## Supporting Information

### General Information

$^1H$ NMR and $^{13}C$ NMR spectra were recorded on VXL-300 instruments using TMS as internal standard in $CDCl_3$ solution. $^{19}F$ NMR spectra were recorded on VXL-300 instruments using TFA as external standard in $CDCl_3$ solution. Infrared spectra were recorded on Perkin-Elmer 983 FI-IR spectrometer as liquid films on potassium bromide plates. Mass spectral were performed on Finnigan GC-MS-4021. Elemental analyses were carried out on an MOD-1606 elemental analyzer. High-resolution mass spectra were recorded on an HP5989A mass spectrometer. The vale of ee determined by HPLC with Chiralcel OJ or AD column; Optical rotations were measured using a Perkin-Elmer 241 MC polarimeter with a thermally jacketed 10 cm cell at 20℃ (concentration given as g per 100 mL). All the reaction were performed under a nitrogen atmosphere. All the acyl cholrides were commercial available and used after distillation . The race cyclopropylboronic acids and optically active cyclopropylboronic acids were prepared according to the literature procedures.

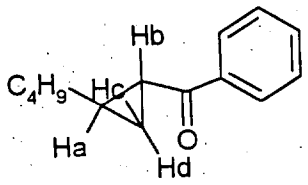
### General Procedure for the cross-coupling reaction:

The preparation of **trans-1-Benzoyl-2-butylcyclopropane(3aa)** is representative of the methods used. To a solution of trans-2-butylcyclopropylboronic acid (1.0mmol, 142 mg) and $Ag_2O$ (2 mmol, 463 mg), $K_2CO_3$ (2 mmol,276.5 mg), $PdCl_2$(dppf) (0.03 mmol, 22 mg) in toluene (4 mL), benzoyl chloride (2 mmol, 281 mmg) were added under a nitrogen atmosphere. The reaction mixture was stirred at 80℃ for 12 h, then cooled to room temperature, water was added and the product was extracted with EtOAc. Organic layer was washed with saturated brine and dried over magnesium sulfate. The solvents were removed in vacuo and the residue purified by flash-column

chromatography (silica gel, eluting with petroleum ether/ EtOAc 20:1) to yield (3aa) as colorless oil (157mg, 78%).

**Spectroscopic data**

**trans-1-Benzoyl-2-butylcyclopropane(3aa)**




$^1$H NMR ($CCl_3D$-TMS, 400Hz ) δppm, 8.0 (m, 2H), 7.56-7.61 (m, 3H), 2.43 (dt, J = 4.5Hz, 7.7Hz, $1H_b$), 1.63(m, $1H_a$), 1.46(ddd, J = 3.5Hz, 4.5Hz, 8.4Hz, $1H_d$), 1.33-1.45 (m, 6H), 0.91(t, J = 7.1Hz, 3H), 0.90-0.93(m,$1H_c$, overlapped with $C\underline{H}_3$),

$^{13}$C NMR 14.057, 19.034, 22.437, 25.279, 27.256, 31.424, 33.264, 128.009, 128.520, 132.616, 138.204, 200.178;

MS m/e 202 ($M^+$, 1.44), 105(100),

IR (neat) 1668$cm^{-1}$;

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.85; H, 9.11.

In the 2D-$^1$H NMR, the proton $H_a$ showed strong NOE interaction with proton $H_d$ but very weak NOE interaction with $H_c$ and $H_b$

**trans-1-(4-Methylbenzoyl)-2-hexylcyclopropane(3bb)**

colorless liquid.

$^1$H NMR ($CCl_3D$-TMS, 300Hz ) δppm, 7.83 (d, J = 8.2Hz, 2H), 7.33 (d, J = 9.5 Hz, 2H), 2.35 (s, 3H), 2.34 (m, $1H_b$ overlapped with Me), 1.53(m, $1H_a$), 1.46(ddd, $1H_d$ overlapped with $C\underline{H}_2$), 1.21-1.45 (m, 10H), 0.81(t, J = 7.0Hz, 3H), 0.78-0.82 (m,$1H_c$, overlapped with $C\underline{H}_3$),

MS m/e 245 ($M+1^+$, 16.36), 119(100),

IR (neat) 1666$cm^{-1}$;

Anal. Calcd for $C_{14}H_{18}O$: C, 83.55; H, 9.90. Found: C, 83.19; H, 10.18.

**trans-1-(3-Methoxybenzoyl)-2-butylcyclopropane(3ad)**

colorless liquid.

