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Joel Jones Jr [a] & W. Bruce Kover [a]
[a] Instituto de Química, Departamento de Química Org[acaron]nica , Universidade Federal do Rio de Janeiro , Rio de Janeiro, R.J., 21945-970, Brazil E-mail:
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SYNTHESIS OF THE FOUR EPIMERIC TOSYLATES OF (5R)-2,3-EPOXY-5-ISOPROPENYL-CYCLOHEXANOL

Joel Jones Jr & W. Bruce Kover*

Instituto de Química, Departamento de Química Orgânica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, R.J. 21945-970, Brazil
E.Mail: IQG20001@UFRJ.BITNET.BR

Abstract: Described is the synthesis of the four optically pure epoxy-tosylates 5, 6, 9 and 12, each with four chiral centers determined, from a single starting material, (R)(-) carvone.

Epoxy-alcohols and their derivatives are frequently employed in synthetic schemes [1] and used to shed light on questions about the mechanism of reactions [2].

We describe in the present paper simple syntheses of the four epimeric tosylates 5, 6, 9 and 12 of (5R)-2,3-epoxy-5-isopropenyl-cyclohexanol with total control of all stereogenic centers. For their

synthesis we used a single starting material, (-)(R) carvone, 1. First, carvone (1) was epoxidized[3] to β-epoxy-carvone (2) which was reduced [4] with $NaBH_4$ / EtOH producing a mixture of 3 and 4 (1.7:1.0). The compounds 3 and 4 were separated on a spinning band distillation column, and taken to the tosylates 5 and 6 , using Fieser's methodology [5] . To synthesize compound 9, carvone was first reduced [6] to *cis*-carveol (7), epoxidized stereoselectively [7] to 8 and transformed in 9 following the same Fieser methodology[5].

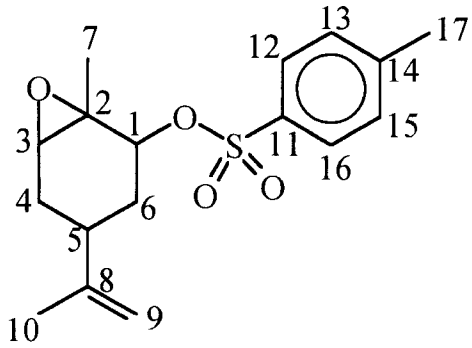
The initial plan for the synthesis of 11 involved epimerizing the hydroxyl group of 8. We tried diverse methodologies[8] without success. A suitable alternative was to oxidize [9,10] 8 to 10 (α-epoxy-carvone) and then reduce it with DIBAL [11], specifically, to 11[12], taking advantage of coordination of aluminum with the epoxide function. Compound 11 was transformed in 12 following Kabalka's method [13] because Fieser's method gave traces of 12 together with various decomposition products.

The table shows all [^{13} C] NMR data of 5, 6, 9 and 12 . Scheme I shows the general outline of the preparations with yields.

