Highly Diastereoselective Addition of Ketone Enolates to *N*-Sulfinyl Imines: Asymmetric Synthesis of *syn*- and *anti*-1,3-Amino Alcohol Derivatives

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Abstract: Lithium enolates derived from ketones may be added to *N*-sulfinyl imines with high diastereoselectivity. Diastereoselective reduction gave either the *syn*- or *anti*-1,3-amino alcohol derivative.

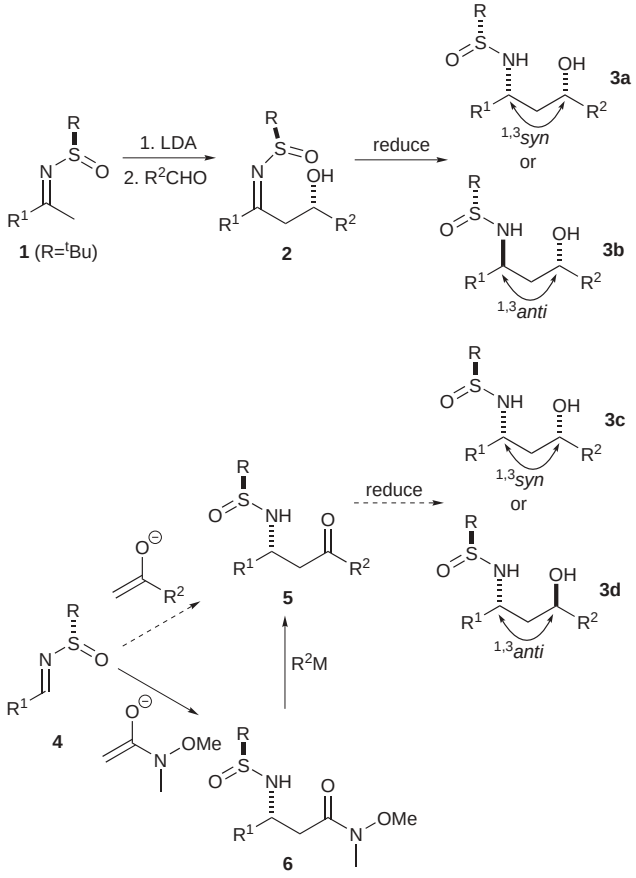
Key words: asymmetric synthesis, chiral auxiliaries, amino alcohols, stereoselective synthesis

N-Sulfinyl chiral auxiliaries have been widely exploited in the asymmetric synthesis of amines.[1] In particular, the additions of organolithium and Grignard reagents to *N*-sulfinyl imines are often highly diastereoselective and may be used to prepare α-branched primary amines.[2]

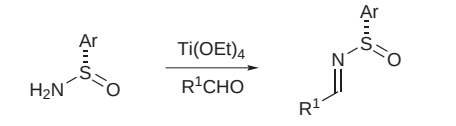
Previously, a convenient asymmetric synthesis of 1,3-amino alcohols has also been developed (Scheme 1). Additions of azaenolates, derived from imines **1** (R = *t*-Bu), to aldehydes often yield β-hydroxy imines **2** with high diastereoselectivity; the imines **2** may be reduced in either sense to give ^{1,3}*syn*- or ^{1,3}*anti*-amino alcohol derivatives (**3a** or **3b**).[3]

In this paper, we describe an alternative approach in which a ketone enolate is added to an *N*-sulfinyl imine **4** (→ **5**);[4] diastereoselective reduction yields the corresponding 1,3-amino alcohol derivatives (e.g. **3c** or **3d**). This approach is more direct than the addition of ester or Weinreb amide enolates[5] to *N*-sulfinyl imine (e.g. → **6**), followed by reaction with an organometallic reagent, R^2M (→ **5**) and reduction (→ **3c**,**d**).[6]

The *N*-sulfinyl imines **7a**–**e** were prepared by treatment of a mixture of an aldehyde R^1CHO and *p*-toluenesulfinamide with 1.5 equivalents of titanium(IV) ethoxide (Scheme 2).[7] The imines **7** were reacted at –78 °C with 1.6 equivalents of lithium enolate, generated by treatment of a ketone (**8**, **10** or **12**) with lithium hexamethyldisilazide (LiHMDS) (Scheme 3 and Table 1). After quenching with methanolic ammonium chloride solution, work-up and purification, the β-amino ketone derivatives **9** and **11** were obtained as single diastereoisomers. Unfortunately, the reaction of the lithium enolate derived from cyclohexanone was less selective, and a mixture of all four possible diastereoisomers (**13**) was obtained (entry 8).