$^1H$ NMR ($CCl_3D$-TMS, 300Hz ) δppm, 7.67 (m, 1H), 7.52 (t, J = 1.8Hz, 1H), 7.38 (t, J = 8.0Hz, 1H), 7.1 9 (m, 1H), 3.91 (s, 3H), 2.39 (dt, J = 4.1Hz, J = 8.1Hz, $1H_b$), 1.60 (m, $1H_a$), 1.46-1.53 (m, $1H_d$ overlapped with $C\underline{H}_2$), 1.35-1.46 (m, 6H), 0.95(t, J = 7.1Hz, 3H), 0.94-0.97 (m,$1H_c$, overlapped with $C\underline{H}_3$),

$^{13}C$ NMR 199.995, 159.855, 139.610, 129.505, 120.705, 119.077, 112.381, 55.484, 33.266, 31.426, 27.373, 25.433, 22.493, 19.110, 14.057.

MS m/e 232 ($M^+$, 9.14), 135(100),

IR (neat) 1667$cm^{-1}$;

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.54; H, 8.68. Found: C, 77.46; H, 8.70.

In the 2D-$^1H$ NMR, the proton $H_a$ showed strong NOE interaction with proton $H_d$ but very weak NOE interaction with $H_c$ and $H_b$

**trans-1-(2-Fluorobenzoyl)-2-hexylcyclopropane(3bf)**

colorless liquid.

$^1H$ NMR ($CD_3COCD_3$-TMS, 300Hz ) δppm, 7.63 (m, 1H), 7.50 (m, 1H), 7.11 (m, 2H), 2.31 (m, $1H_b$), 1.45(m, $1H_a$), 1.21-1.45 (m, 10H+$1H_d$), 0.78-0.85 (m,$1H_c$, overlapped with $C\underline{H}_3$), 0.78(t, J = 7.0Hz, 3H),

MS m/e 248 ($M^+$, 0.27), 123(100),

IR (neat) 1672$cm^{-1}$;

Anal. Calcd for $C_{16}H_{20}OF$: C,77.70; H, 8.15. Found: C, 77.55; H, 8.37.

In the 2D-$^1$H NMR, the proton $H_a$ showed strong NOE interaction with proton $H_d$ but very weak NOE interaction with $H_c$ and $H_b$

**trans-1-(4-Phenylbenzoyl)-2-butylcyclopropane(3aj)**

White solid.

$^1$H NMR ($CCl_3D$-TMS, 300Hz ) δppm, 8.10 (d, J = 8.6Hz, 2H), 7.70 (m, 4H), 7.38-7.50 (m, 3H), 2.50 (dt, J = 4.3Hz, J = 8.7Hz, $1H_b$), 1.63(m, $1H_a$), 1.56(ddd, $1H_d$ overlapped with $C\underline{H}_2$), 1.34-1.56 (m, 6H), 0.91(t, J = 7.0Hz, 3H), 0.90-0.92 (m,$1H_c$, overlapped with $C\underline{H}_3$),

MS m/e 278 ($M^+$, 10.02), 181(100),

IR (neat) 1658$cm^{-1}$;

Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.97. Found: C, 85.97; H, 8.37.

**trans-1-(2-Naphthoyl)-2-hexylcyclopropane(3bk)**

colorless liquid.

$^1$H NMR ($CCl_3D$-TMS, 300Hz ) δppm, 8.41 (d, J = 9.5Hz, 2H), 8.00 (d, J = 8.2Hz, 1H), 7.88(m, 2H), 7.58 (m, 3H), 2.38 (dt, J = 4.2Hz, J = 8.1Hz, $1H_b$), 1.80(m, $1H_a$), 1.67(ddd, $1H_d$), 1.30-1.51 (m, 10H), 1.07 (ddd,$1H_c$,), 0.91(t, J = 6.8Hz, 3H),

MS m/e 280 ($M^+$, 20.11), 155(100),

IR (neat) 1666$cm^{-1}$;

Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.80; H, 8.54.

**trans-1-(2-Furoyl)-2-pentylcyclopropane(3co)**

colorless liquid.

