HETEROCYCLES, Vol. 99, No. 2, 2019, pp. 1423 - 1433. © 2019 The Japan Institute of Heterocyclic Chemistry
Received, 2nd October, 2018, Accepted, 7th November, 2018, Published online, 5th February, 2019
DOI: 10.3987/COM-18-S(F)90

A NOVEL ROUTE TO (*R*)-2-(3-CHLOROPHENYL)PROPAN-1-AMINE, A KEY INTERMEDIATE FOR THE SYNTHESIS OF LORCASERIN

Ivana Gazic Smilovic,[1] Sven Nerdinger,[2]* Sandro Neuner,[3,4] Herwig Schottenberger,[3] Thomas Gelbrich,[3] and Klaus Wurst[3]

[1] Lek Pharmaceuticals DD, Kolodvorska 27, 1234 Mengeš, Slovenia. [2] Sandoz GmbH, Biochemiestrasse 10, 6250 Kundl, Austria. [3] University of Innsbruck, Faculty of Chemistry and Pharmacy, Innrain 80-82, 6020 Innsbruck, Austria. [4] University for Health Sciences, Medical Informatics and Technology, Eduard-Wallnöfer-Zentrum 1, 6060 Hall in Tirol. E-mail: sven.nerdinger@sandoz.com

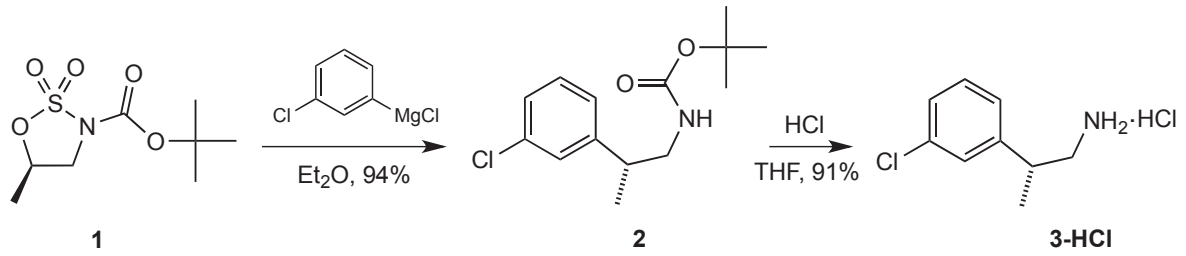
This paper is dedicated to Professor Tohru Fukuyama on the occasion of his 70th birthday.

Abstract – A new and efficient three-step synthesis of (*R*)-2-(3-chlorophenyl)propan-1-amine is reported, which serves as an intermediate in the synthesis of the antiobesity drug lorcaserin. The key step is a chiral resolution due to the formation of a salt with l-(-)-3-phenyllactic acid. The structure of the relevant salt phase is reported.

Obesity is defined as excessive fat accumulation and poses a substantial public health challenge. Recent estimates indicate that roughly >650 million adults worldwide are obese.[1] Whereas lifestyle modification is considered first-line therapy for obese patients, concomitant pharmacotherapy may be beneficial to maintain the weight loss achieved. (*R*)-8-Chloro-1-methyl-2,3,4,5-tetrahydro-1*H*-benzo[*d*]azepine, also known as lorcaserin, is one of the few drugs currently on the market for the treatment of obesity.[2-4] There are several methods of preparation disclosed in the patent literature, frequently necessitating separation of enantiomers.[5-10] We recently reported a new synthesis of enantiopure lorcaserin using an enantiopure cyclic sulfamidate derivative for the introduction of the chiral center.[11]

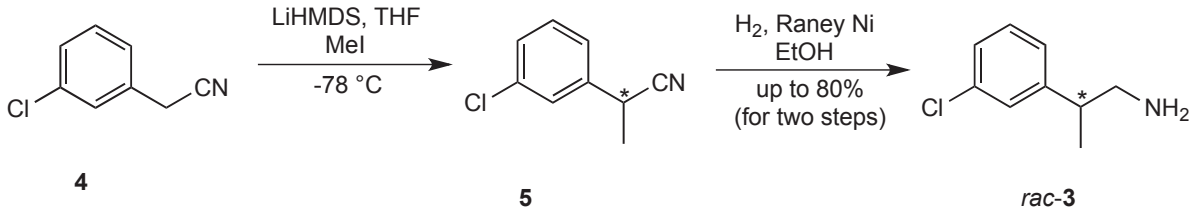
Herein we describe a new and short synthesis of an enantiopure intermediate which can be converted in three steps into lorcaserin.[11]

