

Supporting Information

Oxidation of bis-Sulfinyl Carbanion as the Pivot of Ionic/Radical Tandem Reactions

Réactions tandem ioniques/radicalaires fondées sur l'oxydation de carbanion bis-sulfinyle

Guillaume Vincent,^[a] Saloua Cheli,^[a] Rocio Martinez Mallorquin,^[a] Adi Abramovitch,^[b] Sophie Beauvière,^[a] Catherine Gomez,^[a] Franck Brebion,^[a] Ilan Marek,^[b] Max Malacria,^[a] Jean Philippe Goddard*^[a] and Louis Fensterbank*^[a]

[a] Sorbonne Universités UPMC Univ Paris 06, UMR CNRS 8232, Institut Parisien de Chimie Moléculaire, 4 place Jussieu, C.229, F-75005 Paris, France
Fax: +33-1-44277360

[b] Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel
Fax: +972-4-8293709

Contents

Procedures and spectral data	1 - 13
X-ray parameters and ellipsoid plots	13 - 17

Generalities: All reactions were run under an argon or nitrogen atmosphere in anhydrous solvents and dried flasks. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F 254 and revealed with either an ultraviolet lamp (254 nm) or a *p*-anisaldehyde solution. Flash column chromatography was performed with Silica gel Merck Geduran SI (40-63 nm). Solvents were systematically distilled prior to be used. TEMPO was sublimated under vacuum (80 °C, 0.05 atm) prior to be used. IR spectra were recorded on a Bruker Tensor 27. ¹H and ¹³C NMR spectra were recorded at room temperature at 400 MHz and 100 MHz respectively on an ARX400 Bruker spectrometer. Shifts are given in ppm and referenced from the solvent residual signal (7.26 ppm for CDCl₃) for proton NMR. For carbon NMR, shifts are referenced from the solvent central peak (77.16 ppm for CDCl₃). Coupling constants (*J*) are given in Hertz (Hz). The letters m, s, d, t, q, hept mean respectively multiplet, singlet, doublet, triplet, quadruplet, heptuplet. Optical rotations were measured on a Perkin Elmer 343 polarimeter. Exact Masses were performed by the Plateforme de Spectrométrie masse (IPMC UMR7201). Melting points were obtained on a Reichert apparatus and are uncorrected.

Compounds **6**, **7**, **1a-c**, **9aa**, **9ab**, **9ba**, **9ca** have been previously described.^{1,2}

General procedure A for the tandem alkoxide or carbamate addition /radical cyclisation (ionic add. -40°C / ox. -40°C to -20°C).

To a solution of allyl alcohol **8a,b** or *N*-Boc allyl amine **18a,b** (1.7 eq.) in anhydrous THF (0.2M), cooled to 0°C, is added dropwise *n*-BuLi (1.75 eq.) and the solution is stirred for 30 min at this temperature. Then, the solution is cooled to -40°C and the alkylidene bis-sulfoxide **1a-f** or bis-sulfone (1 eq.) **10a,b** is added as an anhydrous THF (1M) solution. The reaction is stirred for 1 h (disappearance of starting material monitored by TLC). TEMPO (2 eq.) and ferrocenium tetrafluoroborate (3 eq.) are added in one portion at -40°C. The reaction is then warmed up to -20°C and after 2 hours at -20°C, the reaction is hydrolyzed by a saturated aqueous solution of NH₄Cl. The crude mixture is extracted with Et₂O and the resulting organic phases are dried over anhydrous MgSO₄, filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel.

General procedure B for the tandem enolate addition/radical cyclisation

To a solution of di-*iso*-propylamine (2.4 eq.) in anhydrous THF (0.3M), cooled to 0°C, is added dropwise *n*-BuLi (2.7 eq.) and the solution is stirred for 30 min at this temperature. Then, the solution is cooled to -78°C and the ester (2 eq.) is added as an anhydrous THF (1M) solution. The reaction is stirred 45 min at -78°C and alkylidene bis-sulfoxide **1** (1 eq.) is added as an anhydrous THF (0.3M) solution. The reaction is stirred 1.5 h (disappearance of starting material monitored by TLC, diethyl ether/petroleum ether: 8/2). TEMPO (3 eq.) and ferrocenium tetrafluoroborate (3.5 eq.) are added in one portion at -78°C. The reaction is warmed up to -20°C over 30 min and after 2 hours at -20 °C, the reaction is hydrolyzed by a saturated aqueous solution of NH₄Cl. The crude mixture is extracted with Et₂O and the resulting organic phases are dried over anhydrous MgSO₄, filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel.

¹ (a) B. Delouvrié, F. Najera, L. Fensterbank, M. Malacria *J. Organometallic Chem.* **2002**, 643-644, 130-135. (b) F. Brebion, B. Delouvrié, F. Najera, L. Fensterbank, M. Malacria, J. Vaissermann, *Angew. Chem. Int. Ed.*, **2003**, 42, 5342-5345. (c) F. Brebion, J.-P. Goddard, C. Gomez, L. Fensterbank, M. Malacria, *Synthesis*, **2005**, 2449.

² J.-P. Goddard, C. Gomez, F. Brebion, S. Beauvière, L. Fensterbank, M. Malacria *Chem. Commun.* **2007**, 2929-2931.

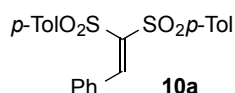
General procedure **C** for the allylic oxidation

To a solution of *t*-BuOK (1.5 eq.) in anhydrous THF (0.2M), cooled to -40°C, is added dropwise the alkylidene bis-sulfoxide **1** (1 eq.) as an anhydrous THF solution (1M). The reaction is stirred for 1 h at -40°C and 30 min at -20°C. TEMPO (2 eq.) and ferrocenium tetrafluoroborate (3 eq.) are added in one portion. After 2 hours at -20 °C, the reaction is hydrolyzed by a saturated aqueous solution of NH₄Cl. The crude mixture is extracted with Et₂O and the resulting organic phases are dried over anhydrous MgSO₄, filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel.

General procedure **D** for the tandem cuprate addition/allylic oxidation

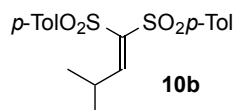
To a suspension of Cu salt (CuI or CuBr.DMS) (4 eq.) in anhydrous THF (0.2M), cooled to -10°C, is added dropwise the Grignard or lithium reagent (3.5 eq.) and the solution is stirred for 30 min at this temperature. Then, the solution is cooled to -65°C and the vinylidene bis-sulfoxide **1** (1 eq.) is added as an anhydrous THF solution. The reaction is allowed to warm up to -15°C over 1 h. TEMPO (4 eq.) and ferrocenium tetrafluoroborate (4 eq.) are added in one portion. After 2 hours at -15 °C, the reaction is hydrolyzed by a saturated aqueous solution of NH₄Cl. The crude mixture is extracted with Et₂O and the resulting organic phases are dried over anhydrous MgSO₄, filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel.

Bis-sulfone **10a**.



