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Diastereoselective synthesis of 10b-substituted hexahydropyrroloisoquinolines from L-tartaric acid. Creation of a quaternary carbon stereocentre via *N*-acyliminium ion cyclization

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Abstract—A simple, three-step synthesis of **10b**-substituted-hexahydropyrroloisoquinolines **12–17** starting from an L-tartaric acid derived imide is described. The methodology presented employs the addition of a Grignard reagent to the imide carbonyl group, followed by a one-pot acetylation–cyclization sequence. The crucial step, an acid-catalyzed carbon–carbon bond forming reaction via an *N*-acyliminium ion offers moderate to high stereoselectivity, which has been shown to be strongly dependent on the size of the R-substituent. The mixtures of pyrroloisoquinolines obtained can be separated as enantiomerically pure 2-silyloxy-derivatives.

The pyrrolo[2,1-*a*]isoquinoline ring system is a key subunit of *Erythrina* alkaloids,[1] which have been widely applied in folk medicine in tropical and sub-tropical regions.[2] Consequently, the stereoselective synthesis of pyrroloisoquinolines has attracted significant attention over recent years.[3–8] The most common approach to the asymmetric synthesis of **10b**-substituted hexahydropyrroloisoquinolines involves Wittig olefination[3–5] or addition of an organometallic reagent[6,7] to the imide carbonyl group of **1** (Scheme 1). The crucial step is diastereoselective cyclization via *N*-acyliminium ion **4**. Steric control can be exerted by the groups already present within the ring[3–6] or as part of the nitrogen substituent.[7]

Lete and co-workers[9,10] have reported recently on the synthesis of racemic **10b**-substituted pyrroloisoquinolines from succinimide employing a tandem carbophilic addition of the organolithium reagent-*N*-acyliminium ion cyclization sequence. Although this methodology has been successfully applied for the preparation of a variety of heterocycles bearing quaternary carbon stereocentres next to the nitrogen atom,[10–12] asymmetric synthesis of **10b**-substituted pyrrolo[2,1-*a*]isoquinolines from a chiral dicarboxylic acid derived imide is rare,[3–6] as far as we are aware.

Herein, we describe an efficient, stereocontrolled synthesis of **10b**-substituted hexahydropyrroloisoquinolines starting from L-tartaric acid. Initially we planned to prepare compounds **10a** and **10b** starting from the easily available imide **6**[4] using a procedure analogous to that reported by Lete and co-workers[9,10] (Scheme 2).

Silylation of **6** under standard conditions (TMS-Cl/pyridine) gave bis-trimethylsilyl ether **7**, which was subsequently treated with phenylmagnesium bromide.

After an aqueous workup, filtration through a silica gel pad and recrystallization from hexane, the hydroxylactam **8** was isolated in 75% yield. Both trimethylsilyl groups in lactam **8** seem stable under the reaction conditions as well as during the isolation procedure, probably due to the steric hindrance. Treatment of **8** with trifluoroacetic acid (TFA) in refluxing dichloromethane for approx. 1 h led to dihydroxypyrroloisoquinolines **10a** and **10b** isolated in trace amounts only. Further increase in the reaction time resulted in the formation of

