

SUPPORTING INFORMATION

Highly Diastereoselective Ionic/Radical Tandem Reactions: Single Electron Transfer Induced Cyclization of Bis-Sulfoxides

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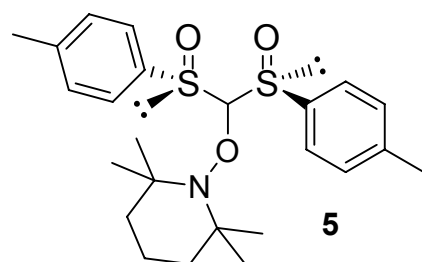
Generalities: All reactions were run under an argon or nitrogen atmosphere in anhydrous solvents and dried flasks. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F 254 and revealed with either an ultraviolet lamp ($\lambda=254$ nm) or a *p*-anisaldehyde solution. Flash column chromatography 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 Perkin-Elmer 1420 spectrometer and on a Bruker Tensor 27. ^1H and ^{13}C 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 CDCl_3) for proton NMR. For carbon NMR, shifts are referenced from the solvent central peak (77.3 ppm for CDCl_3). 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. Elemental analysis were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie. Melting points were obtained on a Reichert apparatus and are uncorrected.

Alkylidene bis-sulfoxides

The general procedure for the synthesis of alkylidene bis-sulfoxides and spectral data of **8**, **14**, **15** and **24** were previously described.^{1,2}

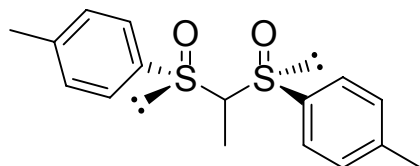
¹ F. Brebion, B. Delouvrié, F. Nájera, L. Fensterbank, M. Malacria, J. Vaissermann, *Angew. Chem. Int. Ed.*, 2003, **42**, 5342.

² F. Brebion, J.-P. Goddard, C. Gomez, L. Fensterbank, M. Malacria, *Synthesis*, 2005, 2449.



$C_{24}H_{33}NO_3S_2$
Mol. Wt.: 447.65 g/mol

A solution of the bis-sulfoxide **1-H** (292 mg, 1 mmol, 1 equiv) in 5 mL of anhydrous THF at $-40\text{ }^\circ\text{C}$ is added *n*-BuLi (0.480 mL, 1.1 mmol, 1.1 equiv, 2.3 M in hexanes). The resulting solution is stirred at this temperature for 30 min. Then, TEMPO (312 mg, 2 mmol, 2 equiv) and ferrocenium hexafluorophosphate **4a** (331 mg, 1 mmol, 1 equiv) are added in one portion. The reaction mixture is stirred at this temperature for 2 h. Then, the reaction is stopped by addition of a saturated aqueous NH_4Cl solution. The crude mixture is filtered over a celite pad to remove solid residues and the resulting solution is dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The crude is purified by flash chromatography over silica gel (petroleum ether/ethyl acetate : 6/4) to afford **5** as a yellow solid (161 mg, 34%). M.p. $92\text{ }^\circ\text{C}$; $[\alpha]_D^{20} +138$ (c 1.00; $CHCl_3$). IR (neat) 3042, 2922, 1096, 1063, 1050, 809 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.78 (s, 3H), 1.02 (s, 3H), 1.24 (s, 3H), 1.28-1.39 (m, 2H), 1.40-1.60 (m, 7H), 2.37 (s, 3H), 2.45 (s, 3H), 5.40 (s, 1H), 7.17 (d, $J = 8.1\text{ Hz}$, 2H), 7.23 (d, $J = 8.1\text{ Hz}$, 2H), 7.33 (d, $J = 8.1\text{ Hz}$, 2H), 7.49 (d, $J = 8.1\text{ Hz}$, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.9 (CH_2), 20.9 (CH_3), 21.1 (CH_3), 21.6 (2 CH_3), 33.5 (CH_3), 34.2 (CH_3), 40.7 (CH_2), 40.8 (CH_2), 62.0 (C), 62.9 (C), 116.5 (C), 125.2 (2 CH), 125.3 (2 CH), 129.8 (2 CH), 130.0 (2 CH), 137.7 (C), 138.7 (C), 141.6 (C), 141.8 (C). Anal. Calc. for $C_{24}H_{33}NO_3S_2$: C 64.39; H 7.43; N 3.13. Found: C 64.51; H 8.18; N 2.52.