$^1$H NMR ($CCl_3D$-TMS, 300Hz ) δppm, 7.50 (d, J = 1.4Hz, 1H), 7.19 (d, J = 3.6Hz, 1H), 6.67(dd, J = 3.6Hz, J = 1.6Hz, 1H), 2.34 (dt, J = 4.1Hz, J = 8.2Hz, $1H_b$), 1.65(m, $1H_a$), 1.47(ddd, $1H_d$, overlapped with $C\underline{H}_2$), 1.30-1.48 (m, 8H), 0.91 (t, J = 6.8Hz, 3H), 0.89-0.91 (m,$1H_c$, overlapped with $C\underline{H}_3$),

MS m/e 206 ($M^+$, 1.54), 95(100),

IR (neat) 1662cm$^{-1}$;

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.44; H, 9.00.

**trans-1-(2-Thiophenecarbonyl)-2-butylcyclopropane(3an)**

colorless liquid.

$^1$H NMR ($CCl_3D$-TMS, 300Hz ) δppm, 7.82 (d, J = 3.7Hz, 1H), 7.66 (d, J = 4.7Hz, 1H), 6.67(t, J = 4.3Hz, 1H), 2.31 (dt, J = 4.0Hz, J = 8.2Hz, $1H_b$), 1.55(m, $1H_a$), 1.43(ddd, $1H_d$, overlapped with $C\underline{H}_2$), 1.32-1.44 (m, 6H), 0.91 (t, J = 7.8Hz, 3H), 0.89-0.91 (m,$1H_c$, overlapped with $C\underline{H}_3$),

$^{13}$C NMR 192.65, 145.24, 133.101, 131.325, 128.151, 33.205, 31.392, 26.918, 26.209, 22.434, 18.736, 14.089.

MS m/e 208 ($M^+$, 9.31), 111(100),

IR (neat) 1647cm$^{-1}$;

Anal. Calcd for $C_{12}H_{16}OS$: C, 69.19; H,7.75. Found: C, 68.79; H, 8.20.

The vale of ee of product (**3aa**) determined by HPLC with Chiralcel AD;

Mobilephase $C_6H_{14}$/IPA = 90/10;

Detector UV254nm;

Flow Rate 0.6ml/min;

tR(min) = 10.133(S, S) and 12.020(R, R).

The vale of ee of product chiral (**3aj**) determined by HPLC with Chiralcel OJ;

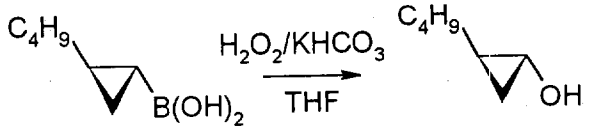
Mobilephase $C_6H_{14}$/IPA = 90/10;

Detector UV254nm;

Flow Rate 0.6ml/min;

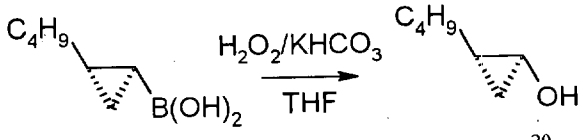
tR(min) = 13.75(S,S) and 15.71(R,R).

The enantiomeric purities were established on the corresponding carbinols generated by the alkali oxidation of the cyclopropylboronic acids as fellow:




**1a**
$[\alpha]^{20}_D$ = -24° (in EtOH)

**4a**
$[\alpha]^{20}_D$ = -54.1°
(in EtOH, c = 1.021)




$[\alpha]^{20}_D$ = 25.6° (in EtOH)

$[\alpha]^{20}_D$ = 56.4°
(in EtOH, c = 1.200)