Procedure from literature.³ A mixture of benzaldehyde (570 μL, 5.6 mmol), bis(tolylsulfonyl)methane (2 g, 6.16 mmol), diethylammonium chloride (1.2 g, 10.6 mmol) and potassium fluoride (49 mg, 0.84 mmol) in dry toluene (26 mL) is heated at reflux with a Dean Stark for 24 h. After cooling, the solvent is evaporated and the residue is partitioned between water (20 mL) and CH₂Cl₂ (60 mL). The organic phase is separated and the aqueous phase is extracted with CH₂Cl₂ (3×50 mL). The combined organic layer is dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude is purified by flash chromatography over silica gel (pentane/ethyl acetate: from 10/0 to 8/2) to afford **10a** as a yellow powder (580 mg, 25 %): IR (neat) 3064, 2923, 1595, 1305, 1121, 1211, 912, 811. ¹H NMR (400 MHz, CDCl₃) δ 8.62 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.51-7.34 (m, 9H), 7.09 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 145.0, 144.6, 137.4, 136.8, 133.5, 131.0, 130.3, 129.6, 129.2, 128.9, 128.1, 128.0, 21.7, 21.6. HRMS: Calc. for C₂₂H₂₀O₄S₂Na [M+Na]⁺ 435.0695, found 435.0690.

Bis-sulfone **10b**.

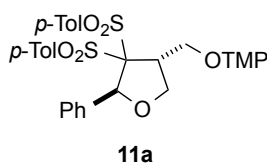


To *iso*-propylidene bis-sulfoxide **1b** (1.15 g, 3.3 mmol) in ether (15 mL), was added *m*CPBA (1.36 g, 5.94 mmol) portionwise at 0°C. After stirring 15 h at 0°C, the reaction is hydrolyzed

³ Sulzer-Mossé, S.; Alexakis, A.; Mareda, J.; Bollot, G.; Bernardinelli, G.; Filinchuk, Y. Chem. Eur. J. 2009, 15, 3204-3220.

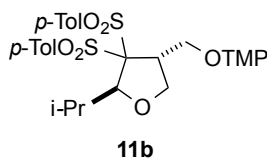
by a saturated aqueous solution of NaHCO_3 . The crude mixture is extracted with AcOEt (3x10 mL) and the resulting organic phases are dried over anhydrous MgSO_4 , filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel (pentane/diethyl ether: from 9/1 to 8/2) to afford **10b** as a white amorphous powder (287.0 mg, 23%): IR (neat) 2961, 2927, 2871, 1726, 1336, 1316, 1290, 1144, 1082, 913, 813, 691, 630. ^1H NMR (CDCl_3 , 400 MHz) δ 7.89 (d, $J = 8.3$ Hz, 2H), 7.83 (d, $J = 8.3$ Hz, 2H), 7.49 (d, $J = 11.6$ Hz, 1H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.32 (d, $J = 8.3$ Hz, 2H), 3.59 (m, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 1.02 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.2, 145.4, 145.0, 142.5, 138.5, 137.2, 129.9, 129.8, 128.9, 128.1, 29.1, 21.8, 21.3. HRMS: Calc. for $\text{C}_{19}\text{H}_{22}\text{O}_4\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 401.0852, found 401.0851.

Tetrahydrofurane 11a.



Procedure **A** with benzylidene bis-sulfone **10a** (329.0 mg, 0.74 mmol) afforded **11a** as a white foam (360.0 mg, 78%): IR (neat) 2931, 2929, 1359, 1332, 1257, 1145, 1077, 1058, 907, 807. ^1H NMR (CDCl_3 , 400 MHz) δ 8.19 (d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.15 (t, $J = 7.2$ Hz, 1H), 7.05 (t, $J = 7.6$ Hz, 2H), 6.62 (d, $J = 8.0$ Hz, 2H), 5.78 (s, 1H), 4.68 (t, $J = 7.6$ Hz, 1H), 4.41 (dd, $J = 10.8$; 9.2 Hz, 1H), 4.21 (dd, $J = 8.5$; 8.4 Hz, 1H), 3.66 (dd, $J = 8.8$; 3.6 Hz, 1H), 3.49-3.56 (m, 1H), 2.56 (s, 3H), 2.40 (s, 3H), 1.07-1.40 (m, 15H), 0.74 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): 146.6, 145.4, 136.1, 135.1, 134.4, 133.0, 131.6, 129.6, 129.4, 128.1, 128.0, 126.9, 96.7, 86.0, 72.9, 72.1, 59.8, 59.7, 49.7, 39.7, 33.0, 32.9, 21.8, 21.6, 20.0, 20.0, 17.1. HRMS: Calc. for $\text{C}_{34}\text{H}_{43}\text{O}_6\text{NS}_2$ $[\text{M}+\text{H}]^+$ 626.2604, found 626.2600.

Tetrahydrofurane 11b.



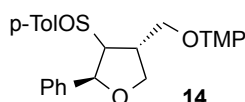
Procedure **A** with *iso*-propylidene bis-sulfone **10b** (128.0 mg, 0.338 mmol) afforded **11b** as a white foam (149 mg, 74%): IR (neat) 2929, 1721, 1596, 1470, 1374, 1334, 1141, 1079, 972, 806, 666, 568. ^1H NMR (CDCl_3 , 400 MHz) δ 8.10 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 7.37 (d, $J = 8.4$ Hz, 2H), 4.51 (t, $J = 7.5$ Hz, 1H), 4.31-4.26 (m, 2H), 3.88 (dd, $J = 10.6$; 8.4 Hz, 1H), 3.50 (dd, $J = 9.0$; 3.6 Hz, 1H), 3.36-3.28 (m, 1H), 2.51-2.45 (m, 1H), 2.48 (s, 3H), 2.44 (s, 3H), 1.50-1.19 (m, 6H), 1.07 (br s, 3H), 1.04 (d, $J = 6.6$ Hz, 3H), 1.00 (br s, 3H), 0.99 (br s, 3H), 0.58 (br s, 3H), 0.43 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 143.9, 143.1, 133.8, 132.6, 130.1, 139.5, 127.1, 126.8, 93.6, 90.4, 70.4, 69.3, 57.2, 57.1, 47.6, 37.2, 30.4, 30.2, 26.1, 19.5, 19.3, 18.8, 17.7, 17.4, 17.4, 14.5. HRMS: Calc. for $\text{C}_{31}\text{H}_{46}\text{O}_6\text{NS}_2$ $[\text{M}+\text{H}]^+$ 592.2761, found 592.2749.

Reduction of **9aa** with SmI_2

To a freshly prepared solution of SmI_2 in THF (0.1 M, 1.51 mmol) and HMPA (262 μL , 1.51 mmol) is added a solution of **9aa** (128 mg, 0.215 mmol) and *t*-BuOH (144 μL , 1.51 mmol) in THF. The reaction mixture is stirred at RT with monitoring by TLC. The reaction is usually

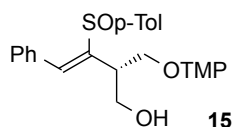
complete within 2-3 h. After quenching with a saturated aq. NH_4Cl solution, the crude mixture is extracted with EtOAc. The combined organic phases are washed with brine and dried over MgSO_4 and concentrated under vacuum. The crude is purified by flash chromatography over silica gel. The crude is purified by flash chromatography over silica gel (pentane/ethyl acetate: from 10/0 to 7/3) to afford **14** (42 mg, 43%) and (S)-**16** (23 mg, 33%) and **15** (5 mg, 5%) by order of elution.

Tetrahydrofuran **14**.



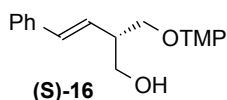
Viscous oil. $\alpha_D = 18^\circ$ (c 1.05, CHCl_3). IR (neat) 3066, 3003, 2977, 1596, 1541, 1493, 1360, 1084, 812. ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.06 (m, 9H), 5.04 (d, $J = 6.6$, 1H), 4.47 (m, 1H), 3.97 (dd, $J = 4.3, 6.6$ Hz, 1H), 3.82 (m, 3H), 3.29 (m, 1H), 2.35 (s, 3H), 1.09-1.44 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.9, 140.0, 136.8, 129.9, 128.6, 128.4, 127.2, 124.1, 83.3, 77.2, 76.5, 71.7, 71.1, 60.0, 39.6, 33.6, 21.3, 20.2, 17.0. HRMS: Calc. for $\text{C}_{27}\text{H}_{37}\text{N}_1\text{O}_3\text{S}_1\text{Na}$ $[\text{M}+\text{Na}]^+$ 478.2386, found 478.2376.