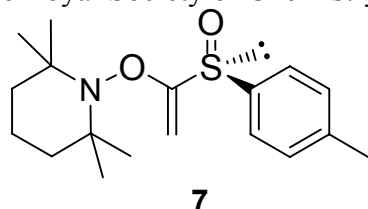


$C_{16}H_{18}O_2S_2$
Mol. Wt.: 306.44 g/mol

1-Me

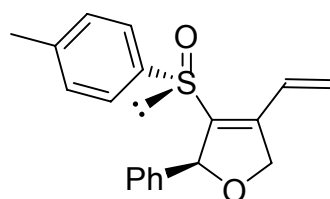
Following the reported procedure³ from bis-sulfoxide **1-H** (1 g, 3.4 mmol), **1-Me** is obtained (769 mg, 73%) as a white solid: m.p. $119\text{-}121\text{ }^\circ\text{C}$; $[\alpha]_D^{20} +308.9$ (c 1.00; $CHCl_3$). IR (neat) 3051, 2923, 2868, 1650, 1492, 1084, 1051, 1016, 811 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.10 (d, $J = 7.1\text{ Hz}$, 3H), 2.40 (s, 3H), 2.44 (s, 3H), 3.55 (q, $J = 7.0\text{ Hz}$, 1H), 7.31 (d, $J = 8.1\text{ Hz}$, 2H), 7.36 (d, $J = 8.3\text{ Hz}$, 2H), 7.41 (d, $J = 8.3\text{ Hz}$, 2H), 7.63 (d, $J = 8.3\text{ Hz}$, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1 (CH_3), 21.4 (CH_3), 21.6 (CH_3), 85.1 (CH), 124.2 (CH), 125.4 (CH), 130.1 (CH), 130.2 (CH), 137.8 (C), 138.3 (C), 141.8 (C), 143.0 (C).

³ N. Khiar, I. Fernandez, F. Alcudia, *Tetrahedron Lett.*, 1993, **34**, 123.



$C_{18}H_{27}NO_2S$
Mol. Wt.: 321.47 g/mol

A solution of the **1-Me** (950 mg, 3.1 mmol, 1 equiv) in anhydrous THF (10 mL) is cooled to $-78^{\circ}C$. To this solution, *n*-BuLi (1.55 mL, 3.75 mmol, 1.2 equiv, 2.4 M in hexanes,) is added dropwise and the solution is stirred for 40 min at this temperature. Then, the solution is warmed to $-40^{\circ}C$ and TEMPO (967 mg, 6.2 mmol, 2 equiv) and ferrocenium hexafluorophosphate (1.03g, 3.1 mmol, 1 equiv) are added in one portion. The reaction is monitored by TLC and after 10 hours at $-40^{\circ}C$, the reaction is hydrolyzed by a saturated aqueous solution of NH_4Cl . The aqueous phase is extracted by ethyl acetate (3x20 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 (petroleum ether/diethyl ether: 8/2) to afford **7** as a pink oil (766 mg, 77%). $[\alpha]_D^{20} +111$ (c 1.50; $CHCl_3$). IR (neat) 3030, 2976, 1628, 1492, 1086, 1060, 810 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.72 (s, 3H), 0.86 (s, 3H), 0.96 (s, 3H), 0.99 (s, 3H), 1.25-1.6 (m, 6H), 2.40 (s, 3H), 5.07 (d, $J = 2.3$ Hz, 1H), 5.17 (d, $J = 2.3$ Hz, 1H), 7.29 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.3$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8 (CH_2), 20.2 (CH_3), 20.8 (CH_3), 21.5 (CH_3), 31.7 (CH_3), 32.2 (CH_3), 39.7 (2 CH_2), 61.1 (C), 61.3 (C), 88.7 (CH_2), 125.3 (2 CH), 129.5 (2 CH), 139.3 (C), 141.7 (C), 166.7 (C). Anal. Calc. for $C_{18}H_{27}NO_2S$: C 67.25; H 8.47; N 4.36. Found: C 67.62; H 8.51; N 4.09.