EXPERIMENTAL

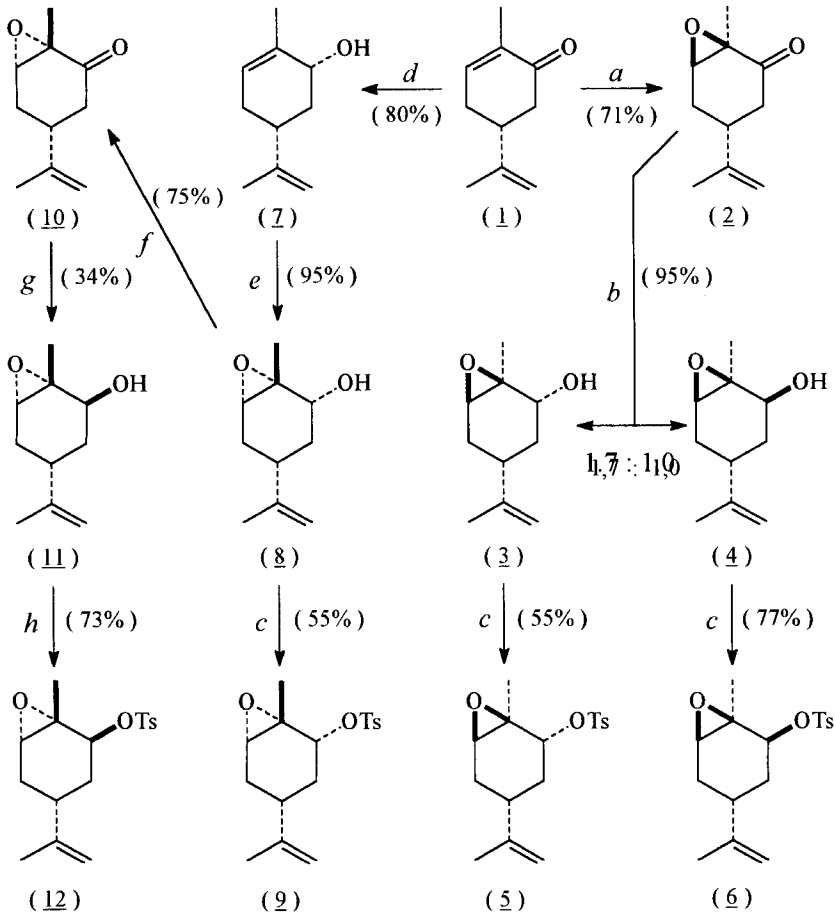
Carvone (R-(-)-carvone, Aldrich 98% ee GLC) was previously distilled. The solvents were distilled prior to use and other chemicals were used without further purification.

TABLE - [^{13}C] NMR



	Compounds				C	Compounds			
#	5	6	9	12	#	5	6	9	12
C_1	78.2	79.8	82.9	80.4	C_{10}	20.4	21.3	19.9	20.2
C_2	58.3	56.6	57.6	56.5	C_{11}	144.7	144.6	144.7	144.8
C_3	61.4	60.6	61.3	59.8	C_{12}	127.7	127.6	127.5	127.7
C_4	30.2	28.5	28.5	28.2	C_{13}	129.7	129.7	129.7	129.7
C_5	33.6	34.4	40.1	33.0	C_{14}	133.7	135.8	134.1	134.0
C_6	34.2	31.0	30.8	29.8	C_{15}	129.7	129.7	129.7	129.7
C_7	19.3	20.2	18.9	19.1	C_{16}	127.7	127.6	127.5	127.7
C_8	146.8	146.4	146.3	147.0	C_{17}	21.6	21.5	21.5	21.6
C_9	109.8	110.0	110.1	109.7					

SCHEME I



a: H_2O_2 / MeOH / KOH ; *b*: $NaBH_4$ / EtOH ; *c*: TsCl / Py ; *d*:$LiAlH_4$ / THF ; *e*: AcOOH / CH_2Cl_2 ; *f*: CrO_3 / Py / CH_2Cl_2 ; *g*: DIBAL / Toluene ; *h*: TsCl / Py / $HCCl_3$

The reactions were monitored by TLC using Merck silica gel 60 HF_{254}. Flash chromatography (as described by Still [14]) used Merk silica gel 60, 400-230 mesh.

Melting points were determined on a Kofler apparatus and are corrected.

[^{1}H] and [^{13}C] NMR spectra of $CDCl_3$ solutions (TMS as internal standard) were recorded on Varian XL-100 (100 Mz).

HRGC analyses were performed on a HP 5890 gas chromatograph with FID by using a 20 m, 0.25 (i.d.), and 0.25 μm (phase thickness) OV-31 (OH) glass capillary column and H_2 (rate flow: 50 cm/s) as carrier gas (split: 1/20). Oven temp.: 60° C (2 min) to 230° C (5 min.), 10° C/min; injector temp: 200° C; detector temp.: 220° C.

Optical rotations were measured with a JASCO-DIP-370 digital polarimeter.

IR spectra were obtained using a Perkin Elmer 257 spectrometer.

MS spectra were determined on HP 5987-A HRGS-MS and Micromass LTD, Micromass 12, Winsford England spectrometers using electron impact (70 eV).

Spinning band , Nester / Faust , teflon band (60 cm)

CHN analyses were performed on Perkin-Elmer 2400 CHN Elementar Analysis.

