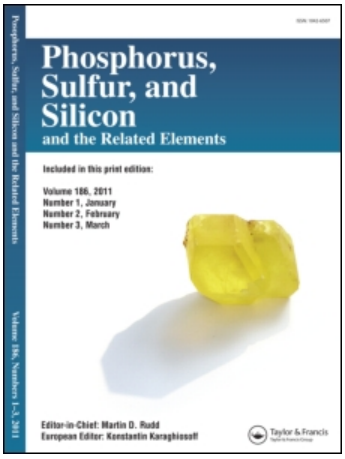

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π-Face-Selective 1,3-Dipolar Cycloadditions of 3,4-Di-*tert*-butylthiophene 1-Oxide with 1,3-Dipoles

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3,4-Di-tert-butylthiophene 1-oxide underwent 1,3-dipolar cycloadditions with 1,3-dipoles such as nitrile oxide, diazomethane, nitrile imide, nitrone, and azomethine ylide at its syn-π-face with respect to the S=O bond.

Keywords 1,3-Dipolar cycloaddition; π-face selectivity; heterocycles; stereochemistry; thiophene 1-oxide

INTRODUCTION

π-Facial selectivity (diastereofacial selectivity) in Diels–Alder reactions has been attracting considerable attention. It has been investigated most extensively by using 5-substituted cyclopentadienes as the diene.[1] Thiophene 1-oxides, which have the general structure shown in Figure 1, are no longer aromatic and hence highly reactive. They serve as a type of cyclic diene that possesses two π-faces, i.e., *syn*- and *anti*-faces, for Diels–Alder reactions, with respect to the S=O bond. We have reported that 3,4-di-*tert*-butylthiophene 1-oxide (**1**) undergoes *syn*-π-face-selective Diels–Alder reactions with a wide range of dienophiles.[2–4] Recently, we also reported that the S_2O, formed by retro-Diels–Alder reaction of bicyclic compound **2**, disproportionates to S_3 (triatomic sulfur) and SO_2, and the resulting S_3 undergoes a *syn*-π-face-selective 1,3-dipolar cycloaddition to **1**, the counterpart of the S_2O formation, to give the final product **3**; the stereochemistry of **3** was determined by X-ray diffraction analysis (Scheme 1).[5] We have now examined 1,3-dipolar

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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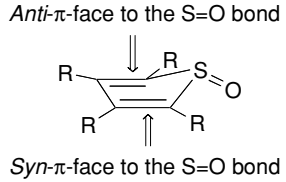
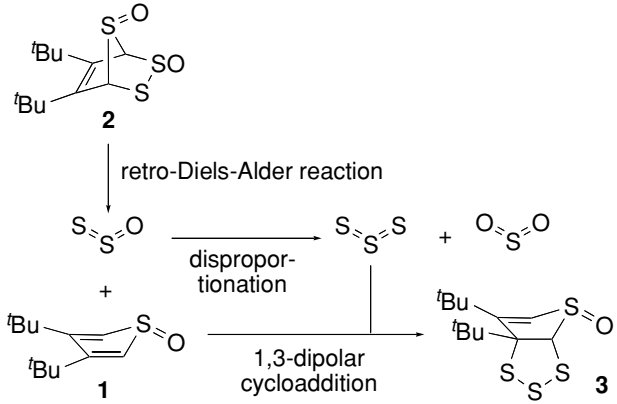


FIGURE 1 General structure and two π-faces of thiophene 1-oxides.