As shown in Scheme **1,** (*R*)-2-(3-chlorophenyl)propan-1-amine (**3**) was obtained via selective ring opening[12] of cyclic sulfamidate **1**,[13] prepared from commercial (*S*)-(-)-1-amino-2-propanol. Subsequent removal of a Boc group from **2** provided the enantiomerically pure amine **3** which was isolated as hydrochloride salt **3-HCl**.[11]



Scheme 1. Preparation of chiral amine **3** hydrochloride

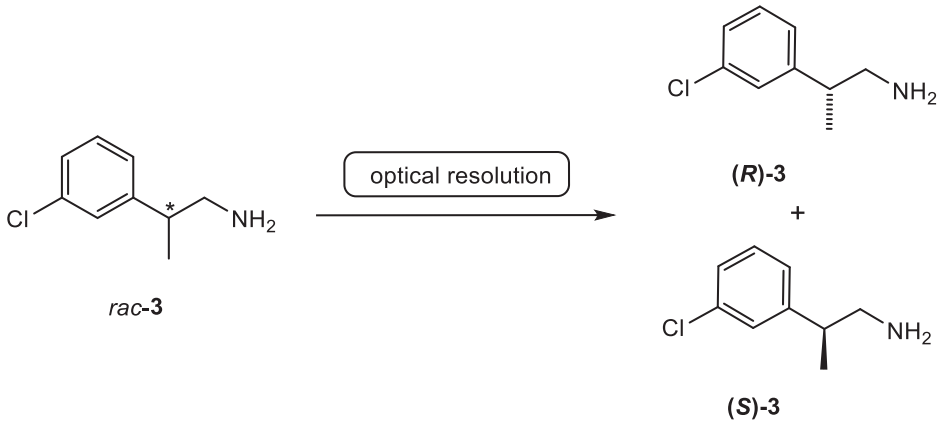
Since sulfamidates can be very cost-relevant when used on a larger scale, we were looking for an improved synthesis of the chiral intermediate with a limited number of steps and increased yield. Starting from commercially available 3-chlorobenzeneacetonitrile (**4**), alkylation with iodomethane in the presence of LiHMDS at -78 °C, and subsequent hydrogenation of the cyano-group with Raney-Ni in ethanol gave the racemic amine (**3**) in 58% yield over two steps. Notably, alternatives using sodium hydride as a base during the alkylation, and BH_3•THF for the reduction of the cyano-group gave a lower yield (32% over two steps). By using dimethyl carbonate and K_2CO_3 as base and performing the reaction in an autoclave at elevated temperatures yields could be improved to nearly 80% for these two steps.

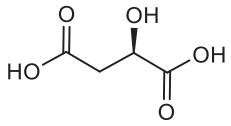
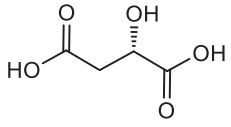
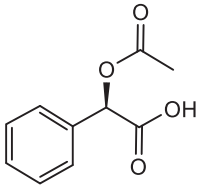
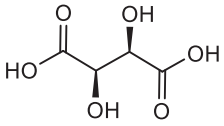
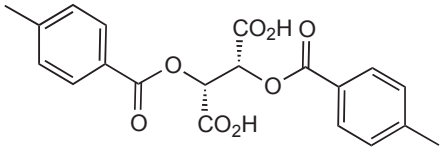
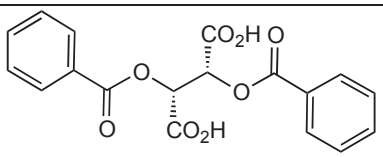


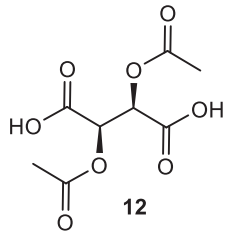
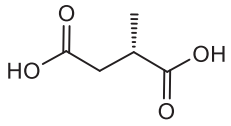
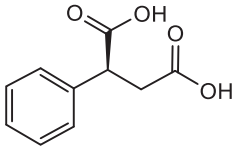
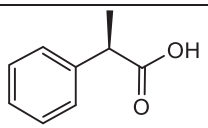
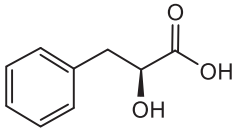
Scheme 2. Preparation of racemic amine *rac*-**3**

Next, the optical resolution of the racemic amine *rac*-**3** was investigated.