Vinylsulfoxide **15**.



Viscous oil. $\alpha_D = -350^\circ$ (c 1.05, CHCl_3). IR (neat) 3420, 3058, 2973, 2928, 2871, 1573, 1359, 1079, 809, 732. ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.0$ Hz, 2H), 7.31-7.16 (m, 5H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.35 (s, 1H), 4.04 (d, $J = 7.2$ Hz, 2H), 3.91-3.77 (m, 2H), 3.66 (p, $J = 7.0$ Hz, 1H), 2.38 (s, 3H), 2.01 (m, 1H), 1.55-1.08 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 138.4, 136.9, 134.1, 130.7, 130.2, 129.1, 128.5, 128.2, 126.7, 75.8, 69.5, 59.9, 44.3, 39.7, 33.0, 32.8, 29.6, 20.2, 17.0.

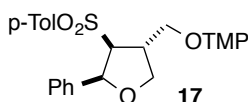
Alkene **16**.



Oil. $\alpha_D = -85^\circ$ (c 0.09, CHCl_3). IR (neat) 3357, 3004, 2927, 1491, 1359, 913, 747. ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.22 (m, 5H), 6.51 (d, $J = 16.0$ Hz, 1H), 6.13 (dd, $J = 16.0$ Hz ; 8.0 Hz, 1H), 4.00-3.75 (m, 4H), 2.77 (m, 1H), 2.28 (s, 1H, OH), 1.46-1.11 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.3, 132.4, 128.6, 127.6, 127.5, 126.2, 79.4, 65.7, 60.1, 45.3, 39.8, 33.3, 33.1, 17.1. HRMS: Calc. for $\text{C}_{20}\text{H}_{31}\text{N}_1\text{O}_2$ $[\text{M}+\text{H}]^+$ 318.2428, found 318.2420.

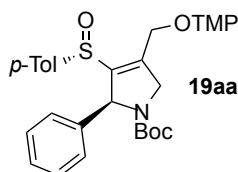
Tetrahydrofuran **17**.

Reduction of **11a** (100 mg, 0.16 mmol) with SmI_2 was accomplished with the same procedure as from **9aa** and afforded rac-**16** (7mg, 28%) and **17** (8 mg, 21%) by order of elution.

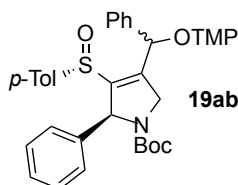


White paste. IR (neat) 2974, 2928, 2870, 1597, 1494, 1360, 1183, 1146, 813. ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.06 (m, 9H), 5.04 (d, $J = 6.6$ Hz, 1H), 4.47 (m, 1H), 3.97 (dd, $J = 6.6$; 4.3 Hz, 1H), 3.82 (m, 3H), 3.29 (m, 1H), 2.35 (s, 3H), 1.44-1.09 (m, 18H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 136.5, 135.2, 129.5, 127.9, 127.8, 127.7, 82.4, 75.8, 69.5, 69.2, 60.2, 41.6, 39.7, 33.5, 33.2, 21.6, 20.4, 20.3, 17.1.

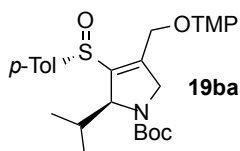
Synthesis of the dihydropyrroles **19**.



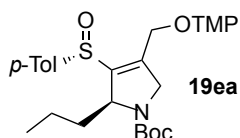
Procedure **A** with benzylidene bis-sulfoxide **1a** (136.0 mg, 0.288 mmol) afforded the desired compound **19aa** as a white foam (114.0 mg, 55%) and as 2 rotamers in solution: $[\alpha]_{\text{D}} = +40.5$ (c 1.24 CHCl_3). IR (neat) 2974, 2929, 1699, 1391, 1260, 1168, 1127, 1083, 1045, 807, 763, 698. ^1H NMR (CDCl_3 , 400 MHz) δ 6.98-6.84 (m, 9H), 5.75 (d, $J = 4.5$ Hz, 0.8 H), 5.69 (br, 0.2H), 4.96 (d, $J = 12.6$ Hz, 0.8H), 4.92 (1/2AB, $J_{\text{AB}} = 12.1$ Hz, 0.2H), 4.79 (1/2AB, $J_{\text{AB}} = 12.6$ Hz, 1H), 4.65 (1/2AB, $J_{\text{AB}} = 16.8$ Hz, 1H), 4.58 (dd, $J = 16.8$; 4.5 Hz, 1H), 2.26 (s, 0.6 H), 2.22 (s, 2.4H), 1.49-1.33 (m, 6H), 1.25 (br s, 3H), 1.24 (br s, 3H), 1.15-1.13 (br s, 15H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.7, 142.5, 140.2, 140.0, 139.9, 137.7, 129.3, 127.9, 127.7, 127.0, 123.4, 80.3, 71.0, 65.7, 60.3, 55.7, 39.7, 33.3, 33.1, 28.1, 28.5, 21.2, 20.3, 20.2, 17.0. HRMS: Calc. for $\text{C}_{32}\text{H}_{45}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 553.3100, found 553.3094.



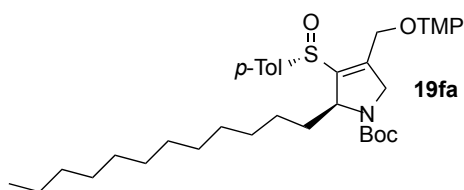
Procedure **A** with benzylidene bis-sulfoxide **1a** (150.0 mg, 0.394 mmol) afforded a white foam of the desired compound **19ab** (139.5 mg, 56%) that evolved to a 1:1 mixture of 2 diastereoisomers (2 rotamers for each in solution) after standing 24 h in CDCl_3 at rt: IR (neat) 2930, 1697, 1493, 1390, 1242, 1167, 1126, 1048, 809, 753, 667. ^1H NMR (CDCl_3 , 400 MHz) δ 7.63 (d, $J = 7.3$ Hz, 1H), 7.50-6.95 (m, 10H), 6.89-6.85 (m, 2H), 6.66 (d, $J = 7.3$ Hz, 1H), 6.45 (s, 0.5H), 6.37 (s, 0.5H), 5.68 (d, $J = 5.0$ Hz, 0.5H), 5.40 (dd, $J = 5.2$; 1.8 Hz, 0.5H), 4.82 (dd, $J = 16.9$; 5.2 Hz, 0.5H), 4.81 (1/2AB, $J_{\text{AB}} = 16.8$ Hz, 0.5H), 4.50 (dd, $J = 16.8$; 5.0 Hz, 0.5H), 4.46 (dd, $J = 16.9$, 1.8 Hz, 0.5H), 2.34 (s, 1.5H), 2.25 (s, 1.5H), 1.61-1.15 (m, 15H), 1.14 (br s, 4.5H), 1.11 (br s, 4.5H), 0.87 (s, 1.5H), 0.82 (s, 1.5H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.3, 153.2, 149.9, 147.3, 140.8, 140.3, 140.2, 140.1, 139.9, 136.8, 136.7, 136.4, 136.2, 128.9, 128.8, 128.4, 128.3, 127.7, 127.4, 127.3, 127.2, 126.9, 126.4, 126.3, 125.2, 124.3, 82.3, 79.8, 79.7, 66.0, 64.9, 59.9, 59.8, 59.5, 59.4, 53.0, 40.0, 39.9, 39.8, 33.6, 33.5, 33.4, 33.3, 28.0, 27.6, 21.0, 20.9, 20.3, 20.0, 19.9, 16.7. HRMS: Calc. for $\text{C}_{38}\text{H}_{49}\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 629.3413, found 629.3390.



