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$Yb(OTf)_3$-MEDIATED RING OPENING OF FUNCTIONALIZED CYCLOPENTANE EPOXIDES WITH ANILINE: ASPECTS OF REGIOCHEMISTRY AND STEREOCHEMISTRY‡

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Abstract – The ring-opening reaction of cyclopentan-1-ol 2,3-epoxides bearing alkoxy and hydroxyl groups with aniline was studied in the presence of $Yb(OTf)_3$ in refluxing toluene. The *syn*- and *anti*- relationship of the alkoxy group has an influence on the regioselectivity of attack affording aniline adducts at the secondary or tertiary position.

The antibiotic pactamycin[1] isolated in 1961 from a fermentation broth of *Streptomyces pactum* var.pactum, is a unique member of a handful of naturally occurring aminocyclopentitols[2] (Figure 1). It exhibits activity against bacterial and also as a cytotoxic agent against cancer cell lines.[3] Among the several functional groups and unusual patterns of substitution is the presence of a 3-acetyl aniline moiety at C-3. A key reaction in our total synthesis of pactamycin[4] was the introduction of a 3-isopropenyl aniline through the highly regioselective ring opening of an epoxide spanning a secondary and a tertiary carbon center mediated by $Yb(OTf)_3$ (Scheme 1).[5] The same type of reaction allowed us to prepare a number of substituted aniline analogs of de-6-methylsalicylyl pactamycin and to study their biological activities (Figure 1).[6]

Intrigued by the exclusive formation of the aniline corresponding to ring opening at the secondary carbon atom as hoped for, we initiated a study of the ring- opening of stereoisomeric model cyclopentan-1-ol 2,3-epoxides with aniline in the presence of $Yb(OTf)_3$ as a Lewis acid.[7]

‡ Dedicated to Professor Victor Snieckus wishing him the best in chemistry and in life.

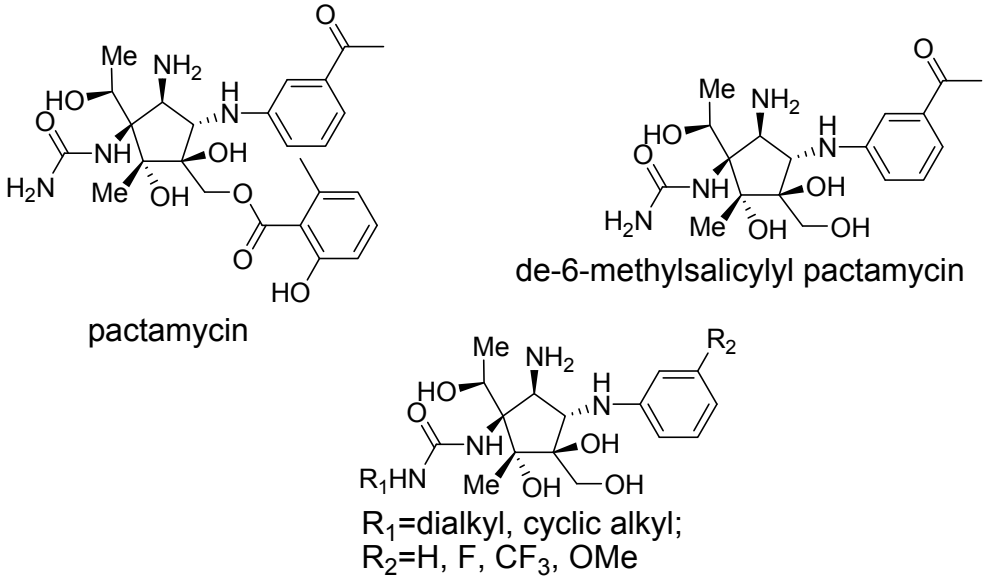
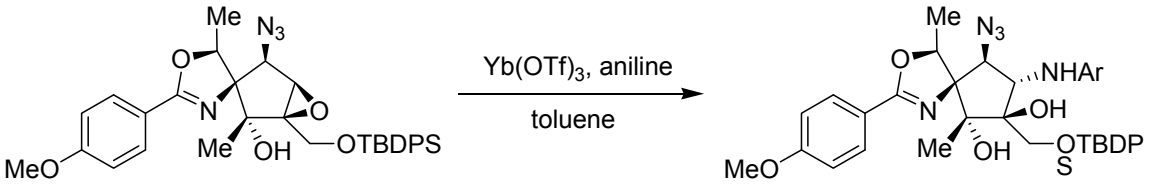


