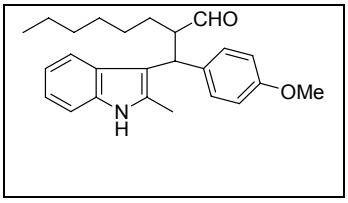
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 12.2, 35.0, 37.8, 55.6, 109.4, 110.7, 118.6, 119.9, 121.3, 124.5, 126.5, 127.0, 128.5, 128.6 (2C), 128.8 (2C), 129.3, 132.3, 132.9, 135.4, 136.2, 138.4, 150.5, 203.0.

ESI MS: rt: 10.9(syn) min; *m/z*: 399 ($M+H^+$); 421 ($M+Na^+$).

HPLC analysis Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. TM (syn): 40.4 min; tm (syn): 33.9min; TM (anti): 43.0 min; tm (anti): 28.7min.

HRMS Calcd for $C_{25}H_{22}N_2O_3$: 398.16034, $[M]^+$, found: 398.1602.

2-((4-methoxyphenyl)(2-methyl-1*H*-indol-3-yl)methyl)octanal, 6a.



$C_{25}H_{31}NO_2$ Fw = 377.52

Colorless oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 0.79 (3Hanti, t, J=7.2Hz), 0.86 (3Hsyn, t, J=7.2Hz),1.09-1.28 (16H, m), 1.46-1.66 (4H, m), 2.42 (3Hsyn, s), 2.44 (3Hanti, s), 3.43-3.55 (2H,m), 3.72 (3Hanti, s), 3.75 (3Hsyn, s), 4.28 (1Hsyn, d, J = 11.6 Hz), 4.40 (1Hanti, d, J = 11.6 Hz), 6.76 (2Hanti, d, J=8.4Hz), 6.81 (2Hsyn, d, J=8.4Hz), 7.02-7.11 (4H, m), 7.19-7.31 (6H,m), 7.62 (1Hanti, d, J=7.6Hz), 7.67 (1Hsyn, d, J=7.6Hz), 7.74 (1Hsyn, bs), 7.79 (1Hanti, bs), 9.40 (1Hsyn, d, J = 4.4 Hz), 9.60 (1Hanti, d, J = 4.4 Hz).

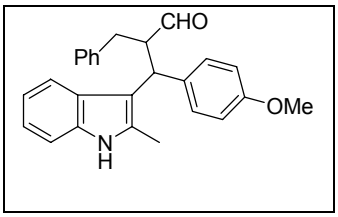
^{13}C NMR ($CDCl_3$, 100 MHz) δ (anti+syn): 12.4, 12.8, 14.0 (2C), 22.5 (2C), 26.7, 27.0, 28.7 (2C), 29.2, 29.3, 31.5, 31.6, 42.2, 43.1, 54.5, 54.6, 55.1, 55.2, 110.3, 110.4, 112.4 (2C), 112.6 (2C), 113.8 (2C), 113.9 (2C), 118.7, 119.0, 119.4, 119.5, 121.0, 121.1, 127.4 (2C), 128.9 (2C), 129.0 (2C), 131.1, 131.4, 134.8, 135.4, 157.9 (2C), 204.3, 205.6.

ESI MS: rt: 12.5 and 13.0 min; *m/z*: 400 ($M+Na^+$).

HPLC analysis: Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 8:2 in 30min, flow 0.5mL/min. TM (anti): 22.2 min; tm (anti): 20.4min; TM (syn): 24.0min; tm (syn): 25.8min.

HRMS Calcd for $C_{25}H_{31}NO_2$: 377.23548, $[M]^+$, found: 377.2353.

2-benzyl-3-(4-methoxyphenyl)-3-(2-methyl-1*H*-indol-3-yl)propanal, 6f.



$C_{26}H_{25}NO_2$ Fw = 383.48

Yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.38 (3Hsyn, s), 2.40 (3Hanti, s), 2.68-3.07 (4H, m), 3.72 (3Hanti, s), 3.78 (3Hsyn, s), 3.89-4.00 (2H, m), 4.37 (1Hsyn, d, J= 11.2 Hz), 4.46 (1Hanti, d, J= 11.2 Hz), 6.77 (2Hanti, dd, J=2.4, 6.8 Hz), 6.87 (2Hsyn, dd, J=2.4, 6.8 Hz), 6.99.7.43 (22H, m), 7.78 (1Hsyn, bs), 7.87 (1Hanti, bs), 9.47 (1Hsyn, d, J = 3.6 Hz), 9.68 (1Hanti, d, J = 3.2 Hz).

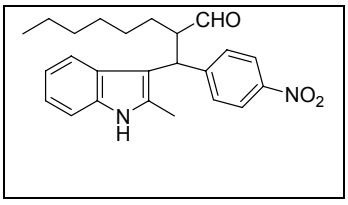
^{13}C NMR ($CDCl_3$, 100 MHz) δ (syn+anti): 12.3, 12.5, 35.3, 35.4, 42.6(2C), 43.5(2C), 55.7, 56.4, 110.5, 110.6, 111.9, 112.2, 113.9(2C), 114.1(2C), 118.9, 119.0, 119.5, 119.6, 121.0, 121.1, 126.2, 126.3, 126.4, 127.2, 127.4, 128.2, 128.3(4C), 128.4, 128.5 (2C), 128.9, 129.0, 129.1, 131.2, 131.8, 134.3, 134.5, 135.3, 135.5, 138.6, 139.0, 157.9, 158.0, 204.5, 205.5.

ESI MS: rt: 10.8 and 11.2 min; *m/z*: 384 ($M+H^+$); 406 ($M+Na^+$).

HPLC analysis IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5 mL/min. TM (anti): 45.8 min; tm (anti): 48.0 min; TM (syn): 42.8 min; tm (syn): 34.1 min.

HRMS Calcd for $C_{26}H_{25}NO_2$: 383.18853, $[M]^+$, found: 383.1884.

2-((2-methyl-1*H*-indol-3-yl)(4-nitrophenyl)methyl)octanal, 7a.



$C_{24}H_{28}N_2O_3$ Fw = 392.49

Yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz) δ : 0.77-0.91 (6H, m), 1.34-1.45 (16H, m), 1.46-1.51 (2H, m), 1.52-1.62 (2H, m), 2.42 (3Hsyn, s), 2.44 (3Hanti, s), 3.49-3.58 (1Hsyn, m), 3.61-3.68 (1Hanti, m), 4.45 (1Hsyn, d, J

= 11.2 Hz), 4.56 (1Hanti, d, J = 11.2 Hz), 7.03-7.14 (4H, m), 7.18-7.34 (4H,m), 7.50 (2Hanti, d, J=8.8 Hz), 7.54 (2Hsyn, d, J=8.8 Hz), 7.89 (1Hsyn, bs), 7.93 (1Hanti, bs), 8.07 (2Hanti, d, J=8.8 Hz), 8.13 (2Hsyn, d, J=8.8 Hz), 9.44 (1Hsyn, d, J = 4.0 Hz), 9.68 (1Hanti, d, J = 4.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz) δ (syn+anti): 12.7 (2C), 14.0 (2C), 22.6 (2C), 26.4, 26.9, 29.1, 29.3, 29.4, 29.7, 31.5, 31.6, 42.4, 43.9, 53.8, 54.0, 110.7 (2C), 118.4, 118.5, 119.9, 120.0, 121.4, 121.5, 123.8 (2C), 123.9 (2C), 128.7 (4C), 127.0 (2C), 131.8 (2C), 132.0 (2C), 135.3 (2C), 150.2 (2C), 150.4 (2C), 203.3, 204.5.

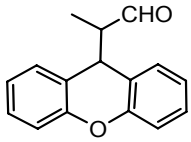
ESI MS: rt: 12.4 and 12.7 min; *m/z*: 393 ($M+H^+$).

HPLC analysis IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 1.0 mL/min. TM (anti): 40.9 min; tm (anti): 31.8 min; TM (syn): 29.3 min; tm (syn): 27.7 min.

HRMS Calcd for $C_{24}H_{28}N_2O_3$: 392.20999, $[M]^+$, found: 392.2098 .

Determination of the absolute configuration.

Synthesis of (R)-2-(*9H*-xanthen-9-yl)propanol

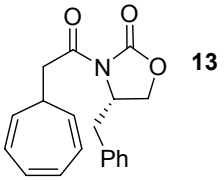


To a solution of N-propionyl oxazolidinone **9** (20 mg, 0.1mmol) in CH_2Cl_2 (2mL) a 1 M solution of $TiCl_4$ in CH_2Cl_2 (0.1mL) was added, followed by DIPEA (0.020mL, 0.12mmol). The resulting violet solution was stirred at 0°C for 30 m, then 9H-Xanthen-9-ol **8** (20 mg, 0.1mmol), immediately followed by 0.1mL of a 1M solution of $TiCl_4$ in CH_2Cl_2, were added. The titanium enolate was immediately decolorized and after few minutes a yellow suspension was formed. The slurry was stirred 2 h at 0 °C then quenched with water and diluted with Et_2O (6 mL). The TiO_2 formed was filtered off and the organic phase was separated. The aqueous phase was extracted with ether, then the organic phases were reunited, dried over Na_2SO_4 and evaporated under reduced pressure. The crude reaction mixture containing 9H-Xanthen-9-ol, propionyl oxazolidinone and the desired products was transferred to a flask and THF (3mL) was added. The solution was stirred at 0 °C for 5 minutes then was treated with SuperHydride (0.20mL of a solution 1M in THF). After 60 min, the reaction was quenched with water and diluted with AcOEt. The separated organic phase was dried over sodium sulfate and concentrated in vacuo. Purification by preparative TLC (5:5 cyclohexane/Et_2O) afforded **11** (3 mg, yield=12% over 2 steps).

^{1}H NMR ($CDCl_3$, 200MHz) δ: 0.65 (3H, t, J=7.0 Hz), 1.50 (1H, bs), 2.0 (1H, m), 3.40-3.59 (2H,m), 4.23 (1H, J=4.2 Hz), 7.03-7.12 (4H,m) 7.19-7.29 (4H, m).

HPLC analysis IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min: TM= 27.5min, tm=30.5min (ee=99%).

Synthesis of (S)-4-benzyl-3-(2-((2Z,4Z,6Z)-cyclohepta-2,4,6-trienyl)acetyl)oxazolidin-2-one 13.



13

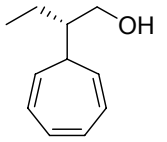
To a solution of diisopropylamine (185 µL, 1.32 mmol) in 12 mL of dry THF under nitrogen, *n*-butyllithium (492 µL of a 2.5M solution in hexanes, 1.23 mmol) was added at 0°C and the resulting solution was stirred for 10 min. Then the flask was cooled to -78°C, EtOAc (119 µL, 1.2 mmol) was added and the solution was stirred at the same temperature for 60min.

In a second flask, tropylium tetrafluoroborate **12** (178mg, 1mmol) and TEA (139 µL, 1mmol) were suspended in 1.5mL of dry THF and the mixture was cooled to -78°C. Then the content of this second flask was slowly transferred by cannula into the solution of the preformed lithium enolate, while keeping the temperature at -78°C. The reaction was allowed to warm during 1h, then it was quenched with water and extracted with EtOAc t. The combined organic phases were dried on sodium sulfate and concentrated in vacuo. The crude product was the dissolved in a mixture of THF/MeOH/H_2O (3.6/1/1, total volume: 15mL) and lithium hydroxyde (114mg, 3 mmol) was added at r.t.. After 1h, the reaction was diluted with EtOAc and acidified with 1M HCl. After the extraction, the organic fraction was dried over sodium sulfate and concentrated in vacuo affording 81mg of 2-((2Z,4Z,6Z)-cyclohepta-2,4,6-trienyl)acetic acid (Y=54% over 2 steps).

The carboxylic acid (81 mg, 0.54 mmol) was dissolved in dry THF (4.0 mL) and TEA (139 µL, 1.0 mmol) and cooled to –78 ºC according to the procedure described by MacMillan at al. in *Science*, **2007**, *316*, 582. Pivaloyl chloride (74 µL, 0.6 mmol) was added and the reaction was gradually warmed to 0 ºC over 90 min. (*S*)-4-benzyloxazolidin-2-one (89 mg, 0.54 mmol) was added followed by lithium chloride (64 mg, 1.5 mmol) and the reaction was warmed to ambient temperature and stirred for 72h. The solution was diluted with ethyl acetate and washed with water, the organic phase was dried over sodium sulfate and concentrated in vacuo. Purification by flash chromatography (silica gel, 9:1 cyclohexane/EtOAc) afforded **13** (90 mg, Y=54%).

^{1}H NMR ($CDCl_3$, 200MHz) δ: 2.30-2.42 (1H, m), 2.80 (1H, dd, J=9.6, 13.2 Hz), 3.24-3.45 (3H, m), 4.08-4.27 (2H, m), 4.65-4.76 (1H, m), 5.29 (2H, pseudo t, J=7.0 Hz), 6.25 (2H, d, J=9.0Hz), 6.70 (2H, pseudo t, J=2.6 Hz), 7.20-7.35 (5H, m).

Synthesis of (S)-2-((2Z,4Z,6Z)-cyclohepta-2,4,6-trienyl)butan-1-ol 14.



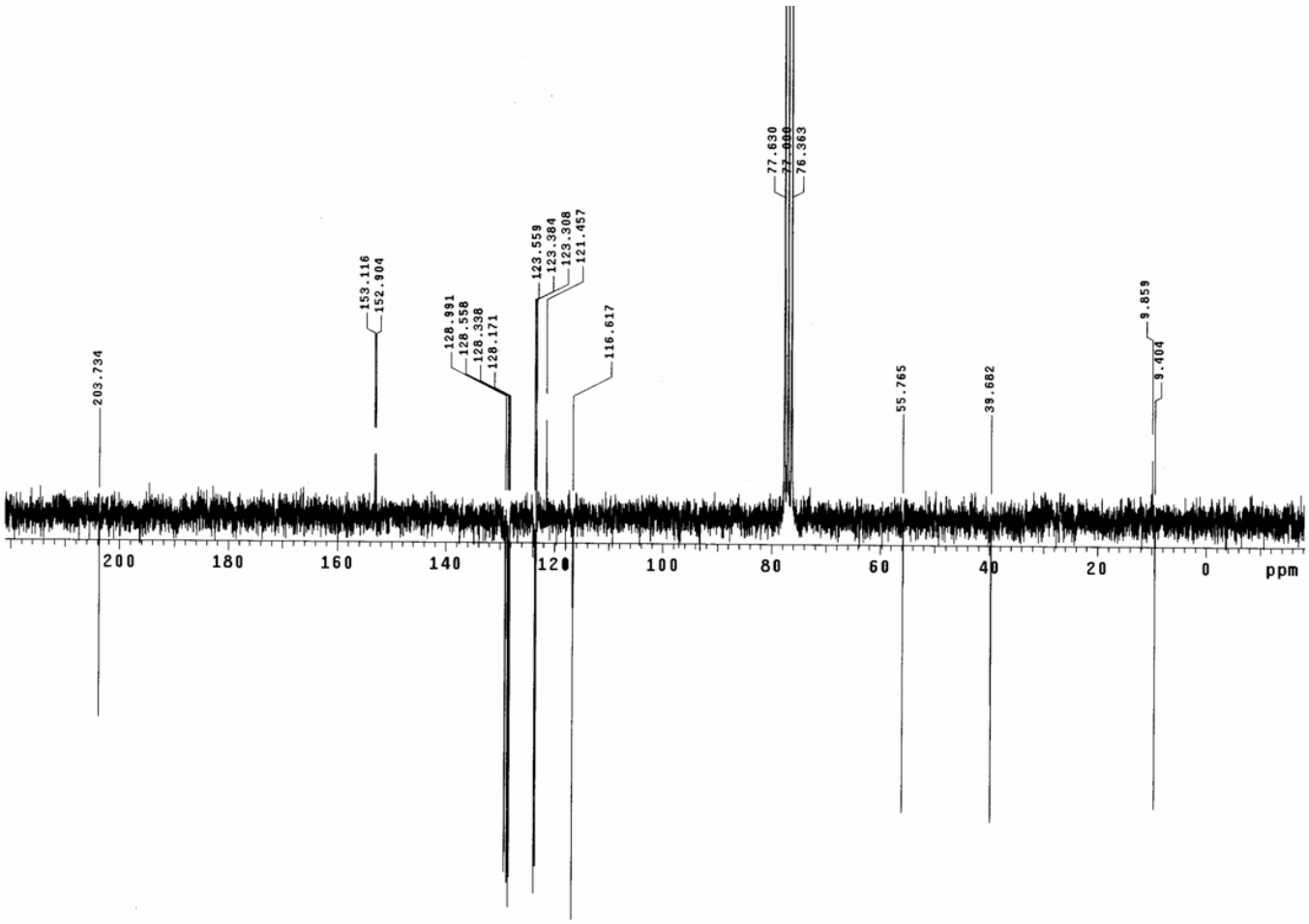
13

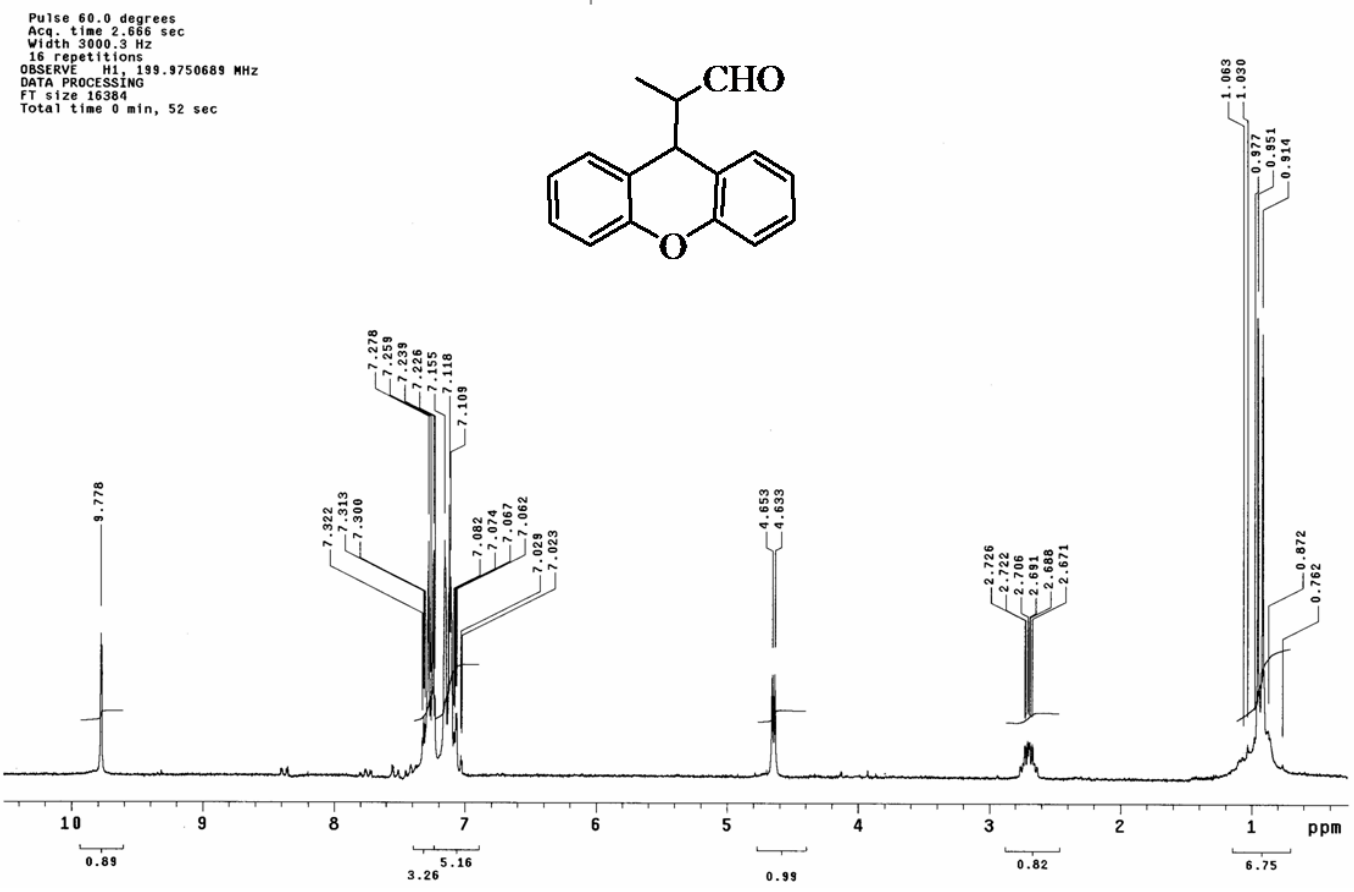
Compound **13** was dissolved in THF (4 mL) and cooled to –78 ºC. $NaN(SiMe_3)_2$ (700 µL, 0.7 mmol) was added and the reaction was stirred for 1 h. Iodoethane (150 µL, 1.88 mmol) was then added and the reaction was warmed to –20 ºC over 4 h, then it was quenched with a saturated NH_4Cl aqueous solution (5 mL). The reaction was diluted with EtOAc and the organic phase was washed with brine, dried over sodium sulfate and concentrated in vacuo. The crude mixture obtained was diluted with 400 µL of dry THF, cooled to 0°C and treated with SuperHydride (0.29mL of a solution 1M in THF). After 30 min, the reaction was quenched with water and diluted with EtOAc. The separated organic phase was dried over sodium sulfate and concentrated in vacuo. Purification by preparative TLC (7:3 cyclohexane/EtOAc) afforded **14** (7 mg, Y=15% over 2 steps).

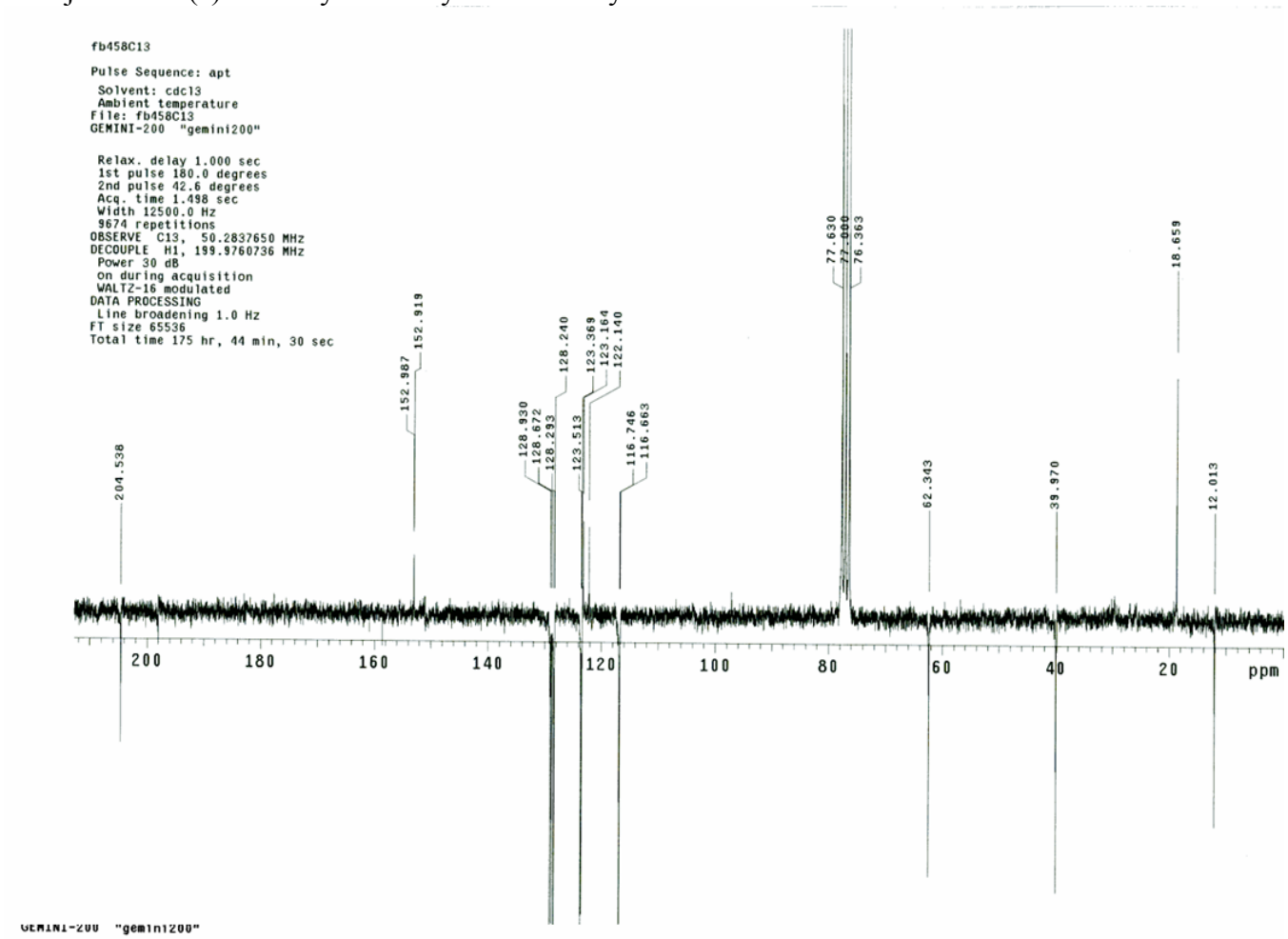
^{1}H NMR ($CDCl_3$, 200MHz) δ: 0.96 (3H, t, J=7.4 Hz), 1.39-1.70 (3H, m), 1.70-1.88 (1H, m), 3.81 (2H, d, J=4.8 Hz), 5.28-5.37 (2H, m), 6.21-6.25 (2H, m), 6.68 (2H, pseudo t, J=3.4 Hz).

