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Asymmetric aldol-Tishchenko reaction catalyzed by Yb-complexes with basic amino acid-derived ligands

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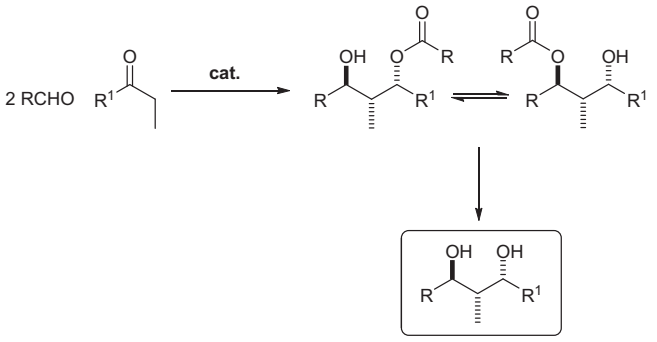
ABSTRACT

Simple amino acid-derived esters have been identified as promising chiral sources for the ytterbium-catalyzed aldol-Tishchenko reaction of aromatic aldehydes with aliphatic ketones. The 1,3-*anti*-diols with three stereogenic centers were isolated in excellent yields, complete *anti*-diastereocontrol and enantioselectivities of up to 50% ee.

1. Introduction

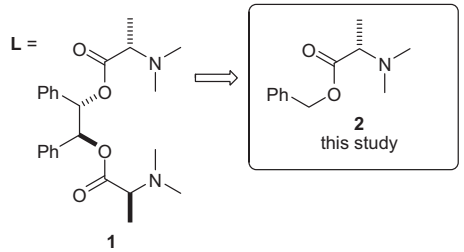
The aldol-Tishchenko reaction is a unique, one step methodology for the synthesis of 1,3-dioxygenated compounds from carbonyl substrates.[1] This transformation is a useful methodology for the construction of defined stereogenic centers and represents a valuable tool for broadening the scope of classical aldol reaction.[2] Despite the enormous synthetic potential of the aldol-Tishchenko reaction of unmodified ketones with aldehydes leading directly to the important class of 1,3-diols, its enantioselective variant requires further exploration. Only a limited number of publications have described an enantioselective aldol-Tishchenko reaction of ketones. In principal, there are two general methodologies available in the field: the direct aldol-Tishchenko the reaction of ketones[3] and reaction of preformed ketone aldols.[4]

In the former direct aldol-type methodology, three stereogenic centers can be created by aldol-Tishchenko reaction of an aldehyde with ethyl ketones leading to 1,3-diols even from demanding aliphatic ketones (Scheme 1).



Scheme 1. Condensation of ketones with aldehydes by means of a catalytic aldol-Tishchenko reaction.

Previously, we reported attempts to carry out the asymmetric aldol-Tishchenko reaction using an amino acid-based chiral ligand along with ytterbium salts, by which the direct asymmetric aldol reaction of 3-pentanone can be efficiently accomplished.[3g] We have presented careful insight into a new class of ytterbium complexes with C_2-symmetric chiral bis(ester) and (bis)amide ligands for the tandem asymmetric aldol reaction. We have shown that the modular design of the catalyst is possible by varying the starting chiral backbone and amino acid parts of the ligands. These findings motivated us to further tune the catalyst and investigate the possible catalytic efficiency of a directly available, less complex ligand composed of selectively blocked simple chiral amino acids, as depicted at Scheme 2.



Scheme 2. Examples of ligands used in previous and current studies.

The discovery and development of novel chiral ligands are of significant importance in asymmetric catalysis, especially when composed of inexpensive and readily available chiral sources.

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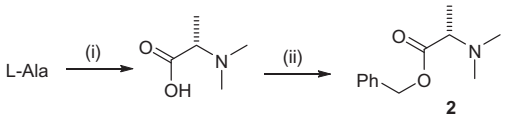
Herein, we report the synthesis and application of new ytterbium-based catalysts armed with chiral amino acids to the valuable direct asymmetric aldol reaction leading directly to 1,3-diols.