Scheme 1 Altenative strategies for the asymmetric synthesis of 1,3-amino alcohols using *N*-sulfinyl imines



7a; R^1=2-furyl, 98%
7b; R^1=Ph, 97%
7c; R^1=$O_2NC_6H_4$-, 91%
7d; R^1=$MeOC_6H_4$-, 94%
7e; R^1=^{c}Hex, 87%

Scheme 2 Preparation of the *N*-sulfinyl imines **7**

The yield of the addition reaction **7** + **8** → **9** was dependent on the substituents R^1 and R^2. Excellent yields of the β-sulfinamino ketones **9a** and **9c** were obtained when 1.6

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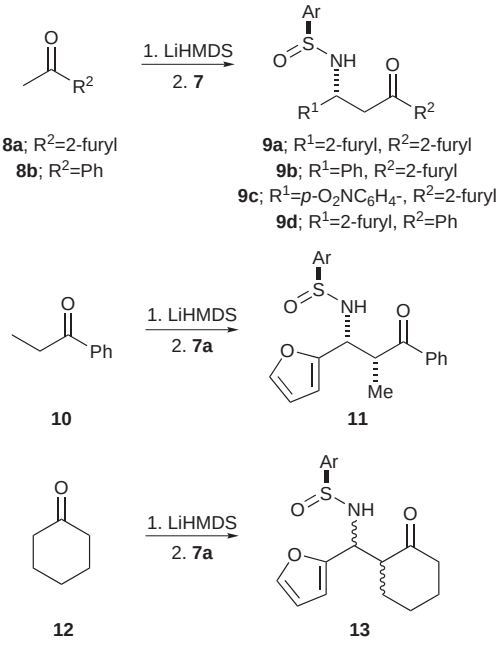
Table 1 Asymmetric Addition of Ketone Enolates to *N*-Sulfinyl Imines[a]

Entry	Imine	Ketone	R^1	R^2	Method	Product	De[b]	Yield (%)[c]
1a	**7a**	**8a**	2-Furyl	2-Furyl	A	**9a**	>95:5	87
1b					B[d]	**9a**	>95:5	69
2	**7b**	**8a**	Ph	2-Furyl	C	**9b**	>95:5	59 (30[e])
3	**7c**	**8a**	*p*-$O_2NC_6H_4$-	2-Furyl	A	**9c**	>95:5	83
4	**7d**	**8a**	*p*-$MeOC_6H_4$-	2-Furyl	A	–	–	–
5	**7e**	**8a**	Cyclohexyl	2-Furyl	A	–	–	–
6	**7a**	**8b**	2-Furyl	Ph	C	**9d**	>95:5	81 (31[e])
7	**7a**	**10**	–	–	A	**11**	>95:5	97
8	**7a**	**12**	–	–	A	**13**	25:20:10:1	82[f]

[a] Methods: **A**: 1. 1.6 equiv lithium enolate, –78 °C, THF; 2. NH_4Cl, MeOH, –78 °C; **B**: 1. 1.6 equiv lithium enolate, –50 °C, THF; 2. HOAc, –50 °C; **C**: 1. 3.0 equiv lithium enolate, –78 °C, THF; 2. NH_4Cl, MeOH.
[b] Detemined by ^1H NMR (500 MHz) spectroscopy of the crude reaction mixture.
[c] Yield of single diastereoisomer.
[d] Final concentration: 0.25 M in **7a** (442 mmol scale).
[e] By method **A**.
[f] Yield of mixture of inseparable isomers.

equivalents of the lithium enolate derived from 2-acetyl furan (**8a**; R^2 = 2-furyl) were added to the imines **7a** and **7c** (R^1 = 2-furyl and *p*-$O_2NC_6H_4$-; R^2 = 2-furyl; entries 1 and 3, Table 1). However, low yields of the β-sulfinamino ketones **9b** and **9d** were obtained under these conditions; these reactions could be optimised by reacting 3 equivalents of lithium enolate with the required imine (entries 2 and 6, Table 1). Attempted addition of the lithium enolate derived from **8a** to the imines **7d** and **7e** (R^1 = *p*-$MeOC_6H_4$- and cyclohexyl) was, however, unsuccessful.