(2R, 3R, 5R) 2,3-Epoxy-5-isopropenyl-2-methyl-cyclohexanone (β-Epoxy-carvone) (2)

To a 1-L flask were added 64 g of KOH, 240 mL of MeOH and 80 mL of water. After this solution was cooled to -15° C, 80 g (0.53 mol) of

carvone (1) in 80 mL of MeOH, (previously cooled to -15° C) , was added. The flask was placed in a refrigerating bath at -15° C and 60 mL of H_2O_2 (30%), previously cooled to -15° C , was added. The internal temperature rose to 40° C. When the temperature returned to 4° C, 68 mL of H_2O_2 as added. The solution was stirred for 3 h at 4° C, and then poured into 400 mL of water and extracted with ether (4 x 150 mL). The organic phase was washed with water (1 x 100 mL), 5 % aqueous hydrochloric acid , water (1 x 100 mL), dried (over anhydrous $MgSO_4$) and distilled at 70° C / 0.05 torr to give 67 g of 2 (71%)

IR (neat) ν: 3060, 2980, 1710, 1680, 1440, 1375, 1110, 1040, 880 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.33 (s, 3H); 1.72 (s, 3H); 1.7 - 2.9 (m, 5H); 3.32 (dd, 1H, J=1 Hz and 3 Hz); 4.7 (m, 2H) ;

[^{13} C] NMR (TMS, $CDCl_3$): 204.9; 146.1; 110.3; 61.2; 58.6; 41.7; 35.0; 28.7; 20.5; 15.2 ppm [Lit.[10] , 204.9, 146.0, 110.2, 61.0, 58.4, 41.5, 34.7, 28.4, 20.3, 15.0 ppm]

MS (%) : m/z 166 (2); 151 (4); 137 (10); 123 (45); 109 (25); 95 (35); 85 (50); 67 (70); 43 (100)

(1R, 2S, 3R, 5S)-2,3-Epoxy-5-isopropenyl-2-methyl-cyclohexenol (3) and (1S, 2S, 3R, 5S)-2,3-Epoxy-5-isopropenyl-2-methyl-cyclohexenol (4)

To a 500-mL flask as added, 12 g of $NaBH_4$ in 250 mL of EtOH . The suspension was stirred until homogenous, 20 g of 2 in 100 mL of EtOH as added and the solution was stirred for 24 h at room temperature. It was poured into 1000 mL of water, extracted with ether (4 x 200 mL), the extract dried over anhydrous $MgSO_4$, and evaporated to give 19.2 g (95%

yield) of 3 / 4 mixture (1.7 : 1.0 by HRGC). Spinning band distillation produced 5.8 g (30%) of 4 (116-118° C / 2-3 torr; lit.[4] 115-120° C / 5 torr) and 9.6 g (47%) of 3 (127-8° C / 2-3 torr; lit.[4] 120-121° C / 2 torr).

Compound 3 :

$[\alpha]_D^{25}$ - 37.1 (c. 1.55, $CHCl_3$), [Lit.[4] $[\alpha]_D^{32}$ - 36 (c. 4.2, acetone)]

IR (neat),:ν 3430; 3060; 2950; 1635; 1440; 1370; 1040; 890; 830 cm^{-1}; free hydroxyl band in CCl_4 at 3616 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$) : δ 1.12 (m, 1H); 1.28 (m, 1H); 1.42 (s, 3H); 1.75 (s, 3H); 1.75-2.50 (m, 3H); 2.35 (m, 1H); 3.15 (s, 1H); 3.90 (d, 1H); 4.72 (s, 3H); [Lit.[4], δ, 1.34 (s, 3H), 1.74 (s, 3H), 3.04 (s. 1H), 3.84 (1H), 4.74 (2H)]

[^{13}C] NMR (TMS, $CDCl_3$): 148.1; 109.3; 69.1; 62.0; 60.7; 36.3; 34.5; 30.8; 20.6; 19.2 ppm

MS (%) : m/z : 150 (8); 135 (15); 121 (20); 107 (20); 95 (20); 87 (98); 74 (42); 67 (38); 55 (35); 43 (100), (molecular ion, m/z 168, not found)

Compound 4 :

$[\alpha]_D^{25}$ - 54 (c. 1.06, $CHCl_3$), [Lit.[4] $[\alpha]_D^{25}$ - 60]