2. Results and discussion

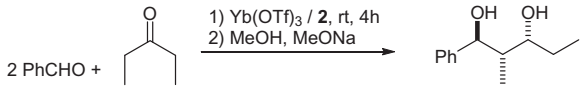
Based on our previous findings, we determined a few structural elements to be necessary for catalyst activity. First, we know that ligands without a tertiary amine group were inferior in this application. Second, the aromatic substituents in the catalyst backbone were indispensable for the reactivity. The most promising levels of enantioselectivity (40%) and yield (95%) were obtained with a catalyst composed of ytterbium triflate and ester type ligands derived from dimethylalanine **1** in a 1:1 ratio.[3d,f] Giving up on C_2-symmetry, we started from a similar amino acid structure **2** containing an ordinary benzyl ester function. Ligand **2** was efficiently prepared by the DCC-promoted esterification of an N-blocked chiral amino acid with benzyl alcohol (Scheme 3).



Scheme 3. Synthesis of a model ligand. Reagents and conditions: (i) CH_2O, H_2, Pd-C (10%), EtOH, 20 h, rt, 100%; (ii) BnOH, DCC, DMAP, DCM, 20 h, rt, 71%.

As a model reaction we selected the addition of benzaldehyde to 3-pentanone in THF at rt since this transformation has already been extensively investigated. The ketone (0.95 mmol, two-fold excess) and aldehyde substrates (1.00 mmol) were added to the catalyst preformed from the chiral ligand and $Yb(OTf)_3$ (20 mol %). As can be seen from Table 1, the conditions applied furnished the diol **3** with varying yields and enantioselectivities.

Table 1
The aldol-Tishchenko reaction of 3-pentanone with benzaldehyde catalyzed by Yb-**2** complex



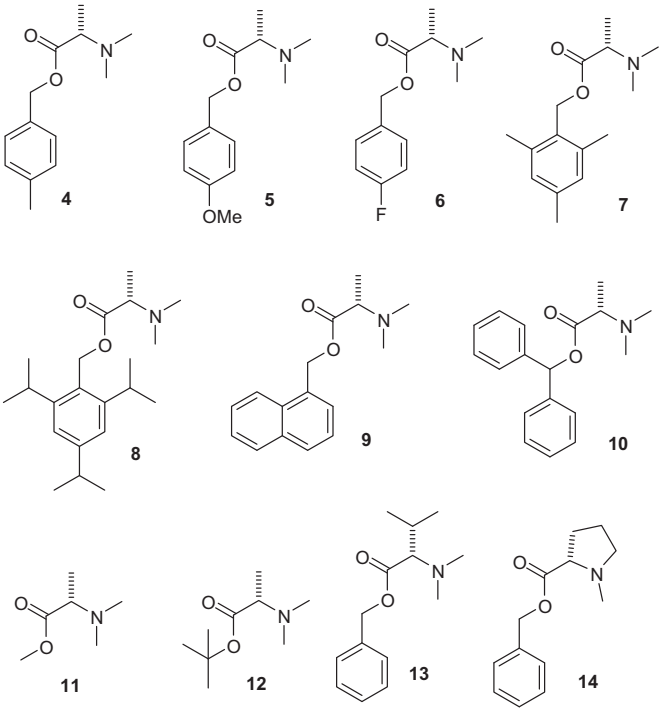
Entry	$Yb(OTf)_3$:**2**	Solvent	Yield[a] (%)	ee[b] (%)
1	1:1 (20 mol %)	THF	85	16
2	1:2 (20 mol %)	THF	93	36
3	1:3 (20 mol %)	THF	93	42
4	1:4 (20 mol %)	THF	98	45
5	1:4 (20 mol %)	MeCN	70	6
6	1:4 (20 mol %)	Dioxane	75	26
7	1:4 (15 mol %)	THF	92	45
8	1:4 (10 mol %)	THF	50	45

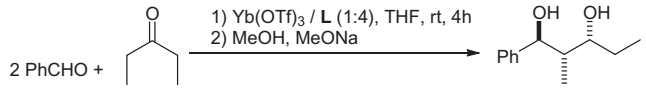
[a] Yield of isolated diol **3**.
[b] The ee of diols was determined by HPLC using a chiral stationary phase AD-H column.[3f]

The most promising level of enantioselectivity was obtained for the (1:4) ratio of Yb-salt to ligand using 20 mol % of catalyst loading (Table 1, entry 4). The desired 1,3-diol was isolated in 98% yield and with full 1,2-*anti*-1,3-*anti* diastereoselectivity. By using HPLC and high resolution NMR's, we did not observe formation of other diastereoisomeric esters, which is in agreement with the previously published findings.[3] For the L-alanine-based ligand, the (1*S*,2*S*,3*R*)-configured product was predominant in the enantiomer mixture. The absolute configurations of the esters and related diols have previously been established in our laboratory using CD technique.[3f] When the catalyst amount was reduced to 15 mol %, a similar yield and stereoselectivity were obtained (Table 1, entry 7). In all cases tested, THF was the best solvent.