Table 1. Chiral resolution of racemic amine *rac*-**3**



entry	chiral acid	ee (%)[1)]	yield (%)
1	 **6**	10	not isolated
2	 **7**	10.6 (undesired enantiomer)	not isolated
3	 **8**	n.a. (racemic)	not isolated
4	 **9**	n.a. (racemic)	not isolated
5	 **10**	3	not isolated
6	 **11**	6 (undesired enantiomer)	not isolated

7	 **12**	10.6	not isolated
8	 **13**	4.5	not isolated
9	 **14**	14.8	not isolated
10	 **15**	74.1	20
11	 **16**	80.5	33

1) Determined via chiral HPLC

The use of both enantiomers of malic acid in the optical resolution resulted in low ee-values (entries 1 and 2). Similar results were obtained when different enantiomerically pure derivatives of tartaric acid were used (entries 4 to 7). The use of other chiral acids e.g. (*R*)-acetylmandelic acid, (*S*)-2-methylsuccinic acid or (*S*)-2-phenylsuccinic acid (entries 3, 8 and 9) resulted in unsatisfactory values for enantiomeric excess as well. Other enantiomerically pure acids which were investigated and not listed in the Table, e. g. (*S*)-2-hydroxyisocaproic acid, (*R*)-2-hydroxyisovaleric acid, (*R*)-mandelic acid, (*S*)-2-chloropropionic acid and (*R*)-lactic acid chiral did not form any crystalline salts together with *rac*-**3**. A good level of enantiomeric excess was observed when using (*R*)-2-phenylpropionic acid (entry 10) which could be improved from 74% to 98% ee by a single recrystallization in ethanol. Fortunately, by switching to (*S*)-3-phenyllactic acid, the level of enantiomeric excess increased to 80% (entry 11) which could again be improved to 97% ee by a single recrystallization, this time using isopropanol as solvent and (*R*)-**3** could be isolated in 33% yield.

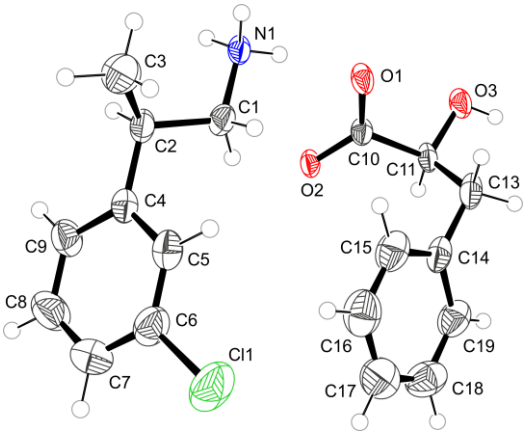


Figure 1. a) Molecular structure of (*R*)**-3-lact** showing non-H atoms as thermal ellipsoids drawn at the 50% probability level.

