Asymmetric Organocatalytic Thio-Diels-Alder Reactions via Trienamine Catalysis

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1. GENERAL METHODS

NMR spectra were acquired on a Varian AS 400 spectrometer, running at 400 MHz for ^1H and 100 MHz for ^{13}C , respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals (CHCl_3 , 7.26 ppm for ^1H NMR, CDCl_3 , 77.0 ppm for ^{13}C NMR). The following abbreviations are used to indicate the multiplicity in NMR spectra: s, singlet; d, doublet; t, triplet; q, quartet; hept, heptet; m, multiplet; br, broad resonance. ^{13}C NMR spectra were acquired on a broad band decoupled mode. For characterization of diastereomeric mixtures, *denotes minor diastereoisomer, +denotes overlap of signals from both diastereoisomers, while the major diastereomer is characterized without further denotations. The number of protons/carbons given in the parenthesis is the sum over both diastereomers. For compounds with diastereomeric ratios above 6:1, only the major diastereomer is characterized. Mass spectra were recorded on a Bruker MicroTOF-Q High-Performance LC-MS system. Analytical thin layer chromatography (TLC) was performed using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation, KMnO_4 or *p*-anisaldehyde dip. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The enantiomeric excess (ee) of the products was either determined by: *i*) Ultrapformance Convergence Chromatography (UPC²) using Daicel Chiralpak IA-3, IB-3, IC-3 and ID-3 columns as chiral stationary phases; or by *ii*) chiral stationary phase HPLC on a Daicel Chiralpak IC-5 column. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (SiO_2 60, 230-400 mesh, Fluka) was used. Racemic samples were prepared using a mixture of enantiomers of **3** (20 mol%) in combination with benzoic acid (20 mol%) in CHCl_3 .

2. STARTING MATERIALS

Dienals **1a-d,f** were prepared from the corresponding alkenyl bromides according to the procedure reported by Fabrizi *et al.*¹ Aldehyde **1e,h**² and dithioester **2b**³ were prepared following literature procedures.

General procedure for the preparation of dithioesters **2a,c-f**

To a stirred solution of sulphur (30 mmol, 3 equiv.) and Et₃N (30 mmol, 3 equiv.) in 15 mL MeCN was added halogen compound (10 mmol, 1 equiv.). After 3 h of stirring at rt, the alkyl iodide (30 mmol, 3 equiv.) was added and the mixture was allowed to stir for an additional 15 h. The formed salts were then removed by filtration and the collected solids were washed with small amounts of MeCN. The organic solution were diluted with water and extracted three times with CH₂Cl₂. The combined organic layers were washed with a saturated solution of NaHCO₃ and 0.5 M Na₂S₂O₃ and dried over Na₂SO₄. After filtration of the solids and removal of excess solvents, the crude product was subjected to purification by FC on silica gel to afford the pure dithioesters.

¹ (a) Battistuzzi, G.; Cacchi, S.; Fabrizi, G. *Org. Lett.* **2003**, *5*, 777. All spectroscopic data matched those previously reported: (b) Jia, Z.-J.; Zhou, Q.; Zhou, Q.-Q.; Chen, P.-Q.; Chen, Y.-C. *Angew. Chem. Int. Ed.* **2011**, *50*, 8638.

² For **1e**, see (a) Liu, Y.-K.; Nappi, M.; Arceo, E.; Vera, S.; Melchiorre, P. *J. Am. Chem. Soc.* **2011**, *133*, 15212. For **1h**, see (b) Halskov, K. S.; Johansen, T. K.; Davis, R. L.; Steurer, M.; Jensen, F.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2012**, *134*, 12943.

³ Thiel, W.; Mayer, R. *J. Prakt. Chem.* **1989**, *331*, 243.

¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 7.6, 1.2 Hz, 2H), 7.61 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.46 (app t, *J* = 7.6 Hz, 2H), 3.45 (q, *J* = 7.5 Hz, 2H), 1.45 (t, *J* = 7.5 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃):** δ 230.7, 190.4, 134.1, 132.5, 130.2 (2C), 128.4 (2C), 29.4, 12.1. **HRMS (ESI+) *m/z* calcd.** for C₁₀H₁₀S₂O [M+Na]⁺: 233.0065; found: 333.0066.

3. PROCEDURES AND PRODUCTS

General Procedure A (the linear trienamine pathway)

A mixture of the aldehyde **1** (0.1 mmol, 1 equiv), PhCO₂H (0.02 mmol, 0.2 equiv) and catalyst **3** in the given amounts (see the specific substrates in the manuscript) was dissolved in 0.5 mL of CHCl₃ and brought to the appropriate temperature. Then, the dithioester was added (0.12 mmol, 1.2 equiv) and the mixture was stirred for the time indicated. When the reaction was completed, the mixture was directly purified by FC on silica gel to afford the corresponding cycloadduct.

General procedure B (reduction/NIS-mediated cyclization sequence)

To a solution of the aldehyde (0.35 mmol, 1 equiv) in MeOH (3 mL) was added NaBH₄ (0.52 mmol, 1.5 equiv) at 0 °C. After stirring for 5 min the reaction was allowed to reach rt and stirred for further 10 min. A saturated solution of aq. NH₄Cl was then added and the resulting solution was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo*. The crude alcohol intermediate was re-dissolved in CHCl₃ (1.5 mL) and NIS (0.42 mmol, 1.2 equiv) was added in one portion. Once the reaction was complete (30 min), the mixture was directly purified by FC on silica gel to afford the pure products.

Following the general procedure A (5 mol% **3**, 4 °C, 72 h), cycloadduct **4a** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 87% yield and 94:6 dr as a pale yellow oil. $[\alpha]_D^{20} = -207.9$ (c 0.3, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.60 (t, *J* = 1.6 Hz, 1H), 7.40–7.32 (m, 5H), 5.54 (d, *J* = 6.1 Hz, 1H), 5.25 (d, *J* = 12.1 Hz, 1H), 5.19 (d, *J* = 12.1 Hz, 1H), 3.30 (d, *J* = 17.9 Hz, 1H), 3.23–3.16 (m, 1H), 2.76–2.68 (m, 2H), 2.66 (dq, *J* = 11.8, 7.4 Hz, 1H), 2.46 (dq, *J* = 11.8, 7.4 Hz, 1H), 2.33 (dd, *J* = 17.5, 3.4 Hz, 1H), 1.72 (s, 3H), 1.15 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 199.7, 170.0, 134.9, 130.5, 128.6 (3C), 128.6 (2C), 122.6, 67.7, 62.7, 48.9, 36.9, 29.4, 25.1, 23.8, 13.6. HRMS (ESI+) *m/z* calcd. for C₁₈H₂₂S₂O₃ [M+Na]⁺: 373.0903; found: 373.0907. UPC²: IC-3, CO₂/MeCN 80:20, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 4.7 min; *t*_{minor} = 7.7 min (92% ee).

Following the general procedure A (5 mol% **3**, rt, 48 h), cycloadduct **4b** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 95% yield and 91:9 dr as a pale yellow oil. $[\alpha]_D^{20} = -214.9$ (c 0.8, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.60 (t, *J* = 2.3 Hz, 1H), 7.41–7.31 (m, 5H), 5.20 (d, *J* = 12.1 Hz, 1H), 5.13 (d, *J* = 12.1 Hz, 1H), 3.35 (d, *J* = 17.6 Hz, 1H), 3.10 (t, *J* = 4.2 Hz, 1H), 2.76 (d, *J* = 16.6 Hz, 1H), 2.63 (dq, *J* = 12.5 Hz, 7.6 Hz, 1H), 2.56 (ddd, *J* = 17.6, 5.0, 2.4 Hz, 1H), 2.45–2.37 (m, 2H), 1.70 (s, 6H), 1.12 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 200.1, 169.9, 134.9, 128.7 (2C), 128.6, 128.6 (2C), 126.7, 123.1, 67.8, 64.2, 48.2, 42.2, 30.5, 25.2, 19.8, 19.3, 13.6. HRMS (ESI+) *m/z* calcd. for C₁₉H₂₄S₂O₃ [M+Na]⁺: 387.1059; found: 387.1063. UPC²: IC-3, first CO₂/iPrOH

99:1 (0.5 min), then linear gradient (10%/min) from 99:1 to 60:40 CO₂/*i*PrOH, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 4.0 min; *t*_{minor} = 5.3 min (93% ee).

Following the general procedure A (10 mol% **3**, rt, 48 h), cycloadduct **4c** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 82% yield and 90:10 dr as a pale yellow oil. $[\alpha]_D^{20} = -219.1$ (c 0.4, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.60 (t, *J* = 2.1 Hz, 1H), 7.41–7.31 (m, 5H), 5.53–5.52 (m, 1H), 5.20 (d, *J* = 12.1 Hz, 1H), 5.14 (d, *J* = 12.1 Hz, 1H), 3.40 (ddd, *J* = 17.4, 4.4, 2.4 Hz, 1H), 3.14–3.12 (m, 1H), 2.96–2.90 (m, 1H), 2.68–2.60 (m, 1H), 2.55 (ddd, *J* = 17.4, 4.4, 2.4 Hz, 1H), 2.50–2.39 (m, 2H), 1.74 (s, 3H), 1.13 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 199.7, 169.8, 134.8, 134.7, 128.7 (2C), 128.6, 128.6 (2C), 117.6, 67.8, 64.2, 48.2, 40.3, 25.6, 25.3, 23.6, 13.5. HRMS (ESI+) *m/z* calcd. for C₁₈H₂₂S₂O₃ [M+Na]⁺: 373.0903; found: 373.0907. UPC²: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar, *t*_{major} = 5.4 min; *t*_{minor} = 10.1 min (93% ee).

Following the general procedure A (10 mol% **3**, rt, 48 h), cycloadduct **4d** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 78% yield and >95:5 dr as a pale yellow oil. $[\alpha]_D^{20} = -191.0$ (c 0.8, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.59 (s, 1H), 7.41–7.19 (m, 10H), 6.09 (d, *J* = 6.1 Hz, 1H), 5.24 (d, *J* = 12.0 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 3.70 (dt, *J* = 17.1, 2.1 Hz, 1H), 3.38 (ddd, *J* = 11.2, 5.6, 3.1 Hz, 1H), 3.26 (d, *J* = 17.1 Hz, 1H), 2.79 (ddd, *J* = 17.8, 8.9, 1.5 Hz, 1H), 2.65 (dq, *J* = 11.9, 7.6 Hz, 1H), 2.52–2.44 (m, 1H), 2.40 (dd, *J* = 17.8, 3.3 Hz, 1H), 1.11 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 199.3, 169.9, 140.7, 134.9, 133.8, 128.7 (3C), 128.6 (2C), 128.4 (2C), 127.7, 125.7 (2C), 125.6, 67.8, 62.5, 48.9, 37.3, 27.9, 25.2, 13.6. HRMS (ESI+) *m/z* calcd. for C₂₃H₂₄S₂O₃ [M+Na]⁺: 435.1059; found: 435.1061. UPC²: IC-3, CO₂/MeCN 80:20, 3.0 mL·min⁻¹, 40 °C, 120 bar, *t*_{major} = 2.6 min; *t*_{minor} = 8.5 min (85% ee).

Following the general procedure A (20 mol% **3**, 40 °C, 48 h), cycloadduct **4e** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 84% yield and 80:20 dr as a pale yellow oil. $[\alpha]_D^{20} = -187.9$ (c 1.3, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.88* (t, *J* = 1.4 Hz, 1H*), 9.62 (t, *J* = 2.0 Hz, 1H), 8.08* (t, *J* = 7.5 Hz, 1H, 1H*), 7.52–7.00* (m, 8H, 8H*), 5.29 (d, *J* = 12.0 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.12* (d, *J* = 12.0 Hz, 1H), 4.95* (d, *J* = 12.0 Hz, 1H), 4.67–4.61* (m, 1H*), 4.27 (t, *J* = 5.0 Hz, 1H), 4.18 (s, 2H), 4.14* (d, *J* = 17.6 Hz, 1H*), 3.95* (d, *J* = 17.6 Hz, 1H), 3.37* (ddd, *J* = 17.9, 6.7, 1.5 Hz, 1H*), 2.87–2.66* (m, 3H, 2H*), 2.63–2.55* (m, 1H*), 2.46 (dq, *J* = 11.7, 7.4 Hz, 1H), 1.69 (s, 9H), 1.65* (s, 9H*), 1.18* (t, *J* = 7.5 Hz, 3H*), 1.09 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 200.0*, 199.4, 169.6, 168.4*, 150.4, 150.0*, 135.4, 135.4*, 134.9*, 134.7, 129.6* (1C,1C*), 128.8 (2C), 128.7, 128.6 (2C), 128.1–128.0* (m, 1C,6C*), 124.9*, 124.6, 123.0*, 123.0, 118.0* (1C,1C*), 117.8*, 117.7, 115.7, 115.7*, 84.5, 84.4*, 68.1, 67.9*, 64.0* (1C,1C*), 49.2, 47.8*, 35.5, 34.7*, 28.3 (3C), 28.2* (3C*), 25.7* (1C,1C*), 25.5, 24.7*, 13.8*, 13.4. HRMS (ESI+) *m/z* calcd. for C₂₈H₃₁S₂O₅ [M+Na]⁺: 548.1536; found: 548.1543. UPC²: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar; major diastereomer: *t*_{major} = 12.4 min; *t*_{minor} = 14.3 min (92% ee).

Following the general procedure A (5 mol% **3**, rt, 48 h), cycloadduct **4f** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 84% yield and 86:14 dr as a pale yellow oil. $[\alpha]_D^{20} = -247.2$ (c 1.2, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.63 (s, 1H), 7.43–7.28 (m, 5H), 5.54 (d, *J* = 6.6 Hz, 1H), 5.24 (d, *J* = 12.1 Hz, 1H), 5.17 (d, *J* = 12.1 Hz, 1H), 3.44–3.35 (m, 1H), 3.26–3.17 (m, 1H), 2.82–2.63 (m, 2H), 2.54–2.41 (m, 1H), 2.35 (dd, *J* = 17.4, 3.4 Hz, 1H), 2.27–2.18 (m, 1H), 2.10–1.93 (m, 2H), 1.87–1.67 (m, 2H), 1.48–1.20 (m, 3H), 1.14 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 199.9, 169.8, 137.8, 135.0, 128.6 (3C), 128.6 (2C), 120.5, 67.6, 63.3, 49.4, 40.5, 37.1, 35.5, 32.3, 27.1, 26.0, 25.2, 13.5. HRMS (ESI+) *m/z* calcd. for C₂₁H₂₆S₂O₃ [M+Na]⁺: 413.1216; found: 413.1218. UPC² IC-3, first CO₂/iPrOH 99:1 (0.5 min), then linear gradient (10%/min) from 99:1 to 60:40 CO₂/iPrOH, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 4.1 min; *t*_{minor} = 4.3 min (90% ee).

Following the general procedure A (10 mol% **3**, 40 °C, 48 h), cycloadduct **4g** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 82% yield and 90:10 dr as a pale yellow oil. $[\alpha]_D^{20} = -198.7$ (c 0.4, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.61 (t, *J* = 1.4 Hz, 1H), 7.44–7.30 (m, 5H), 5.90–5.83 (m, 1H), 5.81–5.73 (m, 1H), 5.26 (d, *J* = 12.1 Hz, 1H), 5.20 (d, *J* = 12.1 Hz, 1H), 3.41 (dq, *J* = 17.6, 2.3 Hz, 1H), 3.26–3.19 (m, 1H), 2.93 (ddd, *J* = 17.6, 5.1, 1.3 Hz, 1H), 2.75 (ddd, *J* = 17.6, 8.9, 1.7 Hz, 1H), 2.71–2.62 (m, 1H), 2.48 (dq, *J* = 11.8, 7.4 Hz, 1H), 2.38 (ddd, *J* = 17.6, 3.5, 1.1 Hz, 1H), 1.15 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 199.3, 169.9, 134.9, 128.7, 128.6 (2C), 128.6 (2C), 128.2, 123.2, 67.7, 62.6, 48.8, 36.2, 25.8, 25.1, 13.6. HRMS (ESI+) *m/z* calcd. for C₁₇H₂₀S₂O₃ [M+Na]⁺: 359.0746; found: 359.0746. UPC²: IC-3, first CO₂/iPrOH 99:1 (0.5 min), then linear gradient (10%/min) from 99:1 to 60:40 CO₂/iPrOH, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 3.6 min; *t*_{minor} = 3.8 min (91% ee).