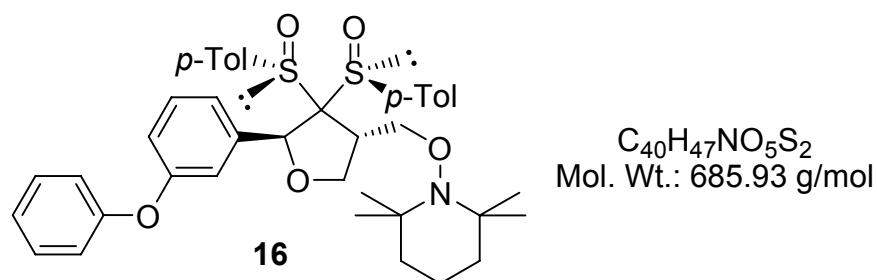


$C_{19}H_{18}O_2S$
Mol. Wt.: 310.41 g/mol

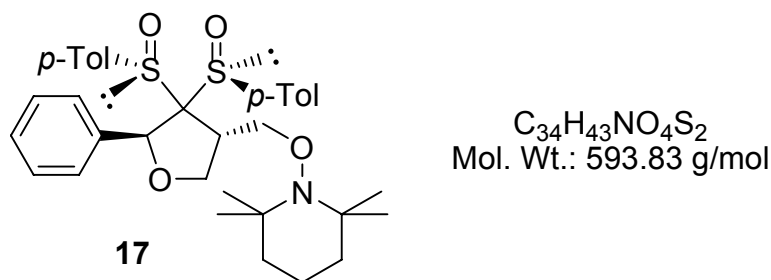
To a solution of alcohol **9**⁴ (104 mg, 0.58 mmol, 1 equiv) in anhydrous THF (3 mL) at $0^{\circ}C$ is added a suspension of NaH 60% in mineral oil (27 mg, 0.68 mmol, 1.3 equiv). The solution is stirred at $0^{\circ}C$ for 30 min and cooled to $-20^{\circ}C$. Then, a solution of benzylidene **8** (200 mg, 0.52 mmol, 1 equiv) in anhydrous THF (3 mL) is added. The solution is stirred at $-20^{\circ}C$ and monitored by TLC. After 3 hours, ferrocenium hexafluorophosphate (522 mg, 1.58 mmol, 3 equiv) is added in one portion and the reaction is gently warmed to room temperature during 6 hours. The reaction is hydrolyzed by addition of a saturated aqueous solution of NH_4Cl . The crude mixture is extracted by diethyl ether (3x30 mL) and the resulting organic phases are washed with water (2x10 mL), 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 8/2 to 5/5) to afford **10** as a colorless oil (56 mg, 35%). $[\alpha]_D^{20} +171$ (c 1.09; $CHCl_3$). IR (neat) 3019, 2953, 2924, 2868, 1710, 1578, 1492, 1046, 807 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 2.30 (s, 3H), 5.00 (dd, $J = 13.2, 2.9$ Hz, 1H), 5.17 (dd, $J = 13.2, 5.0$ Hz, 1H), 5.41 (d, $J = 17.7$ Hz, 1H), 5.61 (d, $J = 10.8$ Hz, 1H), 5.87 (dd, $J = 5.0, 2.9$ Hz, 1H), 6.96-7.15 (m, 9H), 7.34 (dd, $J = 17.7, 10.8$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (CH_3), 75.2 (CH_2), 87.5 (CH), 122.1 (CH_2), 124.3 (CH), 126.0 (CH), 127.7 (CH), 128.1 (2CH), 129.5 (CH), 138.0 (C), 139.1 (C), 139.2 (C), 140.9 (C), 143.7 (C). HRMS: Calc. for $C_{19}H_{18}O_2SNa$ $[M+Na]^+$ 333.0925, found 333.0901

⁴ For the preparation of alcohol **9**, see: Y. Ichinose, K. Oshima, K. Utimoto, *Chem. Lett.*, 1988, 1437.

Typical procedure for the preparation tetrahydrofuran derivatives by 5-exo-cyclization.