IR (neat) ν: 3430, 3060, 2960, 1635, 1435, 1370, 1248, 1060, 950, 890, 860 cm^{-1}, free hydroxyl band in CCl_4 at 3552 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.46 (s, 3H); 1.49 (d, 1H, J=2Hz); 1.65 (d, 1H, J=2Hz); 1.73 (s, 3H); 1.78 (m, 1H); 2.10 (d, 1H, J=4Hz); 2.24 (s, br, 1H); 2.24 (s, br, 1H); 3.30 (t, 1H, J=2Hz); 3.92 (t, 1H, J=4Hz); 4.78 (s, br, 2H); [Lit.[4] , δ, 1.40 (s, 3H), 1.70 (s, 3H), 3.52)1H, t, J=1,5 Hz), 3.79 91H), 4.69 (2H)]

[^{13}C] NMR (TMS, $CDCl_3$): 147.4; 109.3; 67.9; 62.8; 57.7; 35.5; 32.0; 30.0; 21.4; 21.0 ppm

MS (%) m/z: 150 (3); 135 (11); 121 (6); 107 (28); 91 (16); 87 (16); 74 (30); 67 (35); 55 (30); 43 (100), (molecular ion, m/z 168, not found)

(1R, 2R, 3S, 5S)-2,3-Epoxy-5-isopropenyl-2-methyl-cyclohexenol (8)

In a two-neck 250-mL round-bottomed. flask, were placed 20 g (0.13 mol) of *cis*- carveol (7)[6] in 80 mL of chloroform and 35.6 g of Na_2CO_3 . The flask was fitted with a reflux condenser and an addition funnel containing 40.6 g of 30 % peracetic acid in acetic acid. While cooling in an ice bath, peracetic acid was added at a rate which gave little reflux. After complete addition the suspension was stirred for 2.5 h at 0-5°C, and poured into 400 mL of saturated aqueous solution of sodium carbonate. The organic phase was separated and joined to the chloroform extract (1 x 100 mL), of the aqueous phase. This solution was washed with water (1 x 30 mL), saturated aqueous solution of sodium thiossulphate (1 x 30 mL), dried (anhydrous Na_2SO_4), and distilled at 110-5° C / 3-4 torr [lit.[4] 115-120° C / 2 torr] to give 21g of 8 (90%); $[\alpha]_D^{25}$ - 27 (c. 1.04, $CHCl_3$), [Lit.[4] $[\alpha]_D^{25}$ - 29 (c 5.1, acetone)], **IV** (neat) ν: 3400, 3060, 2960, 2920, 1640, 1440, 1370, 1050, 890, cm^{-1}; free hydroxyl band in CCl_4 at 3572 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.0-1.5 (m, 2H); 1.48 (s, 3H); 1.6-2.7 (m, 3 H); 1.65 (s, 3H); 1.88 (s, br, 1H); 3.26 (d, 1H, J=5Hz); 3.85 (dt, 1H, J=9Hz and 5Hz); 4.68 (s, br, 2H); [Lit.[4], δ, 1.40 (s, 3H), 1.72 (s, 3H), 3.03 (d, 1H, J=4.5 Hz), 3.85 (b, 1H), 4.73 (b, 1H)]

[^{13}C] NMR (TMS, $CDCl_3$) :147.5; 109.5; 71.9; 62.0; 60.5; 40.4; 33.7; 29.1; 20.1; 19.1 ppm

MS (%) : m/z: 168 (4); 150 (8); 139 (8); 135 (10); 125 (50); 109 (80); 95 (85); 85 (75); 79 (78); 71 (100); 69 (90); 67 (95); 55 (80); 43 (48)

(2S, 3S, 5R) 2,3-Epoxy-5-isopropenyl-2-methyl-cyclohexanone (α-epoxy-carvone) (10)