Following the general procedure A (20 mol% **3**, 40 °C, 48 h), cycloadduct **4h** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 62% yield and 85:8:7 dr as a pale yellow oil. $[\alpha]_D^{20} = -127.7$ (c 0.3, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.60 (s, 1H), 7.48–7.28 (m, 5H), 5.85 (ddd, *J* = 10.7, 6.0, 2.3 Hz, 1H), 5.66 (d, *J* = 10.7 Hz, 1H), 5.26 (d, *J* = 12.1 Hz, 1H), 5.19 (d, *J* = 12.1 Hz, 1H), 3.60–3.47 (m, 1H), 3.26–3.14 (m, 1H), 2.78–2.61 (m, 2H), 2.55–2.42 (m, 1H), 2.36 (dd, *J* = 17.6, 3.2 Hz, 1H), 1.75–1.61 (m, 2H), 1.14 (t, *J* = 7.5 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 199.4, 169.9, 134.9, 128.7 (2C), 128.6 (2C), 128.6 (2C), 127.6, 67.7, 63.8, 49.2, 41.2, 36.3, 26.5, 25.3, 13.5, 11.2. HRMS (ESI+) *m/z* calcd. for C₁₉H₂₄S₂O₃ [M+Na]⁺: 387.1059; found: 387.1060. UPC²: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 2.9 min; *t*_{minor} = 4.9 min (85% ee).

Following the general procedure A (20 mol% **3**, rt, 24 h), cycloadduct **4i** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 73% yield and 92:8 dr as a pale yellow oil. $[\alpha]_D^{20} = -163.4$ (c 0.6, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.62 (t, *J* = 1.4 Hz, 1H), 7.45–7.30 (m, 5H), 5.56 (d, *J* = 4.4 Hz, 1H), 5.25 (d, *J* = 12.1 Hz, 1H), 5.19 (d, *J* = 12.1 Hz, 1H), 3.29 (d, *J* = 17.1 Hz, 1H), 3.25–3.18 (m, 1H), 2.79–2.69 (m, 2H), 2.36 (ddd, *J* = 17.5, 3.4, 0.9 Hz, 1H), 2.04 (s, 3H), 1.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 199.7, 169.5, 135.0, 130.6, 128.6, 128.6 (2C), 128.6 (2C), 122.5, 67.7, 62.7, 49.1, 36.6, 29.2, 23.8, 13.9. HRMS (ESI+) *m/z* calcd. for C₁₇H₂₀S₂O₃ [M+Na]⁺: 359.0746; found: 359.0752. UPC²: IC-3, CO₂/MeCN 90:10, 2.5 mL·min⁻¹; 55 °C, 120 bar, *t*_{major} = 5.9 min; *t*_{minor} = 7.7 min (84% ee).

Following the general procedure A (20 mol% **3**, rt, 24 h), cycloadduct **4j** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 73% yield and 90:10 dr as a pale yellow oil.

$[\alpha]_D^{20} = -179.4$ (c 0.6, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.59 (t, *J* = 1.4 Hz, 1H), 7.40–7.31 (m, 5H), 7.29–7.17 (m, 5H), 5.52 (d, *J* = 4.3 Hz, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 3.86 (d, *J* = 12.4 Hz, 1H), 3.65 (d, *J* = 12.4 Hz, 1H), 3.34 (d, *J* = 17.1

Hz, 1H), 3.25–3.16 (m, 1H), 2.82–2.67 (m, 2H), 2.33 (ddd, *J* = 17.4, 3.5, 1.0 Hz, 1H), 1.72 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 199.6, 169.6, 136.5, 134.9, 130.5, 129.3 (2C), 128.7 (2C), 128.7, 128.6 (2C), 128.4 (2C), 127.1, 122.5, 67.7, 63.2, 48.9, 36.8, 35.7, 29.4, 23.8. HRMS (ESI+) *m/z* calcd. for C₂₃H₂₄S₂O₃ [M+Na]⁺: 435.1059; found: 435.1065. UPC²: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 9.4 min; *t*_{minor} = 12.8 min (87% ee).

Following the general procedure A (20 mol% **3**, rt, 24 h), cycloadduct **4k** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 96% yield and 97:3 dr as a white solid.

$[\alpha]_D^{20} = -278.6$ (c 0.7, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.78 (dd, *J* = 1.9, 1.3 Hz, 1H), 5.56 (d, *J* = 6.1 Hz, 1H), 5.07 (hept, *J* = 6.3 Hz, 1H), 3.31 (d, *J* = 17.1 Hz, 1H), 3.22–3.14 (m, 1H), 2.84–2.48 (m, 5H), 1.74 (s, 3H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.23

(t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ ppm 200.0, 169.6, 130.6, 122.7, 70.3, 62.7, 48.9, 36.9, 29.5, 25.1, 23.8, 21.6, 21.5, 13.8. HRMS (ESI+) *m/z* calcd. for C₁₄H₂₂S₂O₃ [M+Na]⁺: 325.0903; found: 325.0905. UPC²: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 2.4 min; *t*_{minor} = 3.7 min (94% ee).

Following the general procedure A (20 mol% **3**, rt, 48 h), cycloadduct **4l** was obtained after FC on silica gel (pentane/EtOAc 9:1 to 4:1) in 62% yield and 65:35 dr as a pale yellow oil.

$[\alpha]_D^{20} = -8.0$ (c 1.5, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.86* (s, 1H*), 9.50 (s, 1H), 8.31 (d, *J* = 7.4 Hz, 2H), 8.14* (d, *J* = 8.0 Hz, 2H*), 7.56–7.33* (m, 3H, 3H*), 5.61 (d, *J* = 6.2

Hz, 1H), 5.50* (d, *J* = 6.5 Hz, 1H*), 3.67–3.59* (m, 1H*), 3.55–3.45 (m, 1H), 3.38 (d, *J* = 17.6 Hz, 1H), 3.24* (dd, *J* = 17.5, 5.1 Hz, 1H*), 3.08* (d, *J* = 17.5 Hz, 1H*), 2.86–2.41* (m, 4H, 4H), 2.25 (dd, *J* = 17.6, 3.0 Hz, 1H), 1.77 (s, 3H), 1.62* (s, 3H*), 1.16 (t, *J* = 7.4 Hz, 3H), 1.14* (t, *J* = 7.2 Hz, 3H*). ¹³C NMR (100 MHz, CDCl₃): δ ppm 200.3*, 199.4, 195.3, 194.9*, 136.5*, 135.1, 133.1, 131.8*, 131.4, 131.2*, 129.7(2C), 129.4*(2C*), 128.4(2C), 127.7*(2C*), 125.4*, 122.6, 69.1, 63.4*, 48.6, 47.7*, 37.5, 35.4*, 31.4*, 29.5, 25.1, 24.2*, 23.9*, 23.8, 13.7, 13.6*. HRMS (ESI+) *m/z* calcd. for C₁₇H₂₀S₂O₂ [M+Na]⁺: 343.0797; found: 343.0800. UPC²: IC-3, CO₂/MeCN 70:30, 3.0 mL·min⁻¹; major diastereomer: *t*_{major} = 1.3 min; *t*_{minor} = 1.5 min (6% ee); minor diastereomer: *t*_{major} = 1.0 min; *t*_{minor} = 1.6 min (53% ee).

Following the general procedure A (20 mol% **3**, rt, 24 h), cycloadduct **4m** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 78% yield and 92:8 dr as a pale yellow oil.

$[\alpha]_D^{20} = -240.5$ (c 0.5, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃): δ ppm 9.77 (t, *J* = 2.2 Hz, 1H), 5.05 (hept, *J* = 6.3 Hz, 1H), 3.36 (d, *J* = 17.0 Hz, 1H), 3.10 (t, *J* = 4.5 Hz, 1H), 2.81–2.42 (m, 5H), 1.71 (s, 6H), 1.29 (d, *J* = 6.3 Hz, 3H), 1.27 (d, *J* = 6.4 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ ppm 200.4, 169.6, 126.8, 123.0, 70.5, 64.2, 48.3, 42.1, 30.6, 25.2, 21.5 (2C), 19.8, 19.3, 13.8. HRMS (ESI+) *m/z* calcd. for C₁₅H₂₄S₂O₃ [M+Na]⁺: 339.1059; found: 339.1065. UPC²: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar, *t*_{major} = 2.4 min; *t*_{minor} = 7.4 min (97% ee).

Following the general procedure A (20 mol% **3**, rt, 24 h), cycloadduct **4n** was obtained after FC on silica gel (pentane/EtOAc 9:1 to 4:1) in 76% yield and 90:10 dr as a pale yellow oil. $[\alpha]_D^{20} = -252.9$ (c 0.7, CH₂Cl₂). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 9.79 (t, *J* = 2.0 Hz, 1H), 5.56–5.50 (m, 1H), 5.06 (hept, *J* = 6.3 Hz, 1H), 3.45–3.36 (m, 1H), 3.15–3.10 (m, 1H), 2.93 (ddd, *J* = 17.4, 5.2, 1.5 Hz, 1H), 2.80–2.46 (m, 4H), 1.76 (s, 3H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 199.9, 169.5, 134.9, 117.6, 70.5, 64.2, 48.3, 40.2, 25.6, 25.3, 23.6, 21.5 (2C), 13.8. **HRMS (ESI+)** *m/z* calcd. for C₁₄H₂₂S₂O₃ [M+Na]⁺: 325.0903; found: 325.0905. **UPC²**: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 2.9 min; *t*_{minor} = 4.7 min (94% ee).

Following the general procedure A (10 mol% **3**, rt, 48 h), cycloadduct **4o** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 70% yield and >98:2 dr as a pale yellow oil. $[\alpha]_D^{20} = -230.7$ (c 0.5, CH₂Cl₂). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 9.83 (t, *J* = 1.4 Hz, 1H), 7.36–7.26 (m, 5H), 6.18–6.14 (m, 1H), 5.11 (hept, *J* = 6.3 Hz, 1H), 3.77 (dt, *J* = 17.1, 2.1 Hz, 1H), 3.46–3.39 (m, 1H), 3.33 (d, *J* = 17.0 Hz, 1H), 2.93 (ddd, *J* = 17.6, 8.8, 1.7 Hz, 1H), 2.82–2.61 (m, 3H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.31 (d, *J* = 6.3 Hz, 3H), 1.25 (t, *J* = 7.5 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 199.6, 169.5, 140.8, 133.9, 128.5 (2C), 127.7, 125.7 (3C), 70.4, 62.5, 49.0, 37.3, 28.0, 25.2, 21.6, 21.6, 13.8. **HRMS (ESI+)** *m/z* calcd. for C₁₉H₂₄S₂O₃ [M+Na]⁺: 387.1059; found: 387.1061. **UPC²**: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar, *t*_{major} = 3.7 min; *t*_{minor} = 17.3 min (95% ee).

Following the general procedure A (20 mol% **3**, 40 °C, 48 h), cycloadduct **4p** was obtained after FC on silica gel (pentane/EtOAc 9:1 to 4:1) in 84% yield and 93:7 dr as a pale yellow oil. $[\alpha]_D^{20} = -212.9$ (c 0.8, CH₂Cl₂). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 9.78 (t, *J* = 1.9 Hz, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.32–7.20 (m, 2H), 5.12 (hept, *J* = 6.3 Hz, 1H), 4.25 (t, *J* = 4.9 Hz, 1H), 4.18 (s, 2H), 2.90 (ddd, *J* = 17.6, 5.0, 2.2 Hz, 1H), 2.85–2.74 (m, 2H), 2.63 (dq, *J* = 11.7, 7.4 Hz, 1H), 1.69 (s, 9H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.34 (d, *J* = 6.3 Hz, 3H), 1.19 (t, *J* = 7.5 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 199.6, 169.2, 150.4, 135.5, 129.6, 128.1, 124.6, 123.0, 118.2, 117.8, 115.7, 84.5, 70.9, 64.0, 49.3, 35.4, 28.3 (3C), 25.7, 25.5, 21.6 (2C), 13.6. **HRMS (ESI+)** *m/z* calcd. for C₂₄H₃₁NS₂O₅ [M+Na]⁺: 500.1536; found: 500.1540. The ee was determined after transformation into compound **5a**.

Following the general procedure A (20 mol% **3**, 40 °C, 48 h), cycloadduct **4q** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 92% yield and 86:9:5 dr as a pale yellow oil. $[\alpha]_D^{20} = -130.2$ (c 0.3, CH₂Cl₂). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 9.78 (t, *J* = 1.5 Hz, 1H), 5.87 (ddd, *J* = 10.7, 6.0, 2.4 Hz, 1H), 5.68 (ddd, *J* = 10.7, 2.4, 1.3 Hz, 1H), 5.09 (hept, *J* = 6.2 Hz, 1H), 3.57–3.53 (m, 1H), 3.23–3.18 (m, 1H), 2.81 (ddd, *J* = 17.5, 8.8, 1.8 Hz, 1H), 2.77 (dq, *J* = 11.8, 7.6 Hz, 1H), 2.63 (dq, *J* = 11.8, 7.6 Hz, 1H), 2.56 (ddd, *J* = 17.4, 3.4, 1.0 Hz, 1H), 1.74–1.64 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H), 1.04 (t, *J* = 7.4 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 199.6, 169.5, 128.7, 127.6, 70.3, 63.8, 49.2, 41.3, 36.3, 26.6, 25.3, 21.6, 21.5, 13.7, 11.2. **HRMS (ESI+)** *m/z* calcd. for C₁₅H₂₄S₂O₃ [M+Na]⁺: 339.1059; found: 339.1063. **UPC²**: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 1.4 min; *t*_{minor} = 3.1 min (83% ee).

Following the general procedure A (20 mol% **3**, 40 °C, 48 h), cycloadduct **4r** was obtained after FC on silica gel (pentane/EtOAc 9:1) in 89% yield and 92:8 dr as a pale yellow oil. $[\alpha]_D^{20} = -253.7$ (c 0.3, CH₂Cl₂). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 9.78 (t, *J* = 1.4 Hz, 1H), 5.91–5.84 (m, 1H), 5.83–5.76 (m, 1H), 5.08 (hept, *J* = 6.3 Hz, 1H), 3.46–3.36 (m, 1H), 3.25–3.17 (m, 1H), 2.94 (dd, *J* = 17.6, 5.1 Hz, 1H), 2.84 (ddd, *J* = 17.5, 8.8, 1.7 Hz, 1H), 2.78–2.69 (m, 1H), 2.67–2.53 (m, 2H), 1.30 (d, *J* = 6.7 Hz, 3H), 1.27 (d, *J* = 6.7 Hz, 3H), 1.23 (t, *J* = 7.5 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 199.6, 169.5, 128.2, 123.3, 70.3, 62.5, 48.8, 36.1, 25.8, 25.1, 21.6, 21.5, 13.8. **HRMS (ESI+)** *m/z* calcd. for C₁₃H₂₀S₂O₃ [M+Na]⁺: 311.0746; found: 311.0750. The ee was determined after transformation to compound **5b**.

Following the general procedure B, compound **5a** was obtained after FC on silica gel (pentane/EtOAc 5:1) in 72% yield over two steps. $[\alpha]_D^{20} = -8.0$ (c 1.1, CHCl₃). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 5.99–5.94 (m, 1H), 5.84–5.81 (m, 1H), 5.06 (hept, *J* = 6.2 Hz, 1H), 4.07 (dd, *J* = 6.6, 2.6 Hz, 1H), 4.05 (dd, *J* = 6.6, 2.6 Hz, 1H), 3.28–3.22 (m, 1H), 3.20–3.14 (m, 1H), 3.10–3.04 (m, 1H), 2.36–2.27 (m, 1H), 2.00–1.91 (m, 1H), 1.29 (d, *J* = 6.2 Hz, 3H), 1.27 (d, *J* = 6.2 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 169.7, 129.1, 123.6, 86.7, 69.4, 68.3, 41.8, 32.0, 26.0, 21.6, 21.4. **HRMS (ESI+)** *m/z* calcd. for C₁₁H₁₆SO₃ [M+Na]⁺: 251.0712; found: 251.0710. **UPC²**: IC-3, CO₂/MeCN 90:10, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 3.4 min; *t*_{minor} = 4.1 min (92% ee).