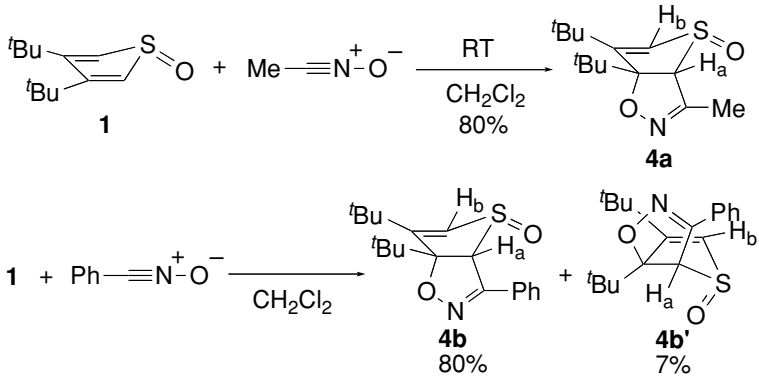
cycloadditions of **1** with a series of 1,3-dipoles to know more about the stereochemical course of the reaction. To our knowledge, π-facial selectivity in 1,3-dipolar cycloadditions has been far less investigated.[6–9]



SCHEME 1 *Syn*-π-face-selective 1,3-dipolar cycloaddition of S_3 to thiophene 1-oxdide **1**.

Initially, 1,3-dipolar cycloadditions of **1** with propargyl-allenyl type 1,3-dipoles were examined. The reaction of **1** with acetonitrile oxide, generated in situ by reaction of nitroethane with phenyl isocyanate in the presence of Et_3N in CH_2Cl_2 at room temperature,[10] furnished the single 1,3-dipolar cycloadduct **4a**[11] in 80% yield (Scheme 2). On the other hand, the reaction of **1** with benzonitrile oxide in CH_2Cl_2, generated by treatment of α-chlorobenzaldehyde oxime (PhCCl=NOH) with Et_3N,[12] afforded a 10:1 mixture of the two diastereomers **4b** and **4b**′,[11] which were isolated in 80% and 7% yields, respectively. The ratio **4b**:**4b**′ showed solvent dependency; it was 23:1 and 24:1 in benzene and toluene, respectively.

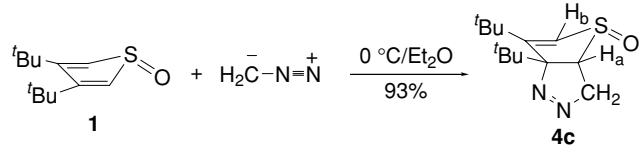
The regiochemistry of the addition in the formation of **4a** was determined by observation of the coupling (1.1 Hz) between H_a and the



SCHEME 2 1,3-Diploar cycloaddition of **1** with nitrile oxides.

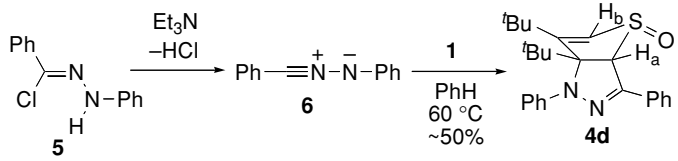
oxazole methyl protons. The configuration of the sulfinyl group was determined on the basis of aromatic solvent-induced shift (ASIS) and Eu(thd)$_3$-induced shift [Eu(thd)$_3$; europium tris(2,2,6,6-tetramethyl-3,5-heptanedionate)]. It is well documented that benzene coordinates to the sulfur atom of the sulfinyl group,[13–17] whereas the europium atom of Eu(thd)$_3$ coordinates to the oxygen atom. Thus, for the adduct **4a**, the ^{1}H NMR spectrum in C_6D_6 would result in the high field shift of H_a and H_b, while the oxazole methyl signal remains virtually unchanged. On the other hand, Eu(thd)$_3$ would bring about the low field shift of H_a, H_b, and the methyl protons. Indeed, the spectrum in C_6D_6 resulted in the high field shift of H_a and H_b by 0.60 and 0.43 ppm, respectively, keeping the methyl signal virtually unchanged. Meanwhile, Eu(thd)$_3$ (0.2 molar amount) brought about the low field shift of H_a, H_b, and methyl signals by 0.52, 0.45, and 0.56 ppm, respectively. The ASIS and Eu(thd)$_3$-induced shift for **4b** were similar to those described above. Meanwhile, H_a of **4b'** remote from the coordinated benzene showed a negligibly small ASIS (0.03 ppm low field shift), whereas H_b moved to a high field by 0.59 ppm. The above methods were also used for the determination of the stereochemistry of the other 1,3-dipolar cycloadducts described below.