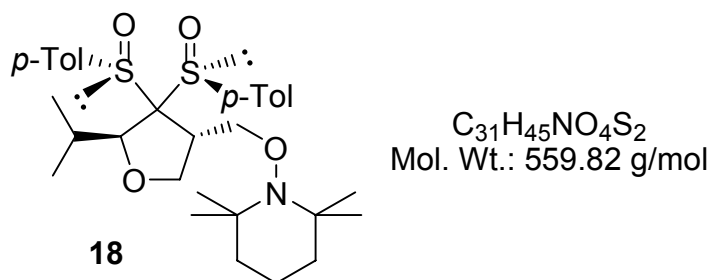


To a solution of allylic alcohol (43 μ L, 0.63 mmol, 1.5 equiv) in anhydrous THF (5 mL), cooled to -40 $^{\circ}$ C, is added dropwise *n*-BuLi (0.270 mL, 0.59 mmol, 1.4 equiv, 2.2 M in hexanes) and the solution is stirred for 30 min at this temperature. Then, phenoxybenzylidene bis-sulfoxide **14** (200 mg, 0.42 mmol, 1 equiv) is added as an anhydrous THF (5 mL) solution. The reaction is stirred until disappearance of starting material (monitored by TLC, diethyl ether/petroleum ether: 8/2) and the solution is warmed to -20 $^{\circ}$ C. TEMPO (132 mg, 0.84 mmol, 2 equiv) and ferrocenium tetrafluoroborate (366 mg, 1.26 mmol, 3 equiv) are added in one portion. The reaction is monitored by TLC and after 2 hours at -20 $^{\circ}$ C, the reaction is hydrolyzed by a saturated aqueous solution of NH_4Cl . The crude mixture is extracted with ethyl acetate (3x30 mL) and the resulting organic phases are washed with brine (2x10 mL), dried over anhydrous $MgSO_4$, filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel (petroleum ether/diethyl ether: from 8/2 to 6/4) to afford **16** as a colorless oil (162 mg, 56%). $[\alpha]_D^{20} + 93$ (c 1.00; $CHCl_3$). IR (neat) 3028, 2971, 2930, 1584, 1490, 1243, 1083, 1052, 808 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.77 (s, 3H), 1.07 (s, 3H), 1.08 (s, 3H), 1.14 (s, 3H), 1.22-1.56 (m, 6H), 2.36 (s, 3H), 2.44 (s, 3H), 3.17 (dd, $J = 7.8, 4.0$ Hz, 1H), 3.67-3.76 (m, 1H), 3.93 (dd, $J = 10.9, 8.1$ Hz, 1H), 4.40 (dd, $J = 11.1, 7.8$ Hz, 1H), 4.52 (m, 1H), 5.47 (s, 1H), 5.51 (s, 1H), 6.80-6.88 (m, 4H), 7.05 (m, 1H), 7.14 (m, 1H), 7.27-7.32 (m, 4H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.74-7.79 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0 (CH_2), 20.0 (CH_3), 21.5 (CH_3), 22.7 (2 CH_3), 33.1 (2 CH_3), 39.6 (CH and 2 CH_2), 59.6 (C), 59.9 (C), 72.3 (CH_2), 74.1 (CH_2), 80.5 (CH), 88.2 (C), 117.3 (2CH), 119.6 (CH), 120.2 (CH), 122.3 (CH), 125.1 (2 CH), 126.2 (3 CH), 128.5 (CH), 129.5 (2 CH), 130.4 (2 CH), 130.7 (2 CH), 135.9 (C), 136.0 (C), 137.6 (C), 142.5 (C), 143.6 (C), 154.8 (C), 158.2 (C). HRMS: Calc. for $C_{40}H_{47}NO_5S_2Na$ $[M+Na]^+$ 708.2794, found 708.2780.