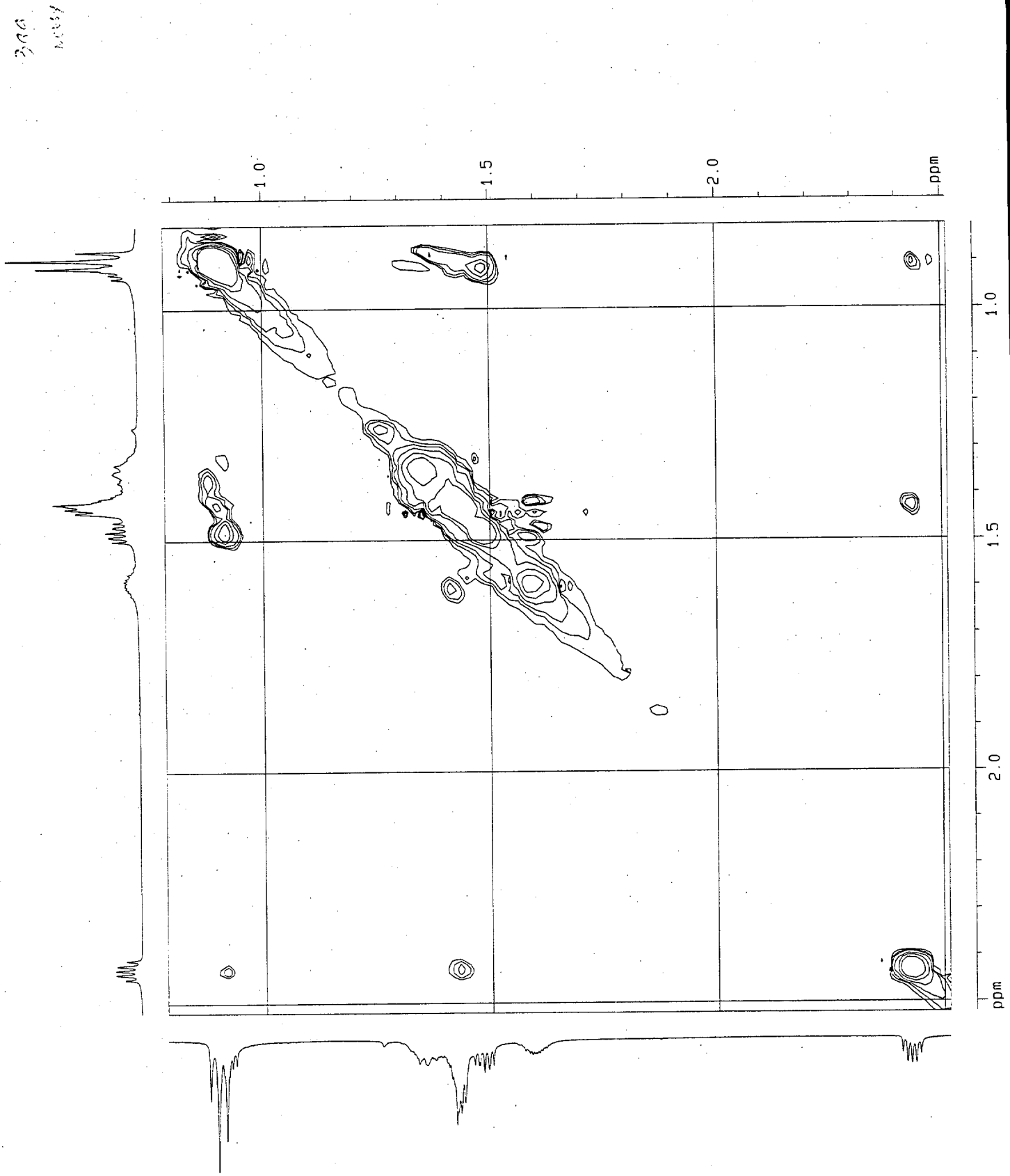
The ee values were determined by a polarimeter based on the reported rotation of Imai's results: (1R, 2R)-**4a**, $[\alpha]^{20}_D$ = -56.3° (in EtOH) ee% = 94%;

(1S, 2S)-**4a,** $[\alpha]^{20}_{D} = 54.1^{\circ}$ (in EtOH) ee% = 90%;

**General Procedure for the oxidation reaction**:

The chiral trans-2-butylcyclopropylboronic acid (71mg, 0.5mmol) was added to 10mL THF as solvent, a mixture containing 30% $H_2O_2$ (0.3mL) and 2N $KHCO_3$ (0.3mL) was also added, after stirring 2h at rt, Diethyl ether and water were added, the aqueous layer exacted twice with diethyl ether (15mL). The combined organic layer were washed with $NH_4Cl$ solution and brine, dried by $MgSO_4$, concentrated under reduced pressure. The crude product was purified by flash column chromatography (PE: EA = 4:1) to afford the product as a colorless oil.( 60mg, yield :94%)