To improve the enantioselectivity further, we changed the ligand structure to tune the electronic nature and steric hindrance around catalytic center. Thus, we prepared a series of ligands based on alanine **4**–**12**, valine **13** and proline **14**; all collected data are shown in Table 2.

Table 2
The aldol-Tishchenko reaction of 3-pentanone with benzaldehyde catalyzed by Yb complex with various ligands





Entry	Ligand	Cat. loading (mol %)	Yield[a] (%)	ee[b] (%)
1	**4**	20	98	44
2	**5**	20	Trace	—
3	**6**	20	Trace	—
4	**7**	15	92	50
5	**8**	15	50	32
6	**9**	15	93	44
7	**10**	20	93	46
8	**11**	15	96	28
9	**12**	15	77	22
10	**13**	15	95	8
11	**14**	15	90	24

[a] Yield of isolated diol **3**.
[b] The ee of diols was determined by HPLC using a chiral stationary phase AD-H column.[3f]

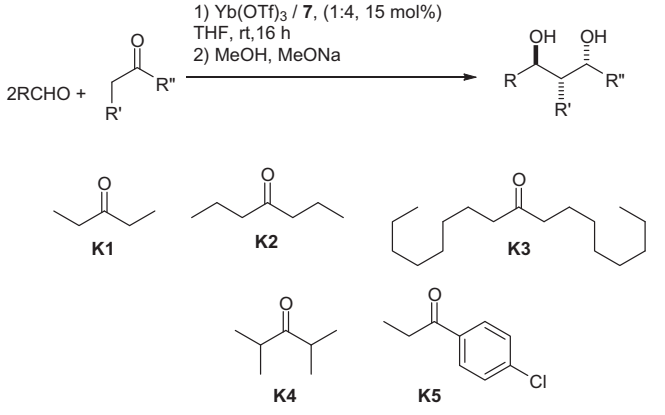
While the application of a backbone with a *para*-methyl-substituted ring was not progressive, the most promising level of enantioselectivity was obtained with the sterically hindered mesityl-derived ester **7** (Table 2, entry 4). Application of tri-*O*-isopropyl-substituted ring in ligand **8** led to a decrease in yield and enantioselectivity. When the *para*-methyl group in the ring was changed to *para*-methoxy or *para*-fluoro groups, the reactivity dropped sharply, and the formation of only trace amounts of

condensation products was observed. Alkyl esters **11** and **12** showed high activity but the observed levels of selectivity were unsatisfactory. The application of valine and proline based ligand was also not promising.

With the optimal reaction conditions identified and by using a ligand **7** combined with ytterbium triflate, the scope of the tandem aldol-Tishchenko procedure was investigated by employing various ketone substrates as well as differently substituted aldehydes. As demonstrated in Table 3, the elaborated catalyst was found active or very active for a wide range of ketones.

In addition to benzaldehyde, other aromatic aldehydes reacted effectively to give diols in good yields with high stereoselectivity (Table 3, entries 1 and 2). A number of ketones can be used as donors without a loss of efficiency or enantiocontrol (entries 5–9). Only the less hindered diisobutyl aldehyde was unreactive under reaction conditions.

Table 3
$Yb(OTf)_3$-promoted asymmetric aldol-Tishchenko reaction



Entry	Ketone	Aldehyde	Yield[a] (%)	ee[b] (%)
1	**K1**	R = Ph	92	50
2	**K1**	R = pMeOC_6H_4	75	52
3	**K1**	R = pClC_6H_4	92	40
4	*After one recrystallisation*		60–65%	98
5	**K2**	R = Ph	93	40
6	**K2**	R = pClC_6H_4	75	36
7	**K3**	R = Ph	35	44
8	**K4**	R = Ph	0	—
9	**K6**	R = Ph	95	40

[a] Yield of isolated diol **3**.
[b] The ee of diols was determined by HPLC using a chiral stationary phase AD-H column.[3f]

It is noteworthy that one recrystallization (hexane with 2-propanol) of the 1,3-diol derived from 4-chlorbenzaldehyde and 3-pentanone gave the diol with high enantiomeric purity (98% ee) in good yield of ca. 60% (entry 4, calculated from the starting carbonyl reactants). In this case, the chiral diol crystallizes easily as racemic crystals leaving in the solution enantiomerically enriched products. This observation is very important for the synthetic application of the presented asymmetric methodology.