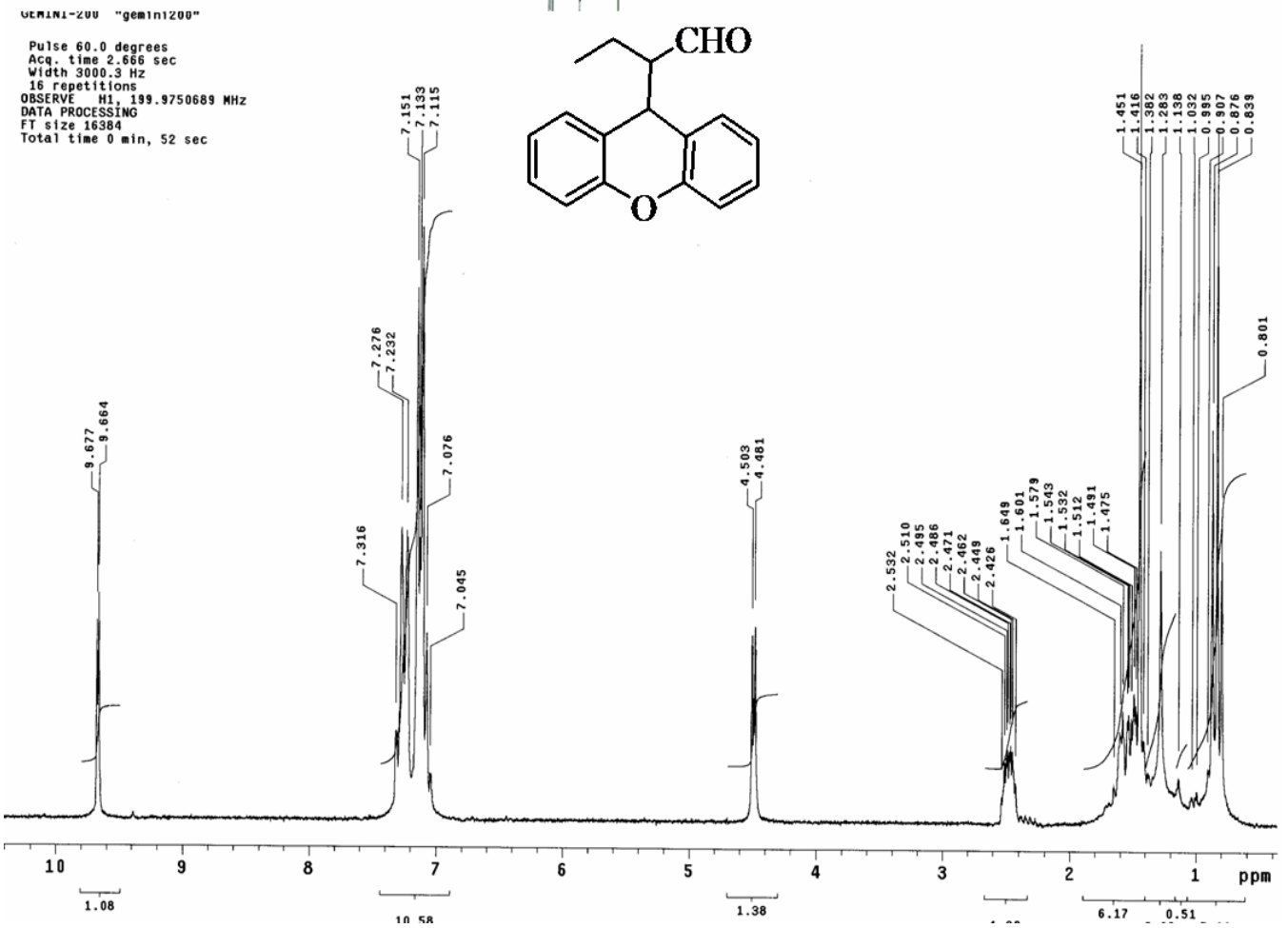
HPLC analysis OD-H 99:1 (hexane: *i*-PrOH), flow 0.6 mL/min. tm= 28.6min, TM=26.9min (ee=90%).