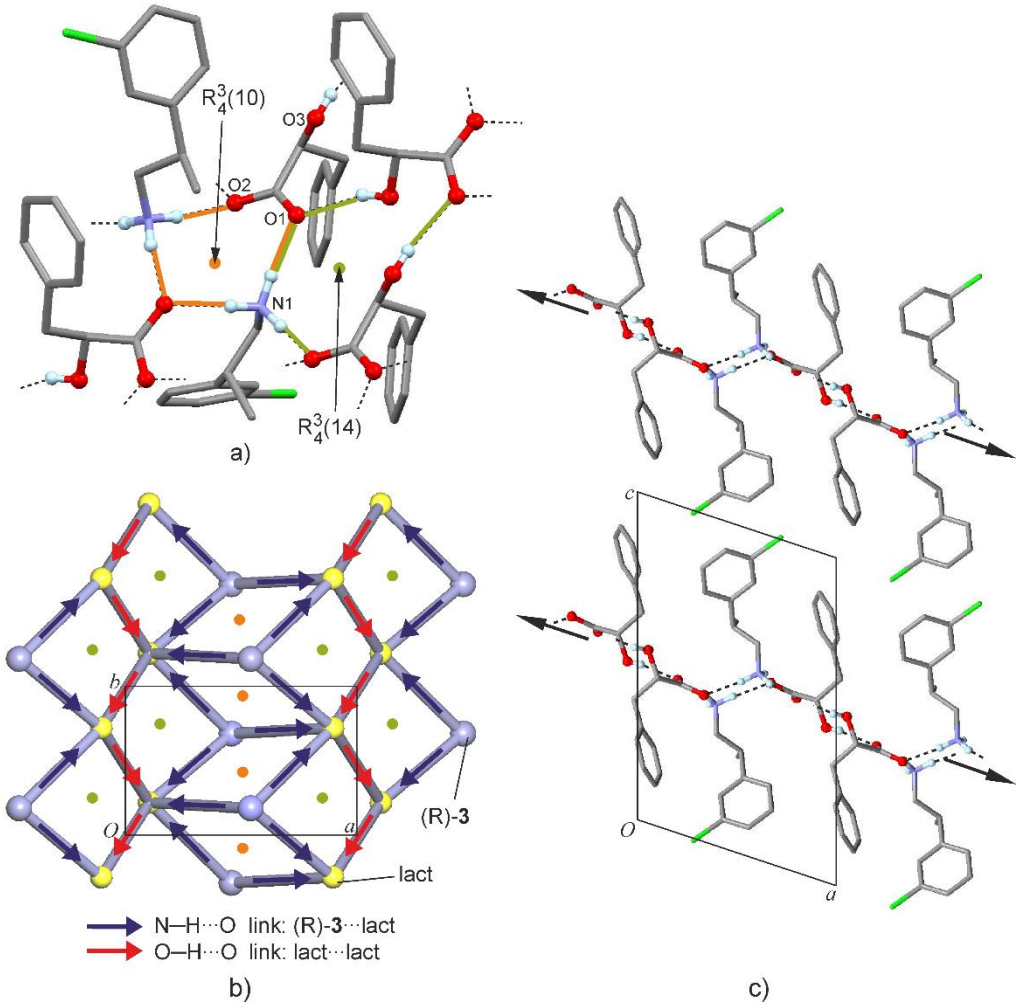
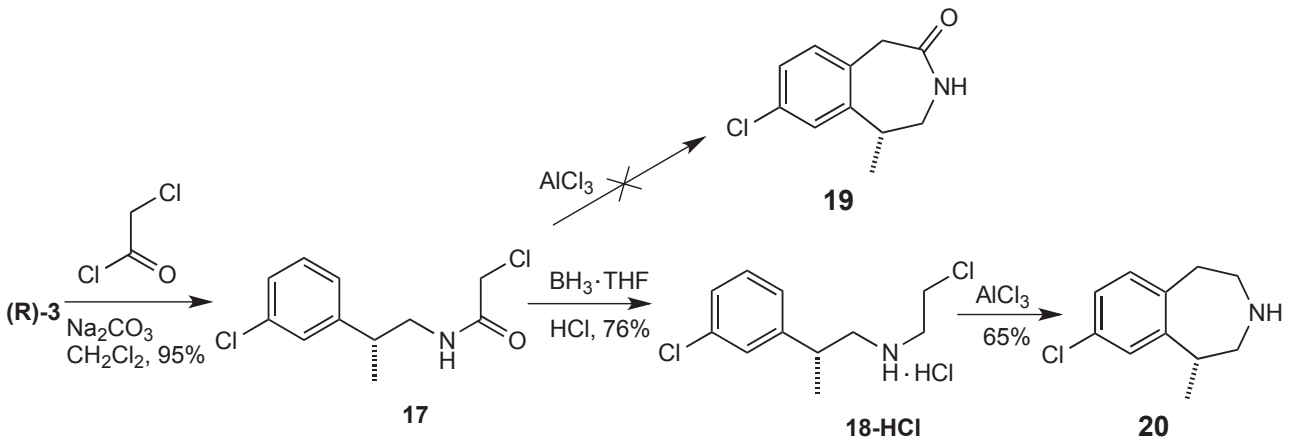


Figure 2. Crystal structure of (*R*)**-3-lact**: a) detail of the H-bonded layer structure showing fused $R^3_4(10)$ and $R^3_4(14)$ rings, colored orange and green, respectively; b) topology graph according to Hursthouse *et al.*[14] showing the underlying **3,5L24** net of the H-bonded structure with (*R*)**-3** (blue) and lact (yellow) units serving as three-connected and five-connected nodes, respectively; different ring types are labelled orange and green in correspondence with a); c) stacking of two adjacent H-bonded layer structures.