$^1H$ NMR ($CCl_3D$-TMS, 300Hz ) δppm, 3.20(m, 1H), 2.02(br, 1H), 1.00-1.70(m, 6H), 0.94(m, 1H), 0.90(t, J = 7.0Hz, 3H), 0.68(m, 1H), 0.30(m, 1H).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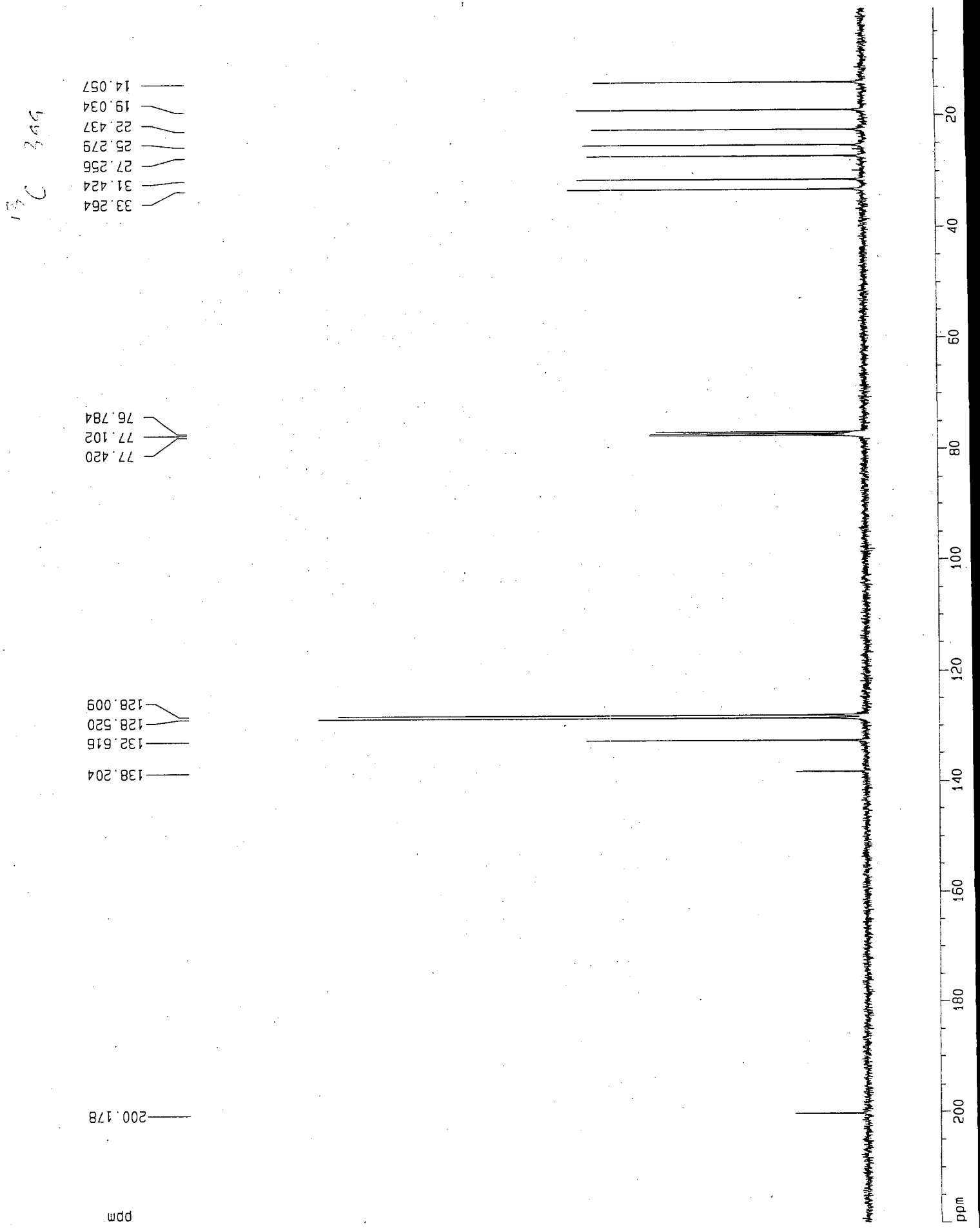
1.0
1.5
2.0
ppm


14.057
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77.420
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ppm
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40
60
80
100
120
140
160
180
200
ppm

File : CH-3__43.D01 RAC-CH-99-X-39 Type : Sample
Run : 01 Inst : 1022 LC Plus
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Collection : 13:02:57 Nov 12 1999 Method : LCTEST [ 10:56:45 Nov 12 1999 ]
Integration: 09:42:26 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]
Report : 09:42:28 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]

PERCENT ( AREA )