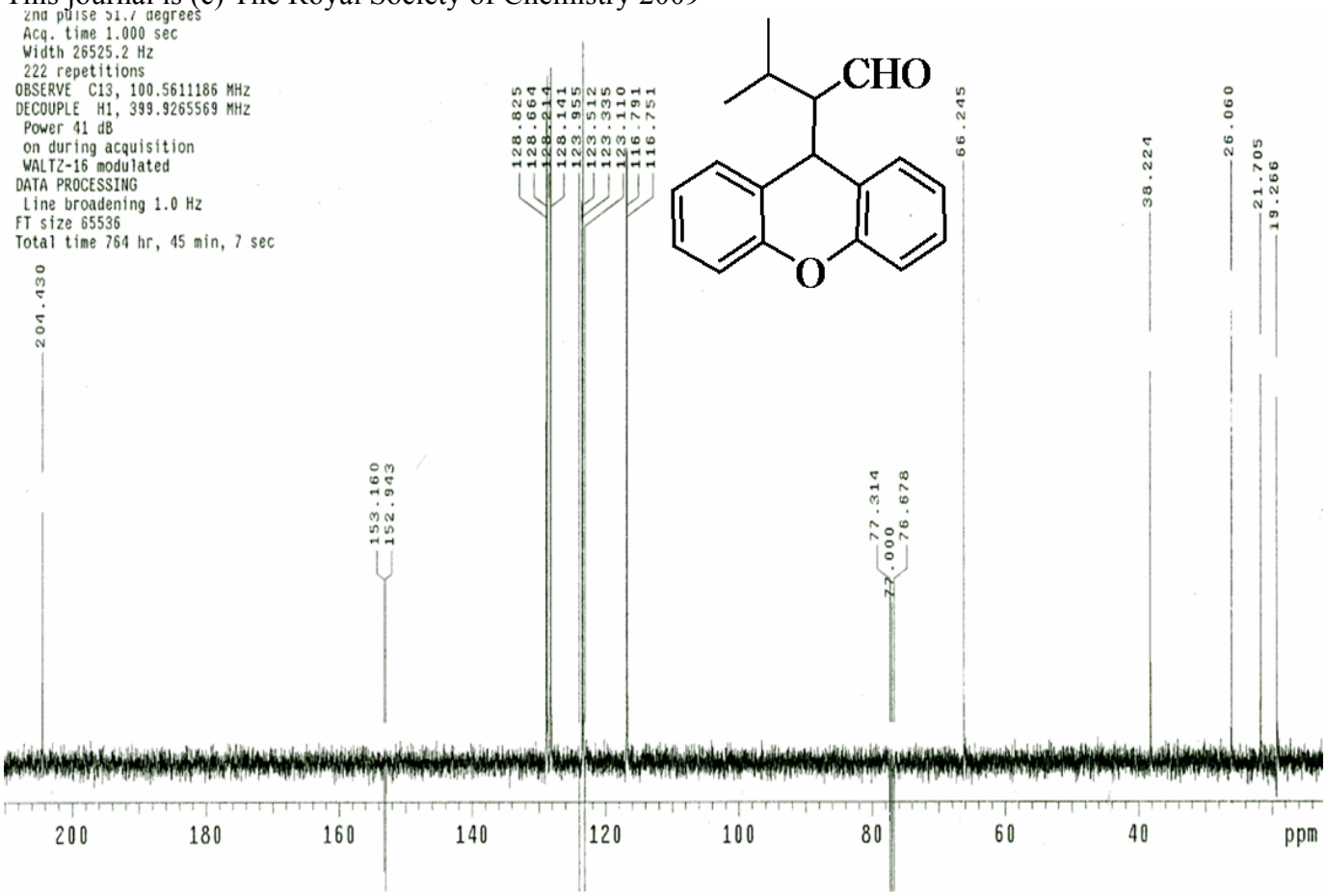
NMR Spectra

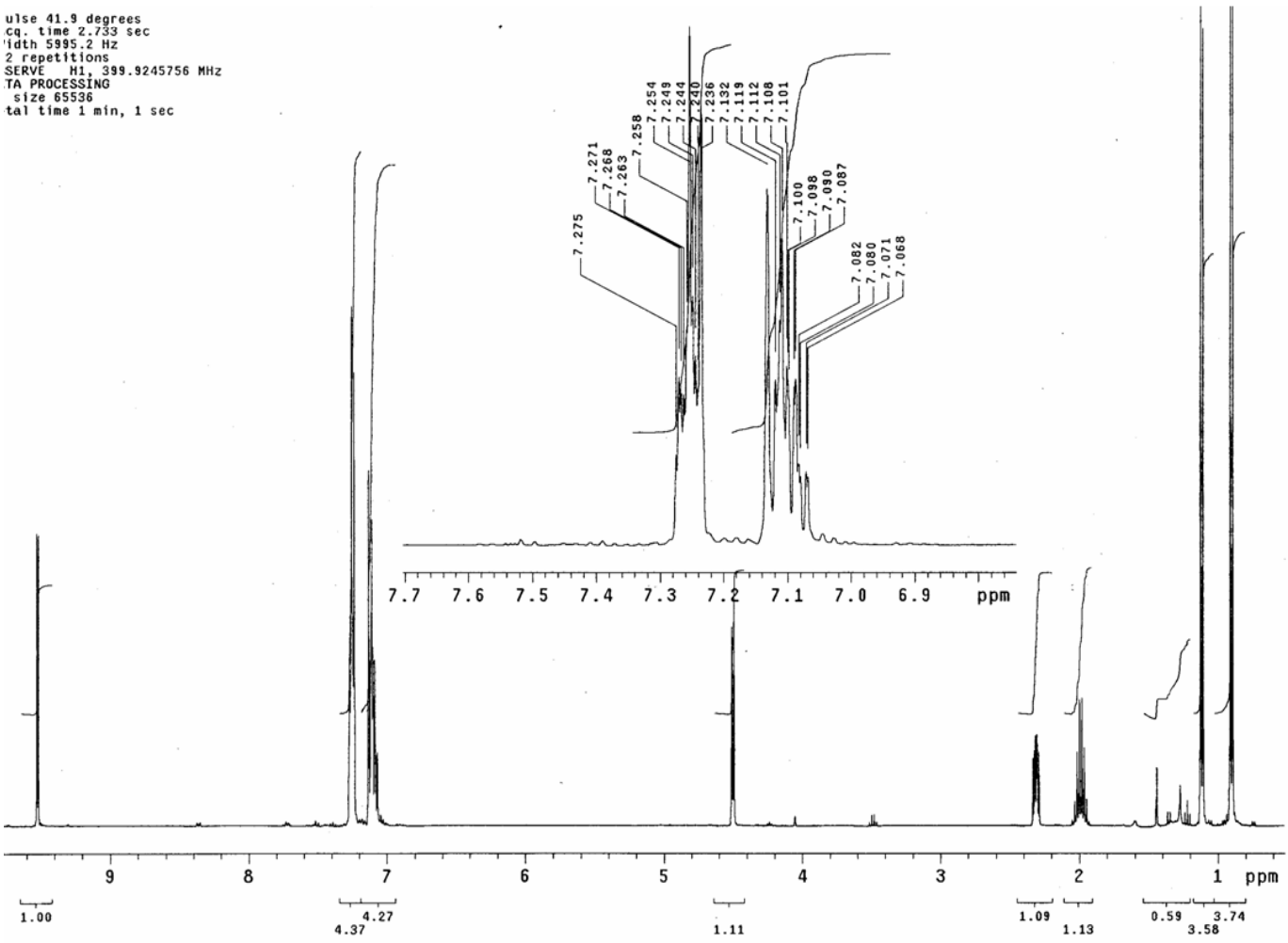


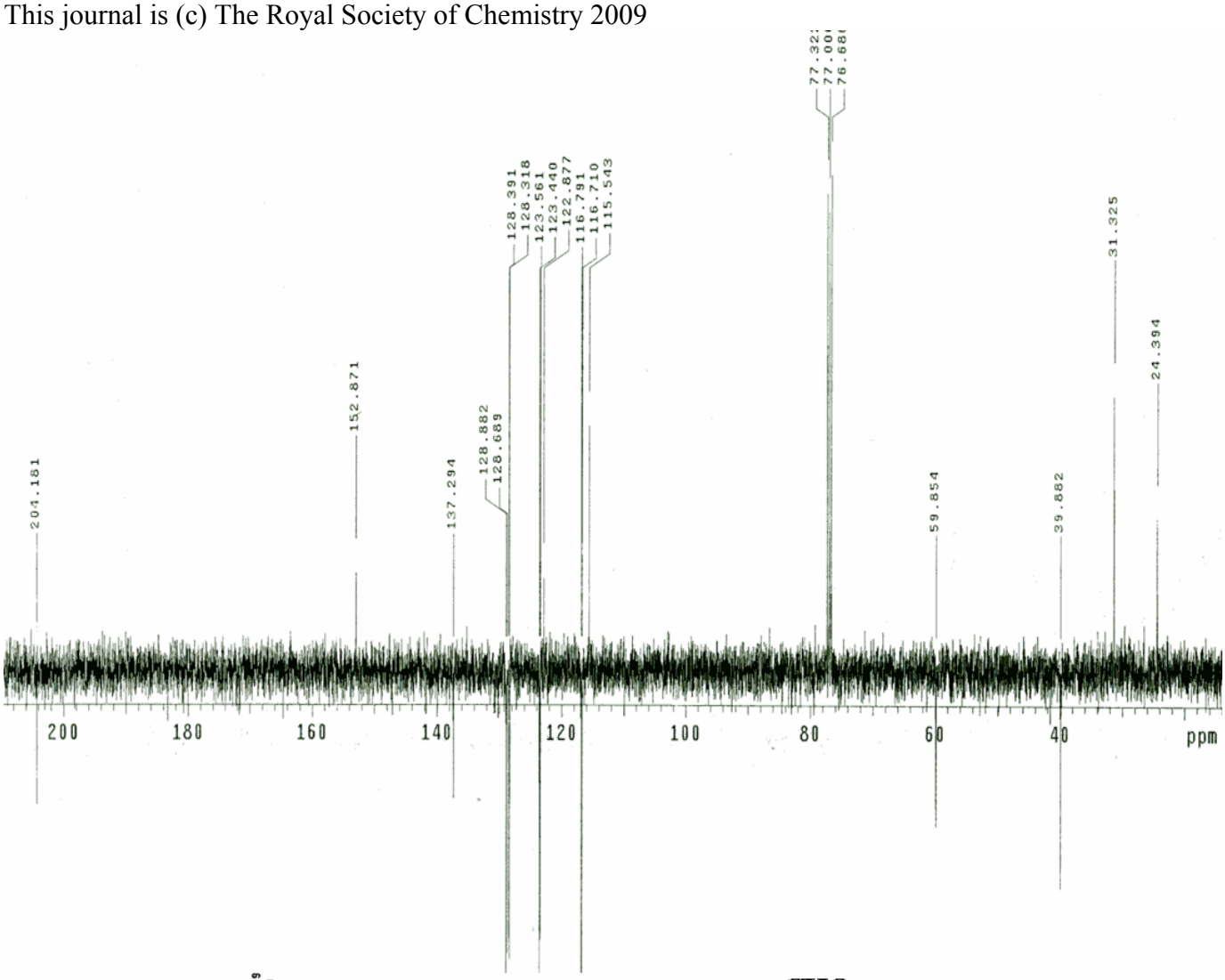


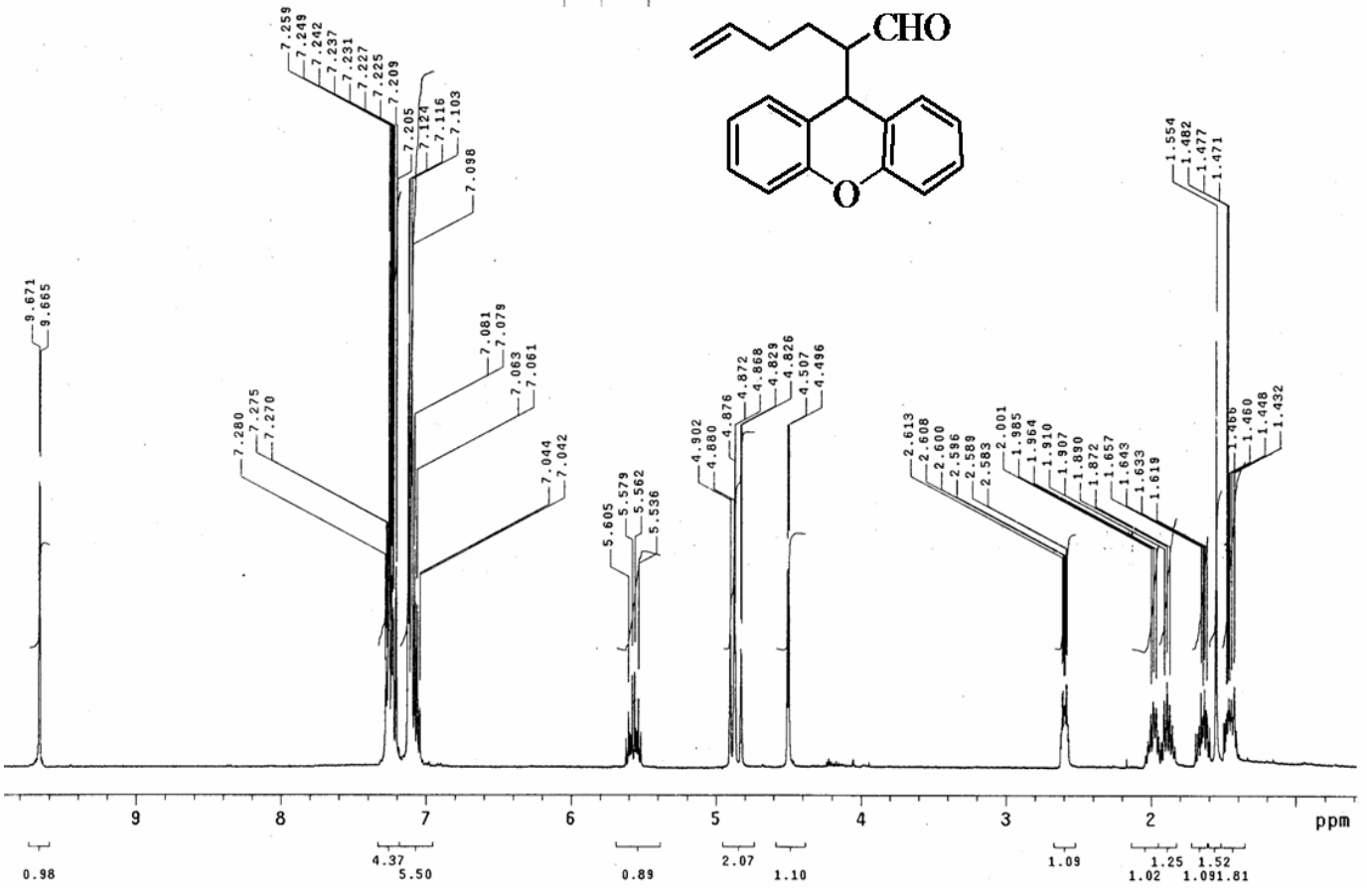


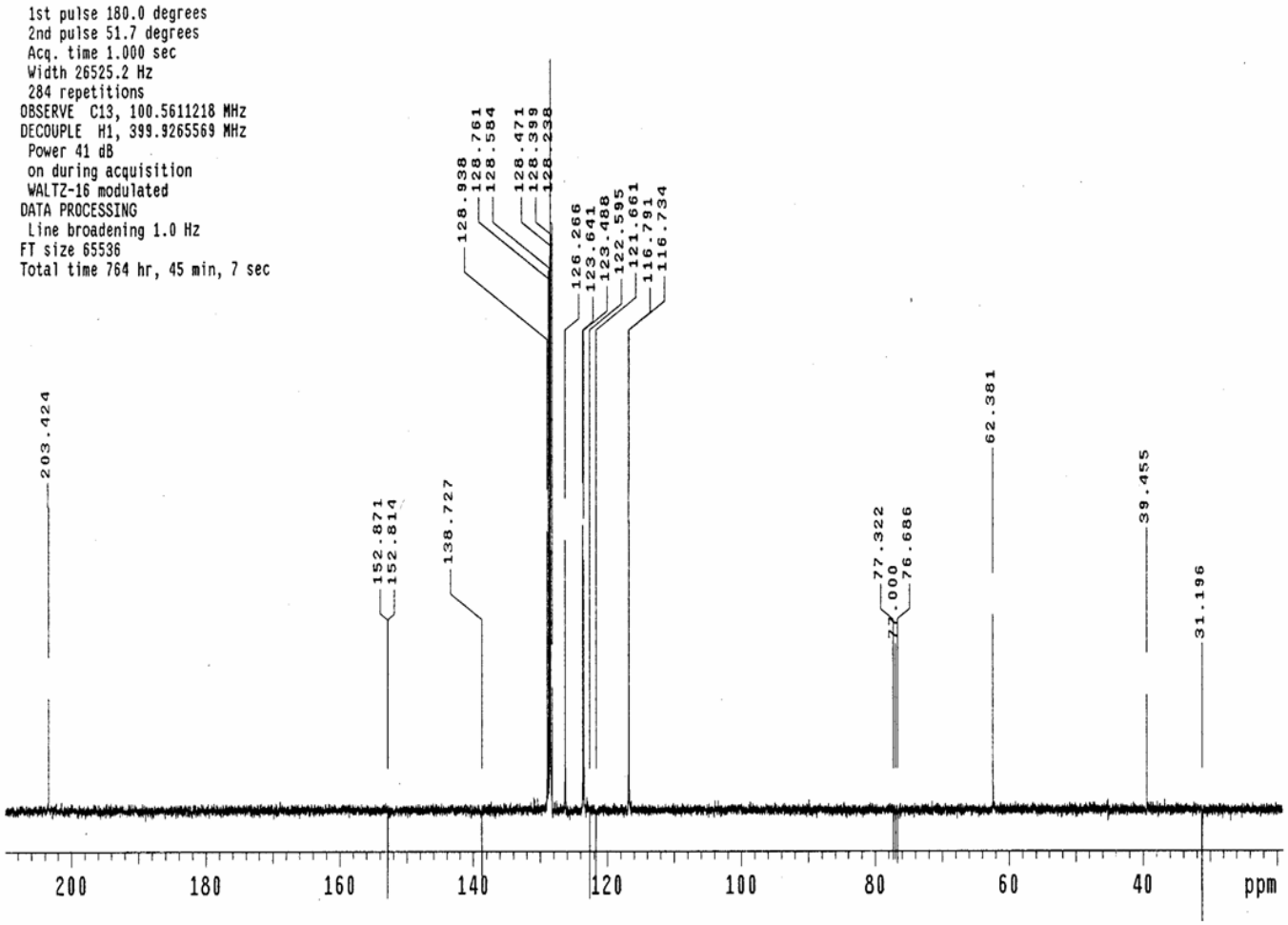


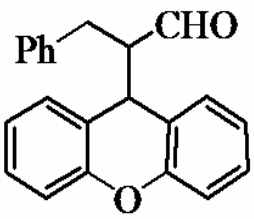


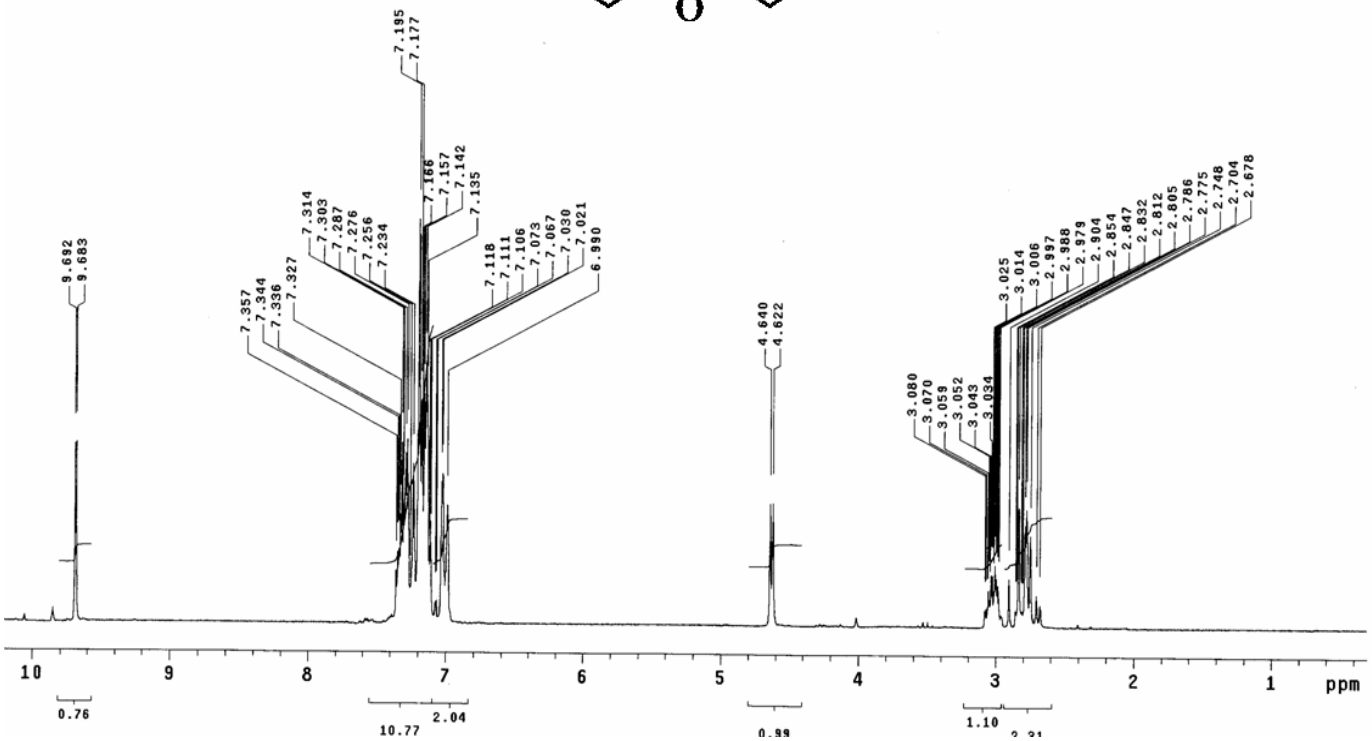


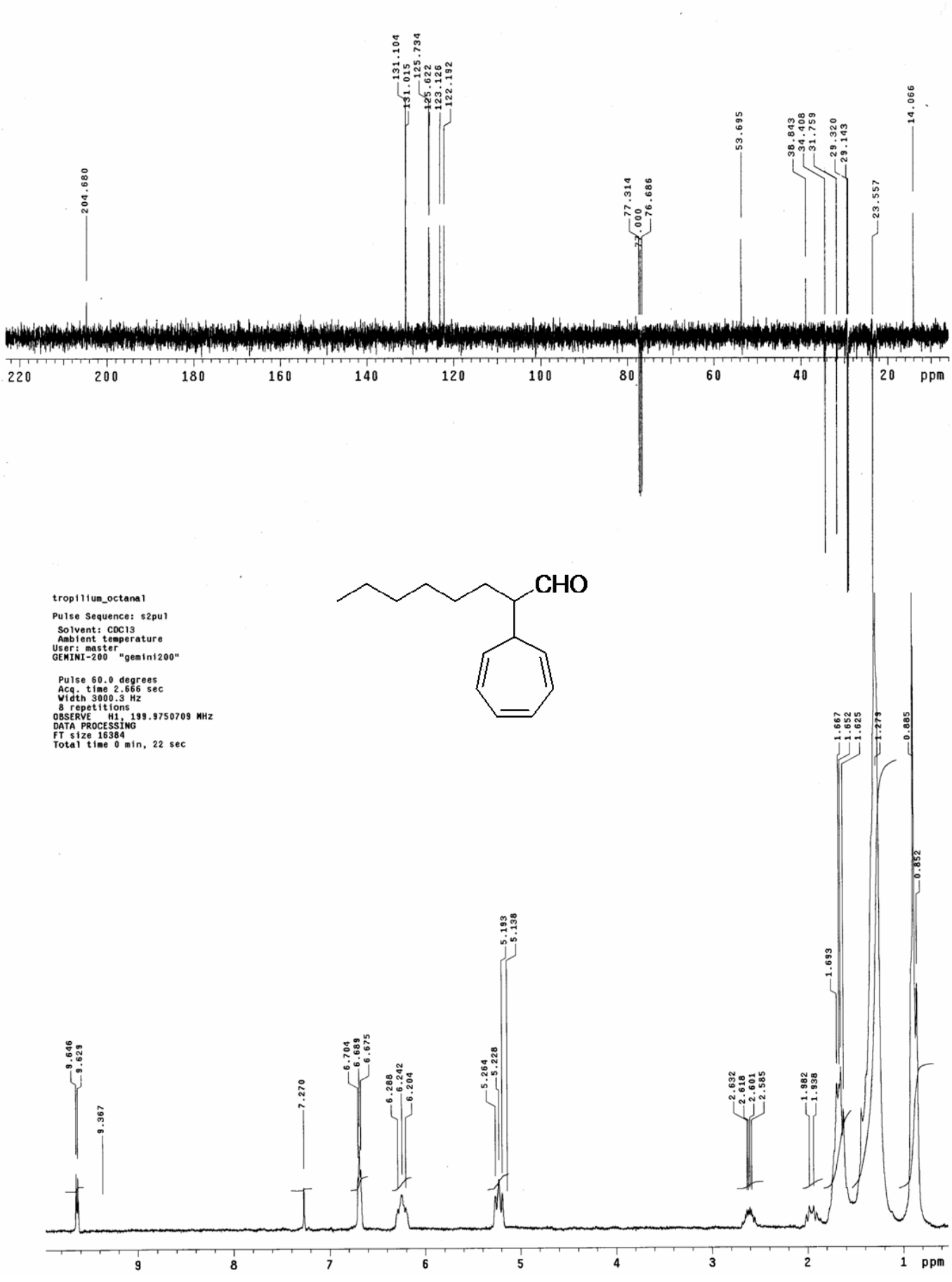


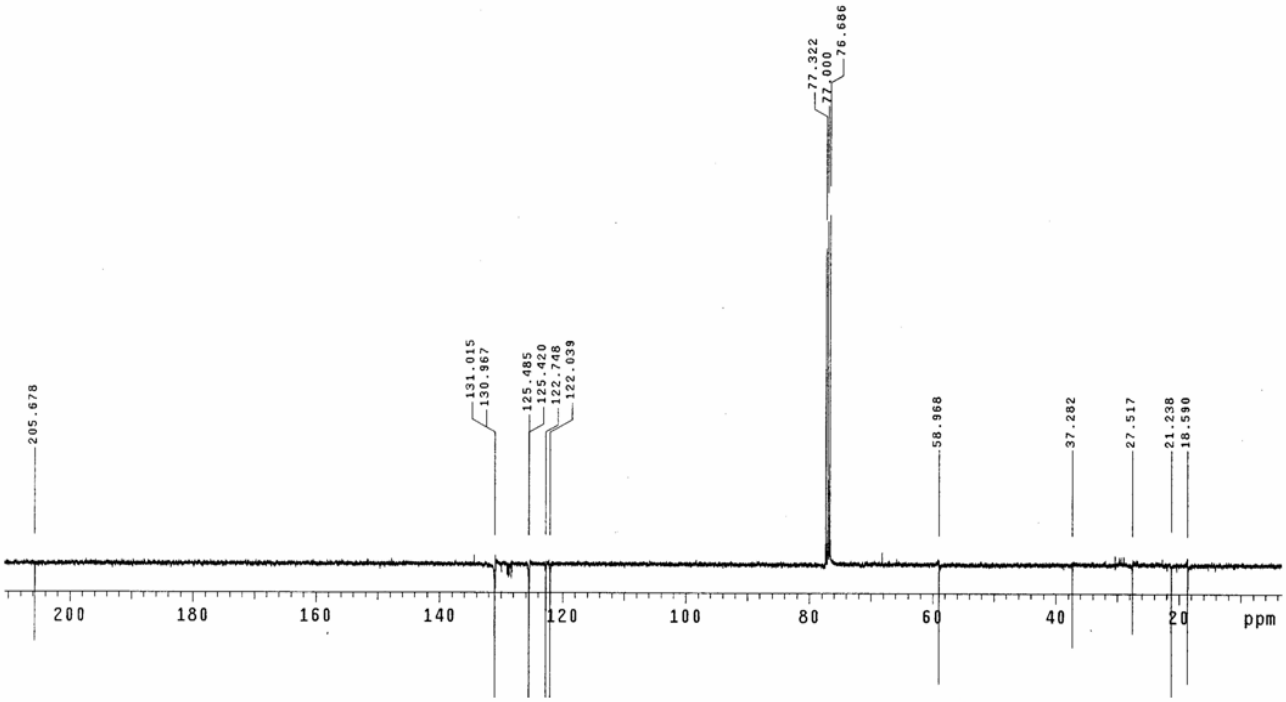



1st pulse 180.0 degrees
2nd pulse 51.7 degrees
Acq. time 1.000 sec
Width 26525.2 Hz
284 repetitions
OBSERVE C13, 100.5611218 MHz
DECOUPLE H1, 399.9265569 MHz
Power 41 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 764 hr, 45 min, 7 sec
203.424
152.871
152.814
138.727
128.938
128.761
128.584
128.471
128.399
128.238
126.266
123.641
123.488
122.595
121.661
116.791
116.734
77.322
77.000
76.686
62.381
39.455
31.196
200
180
160
140
120
100
80
60
40
ppm


Ph
CHO
O

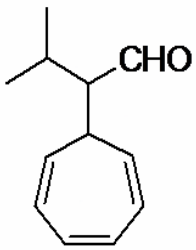

9.692
9.683
7.357
7.344
7.336
7.327
7.314
7.303
7.287
7.276
7.256
7.234
7.195
7.177
7.166
7.157
7.142
7.135
7.118
7.111
7.106
7.073
7.067
7.030
7.021
6.990
4.640
4.622
3.080
3.070
3.059
3.052
3.043
3.034
3.025
3.014
3.006
2.997
2.988
2.979
2.904
2.854
2.847
2.832
2.812
2.805
2.786
2.775
2.748
2.704
2.678
10
9
8
7
6
5
4
3
2
1
ppm
0.76
10.77
2.04
0.99
1.10

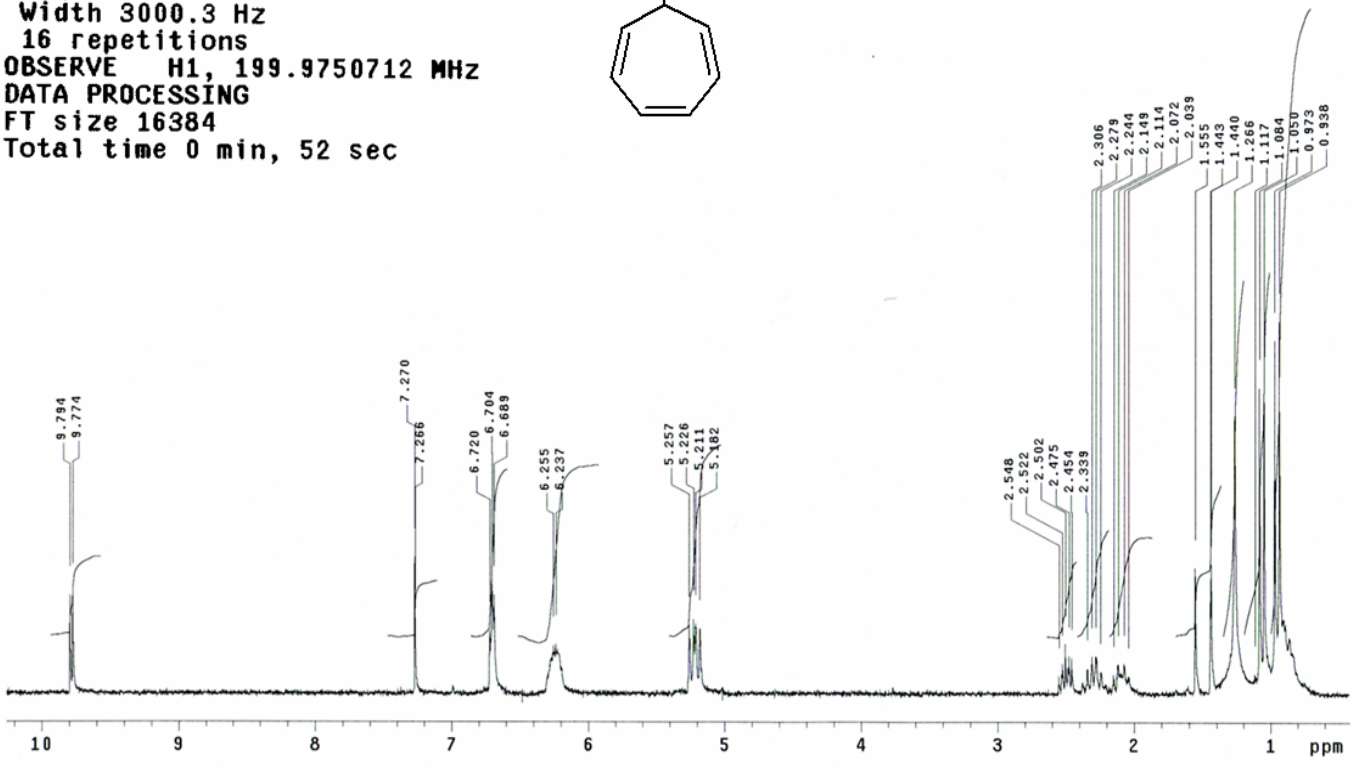


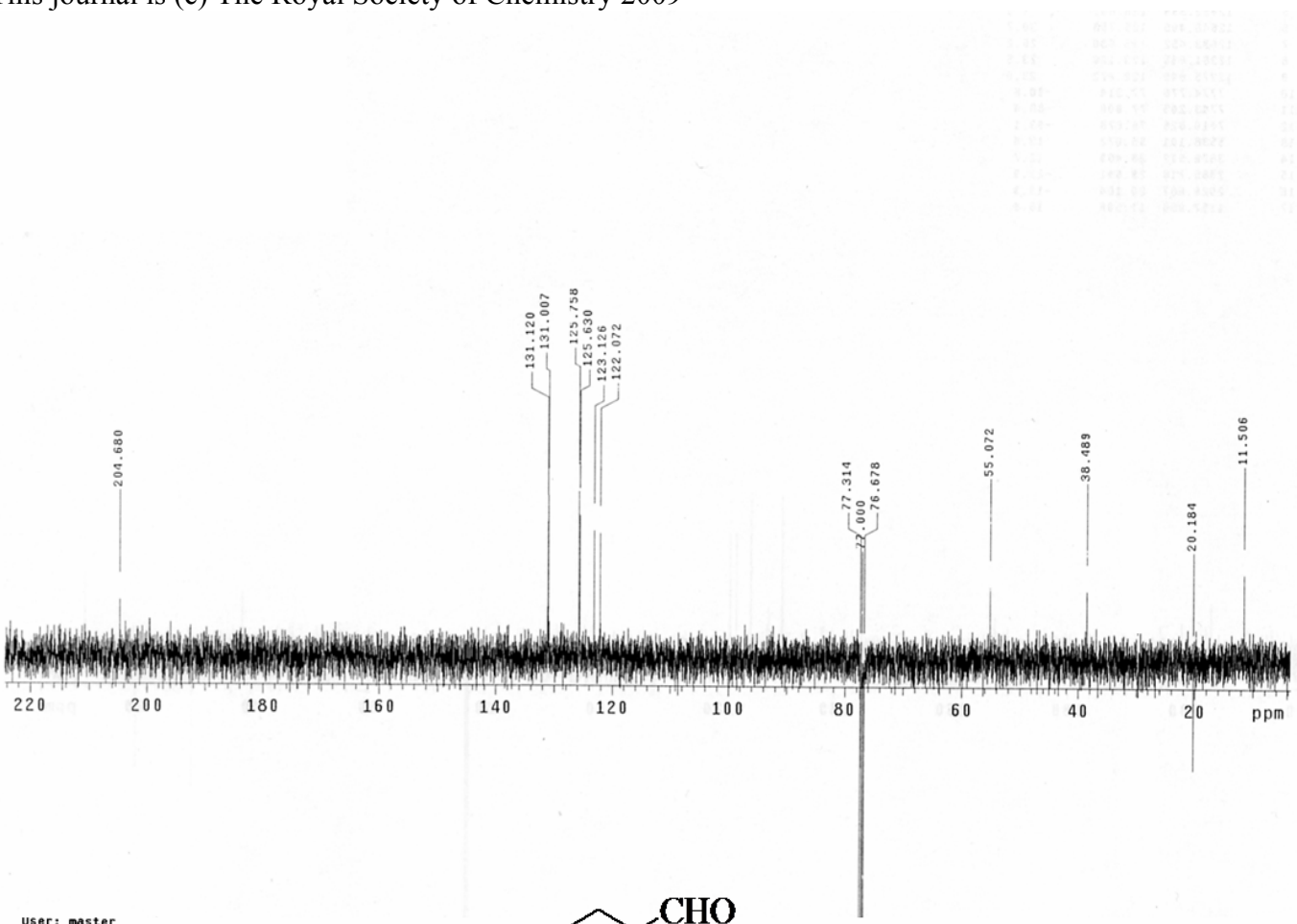


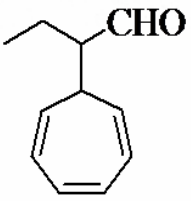
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
User: master
GEMINI-200 "gemini200"

Pulse 60.0 degrees
Acq. time 2.666 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9750712 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 52 sec



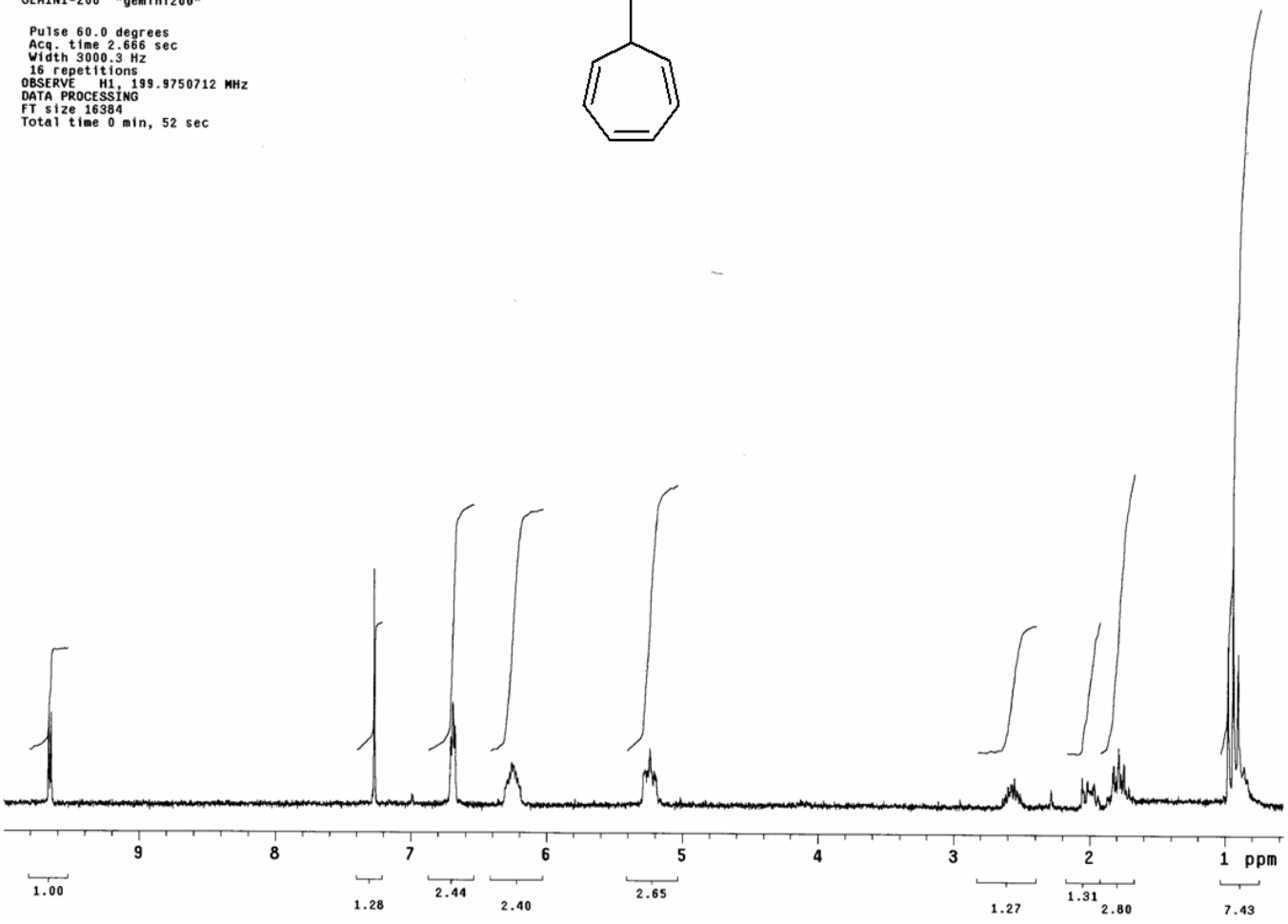


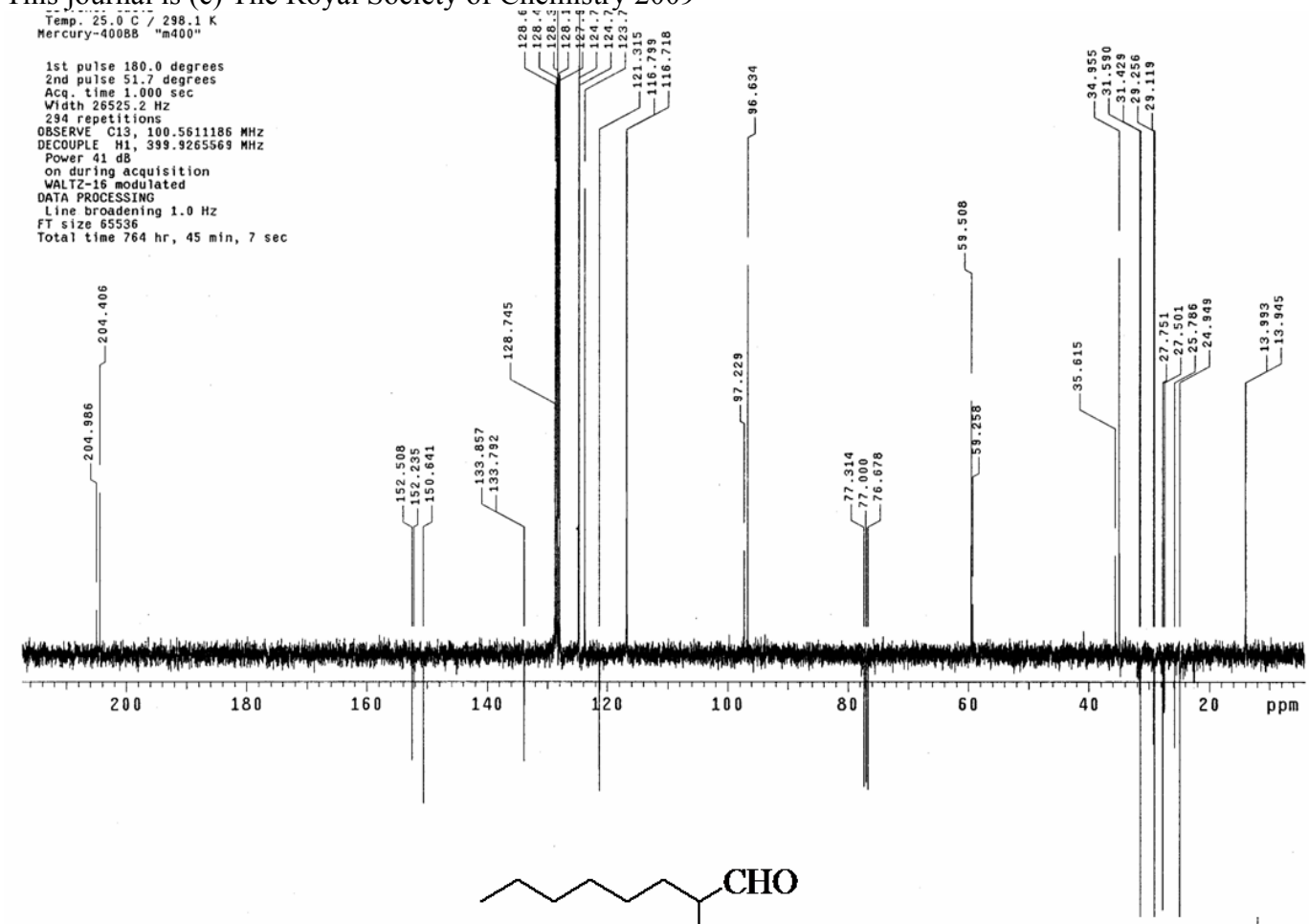


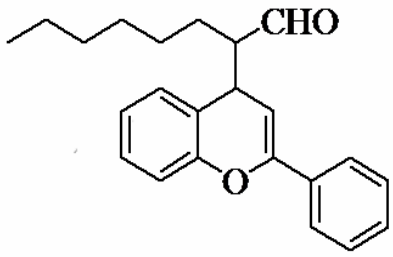


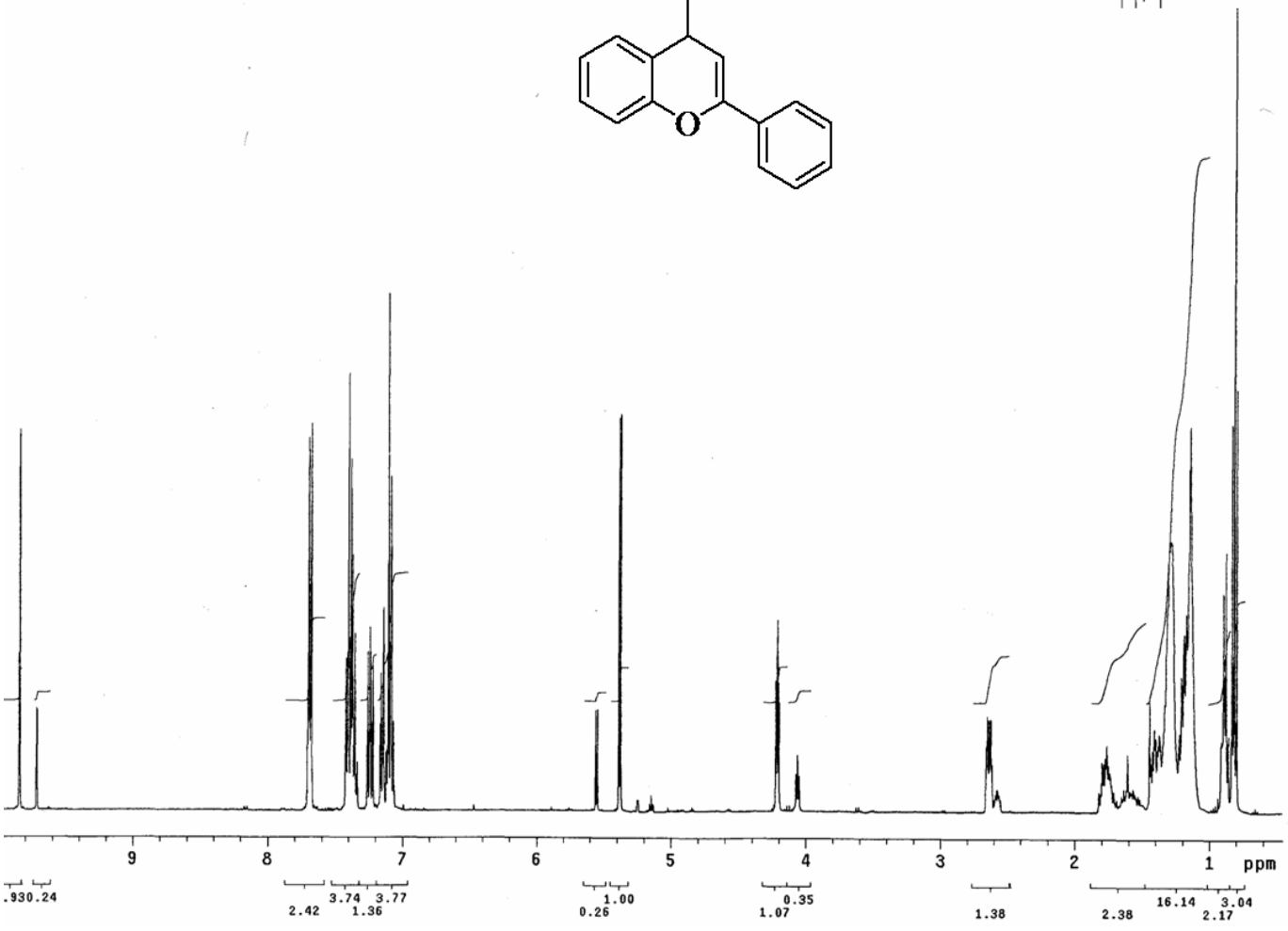
User: master
GEMINI-200 "gemini200"