To a 500-mL flask fitted with $CaCl_2$ tube, 270 mL of anhydrous dichloromethane and 17.3 mL of dry pyridine were added. After cooling with an ice bath, 10.71 g of CrO_3 as added in small portions. The ice bath was removed and the solution allawed to warm to room temperature (a dark red wine color was formed) and 3g (1.8×10^{-2} moles) of 8 in 2 mL of CH_2Cl_2 were added. Immediately a dark precipitate formed. The suspension was stirred for 30 min, the organic phase removed and the residue was washed with ether (4 x 50 mL). All organic phases were combined and washed with 5% NaOH solution (1 x 150 mL), 5% HCl solution (1 x 150 mL), 5% $NaHCO_3$ solution, brine, then dried over $MgSO_4$ and distilled at 70° C / 2 torr producing 2.0 g of 10 (67%)

IR (neat) ν: 3060, 2980, 2940, 1705, 1635, 1440, 1370, 1130, 890, cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.40 (s, 3H); 1.71 (s, 3H); 1.8-2.4 (m, 3H); 2.4-3.0 (m, 2H); 3.45 (d, 1H, J=5Hz); 4.72 (s, br, 2H)

[^{13}C] NMR (TMS, $CDCl_3$): 207.8; 145.8; 110.4; 64.8; 59.2; 45.0; 40.5; 29.0; 19.6; 14.8 ppm; [Lit.[10] , 208.2, 146.0, 110.7, 64.8, 59.3, 44.9, 40.5, 28.9, 19.6, 14.8 ppm]

MS (%) : m/z 166 (1); 150 (2); 135 (4); 123 (10); 109 (80); 108 (65); 95 (30); 82 (30); 81 (34); 79 (32); 67 (65); 55 (34); 43 (100)

(1S, 2R, 3S, 5S)-2,3-Epoxy-5-isopropenyl-2-methyl-cyclohexenol (11)

In a 100-mL flask fitted with a rubber septum as placed 6.2 mL of 1.5 N DIBAL solution in toluene. After cooling to 0° C, 1.2 g (7.23×10^{-3} mol) of 10 in 38 mL of anhydrous toluene as added by syringe. The solution was stirred for 6 h at 0° C under nitrogen. A saturated solution of NH_4Cl was added and the mixture was stirred for 30 min. The aqueous phase was extracted with ether (2 x 10 mL). The ether extract was joined with the organic phase and both were washed with water (1 x 20 mL). After drying over anhydrous $MgSO_4$, the solvent were evaporated to give 1.15 g of a yellow oil. Flash chromatography (hexane/ AcOEt, 5:1) produced 400 mg of 11 (34%, R_f= 0.66) , 210 mg of 8 (17%, R_f= 0.53).

IR (neat)ν: 3400, 3060, 2980, 2940, 1640, 1430, 1370, 1250, 1100, 1080, 1050, 895, 860, 830 cm^{-1};

MS (%) : m/z 168 (1); 150 (3); 135 (8); 125 (8); 109 (45); 97 (30); 95 (38); 85 (38); 79 (38); 71 (42); 69 (35); 67 (50); 55 (35); 43 (100)

General Procedure for tosyl compounds 5, 6 and 9

The epoxy-alchool 3, 4 or 8, tosyl chloride and pyridine (dried over BaO) were placed in a flask, and stirred for 16 h at -18° C. Pouring the mixture into a water/ice slurry led to a white precipitate which after stirring was vacuum filtered and recrystalised from hexane.

(1R, 2R, 3R, 5R)-2,3-Epoxy-5-isopropenyl-2-methyl-1-tosyl-cyclohexyl (5) :

Using 4.4 g of 3 , 9.95 g of tosyl chloride and 80 mL of pyridine, produced 4.6 g of 5 (55% - mp= 67-8° C). $[\alpha]_D^{25}$ - 43.7 (c. 1.00, $CHCl_3$), CHN analysis, found C 63.04 %, H 6.96%; calc. C 63.35%, H 6.83%

IR (2% in KCl) ν: 3080, 3050, 2960, 2920, 1640, 1590, 1440, 1350, 1180, 950, 880, 850, 770, 720 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.2 (s, 3H); 1.2-1.6 (m, 2H); 1.64 (s, 3H); 1.65-2.40 (m, 3H); 2.46 (s, 3H); 3.10 (s, br, 1H); 4.65 (s, br, 2H); 4.72 (s, br, 1H); 7.32 and 7.80 (dd, 4H)