3. Conclusion

In conclusion, we have devised a novel amino acid-based chiral catalyst for the enantioselective aldol-Tishchenko reaction between ketones and aromatic aldehydes. The most reactive ligand for this tandem process was readily prepared (in two steps) from commercially available starting materials. Current studies are being directed at further improving the enantioselectivity of the reactions and the practical application of the asymmetric aldol-Tischenko methodology to the synthesis of more complex molecules.

4. Experimental

4.1. General

All reactions involving organometallic or other moisture sensitive reagents were carried out under argon with standard vacuum line techniques and glassware that was flame dried and cooled under Ar before use. Solvents were dried according to standard procedures. All organic solutions were dried over Na_2SO_4. Thin layer chromatography was performed with aluminum plates coated with 60 F_{254} silica (Merck). Plates were visualized with UV light (254 nm) and ethanolic phosphomolybdic acid solution or ethanolic ninhydrin solution followed by heating. Reaction products were purified by flash chromatography with silica gel 60 (240–400 mesh, Merck). Optical rotations were measured with a JASCO Dip-360 Digital Polarimeter at room temperature. Specific rotations are reported in 10^{-1} deg cm^2 g^{-1} and in concentrations of grams per 100 mL. ^{1}H NMR spectra were recorded with a Varian-200, Varian-400, or Bruker-500 spectrometer in or $CDCl_3$ with Me_4Si as an internal standard. High-resolution mass spectra were recorded with a Mariner PerSeptive Biosystems mass spectrometer with a time-of-flight (TOF) detector. IR spectra were recorded with a Perkin–Elmer FT-IR-1600 spectrophotometer as either a thin film on NaCl plates (film), as a KBr disk (KBr), or as chloroform solutions in 0.1 mm cells ($CHCl_3$), as stated.

4.2. General procedure for the synthesis of ligands

Benzyl alcohol (1.00 mmol), *N*,*N*-dimethylamino acid (1.20 mmol), 1,3-dicyclohexylocarbodiimide (1.20) mmol and DMAP (0.10 mmol) were stirred in dry DCM (5 mL) under an argon atmosphere for 24 h. The precipitate was removed by filtration, and the residue was washed with DCM (5 mL). The solvent was evaporated, and the residue was purified by flash column chromatography.

4.2.1. Benzyl (2*S*)-2-(dimethylamino)propanoate 2

Colorless oil; yield 71%, $[\alpha]_D^{25.1} = -16.5$ (c 0.62, $CHCl_3$); R_f = 0.25 (Hex/AcOEt, 3:2); ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.30 (d, 3H, J = 7.0 Hz), 2.33 (s, 6H), 3.29 (q, 1H, J = 7.0 Hz), 5.16 (s, 2H), 7.27–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 14.9, 41.6, 62.7, 66.0, 128.1, 128.2, 128.4, 135.9, 172.9; IR ($CHCl_3$): 2980, 2940, 2782, 1732, 1455, 1165, 731, 698 cm^{-1}; HRMS (ESI) calculated for $C_{12}H_{17}NO_2Na$ [M+Na]$^+$ 230.1152, found 230.1155.

4.2.2. 4-Methylbenzyl (2*S*)-2-(dimethylamino)propanoate 4

Colorless oil; yield 86%, $[\alpha]_D^{25.9} = -21.8$ (c 0.40, $CHCl_3$); R_f = 0.30 (Hex/AcOEt, 2:3); ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.22 (d, 3H, J = 7.0 Hz), 2.24 (s, 6H), 2.30 (s, 3H), 3.19 (q, 1H, J = 7.0 Hz), 5.03 (s, 2H), 7.05 (ABq, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 14.6, 20.8, 41.2, 62.4, 65.9, 128.1, 128.9, 132.4, 137.8, 172.5; IR ($CHCl_3$): 2980, 2938, 2868, 1732, 1452, 1165, 1107, 806 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{20}NO_2$ [M+H]$^+$ 222.1489, found 222.1499.

4.2.3. 4-Methoxybenzyl (2*S*)-2-(dimethylamino)propanoate 5

Colorless oil; yield, 80%, $[\alpha]_D^{25.7} = -15.5$ (c 0.27, $CHCl_3$); R_f = 0.30 (Hex/AcOEt, 2:3); ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.26 (d, 3H, J = 7.0 Hz), 2.29 (s, 6H), 3.22 (q, 1H, J = 7.0 Hz), 3.78 (s, 3H), 5.07 (s, 2H), 6.85 (d, 2H, J = 8.5 Hz), 7.30 (d, 2H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 15.1, 41.8, 55.4, 63.0, 66.3, 114.1, 128.2, 130.4, 159.8, 173.2; IR ($CHCl_3$): 2967, 2938, 2834, 1728, 1614, 1516, 1248, 1166 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{20}NO_3$ [M+H]$^+$ 238.1438, found 238.1444.