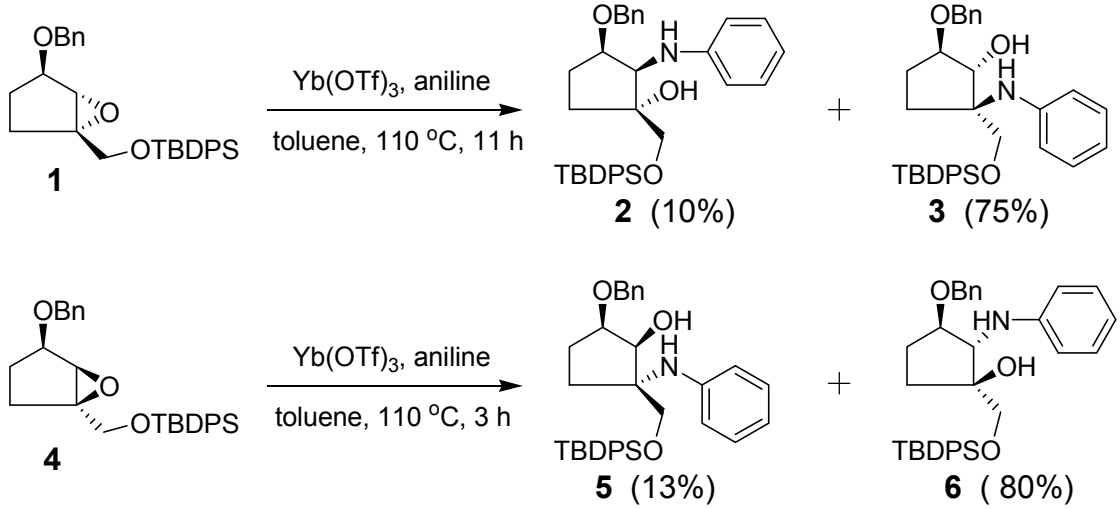
Figure 1



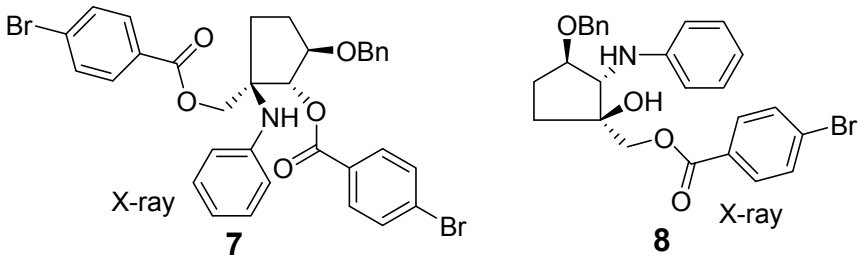
Scheme 1

In this paper, we report on the influence of the orientation of a vicinal alkoxy or alcohol group relative to the epoxide function in $Yb(OTf)_3$-mediated ring opening reactions with aniline using a model 3-hydroxymethylcyclopentan-1-ol 2,3-epoxide derivative, to stimulate the partial structure of the epoxide intermediate shown in Scheme 1.

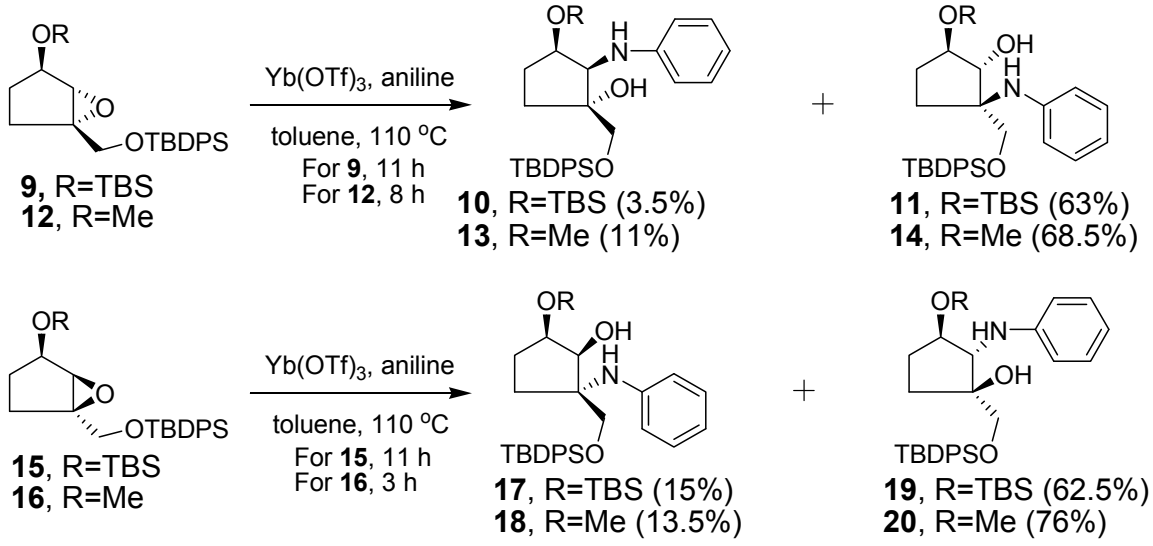
Reaction of the *anti*-oriented benzyl ether **1** with aniline in the presence of 30 mol% $Yb(OTf)_3$ in refluxing toluene led to the aniline adducts **2** and **3** in 10% and 75% yields respectively. In contrast, identical conditions with the *syn*-oriented benzyl ether **4,** afforded **5** and **6** in 13% and 80% yields respectively in a much shorter reaction time. Confirmation of the structure of the major products **3** and **6** was established through single crystal X-ray structure determination of the corresponding di-*p*-bromobenzoate ester **7**, and mono-*p*-bromobenzoate ester **8**, respectively.



