Crystal structure determination of **2f**:

Crystal Data for $C_{26}H_{24}N_2O_4S$ (M =460.53 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 7.27000(10) Å, b = 11.16340(10) Å, c = 14.17310(10) Å, β = 96.9580(10)°, V = 1141.79(2) Å^3, Z = 2, T = 100.01(10) K, μ(CuKα) = 1.556 mm^{-1}, *Dcalc* = 1.340 g/cm^3, 21276 reflections measured (12.264° ≤ 2Θ ≤ 144.218°), 4388 unique (R_{int} = 0.0209, R_{sigma} = 0.0147) which were used in all calculations. The final R_1 was 0.0227 (I > 2σ(I)) and wR_2 was 0.0582 (all data). Flack = -0.004(6).

Crystal structure determination of **4a**:

Crystal Data for $C_{26}H_{26}N_2O$ (M =382.49 g/mol): triclinic, space group P-1 (no. 2), a = 9.9803(5) Å, b = 10.7055(5) Å, c = 11.0770(7) Å, α = 76.953(5)°, β = 64.440(6)°, γ = 72.474(4)°, V = 1011.80(11) Å^3, Z = 2, T = 100.01(10) K, μ(MoKα) = 0.076 mm^{-1}, *Dcalc* = 1.255 g/cm^3, 8126 reflections measured (7.212° ≤ 2Θ ≤ 53.462°), 4266 unique (R_{int} = 0.0201, R_{sigma} = 0.0362) which were used in all calculations. The final R_1 was 0.0451 (I > 2σ(I)) and wR_2 was 0.1063 (all data).

The datasets were measured on an Agilent SuperNova diffractometer using an Atlas detector. The data collections were driven and processed and absorption corrections were applied using CrysAlisPro.[S1] The structure of **2f** was solved using ShelXT[S2] and that of **4a** was solved using ShelXS[S3] and both structures were refined by a full-matrix least-squares procedure on F^2 in ShelXL.[S4] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures and reports were produced using OLEX2.[S5]

The structure of **2f** occupies a chiral space group and the absolute structure has been determined from the diffraction data, with the Flack parameter being -0.004 (6).

In **2f** the thiophene ring, C(7)-S(8)-C(9)-C(10)-C(11), (C(7')-S(8')-C(9')-C(10')-C(11')) is disordered over two positions at a refined percentage occupancy ratio of 63. 9(3) : 36.1 (3).

The structure of **4a** occupies a centrosymmetric space group. Thus in one molecule in the unit cell C(6) is *R* and C(9) is *S* while in the other molecule C(6) is *S* and C(9) is *R*. The relative stereochemistry is the same in all molecules.

The CIFs for the crystal structures of **2f** and **4a** have been deposited with the CCDC and have been given the deposition numbers: CCDC 1880502 and CCDC 1880503 respectively.

[S1] CrysAlisPro, Agilent Technologies, Version 1.171.36.28, **2013**.
[S2] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.
[S3] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
[S4] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.
[S5] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.