Following the general procedure B, compound **5b** was obtained after FC on silica gel (pentane/EtOAc 9:1 to 4:1) in 51% yield over two steps. $[\alpha]_D^{20} = -42.4$ (c 0.9, CH₂Cl₂). **¹H NMR (400 MHz, CDCl₃)**: 8.12 (d, *J* = 8.1 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.38–7.21 (m, 2H), 5.10 (hept, *J* = 6.2 Hz, 1H), 4.32–4.08 (m, 4H), 3.93 (t, *J* = 7.3 Hz, 1H), 2.78–2.63 (m, 1H), 2.32–2.18 (m, 1H), 1.68 (s, 9H), 1.31 (d, *J* = 6.2 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 169.5, 150.3, 135.6, 130.8, 128.7, 124.4, 122.7, 118.4, 117.8, 115.7, 88.1, 84.3, 69.8, 69.2, 41.8, 32.0, 28.3 (3C), 26.1, 21.6, 21.5. **HRMS (ESI+)** *m/z* calcd. for C₂₂H₂₇NSO₅ [M+Na]⁺: 440.1502; found: 440.1506. **UPC²**: IC-3, first CO₂/MeCN 99:1 (0.5 min), then linear gradient (10%/min) from 99:1 to 60:40 CO₂/MeCN, 3.0 mL·min⁻¹, 40 °C, 120 bar; *t*_{major} = 4.1 min; *t*_{minor} = 3.7 min (90% ee).

To a solution of the aldehyde **4r** (0.35 mmol, 1 equiv) in MeOH (3 mL) was added NaBH₄ (0.52 mmol, 1.5 equiv) at 0 °C. After stirring for 5 min the reaction was allowed to reach rt and stirred for further 10 min. A saturated solution of aq. NH₄Cl was then added and the resulting solution was extracted three times with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo*. The crude alcohol intermediate was redissolved in CHCl₃ (1.5 mL) and *p*-TsOH·H₂O (0.175 mmol, 0.5 equiv) was added. This mixture was heated at 50 °C for 36 h in order to reach complete conversion of **4r**. The crude reaction mixture was directly purified by FC (85:15 pentane/EtOAc) on silica gel to afford lactone **6** in 59% yield over two steps as a pale yellow oil. $[\alpha]_D^{20} = -65.3$ (c 0.9, CHCl₃). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 6.08–6.03 (m, 1H), 5.67–5.64 (m, 1H), 4.46–4.41 (m, 1H), 4.34 (ddd, *J* = 12.3, 8.3, 4.2 Hz, 1H), 3.14–3.13 (m, 2H), 3.00 (dq, *J* = 11.6, 7.1 Hz, 1H), 2.88–2.80 (m, 2H), 2.53–2.46 (m, 1H), 1.88–1.81 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). **¹³C NMR (100**

MHz, CDCl₃): δ ppm 167.8, 129.0, 126.2, 68.5, 56.6, 40.8, 27.2, 25.9, 24.8, 13.7. **HRMS** (ESI+) m/z calcd. for C₁₀H₁₄S₂O₂ [M+Na]⁺: 253.0327; found: 253.0327.

Potassium ferricyanide (0.79 mmol, 3equiv), potassium carbonate (0.79 mmol, 3 equiv), osmium (III) chloride (1.8 μ mol), quinuclidine (35 μ mol) and methanesulfonamide (0.26 mmol, 1 equiv) were dissolved in a mixture of H₂O/*t*-BuOH (1:1) 2 mL. Then, a solution of **5a** in 2 mL of the same mixture of solvents was added. The reaction was vigorously stirred for 24 h at rt. Anhydrous sodium sulfite (3.28 mmol, 12.5 equiv) was added and the stirring was continued for 30 min. The product **7** was extracted with CH₂Cl₂, dried over Na₂SO₄ and concentrated *in vacuo*. The product was purified by FC (3:1 pentane/EtOAc) in 71% of yield as a colorless oil. $[\alpha]_D^{20} = -55.4$ (c 2, CHCl₃). **¹H NMR (400 MHz, CDCl₃)** δ ppm 5.20 (d, $J = 10$ Hz, 1H), 5.14 (hept, $J = 6.3$ Hz, 1H), 4.18-4.12 (m, 1H), 4.10-3.95 (m, 3H), 2.98 (ddd, $J = 11.4, 8.6, 2.8$ Hz, 1H), 2.89 (dd, $J = 13.8, 11.1$ Hz, 2H), 2.54 (ddd, $J = 13.8, 4.0, 0.8$ Hz, 1H), 2.42-2.31 (m, 1H), 2.28-2.19 (m, 1H), 1.36 (d, $J = 3.5$ Hz, 3H), 1.34 (d, $J = 3.5$ Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ ppm 171.3, 86.0, 71.2, 69.3, 66.9, 66.1, 49.5, 28.8, 27.3, 21.5, 21.0. **HRMS** (ESI+) m/z calcd. for [M+Na]⁺: 285.0767; measured: 285.0769.

A mixture of the aldehyde **1i** (0.5 mmol, 1 equiv), PhCO₂H (0.1 mmol, 0.2 equiv) and catalyst **3** (0.1 mmol, 0.2 equiv) was dissolved in 1.5 mL of CHCl₃ at rt. Then, the dithioester (1.0 mmol, 2 equiv) and water (2.5 mmol, 5 equiv) were added. The mixture was stirred for the time indicated. When the reaction was completed (20 h), the mixture was directly purified by FC on silica gel (pentane/EtOAc 10:1 to 4:1) to afford the corresponding cycloadduct **8** in 72% yield and 72:28 dr as a pale yellow oil. $[\alpha]_D^{20} = -12.0$ (c 0.5, CH₂Cl₂). **¹H NMR (400 MHz, CDCl₃)**: δ ppm 9.70* (t, $J = 1.9$ Hz, 1H*), 9.62 (s, 1H), 3.80* (s, 3H*), 3.70 (s, 3H), 3.58-3.09* (m, 3H, 4H*), 2.61-2.46 (m, 1H), 2.19-1.86* (m, 2H, 2H*), 2.09 (s, 3H), 2.02* (s, 3H*), 1.76-1.52* (m, 2H, 2H*), 0.95* (s, 9H*), 0.93 (s, 9H), 0.21* (s, 3H*), 0.19* (s, 3H*), 0.14 (s, 3H), 0.10 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ ppm 199.9, 199.7*, 171.4, 169.7*, 154.9, 150.7*, 110.4, 109.0*, 68.3*, 65.4, 53.0*, 52.8, 45.7*, 44.5, 42.0*, 41.7*, 41.6, 41.1, 29.9, 29.7*, 25.6* (3C*), 25.6 (3C), 21.7*, 19.7, 18.0, 18.0*, 15.4, 14.2*, -3.5*, -3.8, -3.9*, -4.6. **HRMS** (ESI+) m/z calcd. for C₁₈H₃₁S₂O₄ [M+H]⁺: 403.1428; found: 403.1428. The ee was determined on HPLC after reduction to the corresponding alcohol (NaBH₄, MeOH, 0 °C, 10 min); IC-5, hx/*i*PrOH 90:10, 1.0 mL·min⁻¹; $t_{\text{major}} = 8.0$ min; $t_{\text{minor}} = 9.4$ min (96% ee).

4. X-RAY STRUCTURE

Crystal data for [**4k**]: C₁₄H₂₂O₃S₂, $M = 302.44$, monoclinic, space group P 1 21 1 (no. 6), $a = 9.2144(0) \text{ \AA}$, $b = 9.3239(0) \text{ \AA}$, $c = 9.5262(0) \text{ \AA}$, $\beta = 109.663(0)^\circ$, $V = 770.71(0) \text{ \AA}^3$, $T = 0 \text{ K}$, $Z = 2$, $d_c = 1.303 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha, \lambda = 0.71073 \text{ \AA}) = 0.347 \text{ mm}^{-1}$, 16358 reflections collected, 5455 unique [$R_{\text{int}} = 0.026$], which were used in all calculations. Refinement on F^2 , final $R(F) = 0.0308$, $R_w(F2) = 0$. CCDC number 909665.

5. COMPUTATIONAL DATA

5.1 Methods

For studying the distinct reaction pathways: All calculations were run using GAUSSIAN09.⁴ All calculations were performed at wB97xd/tzvp level of theory and basis set.⁵ Solvent effects were estimated with IEFPCM, using chloroform as the solvent. Frequency calculations were performed for all stationary points to identify them as local minima or first order saddle points and to obtain the ZPEs and thermochemical corrections for the free energies. All of the reported values are free energies at 298.15 K and 1 atm. Intrinsic reaction coordinate (IRC) calculations were used to characterize transition state structures.⁶ Structural images were created using Chemcraft.⁷

For studying the origin of enantioselectivity and the facial shielding provided by catalyst **3:** All structures were optimized in solvent (IEFPCM, CHCl₃) with wB97xd/6-31G(d). The activation energies reported in the manuscript were obtained with wB97xd/cc-pVDZ single points. Frequency calculations were performed for all stationary points to identify them as local minima or first order saddle points and to obtain the ZPEs and thermochemical corrections for the free energies. All of the reported values are free energies at 298.15 K and 1 atm. Structures were generated with Chemcraft.

5.2 Energies and coordinates: path I-II

Figure S1: Energy profiles for pathways I-II: the formal cycloaddition of **A** and **2b** (initial attack at sulfur). Reported values in plain text are wB97xd/tzvp free energies in solvent (IEFPCM, CHCl₃), relative to **A** + **2b**.

⁴ S1. GAUSSIAN09, Revision A.02 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. D.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, 2009.

⁵ (a) Chai, J.-D.; Head-Gordon, M. *J. Chem. Phys.* **2008**, *10*, 6615. (b) Schaefer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

⁶ (a) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

⁷ Zhurko, G. A. Chemcraft, Version 1.7 (build 365).

A

HF = -484.1123161 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.259331 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -483.893431 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	5.078540	-0.961156	0.448109
2	1	4.823507	-1.325694	1.446707
3	1	6.077182	-0.525350	0.481180
4	1	5.105222	-1.832965	-0.212010
5	6	4.053631	0.031447	-0.036216
6	6	2.679299	-0.480418	-0.114965
7	1	2.577710	-1.557781	-0.229588
8	6	1.563237	0.260918	-0.015766
9	1	1.672276	1.330814	0.157220
10	6	0.212547	-0.230000	-0.100266
11	1	0.062798	-1.290122	-0.275469
12	6	-0.852035	0.598001	0.036209
13	1	-0.678745	1.657105	0.207447
14	6	-2.614444	-1.108943	-0.208476
15	6	-3.251043	1.204116	0.130401
16	6	-4.134091	-0.968922	-0.323344
17	1	-2.167803	-1.548084	-1.105701
18	1	-2.322966	-1.732732	0.645536
19	6	-4.438374	0.306630	0.467254
20	1	-3.032464	1.933999	0.911582
21	1	-3.425042	1.745999	-0.807047
22	1	-4.658421	-1.844105	0.057046
23	1	-4.415959	-0.833965	-1.369684
24	1	-4.450001	0.093978	1.538472
25	1	-5.391772	0.759137	0.198361
26	7	-2.154007	0.255053	-0.012169
27	6	4.402055	1.277590	-0.371352
28	1	3.683464	1.985413	-0.767972
29	1	5.423138	1.623409	-0.260419

2b

HF = -1102.8699914 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.099701 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1102.806393 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.345812	-0.014575	-0.304450
2	1	-3.924343	0.758886	-0.799262
3	1	-3.655998	-0.120208	0.734323
4	1	-3.458926	-0.967863	-0.819243
5	8	-1.982581	0.428343	-0.369710
6	6	-1.082841	-0.378512	0.156252
7	8	-1.317198	-1.450105	0.653372
8	6	0.326568	0.191505	0.068763
9	16	0.638704	1.789284	0.213765
10	16	1.470064	-1.094042	-0.144785
11	6	3.041389	-0.209088	-0.218426
12	1	3.224744	0.306675	0.721993
13	1	3.800644	-0.970552	-0.385883
14	1	3.036001	0.507296	-1.037744

TS₁-I

HF = -1586.984029 hartrees

Imaginary Frequencies: 1 (-271.8276 1/cm)

Zero-point correction = 0.360525 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.677598 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	3.708521	-2.543421	-0.993773
2	1	3.359498	-3.512242	-1.354545
3	1	3.787468	-2.607268	0.095820
4	1	4.705971	-2.361380	-1.393046
5	6	2.745962	-1.449929	-1.370164
6	6	1.373610	-1.733163	-1.263529
7	1	1.102223	-2.744720	-0.972942
8	6	0.356927	-0.812258	-1.383085
9	1	0.600674	0.198273	-1.693135
10	6	-0.998049	-1.070020	-1.119688
11	1	-1.291141	-2.056417	-0.779063
12	6	-1.914987	-0.048977	-1.162461
13	1	-1.589894	0.930995	-1.497742
14	6	-3.779362	-1.313124	-0.189612
15	6	-4.101998	1.018142	-0.783859
16	6	-5.226870	-0.903852	0.081678
17	1	-3.700833	-2.172542	-0.859048
18	1	-3.240484	-1.548705	0.734343
19	6	-5.140147	0.614369	0.257549
20	1	-3.562262	1.929509	-0.527095
21	1	-4.562339	1.148637	-1.768375
22	1	-5.638443	-1.411398	0.952187
23	1	-5.852314	-1.147101	-0.779763
24	1	-4.774421	0.857744	1.256876
25	1	-6.094363	1.116692	0.107680
26	7	-3.188558	-0.125425	-0.799642
27	6	3.240416	-0.176916	-1.627281
28	1	2.620728	0.562174	-2.117144
29	1	4.303921	-0.056457	-1.794844
30	6	0.601408	-1.974081	2.717646

31	1	1.298799	-2.751661	3.018251
32	1	-0.164416	-2.389696	2.060521
33	1	0.121761	-1.540520	3.595646
34	8	1.380551	-1.004821	2.027077
35	6	0.706798	0.058783	1.560713
36	8	-0.472634	0.238873	1.801266
37	6	1.514609	0.987816	0.763490
38	16	3.126209	0.784685	0.443264
39	16	0.526126	2.385242	0.229807
40	6	1.774403	3.469275	-0.506968
41	1	1.234601	4.355732	-0.838141
42	1	2.524550	3.750477	0.230302
43	1	2.262486	3.000739	-1.359064

IRC path for TS₁-I:

TS₁-II

HF = -1586.9825849 hartrees

Imaginary Frequencies: 1 (-288.6569 1/cm)

Zero-point correction = 0.360557 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.675982 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	3.911580	-2.320274	-1.133468
2	1	4.007079	-2.493925	-0.056377
3	1	4.887092	-2.009823	-1.506714
4	1	3.649627	-3.274271	-1.593769
5	6	2.856018	-1.283402	-1.405075
6	6	1.511684	-1.670889	-1.264062
7	1	1.324754	-2.702300	-0.975724
8	6	0.421969	-0.832493	-1.352711
9	1	0.571702	0.178309	-1.720624
10	6	-0.891849	-1.195061	-1.008845
11	1	-1.076544	-2.190425	-0.622639
12	6	-1.901107	-0.266094	-1.038573
13	1	-1.687936	0.728298	-1.415423
14	6	-3.629154	-1.672899	-0.005521
15	6	-4.140752	0.632329	-0.573584
16	6	-5.102075	-1.384007	0.280750
17	1	-3.484232	-2.528041	-0.668920
18	1	-3.062876	-1.854577	0.914702
19	6	-5.133350	0.134280	0.472550
20	1	-3.657489	1.569423	-0.297002
21	1	-4.623557	0.757961	-1.547795
22	1	-5.464543	-1.931625	1.148848
23	1	-5.712772	-1.667594	-0.579037
24	1	-4.778293	0.394398	1.471537
25	1	-6.124937	0.563028	0.337571
26	7	-3.152004	-0.445517	-0.634368
27	6	3.236604	0.037877	-1.594773
28	1	2.546876	0.758113	-2.012529
29	1	4.283226	0.255483	-1.771855
30	6	-0.061892	3.490994	-1.008409

31	1	0.451317	4.038774	-1.794146
32	1	-0.356773	4.169277	-0.207541
33	1	-0.954067	3.010365	-1.412321
34	8	0.874179	2.525758	-0.538455
35	6	0.455279	1.737541	0.468720
36	8	-0.679543	1.795054	0.903908
37	6	1.471977	0.801011	0.951594
38	16	3.069544	0.901567	0.513481
39	16	0.781011	-0.314278	2.170338
40	6	2.150655	-1.460289	2.440077
41	1	1.794563	-2.179895	3.176333
42	1	2.400547	-1.978178	1.514344
43	1	3.031745	-0.949042	2.822921

IRC path for TS₁-II:

B₁

HF = -1586.9934003 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.363024 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.682742 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	4.155360	-2.249403	-0.328216
2	1	3.812340	-3.239570	-0.030244
3	1	4.593389	-1.754911	0.543111
4	1	4.952019	-2.361551	-1.068697
5	6	3.043687	-1.412519	-0.881178
6	6	1.780753	-1.898650	-0.947442
7	1	1.591282	-2.894770	-0.558342
8	6	0.647002	-1.143379	-1.357770
9	1	0.808940	-0.250262	-1.948992
10	6	-0.647442	-1.486763	-1.064609
11	1	-0.851468	-2.353524	-0.448539
12	6	-1.668264	-0.579340	-1.362949
13	1	-1.439412	0.268673	-1.999187
14	6	-3.317699	-1.558296	0.150710
15	6	-3.880740	0.428973	-1.129797
16	6	-4.736283	-1.101864	0.488597
17	1	-3.269895	-2.587312	-0.206631
18	1	-2.633382	-1.437795	0.994915
19	6	-4.723480	0.388257	0.138692
20	1	-3.377764	1.380207	-1.296271
21	1	-4.476730	0.179105	-2.011283
22	1	-4.980195	-1.291602	1.531955
23	1	-5.462020	-1.630129	-0.132775
24	1	-4.227617	0.957021	0.927090
25	1	-5.718618	0.801078	-0.015636
26	7	-2.885764	-0.625845	-0.898393
27	6	3.373930	-0.009035	-1.186617
28	1	2.825512	0.417753	-2.023345
29	1	4.440741	0.132652	-1.353784
30	6	0.376449	-1.230426	2.954141

31	1	1.088040	-1.813047	3.536059
32	1	-0.284485	-1.902587	2.402043
33	1	-0.230881	-0.615617	3.620874
34	8	1.152172	-0.436454	2.074758
35	6	0.446067	0.394591	1.249699
36	8	-0.779829	0.454183	1.349137
37	6	1.242848	1.120737	0.321255
38	16	2.980596	1.063522	0.319715
39	16	0.416995	2.238499	-0.774010
40	6	-0.061157	3.622123	0.314189
41	1	-0.583831	4.357894	-0.297804
42	1	-0.726552	3.257396	1.094719
43	1	0.824550	4.077624	0.754844

B_{II}

HF = -1586.9939022 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.362850 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.684210 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.982629	2.694517	-0.057840
2	1	-4.545778	2.155128	0.708350
3	1	-4.689903	2.964117	-0.846946
4	1	-3.585022	3.608172	0.382444
5	6	-2.898104	1.818925	-0.605478
6	6	-1.595810	2.186308	-0.514199
7	1	-1.352831	3.115364	-0.007263
8	6	-0.505032	1.381771	-0.945471
9	1	-0.709335	0.570163	-1.633659
10	6	0.801585	1.604408	-0.587530
11	1	1.043955	2.394556	0.111931
12	6	1.784174	0.697385	-0.989171
13	1	1.521008	-0.082393	-1.692914
14	6	3.559155	1.576556	0.458359
15	6	3.979384	-0.372882	-0.936964
16	6	5.018194	1.144393	0.589421
17	1	3.443319	2.617519	0.155527
18	1	3.001209	1.418781	1.385323
19	6	4.984869	-0.337230	0.207914
20	1	3.455727	-1.322568	-1.034087
21	1	4.452724	-0.121593	-1.889508
22	1	5.403051	1.318534	1.592217
23	1	5.639042	1.702174	-0.114337
24	1	4.615268	-0.934887	1.042819
25	1	5.957657	-0.724394	-0.089134
26	7	3.021973	0.680135	-0.571714
27	6	-3.304235	0.491731	-1.095938
28	1	-2.719145	0.105857	-1.926616
29	1	-4.362237	0.452794	-1.350986
30	6	-0.341659	-2.788252	-2.284931

31	1	-0.988781	-3.070146	-3.112979
32	1	0.020446	-3.683575	-1.777207
33	1	0.518779	-2.233574	-2.665834
34	8	-1.139286	-1.992553	-1.424362
35	6	-0.541404	-1.578164	-0.259116
36	8	0.654779	-1.806722	-0.077777
37	6	-1.407198	-0.846241	0.595070
38	16	-3.122704	-0.754525	0.311372
39	16	-0.736147	-0.177177	2.087249
40	6	-0.565465	-1.655474	3.144858
41	1	-0.143440	-1.330407	4.096550
42	1	-1.536855	-2.116854	3.318498
43	1	0.110037	-2.368784	2.675088

TS₂-I

HF = -1586.990859 hartrees

Imaginary Frequencies: 1 (-206.2525 1/cm)

Zero-point correction = 0.362215 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.680794 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	4.019717	-2.503327	-0.592773
2	1	3.610607	-3.444224	-0.225275
3	1	4.624431	-2.055623	0.201487
4	1	4.691643	-2.716240	-1.428335
5	6	2.938731	-1.553022	-1.005163
6	6	1.633256	-1.850208	-0.849236
7	1	1.363123	-2.798136	-0.393567
8	6	0.558631	-0.941854	-1.134985
9	1	0.695172	-0.238893	-1.948507
10	6	-0.762084	-1.243236	-0.762450
11	1	-0.926160	-2.001768	-0.006823
12	6	-1.813592	-0.481921	-1.212793
13	1	-1.630774	0.270046	-1.973182
14	6	-3.476273	-1.372785	0.350398
15	6	-4.138947	0.320459	-1.258390
16	6	-4.963803	-1.058204	0.508982
17	1	-3.286549	-2.431331	0.161438
18	1	-2.891454	-1.067966	1.224565
19	6	-5.096505	0.352083	-0.072079
20	1	-3.736370	1.298635	-1.519891
21	1	-4.619959	-0.109919	-2.141969
22	1	-5.285145	-1.124991	1.546788
23	1	-5.560640	-1.760743	-0.076329
24	1	-4.759969	1.093871	0.654525
25	1	-6.115212	0.596521	-0.368485
26	7	-3.065098	-0.558480	-0.791421
27	6	3.349184	-0.192225	-1.399273
28	1	2.799043	0.228073	-2.239267
29	1	4.416579	-0.112062	-1.597153
30	6	0.741497	-0.964085	3.235588

31	1	1.487103	-1.602080	3.704324
32	1	-0.127606	-1.557500	2.946857
33	1	0.422149	-0.189239	3.934101
34	8	1.378145	-0.400645	2.097274
35	6	0.617528	0.433043	1.347759
36	8	-0.535336	0.680304	1.658812
37	6	1.278961	0.900632	0.143793
38	16	3.035993	0.921211	0.078502
39	16	0.416245	2.137211	-0.806229
40	6	0.548022	3.610838	0.254352
41	1	0.070555	4.437031	-0.272080
42	1	0.034974	3.435669	1.198401
43	1	1.595939	3.851073	0.430887

IRC path for TS₂-I:

TS₂-II

HF = -1586.9911468 hartrees

Imaginary Frequencies: 1 (-227.7800 1/cm)

Zero-point correction = 0.362659 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.680975 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	4.005806	-2.770253	-0.287409
2	1	4.666828	-2.286392	0.437359
3	1	4.620636	-3.052750	-1.146214
4	1	3.601836	-3.675686	0.164864
5	6	2.919964	-1.825581	-0.699109
6	6	1.618123	-2.081251	-0.459718
7	1	1.342586	-2.993504	0.060410
8	6	0.561917	-1.157066	-0.768336
9	1	0.714874	-0.494489	-1.611975
10	6	-0.768549	-1.410544	-0.392090
11	1	-0.963747	-2.150252	0.374346
12	6	-1.793195	-0.642385	-0.889410
13	1	-1.575067	0.090898	-1.658276
14	6	-3.548676	-1.527734	0.578666
15	6	-4.092309	0.214234	-1.024287
16	6	-5.040459	-1.202503	0.649874
17	1	-3.354294	-2.584541	0.385130
18	1	-3.022053	-1.246062	1.496322
19	6	-5.121537	0.224301	0.101214
20	1	-3.655815	1.193351	-1.220610
21	1	-4.525515	-0.173116	-1.951553
22	1	-5.430195	-1.294579	1.662016
23	1	-5.603631	-1.882795	0.007673
24	1	-4.823221	0.942230	0.867373
25	1	-6.116772	0.489853	-0.251416
26	7	-3.064789	-0.701342	-0.524800
27	6	3.324531	-0.504431	-1.216491
28	1	2.747883	-0.150685	-2.068568
29	1	4.385253	-0.451794	-1.455829
30	6	0.125608	2.855031	-2.162017

31	1	0.663038	3.056914	-3.085280
32	1	-0.043172	3.785095	-1.617970
33	1	-0.840093	2.399057	-2.385986
34	8	0.953750	1.971021	-1.417016
35	6	0.469561	1.573427	-0.210896
36	8	-0.645741	1.904826	0.152910
37	6	1.353824	0.653547	0.477477
38	16	3.087448	0.741488	0.167961
39	16	0.849916	0.136470	2.103286
40	6	1.004617	1.673096	3.071203
41	1	0.732472	1.433740	4.099203
42	1	2.030210	2.040128	3.049761
43	1	0.324233	2.429338	2.683684

IRC path for TS₂-II:

C₁

HF = -1587.0211442 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.364160 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.709780 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	3.748576	-1.695675	-2.385104
2	1	3.215335	-2.576123	-2.744509
3	1	4.518588	-2.022030	-1.679742
4	1	4.263299	-1.234225	-3.232497
5	6	2.817494	-0.724345	-1.728096
6	6	1.521595	-0.941079	-1.542927
7	1	1.063450	-1.863689	-1.881137
8	6	0.618796	0.054662	-0.856799
9	1	0.619371	0.967257	-1.460576
10	6	-0.789514	-0.452772	-0.753787
11	1	-0.916775	-1.475634	-0.416546
12	6	-1.857562	0.317401	-1.016993
13	1	-1.706960	1.336191	-1.362946
14	6	-3.563999	-1.272571	-0.252203
15	6	-4.258154	0.923715	-0.993992
16	6	-5.084958	-1.156431	-0.154238
17	1	-3.245276	-2.143881	-0.832119
18	1	-3.097224	-1.347699	0.740128
19	6	-5.311682	0.353264	-0.046432
20	1	-3.926740	1.922112	-0.702607
21	1	-4.644325	0.978560	-2.018540
22	1	-5.487261	-1.711386	0.692017
23	1	-5.549656	-1.542403	-1.064345
24	1	-5.112399	0.688813	0.973658
25	1	-6.323579	0.655185	-0.314334
26	7	-3.162446	-0.035583	-0.897524
27	6	3.398758	0.549500	-1.196111
28	1	3.044781	1.416658	-1.757553
29	1	4.487958	0.550482	-1.231315
30	6	0.992264	-2.836513	2.126135

31	1	1.399021	-3.723788	1.650091
32	1	-0.081026	-2.946538	2.281742
33	1	1.481578	-2.660942	3.083524
34	8	1.257418	-1.761321	1.222394
35	6	0.857448	-0.555570	1.608921
36	8	0.312881	-0.340838	2.661327
37	6	1.160877	0.515588	0.555771
38	16	2.985954	0.806711	0.574650
39	16	0.294724	2.032290	1.163862
40	6	0.809179	3.234297	-0.090547
41	1	0.518138	4.210605	0.294322
42	1	1.892273	3.210294	-0.212649
43	1	0.316598	3.073709	-1.048960

C_{II}

HF = -1587.023792 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.364913 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.710616 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	3.800428	-2.529356	-1.531648
2	1	3.346145	-3.513095	-1.410256
3	1	4.638796	-2.448238	-0.832906
4	1	4.216094	-2.460304	-2.540508
5	6	2.808050	-1.437366	-1.279466
6	6	1.562318	-1.639248	-0.862313
7	1	1.181787	-2.642346	-0.702079
8	6	0.642286	-0.482545	-0.582759
9	1	0.586601	0.116037	-1.496118
10	6	-0.753491	-0.886793	-0.219204
11	1	-0.871240	-1.589695	0.597191
12	6	-1.827311	-0.369764	-0.839961
13	1	-1.681446	0.343117	-1.647373
14	6	-3.538069	-1.452445	0.559510
15	6	-4.242150	0.078167	-1.180984
16	6	-5.065064	-1.420003	0.493724
17	1	-3.135645	-2.466835	0.478471
18	1	-3.159603	-1.021089	1.496390
19	6	-5.357574	-0.060920	-0.146473
20	1	-3.978752	1.120207	-1.374988
21	1	-4.532373	-0.381942	-2.133159
22	1	-5.524636	-1.540224	1.473677
23	1	-5.427652	-2.223297	-0.151613
24	1	-5.269886	0.730344	0.601395
25	1	-6.349528	-0.000545	-0.592611
26	7	-3.129554	-0.637952	-0.569803
27	6	3.266187	-0.017438	-1.441593
28	1	2.747538	0.488311	-2.258360
29	1	4.337313	0.048030	-1.630196
30	6	-0.426532	3.480818	-0.998845

31	1	-0.452356	3.662354	-2.069310
32	1	0.074442	4.301228	-0.486054
33	1	-1.437109	3.369988	-0.606066
34	8	0.306448	2.264661	-0.832699
35	6	0.448109	1.828312	0.417579
36	8	0.005134	2.408312	1.374250
37	6	1.243565	0.517980	0.479093
38	16	3.007138	0.932764	0.110341
39	16	1.101066	-0.022778	2.237591
40	6	2.047841	-1.568334	2.233051
41	1	2.201871	-1.818681	3.282006
42	1	1.507838	-2.375821	1.743150
43	1	3.013202	-1.421783	1.750368

5.3 Energies and coordinates: path III-IV

Figure S2: Energy profiles for pathways III-IV: the formal cycloaddition of **A** and **2b** (initial attack at carbon). Reported values in plain text are wB97xd/tzvp free energies in solvent (IEFPCM, CHCl₃), relative to **A** + **2b**.

TS-III

HF = -1586.9742041 hartrees

Imaginary Frequencies: 1 (-444.9298 1/cm)

Zero-point correction = 0.360882 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.667338 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	2.400952	-2.638355	-1.385093
2	1	2.306039	-3.194165	-0.450187
3	1	3.444788	-2.354304	-1.519083
4	1	2.129263	-3.316034	-2.198329
5	6	1.494433	-1.437589	-1.386524
6	6	0.157911	-1.636964	-1.011136
7	1	-0.125199	-2.640694	-0.705672
8	6	-0.816407	-0.660280	-0.948506
9	1	-0.589095	0.330616	-1.325730
10	6	-2.140278	-0.882538	-0.519783
11	1	-2.412286	-1.863095	-0.147414
12	6	-3.060300	0.133696	-0.535321
13	1	-2.753529	1.115357	-0.885600
14	6	-4.936270	-1.165972	0.377397
15	6	-5.258876	1.183698	-0.148073
16	6	-6.405338	-0.787729	0.565866
17	1	-4.798126	-1.993132	-0.322290
18	1	-4.457702	-1.437189	1.323880
19	6	-6.357268	0.723582	0.804028
20	1	-4.755958	2.093451	0.178774
21	1	-5.654752	1.344541	-1.155753
22	1	-6.866813	-1.334545	1.385980
23	1	-6.965513	-1.005696	-0.345568
24	1	-6.068402	0.934566	1.835578
25	1	-7.307358	1.217137	0.607136
26	7	-4.326853	0.053904	-0.146205
27	6	2.025803	-0.179413	-1.625988
28	1	1.373933	0.634054	-1.910356
29	1	3.038422	-0.100067	-2.000441
30	6	4.173058	-2.094109	1.680451

31	1	3.698557	-2.913905	2.212196
32	1	4.907812	-1.603258	2.317984
33	1	4.664542	-2.462248	0.779764
34	8	3.116370	-1.193058	1.345798
35	6	3.467693	-0.112416	0.659392
36	8	4.609137	0.131722	0.343731
37	6	2.299590	0.778445	0.303179
38	16	0.844608	0.692911	1.151622
39	16	2.971402	2.349460	-0.308510
40	6	1.467807	3.333912	-0.498931
41	1	1.796369	4.293143	-0.897939
42	1	0.777808	2.868952	-1.202943
43	1	0.969895	3.474126	0.457678

IRC path for TS-III:

TS-IV

HF = -1586.9736831 hartrees

Imaginary Frequencies: 1 (-423.9000 1/cm)

Zero-point correction = 0.360803 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.667226 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	2.302974	-2.792868	-1.625721
2	1	2.515440	-2.976523	-2.682111
3	1	1.805156	-3.675800	-1.224035
4	1	3.261076	-2.664419	-1.117891
5	6	1.462575	-1.553782	-1.475015
6	6	0.102216	-1.698422	-1.162014
7	1	-0.270034	-2.707689	-1.010620
8	6	-0.792869	-0.661481	-0.983723
9	1	-0.470526	0.349200	-1.208503
10	6	-2.144925	-0.823351	-0.620772
11	1	-2.516376	-1.816988	-0.399393
12	6	-2.967295	0.268007	-0.510491
13	1	-2.557297	1.254078	-0.709686
14	6	-4.991096	-0.951419	0.173647
15	6	-5.068762	1.467061	-0.038586
16	6	-6.426102	-0.458583	0.359147
17	1	-4.897717	-1.693181	-0.622522
18	1	-4.584967	-1.387115	1.092358
19	6	-6.250509	0.995951	0.802067
20	1	-4.498566	2.269467	0.429132
21	1	-5.398429	1.802524	-1.026986
22	1	-6.976713	-1.062025	1.078417
23	1	-6.957994	-0.497605	-0.593525
24	1	-5.995229	1.041335	1.862654
25	1	-7.140375	1.601123	0.637996
26	7	-4.248445	0.260211	-0.163081
27	6	2.090088	-0.319745	-1.549096
28	1	1.511418	0.570619	-1.750304
29	1	3.122991	-0.291192	-1.876293
30	6	2.825994	3.657569	-0.803314