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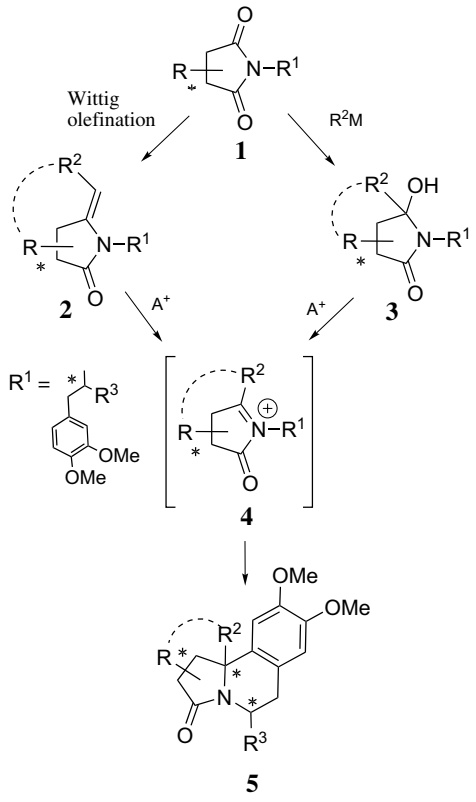
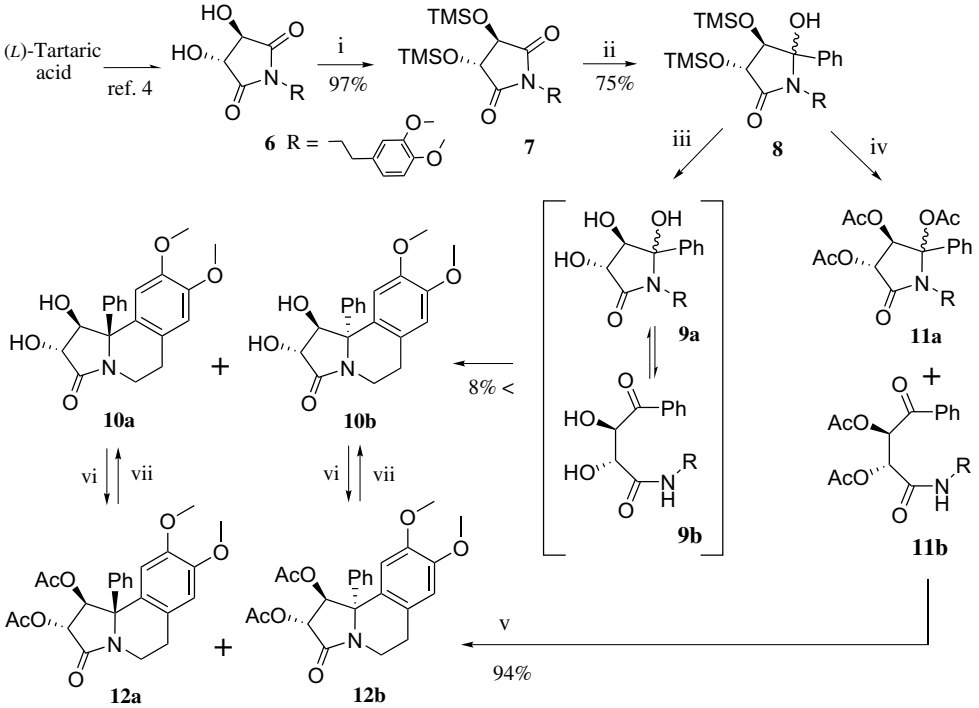


Scheme 1.

tar-like products. Several other protic and/or Lewis acids were tested as catalysts for the cyclization, but no significant improvement was achieved in respect to the yield of **10a** and **10b**. Available literature reports[6,9,11,13] suggest that the synthesis of nitrogen heterocycles via *N*-acyliminium formation of a quaternary carbon atom usually requires prolonged heating of hydroxy-lactams with protic acids. For example, the racemic 1,2-unsubstituted analogue of **10** was obtained from the respective hydroxy-lactam after 36 h heating with TFA.[9] Compound **8**, when treated with TFA gave desilylated **9a** and its open chain tautomer **9b**, both of which apparently are not stable under the reaction conditions.