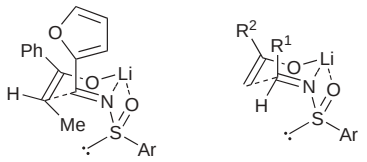


Scheme 3 Asymmetric addition of ketone enolates to *N*-sulfinyl imines

The preparation of the β-amino ketone **9a** on a large (442 mmol) scale (entry 1b, Table 1) required considerable optimisation since the product was susceptible to β-elimination under the concentrated reaction conditions (final concentration: 0.25 M in the sulfinamide **7a**). The elimination of the product could be suppressed by quenching the reaction with acetic acid (in place of methanolic ammonium chloride solution) after 30 minutes below –40 °C. Lower yields of the β-sulfinamino ketone **9a** were obtained when LDA, rather than LiHMDS, was used as the base.

The configurations of the β-amino ketone derivatives **9a**–**d** were assigned by analogy with that of **11** which was determined by X-ray crystallography (Figure 1). The sense of induction observed in the synthesis of **11** is consistent with attack of the *Z*-configured[8] lithium enolate on the *N*-sulfinyl imine via a fused transition state **14** in which the *S*-(*p*-tolyl) substituent occupies an 'outside' position. The transition state **15**, which would lead to the β-amino ketone derivatives **9a**–**d**, is similar to a model which has been proposed to explain the diastereoselective attack of ester enolates on *N*-sulfinyl imines (Figure 2).[5b]

Figure 1 X-ray crystal structure of the β-sulfinamino ketone **11**



14 → 11 **15 → 9a–d**

Figure 2 Proposed transition states for the addition reaction

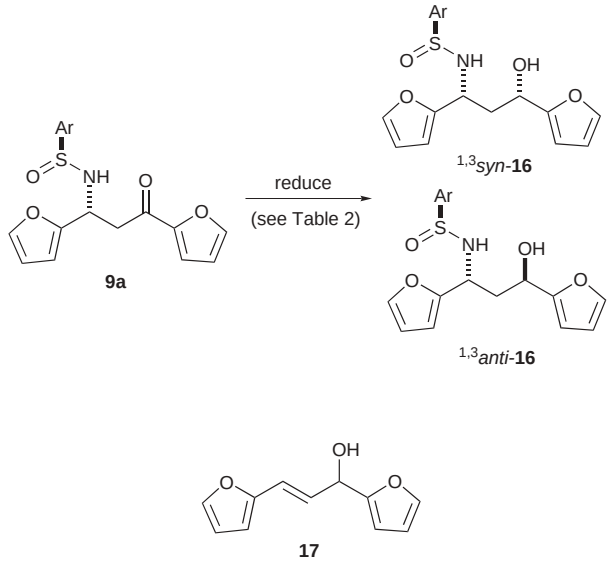
A range of reaction conditions was screened for the reduction of the ketone **9a** (Scheme 4 and Table 2); the diastereoselectivity of each process was determined by analytical HPLC and/or by ^{1}H NMR (500 MHz) spectroscopy. The reduction of **9a** with $NaBH_4$ was unselective (entries 1 and 2) and, in THF, competing β-elimination and subsequent reduction (→ **17**) was observed. We have, however, been able to identify conditions under which the ketone **9a** may be selectively converted into either of the diastereoisomeric 1,3-amino alcohols ^{1,3}*syn*- or ^{1,3}*anti*-**16**. The reductions with Superhydride (entry 3), K-selectride (entry 4) and DIBALH (entries 5a,b) were selective in favour of the alcohol ^{1,3}*syn*-**16**. In contrast, the use of $LiAlH_4$ (entry 6) gave a 71:29 mixture in favour of ^{1,3}*anti*-**16**.