Procedure **A** with *iso*-propylidene bis-sulfoxide **1b** (140.0 mg, 0.400 mmol) afforded the desired compound **19ba** as a white foam (120.7 mg, 58%) and as 2 rotamers in solution: $[\alpha]_D = +17.4$ (c = 0.47 CHCl₃). IR (neat) 2970, 2930, 1697, 1456, 1356, 1256, 1167, 1116, 1083, 1049, 958, 878, 808, 770, 735, 621. ¹HNMR (CDCl₃, 400 MHz) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.96 (br, 0.8H), 4.88 (br, 0.2H), 4.85 (1/2AB, *J*_{AB} = 12.9 Hz, 1H), 4.76 (1/2AB, *J*_{AB} = 12.9 Hz, 1H), 4.67 (1/2AB, *J*_{AB} = 16.9 Hz, 0.8H), 4.47 (1/2AB, *J*_{AB} = 16.8 Hz, 0.2H), 4.11 (dd, *J* = 16.8; 3.6 Hz, 1H), 2.39 (s, 3H), 1.49-1.04 (m, 7H), 1.43 (br s, 9H), 1.21 (s, 3H), 1.19 (s, 3H), 1.12 (s, 3H), 1.09 (s, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.32 (d, *J* = 6.7 Hz, 3H). ¹³CNMR (CDCl₃, 100 MHz) δ 155.3, 144.7, 141.0, 139.0, 138.7, 130.0, 129.7, 124.9, 124.3, 80.7, 71.2, 70.9, 67.2, 60.3, 60.1, 57.1, 39.6, 33.3, 33.1, 33.0, 28.6, 21.5, 21.2, 20.5, 20.3, 17.1, 15.4. HRMS: Calc. for C₂₉H₄₇N₂O₄S [M+H]⁺ 519.3257, found 519.3276.



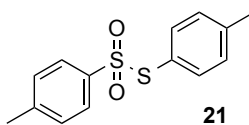
Procedure **A** with *n*-propylidene bis-sulfoxide **1e** (100.0 mg, 0.288 mmol) afforded the desired compound **19ea** as a white foam (110.1 mg, 73%) and as 2 rotamers in solution: $[\alpha]_D = -4.0$ (c 1.09 CHCl₃). IR (neat) 2928, 2810, 2241, 1696, 1452, 1391, 1258, 1165, 1131, 1046, 921, 810, 730. ¹HNMR (CDCl₃, 400 MHz) δ 7.52 (d, *J* = 8.3 Hz, 0.4H), 7.48 (d, *J* = 8.2 Hz, 1.6H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.08 (br, 0.8H), 4.98 (br, 0.2H), 4.80 (1/2AB, *J*_{AB} = 12.5 Hz, 1H), 4.78 (1/2AB, *J*_{AB} = 12.5 Hz, 0.2H), 4.69 (1/2AB, *J*_{AB} = 12.5 Hz, 0.8H), 4.54 (1/2AB, *J*_{AB} = 16.8 Hz, 0.8H), 4.38 (1/2AB, *J*_{AB} = 16.8 Hz, 0.2H), 4.19 (dd, *J* = 16.8; 5.2 Hz, 1H), 2.38 (s, 3H), 1.66-0.90 (m, 10H), 1.46 (br s, 1.8H), 1.41 (br s, 7.2H), 1.20 (s, 6H), 1.11 (s, 3H), 1.09 (s, 3H), 0.42 (t, *J* = 6.8 Hz, 0.6H), 0.29 (t, *J* = 6.8 Hz, 2.4H). ¹³CNMR (CDCl₃, 100 MHz) δ 153.9, 153.2, 143.7, 143.0, 141.2, 140.9, 138.9, 138.8, 138.3, 129.9, 124.7, 124.0, 80.0, 79.7, 71.0, 62.6, 61.9, 60.2, 56.0, 55.8, 39.7, 34.1, 33.3, 33.2, 33.0, 30.4, 29.7, 28.4, 21.3, 20.3, 20.2, 17.0, 16.0, 15.8, 13.5. HRMS: Calc. for C₂₉H₄₇N₂O₄S [M+H]⁺ 519.3257, found 519.3241.



Procedure **A** with *n*-C₁₂H₂₅ alkylidene bis-sulfoxide **1f** (136.0 mg, 0.288 mmol) afforded the desired compound **19fa** as a white foam (132.6 mg, 71%) and as 2 rotamers in solution: $[\alpha]_D = -16.8$ (c 0.85 CHCl₃). IR (neat) 2923, 2852, 2230, 1698, 1451, 1391, 1259, 1166, 1118, 1082, 1048, 991, 809, 731. ¹HNMR (CDCl₃, 400 MHz) δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.08 (br, 0.8H), 5.00 (br, 0.2H), 4.85 (1/2AB, *J*_{AB} = 12.4 Hz, 1H), 4.77 (1/2AB, *J*_{AB} = 12.4 Hz, 0.2H), 4.69 (1/2AB, *J*_{AB} = 12.4 Hz, 0.8H), 4.54 (1/2AB, *J*_{AB} = 16.9 Hz, 0.8H), 4.38 (1/2AB, *J*_{AB} = 16.4 Hz, 0.2H), 4.19 (dd, *J* = 16.9; 5.3 Hz, 1H), 2.38 (s, 3H), 1.72-1.64 (m, 1H), 1.60-1.50 (m, 1H), 1.46 (br s, 1.8H), 1.41 (br s, 7.2H), 1.36-1.00 (br, 30H), 1.10 (s, 3H), 1.09 (s, 3H), 0.99-0.32 (m, 2H), 0.86 (t, *J* = 6.8 Hz, 3H). ¹³CNMR (CDCl₃, 100

MHz) δ 154.0, 143.6, 141.0, 138.9, 138.5, 129.9, 124.5, 124.1, 80.2, 71.1, 62.1, 60.3, 56.0, 39.8, 33.3, 33.1, 32.1, 32.0, 29.8, 29.7, 29.5, 28.5, 22.8, 22.6, 21.4, 20.4, 20.3, 17.1, 14.3. HRMS: Calc. for $C_{38}H_{65}N_2O_4S$ $[M+H]^+$ 645.4660, found 645.4654.

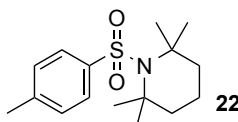
Sulfonesulfide 21.



IR (neat) 2923, 1594, 1490, 1325, 1140, 1078, 1017, 808. 1H NMR ($CDCl_3$, 400 MHz) δ 7.46 (d, $J = 8.3$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.3$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.5, 142.0, 140.3, 136.5, 130.2, 129.3, 127.6, 124.5, 21.7, 21.21.4. HRMS: Calc. for $C_{14}H_{14}O_2S_2Na$ $[M + Na]^+$ 301.0327, found: 301.0331.

The spectral data for this compounds match the literature.⁴

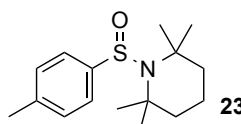
Tosylpiperidine 22.