To facilitate the synthesis of the **10b**-substituted pyrroloisoquinolines we prepared the triacetate **11a**. We assumed that the presence of an acetoxy group at C-1 would speed up the slowest step of the reaction, namely the *N*-acyliminium ion formation.[14] Furthermore, we also expected to see improved stereoselection in favor of *trans*-addition of the nucleophile, due to the known ability of acetoxy groups to bridge adjacent cationic centres.[15] Treatment of **8** with acetic anhydride (4 equiv) and DMAP (1.1 equiv) in acetonitrile resulted in clean conversion to a mixture of acetates **11a** and **11b** in a ratio of ~11:1, as established by ^{1}H NMR analysis of the crude reaction mixture. However, pure **11a** could be isolated by chromatography, on silica gel but in only 15% yield. The ^{1}H NMR experiment indicated that **11a**, on standing in chloroform solution, slowly cyclized to give **12**. Consequently, the crude reaction mixture of acetates **11a** and **11b** was treated with $BF_3{\cdot}Et_2O$ (4 equiv) to give hexahydropyrroloisoquinolines **12a** and **12b** in 94% overall yield and in a 3:1 ratio, respectively.[16] We found that the mixture of **12a** and **12b** was very difficult to separate by chromatography. However, treatment of this mixture with NaOMe in anhydrous



Scheme 2. Reagents and conditions: (i) TMS-Cl, pyridine, 0 °C gradually to rt, 1 h; (ii) PhMgBr (2 equiv), THF, 0 °C gradually to rt, 2 h; (iii) CF_3CO_2H (4 equiv), CH_2Cl_2 reflux, 1 h; (iv) Ac_2O (4 equiv), DMAP (1.1 equiv), MeCN, rt, 4 h; (v) $BF_3{\cdot}Et_2O$ (4 equiv), rt, 10 min then semi-satd $NaHCO_3/H_2O$; (vi) MeONa, MeOH; (vii) Ac_2O, pyridine.

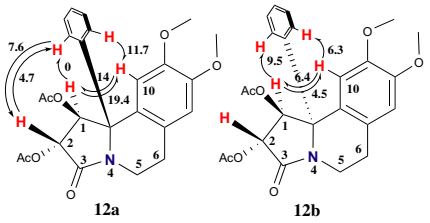


Figure 1.

methanol followed by separation on silica gel of the resulting respective dihydroxy derivatives **10a**,**b** and subsequent re-acetylation gave pure **12a** and **12b**. NOESY experiments, carried out with epimeric **12a** and **12b**, indicated an interaction between the *ortho*-phenylic protons with the protons at C-2 of **12a** and C-1 of **12b** (Fig. 1). Interestingly, the C-1 and C-10 protons of **12a** showed a very strong positive NOE effect. The respective spin interaction in the case of compound **12b** was substantially weaker, indicating that pyrroloisoquinolines **12a** and **12b** possess **10b***S* and **10b***R*-configurations, respectively.

Single crystal X-ray analysis of **12a** confirmed our deduction and provided an unequivocal proof of the absolute configuration of both epimers (Fig. 2).[17]

In order to study the scope of this new methodology, several other **10b**-substituted pyrroloisoquinolines **12**–**17** were obtained (Scheme 3; Table 1). For the preparation

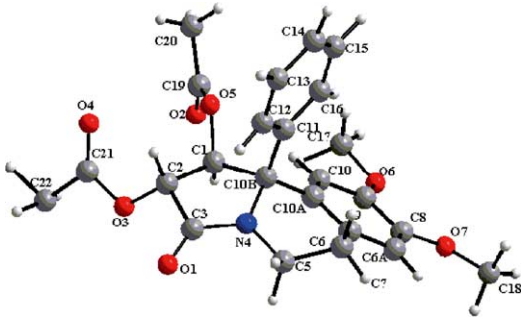
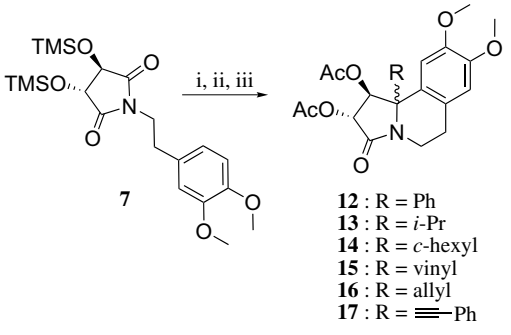


Figure 2.