4.2.4. 4-Fluorobenzyl (2*S*)-2-(dimethylamino)propanoate 6

Colorless oil; yield 62%, $[\alpha]_D^{25.9} = -24.4$ (*c* 0.06, $CHCl_3$); $R_f = 0.30$ (Hex/AcOEt, 2:3); ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.29 (d, 3H, $J = 6.8$ Hz), 2.28 (s, 6H), 3.30 (q, 1H, $J = 6.8$ Hz), 5.13 (s, 2H), 7.00–7.18 (m, 2H), 7.38–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 15.1, 41.9, 63.0, 65.7, 115.7 (d, $J = 85.8$ Hz), 130.6 (d, $J = 33.4$ Hz), 132.5, 162.9 (d, $J = 981.6$ Hz), 173.1; IR ($CHCl_3$): 2968, 2931, 2874, 1615, 1572, 1220, 772, 635 cm^{-1}; HRMS (ESI) calculated for $C_{12}H_{17}NO_3$ $[M+H]^+$ 226.1238, found 238.1241.

4.2.5. 2,4,6-Trimethylbenzyl (2*S*)-2-(dimethylamino)-propanoate 7

Colorless oil; yield 90%, $[\alpha]_D^{25.6} = -14.9$ (*c* 1.08, $CHCl_3$); $R_f = 0.40$ (Hex/AcOEt, 3:2); ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.28 (d, 3H, $J = 7.0$ Hz), 2.27 (s, 3H), 2.33 (d, 6H, $J = 3.8$ Hz), 3.25 (q, 1H, $J = 7.0$ Hz), 5.20 (s, 2H), 6.85 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 15.3, 19.4, 20.9, 41.6, 60.8, 62.6, 129.0, 138.0, 138.3, 173.3; IR ($CHCl_3$): 2977, 2939, 2866, 1728, 1451, 1215, 1164, 850 cm^{-1}; HRMS (ESI) calculated for $C_{15}H_{24}NO_2$ $[M+H]^+$ 250.1802, found 250.1803.

4.2.6. 2,4,6-Triisopropylbenzyl (2*S*)-2-(dimethylamino)-propanoate 8

Colorless oil; yield 80%, $[\alpha]_D^{25.5} = -11.3$ (*c* 0.32, $CHCl_3$); $R_f = 0.30$ (Hex/AcOEt, 7:3); ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.24–1.35 (m, 21H), 2.35 (s, 6H), 2.83–2.96 (m, 1H), 3.13–3.29 (m, 3H), 5.26 (s, 2H), 7.05 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 15.4, 23.9, 24.3, 29.4, 34.3, 41.7, 59.1, 62.8, 121.1, 126.3, 148.7, 149.6, 173.4; IR ($CHCl_3$): 2963, 2935, 2870, 2830, 2780, 1730, 1458, 1164 cm^{-1}; HRMS (ESI) calculated for $C_{21}H_{36}NO_2$ $[M+H]^+$ 334.2741, found 334.2740.

4.2.7. 1-Naphthylmethyl (2*S*)-2-(dimethylamino)propanoate 9

Colorless oil; yield 81%, $[\alpha]_D^{25.7} = -12.8$ (*c* 1.06, $CHCl_3$); $R_f = 0.30$ (Hex/AcOEt, 2:3); ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.29 (d, 3H, $J = 7.12$ Hz), 2.28 (s, 6H), 3.30 (q, 1H, $J = 7.12$ Hz), 5.13 (s, 2H), 7.40–7.60 (m, 4H), 7.80–7.88 (m, 2H), 7.95–8.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 15.0, 41.5, 62.6, 64.1, 123.3, 125.0, 125.7, 126.3, 127.4, 128.5, 129.1, 131.3, 131.4, 133.5, 172.9; IR ($CHCl_3$): 2979, 2937, 2829, 2781, 1730, 1169, 1151, 776 cm^{-1}; HRMS (ESI) calculated for $C_{16}H_{20}NO_2$ $[M+H]^+$ 258.1489, found 258.1490.