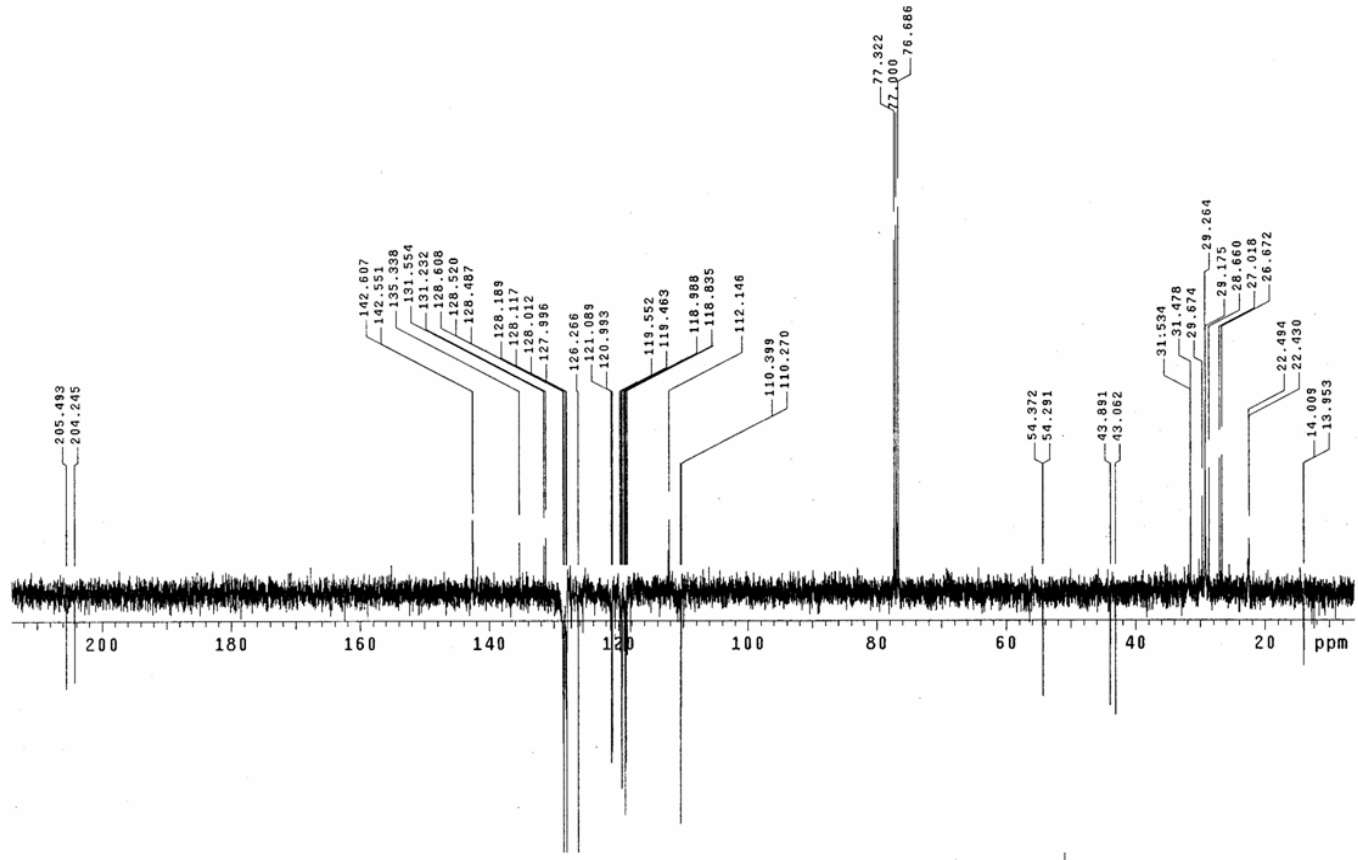
Pulse 60.0 degrees
Acq. time 2.666 sec
Width 3000.3 Hz
16 repetitions
OBSERVE H1, 199.9750712 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 52 sec