Scheme 3. Reagents and conditions: (i) RMgX (1.5–3 equiv), 0 °C gradually to rt, (R = Ph, *i*-Pr, *c*-hexyl, PhC≡C), or −78 °C gradually to 0 °C, (R = allyl, vinyl), THF or Et_2O (see Table 1); (ii) Ac_2O (4 equiv), DMAP (1.1 equiv), MeCN, rt, 2–4 h; (iii) $BF_3{\cdot}Et_2O$ (4 equiv), rt, 10–30 min then satd $NaHCO_3/H_2O$.

of compounds **12**–**17** we applied the modified procedure, consisting of the use of crude hydroxy-lactams for the one-pot acetylation–cyclization reaction sequence.[16]

As is evident from Table 1, the overall yields of **12**–**17**, based on the starting imide **7**, were high, except for entry **5**. Interestingly, even the pyrroloisoquinoline **17**, bearing the phenylethynyl substituent at C**10b** was obtained in a high yield. Previous attempts to synthesise C**10b**-phenylethynyl pyrroloisoquinolines were unsuccessful.[10]

Although the diastereomers **12**–**17** or their respective dihydroxy derivatives **10**, **18**–**22** can be separated by careful chromatography on silica gel, we have found that the 2-*t*-butyldimethylsilyloxy-pyrroloisoquinolines **23ab**–**28ab** are much easier to purify due to improved differentiation in the polarity of the **10b** epimers (Scheme 4). The reaction sequence—alkaline hydrolysis of the acetates **12**–**17** and silylation (TBS-Cl, imidazole, DMF) of the crude diols followed by their separation, on silica gel—resulted in the isolation of enantiomerically pure pyrroloisoquinolines **23ab**–**28ab** in approx. 90% yields. The NOESY experiments, carried out with **24ab**–**27ab** showed an interaction between the protons of the R substituent at the carbon atom bonded to C-**10b** with the protons at C-2 and the OH group of the C-**10b***S* epimers. For the C-**10b***R* epimers the respective protons of the R substituent only interact with the proton at C-1. The configuration at C-**10b** in pyrroloisoquinolines **28ab** possessing a phenylethynyl substituent could not be directly established on the basis of NOESY experiments, due to the lack of diagnostic protons able to interact with protons at C-1 or C-2. However, the epimeric mixture of pyrroloisoquinolines **22** when subjected to palladium catalyzed cyclization[18] [0.2 equiv $Pd(OAc)_2$, TEA, THF, rt, 2 h], gave dihydrofuranyl derivative **29a** in 82% yield. The formation of **29a** indicates that the major diastereomer of **22** possesses the *S*-configuration at C-**10b**. Compound **29b** was not detected in the crude reaction mixture, however, a small amount (~4%) of unreacted pyrroloisoquinoline **10b**(*R*) **22** was isolated. Prolonging the reaction time resulted in complete decomposition of **10b**(*R*) **22**. While both processes—5- and 6-*endo-dig* cyclization, according to Baldwin's rules are favorable—the latter was not observed, probably due to the rigidity of the pyrroloisoquinoline skeleton.