Table 2 Diastereoselective Reduction of the β-Sulfinamido Ketone **9a**

Entry	Conditions	De ^{1,3}*syn*:^{1,3}*anti*
1	$NaBH_4$, THF, 25 °C	40:60[a,b]
2	$NaBH_4$, EtOH, 25 °C	48:52[c,d]
3	Li $BHEt_3$, THF, –78 °C	92:8[c]
4	K BH^sBu_3, THF, –78 °C	79:21[c]
5a	*i*-Bu_2AlH, THF, –78 °C	86:14[c,e]
5b	*i*-Bu_2AlH, THF, 25 °C	72:28[c,f]
6	$LiAlH_4$, THF, –78 °C	29:71[c]
7	Li $AlH(Ot\text{-}Bu)_3$	48:52[c]

[a] Determined by ^{1}H NMR (500 MHz) spectroscopy of the crude reaction mixture.
[b] Flash column chromatography gave ^{1,3}*syn*-**16** (12%), ^{1,3}*anti*-**16** (24%), **17** (51%) and *p*-toluenesulfinamide (63%).
[c] Determined by analytical HPLC.
[d] A >98% yield of a 48:52 mixture of diastereoisomers was obtained; flash column chromatography gave ^{1,3}*syn*-**16** (44%) and ^{1,3}*anti*-**16** (46%).
[e] Flash column chromatography gave ^{1,3}*syn*-**16** (68%).
[f] Flash column chromatography gave ^{1,3}*syn*-**16** (58%).

In conclusion, we have developed an approach to the synthesis of 1,3-amino alcohols with relies on the diastereoselective addition of a ketone enolate to a *N*-sulfinyl imine. The methods have been optimised to avoid competing β-elimination, and have been exploited on a large scale. Complementary reaction conditions have been identified for the stereoselective reduction of **9a** to give the ^{1,3}*syn*- or the ^{1,3}*anti*- 1,3-amino alcohol derivatives **16**.



9a ^{1,3}*syn*-**16** ^{1,3}*anti*-**16** **17**

Scheme 4 Diastereoselective reduction of the β-sulfinamino ketone **9a**

Diastereoselective Addition of Ketone Enolates to *N*-Sulfinyl Imines

Synthesis of 9a: A solution of acetyl furan (151 mg, 1.37 mmol) in THF (3 mL) was added dropwise to a stirred solution of LiHMDS (1.37 mL of a 1 M solution in THF, 1.37 mmol) in THF (5 mL) at –78 °C. After 0.5 h, a solution of the imine **7a** (200 mg, 0.859 mmol) in THF (5 mL) was added dropwise and the resulting reaction mixture stirred at –78 °C for 1 h. The reaction was quenched at –78 °C by addition of a sat. methanolic NH_4Cl solution (4 mL), warmed to r.t. and poured onto H_2O (10 mL) and EtOAc (10 mL). The layers were separated and the aqueous phase was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product which was purified by flash chromatography, eluting with 3:7 EtOAc–petrol ether, to give the ketosulfinamide **9a** (256 mg, 87%) as a colourless oil; R_F 0.7 (EtOAc); $[\alpha]_D^{20}$ +103.7 (*c* 1.1 in $CHCl_3$). IR (thin film): ν_{max} = 3148, 2922, 1671, 1467 and 1089 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (2 H, d, *J* = 8.2 Hz, 2′- and 6′-H), 7.55 (1 H, dd, *J* = 1.4 and 0.8 Hz, 3-furyl 5-H), 7.35 (1 H, dd, *J* = 1.9 and 0.9 Hz, 1-furyl 5-H), 7.27 (2 H, d, *J* = 8.2 Hz, 3′- and 5′-H), 7.15 (1 H, dd, *J* = 3.5 and 0.8 Hz, 3-furyl 3-H), 6.51 (1 H, dd, *J* = 3.5 and 1.4 Hz, 3-furyl 4-H), 6.36 (1 H, dd, *J* = 3.2 and 0.9 Hz, 1-furyl 3-H), 6.32 (1 H, dd, *J* = 3.2 and 1.9 Hz, 1-furyl 4-H), 5.07 (2-H, m, NH and 1-H), 3.49 (1 H, dd, *J* = 17.1 and 5.9 Hz, 2-H), 3.37 (1 H, dd, *J* = 17.1 and 5.2 Hz, 2-H) and 2.39 (3 H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.6, 153.7, 152.6, 147.1, 142.7, 142.2, 141.8, 130.0, 126.0, 118.2, 112.8, 110.9, 108.3, 49.1, 43.5 and 21.8. MS (ES): *m/z* (%) = 344 (85%) [MH^+] and 190 (100) [M – C_7H_7SON]. Found: MNa^+, 366.0760. $C_{18}H_{17}NO_4S$ requires MNa, 366.0776.