The reaction of **1** with an equimolar amount of diazomethane at 0 °C produced the single adduct **4c**[11] in 93% yield (Scheme 3). In the ^{1}H NMR of **4c**, H_a appeared as a d/d (J = 9.5/8.0 Hz) due to the coupling with the methylene protons in agreement with the assigned regiochemistry. Incidentally, diphenyldiazomethane, trimethylsilyl azide, and phenyl azide failed to react with **1**.



SCHEME 3 1,3-Diploar cycloaddition of **1** with diazomethane.

Benzonitrile *N*-phenylimide (**6**), generated from **5**,[18] added to **1** to furnish **4d**[11] in about 50% yield (Scheme 4).[19] The structure of **4d** was determined by X-ray diffraction analysis (Figure 2).[20] Interestingly, methyl protons and methyl carbons of the*tert*-butyl group attached to the sp^3 carbon appeared as a broad singlet both in the ^1H and ^{13}C NMR spectra, probably because of the restricted rotation.

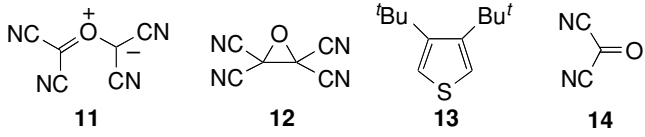


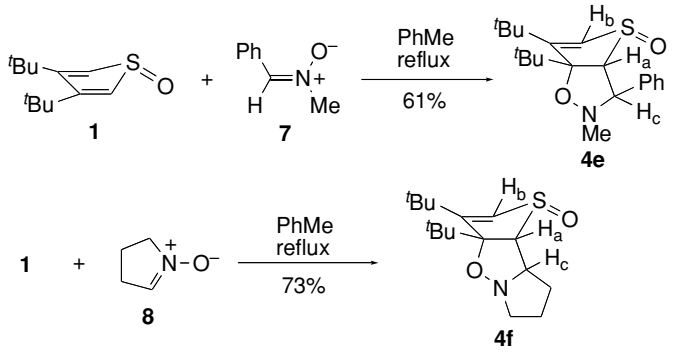
SCHEME 4 1,3-Diploar cycloaddition of **1** with nitirile imine **6**.

Next, reactions with allyl type 1,3-dipoles were investigated. Heating equimolar amounts of **1** and nitrone **7** in refluxing toluene provided the sole adduct **4e**[11] in 61% yield (Scheme 5). Similarly, the reaction with nitrone **8** gave the adduct **4f**[11] in 73% yield.

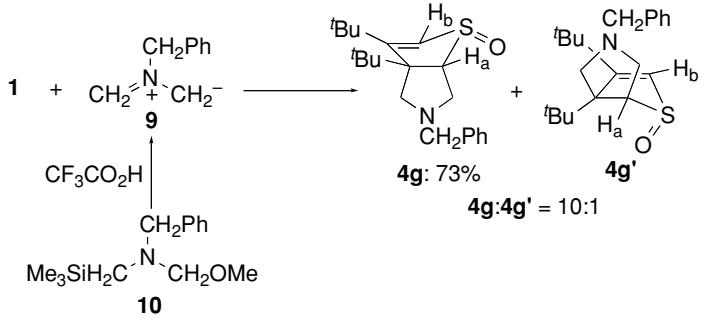
The reaction of **1** with azomethine ylide **9**,[21] generated from three molar amounts of amine **10**, gave a 10:1 diastereomeric mixture of **4g** and **4g′**[11] in good combined yield; only **4g** was isolated in pure form in 73% yield (Scheme 6).