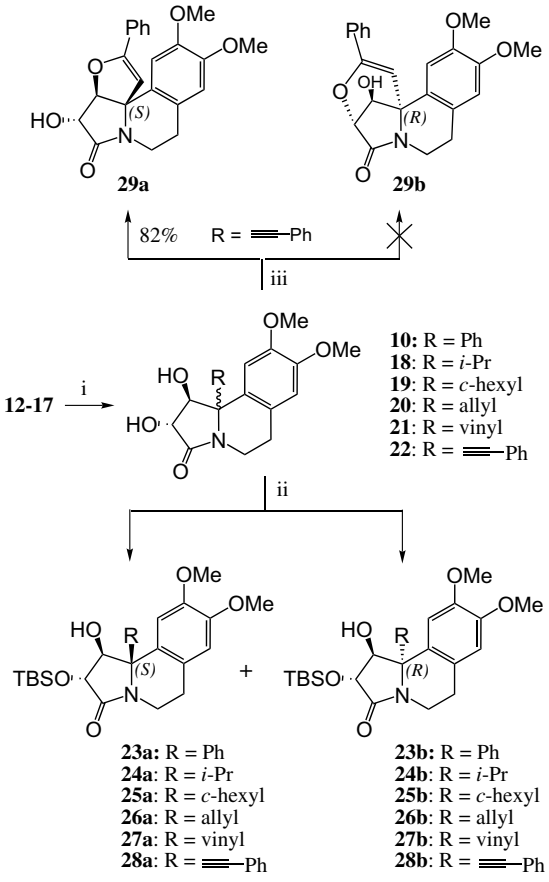
Unequivocal establishment of the configuration at C-**10b** of all pyrroloisoquinolines **12**–**17** allowed for the rationalization of the observed stereoselectivity of cyclization (Table 1). The C-**10b**(*S*) diastereomer is created via *trans*-addition of the nucleophile (dimethoxyphenyl moiety) with respect to the acetoxy group involved in bridging the adjacent cationic centre (Fig. 3).

Consequently, the C-**10b**(*R*) epimer is a product of *syn*-addition. The stereochemical outcome of cyclizations described in this paper can be rationalized by assuming the importance of the differences in steric interactions of the approaching nucleophile with the R substituent versus the acetoxy group. The prevalent *trans*-addition of the nucleophile was observed for the relatively small

Table 1

Entry	RMgX/solvent	Product[a]	Yield [%][b]	*S*:*R*[c]
1	PhMgBr/THF	**12**	82	3:1
2	*i*-PrMg$_2$/Et$_2$O	**13**	80	1:6.3
3	*c*-HexylMgBr/Et$_2$O	**14**	50	1:10
4	AllylMgCl/THF	**15**	62	1:1.2
5	VinylMgBr/THF	**16**	38	4.6:1
6	PhC≡CMgBr/THF	**17**	81	9.5:1

[a] All reactions were carried out at 1 mmol scale, applying the standard procedure, see Scheme 3.
[b] Isolated yields of the mixture of diastereomers calculated for three steps.
[c] Diastereomeric ratio was determined by ^{1}H NMR analysis.



Scheme 4. Reagents and conditions: (i) MeONa, MeOH; (ii) TBS-Cl, imidazole, DMF, rt, 24 h; (iii) Pd(OAc)$_2$ (0.2 equiv), TEA, THF, rt, 2 h.

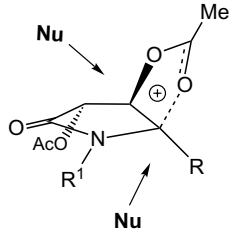


Figure 3.

R groups (phenyl, vinyl, phenylethynyl, entries 1, 5 and 6, Table 1). In contrast, when bulky R groups (*i*-propyl, *c*-hexyl, allyl; entries 2, 3 and 4, Table 1) are present, *syn*-addition occurs predominantly.

In summary, we have successfully developed a simple, three-step synthesis of the C-**10b**-substituted-1,2-diacetoxy-hexahydropyrroloisoquinolines **12**–**17**, starting from the imide **6**, derived from L-tartaric acid. The presented methodology employs the addition of a Grignard reagent to the imide carbonyl group of **9**, followed by an one-pot acetylation–cyclization sequence. The crucial step, an acid-catalyzed carbon–carbon bond forming reaction via an *N*-acyliminium ion offers moderate to high stereoselectivity, which, it has been shown, is strongly dependent on the size of the R substituent. The mixtures of pyrroloisoquinolines obtained can be separated as enantiomerically pure 2-silyloxy-derivatives. Additionally, the C-**10b**-substituted pyrroloisoquinolines, obtained using this methodology, can be regarded as valuable synthons for the preparation of *Erythrina* alkaloids.