Scheme 2



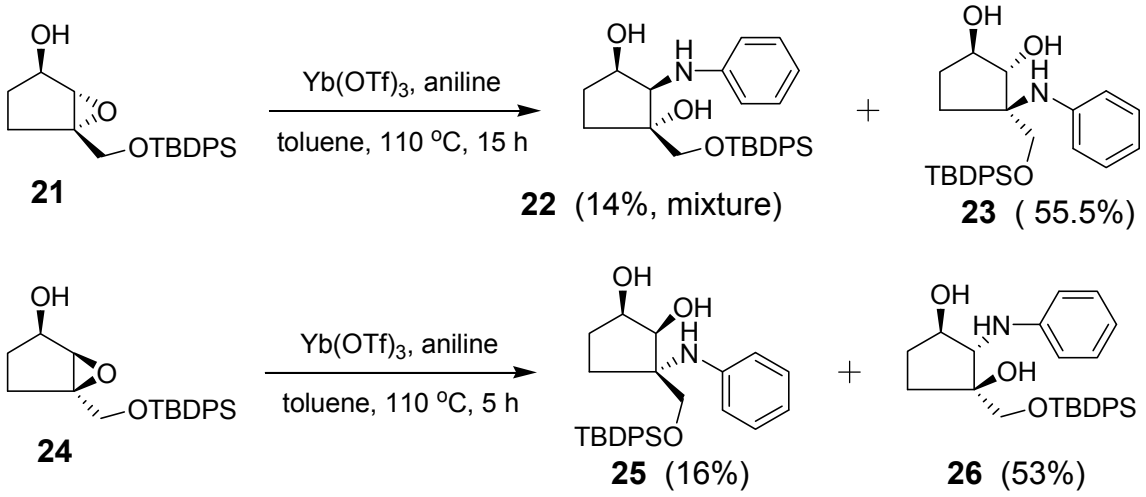
The corresponding OTBS and *O*-methyl ethers were studied next. Thus, treatment of the *anti*-oriented OTBS ether **9** with the same condition as shown in Scheme 2, led to the aniline adducts **10** and **11** (Scheme 3). However, the presumed **10** was obtained as a mixture of products in 3.5% only. The major isomer **11** was obtained in 63% yield. The analogous *O*-methyl ether **12** afforded **13** and **14**, also favoring ring-opening at the tertiary carbon atom.



Scheme 3

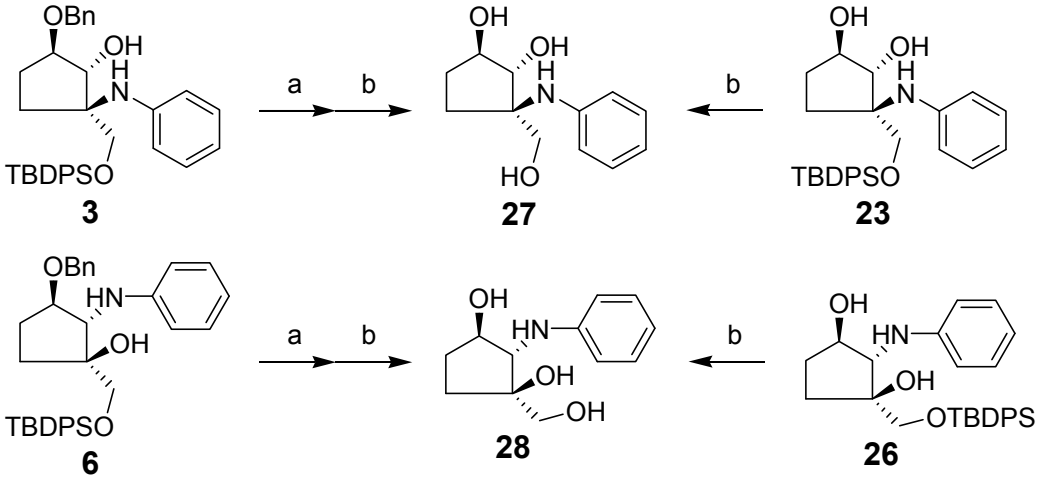
As observed in the *syn*-oriented *O*-benzyl series, the corresponding OTBS and *O*-methyl ethers **15** and **16** led to major ring-opening products corresponding to attack at the secondary epoxide carbon atom to give aniline adducts **19** and **20** respectively.