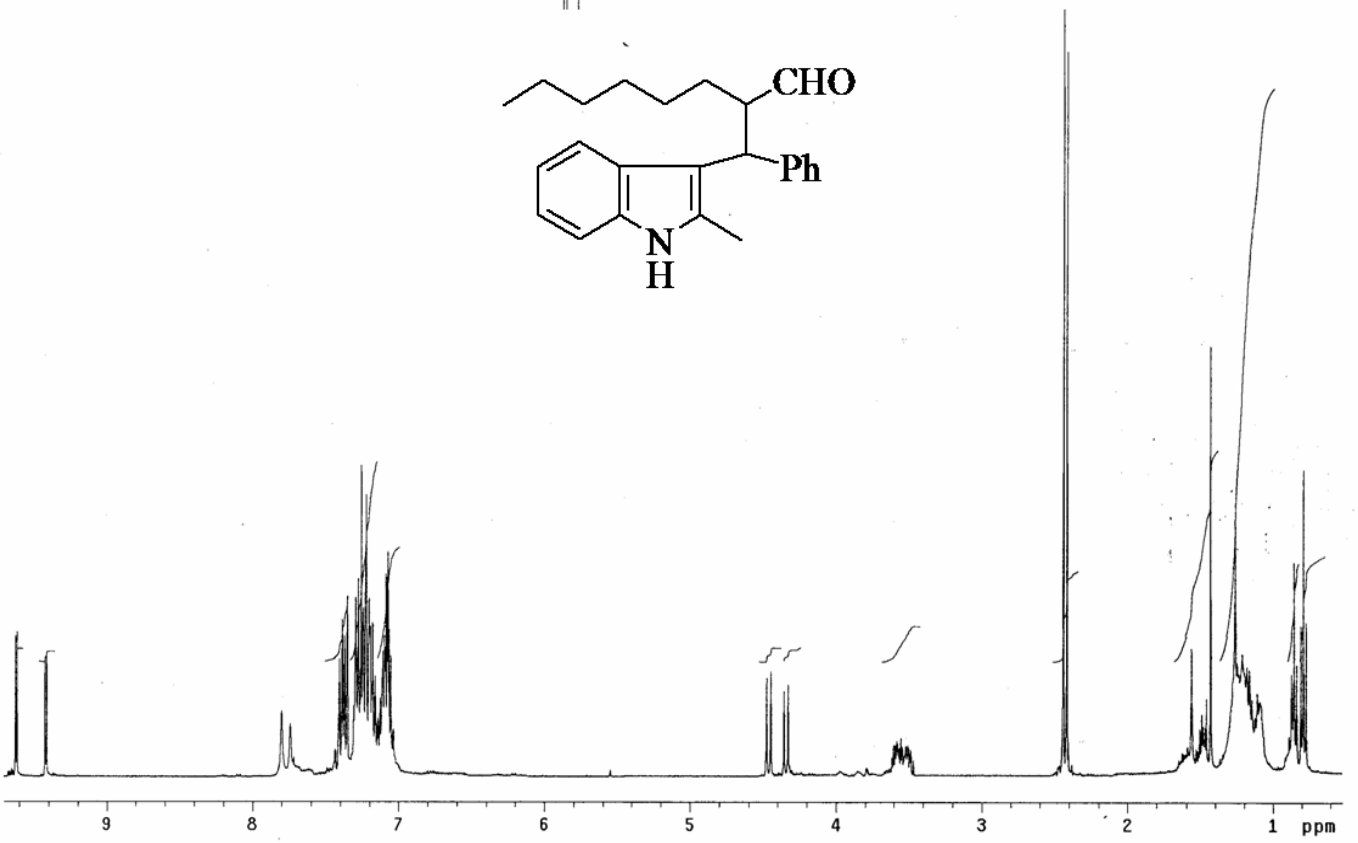


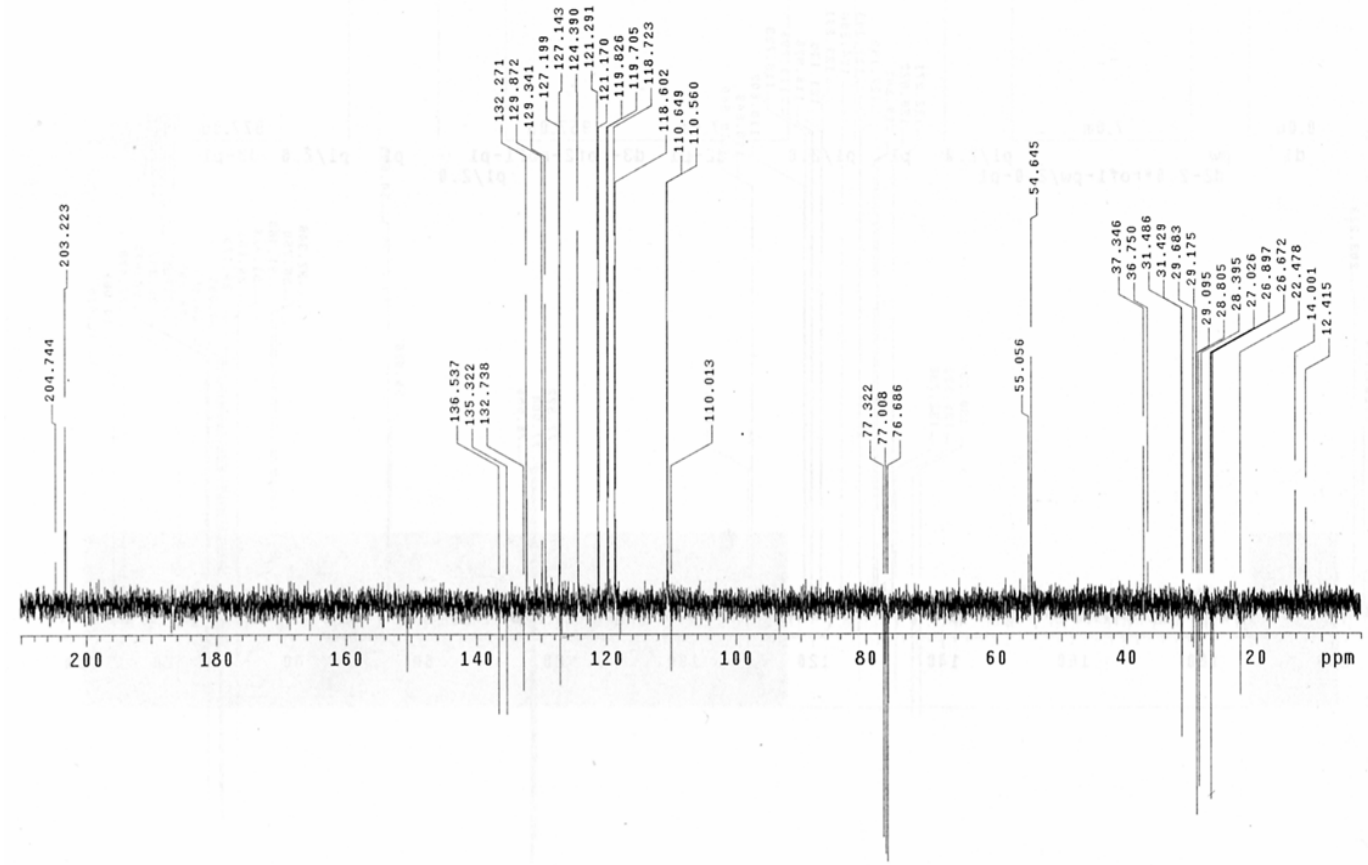


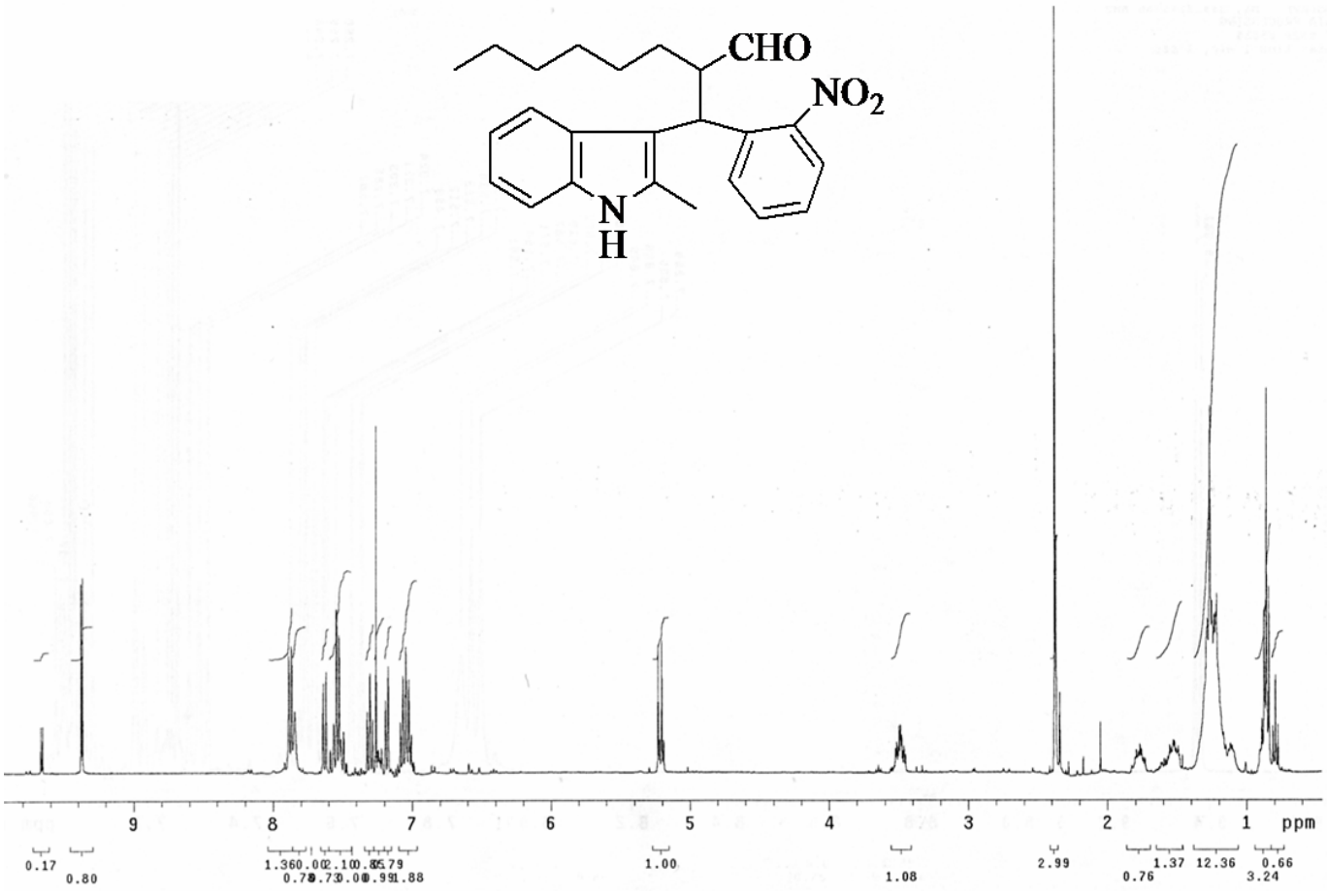


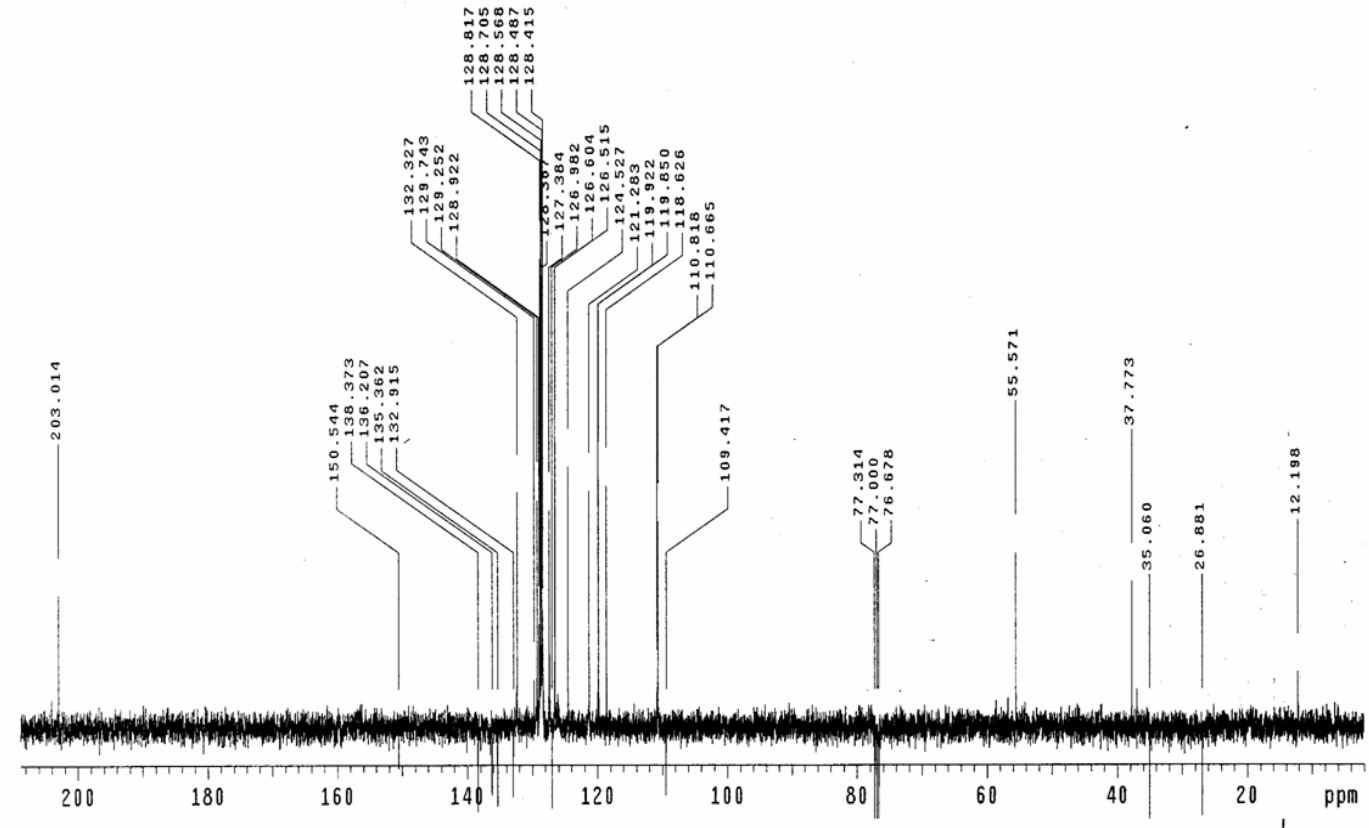


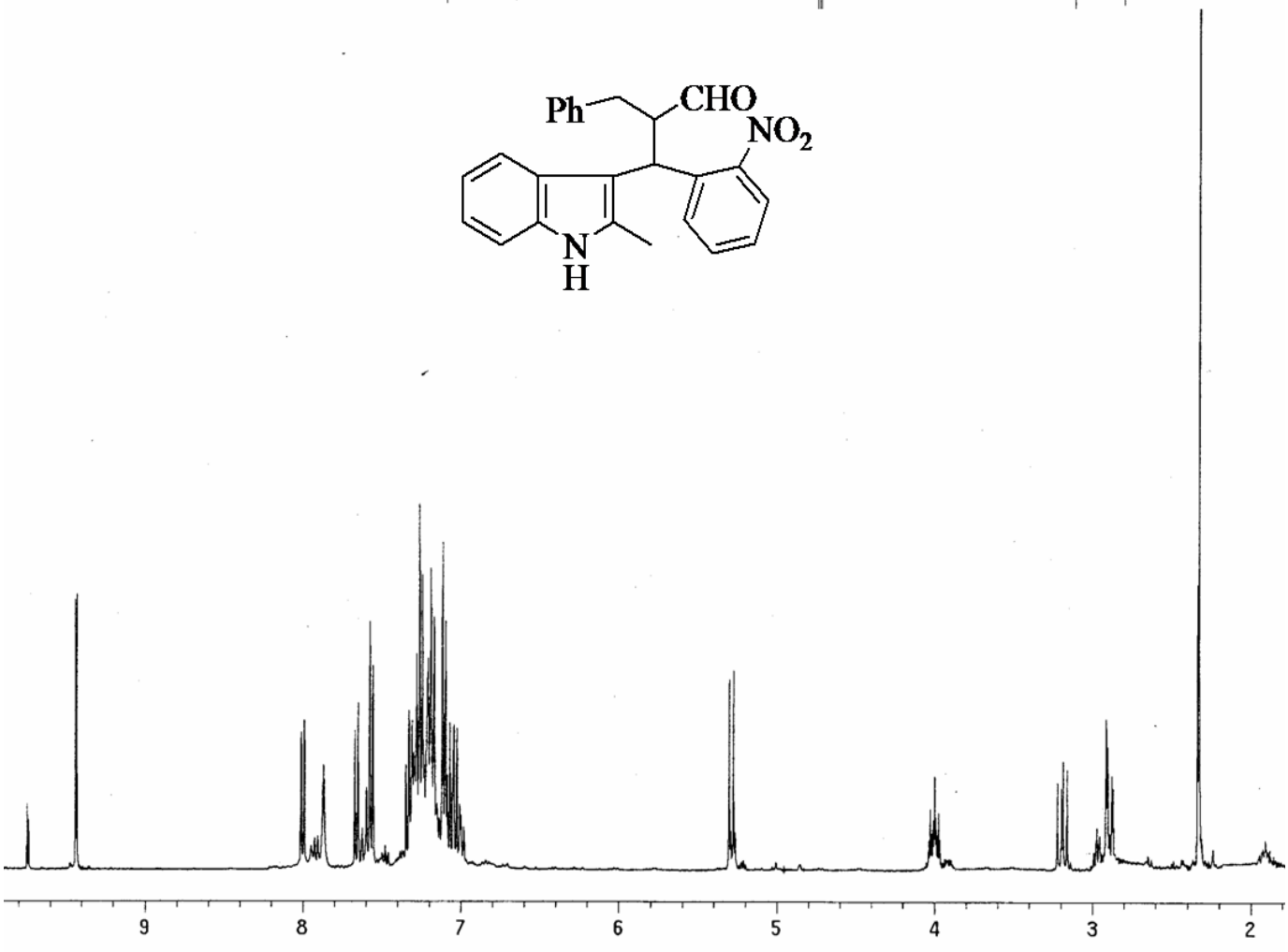


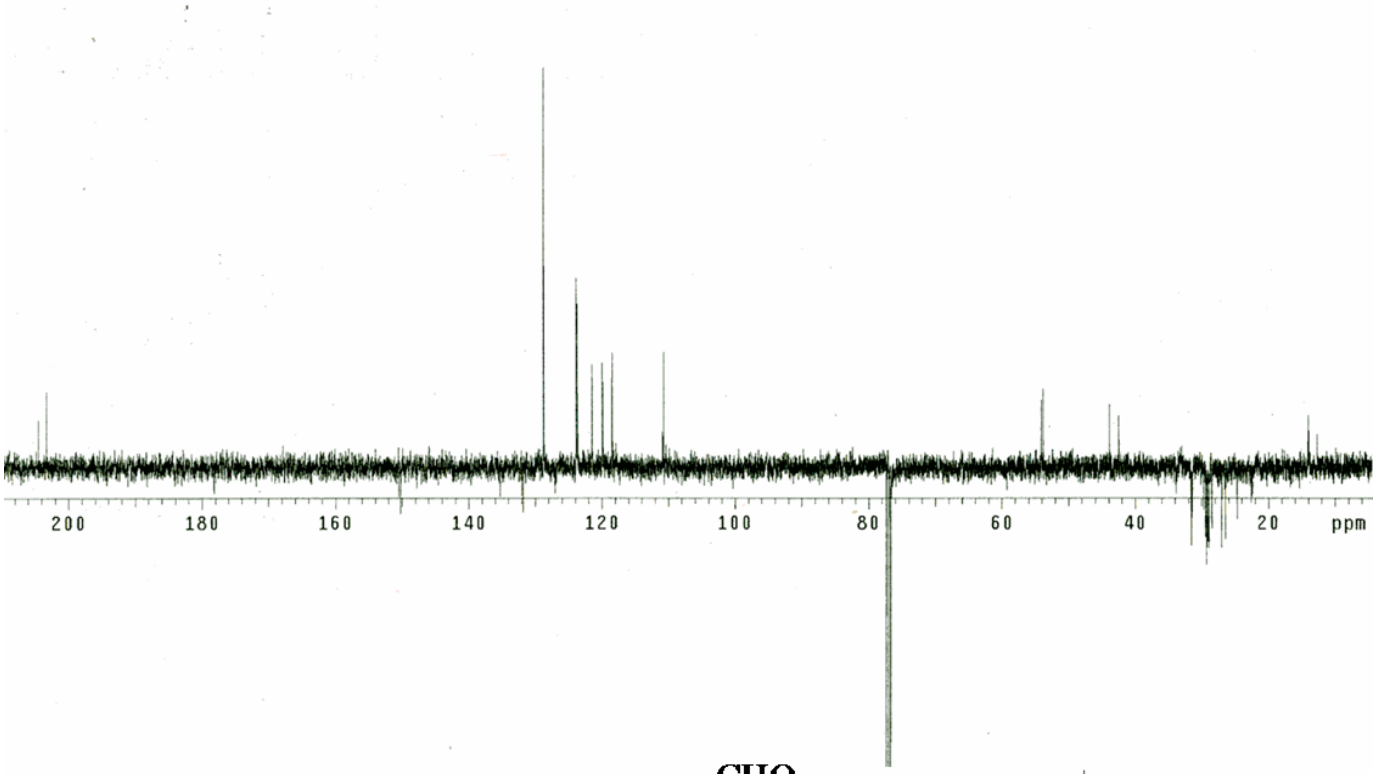


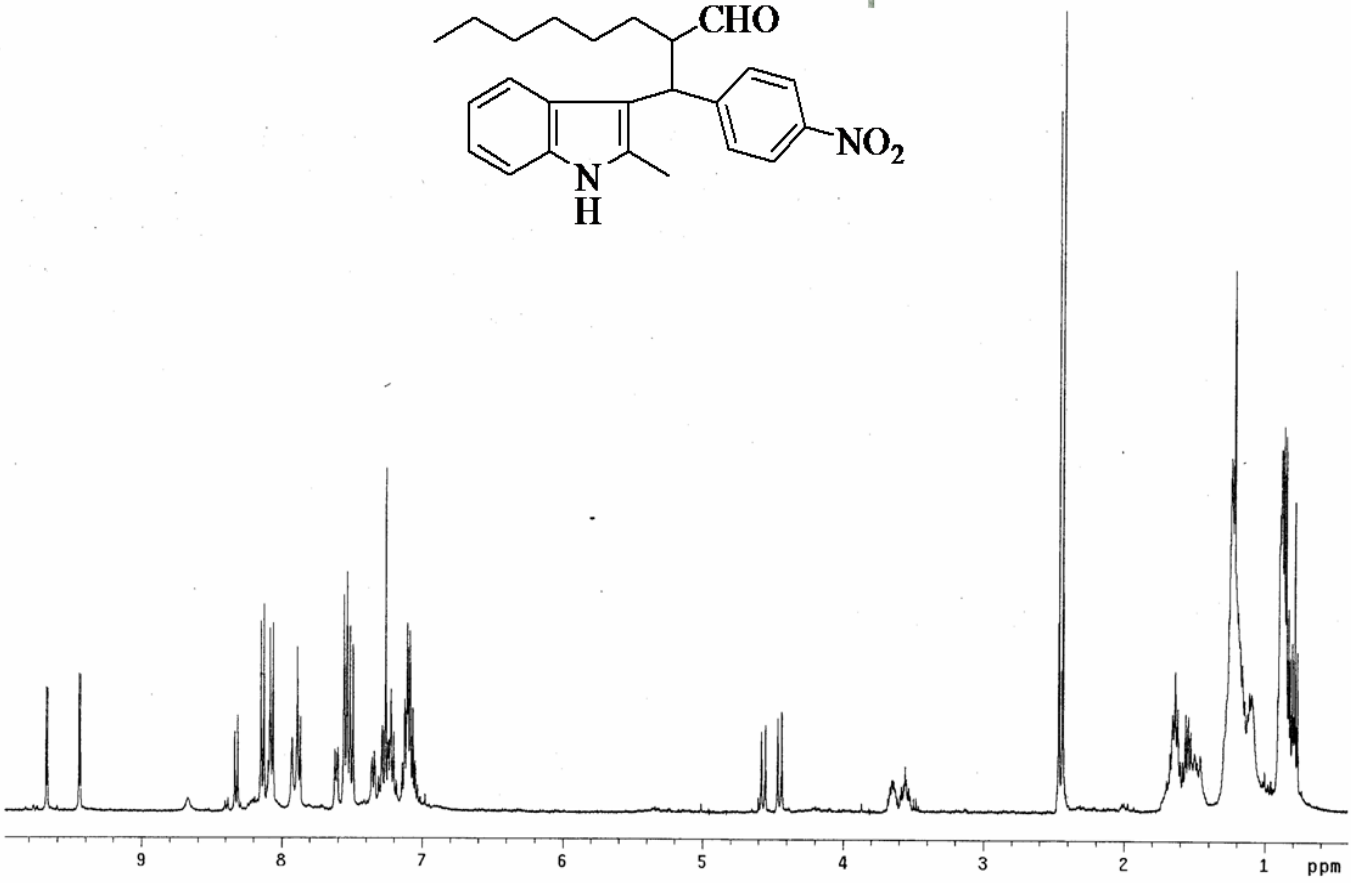


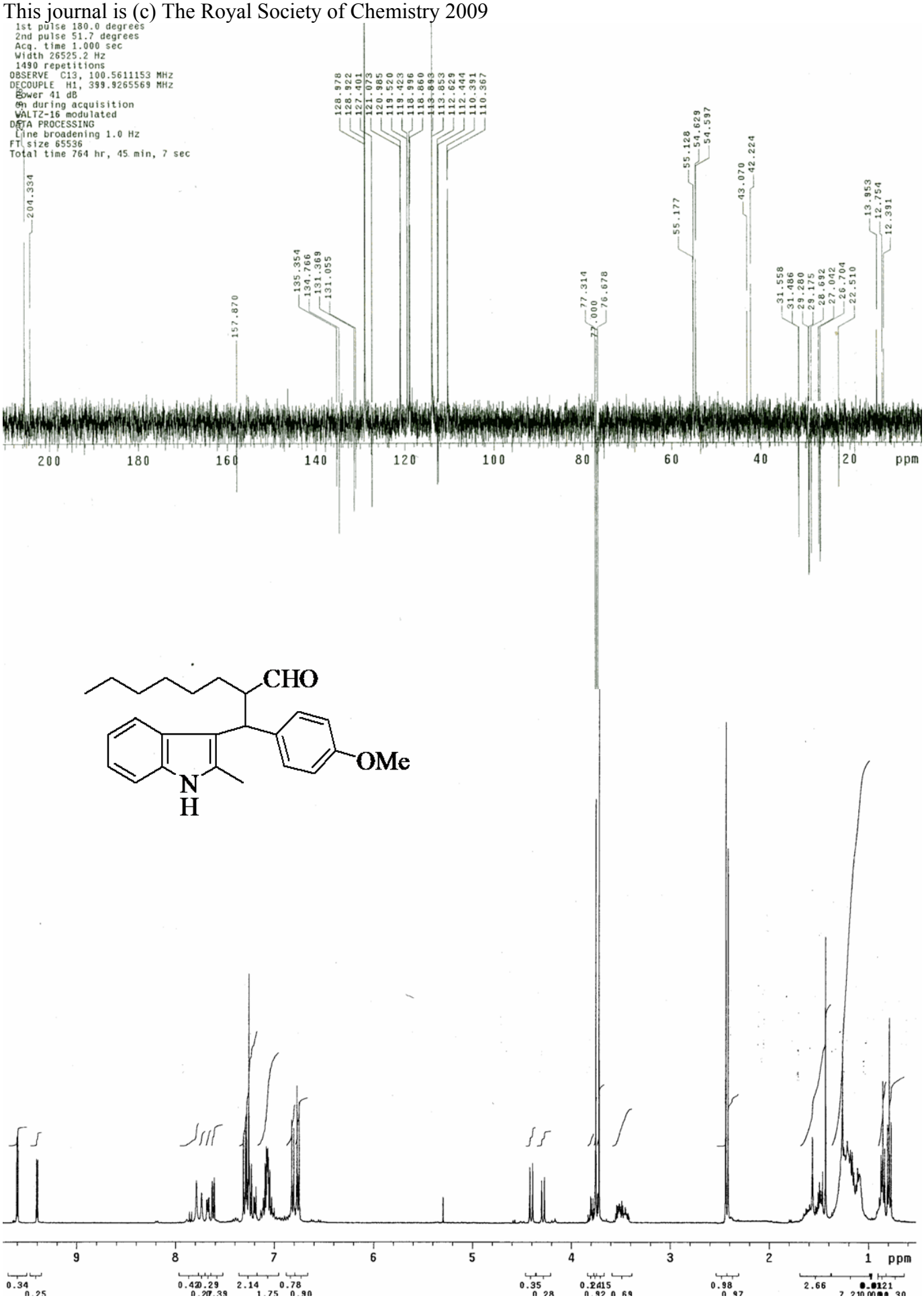


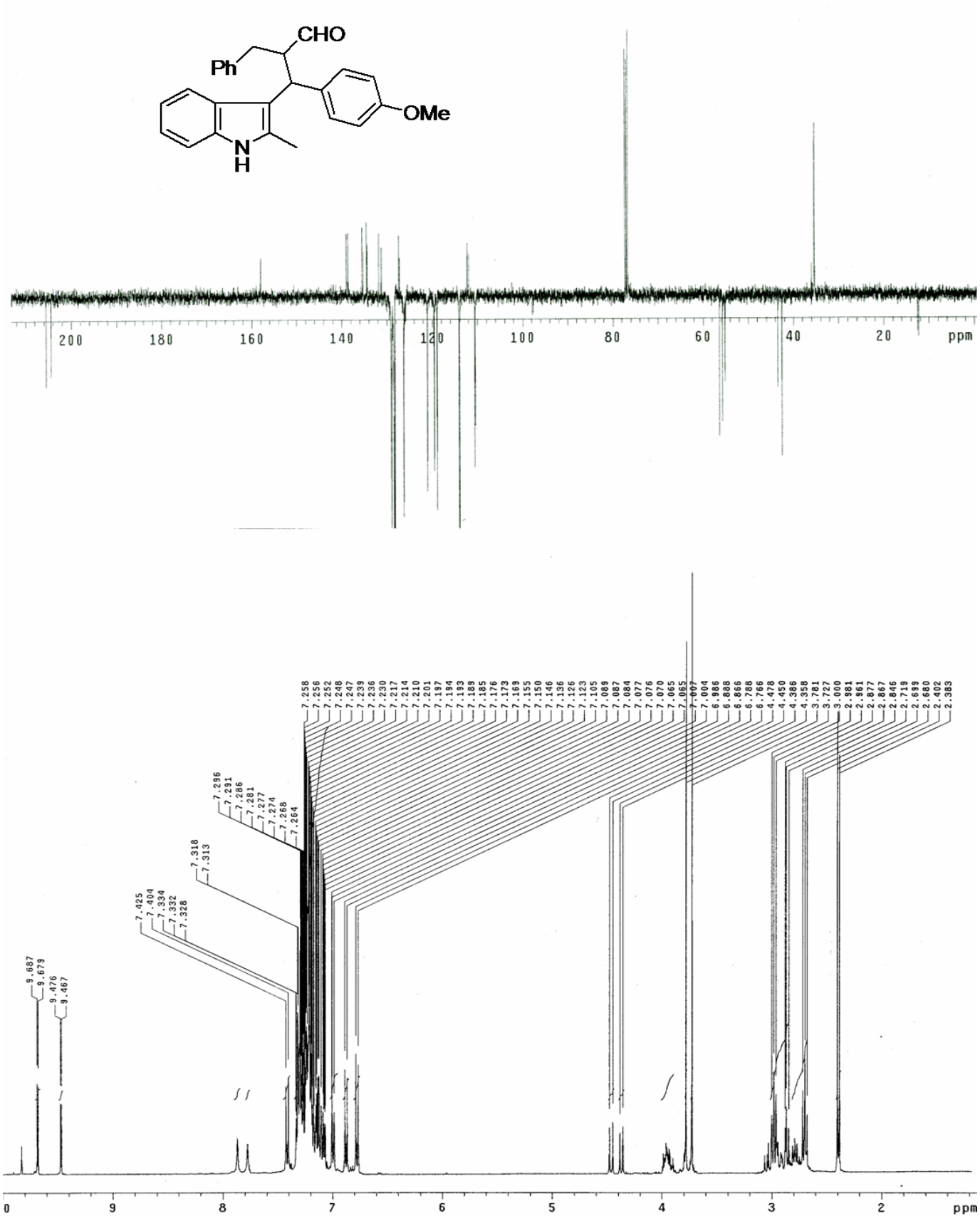


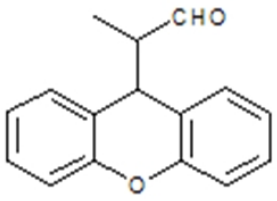






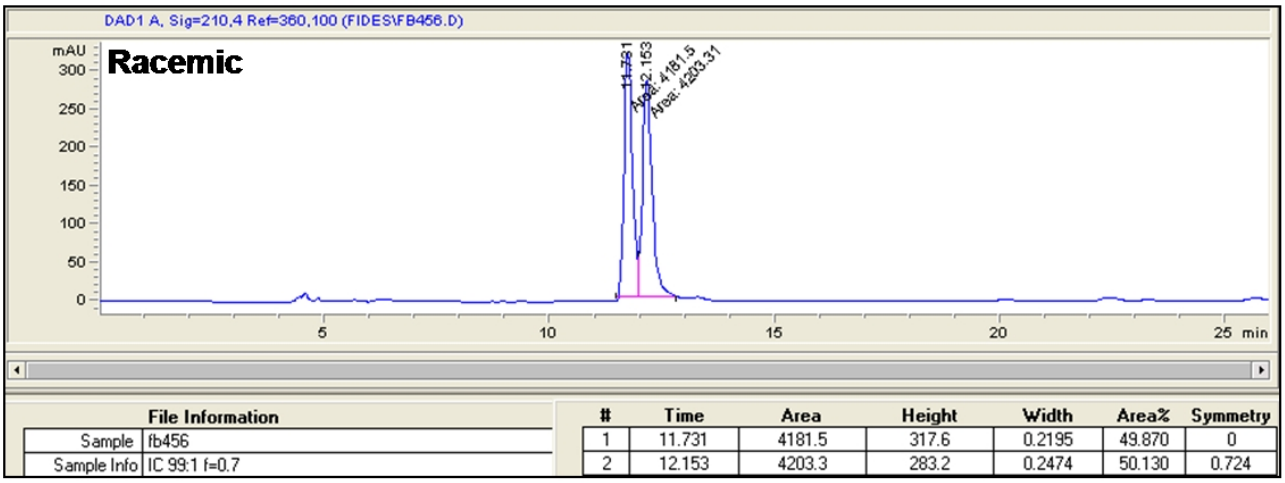






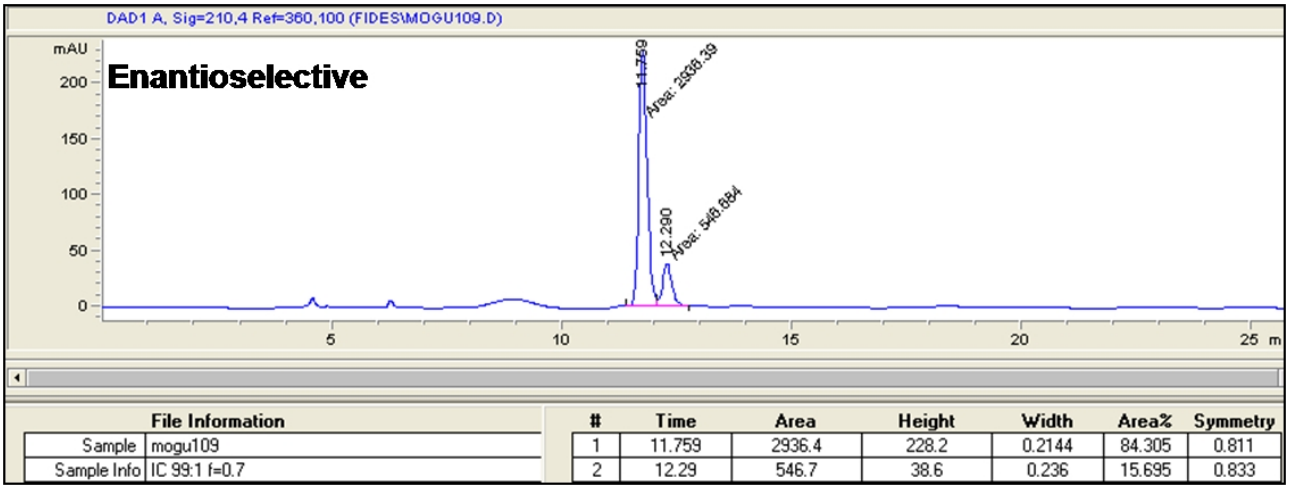
1b

Chiracel IC: 99:1 (hexane: *i*-PrOH), flow 0.7mL/min. tm:12.2 min; TM: 11.7 min.



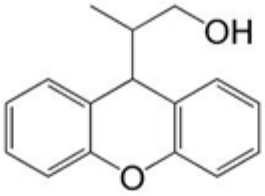
File Information	
Sample	fb456
Sample Info	IC 99:1 f=0.7

#	Time	Area	Height	Width	Area%	Symmetry
1	11.731	4181.5	317.6	0.2195	49.870	0
2	12.153	4203.3	283.2	0.2474	50.130	0.724



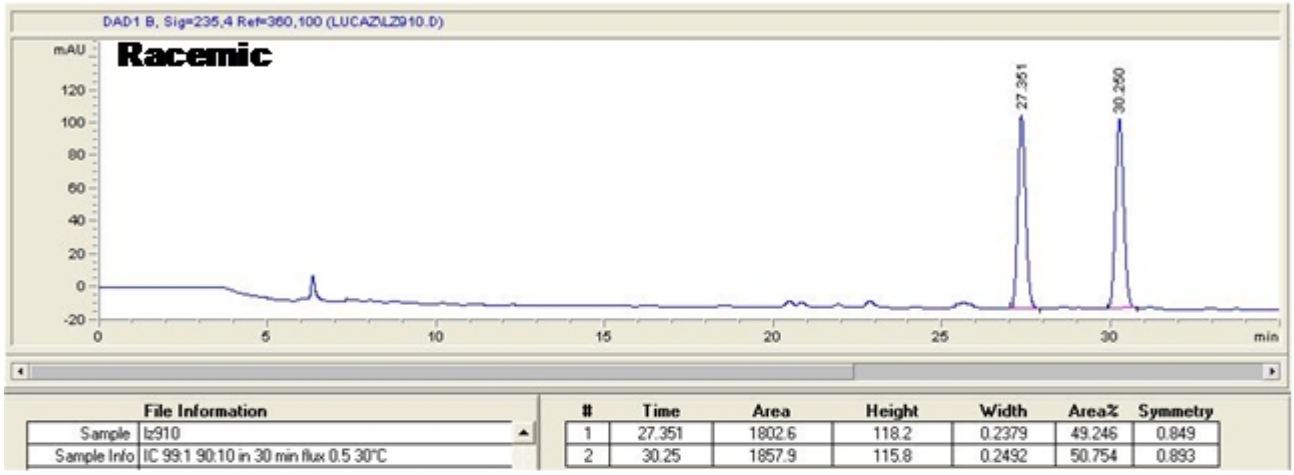
File Information	
Sample	mogu109
Sample Info	IC 99:1 f=0.7

#	Time	Area	Height	Width	Area%	Symmetry
1	11.759	2936.4	228.2	0.2144	84.305	0.811
2	12.29	546.7	38.6	0.236	15.695	0.833



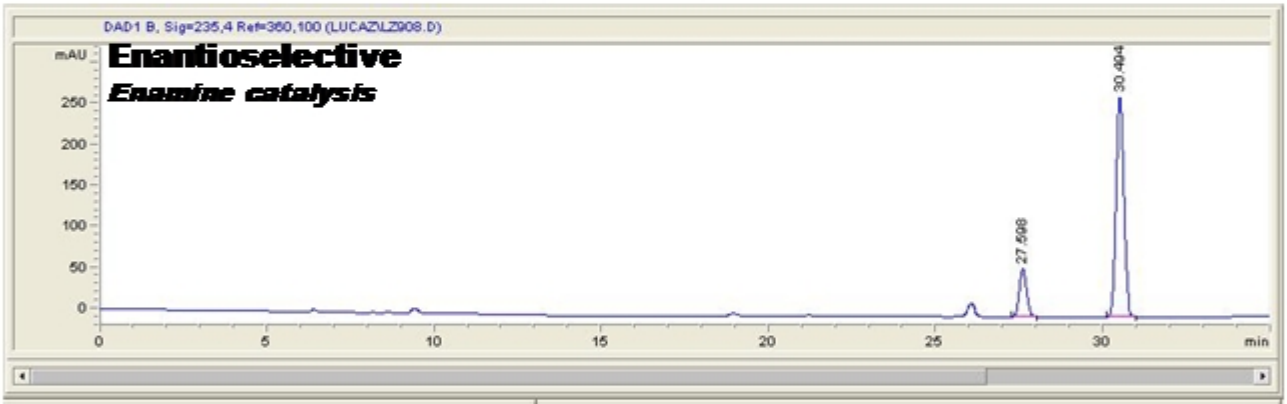
11

Chiracel IC: 99:1 (hexane: *i*-PrOH), flow 0.5mL/min. t: 27.5 min; t: 30.5 min.