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Bailey, P. D.; Morgan, K. M.; Smith, D. I.; Vernon, J. M. *Tetrahedron* **2003**, *59*, 3369–3378.
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16. All compounds gave satisfactory spectroscopic and analytical data. Typical procedure for **12a** and **12b**: To a solution of imide **7** (439 mg, 1 mmol) in dry THF (5 mL), freshly prepared PhMgBr (2 mmol) in THF (5 mL) was added at 0 °C, and gradually warmed up to rt. The resulting mixture was stirred at rt until TLC indicated the disappearance of **7** (approx. 0.5 h), then was poured into ice-cold semi-saturated aqueous $NaHCO_3$ (30 mL) and extracted with *t*-butyl methyl ether (3×20 mL). The combined extracts were washed with ice-cold water, dried ($MgSO_4$), filtered and evaporated in vacuo. The crude hydroxy-lactam **8** obtained was dissolved in dry MeCN (5 mL), and after cooling to 0 °C, dimethylaminopyridine (135 mg, 1.1 mmol) and Ac_2O (378 μL, 4 mmol) were added. The cooling bath was removed and stirring was continued at rt for 2 h, then $BF_3{\cdot}Et_2O$ (507 μL, 4 mmol) was added in one portion. The mixture was stirred at rt for 10 min then cooled to 0 °C, quenched with saturated aqueous $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (3×20 mL). The combined extracts were washed with water (2×20 mL), dried ($MgSO_4$), filtered and evaporated in vacuo. The product was purified by flash column chromatography on silica gel (EtOAc/hexane = 1:1) to yield pyrroloisoquinolines **12a** and **12b** as a 3:1 mixture in 82% yield. The mixture of **12a** and **12b** (220 mg, 0.5 mmol) obtained was dissolved at rt in dry MeOH (10 mL) containing MeONa (16 mg, 0.3 mmol). The solution was stirred until TLC indicated the disappearance of the substrate (~0.5 h), then the reaction was quenched by the addition of a small piece of dry ice and evaporated in vacuo. The product was purified by flash column chromatography on silica gel (EtOAc/hexane/MeOH, 7.5:4:1) to give **10a** (107 mg, 60% yield) and **10b** (32 mg, 18% yield). Dihydroxy-pyrroloisoquinolines **10a** and **10b** were acetylated (Py/Ac_2O) and crystallized to yield analytically pure acetates **12a** and **12b**.
Selected data for **12a**; mp 230–231 °C (ethanol); $[\alpha]_D$ −57.2 (*c* 2.4, CH_2Cl_2); IR (CH_2Cl_2): 3055, 1753, 1713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm): 1.86 and 2.13 (2s, 6H), 2.47 (m, 1H), 2.82 (m, 1H), 3.43 (m, 1H), 3.87 (m, 1H), 3.88 and 3.91 (2s, 6H), 5.72 (d, 1H, $J = 6.8$ Hz), 5.99 (d, 1H, $J = 6.8$ Hz), 6.65 and 7.14 (2s, 2H), 7.07–7.10 (m, 2H), 7.27–7.34 (m, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) (δ, ppm): 20.60, 20.67, 26.12, 37,59, 55.94, 56.20, 67.86, 74.59, 78.27, 109.19, 111.68, 126.63, 127.42, 128.02, 128.31, 131.06, 138.45, 147.75, 147.68, 166.18, 169.82, 170.17; HRMS (EI) *m/z*: (M^+) calcd for $C_{24}H_{25}O_7N$: 439.1631. Found: 439.1642.