IR (neat) 2977, 2935, 1466, 1307, 1139, 1066, 986, 920, 810, 672. 1H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 2.39 (s, 3H), 1.65 (s, 6H), 1.57 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 141.9, 129.3, 126.3, 60.8, 44.0, 31.2, 21.5, 16.9. HRMS: Calc. for $C_{16}H_{25}O_2NSNa$ $[M+Na]^+$ 318.1498, found 318.1497.

The spectral data for this compounds match literature.⁵

Tosylslyfinyl 23.



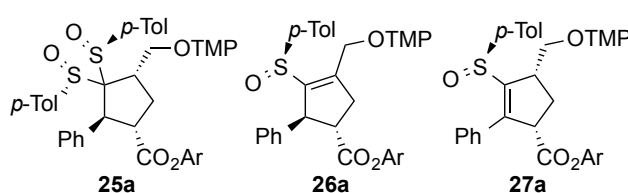
IR (neat) 2930, 1462, 1383, 1367, 1242, 1172, 1084, 1060. 1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, $J = 8.3$ Hz, 2H), 7.24 (d, $J = 7.9$ Hz, 2H), 2.39 (s, 3H), 1.83-1.28 (m, 15H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 139.6, 129.4, 126.0, 61.3, 58.8, 43.7, 41.6, 35.5, 32.7, 31.0, 30.5, 21.3, 17.4. HRMS: Calc. for $C_{16}H_{25}NOSNa$ $[M+Na]^+$ 302.1549, found 302.1557.

The spectral data for this compounds match literature.⁴

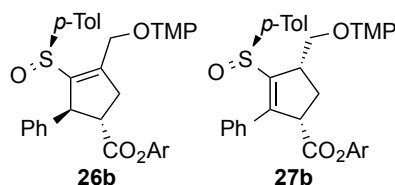
⁴ J. B. Arterburn, M. C. Perry, S. L. Nelson, B. R. Dible, M. S. Holguin, *J. Am Chem. Soc.* **1997**, *119*, 9309-9310.

⁵ P. Carloni, E. Damiani, M. Iacussi, L. Greci, P. Stipa, *Tetrahedron* **1995**, *51*, 12445-12452.

Preparation of cyclopentyl derivatives **25**, **26** and **27**.



Procedure **B** with benzylidene bis-sulfoxyde **1a** (108.0 mg, 0.283 mmol) afforded a yellow oil of a 1.8:1:1.6 mixture of **25a**, **26a** and **27a** (151.8 mg, 81%). After standing 3 days in CDCl_3 , it evolves to a 1:1.7 mixture of **26a/27a**: IR (neat): 2972, 2928, 1750, 1595, 1491, 1470, 1451, 1374, 1359, 1264, 1141, 1077, 1042, 917, 807, 770, 732, 701. ^1H NMR (CDCl_3 , 400 MHz) δ 7.70 (d, $J = 8.3$ Hz, 2H **25a**), 7.66 (d, $J = 8.3$ Hz, 2H **25a**), 7.60-6.85 (m, 12H **25a** + 12H **26a** + 12H **27a**), 4.99 (1/2AB, $J_{AB} = 12.4$ Hz, 1H **26a**), 4.92 (1/2AB, $J_{AB} = 12.4$ Hz, 1H **26a**), 4.84 (d, $J = 4.2$ Hz, 1H **26a**), 4.55 (ddd, $J = 9.9, 5.5, 1.1$ Hz, 1H **27a**), 4.40 (d, $J = 12.4$ Hz, 1H **25a**), 4.34 (dd, $J = 11.1, 7.8$ Hz, 1H **25a**), 3.94-3.86 (m, 1H **27a**), 3.80-3.71 (m, 1H **25a**), 3.56-3.51 (ddd, $J = 12.4, 12.0, 5.6$ Hz, 1H **25a**), 3.38-3.30 (m, 1H **25a** + 1H **27a** + 3H **26a**), 3.25 (dd, $J = 10.8, 8.8$ Hz, 1H **27a**), 2.89 (ddd, $J = 13.5, 9.9, 9.5$ Hz, 1H **27a**), 2.83-2.77 (m, 1H **25a**), 2.46 (ddd, $J = 13.5, 10.8, 5.5$ Hz, 1H **26a**), 2.42 (s, 3H **27a**), 2.41 (s, 3H **25a**), 2.40 (s, 3H **25a**), 2.27 (s, 3H **26a**), 2.06 (s, 6H **26a**), 2.05 (q, $J = 12.2$ Hz, 1H **25a**), 1.84 (s, 6H **27a**), 1.80-1.55 (br, 6H **25a**), 1.52-0.89 (m, 15H **25a** + 18H **26a** + 18H **27a**), 0.71 (br s, 3H **25a**). ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.7, 171.3, 170.9, 150.9, 148.1, 148.0, 147.4, 144.3, 142.6, 142.4, 142.2, 141.9, 141.0, 140.9, 140.6, 140.2, 139.9, 138.8, 136.2, 135.5, 135.0, 134.9, 133.2, 131.5, 130.4, 130.2, 130.1, 130.0, 129.9, 129.8, 129.7, 129.3, 128.9, 128.7, 128.6, 128.4, 128.3, 128.1, 127.5, 127.1, 126.7, 126.6, 126.3, 126.0, 125.7, 124.8, 124.4, 124.1, 88.9, 78.2, 77.4, 76.9, 72.3, 68.2, 60.2, 60.0, 59.6, 54.4, 53.4, 51.7, 50.9, 50.4, 43.5, 39.8, 39.6, 39.0, 38.3, 36.5, 33.4, 33.3, 33.2, 33.1, 32.3, 30.4, 21.7, 21.5, 21.5, 21.4, 21.3, 20.4, 20.3, 20.1, 20.0, 17.1, 16.6, 16.4, 16.2, 15.8. HRMS: **25a** Calc. for $\text{C}_{44}\text{H}_{54}\text{NO}_5\text{S}_2$ $[\text{M}+\text{H}]^+$ 740.3438, found 740.3439. HRMS: **26a/27a** Calc. for $\text{C}_{37}\text{H}_{46}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 600.3142, found 600.3141.



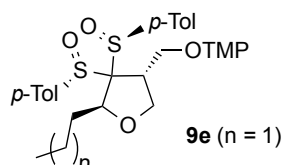
Procedure **B** with *iso*-propylidene bis-sulfoxyde **1b** (100.2 mg, 0.289 mmol) afforded a yellow foam of a 1.5:1 mixture of **26b** and **27b** (146.8 mg, 89%): IR (neat) 2927, 2870, 1750, 1595, 1373, 1359, 1131, 1092, 1042, 991, 910, 806, 768, 729. ^1H NMR (CDCl_3 , 400 MHz) δ 7.53 (d, $J = 8.0$ Hz, 2H **26b**), 7.48 (d, $J = 8.0$ Hz, 2H **27b**), 7.27 (d, $J = 8.0$ Hz, 2H **26b**), 7.27 (d, $J = 8.0$ Hz, 2H **27b**), 7.05 (s, 3H **27b**), 7.05 (s, 3H **26b**), 4.89 (1/2 AB, $J_{AB} = 12.4$ Hz, 1H **26b**), 4.77 (1/2 AB, $J_{AB} = 12.4$ Hz, 1H **26b**), 4.02 (dd, $J = 10.3, 2.7$ Hz, 1H **27b**), 3.82 (br s, 1H **26b**), 3.64-3.57 (m, 1H **27b**), 3.45 (m, 1H **27b**), 3.27 (dd, $J = 17.4, 2.5$ Hz, 1H **26b**), 3.19 (dd, $J = 9.9; 1.5$ Hz, 1H **27b**), 3.03 (dd, $J = 9.9, 4.5$ Hz, 1H **27b**), 3.14 (dt, $J = 9.4, 2.5$ Hz, 1H **26b**), 3.00 (dd, $J = 17.4, 9.4$ Hz, 1H **26b**), 2.60-2.49 (m, 1H **27b**), 2.43-2.38 (m, 1H **27b**), 2.39 (s, 3H **27b**), 2.37 (s, 3H **26b**), 2.18 (s, 6H **27b**), 2.10 (s, 6H **26b**), 1.83-1.74 (m, 1H **26b**), 1.52-1.00 (m, 24H **27b**), 1.47-1.10 (m, 18H **26b**), 0.94 (d, $J = 6.8$ Hz, 3H **27b**), 0.35 (d, $J = 6.8$ Hz, 3H **26b**). ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.8, 172.4, 156.6, 148.0, 147.9, 146.8, 134.4, 142.1, 141.0, 140.9, 140.8, 140.6, 140.1, 139.6, 135.4, 130.1, 130.0, 129.9, 129.7, 129.6, 128.8, 128.6, 126.0, 125.5, 124.4, 124.3, 77.7, 72.3, 68.1, 60.0, 59.4, 59.2, 54.5, 49.8,