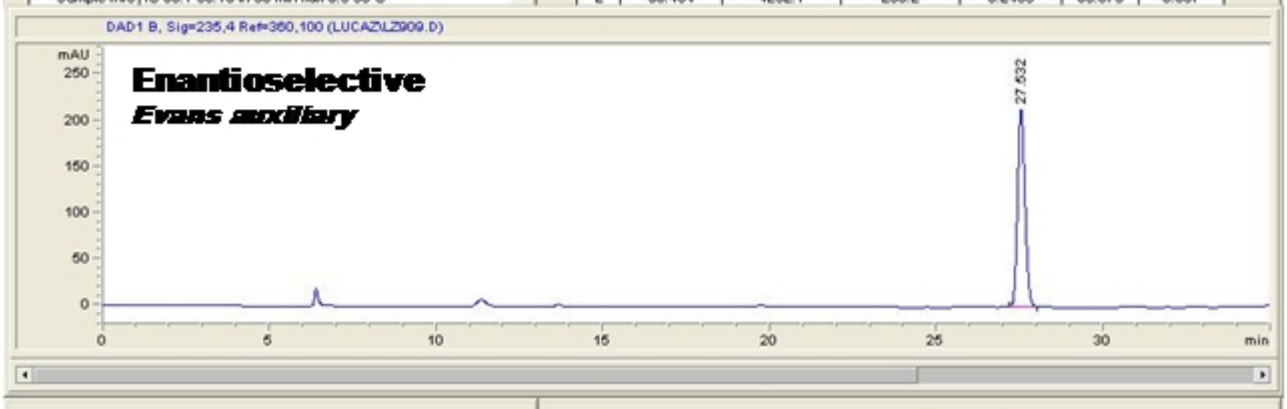
File Information	
Sample	lz910
Sample Info	IC 99:1 90:10 in 30 min flux 0.5 30°C

#	Time	Area	Height	Width	Area%	Symmetry
1	27.351	1802.6	118.2	0.2379	49.246	0.849
2	30.25	1857.9	115.8	0.2492	50.754	0.893



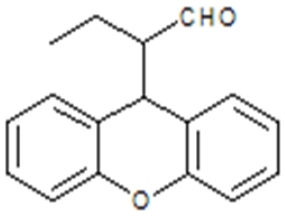
File Information	
Sample	lz908
Sample Info	IC 99:1 90:10 in 30 min flux 0.5 30°C

#	Time	Area	Height	Width	Area%	Symmetry
1	27.598	866.4	59.1	0.2271	16.927	0.877
2	30.494	4252.1	268.2	0.2469	83.073	0.867



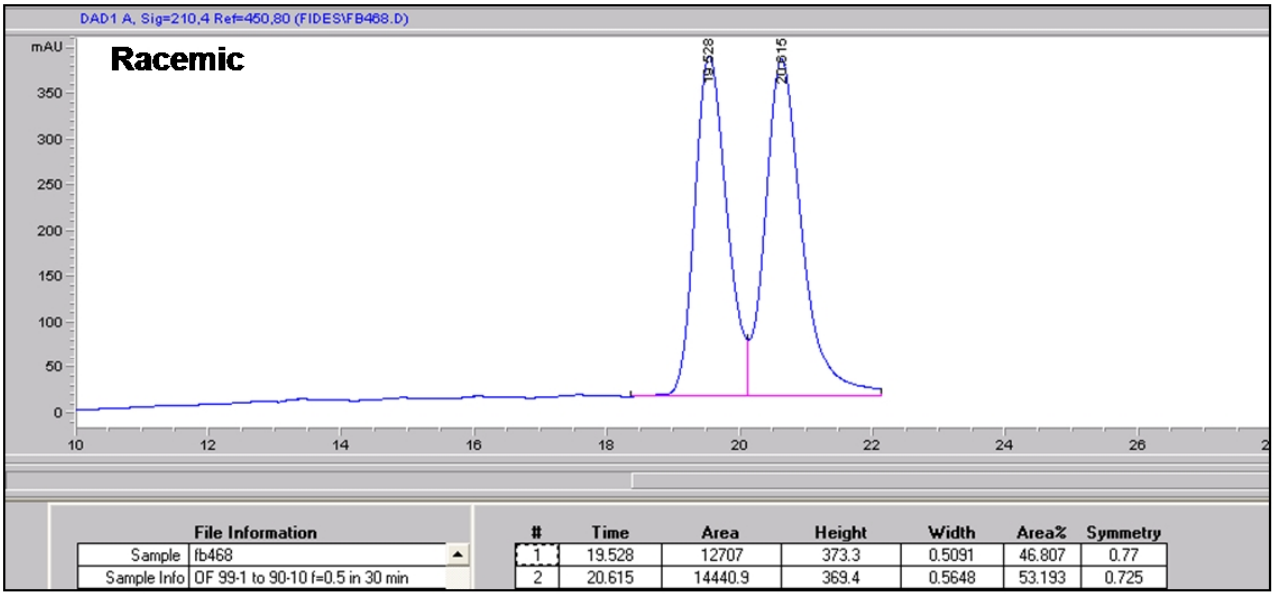
File Information	
Sample	lz909
Sample Info	IC 99:1 90:10 in 30 min flux 0.5 30°C

#	Time	Area	Height	Width	Area%	Symmetry
1	27.532	3177.1	214.1	0.2292	100.000	0.836



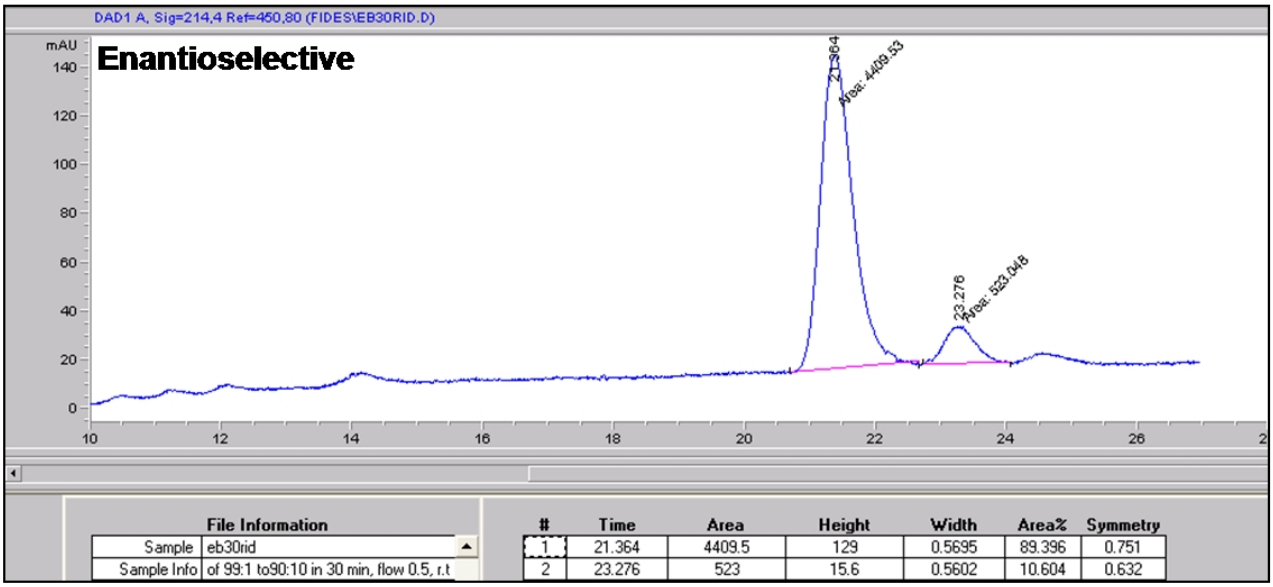
1c
(Derivatized to alcohol)

Chiracel OF: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:23.3 min; TM: 21.4 min.



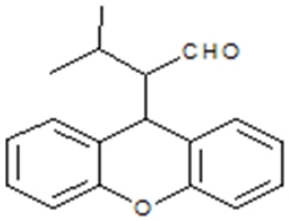
File Information	
Sample	fb468
Sample Info	OF 99-1 to 90-10 f=0.5 in 30 min

#	Time	Area	Height	Width	Area%	Symmetry
1	19.528	12707	373.3	0.5091	46.807	0.77
2	20.615	14440.9	369.4	0.5648	53.193	0.725



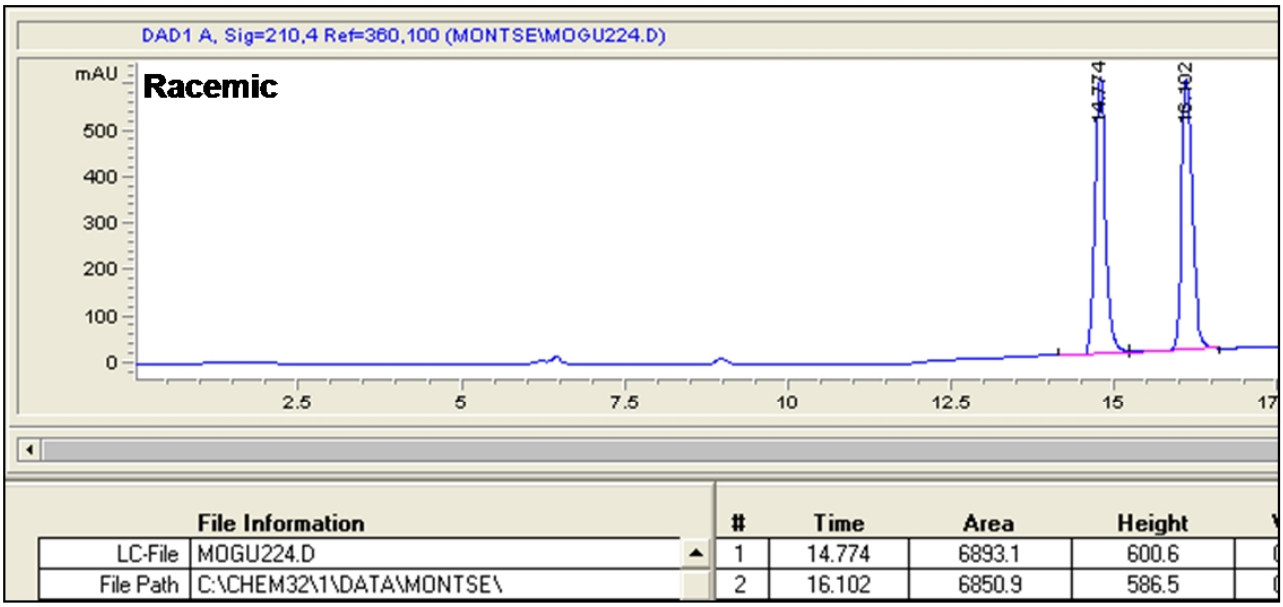
File Information	
Sample	eb30rid
Sample Info	of 99:1 to90:10 in 30 min, flow 0.5, r.t

#	Time	Area	Height	Width	Area%	Symmetry
1	21.364	4409.5	129	0.5695	89.396	0.751
2	23.276	523	15.6	0.5602	10.604	0.632



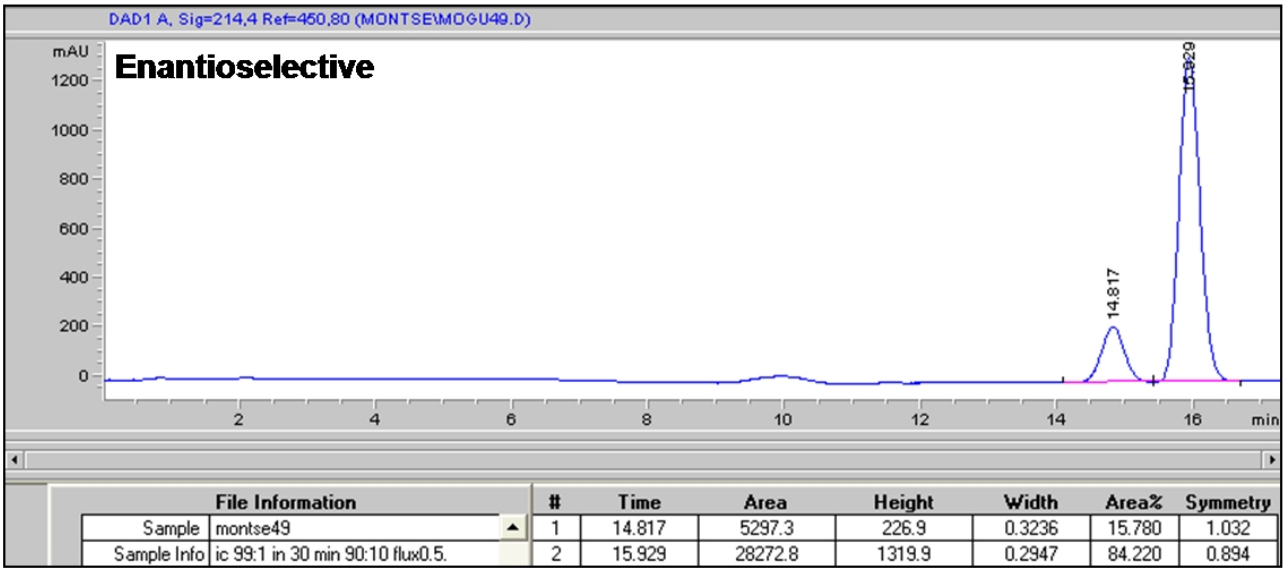
1d

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:14.8 min; TM: 15.9 min.



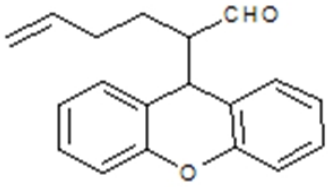
File Information	
LC-File	MOGU224.D
File Path	C:\CHEM32\1\DATA\MONTSE\

#	Time	Area	Height
1	14.774	6893.1	600.6
2	16.102	6850.9	586.5



File Information	
Sample	montse49
Sample Info	ic 99:1 in 30 min 90:10 flux0.5.

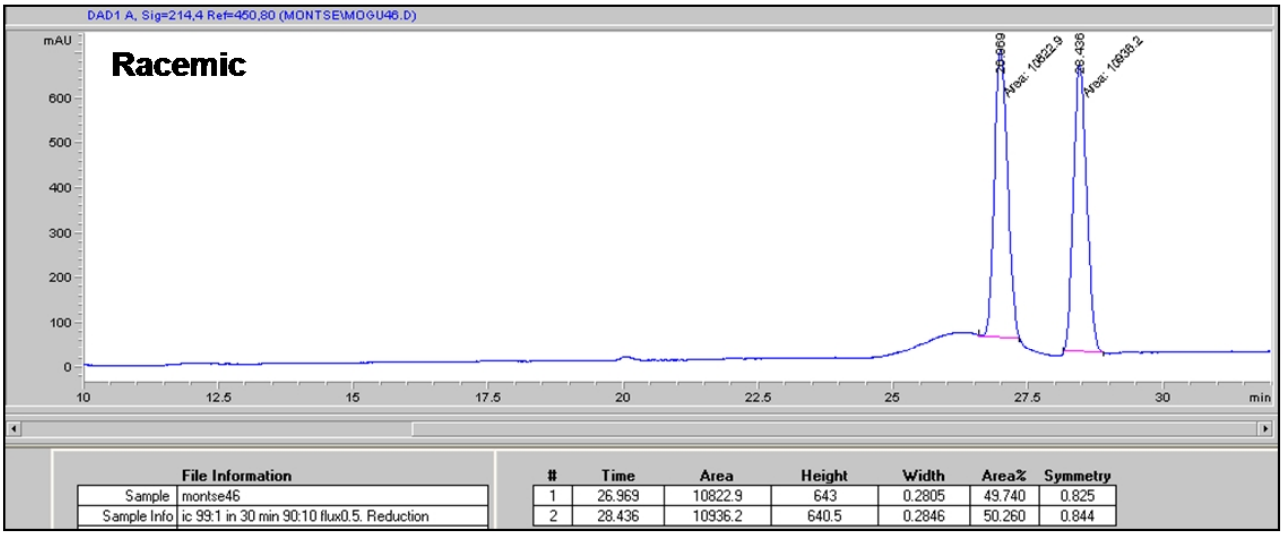
#	Time	Area	Height	Width	Area%	Symmetry
1	14.817	5297.3	226.9	0.3236	15.780	1.032
2	15.929	28272.8	1319.9	0.2947	84.220	0.894



1e

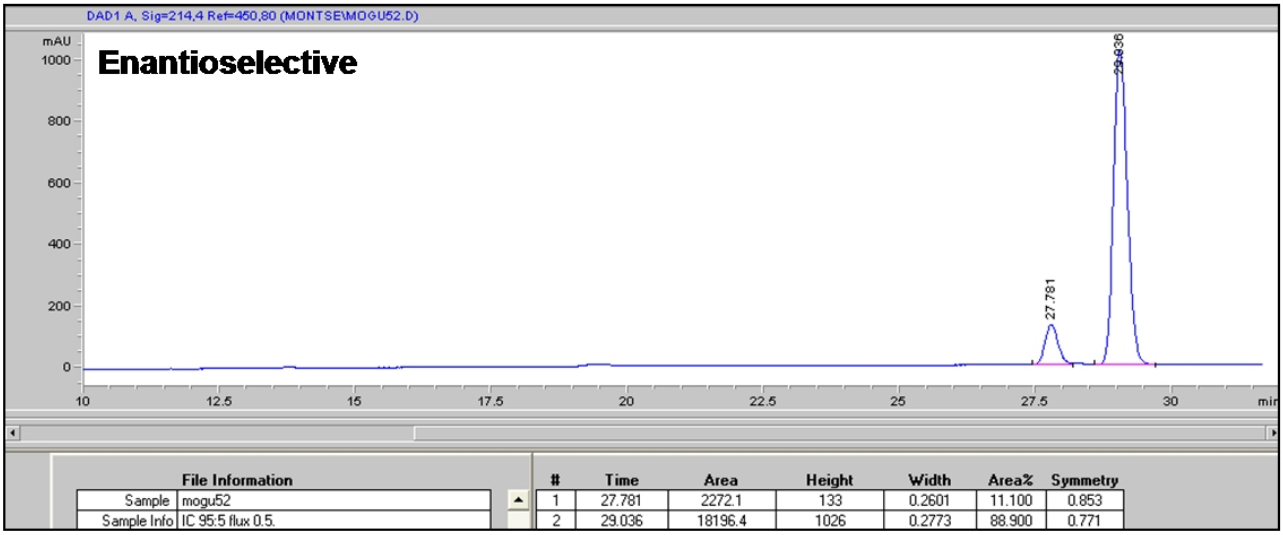
(Derivatized to alcohol)

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:27.8 min; TM: 29.0 min.



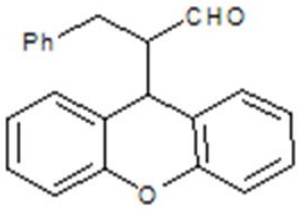
File Information	
Sample	montse46
Sample Info	ic 99:1 in 30 min 90:10 flux0.5. Reduction

#	Time	Area	Height	Width	Area%	Symmetry
1	26.969	10822.9	643	0.2805	49.740	0.825
2	28.436	10936.2	640.5	0.2846	50.260	0.844



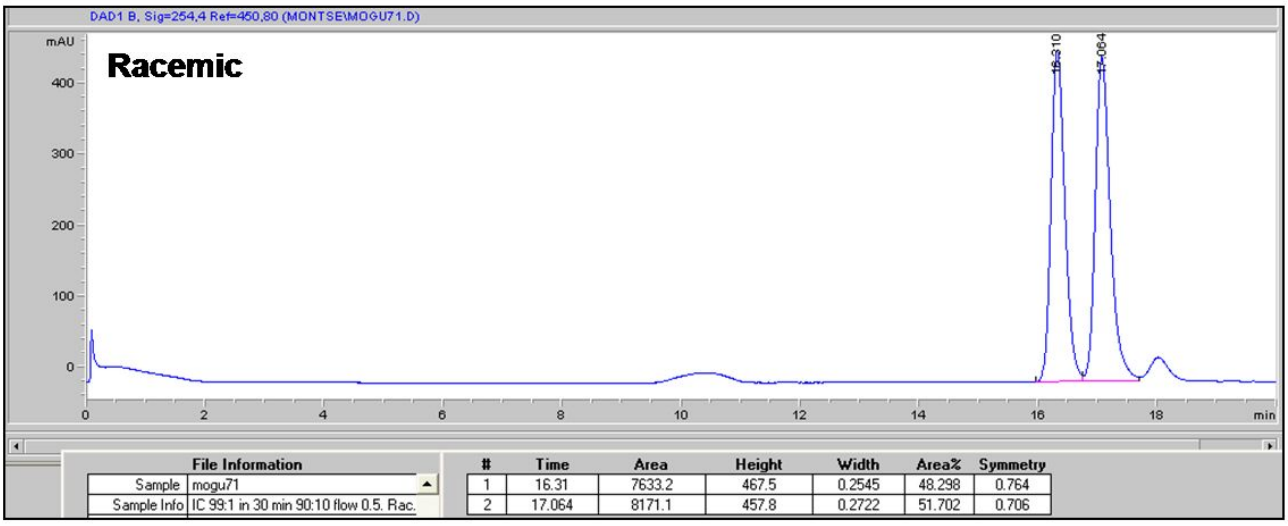
File Information	
Sample	mogu52
Sample Info	IC 95:5 flux 0.5.

#	Time	Area	Height	Width	Area%	Symmetry
1	27.781	2272.1	133	0.2601	11.100	0.853
2	29.036	18196.4	1026	0.2773	88.900	0.771



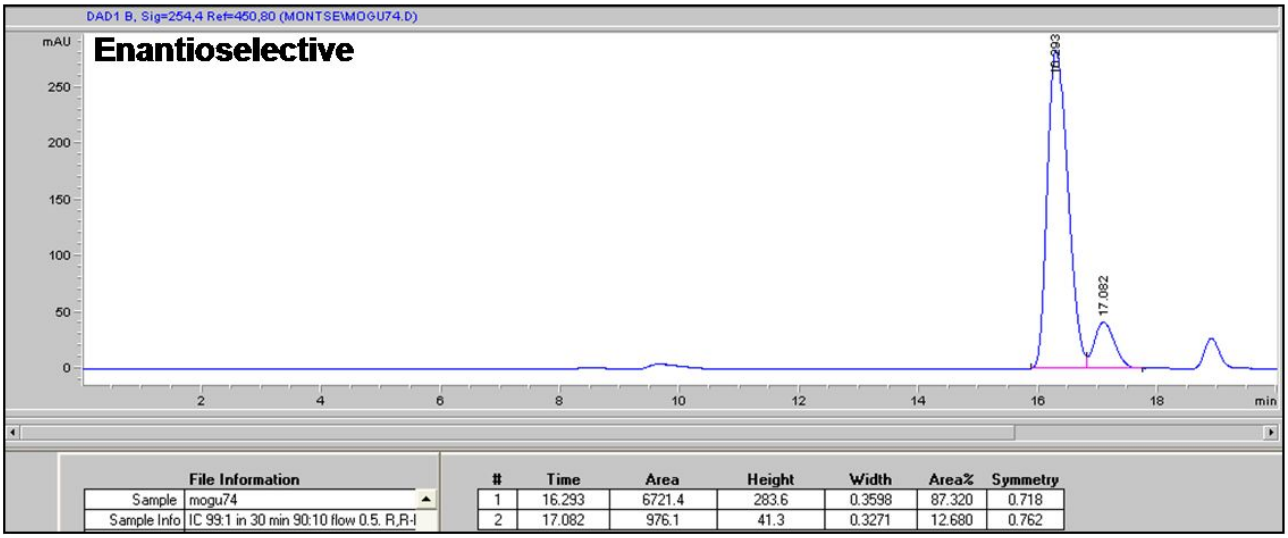
1f

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm:17.1 min; TM: 16.3 min.



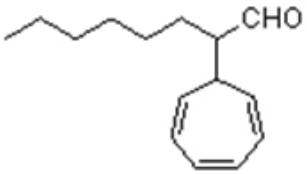
File Information	
Sample	mogu71
Sample Info	IC 99:1 in 30 min 90:10 flow 0.5. Rac.

#	Time	Area	Height	Width	Area%	Symmetry
1	16.31	7633.2	467.5	0.2545	48.298	0.764
2	17.064	8171.1	457.8	0.2722	51.702	0.706



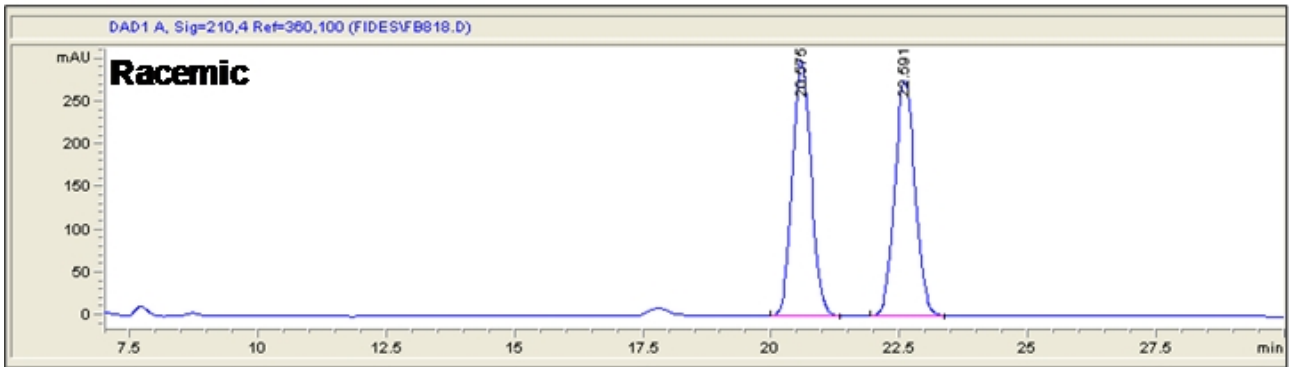
File Information	
Sample	mogu74
Sample Info	IC 99:1 in 30 min 90:10 flow 0.5. R,R-I

#	Time	Area	Height	Width	Area%	Symmetry
1	16.293	6721.4	283.6	0.3598	87.320	0.718
2	17.082	976.1	41.3	0.3271	12.680	0.762



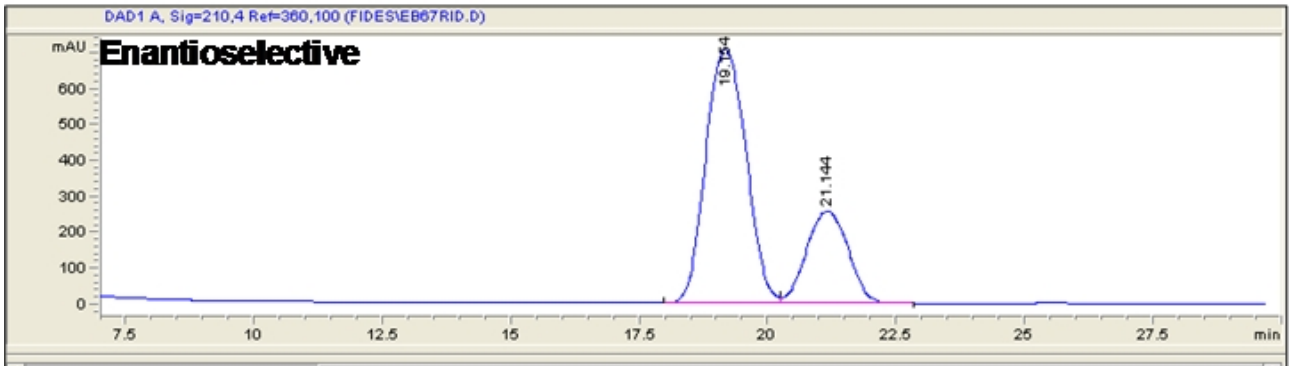
2a
(Derivatized to alcohol)

Chiracel OD-H: 99:1 (hexane: *i*-PrOH), flow 0.6mL/min. tm:21.1 min; TM: 19.2 min.