For the attempted reaction with carbonyl ylide **11**, its precursor tetracyanoethylene oxide **12** reduced **1** to give thiophene **13** and carbonyl cyanide**14**, as was reported by us.[22] The reaction with ozone proceeded smoothly, but gave a complex mixture after treatment with Zn in acetic acid, from which a crystalline product, the structure of which could not be determined unambiguously, was isolated in low yield.





SCHEME 5 1,3-Diploar cycloaddition of **1** with nitrones **7** and **8**.



SCHEME 6 1,3-Diploar cycloaddition of **1** with azomethine imide **9**.

A Mulliken population analysis (B3LYP/6-31G* level[23]) of **1** predicted that the positive charges are located at the 3- and 4-positions, while the negative charges are located at the 2- and 5-positions (Figure 3). Thus, the observed regioselectivity is in agreement with the electronic demand, where the positive end of 1,3-dipoles adds to the 2-position, and the negative end adds to the 3-position. The observed regioselectivity is also in harmony with the steric demand that is brought about by bulky *tert*-butyl group. Only in the case of diazomethane, the steric demand governs the regiochemistry, where the less bulky negative end (diazo nitrogen) added to the congested 3-position, while the bulkier negative end (CH_2) added to the less congested 2-position.

As described above, the 1,3-dipolar cycloadditions of **1** took place preferentially at the *syn*-π-face to the S=O bond. This would best be explained as follows. The 1-oxide **1** has a bent structure at C_1 and C_4 with a tilt angle of 9.3° (Figure 4). Thus, for the *syn*-π-face addition, the transition state can be easily reached with a smaller conformational

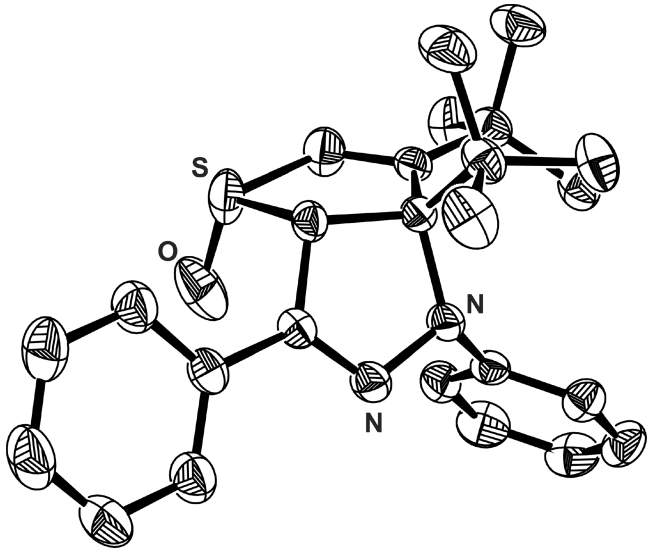


FIGURE 2 ORTEP plot of molecular structure of **4d** in the crystal. Ellipsoids are drawn at 50% probability level.

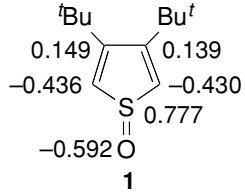


FIGURE 3 Mulliken population analysis of **1** (B3LYP/6-31G* level).

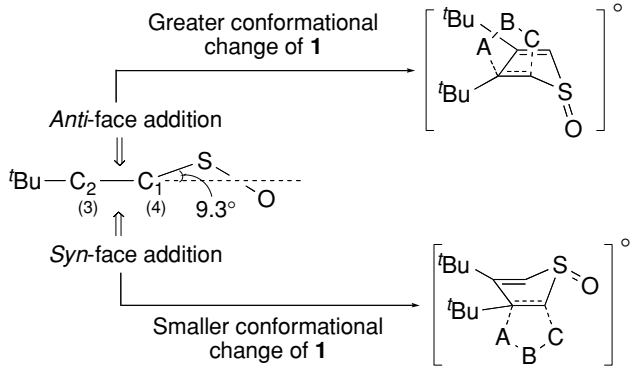


FIGURE 4 Conformational changes required at the transition states.

change of **1**, whereas, for the *anti*-face addition, a larger conformational change is required to reach the transition state, where the inversion at C_1 and C_4 is required.[2–4] Accordingly, the activation energy of the reaction would be smaller for the *syn*-π-face addition than for the *anti*-π-face addition, thus making the former process more favorable.