42.2, 40.3, 39.7, 39.6, 39.2, 33.2, 33.0, 32.0, 30.3, 28.9, 28.6, 22.2, 22.0, 21.5, 21.4; 21.3, 21.2; 20.3, 20.1; 19.8, 17.0, 16.8, 16.5, 15.4. HRMS: **26b/27b** Calc. for C₃₄H₄₈NO₄S [M+H]⁺ 566.3299, found 566.3297.

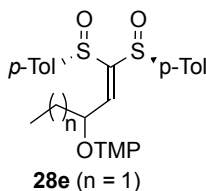
Allylic oxidations.

Procedure **C** with *n*-propylidene bis-sulfoxide **1e** (125.1 mg, 0.361 mmol) afforded the desired compound **28e** as a yellow oil (116.7 mg, 64%) and as a 1.5:1 mixture of diastereoisomers.

Tetrahydrofuran **9e** is a side product.



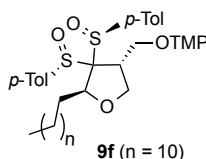
Yellowish paste. $[\alpha]_D = -39.5$ (c 0.66 CHCl₃). IR (neat) 2929, 2868, 2245, 1595, 1453, 1374, 1079, 1045, 909, 838, 807, 730. ¹HNMR (CDCl₃, 400 MHz) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 4.34-4.22 (m, 3H), 3.50 (dd, *J* = 10.4; 8.4 Hz, 1H), 3.26 (m, 1H), 3.04 (dd, *J* = 7.8; 3.8 Hz, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 2.02-1.92 (m, 1H), 1.51-0.87 (m, 8H), 1.04 (br s 3H), 0.98 (br s, 6H), 0.62 (t, *J* = 7.4 Hz, 3H), 0.58 (br s, 3H), 0.26-0.16 (m, 1H). ¹³CNMR (CDCl₃, 100 MHz) δ 143.1, 142.8, 135.7, 135.2, 130.4, 129.9, 126.2, 126.0, 86.0, 80.2, 74.3, 72.4, 59.9, 59.6, 40.7, 39.7, 33.1, 32.9, 32.8, 21.6, 21.4, 20.0, 19.9, 17.0, 13.9. HRMS: Calc. for C₃₁H₄₆O₄NS₂ [M+H]⁺ 560.2863, found 560.2856.



Viscous oil. dr = 1.5:1. IR (neat) 2969, 2929, 1595, 1461, 1377, 1361, 1131, 1082, 1050, 1015, 970, 805, 623. ¹HNMR (CDCl₃, 400 MHz) δ 7.57 (d, *J* = 8.2 Hz, 1.2H), 7.22-7.19 (m, 1.2H), 7.08 (d, *J* = 8.2Hz, 1.2H), 7.06 (m, 4.2H), 6.88 (d, *J* = 7.9 Hz, 1.2H), 5.24-5.12 (m, 1H), 2.36 (s, 1.8H), 2.31 (s, 2.4H), 2.26 (s, 1.8H), 1.95-1.90 (m, 0.6H), 1.82-1.62 (m, 1.4H), 1.60-1.35 (m, 6H), 1.29 (br s, 1.2H), 1.20-1.17 (br s, 6H), 1.12-1.08 (br s, 4.8H), 0.98 (t, *J* = 7.5 Hz, 1.2H), 0.91 (br s, 1.8H). ¹³CNMR (CDCl₃, 100 MHz) δ 148.8, 148.2, 145.7, 145.0, 142.3, 142.1, 141.3, 140.8, 140.3, 139.0, 137.9, 137.4, 129.6, 129.4, 129.3, 126.3, 126.1, 125.0, 124.9, 80.6, 78.8, 61.1, 59.4, 40.5, 40.4, 40.3, 40.2, 35.0, 34.0, 33.9, 33.5, 30.4, 27.8, 27.7, 21.6, 21.5, 21.4, 20.5, 20.4, 17.3, 10.0, 9.9. HRMS: Calc. for C₂₈H₄₀O₃NS₂ [M+H]⁺ 502.2444, found 502.2438.

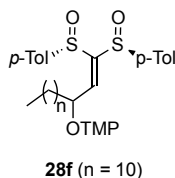
Procedure **C** with *n*-C₁₂H₂₅ alkylidene bis-sulfoxide **1e** (100.0 mg, 0.211 mmol) afforded a yellow oil of **6e** (90.2 mg, 68%) as a 1.5:1 mixture of diastereoisomers.

Tetrahydrofuran **9f** is a side product.

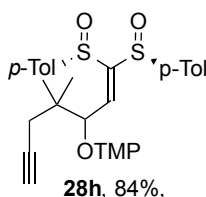


Viscous oil. dr = 5.6:1.

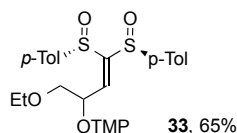
IR (neat) 2922, 2852, 1595, 1453, 1373, 1359, 1242, 1131, 1079, 1046, 1015, 807, 620. ¹HNMR (CDCl₃, 400 MHz) δ 7.76 (d, *J* = 8.4 Hz, 1.7H), 7.72 (d, *J* = 8.4 Hz, 1.7H), 7.53 (d, *J* = 8.2 Hz, 0.3H), 7.49 (d, *J* = 8.2 Hz, 0.3H), 7.40 (d, *J* = 8.4 Hz, 1.7H), 7.38 (d, *J* = 8.4 Hz, 1.7H), 7.29 (d, *J* = 8.2 Hz, 0.3H), 7.22 (d, *J* = 8.2 Hz, 0.3H), 5.17-5.13 (m, 0.15H), 4.85-4.73 (m, 0.3H), 4.31-4.21 (m, 2.55H), 3.51-3.43 (m, 1H), 3.30-3.21 (m, 1H), 3.03 (dd, *J* = 7.8; 3.8 Hz, 1H), 2.46 (s, 2.55H), 2.41 (s, 2.55H), 2.39 (s, 0.45H), 2.37 (s, 0.45H), 1.98-1.86 (m, 1H), 0.57 (br s, 3H), 1.46-0.85 (m, 38H), 0.33-0.26 (m, 1H). ¹³CNMR (CDCl₃, 100 MHz) δ 143.1, 142.7, 135.7, 135.3, 130.4, 129.9, 129.4, 86.0, 85.1, 80.6, 76.4, 74.3, 72.4, 70.5, 60.2, 59.9, 59.6, 40.7, 39.7, 34.7, 33.3, 33.1, 32.9, 32.8, 32.1, 31.0, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 28.1, 24.5, 22.8, 21.6, 21.4, 21.3, 20.3, 20.2, 20.0, 19.9, 17.4, 17.0, 14.3. HRMS: Calc. for C₄₀H₆₄O₄NS [M+H]⁺ 686.4271, found 686.4268.