31	1	2.001662	4.335506	-1.005003
32	1	3.373158	3.443627	-1.721738
33	1	3.505248	4.094060	-0.071807
34	8	2.226974	2.467246	-0.286866
35	6	3.067526	1.497954	0.062282
36	8	4.268354	1.600268	-0.023838
37	6	2.377501	0.250075	0.565427
38	16	0.854188	0.329658	1.281934
39	16	3.653385	-0.893718	1.146866
40	6	2.649160	-2.198063	1.897010
41	1	2.114645	-1.822749	2.766461
42	1	1.936475	-2.601746	1.180581
43	1	3.353428	-2.974565	2.194124

IRC path for TS-IV:

D_{III}

HF = -1587.0255809 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.363855 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.715990 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-2.414354	-2.405167	2.208884
2	1	-1.790376	-3.282162	2.383306
3	1	-3.236923	-2.683484	1.546332
4	1	-2.855947	-2.102869	3.163021
5	6	-1.626463	-1.280871	1.613521
6	6	-0.326686	-1.358903	1.350007
7	1	0.221430	-2.277634	1.532999
8	6	0.452360	-0.203414	0.801854
9	1	0.513412	0.591583	1.550135
10	6	1.818745	-0.550331	0.322512
11	1	1.915341	-1.450431	-0.274177
12	6	2.883111	0.237388	0.568854
13	1	2.748837	1.142137	1.156354
14	6	4.537431	-1.081938	-0.690958
15	6	5.252687	0.955246	0.409578
16	6	6.052355	-0.924650	-0.832682
17	1	4.257490	-2.036044	-0.233539
18	1	4.025900	-1.017352	-1.660115
19	6	6.269775	0.581500	-0.665966
20	1	4.917232	1.991107	0.332227
21	1	5.672217	0.804980	1.411850
22	1	6.421808	-1.309197	-1.782162
23	1	6.558657	-1.464756	-0.029527
24	1	6.032106	1.100649	-1.597008
25	1	7.290200	0.836808	-0.383123
26	7	4.153418	0.033228	0.154807
27	6	-2.359541	0.010404	1.344551
28	1	-1.990110	0.765005	2.043233
29	1	-3.425188	-0.106660	1.544405
30	6	-3.925551	-2.278330	-1.691972

31	1	-4.073899	-3.229054	-1.188376
32	1	-3.294639	-2.407728	-2.570624
33	1	-4.881990	-1.850335	-1.989918
34	8	-3.277083	-1.434615	-0.735306
35	6	-2.980120	-0.204214	-1.138082
36	8	-3.268320	0.229451	-2.224062
37	6	-2.210103	0.585373	-0.077299
38	16	-0.450457	0.567571	-0.650218
39	16	-2.921369	2.291229	-0.180466
40	6	-1.883278	3.173173	1.014335
41	1	-2.053775	4.233767	0.836561
42	1	-2.141613	2.940891	2.045904
43	1	-0.833872	2.947096	0.821639

D_{IV}

HF = -1587.024408 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.364332 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.714105 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-2.287643	-2.922762	1.988729
2	1	-2.706224	-2.684675	2.970955
3	1	-1.595023	-3.756563	2.105480
4	1	-3.124480	-3.248362	1.364710
5	6	-1.606044	-1.722566	1.406952
6	6	-0.298979	-1.670330	1.169954
7	1	0.330477	-2.537306	1.344493
8	6	0.376261	-0.431670	0.663065
9	1	0.317647	0.364779	1.409552
10	6	1.790399	-0.633708	0.242050
11	1	2.003442	-1.509488	-0.361026
12	6	2.760274	0.246534	0.555259
13	1	2.510357	1.119266	1.153399
14	6	4.593352	-0.869213	-0.653534
15	6	5.057428	1.181910	0.549848
16	6	6.091306	-0.563659	-0.714081
17	1	4.386839	-1.859947	-0.236381
18	1	4.123509	-0.823298	-1.644470
19	6	6.156478	0.948804	-0.483835
20	1	4.630248	2.184876	0.495744
21	1	5.439456	1.026357	1.566238
22	1	6.538973	-0.873063	-1.657266
23	1	6.609889	-1.085705	0.093125
24	1	5.915980	1.480378	-1.407100
25	1	7.132337	1.287328	-0.137980
26	7	4.062577	0.176690	0.201019
27	6	-2.445151	-0.496769	1.160214
28	1	-2.168065	0.259073	1.898148
29	1	-3.502891	-0.717739	1.311319
30	6	-2.558012	3.657094	0.967879

31	1	-2.047959	4.002485	1.862206
32	1	-3.632374	3.812707	1.059182
33	1	-2.186359	4.184526	0.089999
34	8	-2.259733	2.261303	0.870153
35	6	-2.771641	1.620654	-0.178868
36	8	-3.494476	2.143757	-0.986773
37	6	-2.306866	0.160228	-0.238166
38	16	-0.556644	0.211477	-0.827441
39	16	-3.378667	-0.619334	-1.525694
40	6	-2.679592	-2.289685	-1.619896
41	1	-1.595831	-2.232315	-1.712071
42	1	-2.951354	-2.900818	-0.763162
43	1	-3.097398	-2.733257	-2.522533

5.4 Energies and coordinates for alternative pathways: path I_c-II_c with *s-cis*-2b

The *s-cis*-conformer of the dithioester (*s-cis*-2b) is energetically close to 2b. The approach of *s-cis*-2b to A was also investigated. The energy profiles for these alternative pathways are described below. The activation energies are higher than those obtained for 2b.

Figure S3: Energy profiles for reaction pathways I_c-II_c: the formal cycloaddition of A and *s-cis*-2b (initial attack at sulfur). Reported values in plain text are wb97xd/tzvp free energies in solvent (IEFPCM, CHCl₃), relative to A + 2b.

s-cis-2b

HF = -1102.8696264 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.099593 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1102.806131 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.144247	-0.779049	-0.278827
2	1	-3.421900	-1.680418	-0.815749
3	1	-3.614848	0.095013	-0.726540
4	1	-3.428482	-0.854173	0.769895
5	8	-1.716639	-0.686677	-0.397431
6	6	-1.144683	0.363847	0.176048
7	8	-1.726438	1.232104	0.763639
8	6	0.367628	0.332114	-0.000209
9	16	1.182722	1.717197	-0.295128
10	16	1.023119	-1.262615	0.182720
11	6	2.800656	-0.979448	0.037513
12	1	3.136076	-0.283782	0.804309
13	1	3.266612	-1.952838	0.178281
14	1	3.037589	-0.585295	-0.948487

TS₁-I_{cis}

HF = -1586.9833399 hartrees

Imaginary Frequencies: 1 (-273.7760 1/cm)

Zero-point correction = 0.360687 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.676441 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.638886	3.042524	0.072697
2	1	-3.521191	2.941565	1.154893
3	1	-4.692833	2.910463	-0.168973
4	1	-3.343751	4.059547	-0.193279
5	6	-2.771782	2.034725	-0.630442
6	6	-1.378304	2.203551	-0.528490
7	1	-1.031721	3.085206	0.003841
8	6	-0.430420	1.293571	-0.929956
9	1	-0.744909	0.405135	-1.467244
10	6	0.953178	1.420226	-0.685964
11	1	1.316962	2.294517	-0.158323
12	6	1.805886	0.398092	-1.008782
13	1	1.406136	-0.477834	-1.510800
14	6	3.827056	1.387492	-0.016190
15	6	3.957559	-0.805370	-1.050270
16	6	5.276256	0.899552	-0.016555
17	1	3.704658	2.350765	-0.516532
18	1	3.427754	1.483865	0.999005
19	6	5.143032	-0.622694	-0.108361
20	1	3.416499	-1.738036	-0.889781
21	1	4.276486	-0.762179	-2.096672
22	1	5.818558	1.228907	0.867856
23	1	5.797431	1.282681	-0.895917
24	1	4.908880	-1.043220	0.871933
25	1	6.044133	-1.107455	-0.480027
26	7	3.105080	0.339829	-0.730710
27	6	-3.364635	0.916295	-1.208104
28	1	-2.811467	0.315860	-1.918887
29	1	-4.436615	0.924285	-1.363856
30	6	1.454255	-0.588176	2.288367

31	1	2.377975	-1.069566	1.976152
32	1	1.221985	-0.852891	3.320246
33	1	1.548952	0.495092	2.207931
34	8	0.450972	-1.067260	1.401351
35	6	-0.781064	-0.533143	1.544442
36	8	-1.039389	0.265169	2.418204
37	6	-1.710176	-1.068903	0.538135
38	16	-3.284989	-0.563265	0.481962
39	16	-1.005709	-2.278687	-0.585890
40	6	-2.475280	-2.958252	-1.396717
41	1	-2.104927	-3.733502	-2.066743
42	1	-3.149966	-3.397041	-0.663414
43	1	-3.006133	-2.203951	-1.972902

TS₁-II_{cis}

HF = -1586.981866 hartrees

Imaginary Frequencies: 1 (-267.0372 1/cm)

Zero-point correction = 0.361221 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.673600 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.896269	2.430861	0.641907
2	1	-4.782270	1.835215	0.414221
3	1	-4.148292	3.476972	0.446760
4	1	-3.674111	2.335601	1.705459
5	6	-2.733666	2.009865	-0.212847
6	6	-1.448654	2.007229	0.344618
7	1	-1.347931	2.307835	1.383037
8	6	-0.320838	1.559035	-0.309731
9	1	-0.405459	1.284440	-1.355923
10	6	0.964881	1.456515	0.248147
11	1	1.111638	1.673735	1.299396
12	6	2.013037	1.046180	-0.537172
13	1	1.830517	0.853967	-1.590358
14	6	3.691357	0.914306	1.254619
15	6	4.341601	0.400575	-1.026952
16	6	5.190291	0.615846	1.194201
17	1	3.474828	1.901127	1.669257
18	1	3.144827	0.171663	1.845260
19	6	5.337774	-0.239181	-0.066928
20	1	3.962838	-0.285518	-1.785252
21	1	4.781943	1.265725	-1.532193
22	1	5.543908	0.116028	2.093977
23	1	5.750086	1.546308	1.081713
24	1	5.046209	-1.271696	0.137639
25	1	6.350866	-0.242519	-0.465239
26	7	3.261044	0.830483	-0.138549
27	6	-2.991652	1.503330	-1.488172
28	1	-2.218065	1.515592	-2.242620
29	1	-3.997744	1.606338	-1.879366
30	6	1.695281	-2.441052	-0.328018

31	1	2.195950	-2.853007	0.544342
32	1	2.279143	-1.618395	-0.737992
33	1	1.575987	-3.211070	-1.090824
34	8	0.428518	-1.987975	0.133343
35	6	-0.398144	-1.446841	-0.785169
36	8	-0.049049	-1.274065	-1.936496
37	6	-1.706874	-1.128775	-0.209180
38	16	-2.987329	-0.711487	-1.182999
39	16	-1.840692	-1.403302	1.562285
40	6	-3.607980	-1.170701	1.867894
41	1	-3.742559	-1.356461	2.933297
42	1	-3.924748	-0.156508	1.634188
43	1	-4.203145	-1.878962	1.294403

B_{I-cis}

HF = -1586.9925359 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.363151 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.681483 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	3.834260	-2.954418	0.259916
2	1	4.394930	-2.422490	1.033127
3	1	4.561707	-3.322228	-0.468928
4	1	3.333760	-3.806341	0.717916
5	6	2.868106	-2.020332	-0.400153
6	6	1.534367	-2.280622	-0.378702
7	1	1.194128	-3.161032	0.157784
8	6	0.533079	-1.417687	-0.885889
9	1	0.820309	-0.632764	-1.572975
10	6	-0.806354	-1.561263	-0.587389
11	1	-1.127403	-2.363798	0.065206
12	6	-1.704726	-0.573162	-0.977462
13	1	-1.332499	0.273782	-1.545460
14	6	-3.669819	-1.554669	0.122780
15	6	-3.861944	0.590278	-1.011729
16	6	-5.126814	-1.095455	0.115891
17	1	-3.526585	-2.539009	-0.323995
18	1	-3.251546	-1.569809	1.132689
19	6	-5.022237	0.423462	-0.037835
20	1	-3.326266	1.532056	-0.902848
21	1	-4.196199	0.488191	-2.047147
22	1	-5.650886	-1.398249	1.020039
23	1	-5.649107	-1.524920	-0.740858
24	1	-4.777420	0.886013	0.920268
25	1	-5.937431	0.878182	-0.411694
26	7	-2.976969	-0.532383	-0.669598
27	6	3.433407	-0.772836	-0.937737
28	1	2.940914	-0.386665	-1.828037
29	1	4.502010	-0.857656	-1.127483
30	6	-1.505142	0.909007	2.129086

31	1	-2.449733	1.326006	1.782164
32	1	-1.230649	1.367799	3.080534
33	1	-1.605931	-0.167363	2.279138
34	8	-0.559457	1.203858	1.117551
35	6	0.703103	0.696272	1.314947
36	8	0.942652	0.045694	2.325462
37	6	1.594796	1.009729	0.247265
38	16	3.269195	0.567277	0.378192
39	16	1.091726	1.969619	-1.150527
40	6	1.474427	3.681022	-0.646736
41	1	1.229718	4.336832	-1.482822
42	1	0.876794	3.957010	0.220670
43	1	2.534827	3.770422	-0.414355

B_{II-cis}

HF = -1586.9918164 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.362740 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.683307 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	4.030081	-2.667923	0.471819
2	1	4.705289	-1.918158	0.892085
3	1	4.614053	-3.269020	-0.230575
4	1	3.680636	-3.313020	1.276999
5	6	2.898439	-1.992443	-0.237196
6	6	1.610213	-2.210729	0.137668
7	1	1.415258	-2.866135	0.980877
8	6	0.496513	-1.568492	-0.457637
9	1	0.641014	-1.057199	-1.402065
10	6	-0.789755	-1.634772	0.035910
11	1	-0.983680	-2.123255	0.982490
12	6	-1.813315	-0.991998	-0.651164
13	1	-1.585590	-0.532340	-1.608148
14	6	-3.553770	-1.351818	1.042672
15	6	-4.103305	-0.189160	-1.019856
16	6	-5.042257	-1.003203	1.015123
17	1	-3.368638	-2.420413	1.157377
18	1	-3.020231	-0.820454	1.834912
19	6	-5.118236	0.183876	0.051578
20	1	-3.680920	0.664376	-1.546025
21	1	-4.534190	-0.878404	-1.750865
22	1	-5.422176	-0.772823	2.008269
23	1	-5.615466	-1.843500	0.619403
24	1	-4.808449	1.102892	0.552837
25	1	-6.113356	0.334767	-0.362126
26	7	-3.056911	-0.880830	-0.255836
27	6	3.250355	-0.978037	-1.238307
28	1	2.562921	-0.888873	-2.075226
29	1	4.266093	-1.095465	-1.612110
30	6	-1.388168	2.455634	-1.318901

31	1	-2.302386	2.669260	-0.767572
32	1	-1.600881	1.787651	-2.155711
33	1	-0.977790	3.383167	-1.722915
34	8	-0.499036	1.867116	-0.385239
35	6	0.697823	1.432593	-0.893080
36	8	0.873734	1.424825	-2.110057
37	6	1.612795	0.977580	0.099026
38	16	3.263504	0.704575	-0.373089
39	16	1.180989	0.920872	1.812186
40	6	1.397717	2.654903	2.342107
41	1	1.147390	2.711716	3.402178
42	1	2.430568	2.970690	2.198829
43	1	0.728656	3.301595	1.776154

TS₂-I_{cis}

HF = -1586.990177 hartrees

Imaginary Frequencies: 1 (-199.4218 1/cm)