Finally, treatment of the *anti*-oriented cyclopentanol epoxide **21** under the same conditions afforded the major product **23** after 15 h at reflux (Scheme 4). A small amount of a mixture of isomeric anilines **22** presumably resulting from a Payne rearrangement prior to ring opening was not investigated further.



Scheme 4

The *syn*-oriented epoxide **24** reacted within 5 h to give **25** and **26** as aniline adducts in 16% and 53% yields respectively. Correlation of structures was possible by treatment with TBAF in the case of **23** and **26**, which gave the same products derived from the hydrogenation of **3** and **6** respectively, followed by removal of the silyl protecting group to give **27** and **28** (Scheme 5).



a, Pd/C, H_2, 1 atm, MeOH, AcOH, rt, 96 h;
b, TBAF, THF, 0 °C~rt, 3 h

Scheme 5

As seen in the preceding reactions, the *anti*-oriented epoxides harboring the vicinal alkoxy or hydroxyl groups consistently led to ring-opening at the tertiary carbon atom of the corresponding epoxide. On the other hand, the *syn*-oriented epoxides with regard to the alkoxy group led to the corresponding aniline adducts resulting from attack at the secondary carbon atom. It is noteworthy that reaction times were considerably shorter in the *syn*-oriented epoxides. A plausible rationale for these results may be given by considering a combination of coordination effects and conformational bias.[5] Thus, in the case of the *anti*-oriented epoxides **A**, a monodentate chelated Yb^{3+} coordination will render the tertiary carbon atom more susceptible to attack to release a 1,3-*syn*- interaction of the two ether sunstituents, in addition to stabilization of the developing positive charge in the transition state by an inductive effect of the hydroxymethyl substituent. It is of interest that in spite of the steric effects of the alkoxy and bulky *O*-silylated hydroxymethyl groups, attack is favored at the tertiary carbon center in an S_N2-like process, allowing for a better overlap of the nucleophilic aniline with the σ^* orbital of the C-O bond as it begins break.

In contrast, the *syn*-oriented epoxide **B** can engage in a bidentate coordination which activates the secondary carbon atom of the epoxide toward attack, in addition to a more favorable trajectory of approach of the nucleophilic aniline (Figure 2).

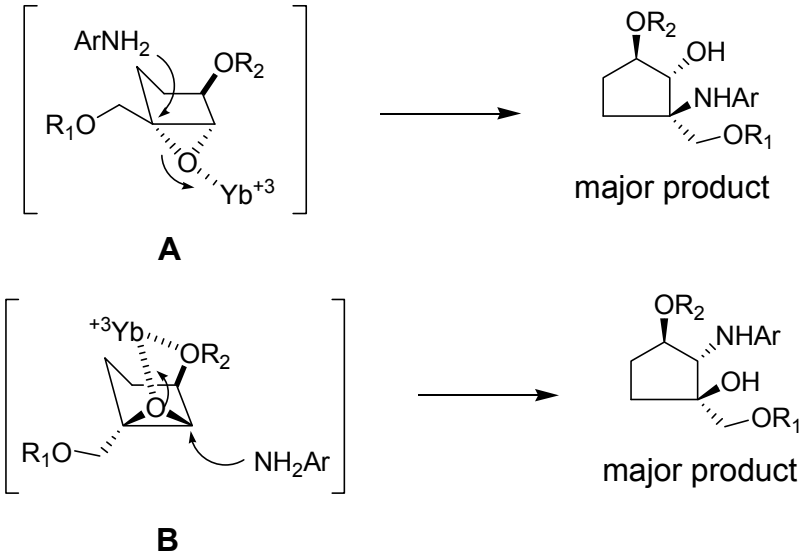


Figure 2

In conclusion, we have shown that a vicinal polar ether or hydroxyl group can dramatically influence the direction of ring opening of 2,3-epoxides in model cyclopentan-1-ols bearing a bulky hydroxymethyl substituent. It is also interesting that no ring opening was observed at the tertiary C-4 site in the case of the more densely functionalized pactamycin intermediate (Scheme 1). This would have necessitated a major change in synthetic strategy. Further studies in the synthesis of related substituted aniline

derivatives of hydroxycycloalkane epoxides are in progress and will be reported in due course.

