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TETRAHEDRON: *ASYMMETRY*

Diastereoselective synthesis of 3,6-dihydro-2*H*-1,3,4-thiadiazines

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Abstract

Thionation of the benzil hydrazones **3** with Lawesson's reagent afforded the 3,6-dihydro-2*H*-1,3,4-thiadiazines **4** by an intramolecular cyclisation. This reaction was shown to be diastereospecific and allowed the formation of the *exo* compounds **4b–e**. When the homochiral SAMP–hydrazone **3f** was used, the reaction afforded enantiomerically pure (4*R*,6*R*,9*S*)-**4f**.

1. Introduction

1,3,4-Thiadiazines are of great interest since many compounds possessing this structure have useful applications in very different areas such as pharmacology,[1] agriculture[2] or photography.[3] Several reviews[4] report the preparation of this six-membered heterocyclic system and its use in the synthesis of other heterocycles. In this report, we describe an original method leading to the 3,6-dihydro-2*H*-1,3,4-thiadiazines **4** using a diastereospecific reaction.

2. Results and discussion

We have recently shown in our studies on 4-amino-1-thia-4-azabutadienes that the α-hydrazonothioamides **1** can isomerise into 3,6-dihydro-2*H*-1,3,4-thiadiazines **2** by simple heating[5] (Scheme 1).

The dialkylhydrazones **3** were prepared as previously described[6] by condensation of benzil with one equivalent of a dialkylhydrazine. The compounds **3** thus obtained were treated with Lawesson's reagent (LR) to give the dihydrothiadiazines **4** without isolation of any intermediates (Scheme 2).

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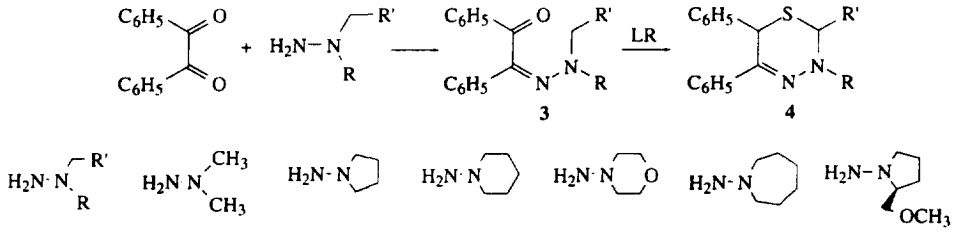
Scheme 1.

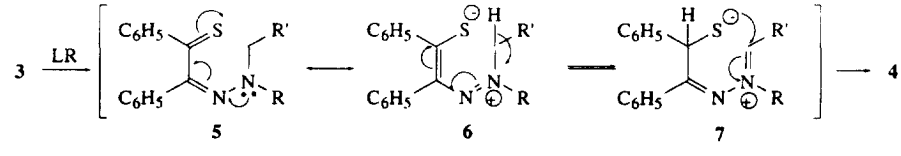


compounds (yield%)	3a (77) 4a (89)	3b (58) 4b (85)	3c (86) 4c (83)	3d (90) 4d (61)	3e (58) 4e (57)	3f (82) 4f (70)

Scheme 2.

This type of intramolecular cyclisation has already been described by D. N. Reinhoudt[7] and J. P. Pradère[8] who obtained 1,3-thiazines from thioamide vinylogues. M. Hojo also prepared thiadiazines by a similar method.[9]

The mechanism for the transformation of **3** into **4** involves an intermediate thiocarbonyl compound **5** whose mesomeric form **6** is transformed by [1,5]-proton shift to the intermediate **7**. Cyclisation resulting from nucleophilic addition of the thiolate to the iminium ion in **7** then leads to the dihydrothiadiazine **4** (Scheme 3).