Selected data for **12b**; mp 211–212 °C (EtOAc/hexane); $[\alpha]_D$ −27.0 (*c* 1, CH_2Cl_2); IR (CH_2Cl_2): 3066, 1755, 1708 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm): 1.90 and 2.02 (2s, 6H), 2.64 (m, 1H), 2.98 (m, 1H), 3.18 (m, 1H), 3.83 and 3.88 (2s, 6H), 4.21(m, 1H), 5.22 (d, 1H, $J = 2.7$ Hz), 5.99 (d, 1H, $J = 2.7$ Hz), 6.64 and 6.81 (2s, 2H), 7.27–7.36 (m, 5H); ^{13}C NMR (125.76 MHz, $CDCl_3$) (δ, ppm): 20.51, 20.92, 27.50, 36.55, 55.80, 55.95, 69.12, 75.35, 76.91, 110.72, 111.58, 125.97, 127.02, 127.19, 128.11, 128.55, 141.83, 146.90, 148.36, 167.20, 169.29, 169.66; HRMS (LSIMS+) *m/z*: ($M + H^+$) calcd for $C_{24}H_{26}O_7N$: 440.1709. Found: 440.1713.
Typical procedure for the preparation of pyrroloisoquinolines **23a** and **23b**: To a stirred solution of the crude reaction mixture of **10a** and **10b** obtained as above from **12a**, **12b** (220 mg, 0.5 mmol), imidazole (102 mg, 1.5 mmol) in DMF (3 mL) was added followed by *tert*-butyldimethylchlorosilane (150 mg, 1 mmol) and the mixture was stirred for 24 h at room temperature. The mixture was poured into water, extracted with ethyl acetate (2×10 mL), washed with water and brine then dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/hexane, 35:65) to give **23a**, (167 mg, 71% yield) and **23b** (54 mg, 23% yield).
Selected data for **23a**: oil; $[\alpha]_D$ −120.2 (*c* 1.1, CH_2Cl_2); IR (CH_2Cl_2): 3683, 1705, 1608 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm): 0.14 and 0.20 (2s, 6H), 0.93 (s, 9H), 1.64 (d, 1H, $J = 10.0$ Hz), 2.45 (m, 1H), 2.72 (m, 1H), 3.57 (m, 1H), 3.71 (m, 1H), 3.86 and 3.98 (2s, 6H), 4.23 (d, 1H, $J = 8.3$ Hz), 4.57 (dd, 1H, $J = 8.3$, 10.0 Hz), 6.62 and 7.34 (2s, 2H), 7.16–7.20 (m, 2H), 7.29–7.38 (m, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) (δ, ppm): 18.37, 25.76, 26.26, 37.75, 55.96, 56.41, 66.39, 76.60, 82.10, 108.94, 111.35, 126.6, 127.54, 128.21, 128.86, 132.85, 137.77, 147.87, 148.53, 170.24. HRMS (EI) *m/z*: (M^+) calcd for $C_{26}H_{35}O_5NSi$: 469.2287. Found: 469.2285.
Selected data for **23b**: mp 216–218 °C; $[\alpha]_D$ −4.4 (*c* 1.2, CH_2Cl_2); IR (CH_2Cl_2): 3559, 1705, 1611 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm): 0.15 and 019 (2s, 6H), 0.88 (s, 9H), 2.00 (d, 1H, $J = 3.9$ Hz), 2.27 (m, 1H), 2.89 (m, 1H), 3.10 (m, 1H), 3.87 and 3.88 (2s, 6H), 4.11 (m, 1H), 4.20 (d, 1H, $J = 3.1$), 4.55 (dd, 1H, $J = 3.1$, 3.9 Hz), 6.67 and 7.08 (2s, 2H), 7.22–7.29 (m, 3H), 7.35–7.39 (m, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$) (δ, ppm): 18.11, 25.64, 27.46, 35.78, 55.87, 56.27, 69.54, 77.70, 80.89, 110.61, 112.34, 126.67, 127.57, 127.64, 128.23, 128.75, 142.75, 147.50, 148.61, 171.03. HRMS (EI) *m/z*: (M^+) calcd for $C_{26}H_{35}O_5NSi$: 469.2287. Found: 469.2279.
17. The crystallographic data for compound **12a** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC 222580. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].
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