ACKNOWLEDGEMENT

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EXPERIMENTAL

General procedure for epoxide ring opening reactions:

The stirred solution of epoxide (1 equiv.), aniline (5.8 equiv.) and $Yb(OTf)_3$ (0.3 equiv.) in toluene (0.28 mmol/mL) was heated to 110 °C for several hours with TLC monitoring. The reaction mixture was then concentrated in vacuum, and the residue was purified by flash column chromatography to give the corresponding aniline adducts.

(1*R*,2*R*,3*R*)-3-(Benzyloxy)-1-((*tert*-butyldiphenylsilyloxy)methyl)-2-(phenylamino)cyclopentanol (**2**) and (1*R*,2*R*,5*R*)-5-(Benzyloxy)-2-((*tert*-butyldiphenylsilyloxy)methyl)-2-(phenylamino)cyclopentanol (**3**).

Prepared according to the general procedure. From 504 mg (1.1 mmol) of epoxide **1**, after 11 h reaction, were obtained product **2** (64 mg, 10.5%) as a sticky solid, and product **3** (435 mg, 72%) as a light yellow solid.

For compound **2:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{35}H_{42}NO_3Si$, Calc. *m/z*: 552.29285, found *m/z*: 552.29425; $[M+Na]^+$, $C_{35}H_{41}NNaO_3Si$, Calc. *m/z*: 574.27479, found *m/z*: 574.27487.

^1H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.65 (m, 4H), 7.17-7.43 (m, 11H), 7.10-7.14 (m, 2H), 6.65-6.74 (m, 3H), 4.38 (d,d, J_1= 11.6 Hz, J_2=11.6 Hz, 2H), 4.40 (b, 1H), 4.20-4.21 (m, 1H), 3.79 (d,d, J_1 = 10 Hz, J_2= 10.4 Hz, 2H), 3.81 (d, *J*= 5.2 Hz, 1H), 3.01 (s, 1H), 2.00-2.09 (m, 1H), 1.87-1.95 (m, 1H), 1.64-1.75 (m, 2H), 1.07 (s, 9H).

For compound **3:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{35}H_{42}NO_3Si$, Calc. *m/z*: 552.29285, found *m/z*: 552.29438; $[M+Na]^+$, $C_{35}H_{41}NNaO_3Si$, Calc. *m/z*: 574.27479, found *m/z*: 574.27491.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.62 (m, 4H), 7.28-7.49 (m, 11H), 7.09-7.13 (m, 2H), 6.61-6.77 (m, 3H), 4.70 (d,d, J_1= 12.4 Hz, J_2=12 Hz, 2H), 4.25 (d, *J*= 6.0 Hz, 1H), 3.93-3.98 (m, 1H), 3.93 (d,d, J_1 = 10.8 Hz, J_2= 10.4 Hz, 2H), 1.88-2.06 (m, 3H), 1.72-1.79 (m, 1H), 1.05 (s, 9H).

(1*S*,2*S*,5*R*)-5-(Benzyloxy)-2-((*tert*-butyldiphenylsilyloxy)methyl)-2-(phenylamino)cyclopentanol (**5**) and (1*S*,2*S*,3*R*)-3-(Benzyloxy)-1-((*tert*-butyldiphenylsilyloxy)methyl)-2-(phenylamino)cyclopentanol (**6**).

Prepared according to the general procedure. From 503 mg (1.1 mmol) of epoxide **4**, after 3 h reaction, were obtained product **5** (70 mg, 11.5%) as a light yellow solid and product **6** (480 mg, 80%) as a sticky solid.

For compound **5:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{35}H_{42}NO_3Si$, Calc. *m/z*: 552.29285, found *m/z*: 552.29468; $[M+Na]^+$, $C_{35}H_{41}NNaO_3Si$, Calc. *m/z*: 574.27479, found *m/z*: 574.27573.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.48 (m, 4H), 7.19-7.37 (m, 11H), 7.13-7.17 (m, 2H), 6.73-6.81 (m, 3H), 4.61 (d,d, J_1= 11.6 Hz, J_2=11.6 Hz, 2H), 4.21-4.24 (m, 1H), 4.15-4.19 (m, 1H), 4.13 (b, 1H), 3.98 (d,d, J_1 = 10.4 Hz, J_2= 10.4 Hz, 2H), 3.23 (d, *J*= 6 Hz, 1H), 1.97-2.13 (m, 2H), 1.76-1.87 (m, 2H), 0.97 (s, 9H).