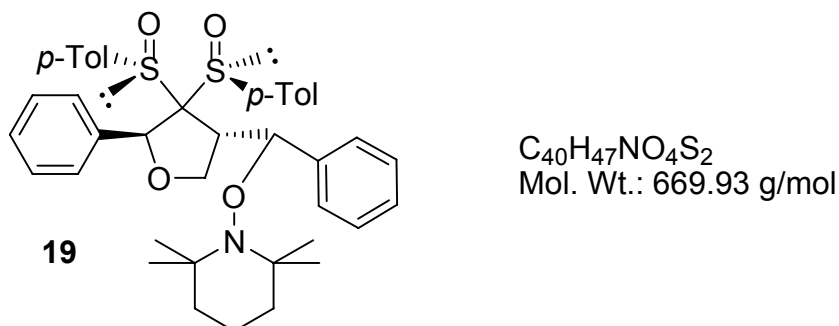


Following the same procedure that gives **16** from **14**, compound **8** (380 mg, 1 mmol) afforded **17** (352 mg, 59%) as a colorless oil: $[\alpha]_D^{20} + 142$ (c 0.98; $CHCl_3$). IR (neat) 3021, 2956, 2891, 1569, 1430, 1086, 807 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.78 (s, 3H, CH_3), 1.05-1.69 (m, 15H), 2.42 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 3.21 (dd, $J = 7.3, 3.5$ Hz, 1H), 3.75 (m, 1H), 3.89 (dd, $J = 10.6, 8.1$ Hz, 1H), 4.40 (dd, $J = 10.6, 8.1$ Hz, 1H), 4.52 (dd, $J = 7.6, 7.3$ Hz, 1H), 5.43 (s, 1H), 6.47 (d, $J = 7.6$ Hz, 2H), 6.90-7.08 (m, 3H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 8.1$ Hz, 2H), 7.71 (d, $J = 7.8$ Hz, 2H), 7.82 (d, $J = 8.1$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1 (CH_2), 20.3 (CH_3), 21.1 (CH_3), 22.2 (2 CH_3), 34.2 (2 CH_3), 38.9 (CH

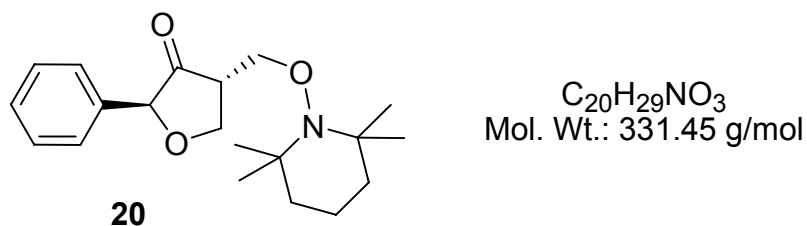
and 2 CH₂), 60.2 (C), 60.7 (C), 72.3 (CH₂), 74.1 (CH₂), 80.5 (CH), 88.2 (C), 121.3 (2 CH), 123.1 (2 CH), 126.1 (CH), 126.6 (2 CH), 128.5 (2 CH), 129.5 (2 CH), 130.4 (CH), 130.7 (CH), 135.9 (C), 136.0 (C), 137.6 (C), 142.5 (C), 143.6 (C). HRMS: Calc. for C₃₄H₄₄NO₄S₂ [M+H]⁺ 594.2712, found 594.2704.



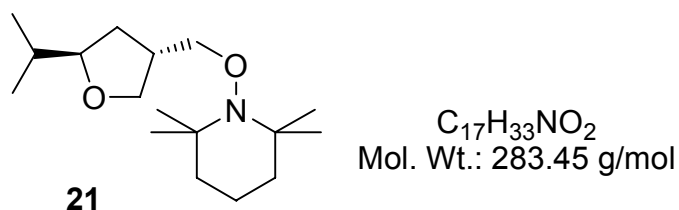
Following the same procedure that gives **16** from **14**, compound **15** (346 mg, 1 mmol) afforded **18** (230 mg, 41%) as a colorless oil: [α]_D²⁰ + 129 (c 1.04; CHCl₃). IR (neat) 3032, 2946, 2851, 1558, 1432 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 0.45 (d, *J* = 6.8 Hz, 3H), 0.60 (s, 3H, CH₃), 1.01 (d, *J* = 6.8 Hz, 3H), 1.05-1.69 (m, 9H), 1.30-1.55 (m, 6H), 2.45 (s, 3H), 2.48-2.58 (m, 4H), 3.28-3.36 (m, 1H), 3.51 (dd, *J* = 8.8, 3.5 Hz, 1H), 3.90 (dd, *J* = 10.8, 8.8 Hz, 1H), 4.26-4.33 (m, 2H), 4.53 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 8.08 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 15.1 (CH₂), 18.0 (2CH₃), 18.3 (CH₃), 19.4 (CH₃), 19.9 (CH₃), 20.1 (CH₃), 26.7 (2 CH₃), 30.8 (CH₂), 31.0 (CH₂), 37.8 (CH), 48.2 (CH), 57.8 (C), 57.9 (C), 69.8 (CH₂), 71.0 (CH₂), 90.9 (CH), 94.2 (C), 127.4 (2 CH), 127.6 (2 CH), 130.1 (2 CH), 130.7 (2 CH), 133.2 (C), 134.4 (C), 143.7 (C), 144.5 (C). HRMS: Calc. for C₃₁H₄₆NO₄S₂ [M+H]⁺ 560.2869, found 560.2880.