MS (%) : m/z 241(10); 172 (25); 155 (48); 150 (98); 135 (49); 121 (77); 107 (100); 93 (30); 92 (28); 91 (25); 41 (52), (molecular ion, m/z 322, not found)

(1S, 2R, 3R, 5R)-2,3-Epoxy-5-isopropenyl-2-methyl-1-tosyl-cyclohexyl (6)

Using 3.0 g of 4 , 5.52 g of tosyl chloride and 30 mL of pyridine, produced 4.4 g of 6 (77% - mp= 87-8° C). $[\alpha]_D^{25}$ - 46.0 (*c* 1.00, $CHCl_3$), CHN analysis, found: C 63.29%, H 6.83%%; calc. C 63.35%, H 6.83%

IR (2% in KCl): 3080, 3050, 2960, 2920, 1635, 1590, 1440, 1350, 1170, 880, 810 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.22 (s, 3H); 1.66 (s, 3H); 1.4-2.4 (m, 5H); 2.46 (s, 3H); 3.14 (dd, 1H, J=3 and 1.5 Hz); 4.70 (d, 2H); 4.85 (d, 1H, J=5Hz); 7.3 and 7.8 (dd, 4H, J=4Hz)

MS (%) : m/z 307 (1); 241 (2); 213 (1); 172 (2); 155 (12); 150 (12); 107 (45); 91 (65); 65 (30); 43 (100), (molecular ion, m/z 322, not found)

(1S, 2S, 3S, 5R)-2,3-Epoxy-5-isopropenyl-2-methyl-1-tosyl-cyclohexyl (9)

Using 4.4 g of 8 , 9.95 g of tosyl chloride and 80 mL of pyridine, produced 4.5 g of 9 (55% - mp= 85-6° C). $[\alpha]_D^{25}$ - 25.4 (*c* 1.00 $CHCl_3$) CHN analysis: found C 63.30%, H 6.79%%; calc. C 63.35%, H 6.83%

IR (2% in KCl) ν: 3060; 2970; 2910; 1650; 1600; 1440; 1350; 1180; 1090; 950; 870; 820; 780; 670 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.28 (s, 3H); 1.64 (s, 3H); 1.40-2.40 (m. 5H); 2.47 (s, 3H); 3.10 (d, 1H, J=4Hz); 4.65 (d, 2 H); 4.90 (dd, 1H, J=6Hz and 9Hz); 7.30 and 7.80 (dd, 2H)

MS (%) : m/z; 264 (2); 172 (10); 167 (8); 155 (43); 150 (12); 135 (10); 107 (80); 93 (70); 92 (95); 91 (91); 57 (100), (molecular ion, m/z 322, not found)

(1R, 2S, 3S, 5R)-2,3-Epoxy-5-isopropenyl-2-methyl-1-tosyl-cyclohexyl (12)

To a 5 mL flask were added 150 mg (9 x 10^{-4} mol) of 11 in 1.0 mL of chloroform and 0.225 mL of pyridine . The flask was placed in an ice bath and 336 mg of tosyl chloride were added. The solution was stirred until total consumption of 11 (monitored by TLC, approximately 17 h). Then, 3.0 mL of ether and 1.0 mL of water were added, the organic phase

was separated and washed with 5% HCl, 5% $NaHCO_3$, dried over anhydrous $MgSO_4$, and the solvent evaporated to give a yellow oil. Flash chromatography (hexane/ AcOEt, 5:1) of the oil produced 210 mg (73%) of 12 (mp=100-2° C , R_f= 0.80).

IR (2% in KCl) ν : 3050, 3030, 2980, 2984, 1660, 1600, 1450, 1380, 1180, 1100, 1030, 950, 920, 890, 820, 740, 710 cm^{-1}

[^{1}H] NMR (TMS, $CDCl_3$), δ : 1.20 (s, 3H); 1.5-2.4 (m, 5H); 2.50 (s, 3H); 3.06 (d, 1H, J=5Hz); 4.62 (d, 2H); 4.90 (t, 1H, J=3Hz); 7.38 and 7.94 (dd, 4H)

MS (%) ; m/z: 264 (2); 173 (3); 167 (5); 155 (18); 150 (20); 135 (30); 121 (18); 107 (70); 91 (100); 79 (28); 65 (30), (molecular ion, m/z 322, not found)

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