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[11] Supporting information of cycloadducts **4a**–**4g** (satisfactory elemental analyses were obtained except **4d** whose analysis sample could not be supplied[19]). **4a**: colorless crystals; mp 193–194°C; IR (KBr) ν 1048 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ1.05 (s, 9H), 1.35 (s, 9H), 2.18 (d, 3H, $J = 1.1$ Hz), 4.86 (d, 1H, $J = 1.1$ Hz, H_a), 6.61 (s, 1H, H_b); ^1H NMR (C_6D_6) δ1.74 (s, 9H), 1.11 (s, 9H), 2.14 (d, 3H, $J = 1.5$ Hz), 4.26 (d, 1H, $J = 1.5$ Hz, H_a), 6.18 (s, 1H, H_b); ^1H NMR ($CDCl_3$/0.2 mol eq. Eu(thd)$_3$) δ1.19 (s, 9H), 1.47 (s, 9H), 2.73 (broad s, 3H), 5.38 (broad s, 1H, H_a), 7.06 (broad s, 1H, H_b); ^{13}C NMR ($CDCl_3$) δ 13.9, 27.9, 32.6, 36.1, 36.6, 74.9, 108.4, 134.4, 153.2, 163.1. **4b**: colorless crystals; mp 167–168 °C; IR (KBr) ν 1048 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.14 (s, 9H), 1.41 (s, 9H), 5.54 (s, 1H, H_a), 6.61 (s, 1H, H_b), 7.35–7.40 (m, 3H), 7.68–7.75 (m, 2H); ^1H NMR (C_6D_6) δ 0.80 (s, 9H), 1.12 (s, 9H), 5.14 (s, 1H, H_a), 6.14 (s, 1H, H_b), 7.02–7.12 (m, 3H), 7.80 (d, 2H, $J = 1.1$); ^1H NMR ($CDCl_3$/0.2 mol eq. Eu(thd)$_3$) δ 1.29 (s, 9H), 1.53 (s, 9H), 6.04 (broad s, 1H, H_a), 7.10 (broad s, 1H, H_b), 7.32–7.35 (m, 3H), 8.32 (br, 2H); ^{13}C NMR ($CDCl_3$) δ 27.6, 32.5, 36.2, 37.6, 73.4, 111.0, 127.1, 128.3, 128.7, 130.0, 134.4, 153.0, 163.5. **4b′**: colorless crystals; mp 169–170°C; IR (KBr) ν 1039 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 1.41 (s, 9H), 4.80 (s, 1H, H_a), 6.63 (s, 1H, H_b), 7.44–7.50 (m, 3H), 7.79–7.86 (m, 2H); ^1H NMR (C_6D_6) δ 1.06 (s, 9H), 1.08 (s, 9H), 4.83 (s, 1H, H_a), 6.04 (s, 1H, H_b), 7.01–7.04 (m, 3H), 7.90–7.93 (m, 2H); ^1H NMR ($CDCl_3$/0.2 mol eq. Eu(thd)$_3$) δ 1.39 (s, 9H), 1.46 (s, 9H), 5.25 (s, 1H, H_a), 6.81 (s, 1H, H_b), 7.43–7.47 (m, 3H), 7.90–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 27.2, 32.5, 36.7, 37.3, 79.8, 111.0, 126.9, 127.8, 129.1, 130.3, 130.7, 151.8, 166.8. **4c**: colorless crystals; mp 153–154 °C; IR (KBr) ν 1031 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.12 (s, 9H), 1.34 (s, 9H), 3.83 (dd, 1H, $J = 8.0$, 9.5 Hz,