Compound **9b**: R_f = 0.1 (3:7 EtOAc–petrol ether); $[\alpha]_D^{20}$ +84.5 (*c* 1.51 in $CHCl_3$). IR (thin film): ν_{max} = 3209, 2922, 1671, 1467, 1089 and 1062 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (2 H, d, *J* = 8.1 Hz, 2′- and 6′-H), 7.52 (1 H, dd, *J* = 1.4 and 0.8 Hz, furyl 5-H), 7.46 (2 H, d, *J* = 7.4 Hz, Ph 2- and Ph 6-H), 7.37 (2 H, t, *J* = 7.4 Hz, Ph 3-H and 5-H), 7.30 (1 H, t, *J* = 7.4 Hz, Ph 4-H), 7.27 (2 H, d, *J* = 8.1 Hz, 3′- and 5′-H), 7.11 (1 H, dd, *J* = 3.4 and 0.8 Hz, furyl 3-H), 6.48 (1 H, dd, *J* = 3.4 and 1.4 Hz, furyl 4-H), 5.13 (1 H, d, *J* = 4.8 Hz, NH), 5.03 (1 H, app. q, *J* = 5.2 Hz, 1-H) 3.39 (1 H, dd, *J* = 16.7

and 5.2 Hz, 2-H_A), 3.33 (1 H, dd, *J* = 16.7 and 7.5 Hz, 2-H_B) and 2.39 (3 H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.1, 152.7, 147.2, 142.7, 141.8, 141.0, 130.0, 129.2, 128.4, 127.9, 125.8, 118.2, 112.9, 55.0, 46.2 and 21.8. MS (ES): *m/z* (%) = 707 (100) [M_2H^+] and 354 (42) [MH^+]. Found: MNa^+, 376.0966. $C_{20}H_{19}NO_3S$ requires MNa, 376. 0983.

Compound **9c**: mp 138.4–139.1 °C ($CHCl_3$–Et_2O); R_f = 0.2 (colourless needles from 3:7 EtOAc–petrol ether). $C_{20}H_{18}N_2SO_5$ requires: C, 60.3; H, 4.55; N, 7.0; S, 8.1%. Found: C, 60.0; H, 4.70; N, 7.0; S, 8.0; $[\alpha]_D^{20}$ +84.3 (*c* 0.56 in $CHCl_3$). IR (thin film): ν_{max} = 3206, 2923, 1671, 1520, 1347 and 1088 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (2 H, d, *J* = 8.7 Hz, Ar 2- and 6-H), 7.65 (2 H, d, *J* = 8.7 Hz, Ar 3- and 5-H), 7.58 (2 H, d, *J* = 8.1 Hz, 2′- and 6′-H), 7.55 (1 H, dd, *J* = 1.6 and 0.8 Hz, furyl 5-H), 7.32 (2 H, d, *J* = 8.1 Hz, 3′- and 5′-H), 7.15 (1 H, dd, *J* = 3.4 and 0.8 Hz, furyl 3-H), 6.53 (1 H, dd, *J* = 3.4 and 1.6 Hz, furyl 4-H), 5.24 (1 H, d, *J* = 6.1 Hz, NH), 5.08 (1 H, app. q, *J* = 6.1 Hz, 1-H), 3.42 (1 H, d, *J* = 6.0 Hz, 2-H_2) and 2.39 (3 H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.4, 152.5, 148.8, 147.8, 147.4, 142.3, 141.8, 130.2, 128.7, 125.8, 142.4, 118.4, 113.1, 54.3, 45.6 and 21.8. MS (ES): *m/z* (%) = 797 (100) [M_2H^+] and 399 (63) [MH^+].