For compound **6:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{35}H_{42}NO_3Si$, Calc. *m/z*: 552.29285, found *m/z*: 552.29477; $[M+Na]^+$, $C_{35}H_{41}NNaO_3Si$, Calc. *m/z*: 574.27479, found *m/z*: 574.276.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.66 (m, 4H), 7.29-7.46 (m, 11H), 7.12-7.16 (m, 2H), 6.62-6.72 (m, 3H), 4.58 (d,d, J_1= 12 Hz, J_2= 12 Hz, 2H), 4.40 (b, 1H), 3.83-3.87 (m, 2H), 3.73 (d,d, J_1 = 10.4 Hz, J_2= 10.4 Hz, 2H), 2.98 (b, 1H), 1.88-2.13 (m, 4H), 1.09 (s, 9H).

(1*R*,2*R*,3*R*)-1-((*tert*-Butyldiphenylsilyloxy)methyl)-3-methoxy-2-(phenylamino)cyclopentanol (**13**) and (1*R*,2*R*,5*R*)-2-((*tert*-Butyldiphenylsilyloxy)methyl)-5-methoxy-2-(phenylamino)cyclopentanol (**14**).

Prepared according to the general procedure. From 170 mg (0.44 mmol) of epoxide **12**, after 8 h reaction, were obtained product **13** (23.3 mg, 11%) as a light yellow sticky solid and product **14** (146.5 mg, 68.5%) as a white solid.

For compound **13:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{29}H_{38}NO_3Si$, Calc. *m/z*: 476.26155, found *m/z*: 476.26284; $[M+Na]^+$, $C_{29}H_{37}NNaO_3Si$, Calc. *m/z*: 498.24349, found *m/z*: 498.24343.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.65 (m, 4H), 7.30-7.44 (m, 6H), 7.10-7.14 (m, 2H), 6.65-6.76 (m, 3H), 4.31 (b, 1H), 3.97-3.98 (m, 1H), 3.75 (d,d, J_1 = 10 Hz, J_2 =10.4 Hz, 2H), 3.78 (d, *J*= 5.6 Hz, 1H), 3.21 (s, 3H), 2.96 (s, 1H), 1.95-2.05 (m, 1H), 1.83-1.91 (m, 1H), 1.61-1.78 (m, 2H), 1.08 (s, 9H).

For compound **14:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{29}H_{38}NO_3Si$, Calc. *m/z*: 476.26155, found *m/z*: 476.2629; $[M+Na]^+$, $C_{29}H_{37}NNaO_3Si$, Calc. *m/z*: 498.24349, found *m/z*: 498.24349.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.63 (m, 2H), 7.26-7.47 (m, 8H), 7.08-7.12 (m, 2H), 6.59-6.76 (m, 3H), 4.08-4.13 (m, 3H), 3.69-3.79 (m, 3H), 3.44 (s, 3H), 1.96-2.05 (m, 2H), 1.85-1.93 (m, 1H), 1.60-1.69 (m, 1H), 1.05 (s, 9H).

(1*S*,2*S*,5*R*)-2-((*tert*-Butyldiphenylsilyloxy)methyl)-5-methoxy-2-(phenylamino)cyclopentanol (**18**) and (1*S*,2*S*,3*R*)-1-((*tert*-Butyldiphenylsilyloxy)methyl)-3-methoxy-2-(phenylamino)cyclopentanol (**20**).

Prepared according to the general procedure. From 153 mg (0.40 mmol) of epoxide **16**, after 3 h reaction, were obtained product **18** (25.5 mg, 13.4%) as a light yellow solid and product **20** (145 mg, 76%) as a light yellow sticky solid.

For compound **18:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{29}H_{38}NO_3Si$, Calc. *m/z*: 476.26155, found *m/z*: 476.26313; $[M+Na]^+$, $C_{29}H_{37}NNaO_3Si$, Calc. *m/z*: 498.24349, found *m/z*: 498.24396.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.53 (m, 4H), 7.22-7.39 (m, 6H), 7.13-7.17 (m, 2H), 6.72-6.81 (m, 3H), 4.20-4.23 (m, 1H), 4.15 (b, 1H), 3.92-3.96 (m, 1H), 3.98 (d,d, J_1= 10 Hz, J_2=10.4 Hz, 2H), 3.41 (s, 3H), 3.31 (d, *J*= 6 Hz, 1H), 1.95-2.07 (m, 2H), 1.74-1.82 (m, 2H), 0.99 (s, 9H).