4.2.8. Diphenylmethyl (2*S*)-2-(dimethylamino)propanoate 10

Colorless oil; yield 71%, $[\alpha]_D^{25.2} = -11.0$ (*c* 1.06, $CHCl_3$); $R_f = 0.20$ (Hex/AcOEt, 3:2); ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.32 (d, 3H, $J = 7.1$ Hz), 2.32 (s, 6H), 2.37 (q, 1H, $J = 7.1$ Hz), 6.93 (s, 1H), 7.24–7.38 (m, 10H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 15.3, 41.6, 62.8, 76.7, 127.1, 127.1, 127.8, 128.4, 128.4, 140.1, 140.2, 172.2; IR ($CHCl_3$): 2980, 2939, 2868, 2830, 2785, 1734, 1453, 1162, 699 cm^{-1}; HRMS (ESI) calculated for $C_{18}H_{21}NO_2Na$ $[M+Na]^+$ 306.1465, found 306.1466.

4.2.9. Methyl (2*S*)-2-(dimethylamino)propanoate 11

Known compound.[5]

4.2.10. *tert*-Butyl (2*S*)-2-(dimethylamino)propanoate 12

Known compound.[6]

4.2.11. Benzyl (2*S*)-2-(dimethylamino)-3-methylbutanoate 13

Colorless oil; yield 82%, $[\alpha]_D^{23.3} = -7.6$ (*c* 0.96, $CHCl_3$); $R_f = 0.40$ (Hex/AcOEt, 9:1); ^1H NMR ($CDCl_3$, 200 MHz) δ: 0.86 (d, 3H, $J = 6.5$ Hz), 0.97 (d, 6H, $J = 6.5$ Hz), 1.93–2.10 (m, 1H), 2.30 (s, 6H), 2.79 (d, 1H, $J = 10.3$ Hz), 5.18 (s, 2H), 7.38–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 19.4, 19.6, 27.5, 41.5, 65.6, 74.3, 128.2, 128.4, 128.5, 136.0, 171.6; IR ($CHCl_3$): 2962, 2938, 2872, 1729, 1455, 1151, 1122, 697 cm^{-1}; HRMS (ESI) calculated for $C_{14}H_{22}NO_2$ $[M+H]^+$ 236.1645, found 236.1647.

4.2.12. Benzyl (2*S*)-1-methyltetrahydro-1*H*-pyrrole-2-carboxylate 14

Colorless oil; yield 80%, $[\alpha]_D^{24.5} = -71.1$ (*c* 0.28, $CHCl_3$); $R_f = 0.20$ (Hex/AcOEt, 2:3); ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.75–2.38 (m, 5H), 2.40 (s, 3H), 2.96–3.20 (m, 2H), 5.18 (s, 2H), 7.35–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 23.1, 29.6, 40.8, 56.3, 66.2, 67.4, 126.8, 128.1, 128.4, 135.9, 173.5; IR ($CHCl_3$): 2947, 2782, 1744, 1455, 1167, 1054, 749, 697 cm^{-1}; HRMS (ESI) calculated for $C_{13}H_{18}NO_2$ $[M+H]^+$ 220.1332, found 220.1336.

4.3. General procedure to obtain the aldol-Tishchenko

At first, Yb(III) triflate (0.15 mmol, 15 mol %) was placed in an oven-dried flask with a magnetic stirring bar, and the flask was heated at 200 °C for 10 min in vacuo and then flushed with argon. After the flask was cooled to room temperature, a solution of ligand **7** (0.15 mmol, 15 mol %) in THF (2 mL) was added. The resulting solution was stirred for 30 min at room temp under argon. To a solution of the catalyst, 3-pentanone (100 μL, 0.95 mmol) and benzaldehyde (101 μL, 1.00 mmol) were added successively. The resulting solution was stirred for 4–16 h at room temperature and then dissolved with MTBE and washed with water and brine. The organic layer was dried with Na_2SO_4, concentrated, and submitted to short column chromatography (Hex/AcOEt, 9:1) to afford a mixture of esters as an oil. The esters obtained were dissolved in MeOH (2 mL) and treated with NaOMe (5–10 mol %) overnight. The resulting mixture was purified by column chromatography on silica gel (Hex/AcOEt, 3:2) to afford diol **3** and, with an analogous procedure all other diols.

Analytical data (NMR, IR, MS and chiral stationary phase HPLC) for all aldol-Tishchenko products from Table 3 have already been published.[3g]

Acknowledgments

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