Compound **9d**: mp 91.0–92.7 °C (colourless needles from EtOAc–petrol ether). R_f = 0.2 (3:7 EtOAc–petrol ether). $C_{20}H_{19}NSO_3$ requires: C, 68.0; H, 5.40; N, 4.0; S, 9.1%. Found: C, 67.8; H, 5.55; N, 3.9; S, 8.9; $[\alpha]_D^{20}$ +87.5 (*c* 0.64 in CH_2Cl_2). IR (thin film): ν_{max} = 3189, 2920, 1683, 1448, 1090 and 1066 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (2 H, d, *J* = 7.4 Hz, Ph 2- and Ph 6-H), 7.59 (2 H, d, *J* = 8.1 Hz, 2′- and 6′-H), 7.56 (1 H, t, *J* = 7.4 Hz, Ph 4-H), 7.43 (2 H, t, *J* = 7.4 Hz, Ph 3- and Ph 5-H), 7.35 (1 H, dd, *J* = 1.8 and 0.8 Hz, furyl 5-H), 7.27 (2 H, d, *J* = 8.1 Hz, 3′- and 5′-H), 6.38 (1 H, dd, *J* = 3.2 and 0.8 Hz, furyl 3-H), 6.33 (1 H, dd, *J* = 3.2 and 1.8 Hz, furyl 4-H), 5.11 (2 H, m, NH and 1-H), 3.66 (1 H, dd, *J* = 17.1 and 5.5 Hz, 2-H_A), 3.52 (1 H, dd, *J* = 17.1 and 5.0 Hz, 2-H_B) and 2.39 (3 H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.6, 153.8, 142.6, 142.3, 141.8, 136.8, 133.9, 130.0, 129.1, 128.5, 126.0, 111.0, 108.4, 49.3, 43.7 and 21.8. MS (ES): *m/z* (%) = 707 (100) [M_2H^+] and 354 (35) [MH^+].

Compound **11**: mp 120.8–121.5 °C (colourless plates from MeOH–H_2O); R_f = 0.3 (3:7 EtOAc–petrol ether); $C_{21}H_{21}NSO_3$ requires: C, 68.6; H, 5.75; N, 3.8; S, 8.7%. Found: C, 68.5; H, 5.70; N, 3.7; S, 8.8; $[\alpha]_D^{20}$ +160 (*c* 0.76 in CH_2Cl_2). IR (thin film): ν_{max} = 3194, 2976, 1679, 1448, 1090 and 1066 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83 (2 H, d, *J* = 7.3 Hz, Ph 2- and Ph 6-H), 7.54 (2 H, d, *J* = 8.1 Hz, 2′- and 6′-H), 7.54 (1 H, t, *J* = 7.3 Hz, Ph 4-H), 7.41 (2 H, t, *J* = 7.4 Hz, Ph 3- and Ph 5-H), 7.34 (1 H, dd, *J* = 1.7 and 0.8 Hz, furyl 5-H), 7.23 (2 H, d, *J* = 8.1 Hz, 3′- and 5′-H), 6.33 (1 H, dd, *J* = 3.1 and 0.8 Hz, furyl 3-H), 6.29 (1 H, dd, *J* = 3.1 and 1.7 Hz, furyl 4-H), 4.89 (1 H, dd, *J* = 6.9 and 6.9 Hz, 1-H), 4.77 (1 H, d, *J* = 6.9 Hz, NH), 3.98 (1 H, app. qn, *J* = 6.9 Hz, 2-H), 2.38 (3 H, s, Me) and 1.22 (3 H, d, *J* = 6.9 Hz, 2-Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.6, 153.2, 142.1, 141.7, 141.4, 135.7, 133.3, 129.5, 128.6, 128.3, 125.6, 110.5, 108.5, 53.1, 44.6, 21.4 and 13.7. MS(ES+): *m/z* (%) = 735 (100) [M_2H^+] and 368 (73) [MH^+].