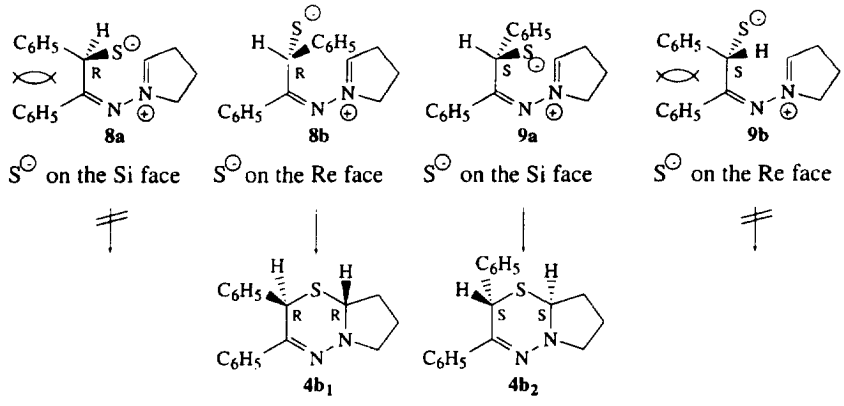


Scheme 3.

When the cyclic hydrazines (*N*-aminopyrrolidine, *N*-aminopiperidine, *N*-aminomorpholine, *N*-aminohomopiperidine) were used in this reaction, the resultant compound **4** possessed two stereogenic centres and so two diastereomers were possible. However, only one diastereomer was detected by ^{1}H and ^{13}C NMR spectroscopy. Furthermore, chiral HPLC[10] showed only two peaks of equal intensity corresponding to the two expected enantiomers.

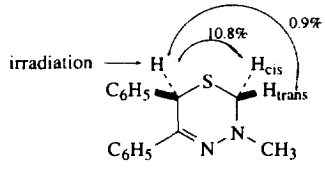
The diastereoselectivity of this reaction is easily explained by considering the geometry of the 'thiolate iminium' species **8** and **9**. In this intermediate, the first chiral centre is already present and its stereochemistry can be either *R* (species **8a,b**) or *S* (species **9a,b**). Attack of the thiolate can then occur only on that face of the iminium ion in which steric interactions between the two bulky aromatic rings are minimised. Addition of a thiolate ion **8** with the *R* configuration thus takes place on the *Re* face of the iminium ion whereas a thiolate ion **9** with the *S* configuration adds to the *Si* face (Scheme 4).

By this mechanism the diastereomer *RR–SS* (**4b**$_1$,**b**$_2$) is obtained. At this stage the sole evidence for the relative stereochemistry of **4** was based on comparison of the ^{1}H NMR spectra of compounds **4a** and **4b–e**. In **4a** the proton in position 6 was coupled (^{4}J=1.8 Hz) to only one of the protons in position 2



Scheme 4.

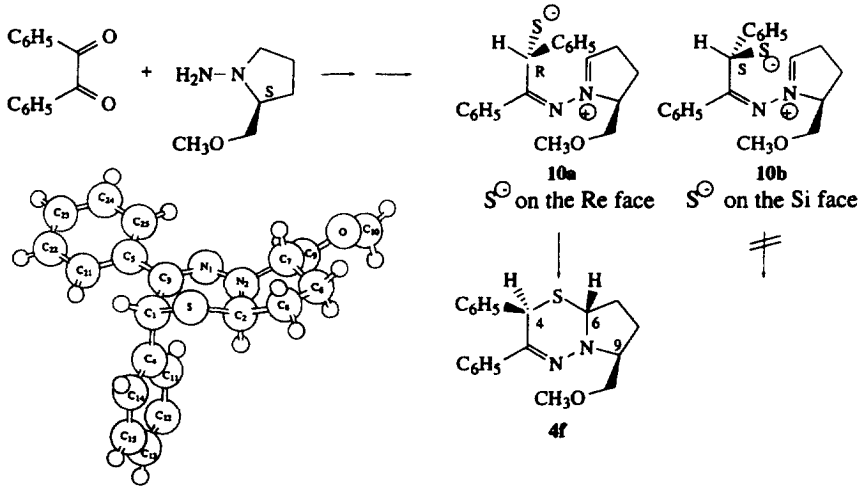
which has been proved to be H_{cis} by an NOE experiment which showed enhancement of H_{cis} when H_6 was irradiated (Scheme 5).



Scheme 5.

For the compounds **4b–e** no coupling constant was observed between H_2 and H_6. Both protons are thus in a *trans* relationship. This observation confirms the stereochemistry expected from the proposed mechanism.