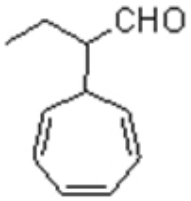
File Information	
Sample	fb818
Sample Info	OD-H 99:1 flow 0.6

#	Time	Area	Height	Width	Area%	Symmetry
1	20.575	7626.6	298.8	0.3978	50.012	0.886
2	22.591	7622.8	275.1	0.4333	49.988	0.921



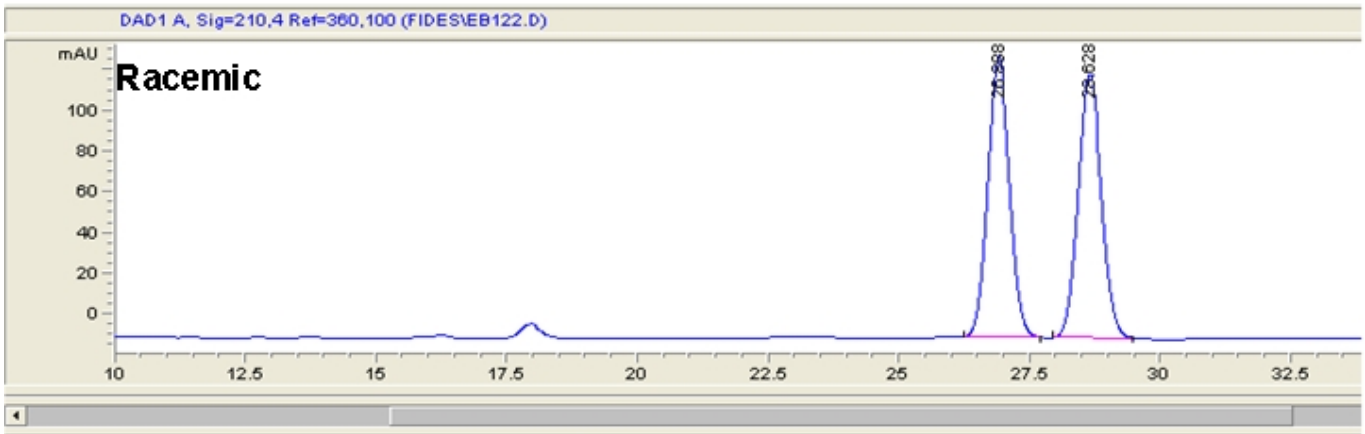
File Information	
LC-File	EB67RID.D
File Path	C:\CHEM32\1\DATA\FIDES\

#	Time	Area	Height	Width	Area%	Symmetry
1	19.154	38646.5	704.6	0.8919	72.779	0.867
2	21.144	14455	255.1	0.9172	27.221	0.94



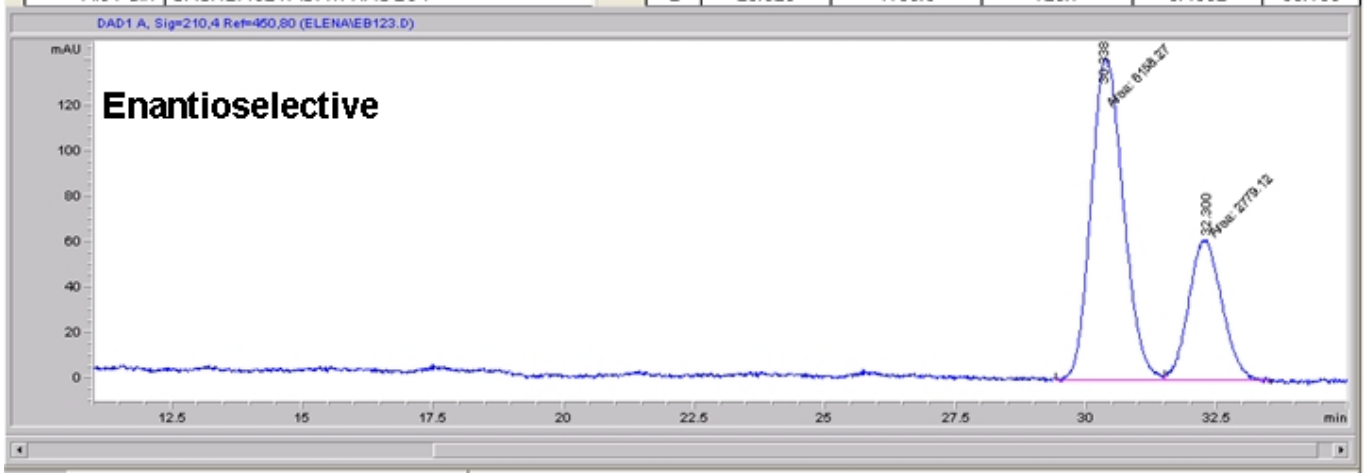
2c
(Derivatized to alcohol)

Chiracel OD-H: 99:1 (hexane: *i*-PrOH), flow 0.6mL/min. tm:28.6min; TM: 26.9min.



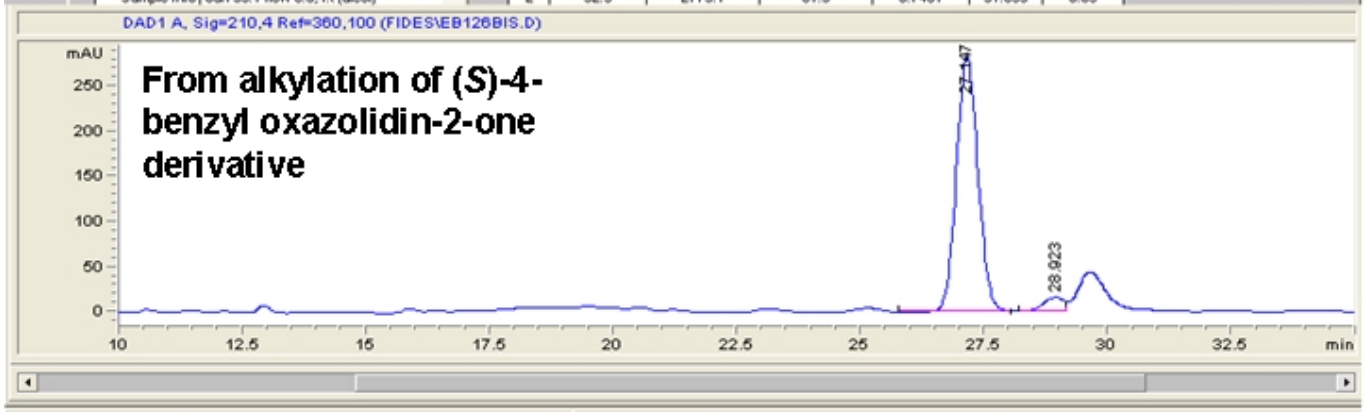
File Information	
LC-File	EB122.D
File Path	C:\CHEM32\1\DATA\FIDES\

#	Time	Area	Height	Width	Area%
1	26.888	4111.2	137.4	0.469	49.844
2	28.628	4136.9	129.7	0.4982	50.156



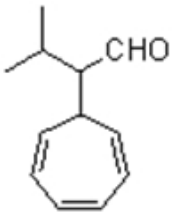
File Information	
Sample	eb123
Sample Info	odh 99:1 flow 0.6, r.t (alcol)

#	Time	Area	Height	Width	Area%	Symmetry
1	30.338	6158.3	142	0.7228	68.905	0.701
2	32.3	2779.1	61.9	0.7481	31.095	0.89



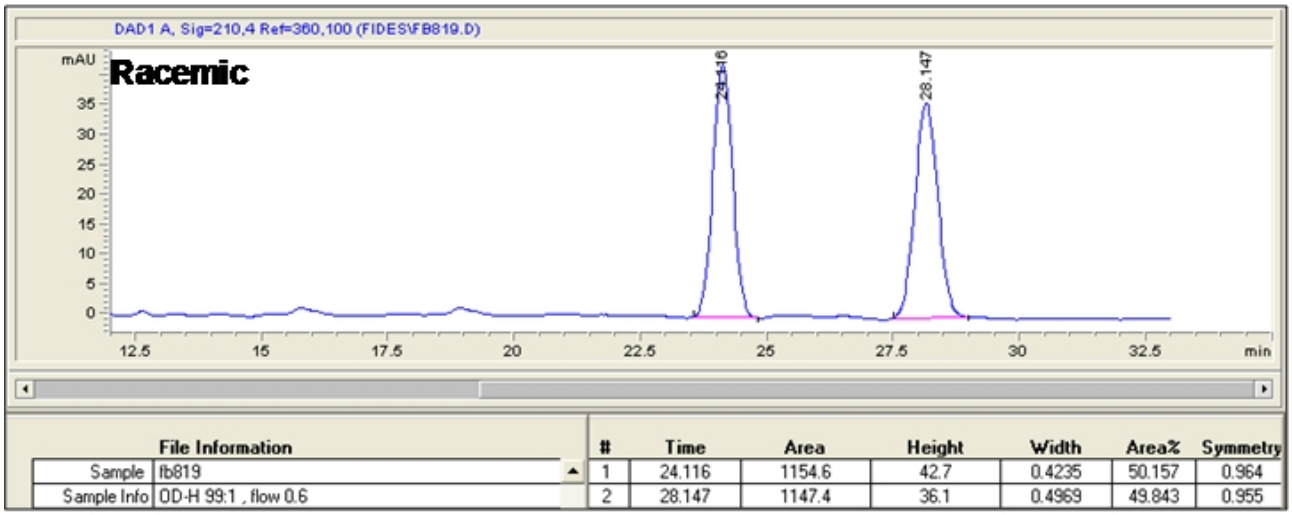
File Information	
Sample	eb126bis
Sample Info	OD-H 99:1 F=0.6

#	Time	Area	Height	Width	Area%	Symmetry
1	27.147	8554.9	282.4	0.4734	95.087	0.907
2	28.923	442	15	0.447	4.913	1.293

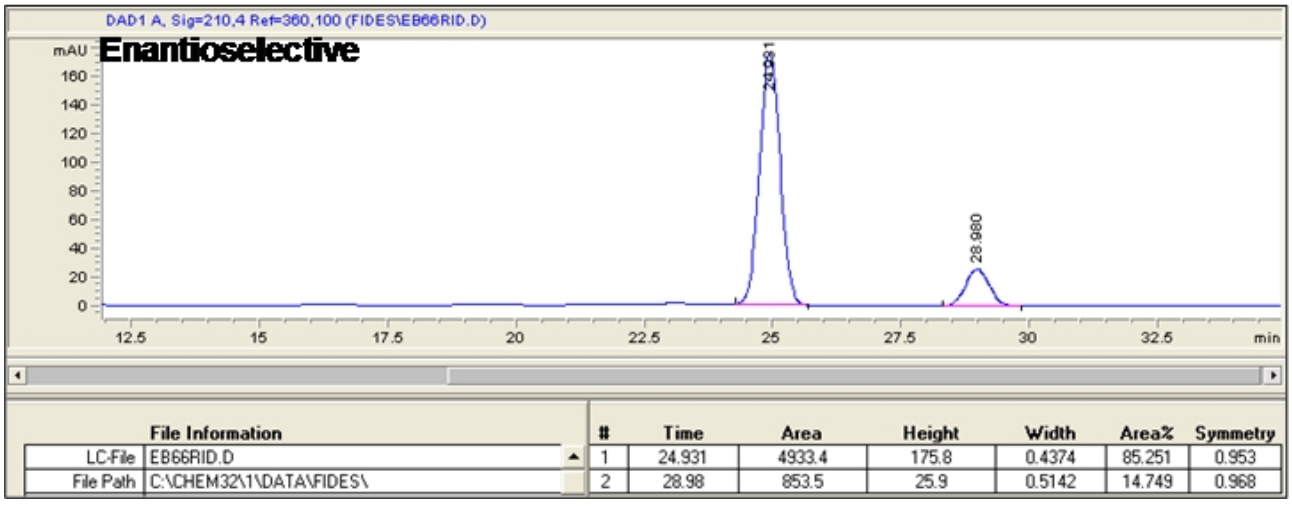


2d
(Derivatized to alcohol)

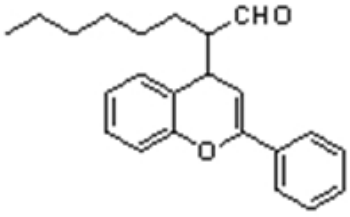
Chiracel OD-H: 99:1 (hexane: *i*-PrOH), flow 0.6mL/min. tm:29.0min; TM: 24.9min.



File Information		#	Time	Area	Height	Width	Area%	Symmetry
Sample	fb819	1	24.116	1154.6	42.7	0.4235	50.157	0.964
Sample Info	OD-H 99:1 , flow 0.6	2	28.147	1147.4	36.1	0.4969	49.843	0.955

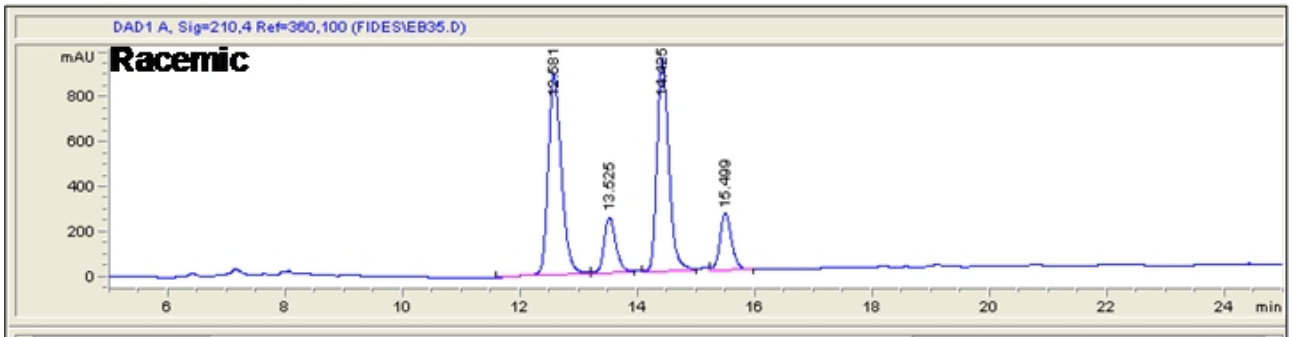


File Information		#	Time	Area	Height	Width	Area%	Symmetry
LC-File	EB66RID.D	1	24.931	4933.4	175.8	0.4374	85.251	0.953
File Path	C:\CHEM32\1\DATA\FIDES\	2	28.98	853.5	25.9	0.5142	14.749	0.968



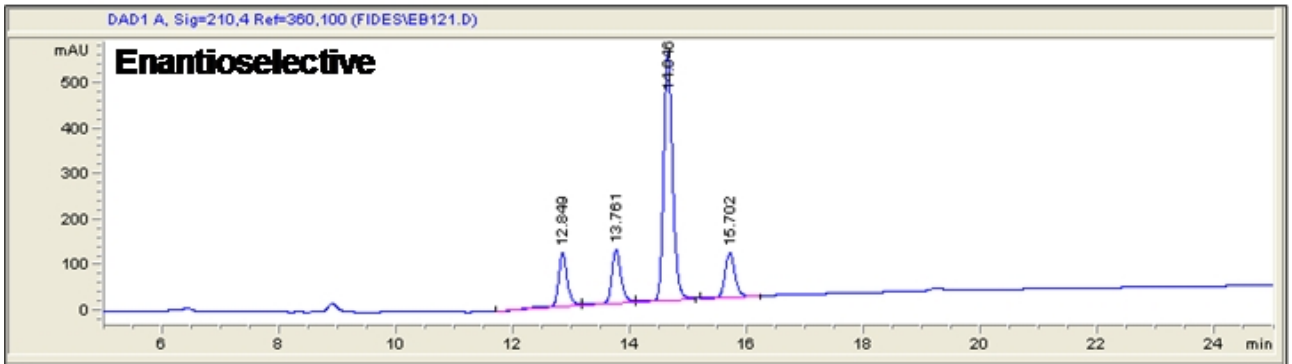
3a

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. tm (major):12.8 min; TM (major): 14.6 min. tm (minor):15.7 min; TM (minor): 13.8 min.



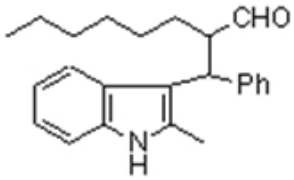
File Information	
Sample	eb35
Sample Info	IC 99:1 to 90:10 in 30min, F=0.5
Barcode	
Operator	ML

#	Time	Area	Height	Width	Area%	Symmetry
1	12.581	14336.3	899	0.244	40.941	0.74
2	13.525	3672.7	253.2	0.2192	10.488	0.763
3	14.425	13508.8	952.3	0.2175	38.578	0.738
4	15.499	3499.3	252.5	0.2117	9.993	0.819



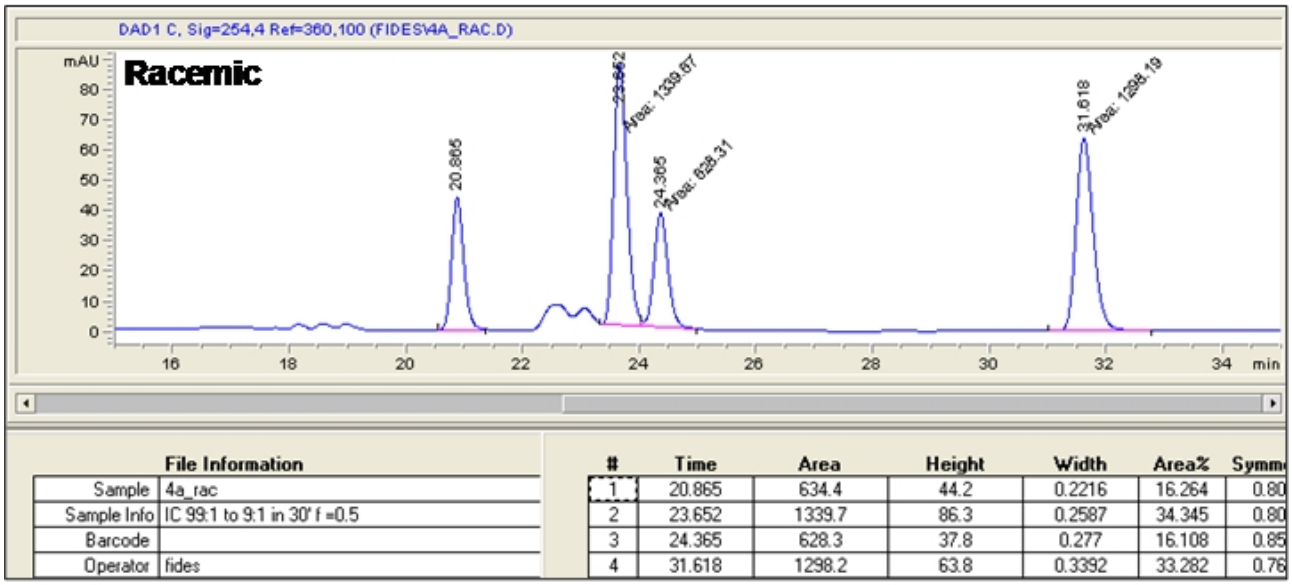
File Information	
Sample	eb121
Sample Info	IC 99:1 to 90:10 in 30 min, flow 0.5
Barcode	
Operator	elena

#	Time	Area	Height	Width	Area%	Symmetry
1	12.849	1459	121.1	0.1765	14.406	1.032
2	13.761	1486.3	121.8	0.1823	14.676	0.968
3	14.646	5963.4	544.3	0.1678	58.884	0.84
4	15.702	1218.8	98.9	0.1878	12.034	0.909



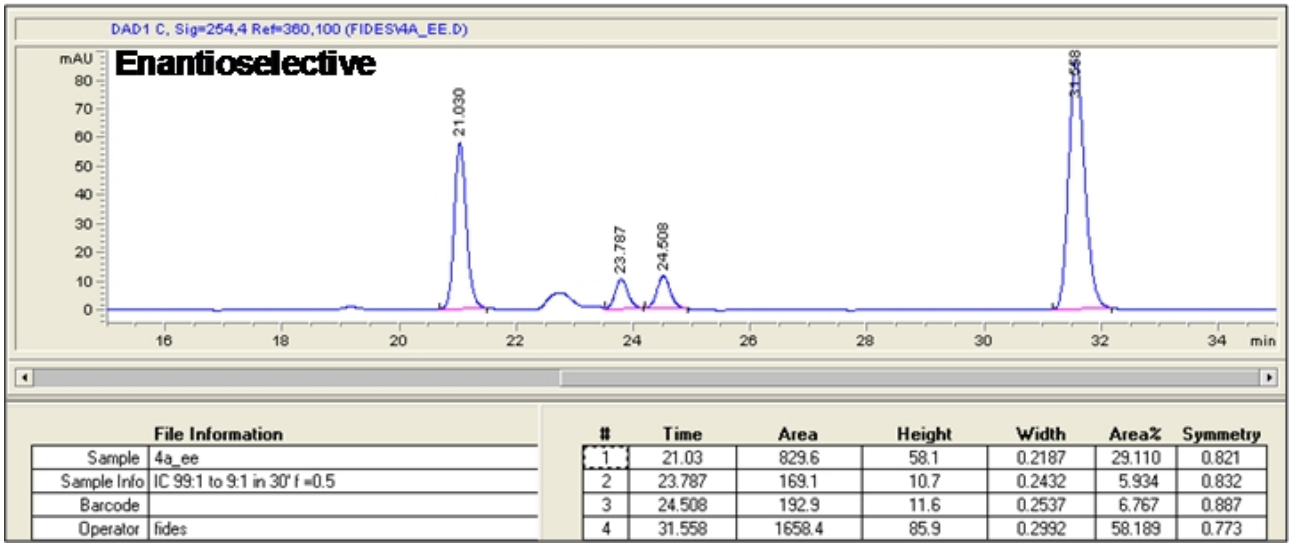
4a

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min.
TM (anti): 31.6 min; tm (anti): 23.8 min; TM (syn): 21.0 min; tm (syn): 24.5 min;



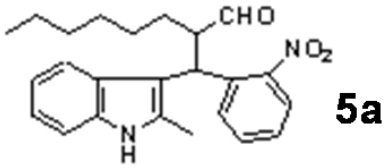
File Information	
Sample	4a_rac
Sample Info	IC 99:1 to 9:1 in 30' f =0.5
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symm
1	20.865	634.4	44.2	0.2216	16.264	0.80
2	23.652	1339.7	86.3	0.2587	34.345	0.80
3	24.365	628.3	37.8	0.277	16.108	0.85
4	31.618	1298.2	63.8	0.3392	33.282	0.76



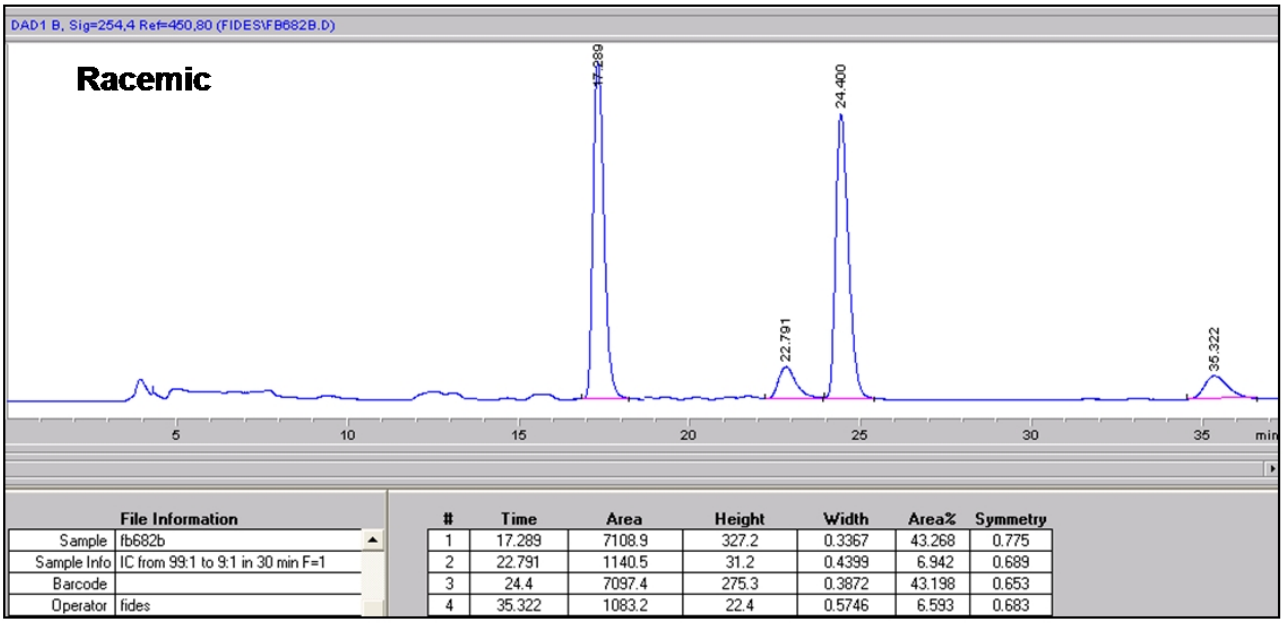
File Information	
Sample	4a_ee
Sample Info	IC 99:1 to 9:1 in 30' f =0.5
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symmetry
1	21.03	829.6	58.1	0.2187	29.110	0.821
2	23.787	169.1	10.7	0.2432	5.934	0.832
3	24.508	192.9	11.6	0.2537	6.767	0.887
4	31.558	1658.4	85.9	0.2992	58.189	0.773



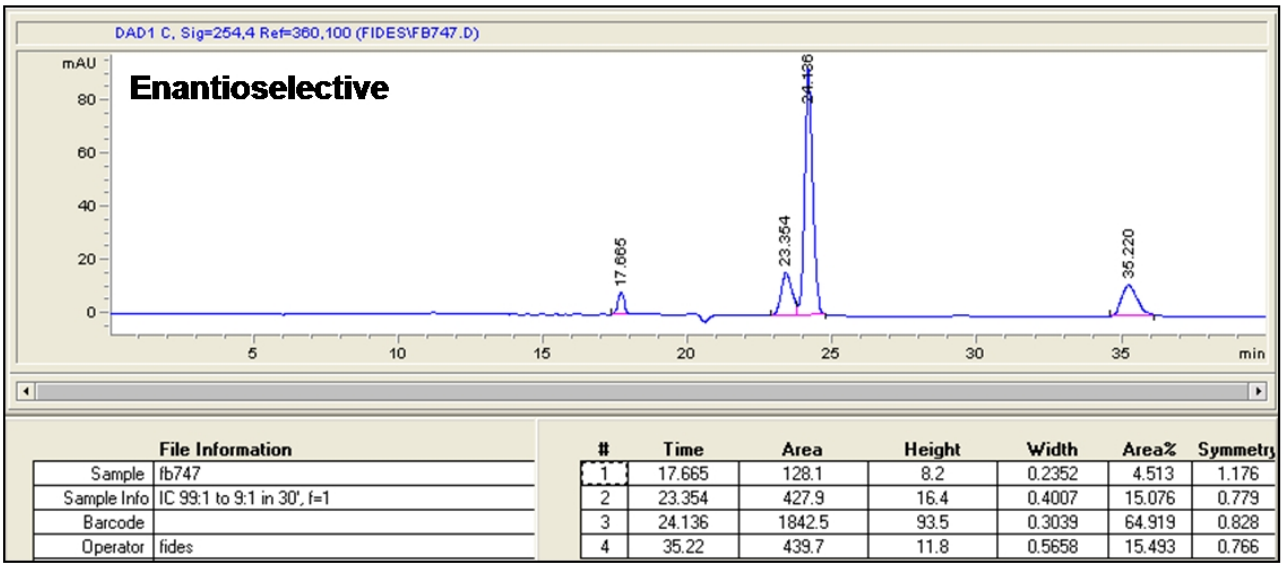
5a

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 1.0mL/min. TM (syn): 24.1 min; tm (syn): 17.7min.