H_a), 4.78 (dd, 1H, $J = 8.0$, 18.7 Hz), 4.81 (dd, 1H, $J = 9.5$, 18.7 Hz), 6.35 (s, 1H, H_b); ^{1}H NMR (C_6D_6) δ 0.74 (s, 9H), 1.03 (s, 9H), 2.99 (dd, 1H, $J = 8.3$, 9.8 Hz, H_a), 4.43 (dd, 1H, $J = 9.8$, 19.0 Hz), 4.93 (dd, 1H, $J = 8.1$, 18.8 Hz), 5.87 (s, 1H, H_b); ^{1}H NMR ($CDCl_3$/0.2 mol eq. Eu(thd)$_3$) δ 1.16 (s, 9H), 1.49 (s, 9H), 4.35 (t, 1H, $J = 9.0$ Hz, H_a), 5.30 (dd, 1H, $J = 9.5$, 18.8 Hz), 5.92 (br, 1H), 6.98 (broad s, 1H, H_b); ^{13}C NMR ($CDCl_3$) δ 28.4, 33.4, 36.4, 37.6, 60.1, 74.1, 119.4, 134.7, 161.7. **4d**: colorless crystals; ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 9H), 1.25 (broad s, 9H), 4.87 (s, 1H, H_a), 6.84 (s, 1H, H_b), 7.28–7.31 (m, 4H), 7.33–7.38 (m, 2H), 7.59–7.61 (m, 2H, $J = 7.6$ Hz), 7.80–7.82 (m, 2H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 28.1 (broad s), 33.7, 37.2, 40.1, 74.6, 97.0, 125.7, 128.2, 128.66, 128.72, 128.9, 131.2, 131.8, 135.4, 143.5, 146.9, 168.6. **4e**: colorless crystals; mp 127–128 °C; IR (KBr) ν 1038 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$): δ 1.09 (s, 9H), 1.40 (s, 9H), 2.61 (s, 3H), 4.33 (d, 1H, $J = 7.6$ Hz, H_c), 4.61 (d, 1H, $J = 7.6$ Hz, H_a), 6.41 (s, 1H, H_b), 7.20–7.37 (m, 3H), 7.42–7.48 (m, 2H);^{1}H NMR (C_6D_6) δ 0.87 (s, 9H), 1.20 (s, 9H), 2.46 (s, 3H), 4.35 (d, 1H, $J = 8.3$ Hz, H_a), 4.57 (d, 1H, $J = 8.8$ Hz, H_c), 6.04 (s, 1H, H_b), 7.07–7.22 (m, 3H), 7.67 (d, 2H, $J = 6.8$ Hz); ^{1}H NMR ($CDCl_3$, 0.2 mol eq. Eu(fod)$_3$, fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) δ 1.27 (s, 9H), 1.55 (s, 9H), 2.91 (s, 3H), 4.34 (broad s, 1H, H_c), 5.37 (m, 1H, H_a), 7.02 (broad s, 1H, H_b), 7.32–7.46 (m, 3H), 8.27 (broad s, 2H);^{13}C NMR ($CDCl_3$) δ 28.0, 33.1, 35.9, 37.7, 43.1, 70.8, 78.0, 104.0, 128.0, 128.5, 128.7, 132.8, 137.1, 165.1. **4f**: colorless crystals; mp 193.5–194.5 °C; IR (KBr) ν 1040 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9H), 1.34 (s, 9H), 1.68–1.83 (m, 2H), 1.95–2.14 (m, 2H), 2.77–2.89 (m, 1H, $J = 13.6$ Hz), 3.38–3.48 (m, 1H, $J = 13.6$ Hz), 4.04 (d, 1H, $J = 3.3$ Hz, H_a), 4.18–4.26 (m, 1H, $J = 4.2$ Hz, H_c), 6.39 (s, 1H, H_b); ^{1}H NMR (C_6D_6) δ 0.79 (s, 9H), 1.26 (s, 9H), 1.52–1.84 (m, 4H), 2.39–2.54 (m, 1H, $J = 13.6$ Hz), 3.15–3.25 (m, 