The synthesis was now investigated using a cyclic hydrazine bearing a chiral centre: SAMP[11] ((*S*)-1-amino-2-methoxymethylpyrrolidine). The bulky methoxymethyl group will hinder the *Si* face of the intermediate 'thiolate iminium' **10b** so that ring closure of this species will be impossible. The thiadiazine **4f** resulting from the ring closure of the species **10a** was thus obtained as a pure stereoisomer with absolute configuration 4*R*,6*R*,9*S* as proved by X-ray structure analysis[12] (Scheme 6).



Scheme 6.

3. Conclusion

Current interest in the 1,3,4-thiadiazines skeleton justifies development of new methods to synthesize compounds with this basic structure. In the novel approach presented here, we show that our method has high diastereoselectivity: the dihydrothiadiazines **4b–e** are obtained as the sole diastereomers. The two stereogenic centres created in these compounds have an *exo* relationship. In the presence of SAMP–hydrazone, complete asymmetric induction yields the single enantiomer (4*R*,6*R*,9*S*)-**4f**.

4. Experimental

Melting points are uncorrected (Reichert microscope), optical rotations were obtained using an AA.10 optical activity polarimeter, NMR spectra were recorded using a Bruker AC 200 spectrometer with Me_4Si as internal reference (δ given in ppm, J in hertz), IR spectra (film or KBr pellets) were measured on a Bruker IFS 85 spectrometer, MS spectra were taken on a Hewlett Packard 5989 spectrometer. Flash chromatography was performed on Merck kieselgel 60 Art. 7734 or 9385 silica gel. All reactions were performed under an inert atmosphere (N_2) and all the solvents were freshly distilled using standard procedures.

4.1. Typical procedure for preparation of benzil monohydrazones 3

The *N,N*-dialkylhydrazine (5×10^{-3} mol) [or its hydrochloride salt (7.5×10^{-3} mol) for **3b**] was added to a solution of benzil (5×10^{-3} mol) and acetic acid (5×10^{-3} mol) [or sodium acetate (7.5×10^{-3} mol) for **3b**] in ethanol (8 mL). The solution was stirred for 20 h under N_2 at room temperature. The solvent was removed under reduced pressure and the residue was dissolved in ethyl acetate (20 mL) and washed with brine (20 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude compounds were purified by flash chromatography using dichloromethane as eluent. The compounds **3a–e** were crystallised from ethyl acetate.

4.2. Benzil N,N-*dimethylmonohydrazone 3a*

Pale yellow crystals: mp 99°C; yield 92%; IR (KBr): 2893, 1619, 1532, 1315, 1293, 1204, 1065, 1022, 874, 739, 725, 701, 694, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.59 (s, 3H, CH_3), 2.88 (s, 3H, CH_3), 7.34–7.87 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 46.9 (CH_3), 127.3 (CH), 127.6 (CH), 127.9 (CH), 130.2 (CH), 130.3 (CH), 130.5 (CH), 135.5 (C), 138.4 (C), 139.6 (C), 192.5 (CO); MS *m/z*: 252 (M^+). Anal. calcd for $C_{16}H_{16}N_2O$: C, 76.17; H, 6.39; N, 11.10. Found: C, 76.44; H, 6.44; N, 11.19.

4.3. Benzil-N-*pyrrolidinomonoimine 3b*

Pale yellow crystals: mp 114°C; yield 58%; IR (KBr): 3042, 2968, 2870, 1628, 1530, 1288, 1082, 1069, 877, 857, 730, 701, 676 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.76 (m, 4H, $2CH_2$), 3.15 (m, 4H, $2NCH_2$), 7.34–7.91 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 24.2 ($2CH_2$), 55.1 ($2NCH_2$), 127.2 (CH), 127.3 (CH), 127.7 (CH), 130.3 (CH), 130.4 (CH), 130.5 (CH), 135.8 (C), 137.9 (C), 139.8 (C), 192.4 (CO); MS *m/z*: 278 (M^+).