Zero-point correction = 0.362639 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.678628 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	3.928474	-2.924898	0.248809
2	1	4.528166	-2.413135	1.006961
3	1	4.621834	-3.312579	-0.502292
4	1	3.419294	-3.764548	0.720850
5	6	2.961507	-1.965025	-0.372623
6	6	1.625809	-2.134603	-0.266175
7	1	1.256104	-2.969666	0.321211
8	6	0.643941	-1.222425	-0.770743
9	1	0.869391	-0.682625	-1.681691
10	6	-0.714286	-1.389557	-0.428530
11	1	-0.961002	-2.076276	0.372675
12	6	-1.691950	-0.608054	-0.989453
13	1	-1.412569	0.124084	-1.740265
14	6	-3.558946	-1.502639	0.336227
15	6	-3.969996	0.289022	-1.250435
16	6	-5.054264	-1.188676	0.281587
17	1	-3.335814	-2.548339	0.114217
18	1	-3.127609	-1.266637	1.313858
19	6	-5.099739	0.254441	-0.227175
20	1	-3.534059	1.278403	-1.385652
21	1	-4.310161	-0.081247	-2.222626
22	1	-5.533828	-1.316414	1.250275
23	1	-5.548931	-1.851808	-0.430726
24	1	-4.885931	0.950761	0.586485
25	1	-6.060186	0.522454	-0.663827
26	7	-2.980391	-0.626312	-0.678865
27	6	3.519927	-0.726464	-0.943594
28	1	3.053047	-0.388661	-1.867610
29	1	4.598408	-0.771936	-1.081653
30	6	-1.462948	1.160909	2.220130

31	1	-2.401932	1.586162	1.871929
32	1	-1.121083	1.688706	3.111696
33	1	-1.595368	0.106896	2.466031
34	8	-0.546398	1.321121	1.147056
35	6	0.666926	0.738917	1.310726
36	8	0.954285	0.170950	2.349387
37	6	1.489113	0.825691	0.118283
38	16	3.215279	0.609346	0.332744
39	16	0.980643	1.844090	-1.256087
40	6	1.338388	3.525743	-0.658100
41	1	1.100724	4.218448	-1.465219
42	1	0.720687	3.752469	0.209517
43	1	2.393966	3.613842	-0.403749

TS₂-II_{cis}

HF = -1586.990187 hartrees

Imaginary Frequencies: 1 (-217.1535 1/cm)

Zero-point correction = 0.362476 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.679273 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	4.145215	-2.643770	0.390100
2	1	4.819976	-1.922078	0.859475
3	1	4.731136	-3.201685	-0.345059
4	1	3.794268	-3.336526	1.154485
5	6	3.011174	-1.924795	-0.270657
6	6	1.729497	-2.097185	0.119811
7	1	1.509861	-2.768178	0.944475
8	6	0.636386	-1.359315	-0.436836
9	1	0.742437	-0.989301	-1.449798
10	6	-0.674002	-1.484794	0.056529
11	1	-0.829055	-1.917690	1.036943
12	6	-1.732279	-0.981825	-0.659664
13	1	-1.546559	-0.576740	-1.650548
14	6	-3.440735	-1.320856	1.071659
15	6	-4.088709	-0.394531	-1.075653
16	6	-4.949171	-1.065247	1.045901
17	1	-3.195044	-2.365034	1.275846
18	1	-2.926940	-0.698361	1.810544
19	6	-5.116769	0.013288	-0.027967
20	1	-3.734629	0.435229	-1.686238
21	1	-4.487410	-1.168625	-1.738625
22	1	-5.327435	-0.760125	2.019730
23	1	-5.476657	-1.973429	0.747981
24	1	-4.863420	0.994933	0.377778
25	1	-6.125581	0.058819	-0.434446
26	7	-2.995993	-0.936141	-0.267094
27	6	3.345160	-0.874406	-1.246720
28	1	2.707352	-0.844126	-2.127001
29	1	4.387541	-0.904071	-1.559132
30	6	-1.518608	2.481620	-1.199192

31	1	-2.408112	2.685358	-0.607380
32	1	-1.761346	1.816983	-2.029042
33	1	-1.119914	3.411413	-1.607660
34	8	-0.587990	1.881477	-0.307831
35	6	0.557080	1.420304	-0.864098
36	8	0.725826	1.465091	-2.073058
37	6	1.465000	0.811117	0.088897
38	16	3.159229	0.783814	-0.375065
39	16	1.095415	0.842262	1.828866
40	6	1.391782	2.587061	2.267035
41	1	1.188728	2.693368	3.332767
42	1	2.428558	2.858759	2.071847
43	1	0.721089	3.234346	1.704147

5.5 Energies and coordinates for alternative pathways: path III-IV with *s-cis*-2b

Figure S4: Energy profiles for pathways III_c-IV_c: the formal cycloaddition of **A** and *s-cis*-2b (initial attack at carbon). Reported values in plain text are wB97xd/tzvp free energies in solvent (IEFPCM, CHCl₃), relative to **A** + 2b.

TS-III_{cis}

HF = -1586.9732948 hartrees

Imaginary Frequencies: 1 (-450.3694 1/cm)

Zero-point correction = 0.361250 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.665772 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	2.313975	-2.837829	-0.954549
2	1	2.456435	-3.038244	0.111012
3	1	3.292419	-2.669171	-1.404138
4	1	1.875471	-3.731344	-1.402457
5	6	1.408390	-1.650541	-1.136578
6	6	0.062292	-1.800201	-0.770380
7	1	-0.232727	-2.758541	-0.351777
8	6	-0.904253	-0.817550	-0.845315
9	1	-0.664958	0.114002	-1.346551
10	6	-2.234464	-0.970067	-0.403419
11	1	-2.518243	-1.885688	0.101756
12	6	-3.143122	0.041840	-0.571564
13	1	-2.822833	0.957762	-1.060040
14	6	-5.041873	-1.074535	0.524345
15	6	-5.329497	1.163145	-0.372111
16	6	-6.504867	-0.647296	0.648501
17	1	-4.918383	-2.005154	-0.033874
18	1	-4.567664	-1.201430	1.502878
19	6	-6.433098	0.881709	0.641528
20	1	-4.814769	2.108377	-0.200838
21	1	-5.724889	1.160273	-1.392920
22	1	-6.973027	-1.050232	1.544617
23	1	-7.070199	-0.998723	-0.216893
24	1	-6.137737	1.252330	1.625214
25	1	-7.375528	1.352348	0.366949
26	7	-4.412468	0.037979	-0.182328
27	6	1.956771	-0.427976	-1.496993
28	1	1.319300	0.362224	-1.867315
29	1	2.974721	-0.401247	-1.862612
30	6	5.437704	-1.021996	0.828462

31	1	6.339954	-0.753445	0.286612
32	1	5.158110	-2.053304	0.612611
33	1	5.591320	-0.905663	1.900863
34	8	4.428390	-0.122851	0.366888
35	6	3.211852	-0.269031	0.903471
36	8	2.956575	-1.100256	1.734456
37	6	2.216228	0.716766	0.326705
38	16	0.708458	0.847555	1.070221
39	16	3.056769	2.147064	-0.408629
40	6	1.673264	3.259030	-0.747830
41	1	2.116748	4.140157	-1.210894
42	1	0.964397	2.804087	-1.438902
43	1	1.160193	3.532917	0.171129

TS-IV_{cis}

HF = -1586.973058 hartrees

Imaginary Frequencies: 1 (-420.3331 1/cm)

Zero-point correction = 0.360762 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1586.666245 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-2.150779	2.886923	-1.420982
2	1	-2.376065	3.146132	-2.458772
3	1	-1.632492	3.732244	-0.967607
4	1	-3.103137	2.739251	-0.907566
5	6	-1.329180	1.626982	-1.370452
6	6	0.034510	1.724154	-1.055871
7	1	0.424104	2.712170	-0.827198
8	6	0.914043	0.661680	-0.965757
9	1	0.577533	-0.320979	-1.276660
10	6	2.267972	0.773761	-0.590491
11	1	2.652808	1.740160	-0.286615
12	6	3.073379	-0.335450	-0.565398
13	1	2.649708	-1.296539	-0.842547
14	6	5.115073	0.798881	0.204979
15	6	5.157553	-1.597503	-0.190520
16	6	6.542779	0.272398	0.354795
17	1	5.034215	1.594419	-0.539071
18	1	4.714859	1.177495	1.151175
19	6	6.347524	-1.210209	0.680857
20	1	4.577585	-2.427158	0.213015
21	1	5.480074	-1.856035	-1.204081
22	1	7.098400	0.809358	1.121445
23	1	7.078456	0.379970	-0.590377
24	1	6.094291	-1.336957	1.735294
25	1	7.228592	-1.812569	0.466199
26	7	4.353304	-0.373932	-0.215343
27	6	-1.977145	0.411885	-1.533816
28	1	-1.415840	-0.471129	-1.804051
29	1	-3.011405	0.426706	-1.858845
30	6	-4.960754	-2.510604	-0.701614

31	1	-6.010049	-2.247429	-0.605720
32	1	-4.753273	-3.439965	-0.172283
33	1	-4.692085	-2.624476	-1.751822
34	8	-4.236344	-1.427200	-0.115916
35	6	-2.906832	-1.547336	-0.083507
36	8	-2.322869	-2.510134	-0.508536
37	6	-2.249266	-0.327281	0.530932
38	16	-0.712797	-0.508243	1.197847
39	16	-3.466447	0.809697	1.242918
40	6	-2.399999	2.016450	2.067272
41	1	-1.877518	1.565476	2.907392
42	1	-1.675587	2.431249	1.369572
43	1	-3.067959	2.803152	2.417347

5.6 Energies and coordinates: Figure 7 in the manuscript

Figure S5: Activation energies for the addition of **A** to thiocarbonyls **E**, **F**, **G** via the two possible pathways (initial attack at sulfur, S-attack pathway; or, initial attack at carbon, C-attack pathway). Reported values in plain text are wB97xd/tzvp free energies in solvent (IEFPCM, CHCl₃). Values in italics are bond distances in Ångström.

TS-E_{C-attack}

HF = -921.5777942 hartrees

Imaginary Frequencies: 1 (-342.8046 1/cm)

Zero-point correction = 0.287179 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -921.335968 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-4.253381	-1.883085	-0.488239
2	1	-4.236485	-1.557099	-1.532800
3	1	-5.263675	-1.750423	-0.102509
4	1	-4.015519	-2.948980	-0.481156
5	6	-3.243083	-1.103584	0.308941
6	6	-1.878714	-1.295103	-0.042063
7	1	-1.674068	-2.032227	-0.813982
8	6	-0.820421	-0.584990	0.451876
9	1	-0.997812	0.137085	1.242947
10	6	0.532411	-0.755697	0.053155
11	1	0.757838	-1.471944	-0.728683
12	6	1.526799	-0.009850	0.615488
13	1	1.270413	0.714696	1.383356
14	6	3.380666	-0.926308	-0.718173
15	6	3.841686	0.789705	0.934603
16	6	4.888945	-0.694564	-0.618500
17	1	3.103113	-1.967853	-0.537461
18	1	2.984376	-0.638093	-1.698101
19	6	4.998642	0.725712	-0.057393
20	1	3.457985	1.799155	1.084592
21	1	4.136364	0.381404	1.907310
22	1	5.386562	-0.814869	-1.579183
23	1	5.328490	-1.407369	0.082222
24	1	4.847689	1.459732	-0.851596
25	1	5.959602	0.924205	0.414419
26	7	2.825897	-0.057343	0.312034
27	6	-3.675276	-0.157269	1.199366
28	1	-2.994050	0.312932	1.895293
29	1	-4.724679	-0.112363	1.463030
30	6	-3.656952	1.663167	-0.119320

31	16	-2.157259	1.955660	-0.780199
32	1	-3.977235	2.195595	0.770174
33	1	-4.461970	1.278449	-0.737378

TS-E_{s-attack}

HF = -921.5684276 hartrees

Imaginary Frequencies: 1 (-394.0095 1/cm)

Zero-point correction = 0.287789 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -921.324139 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-4.288460	-1.891229	-0.293162
2	1	-3.909570	-2.900899	-0.457891
3	1	-4.541025	-1.468846	-1.270659
4	1	-5.208532	-1.959864	0.287693
5	6	-3.257538	-1.030932	0.391755
6	6	-1.909324	-1.240126	0.090483
7	1	-1.667942	-2.063662	-0.577251
8	6	-0.873970	-0.379624	0.428058
9	1	-1.027092	0.314987	1.246408
10	6	0.493745	-0.609428	0.046889
11	1	0.692023	-1.356652	-0.713282
12	6	1.511172	0.104678	0.591143
13	1	1.286029	0.853744	1.345912
14	6	3.332126	-0.920023	-0.711002
15	6	3.867783	0.785790	0.926231
16	6	4.850662	-0.764026	-0.604525
17	1	3.002880	-1.943872	-0.510899
18	1	2.957404	-0.638703	-1.702404
19	6	5.030181	0.652888	-0.052855
20	1	3.543601	1.817763	1.068036
21	1	4.130958	0.369211	1.905373
22	1	5.348054	-0.917130	-1.560810
23	1	5.249412	-1.492507	0.104505
24	1	4.925344	1.387737	-0.853895
25	1	5.996337	0.804594	0.426060
26	7	2.816275	-0.002855	0.293002
27	6	-3.662712	0.095268	1.089495
28	1	-3.008071	0.568325	1.807086
29	1	-4.719841	0.255698	1.266312
30	6	-1.615465	1.427348	-0.851083

31	16	-3.215997	1.755149	-0.501532
32	1	-0.824665	1.984249	-0.363225
33	1	-1.352488	0.939925	-1.782135

TS-F_{C-attack}

HF = -1359.0892375 hartrees

Imaginary Frequencies: 1 (-508.9094 1/cm)

Zero-point correction = 0.317831 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1358.820413 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.014222	3.194538	0.043365
2	1	-3.150245	3.080945	1.124299
3	1	-4.000238	3.247619	-0.417237
4	1	-2.499272	4.142849	-0.118034
5	6	-2.210167	2.038309	-0.483061
6	6	-0.821299	2.056967	-0.235251
7	1	-0.420014	2.934328	0.264586
8	6	0.045932	1.026662	-0.502424
9	1	-0.326860	0.156008	-1.031948
10	6	1.425578	1.026959	-0.192912
11	1	1.844775	1.877211	0.332457
12	6	2.213085	-0.041841	-0.523697
13	1	1.761018	-0.889815	-1.030524
14	6	4.312902	0.832519	0.412693
15	6	4.300635	-1.350410	-0.651000
16	6	5.740514	0.293473	0.317910
17	1	4.197446	1.808212	-0.065099
18	1	3.975570	0.922940	1.450627
19	6	5.547276	-1.221949	0.218093
20	1	3.736798	-2.264084	-0.462216
21	1	4.556823	-1.312332	-1.714891
22	1	6.348267	0.591491	1.170448
23	1	6.220334	0.669741	-0.587706
24	1	5.357325	-1.645988	1.206080
25	1	6.405991	-1.732809	-0.214159
26	7	3.514111	-0.174545	-0.277697
27	6	-2.875478	0.945064	-1.000510
28	1	-2.337383	0.189542	-1.556474
29	1	-3.918848	1.052545	-1.266659
30	6	-3.177973	-0.368149	0.680860

31	16	-1.715258	-0.609777	1.483865
32	16	-4.095072	-1.666226	-0.149367
33	6	-2.793467	-2.821001	-0.643195
34	1	-3.295871	-3.652087	-1.135884
35	1	-2.102503	-2.349596	-1.341679
36	1	-2.247741	-3.175231	0.228469
37	1	-3.898778	0.319515	1.112233

TS-F_{s-attack}

HF = -1359.0816983 hartrees

Imaginary Frequencies: 1 (-366.4687 1/cm)

Zero-point correction = 0.316898 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1358.812975 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-4.071460	-2.601075	-0.088985
2	1	-3.613700	-3.544166	-0.388482
3	1	-4.567749	-2.174260	-0.967056
4	1	-4.844421	-2.813845	0.652099
5	6	-3.047351	-1.635144	0.441675
6	6	-1.699158	-1.871850	0.219864
7	1	-1.425572	-2.786617	-0.299992
8	6	-0.679048	-0.964680	0.491130
9	1	-0.879261	-0.160608	1.188557
10	6	0.687553	-1.181736	0.164604
11	1	0.936269	-1.991474	-0.512484
12	6	1.663924	-0.356591	0.639476
13	1	1.392289	0.439513	1.324184
14	6	3.534543	-1.353029	-0.612994
15	6	3.955729	0.537946	0.845883
16	6	5.032908	-1.048871	-0.580742
17	1	3.310158	-2.386002	-0.334087
18	1	3.101050	-1.173294	-1.604165
19	6	5.088140	0.424998	-0.170569
20	1	3.523224	1.538199	0.897554
21	1	4.298372	0.257610	1.848164
22	1	5.512602	-1.244470	-1.538297
23	1	5.522592	-1.666143	0.175364
24	1	4.878615	1.064008	-1.031008
25	1	6.050844	0.716497	0.246622
26	7	2.970340	-0.418630	0.349897
27	6	-3.490772	-0.382622	0.905978
28	1	-2.885568	0.169464	1.612606
29	1	-4.556030	-0.257190	1.071765
30	6	-1.507571	0.909101	-0.999504