Synthesis of ^{1,3}*Syn*- and ^{1,3}*anti*-16: Sodium borohydride (11 mg, 0.292 mmol) was added to a stirred solution of **9a** (50 mg, 0.146 mmol) in EtOH (8 mL). After 1.5 h, the reaction was quenched with H_2O (10 mL), the layers were separated and the aqueous portion was extracted with EtOAc (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure to give a crude product. Purification by flash chromatography, eluting with 3:7 EtOAc–petrol ether, gave ^{1,3}*syn*-**16** (22 mg, 44%) as a colourless oil, R_f = 0.7 (7:3 EtOAc–petrol ether); $[\alpha]_D^{20}$ +75.6 (*c* 0.27 in $CHCl_3$). IR (thin film): ν_{max} = 3306, 2924, 1596, 1504, 1012 and 737 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (2 H, d, *J* = 8.2 Hz, 2′- and 6′-H), 7.37 (1 H, br s, 1-furyl 5-H), 7.29 (1 H, br s, 3-furyl 5-H), 7.23 (2 H, d, *J* = 8.2 Hz, 3′- and 5′-H), 6.31 (1 H, dd, *J* = 3.0 and 1.8 Hz, 1-furyl 4-H), 6.27 (1 H, dd, *J* = 3.0 and 1.9 Hz, 3-furyl 4-H), 6.24 (1 H, d, *J* = 3.0 Hz, 1-furyl 3-H), 6.19 (1 H, d, *J* = 3.0 Hz, 1-furyl 3-H), 4.90 (1 H, d, *J* = 8.5 Hz, NH), 4.84 (1 H, ddd, *J* = 9.6, 4.7 and 4.7 Hz, 3-H), 4.77 (1 H, td, *J* = 8.5 and 4.7 Hz, 1-H), 3.81 (1 H, d, *J* = 4.7 Hz, OH), 2.41 (1 H, ddd, *J* = 14.0, 9.6 and 4.7 Hz, 2-H), 2.38 (3 H, s, Me) and 2.21 (1 H, ddd, *J* = 14.0, 8.5 and 4.7 Hz, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 155.3, 142.7, 142.4, 142.2, 142.1, 130.1, 126.0, 110.7, 110.6, 107.1, 106.4, 64.4, 50.9, 40.3 and 21.8. MS (ES+): *m/z* (%) = 346 (15) [MH^+], 328 (30) [M – OH] and 234 (100) [M – $FuCHOHCH_2$]. $C_{18}H_{19}NO_4S$ requires MNa, 368.0932. Found: MNa^+, 368.0938. Also isolated was ^{1,3}*anti*-**16** (23 mg, 46%) as a colourless oil, R_f 0.6 (7:3 EtOAc–petrol ether); $[\alpha]_D^{20}$ +53.3 (*c* 0.3 in $CHCl_3$). IR (thin film): ν_{max} = 3306, 2924, 1596, 1504, 1011 and 736 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55 (2 H, d, *J* = 8.1 Hz, 2′- and 6′-H), 7.40 (1 H, br s, 1-furyl 5-H), 7.32 (1 H, br s, 3-furyl 5-H), 7.26 (2 H, d, *J* = 8.1 Hz, 3′- and 5′-H), 6.35 (1 H, dd, *J* = 3.2 and 1.7 Hz, 1-furyl 4-H), 6.33 (1 H, d, *J* = 3.2 Hz, 1-furyl 3-H), 6.28 (1 H, dd, *J* = 3.0 and 1.7 Hz, 3-furyl 4-H), 6.21 (1 H, d, *J* = 3.0 Hz, 3-furyl 3-H), 4.90 (1 H, d, *J* = 6.0 Hz, NH), 4.82 (2 H, m, 1-H and 3-H), 3.44 (1 H, d, *J* = 3.8 Hz, OH), 2.40 (4 H, m, 2-H and Me), and 2.31 (1 H, ddd, *J* = 14.3, 9.3 and 8.3 Hz, 2-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 154.6, 142.8, 142.4, 142.2, 141.9, 130.0, 125.9, 110.7, 110.6, 107.8, 106.3, 66.4, 51.8, 41.0 and 21.8. MS (ES+): *m/z* (%) = 346 (15) [MH^+], 328 (30) [M – OH] and 234 (100) [M – $FuCHOHCH_2$]. $C_{18}H_{19}NO_4S$ requires MNa, 368.0932. Found: MNa^+, 368.0938.

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