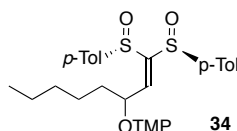
White paste. dr = 1.5:1. IR (neat): 2922, 2852, 1592, 1462, 1376, 1360, 1132, 1082, 1051, 804, 623. ¹HNMR (CDCl₃, 400 MHz) δ 7.57 (d, *J* = 8.2 Hz, 1.2H), 7.21-7.18 (m, 1H), 7.09-6.96 (m, 5.6H), 6.87 (d, *J* = 8.0 Hz, 1.2H), 5.25-5.16 (m, 1H), 2.35 (s, 1.8H), 2.32 (s, 1.2H), 2.31 (s, 1.2H), 2.26 (s, 1.8H), 1.89-1.80 (m, 1H), 1.75-1.24 (m, 25H), 1.17 (br s, 3H), 1.16 (br s, 3H), 1.08 (br s, 3H), 0.91 (br s, 3H), 0.88 (t, *J* = 6.8 Hz, 1.2H), 0.87 (t, *J* = 6.8 Hz, 1.8H). ¹³CNMR (CDCl₃, 100 MHz) δ 148.4, 147.9, 145.9, 145.3, 142.2, 142.0, 141.3, 140.7, 140.4, 139.0, 137.9, 137.4, 79.5, 78.0, 61.0, 59.4, 40.5, 40.3, 40.2, 40.1, 35.0, 34.8, 34.6, 34.0, 33.9, 33.5, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 25.4, 25.3, 22.7, 21.5, 21.4, 21.3, 20.5, 20.4, 17.2, 14.2. HRMS: Calc. for C₃₇H₅₈O₃NS₂ [M+H]⁺ 628.3853, found 628.3843.



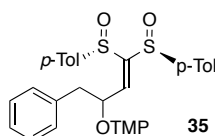
From alkylidene bis-sulfoxide **1h** (210.0 mg, 0.53 mmol) and upon addition of 1.2 equiv. Of PhCH₂OLi afforded a colorless oil of **28h** (246.0 mg, 84%) as a 1.5:1 mixture of diastereoisomers. Major Diastereoisomer : [α]_D + 71.5 (c = 1.0 CHCl₃). IR (neat): 3307, 3238, 3092, 2971, 2929, 2241, 1491, 1466, 1051. ¹H NMR (CDCl₃, 400MHz) δ 7.38 (d, *J* = 10.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.02-6.98 (m, 4H), 5.32 (d, *J* = 10.8 Hz, 1H), 2.51-2.47 (m, 1H), 2.34-2.29 (m, 7H), 2.07-2.05 (m, 1H), 1.69-1.57 (m, 3H), 1.47-1.33 (m, 6H), 1.26 (s, 3H), 1.19 (s, 3H), 1.18 (s, 3H), 1.14 (s, 3H), 1.02 (s, 3H). ¹³C NMR (CDCl₃, 100MHz): δ 151.5, 141.8, 141.7, 141.4, 140.8, 136.9, 129.5, 129.3, 125.6, 125.4, 81.7, 79.7, 71.1, 61.4, 59.8, 40.4, 40.0, 39.1, 34.2, 33.6, 29.0, 23.1, 22.3, 21.3, 21.2, 20.7, 20.5, 17.1.



To a solution of ethanol (0.022 mL, 0.242 mmol) in anhydrous THF (2 mL), cooled to -10°C , is added dropwise *n*-BuLi (0.130 mL, 0.260 mmol, 2.0 M in hexanes) and the solution is stirred for 30 min at this temperature. Then, the solution is cooled to -40°C and the vinylidene bis-sulfoxide **1i** (80.0 mg, 0.242 mmol) is added as an anhydrous THF (1 mL) solution. The reaction is stirred 1 h at -40°C and 1 h at -20°C (disappearance of starting material monitored by TLC, diethyl ether/petroleum ether: 8/2). TEMPO (95 mg, 0.605 mmol) and ferrocenium tetrafluoroborate (231 mg, 0.847 mmol) are added in one portion. The reaction is stirred 2 hours at -20°C , the reaction is then hydrolyzed by a saturated aqueous solution of NH_4Cl . The crude mixture is extracted with Et_2O (3x7 mL) and the resulting organic phases are dried over anhydrous MgSO_4 , filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel (pentane/diethyl ether: from 9/1 to 6/4) to afford a yellow oil of **33** (83.2 mg, 65%) as a 1.2:1 mixture of diastereoisomers: IR (neat) 2972, 2927, 1595, 1454, 1376, 1360, 1114, 1082, 1049, 804, 731, 623. ^1H NMR (CDCl_3 , 400 MHz) δ 7.48 (d, $J = 8.2$ Hz, 1.1H), 7.23 (d, $J = 10.1$ Hz, 0.45H), 7.18 (d, $J = 8.2$ Hz, 0.9H), 7.14 (d, $J = 8.2$ Hz, 1.1H), 7.13 (d, $J = 8.2$ Hz, 1.1H), 7.06 (d, $J = 9.3$ Hz, 0.55H), 6.99 (d, $J = 8.2$ Hz, 1.1H), 6.87 (d, $J = 8.2$ Hz, 2.7H), 5.44-5.40 (m, 0.45H), 5.39-5.34 (m, 0.55H), 3.89 (dd, $J = 9.2$; 4.2 Hz, 0.45H), 3.77 (dd, $J = 10.6$; 5.5 Hz, 0.55H), 3.65 (dd, $J = 10.6$; 5.3 Hz, 0.55H), 3.60-3.49 (m, 2.45H), 2.33 (s, 1.65H), 2.26 (br s, 2.70H), 2.25 (s, 1.65H), 1.59-1.12 (m, 18H), 1.08 (br s, 1.35H), 1.01 (br s, 1.65H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 149.2, 143.8, 142.4, 142.2, 142.1, 140.7, 140.6, 140.3, 139.1, 137.7, 136.7, 129.4, 129.3, 129.2, 126.7, 126.5, 125.6, 124.9, 79.8, 78.3, 71.6, 71.4, 67.4, 67.2, 61.0, 60.9, 59.8, 59.7, 40.6, 40.5, 40.3, 35.3, 34.1, 33.7, 33.0, 30.4, 21.5, 21.4, 21.3, 20.7, 20.4, 17.2, 15.4, 15.3. HRMS: Calc. for $\text{C}_{29}\text{H}_{42}\text{O}_4\text{NS}_2$ $[\text{M}+\text{H}]^+$ 532.2550, found 532.2553.