Following the same procedure that gives **16** from **14** applied to cinnamyl alcohol, compound **8** (380 mg, 1 mmol) afforded **19** (321 mg, 48%) as a colorless oil and a mixture of diastereoisomers (1.1:1). ¹H NMR (400 MHz, CDCl₃) δ 0.78 (s, 3H, major), 0.87 (s, 3H, minor), 1.13 (s, 3H, major), 1.15 (s, 3H, minor), 1.24 (s, 3H, major), 1.25 (s, 3H, minor), 1.30-1.75 (m, 18H), 2.26 (bs, 6H), 2.35 (s, 3H, major), 2.41 (s, 3H, minor), 4.77 (dd, *J* = 13.6, 4.0 Hz, 1H, minor), 5.03 (dd, *J* = 14.2, 5.3 Hz, 1H, major), 5.14-5.22 (m, 4H), 5.43 (dd, *J* = 9.1, 4.5 Hz, 1H, minor), 5.85 (dd, *J* = 5.1, 2.3 Hz, 1H, major), 6.44 (s, 1H, major), 6.59 (s, 1H, minor), 6.74 (d, *J* = 8.3 Hz, 1H, major), 6.88-7.21 (m, 33H), 7.39 (d, *J* = 8.2 Hz, 2H, minor). ¹³C NMR (100 MHz, CDCl₃) δ 17.1 (CH₂), 17.3 (CH₂), 20.3 (2 CH₃), 20.4 (3 CH₃), 20.6 (3 CH₃), 21.3 (2 CH₃), 21.5 (2 CH₃), 33.6 (2 CH₂), 33.8 (2 CH₂), 34.0 (CH), 34.2 (CH), 59.7 (2 C), 60.0 (2 C), 60.2 (C), 74.6 (CH₂), 75.0 (CH₂), 81.9 (CH), 83.1 (CH), 86.6 (CH), 87.6 (CH), 90.2 (C), 91.6 (C), 124.7 (CH), 126.1 (CH), 126.7 (CH), 126.8 (CH), 127.4 (2 CH), 127.8 (2 CH), 127.9 (2 CH), 128.1 (2 CH), 128.2 (2 CH), 128.5 (2 CH), 128.6 (2 CH), 128.8 (2 CH), 129.3 (2 CH), 129.6 (2 CH), 135.7 (C), 135.9 (C), 137.2 (C), 137.8 (C), 138.7 (C), 139.5 (C), 140.8 (C), 141.1 (C), 141.3 (C), 141.8 (C), 149.9 (C), 150.9 (C).