For compound **20:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{29}H_{38}NO_3Si$, Calc. *m/z*: 476.26155, found *m/z*: 476.26302; $[M+Na]^+$, $C_{29}H_{37}NNaO_3Si$, Calc. *m/z*: 498.24349, found *m/z*: 498.24437.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.68 (m, 4H), 7.36-7.46 (m, 6H), 7.15-7.19 (m, 2H), 6.68-6.73 (m, 3H), 4.45 (d, *J*= 5.6 Hz, 1H), 3.67-3.80 (m, 4H), 3.39 (s, 3H), 2.99 (s, 1H), 2.02-2.16 (m, 2H), 1.82-1.96 (m, 2H), 1.13 (s, 9H).

(1*R*,2*R*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-1-((*tert*-butyldiphenylsilyloxy) methyl)-2-(phenylamino)-cyclopentanol (**10**) and (1*R*,2*R*,5*R*)-5-(*tert*-Butyldimethylsilyloxy)-2-((*tert*-butyldiphenylsilyloxy)methyl)-2-(phenylamino)cyclopentanol (**11**).

Prepared according to the general procedure. From 227.5 mg (0.47 mmol) of epoxide **9**, after 11 h reaction, were obtained product **10** (9.4 mg, 3.5%, mixture, containing a unknown impurity, [M+1]=582) as a light yellow sticky solid and product **11** (171 mg, 63%) as a colorless sticky solid.

For compound **11:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{34}H_{50}NO_3Si_2$, Calc. *m/z*: 576.33237, found *m/z*: 576.33362; $[M+Na]^+$, $C_{34}H_{49}NNaO_3Si_2$, Calc. *m/z*: 598.31432, found *m/z*: 598.31507.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65-7.67 (m, 2H), 7.53-7.55 (m, 2H), 7.30-7.50 (m, 8H), 7.09-7.13 (m, 2H), 6.59-6.75 (m, 3H), 3.96 (d,d, J_1 = 10.4 Hz, J_2= 10.4 Hz, 2H), 4.12-4.18 (m, 1H), 4.03 (m, 1H), 3.73 (b, 1H), 1.96-2.00 (m, 3H), 1.65-1.71 (m, 1H), 1.09 (s, 9H), 0.96 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H).

(1*S*,2*S*,5*R*)-5-(*tert*-Butyldimethylsilyloxy)-2-((*tert*-butyldiphenylsilyloxy) methyl)-2-(phenylamino)-cyclopentanol (**17**) and (1*S*,2*S*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-1-((*tert*-butyldiphenylsilyloxy)methyl)-2-(phenylamino)cyclopentanol (**19**).

Prepared according to the general procedure. From 156.5 mg (0.32 mmol) of epoxide **15**, after 11 h reaction, were obtained product **17** (28 mg, 15%) as a white solid and product **19** (116.5 mg, 62.4%) as a light yellow sticky solid.

For compound **17:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{34}H_{50}NO_3Si_2$, Calc. *m/z*: 576.33237, found *m/z*: 576.33318; $[M+Na]^+$, $C_{34}H_{49}NNaO_3Si_2$, Calc. *m/z*: 598.31432, found *m/z*: 598.31389.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51-7.53 (m, 2H), 7.15-7.39 (m, 10H), 6.79-6.84 (m, 3H), 4.36-4.40 (m, 1H), 4.14-4.16 (m, 1H), 3.90 (d,d, J_1 = 10.4 Hz, J_2= 10.4 Hz, 2H), 2.86 (d, *J* = 6 Hz, 1H), 2.18-2.63 (m, 1H), 1.95-2.05 (m, 1H), 1.64-1.78 (m, 2H), 0.98 (s, 9H), 0.88 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H).

For compound **19:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{34}H_{50}NO_3Si_2$, Calc. *m/z*: 576.33237, found *m/z*: 576.33324; $[M+Na]^+$, $C_{34}H_{49}NNaO_3Si_2$, Calc. *m/z*: 598.31432, found *m/z*: 598.31467.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68-7.70 (m, 4H), 7.39-7.48 (m, 6H), 7.16-7.19 (m, 2H), 6.65-6.73 (m, 3H), 4.72 (d, J = 5.6 Hz, 1H), 4.14-4.17 (m, 1H), 3.71-3.74 (m, 1H), 3.77 (d,d, J_1 = 10 Hz, J_2= 10.4 Hz, 2H), 3.35 (s, 1H), 2.20-2.27 (m, 1H), 2.05-2.12 (m, 1H), 1.82-1.91 (m, 2H), 1.16 (s, 9H), 0.91 (s, 9H), 0.10 (s, 6H).