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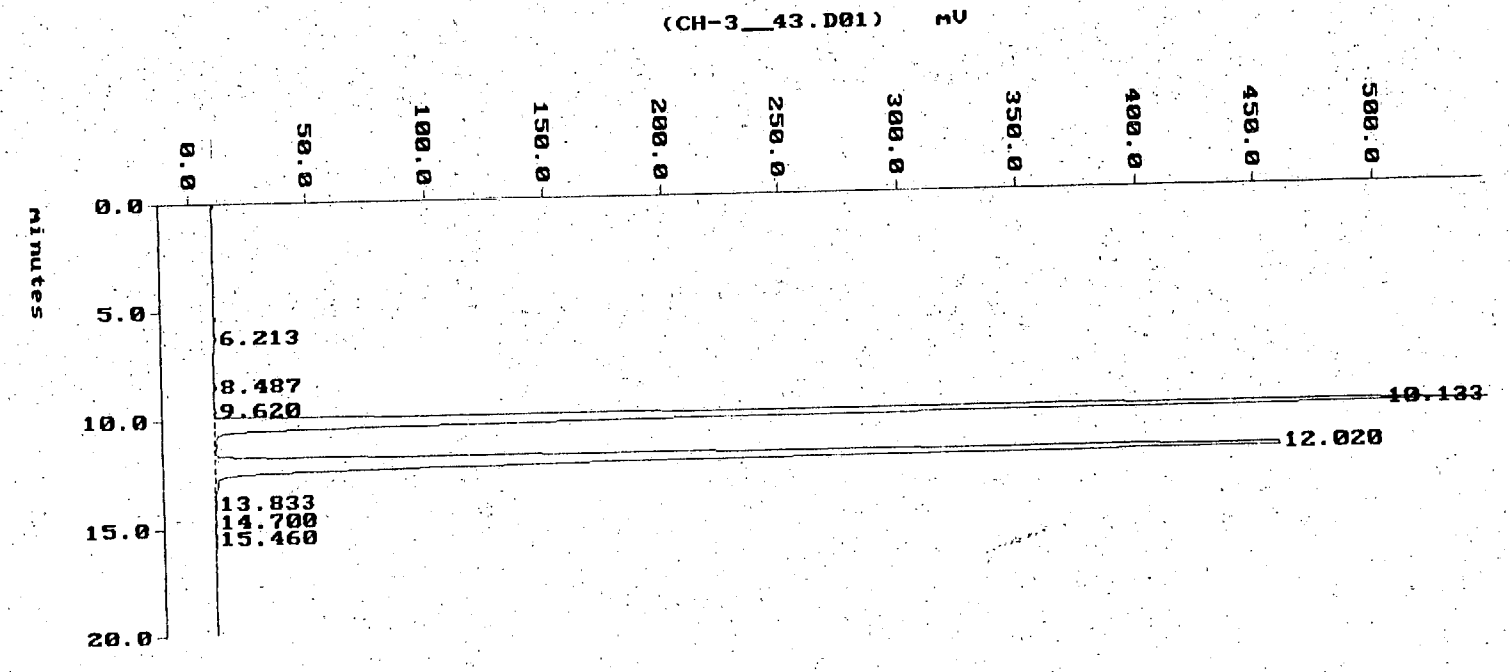
| 1 | 6.213 | 160976 | 1.0264 | V | 0.0888 | 0.1036 |
| 2 | 8.487 | 157422 | 1.2021 | V | 0.0868 | 0.1213 |
| 3 | 9.620 | 134355 | 0.8172 | T | 0.0741 | 0.0825 |
| 4 | 10.133 | 90022648 | 537.4796 | T | 49.6624 | 54.2297 |
| 5 | 12.020 | 90439496 | 449.4610 | T | 49.8923 | 45.3489 |
| 6 | 13.833 | 112000 | 0.4084 | T | 0.0618 | 0.0412 |
| 7 | 14.700 | 71092 | 0.2274 | T | 0.0392 | 0.0229 |
| 8 | 15.460 | 171360 | 0.4952 | V | 0.0945 | 0.0500 |

8 Peaks > Area Reject 181269344 Total Area
8 Peaks > Height Reject 991.117 Total Height



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Integration: 09:42:15 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]
Report : 09:42:21 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]

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| 1 | 3.613 | 750019 | 1.2445 | | 0.6945 | 0.1912 |
| 2 | 6.157 | 109975 | 0.6844 | V | 0.1018 | 0.1052 |
| 3 | 8.430 | 85577 | 0.7106 | V | 0.0792 | 0.1092 |
| 4 | 10.223 | 103392584 | 630.3599 | T | 95.7384 | 96.8727 |
| 5 | 11.223 | 358488 | 1.5705 | T | 0.3319 | 0.2414 |
| 6 | 12.183 | 3161596 | 15.8492 | T | 2.9275 | 2.4357 |
| 7 | 13.723 | 42954 | 0.1624 | | 0.0398 | 0.0250 |
| 8 | 18.470 | 93668 | 0.1281 | | 0.0867 | 0.0197 |