The crystal structure of the (*R*)**-3-lact** formed by the crystallization of (*R*)**-3** with (*S*)-3-phenyllactic acid was determined in order to establish the structural basis for the enantiospecific crystallization behavior of **3** in this system (Figure 1). The protonated primary amine of (*R*)**-3** forms one N–H···O bond to each of three different carboxylate anions of 3-phenyllactic acid (lact). The lact unit accepts in turn three N–H···O bonds from three different (*R*)**-3** molecules and also forms an (hydroxyl)O–H···O(carboxylate) interaction with a neighboring lact unit so that both carboxylate O atoms accept two H-bonds each. Altogether, an H-bonded layer structure parallel to the ab plane is formed (Figure 2a) which contains two different rings of four molecules which can be characterized as $R^3_4(10)$ and $R^3_4(14)$.[15] Its underlying net has the **3,5L24** topology, with (*R*)**-3** and lact units serving as three- und five-connected nodes, respectively (Figure 2b). The H-bonded layers are stacked along the *c* axis (Figure 2c). All classical H-bond donor sites of (*R*)**-3** and lact are employed within a dense chiral H-bonded layer structure, and the hypothetical replacement of every other (*R*)**-3** unit with (*S*)**-3** would probably require major intra-layer geometrical adjustments and therefore make such an arrangement unviable. Likewise, a hypothetical crystal structure in which the H-bonded (*R*)**-3-lact** layers are alternately stacked with analogous (*S*)**-3-lact** layers are likely disadvantaged in comparison to the respective phases with a single layer type.



Scheme 3. Three-step synthesis of enantiopure lorcaserin **20** via amide **17**

Finally the chiral amine (*R*)**-3** was converted in a straight manner in three steps and with 47% overall yield to enantiopure lorcaserin **20** as shown in scheme **4**.[11] Further attempts to modify this route e. g. via *Friedel Crafts*-reaction of **17** were unsuccessful since the desired product **19** could be detected only as minor product in the mixture.

EXPERIMENTAL

Reagents and solvents were purchased from Sigma-Aldrich. NMR spectra were recorded with a Bruker Avance III 500 spectrometer. IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument. High resolution mass spectra were measured with a Finnigan MAT 95 mass spectrometer. HPLC was measured on Waters Alliance 2695 with Dual or PDA UV detector, column: Chiralpak AD-H 250x4.6 mm, mobile phase: A: *n*-hexane; B: 90% n-hexane/10% EtOH/0.20% butylamine; 75%A/25%B, flow 1.20 ml/min, tr(e1) = 12.7 min, tr(e2) = 19.3 min. UPLC was measured on Waters Acquity UPLC with UV detector. LC/Mass spectra were recorded on an Agilent 1200 Series with a Bruker Esquire HCT mass detector.

2-(3-Chlorophenyl)propionitrile (5)

To a solution of 2-(3-chlorophenyl)acetonitrile (**4**) (66.0 mmol; 10.0 g) in dry THF (250 mL) under nitrogen atmosphere at -78 °C was added LiHMDS (66.0 mmol; 66.0 mL; lM in THF). The mixture was stirred for 1 h at -78 °C followed by addition of methyl iodide (66.0 mmol; 4.20 mL). After stirring at -78 °C for 1 h, the reaction mixture was allowed to warm to room temperature and stirred for 2 h. Afterwards, it was quenched with water (200 mL) and extracted with EtOAc (3 x 150 mL). The combined organic phases were dried over $MgSO_4$, filtered and evaporated to the dryness. After purification by flash chromatography (silica gel; mobile phase: *n*-heptane/EtOAc, EtOAc gradient 2-20%), an oily product (**5**) was obtained (7.60 g; 72%). The ^{1}H-NMR data were in agreement with known literature data.[16,17] – ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 3H), 7.26 (m, lH), 3.89 (q, lH, J = 7.2 Hz), 1.65 (d, 3H, J = 7.4 Hz) ppm. – ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.9, 135.0, 130.5, 128.4, 127.0, 125.0, 121.0, 31.0, 21.3 ppm.