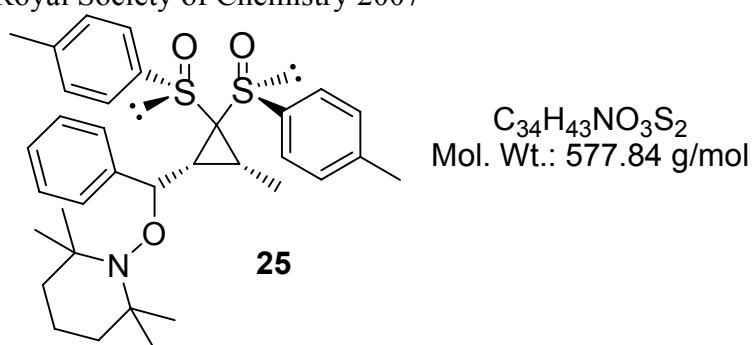
To a suspension of In (118 mg, 1 mmol) in anhydrous THF (20 mL) at room temperature, is added $TiCl_4$ (261 μ L, 2.4 mmol).⁵ The dark-blue mixture is stirred at room temperature for 1 h. To a solution of **17** (190 mg, 0.32 mmol) in anhydrous THF (5 mL) at room temperature is added 6.4 mL (2.4 equiv of Ti species) of the previously prepared Ti/In complex solution. After 30 min, a saturated aqueous solution of NH_4Cl (20 mL) is added, the resulting mixture is stirred for 10 min and extracted by dichloromethane (3x25 mL). The 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/diethylether: 9/1) to afford **20** as a colorless oil (36 mg, 34%): $[\alpha]_D^{20} - 49.8$ (c 1.00; $CHCl_3$). IR (neat) 2991, 2928, 2853, 1762, 1452, 1374, 1055, 968 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.13 (s, 3H), 1.18 (s, 3H), 1.21 (s, 3H), 1.27-1.55 (m, 6H), 2.82-2.89 (m, 1H), 4.01 (dd, $J = 9.1, 3.5$ Hz, 1H), 4.15 (dd, $J = 9.1, 5.8$ Hz, 1H), 4.33 (t, $J = 9.5$ Hz, 1H), 4.69 (t, $J = 9.1$ Hz, 1H), 4.73 (s, 1H), 7.33-7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0 (CH_2), 20.1 (CH), 29.7 (CH_3), 30.3 (CH_3), 32.9 (CH_3), 33.1 (CH_3), 39.6 (CH_2), 39.7 (CH_2), 60.0 (C), 60.2 (C), 68.0 (CH_2), 72.3 (CH_2), 82.1 (CH), 126.2 (2CH), 128.2 (CH), 128.5 (2CH), 135.8 (C), 212.3 (C). HRMS: Calc. for $C_{20}H_{30}NO_3$ $[M+H]^+$ 332.2220, found 332.2222.



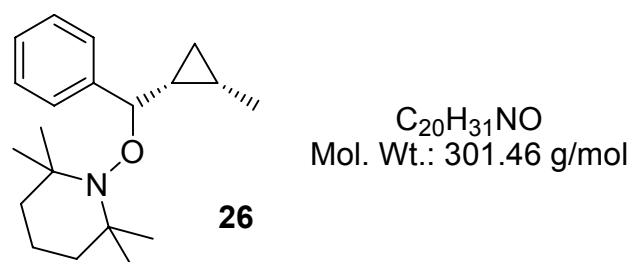
To a solution of **18** (50 mg, 0.09 mmol) in anhydrous THF (1 mL) is added at room temperature a freshly prepared SmI_2 solution⁶ (5.4 mL, 0.54 mmol, 0.1 mol/L in THF). The reaction mixture is stirred until disappearance of the typical blue color. The resulting grey suspension is hydrolyzed by a saturated aqueous solution of NH_4Cl (5 mL) and extracted by dichloromethane (3x10 mL). The 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/diethylether: 95/5) to afford **21** as a colorless oil (22 mg, 88%): $[\alpha]_D^{20} + 38$ (c 1.00; $CHCl_3$). IR (neat) 2960, 2931, 1443, 1376, 1106, 951 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$) δ 0.89 (d, $J = 6.8$ Hz, 3H), 0.98 (d, $J = 6.8$ Hz, 3H), 1.05-1.13 (m, 6H), 1.15-1.19 (m, 6H), 1.29-1.51 (m, 6H), 1.65-1.78 (m, 3H), 2.44-2.52 (m, 1H), 3.54-3.59 (m, 2H), 3.68-3.79 (m, 2H), 4.01 (dd, $J = 8.6, 7.3$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1 (CH_2), 18.6 (CH_3), 19.3 (CH_3), 20.1 (CH), 32.3 (2 CH_2), 33.1 (2 CH_3), 33.2 (2 CH_3), 38.6 (CH), 39.6 (CH_2), 59.8 (2C), 70.9 (CH_2), 78.2 (CH_2), 84.3 (CH). HRMS: Calc. for $C_{17}H_{33}NO_2$ $[M+H]^+$ 284.2590, found 284.2597.

⁵ B. W. Yoo, K. H. Choi, D. Y. Kim, K. I. Choi, J. H. Kim, *Synth. Commun.*, 2003, **33**, 53.

⁶ S. Bezzenine-Lafollée, F. Guibé, H. Villar, R. Zriba, *Tetrahedron*, 2004, **60**, 6931.