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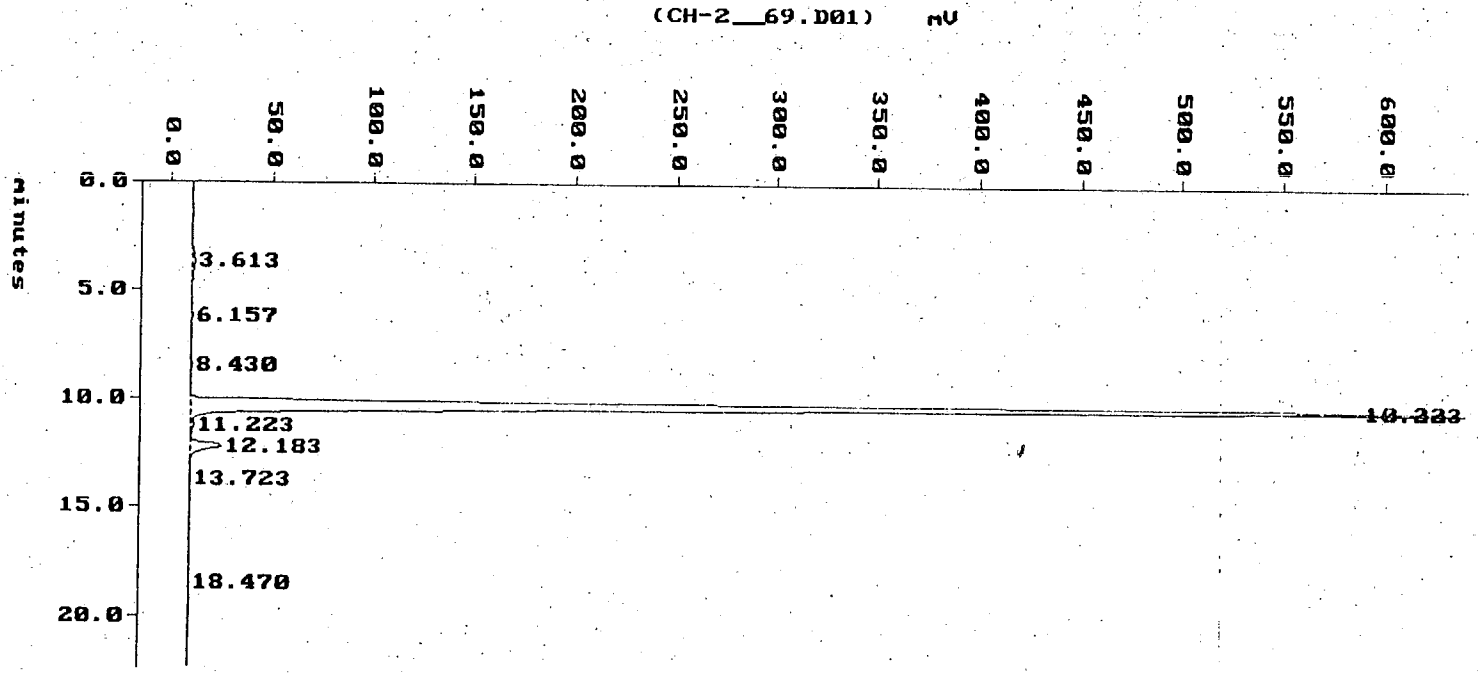

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Integration: 09:42:05 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]
Report : 09:42:08 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]

PERCENT ( AREA )

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| 1 | 6.153 | 108477 | 0.9219 | V | 0.1173 | 0.1852 |
| 2 | 8.447 | 191293 | 1.1072 | T | 0.2069 | 0.2225 |
| 3 | 9.733 | 91511 | 0.4605 | T | 0.0990 | 0.0925 |
| 4 | 10.293 | 44638996 | 267.9766 | T | 48.2766 | 53.8406 |
| 5 | 12.287 | 44762416 | 221.2081 | T | 48.4101 | 44.4441 |
| 6 | 13.860 | 212409 | 0.5258 | T | 0.2297 | 0.1056 |
| 7 | 15.873 | 140906 | 0.2988 | V | 0.1524 | 0.0600 |
| 8 | 17.773 | 1575128 | 3.6283 | T | 1.7035 | 0.7290 |
| 9 | 19.800 | 604026 | 1.2419 | T | 0.6532 | 0.2495 |
| 10 | 21.440 | 139909 | 0.3529 | | 0.1513 | 0.0709 |