Alternative procedure:

a) 2-(3-Chlorophenyl)acetonitrile (**4**) (3.00 g, 19.9 mmol) was dissolved in dry THF (50.0 mL) and cooled to 0 °C under a nitrogen atmosphere. Sodium hydride (1.20 g, 29.9 mmol) was added slowly in several portions. The resulting suspension was stirred at 0 °C for 40 min. Methyl iodide (1.90 mL, 29.9 mmol) was added slowly and the mixture was stirred at 0 °C for 1 h and then warmed up to room temperature. Water (50.0 mL) was added and the mixture was extracted with EtOAc (100 mL). The organic phase is washed first with brine (50.0 mL) and then with 20% aqueous solution of sodium thiosulfate, dried over $MgSO_4$ and evaporated under reduced pressure to give 3.71 g of a yellow to orange oil. After purification by flash chromatography (silica gel; mobile phase *n*-heptane/EtOAc, EtOAc gradient 7-60%), an oily product is obtained (1.51 g, 46%).

b) 2-(3-Chlorophenyl)acetonitrile (**4**) (20.0 g, 132 mmol), potassium carbonate (910 mg, 6.60 mmol) and dimethyl carbonate (214 g, 200 mL, 2.38 mol) were put into an autoclave, the reactor was purged with nitrogen and closed. The temperature was raised to 180 °C and the mixture stirred for 18 h. Then the

mixture was cooled, filtered and evaporated under reduced pressure to give 18.7 g of product as dark red liquid which was used in the next step without purification.

2-(3-Chlorophenyl)propan-1-amine (*rac*-3), isolated as hydrochloride acid salt.
2-(3-Chlorophenyl)propionitrile (**5**) (18.7 g, 113 mmol), EtOH (210 mL), NH_4OH (42.0 mL) and Raney-Ni (5.60 g) were put into an autoclave. The mixture was shaken overnight at room temperature under 5 bar of pressure of H_2. The reaction mixture was then filtered to remove Raney-Ni. The filtrate was partially concentrated under reduced pressure to remove EtOH. The pH was adjusted to 2 by the addition of 2M aqueous HCl solution and the mixture washed with *tert*-butyl methyl ether (2 x 50.0 mL). NaCl was added to the aqueous phase and the mixture extracted with CH_2Cl_2. Three layers were formed, the bottom and middle layer were separated and, the top layer was extracted again with CH_2Cl_2 (2 x 30.0 mL). All organic phases were combined, washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure to give 18.6 g (80% yield) of product as a white solid. The NMR data were in agreement with known literature data.[11] – ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (m, 3H), 7.08 (d, lH), 2.83 (m, 2H), 2.72 (m, lH), 1.23 (d, lH), 1.08 (bs, NH) ppm. – ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 133.2, 130.5, 127.2, 126.9, 126.1, 44.5, 37.1, 19.2 ppm.
Alternative procedure: To a solution of 2-(3-chlorophenyl)propionitrile (**5**) (45.3 mmol; 7.50 g) in toluene (150 mL) under nitrogen atmosphere at 0 °C was added BH_3•THF (136 mmol; 136 mL, lM). The reaction mixture was stirred under reflux for 4 h. After cooling to room temperature, the reaction mixture was quenched with water (150 mL) followed by extraction with EtOAc (l x 300 mL). The organic phase was dried over $MgSO_4$, filtered and solvent was removed by evaporation. The pure product was isolated as a hydrochloride salt by treatment of residue with HCI (Et_2O-solution) in 70% yield (6.60 g) as a white solid.

(*R*)-2-(3-Chlorophenyl)propan-1-amine using (*R*)-2-phenylpropionic acid for the optical resolution
To a solution of 2-(3-chlorophenyl)propan-1-amine (***rac*-3**) (3.00 mmol; 0.50 g) in EtOH (3.00 mL) at 70 °C was added a solution of (*R*)-2-phenylpropionic acid (**15**) (1.50 mmol; 0.20 g) in EtOH (1.00 mL). The reaction mixture was stirred at 70 °C for 30 min and then slowly cooled to room temperature during several hours. After stirring for 16 h, obtained precipitate was filtered, washed with cold EtOH and dried under reduced pressure to give 0.29 g of salt (**3-PP**) (chiral HPLC: 74.1% ee, *R*-enantiomer).
Recrystallization: 0.28 g of obtained precipitated enantiomeric salt mixture was dissolved in EtOH (3.00 mL) at 70 °C. The solution was stirred at 70 °C for 30 min and then cooled to room temperature during several hours. After stirring for 16 h, the formed precipitate was filtered, washed with EtOH and dried under reduced pressure to give 0.19 g (19.8% yield) of salt (*R*)-**3-PP** (chiral HPLC: 98.1% ee, *R*-enantiomer). – ^{1}H (300 MHz, DMSO-d_6): δ 7.17 – 7.35 (m, 9H), 6.01 (bs, 3H), 3.51 (q, J = 7.1 Hz, 1H),