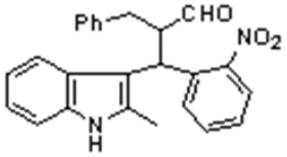
File Information	
Sample	fb682b
Sample Info	IC from 99:1 to 9:1 in 30 min F=1
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symmetry
1	17.289	7108.9	327.2	0.3367	43.268	0.775
2	22.791	1140.5	31.2	0.4399	6.942	0.689
3	24.4	7097.4	275.3	0.3872	43.198	0.653
4	35.322	1083.2	22.4	0.5746	6.593	0.683



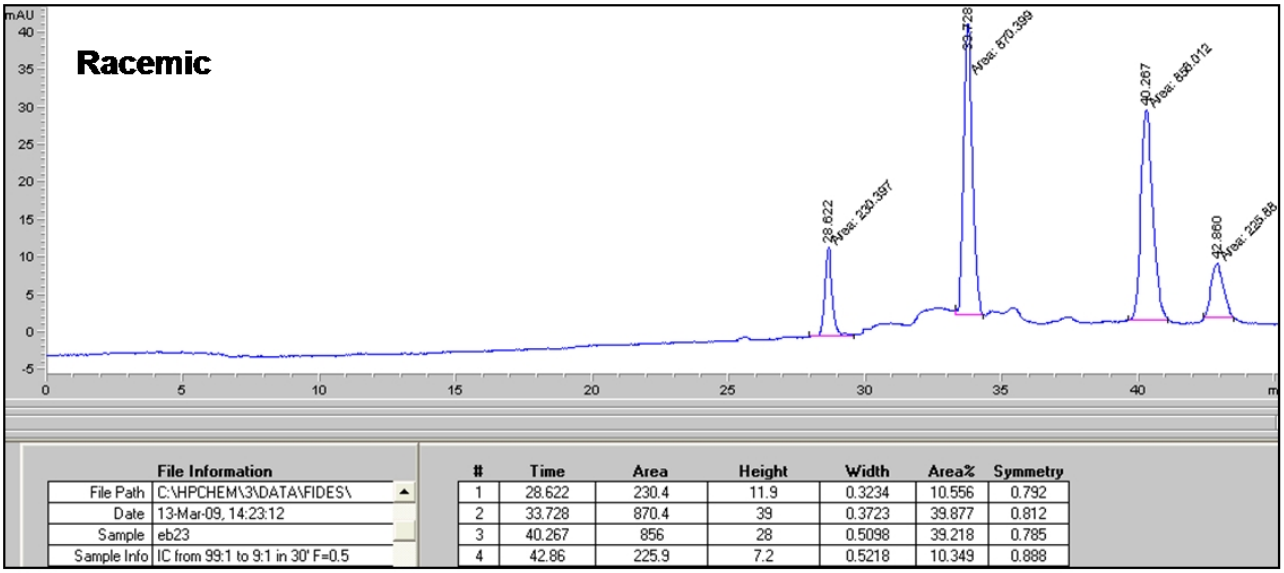
File Information	
Sample	fb747
Sample Info	IC 99:1 to 9:1 in 30', f=1
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symmetry
1	17.665	128.1	8.2	0.2352	4.513	1.176
2	23.354	427.9	16.4	0.4007	15.076	0.779
3	24.136	1842.5	93.5	0.3039	64.919	0.828
4	35.22	439.7	11.8	0.5658	15.493	0.766



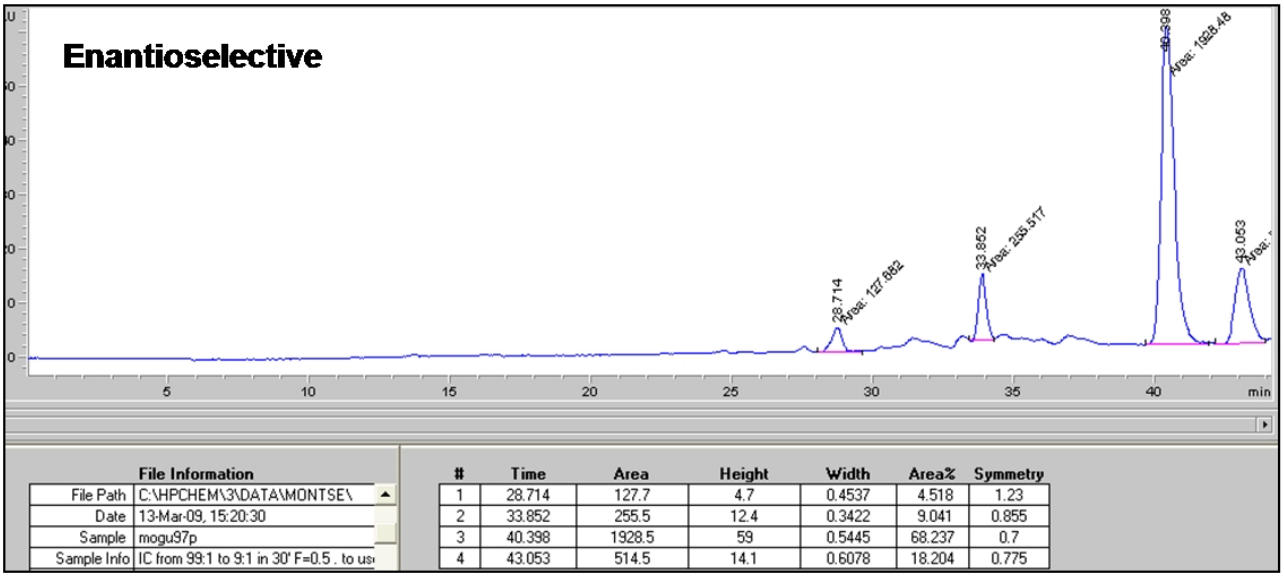
5f

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. TM (syn): 40.4 min; tm (syn): 33.9min; TM (anti): 43.0 min; tm (anti): 28.7min.



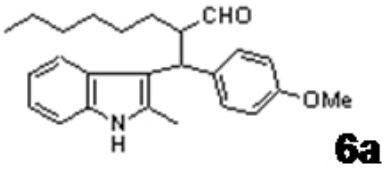
File Information	
File Path	C:\HPCHEM\3\DATA\FIDES\
Date	13-Mar-09, 14:23:12
Sample	eb23
Sample Info	IC from 99:1 to 9:1 in 30' F=0.5

#	Time	Area	Height	Width	Area%	Symmetry
1	28.622	230.4	11.9	0.3234	10.556	0.792
2	33.728	870.4	39	0.3723	39.877	0.812
3	40.267	856	28	0.5098	39.218	0.785
4	42.86	225.9	7.2	0.5218	10.349	0.888



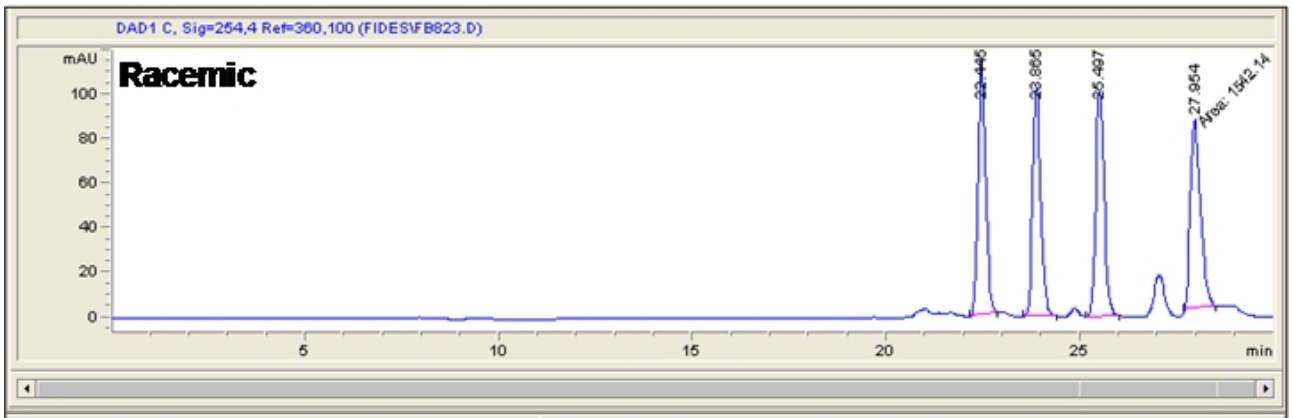
File Information	
File Path	C:\HPCHEM\3\DATA\MONTSE\
Date	13-Mar-09, 15:20:30
Sample	mogu97p
Sample Info	IC from 99:1 to 9:1 in 30' F=0.5 . to us

#	Time	Area	Height	Width	Area%	Symmetry
1	28.714	127.7	4.7	0.4537	4.518	1.23
2	33.852	255.5	12.4	0.3422	9.041	0.855
3	40.398	1928.5	59	0.5445	68.237	0.7
4	43.053	514.5	14.1	0.6078	18.204	0.775



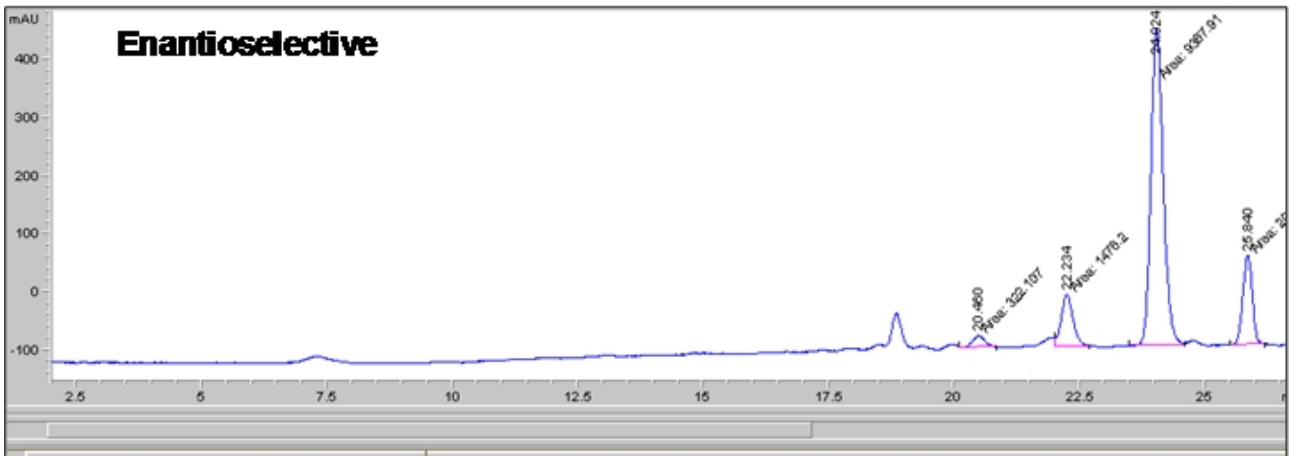
6a

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 8:2 in 30min, flow 0.5mL/min.
TM (anti): 22.2 min; tm (anti): 20.4min; TM (syn): 24.0min; tm (syn): 25.8min.



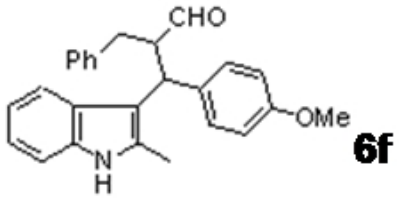
File Information	
Sample	fb823
Sample Info	IC 99:1 to 8:2 in 30', f=0.5
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symmetry
1	22.445	1552.1	113.5	0.2116	25.304	0.815
2	23.865	1511.9	102.8	0.2277	24.648	0.807
3	25.497	1527.8	101.9	0.2309	24.908	0.817
4	27.954	1542.1	84.3	0.305	25.141	0.717



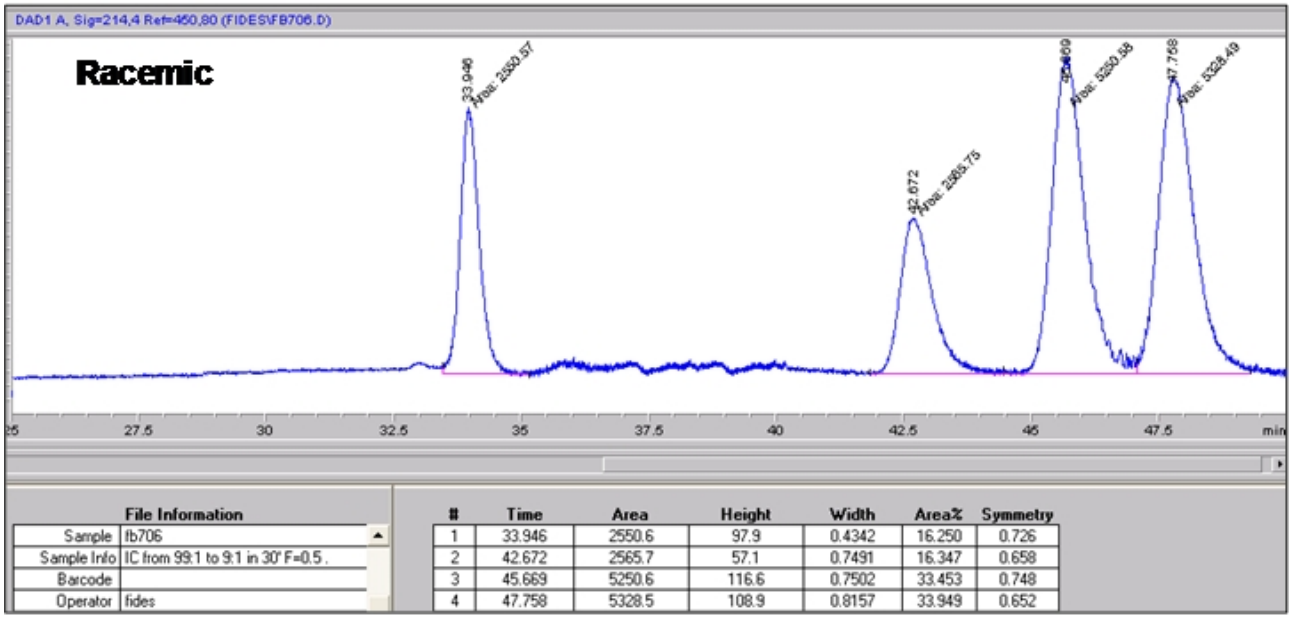
File Information	
Sample	fb686
Sample Info	Ic from 99-1 to 8-2 in 30' f=0.5
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symmetry
1	20.46	322.1	19.8	0.2711	2.446	0.712
2	22.234	1476.2	89.5	0.2749	11.208	0
3	24.024	9367.9	547.6	0.2851	71.125	0.813
4	25.84	2004.8	153.5	0.2177	15.221	1.017



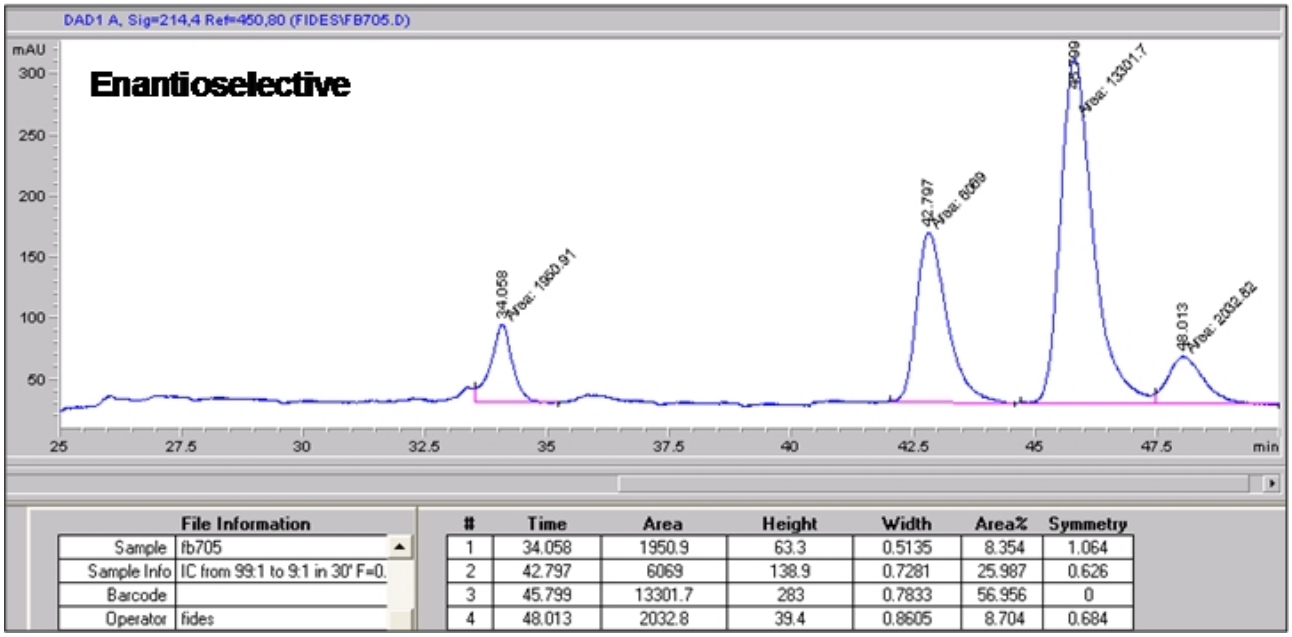
6f

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 0.5mL/min. TM (anti): 45.8 min; tm (anti): 48.0min; TM (syn): 42.8 min; tm (syn): 34.1min.



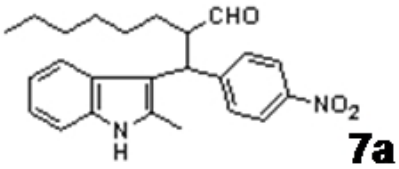
File Information	
Sample	fb706
Sample Info	IC from 99:1 to 9:1 in 30' F=0.5 .
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symmetry
1	33.946	2550.6	97.9	0.4342	16.250	0.726
2	42.672	2565.7	57.1	0.7491	16.347	0.658
3	45.669	5250.6	116.6	0.7502	33.453	0.748
4	47.758	5328.5	108.9	0.8157	33.949	0.652



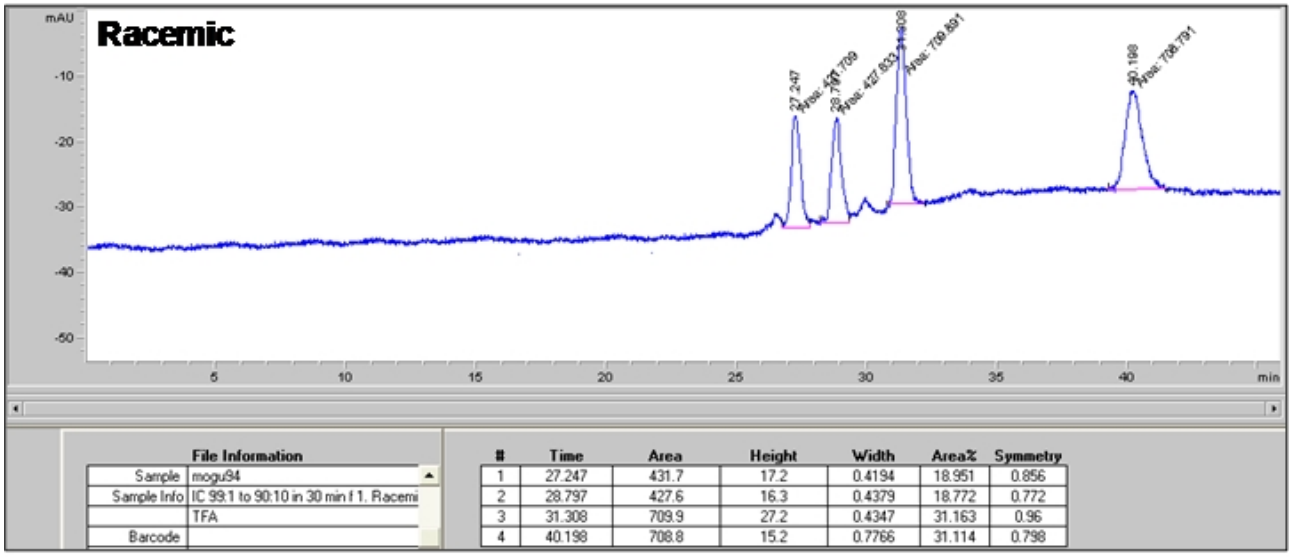
File Information	
Sample	fb705
Sample Info	IC from 99:1 to 9:1 in 30' F=0.
Barcode	
Operator	fides

#	Time	Area	Height	Width	Area%	Symmetry
1	34.058	1950.9	63.3	0.5135	8.354	1.064
2	42.797	6069	138.9	0.7281	25.987	0.626
3	45.799	13301.7	283	0.7833	56.956	0
4	48.013	2032.8	39.4	0.8605	8.704	0.684



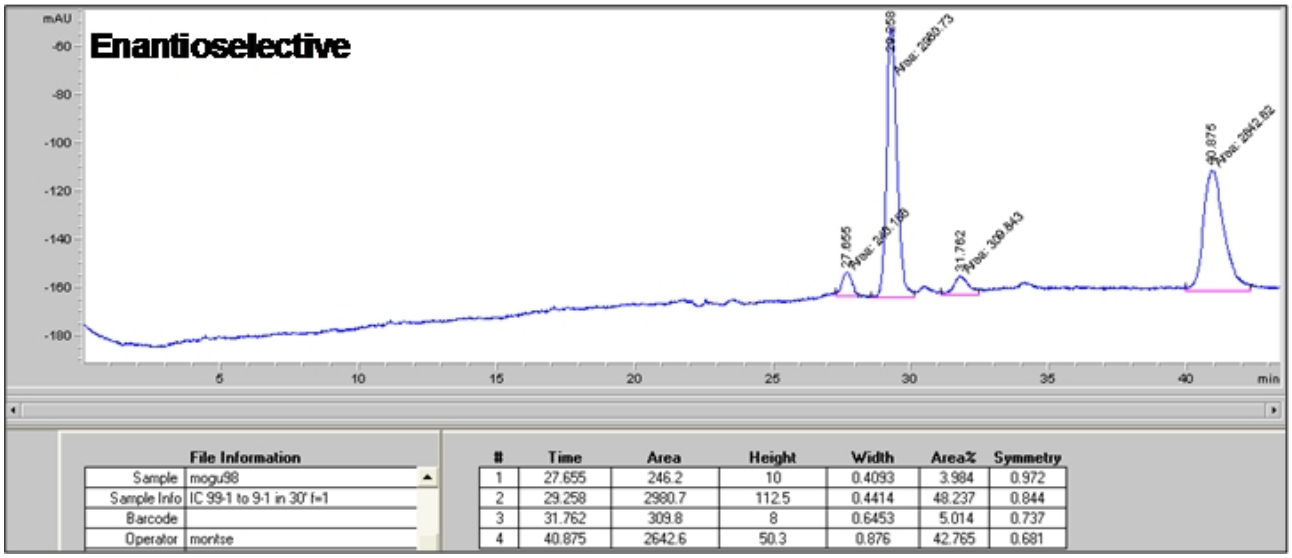
7a

Chiracel IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10 in 30min, flow 1.0mL/min. TM (anti): 40.9 min; tm (anti): 31.8min; TM (syn): 29.3 min; tm (syn): 27.7min.



File Information	
Sample	mogu94
Sample Info	IC 99:1 to 90:10 in 30 min f 1. Racemi
	TFA
Barcode	

#	Time	Area	Height	Width	Area%	Symmetry
1	27.247	431.7	17.2	0.4194	18.951	0.856
2	28.797	427.6	16.3	0.4379	18.772	0.772
3	31.308	709.9	27.2	0.4347	31.163	0.96
4	40.198	708.8	15.2	0.7766	31.114	0.798



File Information	
Sample	mogu98
Sample Info	IC 99-1 to 9-1 in 30' f=1
Barcode	
Operator	montse

#	Time	Area	Height	Width	Area%	Symmetry
1	27.655	246.2	10	0.4093	3.984	0.972
2	29.258	2980.7	112.5	0.4414	48.237	0.844
3	31.762	309.8	8	0.6453	5.014	0.737
4	40.875	2642.6	50.3	0.876	42.765	0.681