4.4. *Benzil-N-piperidinomonoimine* **3c**

Yellow crystals: mp 71°C; yield 86%; IR (KBr): 3057, 2939, 2819, 1675, 1597, 1470, 1449, 1447, 1316, 1229, 1215, 1036, 940, 786, 776, 729, 699, 641 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.34–1.40 (m, 6H, $3CH_2$), 2.73 (m, 4H, $2NCH_2$), 7.34–7.89 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 23.5 (CH_2), 24.8 ($2CH_2$), 55.9 ($2NCH_2$), 127.4 (CH), 128.3 (CH), 128.7 (CH), 129.0 (CH), 130.4 (CH), 130.8 (CH), 133.0 (C), 135.9 (C), 166.3 (CN), 196.4 (CO); MS *m/z*: 292 (M^+). Anal. calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.89; N, 9.58. Found: C, 78.30; H, 6.88; N, 9.40.

4.5. *Benzil-N-morpholinomonoimine* **3d**

Pale yellow crystals: mp 109°C; yield 90%; IR (KBr): 2973, 2893, 2846, 1673, 1596, 1450, 1446, 1329, 1305, 1269, 1262, 1226, 1108, 1073, 969, 946, 907, 861, 776, 734, 707, 698, 693, 652 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 2.80 (m, 4H, $2NCH_2$), 3.53 (m, 4H, $2OCH_2$), 7.31–7.92 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 55.1 ($2NCH_2$), 65.8 ($2OCH_2$), 127.5 (CH), 128.4 (CH), 128.7 (CH), 128.8 (CH), 131.2 (CH), 133.6 (CH), 132.5 (C), 135.6 (C), 168.0 (CN), 196.3 (CO); MS *m/z*: 294 (M^+). Anal. calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.46; H, 6.14; N, 9.30.

4.6. *Benzil-N-homopiperidinomonoimine* **3e**

Pale yellow crystals: mp 99°C; yield 58%; IR (KBr): 3049, 2937, 2858, 1626, 1550, 1442, 1318, 1312, 1304, 1285, 1077, 1070, 877, 726, 704, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.52 (m, 8H, $4CH_2$), 3.30 (m, 4H, $2NCH_2$), 7.25–7.87 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 27.5 ($2CH_2$), 27.6 ($2CH_2$), 57.1 ($2NCH_2$), 127.1 (CH), 127.6 (CH), 127.7 (CH), 130.0 (CH), 130.1 (CH), 130.2 (CH), 136.1 (C), 136.5 (C), 140.2 (C), 193.5 (CO); MS *m/z*: 306 (M^+). Anal. calcd for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14. Found: C, 78.62; H, 7.28; N, 9.03.

4.7. *Benzil-N-((S)-2-methoxymethylpyrrolidino)monoimine* **3f**

Yellow oil: $[\alpha]_D^{20}$ +191 (c 1.00, $CHCl_3$); yield 82%; IR (film): 3056, 3023, 2974, 2925, 2876, 2828, 1636, 1597, 1579, 1543, 1489, 1444, 1283, 1200, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.62–1.95 (m, 4H, $2CH_2$), 2.69 and 2.81 (2m, 2H, NCH_2), 3.32 (s, 3H, CH_3), 3.49 (d, J=5.3 Hz, 2H, OCH_2), 3.72 (m, 1H, CH), 7.32–7.87 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 23.8 (CH_2), 26.10 (CH_2), 53.9 (NCH_2), 59.3 (CH_3), 65.6 (CH), 73.9 (OCH_2), 127.4 (CH), 127.5 (CH), 127.9 (CH), 130.2 (CH), 130.5 (CH), 130.7 (CH), 135.7 (C), 138.1 (CH), 140.2 (C), 192.9 (CO); MS *m/z*: 322 (M^+). Anal. calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.36; H, 6.78; N, 8.43.

4.8. *Typical procedure for preparation of 3,6-dihydro-2H-1,3,4-thiadiazines* **4**

Lawesson's reagent (1.5×10^{-3} mol) was added to a solution of the benzil hydrazone **3** (3×10^{-3} mol) in anhydrous benzene (15 mL). The mixture was refluxed under an inert atmosphere (N_2) for 15 h. Solvents were removed under reduced pressure and the residue was chromatographed using dichloromethane:light petroleum (7:3) as eluent. The compounds **4** were crystallised from diethyl ether.