2.70 – 2.89 (m, 3H), 1.30 (d, J = 7.1 Hz, 3H), 1.18 (d, J = 6.5 Hz, 3H), ppm. – ^{13}C (75 MHz, DMSO-d_6): δ 176.28, 147.24, 143.29, 133.00, 130.18, 127.97, 127.39, 127.13, 126.26, 125.99, 125.93, 46.83, 46.49, 40.13, 19.25, 18.91 ppm. – IR (neat, ATR): v 2977 (m), 2965 (m), 2920 (m), 2746 (b), 2697 (b), 2655 (b), 2200 (bw), 1638 (m), 1596 (m), 1536 (s), 1483 (m), 1383 (s), 1281 (s), 1187 (m), 1049 (m), 995 (m), 879 (m), 794 (s), 771 (m), 747 (s), 700 (s), 671 (m), 573 (m), 504 (m), 484 (m), 471 (m), 453 (m), 431 (s) cm^{-1} – HRMS (EI$^+$, 70 eV): m/z = $(C_9H_{13}ClN)^+(C_9H_9O_2)^-$; calcd. 319.8106; found 319.1321.

(R)-2-(3-Chlorophenyl)propan-1-amine using (*S*)-3-phenyllactic acid for the optical resolution

To a solution of 2-(3-chlorophenyl)propan-1-amine (***rac*-3**) (4.10 mmol; 0.70 g) in toluene (5.00 mL) at 70 °C was added (*S*)-3-phenyllactic acid (2.10 mmol; 0.30 g). The reaction mixture was stirred at 70 °C for 30 min and then cooled to room temperature in several hours. After stirring for 16 h, obtained precipitate was filtered, washed with toluene and dried under reduced pressure to give 0.44 g of salt **3-lact** (chiral HPLC: 80.5% ee, *R*-enantiomer).

Recrystallization: 0.43 g of obtained salt mixture was dissolved in ^{i}PrOH (2.00 mL) at 70 °C. The solution was stirred at 70 °C for 30 min and then cooled to room temperature in several hours. After stirring for 16 h, obtained precipitate was filtered, washed with ^{i}PrOH and dried under reduced pressure to give 0.23 g (32.6% yield) of salt (*R*)-**3-lact** (chiral HPLC: 96.7% ee, *R*-enantiomer). – ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.13 - 7.39 (m, 9H), 5.89 (bs), 3.87 (dd, J = 8.4, 3.6 Hz, 1H), 2.95 - 3.09 (m), 2.64 (dd, J = 13.7, 8.4 Hz, 1H), 1.24 (d, J = 6.6 Hz, 2H). – ^{13}C NMR (75 MHz, DMSO-d_6) δ 176.33, 145.81, 139.75, 133.21, 130.41, 129.36, 127.72, 127.20, 126.77, 126.09, 125.57, 71.84, 44.81, 40.77, 37.73, 19.11 ppm. – IR (neat): v 3283 (b), 3038 (w), 3026 (w), 2962 (b), 2922 (b), 2891 (b), 2795 (b), 2694 (b), 2230 (w), 1571, 1557, 1522(s), 1479, 1461 (s), 1453 (s), 1436, 1359, 1322, 1257 (s), 1083 (s), 861, 786 (s), 749 (s), 698 (s), 535 (s), 477 cm^{-1}. – HRMS (EI$^+$, 70 eV): m/z = $(C_9H_{13}ClN)^+(C_9H_9O_3)^-$; calcd. 335.81; found 335.1284. Single crystals suitable for X-ray crystallography were obtained as follows: (*R*)-2-(3-Chlorophenyl)propan-1-amine hydrochloride (**3-HCl**) (65.0 mg, 0.32 mmol) was partitioned between CH_2Cl_2 and 1M sodium hydroxide solution. The aqueous layer was separated and extracted twice with CH_2Cl_2. The organic layers were combined, dried over Na_2SO_4 and concentrated. The residue was dissolved in 1.00 mL of hot ^{i}PrOH and (*S*)-3-phenyllactic acid (6.03 mg, 0.38 mmol) in 1.50 mL of hot ^{i}PrOH was added. The resulting clear solution was cooled to room temperature, and left at 4 °C overnight and crystallization was observed. Aliquots of the supernatant were covered with petrol ether and let stand to crystallize at room temperature to yield (*R*)-**3-lact** as fine needles.