(1*R*,2*R*,3*R*)-1-((*tert*-Butyldiphenylsilyloxy)methyl)-2-(phenylamino) cyclopentane-1,3-diol (**22**) and (1*R*,2*R*,3*R*)-3-((*tert*-Butyldiphenylsilyloxy) methyl)-3-(phenylamino)cyclopentane-1,2-diol (**23**).

Prepared according to the general procedure. From 143.7 mg (0.39 mmol) of epoxide **21**, after 15 h reaction, were obtained product **22** (25.5 mg, 14.2%, as a mixture of A and B) as a light yellow sticky solid and product **23** (97.6 mg, 55.5%) as a light yellow sticky solid.

For compound **22:**
Compound **A:**

HRMS, (ESI-POS-DI.m), $[M^*]^+$, $C_{28}H_{35}NO_3Si$, Calc. *m/z*: 461.23807, found *m/z*: 461.23746; $[M+H]^+$, $C_{28}H_{36}NO_3Si$, Calc. *m/z*: 462.2459, found *m/z*: 462.24707.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.68 (m, 4H), 7.37-7.46 (m, 6H), 7.15-7.19 (m, 2H), 6.71-6.76 (m, 3H), 4.37-4.39 (m, 1H), 3.82 (d,d, J_1 = 10.4 Hz, J_2 = 10.4 Hz, 2H), 3.78 (d, J = 4.8 Hz, 1H), 2.71 (b, 1H), 2.11-2.15 (m, 1H), 1.90-1.98 (m, 1H), 1.68-1.79 (m, 2H), 1.12 (s, 9H).

Compound **B:**

HRMS, (ESI-POS-DI.m), $[M^*]^+$, $C_{28}H_{35}NO_3Si$, Calc. *m/z*: 461.23807, found *m/z*: 461.23827; $[M+H]^+$, $C_{28}H_{36}NO_3Si$, Calc. *m/z*: 462.2459, found *m/z*: 462.24729.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.67 (m, 4H), 7.39-7.48 (m, 6H), 7.19-7.23 (m, 2H), 6.76-6.82 (m, 3H), 3.98 (s, 1H), 3.80 (d,d, J_1 = 10.4 Hz, J_2 = 10.4 Hz, 2H), 3.72 (m, 1H), 2.42 (b, 1H), 2.17-2.27 (m, 1H), 1.60-1.80 (m, 3H), 1.08 (s, 9H).

For compound **23:**

HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{28}H_{36}NO_3Si$, Calc. *m/z*: 462.2459, found *m/z*: 462.24726; $[M+Na]^+$, $C_{28}H_{35}NNaO_3Si$, Calc. *m/z*: 484.22784, found *m/z*: 484.22865.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.63 (m, 2H), 7.26-7.48 (m, 8H), 7.13-7.17 (m, 2H), 6.69-6.86 (m, 3H), 4.08-4.13 (m, 1H), 4.05 (d, J = 5.2 Hz, 1H), 3.86 (d,d, J_1 = 10.4 Hz, J_2 = 10.8 Hz, 2H), 3.62 (b, 2H), 1.96-2.17 (m, 2H), 1.72-1.82 (m, 2H), 1.07 (s, 9H).

(1*R*,2*S*,3*S*)-3-((*tert*-Butyldiphenylsilyloxy)methyl)-3-(phenylamino)cyclopentane-1,2-diol (**25**) and (1*S*,2*S*,3*R*)-1-((*tert*-Butyldiphenylsilyloxy)methyl)-2-(phenylamino)cyclopentane-1,3-diol (**26**).

Prepared according to the general procedure. From 133 mg (0.36 mmol) of epoxide **24**, after 5 h reaction, were obtained a mixture of product **25** and **26** (115 mg, 69% estimated by NMR) as a light yellow sticky solid. Products can be separated and get exact yield after removing the TBDPS group.
HRMS, (ESI-POS-DI.m), $[M+H]^+$, $C_{28}H_{36}NO_3Si$, Calc. *m/z*: 462.2459, found *m/z*: 462.24688; $[M+Na]^+$, $C_{28}H_{35}NNaO_3Si$, Calc. *m/z*: 484.22784, found *m/z*: 484.22859.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.68 (m, 4H), 7.29-7.50 (m, 6H), 7.10-7.20 (m, 2H), 6.60-6.78 (m, 3H), 3.68-4.26 (m, 4H), 2.99 (b, 2H), 1.81-2.19 (m, 4H), 1.08, 1.11 (s, 9H).

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