4.9. 3-Methyl-5,6-diphenyl-3,6-dihydro-2H-1,3,4-thiadiazine **4a**

Pale yellow crystals: mp 96°C; yield 89%; IR (KBr): 3052, 3022, 2940, 2864, 1578, 1556, 1492, 1445, 1402, 1336, 1212, 1006, 766, 721, 694, 671 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 3.27 (s, 3H, CH_3), 3.99 (d, J=13.0 Hz, 1H, CH), 4.09 (dd, J=13.0 Hz and J=1.8 Hz, 1H, CH), 5.01 (d, J=1.8 Hz, 1H, CH), 7.17–7.63 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 38.6 (CH), 45.5 (CH_2), 46.1 (CH_3), 124.8 (CH), 127.3 (CH), 127.4 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 137.0 (C), 138.8 (C), 141.6 (C); MS *m/z*: 268 (M^+). Anal. calcd for $C_{16}H_{16}N_2S$: C, 71.61; H, 6.01; N, 10.44; S, 11.95. Found: C, 71.65; H, 6.05; N, 10.48; S, 11.80.

4.10. 3,4-Diphenyl-5-thia-1,2-diazabicyclo[4.3.0]non-2-ene **4b**

White crystals: mp 135°C; yield 85%; IR (KBr): 3055, 2941, 2872, 1592, 1543, 1489, 1441, 1203, 1128, 1102, 1006, 880, 831, 762, 726, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.90 (m, 2H, CH_2), 2.41 (m, 2H, CH_2), 3.56 and 3.94 (2m, 2H, NCH_2), 4.10 (t, J=7.0 Hz, 1H, CH), 5.14 (s, 1H, CH), 7.17–7.64 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 21.8 (CH_2), 30.5 (CH_2), 41.6 (CH), 54.3 (CH), 54.4 (CH_2), 124.7 (CH), 127.1 (CH), 127.3 (CH), 128.2 (CH), 128.3 (CH), 128.5 (CH), 136.9 (C), 138.7 (C), 141.0 (C); MS *m/z*: 294 (M^+).

4.11. 3,4-Diphenyl-5-thia-1,2-diazabicyclo[4.4.0]dec-2-ene **4c**

White crystals: mp 142°C; yield 83%; IR (KBr): 2936, 2823, 1581, 1559, 1491, 1450, 1366, 1119, 1103, 1074, 978, 961, 828, 767, 722, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.38–1.86 (m, 6H, $3CH_2$), 3.08 and 3.93 (ddd, J=12.2, 9.1, 6.3 Hz and ddd, J=12.2, 5.0, 3.4 Hz, 2H, NCH_2), 3.69 (dd, J=11.2 Hz and J=2.9 Hz, 1H, CH), 4.97 (s, 1H, CH), 7.18–7.56 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 24.2 (CH_2), 25.9 (CH_2), 30.2 (CH_2), 40.8 (CH), 53.4 (CH), 56.1 (CH_2), 125.4 (CH), 127.3 (CH), 127.6 (CH), 128.0 (CH), 128.2 (CH), 128.7 (CH), 136.7 (C), 138.5 (C), 143.5 (C); MS *m/z*: 308 (M^+). Anal. calcd for $C_{19}H_{20}N_2S$: C, 73.99; H, 6.54; N, 9.08; S, 10.39. Found: C, 73.73; H, 6.55; N, 8.78; S, 10.24.

4.12. 3,4-Diphenyl-8-oxa-5-thia-1,2-diazabicyclo[4.4.0]dec-2-ene **4d**

White crystals: mp 177°C; yield 61%; IR (KBr): 3062, 2966, 2852, 1583, 1560, 1493, 1445, 1143, 1114, 1070, 1007, 982, 762, 717, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 3.35 and 3.73 (ddd, J=12.4, 10.9, 3.9 Hz and dt, J=12.4, 2.1 Hz, 2H, NCH_2), 3.56 (dd, J=10.4, 9.6 Hz, 1H, CH), 3.84–4.05 (m, 4H, $2CH_2$), 5.06 (s, 1H, CH), 7.20–7.58 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 40.1 (CH), 53.0 (CH), 54.6 (CH_2), 67.7 (CH_2), 68.4 (CH_2), 125.5 (CH), 127.6 (CH), 128.0 (CH), 128.3 (CH), 128.9 (CH), 138.0 (C), 138.2 (C), 142.6 (C); MS *m/z*: 310 (M^+). Anal. calcd for $C_{18}H_{18}N_2OS$: C, 69.65; H, 5.84; N, 9.02; S, 10.33. Found: C, 69.53; H, 5.83; N, 8.97; S, 10.15.