Single-crystal structure determination of (*R*)-3-lact

Intensity data were recorded at 203 K with a Bruker D8 Quest Photon 100 diffractometer using Mo*Kα* radiation (λ = 0.71073 Å). The crystal structure was solved by Direct Methods and refined by full-matrix least-squares techniques.[18,19] Visualization of the structures and measurements of distances and angles were performed with the programs Ortep-3[20] and Mercury.[21] The topology of the H-bonded structure was determined and classified with the programs ADS and IsoTest of the TOPOS package.[21] Crystal data: moiety formula $(C_9H_{13}ClN)^+(C_9H_9O_3)^-$; $C_{18}H_{22}ClNO_3$ (M = 335.81 g mol^{-1}); D_x = 1.254 g cm^{-3}; monoclinic space group $P2_1$ with Z = 2; a = 9.9291(7), b = 6.0792(4), c = 15.5430(11) Å; U = 889.71(11) Å^3; 14598 reflections measured and 3127 independent reflections (R_{int} = 0.027); R_1 [$I > 2\sigma(I)$] = 0.028; wR_2 (all data) = 0.069; Flack parameter x = 0.007(18) based on 1283 quotients.[21] CCDC reference number 1868875.

REFERENCES

1. World Health Organization, World Health Organization obesity and overweight fact sheet. <http://www.who.int/mediacentre/factsheets/fs311/en/>, (accessed 08.08.2018.).
2. M. Daubresse and G. Alexander, *Int. J. Obesity*, 2015, **39**, 377.
3. S. Manning, A. Pucci, and N. Finer, *Therap. Adv. Chronic Dis*., 2014, **5**, 135.
4. B. Smith, J. Smith, and J. Tsai, *Bioorg. Med. Chem. Lett*., 2005, **15**, 1467.
5. Q. Zhu, J. Wang, X. Bian, L. Zhang, P. Wei, and Y. Xu, *Org. Process Res. Dev*., 2015, **19**, 1263.
6. B. W. Burbaum, C. A. Gilson, S. Aytes, S. A. Estrada, D. Sengupta, B. Smith, M. Rey, and U. Weigl, *Int. Pat.*, WO2005/019179.
7. U. Weigl, F. Porstmann, C. Straessler, L. Ulmer, and U. Koetz, *Int. Pat.*, WO2007/120517.
8. T. Gharbaoui, S. K. Tandel, Y. Ma, M. Carlos, and J. R. Fritch, *Int. Pat.*, WO2008/070111.
9. J. Demattel, M. Carlos, R. Castro, T.-H. Chuang, M. Hadd, X.-X. Lu, M. Macias, and S. M. Shaw, *Int. Pat.*, WO2010/148207.
10. M. Carlos, R. Castro, T. Ghar-Baoui, X.-X. Lu, Y.-A. Ma, and N. Martin, *Int. Pat.*, WO2009/111004.
11. I. Gazic-Smilovic, J. Cluzeau, F. Richter, S. Nerdinger, E. Schreiner, G. Laus, and H. Schottenberger, *Bioorg. Med. Chem.*, 2018, **26**, 2686.
12. P. Hebeisen, U. Weiss, A. Alker, and A. Staempfli, *Tetrahedron Lett.*, 2011, **52**, 5229.
13. G. Laus, K. Wurst, S. Nerdinger, F. Richter, and H. Schottenberger, *IUCrData*, 2017, **2**, 170869.
14. M. B. Hursthouse, D. S. Hughes, T. Gelbrich, and T. L. Threlfall, *Chem. Cent. J.*, 2015, **9**, 1.
15. M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120; J. Bernstein, R. E. Davis, L. Shimoni, and N.-L. Chang, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1555.
16. J. A. Landgrebe and A. G. Kirk, *J. Org. Chem.*, 1967, **32**, 3499.

17. J. Guin, G. Varseev, and B. List, *J. Am. Chem Soc.*, 2013, **135**, 2100.
18. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
19. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
20. L. J. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849.
21. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, and P. A. Wood, *J. Appl. Cryst.*, 2008, **41**, 466.
22. V. A. Blatov, *IUCr Compcomm Newsl.*, 2006, **7**, 4; I. A. Baburin and V. A. Blatov, *Acta Cryst.*, 2007, **B63**, 791.
23. S. Parsons, H. D. Flack, and T. Wagner, *Acta Cryst.*, 2013, **B69**, 249.