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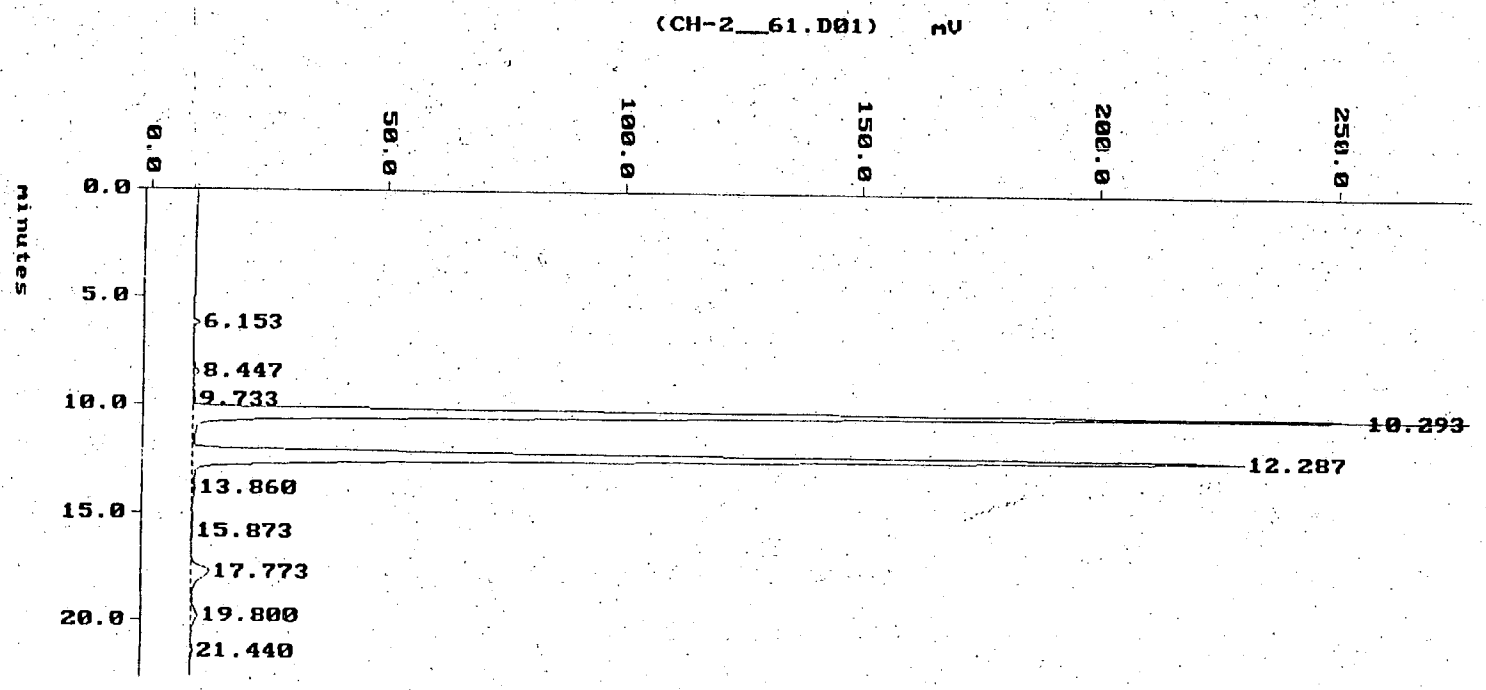

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Integration: 09:42:35 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]
Report : 09:42:43 Jan 13 2000 Method : LCTEST [ 08:43:45 Jan 13 2000 ]

PERCENT ( AREA )

| Pk # | RT | Area | Height | BC | Area Percent | Height Percent |
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| 1 | 1.233 | 124873 | 0.4118 | | 0.2933 | 0.1910 |
| 2 | 6.223 | 63535 | 0.2967 | V | 0.1492 | 0.1376 |
| 3 | 8.530 | 173858 | 0.5735 | | 0.4083 | 0.2661 |
| 4 | 10.190 | 1761459 | 10.5110 | V | 4.1366 | 4.8764 |
| 5 | 12.103 | 40410472 | 203.6706 | | 94.8997 | 94.4902 |
| 6 | 17.870 | 48093 | 0.0833 | | 0.1129 | 0.0386 |

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6 Peaks > Height Reject 215.547 Total Height