Procedure **D** with **CuI** (173 mg, 0.91 mmol), *n*-BuLi (0.395 mL, 0.91 mmol, 2.3M in hexanes) and vinylidene bis-sulfoxide **1j** (74.0 mg, 0.224 mmol) afforded a yellow oil of **12** (87 mg, 72%) as a 2.5:1 mixture of diastereoisomers: IR (neat) 2928, 2870, 1595, 1460, 1377, 1360, 1083, 1051, 805, 623. ^1H NMR (CDCl_3 , 400 MHz) δ 7.57 (d, $J = 8.3$ Hz, 1.2H), 7.21-7.17 (m, 1H), 7.09-6.97 (m, 5.6H), 6.88 (d, $J = 7.8$ Hz, 1.2H), 5.25-5.16 (m, 1 H), 2.35 (s, 1.8H), 2.32 (s, 1.2H), 2.31 (s, 1.2H), 2.26 (s, 1.8H), 1.91-1.27 (m, 14H), 1.17 (br s, 3H), 1.16 (br s, 3H), 1.08 (br s, 3H), 0.93-0.88 (m, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 148.5, 147.9, 145.9, 145.2, 142.2, 142.0, 141.3, 140.7, 140.3, 139.0, 137.8, 137.4, 129.6, 129.5, 129.3, 129.2, 126.2, 126.0, 125.0, 124.8, 79.5, 77.9, 61.0, 60.0, 40.5, 40.3, 40.2, 40.1, 35.0, 34.7, 33.9, 33.8, 33.5, 32.0, 25.0, 24.9, 22.5, 21.5, 21.4, 21.3, 20.5, 20.4, 20.3, 17.2, 14.1, 14.0. HRMS: Calc. for $\text{C}_{31}\text{H}_{46}\text{O}_3\text{NS}_2$ $[\text{M}+\text{H}]^+$ 544.2914, found 544.2906.



Procedure **D** with CuBr.DMS (151.7 mg, 0.738 mmol), PhLi (0.435 mL, 0.738 mmol, 1.7M in Et₂O) and vinylidene bis-sulfoxide **1j** (60.9 mg, 0.184 mmol) afforded a yellow oil of **13** (59.2 mg, 57%) as a 1.8:1 mixture of diastereoisomers: IR (neat) 2972, 2928, 1595, 1493, 1454, 1376, 1361, 1181, 1132, 1083, 1052, 918, 805, 731, 700. ¹HNMR (CDCl₃, 400 MHz) δ 7.46 (d, *J* = 8.0 Hz, 1.28H), 7.38-7.26 (m, 5H), 7.19 (d, *J* = 7.0 Hz, 0.36H), 7.08 (d, *J* = 8.3 Hz, 1.28H), 7.05 (d, *J* = 10.3 Hz, 0.64H), 6.98 (d, *J* = 8.0 Hz, 1.28H), 6.88-6.83 (m, 2.72H), 6.73 (d, *J* = 8.0 Hz, 0.72H), 6.35 (d, *J* = 8.0 Hz, 0.72), 5.45-5.35 (m, 1H), 3.34 (dd, *J* = 13.1; 4.6 Hz, 0.36H), 3.20 (dd, *J* = 13.6; 6.3 Hz, 0.64H), 2.98-2.90 (m, 1H), 2.33 (s, 1.92H), 2.28 (s, 2.16H), 2.24 (s, 1.92H), 1.59-0.96 (m, 18H). ¹³CNMR (CDCl₃, 100 MHz) δ 149.7, 148.7, 144.6, 144.3, 142.1, 141.8, 140.6, 140.5, 140.3, 138.8, 137.5, 136.6, 136.3, 136.1, 130.2, 130.1, 129.4, 129.3, 129.2, 128.8, 128.5, 127.0, 126.7, 126.3, 126.1, 124.7, 124.5, 80.5, 79.5, 61.2, 59.7, 41.3, 40.7, 40.5, 40.3, 40.2, 35.1, 34.3, 34.1, 33.8, 33.2, 30.4, 29.7, 21.5, 21.4, 21.3, 21.2, 20.7, 20.6, 20.5, 20.4, 17.2. HRMS: Calc. for C₃₃H₄₂O₃NS₂ [M+H]⁺ 564.2601, found 564.2595.

X-ray parameters and ellipsoid plots

Structure 17

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell: a=28.123(6) b=17.080(4) c=11.050(2)
 alpha=90 beta=97.334(17) gamma=90

Temperature: 200 K

	Calculated	Reported
Volume	5264.3(19)	5264(2)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C27 H37 N O4 S	C27 H37 N O4 S
Sum formula	C27 H37 N O4 S	C27 H37 N O4 S
Mr	471.64	471.63
Dx,g cm-3	1.190	1.190
Z	8	8
Mu (mm-1)	0.154	0.154
F000	2032.0	2032.0
F000'	2033.85	
h,k,lmax	36,22,14	36,22,14
Nref	6058	6045
Tmin,Tmax	0.989,0.991	0.747,1.000
Tmin'	0.919	

Correction method= # Reported T Limits: Tmin=0.747 Tmax=1.000
AbsCorr = MULTI-SCAN

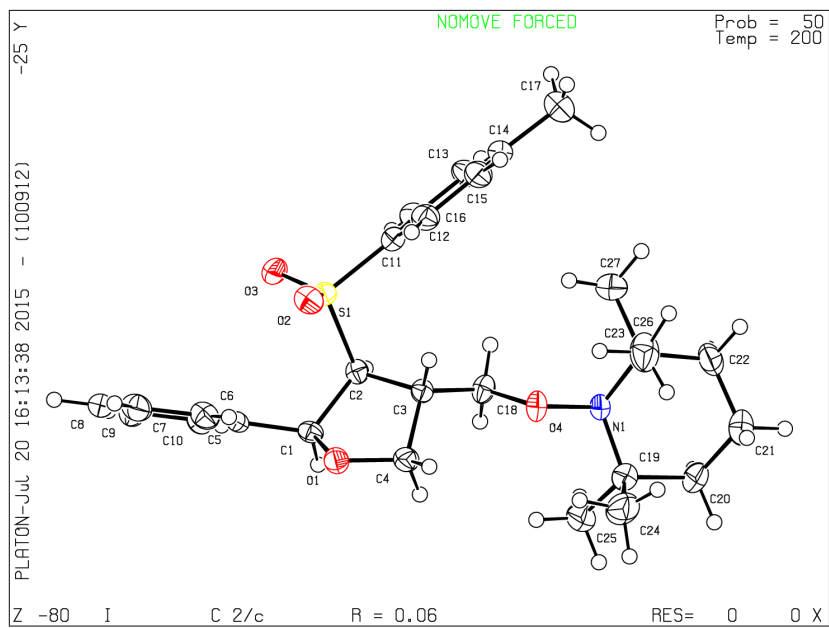
Data completeness= 0.998 Theta(max)= 27.503

R(reflections)= 0.0598(3134) wR2(reflections)= 0.1570(6045)

S = 1.036 Npar= 303

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Datablock I - ellipsoid plot



Structure 27a

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: C-C = 0.0062 A Wavelength=0.71073
Cell: a=6.3790(8) b=21.193(3) c=25.1780(19)
 alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	3403.8(7)	3403.8(7)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C37 H45 N O4 S	C37 H45 N O4 S
Sum formula	C37 H45 N O4 S	C37 H45 N O4 S
Mr	599.80	599.80
Dx, g cm-3	1.171	1.170
Z	4	4
Mu (mm-1)	0.133	0.133
F000	1288.0	1288.0
F000'	1289.02	
h,k,lmax	8,27,32	8,27,32
Nref	7834[4451]	7272
Tmin,Tmax	0.983,0.989	0.749,1.000
Tmin'	0.941	

Correction method= # Reported T Limits: Tmin=0.749 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.63/0.93 Theta(max)= 27.507

R(reflections)= 0.0513(3431) wR2(reflections)= 0.1104(7272)

S = 0.939 Npar= 395

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Datablock I - ellipsoid plot