To a suspension of CuI (375 mg, 1.97 mmol, 4 equiv) in anhydrous THF (5 mL) at 0 °C is added a solution of MeLi (1.23 mL, 1.97 mmol, 4 equiv, 1.6 M in diethyl ether). The suspension disappeared then a yellow precipitate appeared. The resulting yellow mixture is stirred for 30 min and cooled to -78 °C. A solution of dienyl bis-sulfoxide **24** (200 mg, 0.49 mmol, 1 equiv) in anhydrous THF (5 mL) is added to the organocopper suspension and the solution is warmed to -20 °C in 1 hour. Then, TEMPO (384 mg, 2.46 mmol, 5 equiv) and ferrocenium tetrafluoroborate (620 mg, 2.46 mmol, 5 equiv) are added in one portion. The reaction is monitored by TLC and after 3 hours at -20 °C, the reaction is hydrolyzed by a saturated aqueous solution of NH₄Cl. The crude mixture is extracted by ethyl acetate (3x30 mL) and the resulting organic phases are washed with brine (2x10 mL), dried over anhydrous MgSO₄, filtered and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel (ethyl acetate/pentane: 4/6) to afford **25** as a gummy solid (151 mg, 53%). $[\alpha]_D^{20} + 157$ (c 0.90; CHCl₃). IR (neat) 3022, 2932, 2890, 1560, 1452, 1090, 800 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 1.08 (s, 6H), 1.12-1.56 (m, 12H), 1.64 (d, *J* = 6.6 Hz, 3H), 2.26-2.39 (m, 1H), 2.36 (s, 3H), 2.50 (s, 3H), 2.94 (t, *J* = 9.6 Hz, 1H), 5.36 (d, *J* = 9.8 Hz, 1H), 6.43 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 7.37-7.49 (m, 5H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 13.2 (CH), 17.4 (CH₂), 20.6 (CH₃), 20.7 (CH₃), 21.4 (CH₃), 21.6 (CH₃), 30.9 (CH₃), 32.7 (2 CH₃), 33.7 (CH), 33.9 (2 CH₂), 60.0 (C), 60.7 (C), 70.2 (CH), 79.7 (C), 124.0 (CH), 125.6 (2 CH), 127.8 (2 CH), 128.4 (2 CH), 129.5 (2 CH), 129.7 (2 CH), 130.0 (2 CH), 138.8 (C), 139.0 (C), 139.2 (C), 141.1 (C), 142.2 (C). HRMS: Calc. for C₃₄H₄₃NO₃S₂Na [M+Na]⁺ 600.2582, found 600.2577.



To a solution of compound **25** (100 mg, 0.17 mmol) in ethanol (20 mL) is added 2 mL of Raney Ni as a water suspension (50% w/v). The flask is successively purged by an argon flow and an hydrogen flow. Then, the reaction is stirred under an hydrogen atmosphere during 2 hours. The reaction flask is purged by an argon flow and the crude mixture is filtered over a pad of celite. The celite pad is washed by ethanol and the solvent is removed under vacuum. The crude is purified by flash chromatography over silica gel (pentane/diethyl ether: 95/5) to afford the compound **26** (46 mg, 91%) as a pale yellow oil: $[\alpha]_D^{20} + 79$ (c 1.01; CHCl₃). IR (neat) 3062, 2997, 2926, 2870, 1492, 1375, 1359 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ -0.27 (m, 1H), 0.66 (ddd, *J* = 8.8, 8.8, 4.8 Hz, 1H), 0.92 (s, 3H), 1.06 (s, 3H), 1.23-1.60 (m, 11H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.45 (s, 3H), 4.36 (d, *J* = 8.8 Hz, 1H), 7.21-7.43 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 11.8 (CH₂), 13.9 (CH), 15.9 (CH₃), 17.5 (CH₂), 20.5 (CH₃), 20.8 (CH₃), 24.4 (CH₃),

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33.6 (CH), 33.9 (CH₃), 40.1 (CH₂), 40.6 (CH₂), 59.6 (C), 60.4 (C), 84.7 (CH), 126.7 (CH), 127.2 (2 CH), 127.9 (2 CH), 144.3 (C). HRMS: Calc. for C₂₀H₃₂NO [M+H]⁺ 302.2485, found 302.2477.