1H, $J = 13.6$ Hz), 3.60 (d, 1H,$J = 3.4$ Hz, H_a), 4.45–4.54 (m, 1H, $J = 4.2$ Hz, H_c), 6.14 (s, 1H, H_b); ^{1}H NMR ($CDCl_3$/0.2 mol eq. Eu(thd)$_3$) δ 1.08 (s, 9H), 1.39 (s, 9H), 1.69–1.84 (m, 2H), 2.00–2.19 (m, 2H), 2.84–2.95 (m, 1H), 3.44–3.53 (m, 1H), 4.24 (broad s, 1H, H_a), 4.58–4.69 (m, 1H, H_c), 6.61 (s, 1H, H_b); ^{13}C NMR ($CDCl_3$) δ 25.0, 28.1, 32.3, 32.4, 35.90, 35.91, 57.0, 62.4, 78.4, 104.0, 133.5, 166.0. **4g**: colorless crystals; mp 128–129 °C; IR (KBr) ν 1044 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9H), 1.27 (s, 9H), 2.66 (d, 1H, $J = 9.9$ Hz), 2.84–3.03 (m, 3H), 3.61 (s, 2H), 4.12 (t, 1H, $J = 8.3$ Hz, H_a), 6.35 (s, 1H, H_b), 7.23–7.31 (m, 5H); ^{1}H NMR (C_6D_6) δ 0.71 (s, 9H), 0.96 (s, 9H), 2.50 (d, 1H, $J = 9.6$ Hz), 2.65–2.72 (m, 2H), 3.24–3.41 (m, 3H), 3.66 (t, 1H, $J = 8.1$ Hz, H_a), 6.07 (s, 1H, H_b), 7.23–7.31 (m, 5H); ^{1}H NMR ($CDCl_3$/0.2 mol eq. Eu(thd)$_3$) δ 1.09 (s, 9H), 1.36 (s, 9H), 2.84 (m, 1H), 3.07–3.20 (m, 3H), 3.71 (s, 2H), 4.43 (broad s, 1H, H_a), 6.70 (broad s, 1H, H_b), 7.23–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 29.1, 33.5, 36.0, 36.5, 51.7, 60.1, 61.0, 66.4, 76.0, 127.0, 128.2, 128.5, 133.1, 138.4, 166.1. **4g′**: ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 9H), 1.29 (s, 9H), 2.42 (dd, 1H, $J = 7.4$, 9.9 Hz), 2.53 (d, 1H, $J = 9.9$ Hz), 2.79 (d, 1H, $J = 9.9$ Hz), 3.11 (t, 1H, $J = 9.2$ Hz, H_a), 3.47–3.54 (m, 3H), 6.50 (s, 1H, H_b), 7.23–7.31 (m, 5H).

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[19] *Caution!* The precursor compound **5** caused a severe skin eruption. Therefore, the yield of **4d** was not optimized.
[20] Crystal data for **4d**: $C_{25}H_{30}N_2OS$, $M = 406.57$, orthorhombic, space group *Pbca*; $a = 16.6749(19)$, $b = 10.7803(6)$, $c = 24.0477(14)$ Å; $Z = 8$; $V = 4322.8(4)$ Å^3; Dc = 1.249

g/cm^3, $\mu = 0.168$ mm^{-1}; measured reflections 30101, independent reflections 5199 [R(int) = 0.0863], $R = 0.0788$, Rw = 0.1523, GOF = 1.091. Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 671816 for **4d**. Copies of this information can be obtained from The Director, DDCD, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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