4.13. 9,10-Diphenyl-8-thia-1,11-diazabicyclo[5.4.0]undec-10-ene **4e**

White crystals: mp 116°C; yield 57%; IR (KBr): 3057, 3020, 2932, 2918, 2848, 1580, 1545, 1492, 1364, 1223, 1123, 956, 914, 762, 722, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.51–2.20 (m, 8H, $4CH_2$), 3.86 (d, J=7.8 Hz, 1H, CH), 3.86 and 4.24 (d, J=7.8 Hz and t, J=5.2 Hz, 2H, CH_2), 5.17 (s, 1H, CH), 7.12–7.60 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 26.6 (CH_2), 29.3 (CH_2), 30.2 (CH_2), 31.6 (CH_2), 42.6 (CH), 57.6 (CH_2 and CH), 124.5 (CH), 126.5 (CH), 127.1 (CH), 128.2 (CH), 128.3 (CH), 128.5 (CH), 132.1 (C), 139.1

(C), 143.2 (C); MS *m/z*: 322 (M^+). Anal. calcd for $C_{20}H_{22}N_2S$: C, 74.49; H, 6.88; N, 8.69; S, 9.94. Found: C, 74.64; H, 6.80; N, 8.80; S, 9.92.

4.14. (4R,6R,9S)-9-Methoxymethyl-3,4-diphenyl-5-thia-1,2-diazabicyclo[4.3.0]non-2-ene **4f**

White crystals: mp 116°C; $[\alpha]_D^{20}$ −461 (c 1.00, $CHCl_3$); yield 70%; IR (KBr): 3013, 2913, 2895, 2824, 1577, 1544, 1494, 1449, 1281, 1194, 1130, 1089, 712, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.85–2.19 and 2.31–2.52 (2m, 4H, $2CH_2$), 3.47 (s, 3H, CH_3), 3.74–3.81 and 3.95 (m and dd, J=12.7, 6.3 Hz, 3H, CH and CH_2), 4.20 (t, J=7.2 Hz, 1H, CH), 5.12 (s, 1H, CH), 7.11–7.72 (m, 10H, $2C_6H_5$); ^{13}C NMR δ: 25.9 (CH_2), 29.0 (CH_2), 40.8 (CH), 55.0 (CH), 59.4 (CH_3), 64.0 (CH), 74.0 (CH_2), 124.5 (CH), 127.0 (CH), 127.1 (CH), 128.0 (CH), 128.2 (CH), 128.4 (CH), 135.8 (C), 138.6 (C), 140.8 (C); MS *m/z*: 338 (M^+). Anal. calcd for $C_{20}H_{22}N_2OS$: C, 70.97; H, 6.55; N, 8.28; S, 9.47. Found: C, 70.78; H, 6.41; N, 8.00; S, 9.18.

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10. Column: ODH; eluent: hexane:isopropanol (95:5); pressure: 0.7 torr.
11. SAMP is commercially available, but can also be prepared in six steps from (*S*)-proline: D. Enders, P. Fey, H. Kipphardt, *Org. Synth.* **1987**, *65*, 173–182 and references cited therein.
12. Crystals of **4f** (1.2×0.53×0.13 mm) grown from $CHCl_3$. $C_{20}H_{22}N_2OS$, M=338.47, orthorhombic; a=8.217 Å, b=12.595 Å, c=17.300 Å, Z=4, space group: $P2_12_12_1$, ρ_{calc}=1.255 g cm^{-3}. Mo-Kα radiation λ=0.7107 Å, 6425 reflections were measured of which 2496 were unique with $I>2\sigma(I)$. Crystallographic calculations were carried out using the Siemens SHELXTL-PLUS program. The final Rw^2 and R parameters were 0.1379 and 0.054.