31	16	-3.173615	0.913186	-0.799158
32	16	-0.388348	2.188296	-0.475315
33	6	-1.202757	2.852614	1.000509
34	1	-0.655661	3.749794	1.284395
35	1	-2.237082	3.108304	0.775863
36	1	-1.172463	2.137822	1.822668
37	1	-1.077556	0.349190	-1.819935

TS-G_{C-attack}

HF = -1149.4690305 hartrees

Imaginary Frequencies: 1 (-283.2636 1/cm)

Zero-point correction = 0.332005 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1149.187018 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.008782	2.397982	0.019697
2	1	-2.980669	2.221434	1.096455
3	1	-4.014172	2.184527	-0.344035
4	1	-2.810504	3.460358	-0.143824
5	6	-1.976122	1.561322	-0.687441
6	6	-0.677014	1.529373	-0.125878
7	1	-0.530444	2.080365	0.799078
8	6	0.397403	0.832368	-0.622172
9	1	0.297441	0.333334	-1.580668
10	6	1.684383	0.799224	-0.030190
11	1	1.834567	1.295501	0.921504
12	6	2.710016	0.126440	-0.632265
13	1	2.522820	-0.384117	-1.572790
14	6	4.429601	0.609185	1.062072
15	6	5.006369	-0.741439	-0.871010
16	6	5.933762	0.332945	1.051232
17	1	4.196996	1.676512	1.088416
18	1	3.932195	0.133981	1.914336
19	6	6.056156	-0.944179	0.216582
20	1	4.608535	-1.676131	-1.266774
21	1	5.411073	-0.155722	-1.702995
22	1	6.339521	0.227374	2.055820
23	1	6.458553	1.153956	0.558423
24	1	5.801045	-1.817068	0.821070
25	1	7.053012	-1.091899	-0.195445
26	7	3.958106	0.010881	-0.181797
27	6	-2.350446	0.783836	-1.754499
28	1	-1.615186	0.328534	-2.402877
29	1	-3.348433	0.873839	-2.164909
30	6	-4.778473	-0.160584	1.967437

31	1	-4.435008	0.100367	2.964391
32	1	-5.483586	-0.990056	2.013739
33	1	-5.262260	0.696479	1.497822
34	8	-3.606721	-0.532939	1.241992
35	6	-3.793335	-0.917715	-0.017372
36	8	-4.884384	-0.985464	-0.538783
37	6	-2.533899	-1.268141	-0.740241
38	16	-1.100196	-1.662385	0.000961
39	1	-2.747965	-1.626046	-1.740914

TS-G_{S-attack}

HF = -1149.4717753 hartrees

Imaginary Frequencies: 1 (-166.5992 1/cm)

Zero-point correction = 0.331601 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1149.189462 hartrees

Coordinates:

Center	Atomic	Coordinates (Angstroms)		
Number	Number	X	Y	Z

1	6	-3.856250	-0.843911	-1.823486
2	1	-3.607849	-0.965385	-2.879737
3	1	-3.954521	0.226855	-1.626337
4	1	-4.820300	-1.315945	-1.637379
5	6	-2.774598	-1.417815	-0.949041
6	6	-1.445677	-1.028991	-1.243594
7	1	-1.304344	-0.406717	-2.123400
8	6	-0.340356	-1.285026	-0.470735
9	1	-0.447199	-1.928412	0.397663
10	6	0.961048	-0.807720	-0.744739
11	1	1.110502	-0.167968	-1.606335
12	6	1.996190	-1.069919	0.109530
13	1	1.814220	-1.691583	0.981817
14	6	3.685518	0.276544	-1.062432
15	6	4.299881	-0.893760	0.974075
16	6	5.183511	0.436578	-0.803787
17	1	3.470146	-0.151099	-2.044301
18	1	3.150710	1.228707	-0.980961
19	6	5.311215	0.216172	0.705991
20	1	3.896664	-0.874305	1.986639
21	1	4.741221	-1.879311	0.793388
22	1	5.553671	1.408003	-1.126738
23	1	5.739254	-0.333611	-1.342664
24	1	5.021694	1.120424	1.244965
25	1	6.318785	-0.059025	1.013358
26	7	3.244053	-0.622634	-0.001561
27	6	-3.115572	-2.133372	0.173659
28	1	-2.381617	-2.699159	0.729442
29	1	-4.147218	-2.422793	0.330426
30	6	-1.962156	3.028073	-0.959248

31	1	-2.898238	3.253860	-1.463340
32	1	-1.206665	2.729409	-1.687805
33	1	-1.606565	3.904803	-0.417236
34	8	-2.251806	1.956815	-0.068881
35	6	-1.226441	1.516499	0.677204
36	8	-0.127525	2.037105	0.649051
37	6	-1.541574	0.368303	1.531137
38	16	-3.030586	-0.295573	1.754990
39	1	-0.675121	-0.010434	2.061060

5.7 Facial shielding provided by catalyst 3: Structures and energies

Figure S6: Energy profiles for the favored and the dis-favored approach of dithioester **2b** to the catalyst-bound trienamine **SM**. Reported values in plain text are wB97xd/cc-pVDZ/IEFPCM//wB97xd/6-31G(d)/IEFPCM free energies. R = -C(Ph)₂OTMS.

Difference in activation energies with different methods

Method	$\Delta\Delta G^\ddagger_{(TS1-DF-TS1-F)}$
wB97xd/6-31G(d) in CHCl ₃	1.6
wB97xd/tzvp//wB97xd/6-31G(d) in CHCl ₃	1.6
M062X/tzvp//wB97xd/6-31G(d) in CHCl ₃	1.8
wB97xd/cc-pVDZ//wB97xd/6-31G(d) in CHCl₃	1.4
wB97xd/cc-pVTZ//wB97xd/6-31G(d) in CHCl ₃	1.6
wB97xd/cc-pVQZ//wB97xd/6-31G(d) in CHCl ₃	1.7

* All values are free energies at 298.15 K.

Experimental result: When dithioester **2b** is reacted with dienal **1a** at 25 °C in the presence of catalyst **3** (20 mol%) and PhCO₂H (20 mol%) in CHCl₃, the desired cycloadduct was formed in 84% yield, 79:21 dr and 79% ee.

TS₁-F

HF = -2571.8061396 hartrees

Imaginary Frequencies: 1 (-246.7239 1/cm)

Zero-point correction = 0.665721 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy= 0.591201

Sum of electronic and thermal Free Energies = -2571.214939 hartrees

Single Point Energy (wB97xd/cc-pVDZ in chloroform)

HF = -2571.937123 hartrees

Single Point Energy (wB97xd/cc-pVTZ in chloroform)

HF = -2572.397864 hartrees

Single Point Energy (wB97xd/cc-pVQZ in chloroform)

HF = -2572.525082 hartrees

Single Point Energy (wB97xd/tzvp in chloroform)

HF = -2572.33557 hartrees

Single Point Energy (M062x/tzvp in chloroform)

HF = -2572.132897 hartrees

Coordinates:

6	-3.931955000	0.873385000	-1.765165000
6	-5.061222000	0.062160000	-1.984925000
6	-5.057787000	-1.315105000	-1.758247000
6	-2.705644000	0.416808000	-1.318334000
6	-1.641236000	1.224577000	-0.877041000
6	-0.539087000	0.619670000	-0.318703000
7	0.437108000	1.219162000	0.364428000
6	1.529654000	0.473905000	0.982295000
6	1.899619000	1.348101000	2.193088000
6	1.478884000	2.777211000	1.812538000
6	0.307132000	2.593272000	0.844027000
1	-4.071421000	1.951218000	-1.842585000
1	-5.940641000	-1.888688000	-2.028904000
1	-1.764021000	2.303211000	-0.845278000
1	-0.442226000	-0.455281000	-0.402342000
1	1.130976000	-0.494915000	1.299197000
1	2.959940000	1.285254000	2.446919000
1	1.328377000	1.002819000	3.060116000
1	2.300019000	3.299680000	1.317418000
1	1.186401000	3.360390000	2.688513000
1	0.348687000	3.299939000	0.008304000
1	-0.668970000	2.690109000	1.335680000
6	2.686116000	0.176774000	-0.034239000
8	2.100135000	-0.471164000	-1.150804000
14	1.734168000	-2.072373000	-1.511727000
6	3.235727000	-3.042000000	-2.083243000
1	2.904345000	-3.962552000	-2.579384000
1	3.887844000	-3.319626000	-1.249778000
1	3.830521000	-2.467817000	-2.801797000
6	0.516714000	-1.904773000	-2.928797000
1	-0.338043000	-1.275784000	-2.657118000
1	0.134543000	-2.886366000	-3.232116000
1	0.997996000	-1.448042000	-3.800601000
6	0.941251000	-2.975585000	-0.064482000

1	0.686682000	-3.995352000	-0.379319000
1	0.018393000	-2.498445000	0.284388000
1	1.627483000	-3.054815000	0.785489000
6	3.773146000	-0.719947000	0.571594000
6	4.932017000	-0.951689000	-0.179134000
6	3.640388000	-1.373260000	1.798067000
6	5.924895000	-1.808291000	0.278207000
1	5.049103000	-0.457164000	-1.138825000
6	4.633035000	-2.236943000	2.259487000
1	2.762653000	-1.225043000	2.417578000
6	5.777487000	-2.458051000	1.502746000
1	6.813609000	-1.972647000	-0.323572000
1	4.505444000	-2.733940000	3.216303000
1	6.550184000	-3.130770000	1.862208000
6	3.260464000	1.502251000	-0.539977000
6	4.346166000	2.121636000	0.083934000
6	2.629416000	2.161066000	-1.597815000
6	4.781936000	3.378185000	-0.328141000
1	4.859230000	1.623318000	0.900823000
6	3.062279000	3.417959000	-2.009276000
1	1.793433000	1.681541000	-2.094249000
6	4.137636000	4.033918000	-1.373552000
1	5.628487000	3.842458000	0.169024000
1	2.558547000	3.916077000	-2.832716000
1	4.476476000	5.014048000	-1.696007000
1	-2.537448000	-0.657353000	-1.272844000
1	-4.130616000	-1.877090000	-1.801984000
6	-6.375138000	0.756365000	-2.239489000
1	-6.252301000	1.592266000	-2.935701000
1	-6.762892000	1.164311000	-1.297512000
1	-7.126104000	0.073474000	-2.645407000
6	-4.849921000	2.840723000	1.443574000
1	-5.821208000	3.257643000	1.177774000
1	-4.615244000	3.063504000	2.487513000
1	-4.070516000	3.265266000	0.803246000
8	-4.961124000	1.439491000	1.230066000
6	-3.854745000	0.730909000	1.517461000
8	-2.866330000	1.234803000	2.031810000
6	-3.939349000	-0.694717000	1.170186000
16	-5.282652000	-1.413436000	0.521324000
16	-2.424752000	-1.522509000	1.629198000
6	-2.785451000	-3.240217000	1.201196000
1	-3.647797000	-3.613819000	1.758228000
1	-1.895265000	-3.811579000	1.477436000
1	-2.970317000	-3.360057000	0.131122000

TS₁-DF

HF = -2571.8049342 hartrees

Imaginary Frequencies: 1 (-251.5466 1/cm)

Zero-point correction = 0.665684 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy= 0.592512

Sum of electronic and thermal Free Energies = -2571.212422 hartrees

Single Point Energy (wB97xd/cc-pVDZ in chloroform)

HF = -2571.936166 hartrees

Single Point Energy (wB97xd/cc-pVTZ in chloroform)

HF = -2572.396602 hartrees

Single Point Energy (wB97xd/cc-pVQZ in chloroform)

HF = -2572.523673 hartrees

Single Point Energy (wB97xd/tzvp in chloroform)

HF = -2572.334345 hartrees

Single Point Energy (M062x/tzvp in chloroform)

HF = -2572.131352 hartrees

Coordinates:

6	-4.011155000	0.379841000	2.009220000
6	-5.073966000	-0.535115000	1.935974000
6	-4.912478000	-1.846423000	1.467231000
6	-2.675239000	0.094823000	1.779287000
6	-1.657105000	1.063530000	1.724884000
6	-0.330492000	0.695443000	1.651996000
7	0.698580000	1.540506000	1.541316000
6	2.113953000	1.153435000	1.615348000
6	2.829975000	2.497908000	1.824070000
6	1.890995000	3.565818000	1.244096000
6	0.491275000	2.982595000	1.432306000
1	-4.268138000	1.420883000	2.203655000
1	-5.751831000	-2.532041000	1.558733000
1	-1.939276000	2.112022000	1.734413000
1	-0.057391000	-0.353575000	1.686339000
1	2.232815000	0.499520000	2.482913000
1	3.817577000	2.513372000	1.358190000
1	2.972420000	2.659937000	2.896977000
1	2.091884000	3.720751000	0.182661000
1	1.999953000	4.526557000	1.752091000
1	-0.175348000	3.193919000	0.589182000
1	0.012916000	3.352534000	2.348850000
6	2.576123000	0.308905000	0.376969000
8	1.795272000	-0.867795000	0.492744000
14	1.891947000	-2.446872000	-0.076737000
6	1.793890000	-2.486963000	-1.949953000
1	1.750874000	-3.522634000	-2.308340000
1	2.666087000	-2.010863000	-2.410617000

1	0.902273000	-1.962099000	-2.309993000
6	0.387357000	-3.236634000	0.717007000
1	-0.510204000	-2.637138000	0.532436000
1	0.527609000	-3.324850000	1.800470000
1	0.212711000	-4.242818000	0.318452000
6	3.417178000	-3.356540000	0.535926000
1	3.281321000	-4.432095000	0.366347000
1	3.552356000	-3.202696000	1.612154000
1	4.338038000	-3.045761000	0.034994000
6	4.061835000	-0.072785000	0.465122000
6	4.763403000	-0.424187000	-0.693506000
6	4.714420000	-0.215068000	1.692916000
6	6.072061000	-0.891495000	-0.630905000
1	4.281323000	-0.332426000	-1.661087000
6	6.024137000	-0.682199000	1.760997000
1	4.210382000	0.032006000	2.620894000
6	6.709359000	-1.023476000	0.599364000
1	6.590983000	-1.155340000	-1.547545000
1	6.506757000	-0.782202000	2.728489000
1	7.730057000	-1.389826000	0.652772000
6	2.230232000	1.075597000	-0.902118000
6	3.109526000	2.006796000	-1.465562000
6	0.957594000	0.943698000	-1.456385000
6	2.726052000	2.775504000	-2.560555000
1	4.102833000	2.140649000	-1.048145000
6	0.567136000	1.714794000	-2.547318000
1	0.255738000	0.239328000	-1.027705000
6	1.451618000	2.633017000	-3.105057000
1	3.426082000	3.489726000	-2.984507000
1	-0.439341000	1.598267000	-2.935952000
1	1.151243000	3.236405000	-3.956836000
1	-2.369381000	-0.942982000	1.658856000
1	-3.941696000	-2.329099000	1.529955000
6	-6.468627000	0.005207000	2.118069000
1	-6.500631000	0.763617000	2.906272000
1	-7.185317000	-0.783277000	2.362951000
1	-6.795477000	0.481992000	1.185018000
6	-4.789195000	2.830723000	-0.779138000
1	-5.824027000	3.118911000	-0.593493000
1	-4.152982000	3.159322000	0.049069000
1	-4.428009000	3.286549000	-1.704442000
8	-4.796216000	1.413547000	-0.871089000
6	-3.595493000	0.852171000	-1.123719000

8	-2.604981000	1.523008000	-1.380723000
6	-3.596339000	-0.611632000	-1.074251000
16	-4.936765000	-1.525716000	-0.730522000
16	-1.979892000	-1.255828000	-1.479589000
6	-2.298067000	-3.025841000	-1.644048000
1	-2.624181000	-3.471544000	-0.701476000
1	-1.345202000	-3.473560000	-1.939401000
1	-3.048995000	-3.220824000	-2.413765000

Int_r

HF = -2571.8144595 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.667544 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy= 0.593623

Sum of electronic and thermal Free Energies = -2571.220836 hartrees

Single Point Energy (wb97xd/cc-pVDZ in chloroform)

HF = -2571.9442719 hartrees

Coordinates:

6	-4.103634000	0.054342000	2.127231000
6	-5.157171000	-0.768958000	1.867713000
6	-5.012733000	-1.977613000	1.041275000
6	-2.748237000	-0.204720000	1.773328000
6	-1.766495000	0.772340000	1.822947000
6	-0.418394000	0.454572000	1.670866000
7	0.557390000	1.345115000	1.607025000
6	1.998079000	1.029181000	1.670174000
6	2.638000000	2.399477000	1.945875000
6	1.648858000	3.438196000	1.399804000
6	0.281936000	2.785799000	1.585955000
1	-4.307767000	1.025243000	2.576006000
1	-5.867556000	-2.653162000	1.122293000
1	-2.068821000	1.805358000	1.960041000
1	-0.105417000	-0.582338000	1.607589000
1	2.137265000	0.345001000	2.509673000
1	3.627536000	2.486822000	1.492990000
1	2.760483000	2.523805000	3.026295000
1	1.832730000	3.627808000	0.341014000
1	1.716208000	4.389277000	1.932069000
1	-0.418717000	3.002445000	0.773859000
1	-0.181729000	3.076523000	2.536611000
6	2.518093000	0.268376000	0.402450000
8	1.797968000	-0.950909000	0.446597000
14	2.035721000	-2.498551000	-0.177608000
6	1.993227000	-2.448185000	-2.051991000
1	1.967444000	-3.463170000	-2.465573000
1	2.868947000	-1.938916000	-2.467668000
1	1.101895000	-1.913759000	-2.396998000
6	0.590715000	-3.455640000	0.531896000

1	-0.369503000	-3.009253000	0.258170000
1	0.659573000	-3.493172000	1.625562000
1	0.600071000	-4.488278000	0.163191000
6	3.605976000	-3.317902000	0.451479000
1	3.542836000	-4.394928000	0.251337000
1	3.702960000	-3.186095000	1.534801000
1	4.518029000	-2.937112000	-0.014878000
6	4.022595000	-0.033333000	0.513342000
6	4.770497000	-0.290936000	-0.641279000
6	4.656446000	-0.189359000	1.749277000
6	6.104411000	-0.677561000	-0.566585000
1	4.306304000	-0.188505000	-1.616289000
6	5.991348000	-0.576649000	1.829571000
1	4.120397000	-0.014623000	2.675695000
6	6.722352000	-0.822428000	0.671967000
1	6.657644000	-0.868877000	-1.481075000
1	6.458064000	-0.688172000	2.803553000
1	7.763603000	-1.123401000	0.734925000
6	2.164531000	1.081928000	-0.847228000
6	3.022785000	2.072573000	-1.340993000
6	0.907131000	0.938312000	-1.434576000
6	2.638571000	2.886852000	-2.401302000
1	4.001056000	2.219347000	-0.894284000
6	0.515821000	1.762328000	-2.487154000
1	0.205592000	0.196604000	-1.068219000
6	1.379749000	2.735304000	-2.978148000
1	3.324198000	3.644239000	-2.770207000
1	-0.485798000	1.651917000	-2.887956000
1	1.073821000	3.377950000	-3.798672000
1	-2.441390000	-1.228380000	1.573346000
1	-4.091721000	-2.540804000	1.199812000
6	-6.555822000	-0.365089000	2.234414000
1	-6.582303000	0.598388000	2.749820000
1	-7.020633000	-1.119701000	2.880244000
1	-7.171308000	-0.290170000	1.329455000
6	-4.564143000	2.904641000	-0.658529000
1	-5.588975000	3.237129000	-0.484662000
1	-3.919422000	3.250007000	0.156855000
1	-4.188373000	3.323462000	-1.596573000
8	-4.620063000	1.490708000	-0.704487000
6	-3.427598000	0.873235000	-0.962081000
8	-2.424241000	1.543430000	-1.198811000
6	-3.494837000	-0.562790000	-0.896832000

16	-4.998894000	-1.410715000	-0.767238000
16	-2.028521000	-1.469013000	-1.254719000
6	-1.970040000	-1.473385000	-3.074526000
1	-2.869592000	-1.940085000	-3.484838000
1	-1.093592000	-2.050672000	-3.384434000
1	-1.878624000	-0.451473000	-3.450653000

Int_{DF}

HF = -2571.8112075 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.666999 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy= 0.592584

Sum of electronic and thermal Free Energies = -2571.218624 hartrees

Single Point Energy (wb97xd/cc-pVDZ in chloroform)

HF = -2571.941388 hartrees

Coordinates:

6	-4.103634000	0.054342000	2.127231000
6	-5.157171000	-0.768958000	1.867713000
6	-5.012733000	-1.977613000	1.041275000
6	-2.748237000	-0.204720000	1.773328000
6	-1.766495000	0.772340000	1.822947000
6	-0.418394000	0.454572000	1.670866000
7	0.557390000	1.345115000	1.607025000
6	1.998079000	1.029181000	1.670174000
6	2.638000000	2.399477000	1.945875000
6	1.648858000	3.438196000	1.399804000
6	0.281936000	2.785799000	1.585955000
1	-4.307767000	1.025243000	2.576006000
1	-5.867556000	-2.653162000	1.122293000
1	-2.068821000	1.805358000	1.960041000
1	-0.105417000	-0.582338000	1.607589000
1	2.137265000	0.345001000	2.509673000
1	3.627536000	2.486822000	1.492990000
1	2.760483000	2.523805000	3.026295000
1	1.832730000	3.627808000	0.341014000
1	1.716208000	4.389277000	1.932069000
1	-0.418717000	3.002445000	0.773859000
1	-0.181729000	3.076523000	2.536611000
6	2.518093000	0.268376000	0.402450000
8	1.797968000	-0.950909000	0.446597000
14	2.035721000	-2.498551000	-0.177608000
6	1.993227000	-2.448185000	-2.051991000
1	1.967444000	-3.463170000	-2.465573000
1	2.868947000	-1.938916000	-2.467668000
1	1.101895000	-1.913759000	-2.396998000
6	0.590715000	-3.455640000	0.531896000
1	-0.369503000	-3.009253000	0.258170000

1	0.659573000	-3.493172000	1.625562000
1	0.600071000	-4.488278000	0.163191000
6	3.605976000	-3.317902000	0.451479000
1	3.542836000	-4.394928000	0.251337000
1	3.702960000	-3.186095000	1.534801000
1	4.518029000	-2.937112000	-0.014878000
6	4.022595000	-0.033333000	0.513342000
6	4.770497000	-0.290936000	-0.641279000
6	4.656446000	-0.189359000	1.749277000
6	6.104411000	-0.677561000	-0.566585000
1	4.306304000	-0.188505000	-1.616289000
6	5.991348000	-0.576649000	1.829571000
1	4.120397000	-0.014623000	2.675695000
6	6.722352000	-0.822428000	0.671967000
1	6.657644000	-0.868877000	-1.481075000
1	6.458064000	-0.688172000	2.803553000
1	7.763603000	-1.123401000	0.734925000
6	2.164531000	1.081928000	-0.847228000
6	3.022785000	2.072573000	-1.340993000
6	0.907131000	0.938312000	-1.434576000
6	2.638571000	2.886852000	-2.401302000
1	4.001056000	2.219347000	-0.894284000
6	0.515821000	1.762328000	-2.487154000
1	0.205592000	0.196604000	-1.068219000
6	1.379749000	2.735304000	-2.978148000
1	3.324198000	3.644239000	-2.770207000
1	-0.485798000	1.651917000	-2.887956000
1	1.073821000	3.377950000	-3.798672000
1	-2.441390000	-1.228380000	1.573346000
1	-4.091721000	-2.540804000	1.199812000
6	-6.555822000	-0.365089000	2.234414000
1	-6.582303000	0.598388000	2.749820000
1	-7.020633000	-1.119701000	2.880244000
1	-7.171308000	-0.290170000	1.329455000
6	-4.564143000	2.904641000	-0.658529000
1	-5.588975000	3.237129000	-0.484662000
1	-3.919422000	3.250007000	0.156855000
1	-4.188373000	3.323462000	-1.596573000
8	-4.620063000	1.490708000	-0.704487000
6	-3.427598000	0.873235000	-0.962081000
8	-2.424241000	1.543430000	-1.198811000
6	-3.494837000	-0.562790000	-0.896832000
16	-4.998894000	-1.410715000	-0.767238000

16	-2.028521000	-1.469013000	-1.254719000
6	-1.970040000	-1.473385000	-3.074526000
1	-2.869592000	-1.940085000	-3.484838000
1	-1.093592000	-2.050672000	-3.384434000
1	-1.878624000	-0.451473000	-3.450653000

TS₂-F

HF = -2571.8126535 hartrees

Imaginary Frequencies: 1 (-198.5659 1/cm)

Zero-point correction = 0.666571 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy= 0.591921

Sum of electronic and thermal Free Energies = -2571.220732 hartrees

Single Point Energy (wb97xd/cc-pVDZ in chloroform)

HF = -2571.942338 hartrees

Coordinates:

6	-3.847451000	0.818342000	-1.854438000
6	-4.994754000	0.164836000	-2.152483000
6	-5.217606000	-1.216741000	-1.671218000
6	-2.731979000	0.226445000	-1.164354000
6	-1.677545000	1.018981000	-0.674576000
6	-0.549563000	0.427854000	-0.149102000
7	0.404772000	1.043788000	0.542406000
6	1.587002000	0.359626000	1.059585000
6	1.977894000	1.218516000	2.274405000
6	1.420929000	2.623988000	1.991308000
6	0.222258000	2.396373000	1.065365000
1	-3.781418000	1.885251000	-2.061581000
1	-6.127502000	-1.663880000	-2.078198000
1	-1.832500000	2.089367000	-0.578152000
1	-0.411997000	-0.638546000	-0.276756000
1	1.283228000	-0.644854000	1.367879000
1	3.056255000	1.230236000	2.446516000
1	1.505027000	0.795825000	3.165821000
1	2.169909000	3.242789000	1.493736000
1	1.122996000	3.131857000	2.911113000
1	0.191359000	3.124486000	0.247941000
1	-0.738467000	2.419877000	1.594359000
6	2.682421000	0.181794000	-0.048052000
8	2.076641000	-0.522582000	-1.119669000
14	1.824832000	-2.164149000	-1.407581000
6	3.383419000	-3.046729000	-1.966220000
1	3.111478000	-4.016567000	-2.400893000
1	4.072760000	-3.227244000	-1.135691000
1	3.918070000	-2.473292000	-2.730959000
6	0.571167000	-2.138184000	-2.801168000
1	-0.328943000	-1.578000000	-2.525225000

1	0.266869000	-3.157111000	-3.066512000
1	0.993610000	-1.668181000	-3.695944000
6	1.128563000	-3.069179000	0.087361000
1	0.939584000	-4.112292000	-0.195714000
1	0.180862000	-2.654494000	0.449304000
1	1.840932000	-3.082163000	0.919290000
6	3.901460000	-0.603276000	0.451086000
6	5.024327000	-0.671108000	-0.382601000
6	3.922755000	-1.322013000	1.647163000
6	6.133111000	-1.429962000	-0.033564000
1	5.020297000	-0.126269000	-1.321800000
6	5.032678000	-2.089820000	1.999536000
1	3.078116000	-1.298689000	2.327753000
6	6.140704000	-2.146621000	1.162141000
1	6.990378000	-1.467403000	-0.698945000
1	5.025760000	-2.639980000	2.935575000
1	7.005372000	-2.742483000	1.438306000
6	3.081198000	1.560405000	-0.580748000
6	4.126119000	2.291364000	-0.009508000
6	2.332394000	2.147609000	-1.602773000
6	4.406781000	3.585547000	-0.437851000
1	4.729610000	1.850498000	0.777929000
6	2.610534000	3.442527000	-2.031167000
1	1.526686000	1.582245000	-2.057396000
6	3.645989000	4.168317000	-1.447632000
1	5.224012000	4.136134000	0.018524000
1	2.016412000	3.883996000	-2.826066000
1	3.862865000	5.178280000	-1.782632000
1	-2.526632000	-0.826728000	-1.337973000
1	-4.383494000	-1.900837000	-1.843830000
6	-6.158314000	0.861978000	-2.795430000
1	-5.932587000	1.907474000	-3.021911000
1	-7.029000000	0.834046000	-2.128036000
1	-6.449006000	0.358443000	-3.725210000
6	-4.444569000	2.723906000	1.923109000
1	-5.326170000	3.324815000	1.697332000
1	-4.335076000	2.606182000	3.004569000
1	-3.548193000	3.212687000	1.529617000
8	-4.661222000	1.472125000	1.288049000
6	-3.688244000	0.548521000	1.486189000
8	-2.716510000	0.795158000	2.191461000
6	-3.881539000	-0.677732000	0.730033000
16	-5.484540000	-1.127744000	0.181992000

16	-2.723144000	-1.987419000	1.050504000
6	-3.077549000	-2.427569000	2.777629000
1	-2.922083000	-1.554637000	3.414502000
1	-2.381572000	-3.219312000	3.067911000
1	-4.102735000	-2.792937000	2.879916000

TS₂-DF

HF = -2571.8105764 hartrees

Imaginary Frequencies: 1 (-116.2446 1/cm)

Zero-point correction = 0.666066 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy = 0.593016

Sum of electronic and thermal Free Energies = -2571.217561 hartrees

Single Point Energy (wB97xd/cc-pVDZ in chloroform)

HF = -2571.940814 hartrees

Coordinates:

6	-4.130573000	-0.117185000	2.113255000
6	-5.188130000	-0.930150000	1.865717000
6	-5.069225000	-2.047824000	0.909753000
6	-2.804730000	-0.326490000	1.609426000
6	-1.812204000	0.657146000	1.732459000
6	-0.471058000	0.355818000	1.593537000
7	0.513867000	1.253194000	1.606818000
6	1.947954000	0.934476000	1.705457000
6	2.579025000	2.292290000	2.058277000
6	1.600880000	3.350903000	1.531616000
6	0.233539000	2.687762000	1.666798000
1	-4.300360000	0.805487000	2.665798000
1	-5.941140000	-2.706005000	0.911269000
1	-2.125769000	1.680474000	1.913361000
1	-0.152469000	-0.674043000	1.471952000
1	2.066516000	0.214477000	2.518672000
1	3.579871000	2.401133000	1.635326000
1	2.672963000	2.370181000	3.146032000
1	1.805266000	3.575466000	0.482947000
1	1.657085000	4.283509000	2.097308000
1	-0.458666000	2.953766000	0.861418000
1	-0.242568000	2.927150000	2.626996000
6	2.518696000	0.231933000	0.425022000
8	1.813430000	-0.998396000	0.394920000
14	2.061889000	-2.490985000	-0.342445000
6	2.013376000	-2.311401000	-2.209626000
1	2.086457000	-3.293231000	-2.691996000
1	2.836962000	-1.692453000	-2.580942000
1	1.076699000	-1.840474000	-2.526312000
6	0.629377000	-3.516082000	0.295072000
1	-0.336587000	-3.054342000	0.071701000

1	0.708818000	-3.647645000	1.380531000
1	0.641252000	-4.512353000	-0.162607000
6	3.643513000	-3.340467000	0.214825000
1	3.585032000	-4.403025000	-0.052674000
1	3.753913000	-3.276519000	1.302999000
1	4.546465000	-2.922437000	-0.237051000
6	4.022319000	-0.059910000	0.569820000
6	4.810980000	-0.259069000	-0.569088000
6	4.619467000	-0.259398000	1.817937000
6	6.148517000	-0.626865000	-0.467873000
1	4.375681000	-0.126222000	-1.553871000
6	5.957526000	-0.628712000	1.925082000
1	4.051477000	-0.130691000	2.732683000
6	6.729651000	-0.812994000	0.782737000
1	6.733112000	-0.771812000	-1.371351000
1	6.395472000	-0.772874000	2.908176000
1	7.773728000	-1.098599000	0.867085000
6	2.191995000	1.092947000	-0.799186000
6	3.057065000	2.102066000	-1.239844000
6	0.944286000	0.972777000	-1.412204000
6	2.690451000	2.955238000	-2.275992000
1	4.027016000	2.232338000	-0.770391000
6	0.570507000	1.834568000	-2.439705000
1	0.237153000	0.220859000	-1.079692000
6	1.442372000	2.824865000	-2.880115000
1	3.381683000	3.725919000	-2.604699000
1	-0.423150000	1.739574000	-2.863262000
1	1.150165000	3.497402000	-3.681475000
1	-2.479144000	-1.346251000	1.419410000
1	-4.166525000	-2.652479000	1.017327000
6	-6.562445000	-0.606256000	2.375320000
1	-6.565507000	0.296320000	2.992367000
1	-6.963502000	-1.435982000	2.969590000
1	-7.249564000	-0.450888000	1.534060000
6	-4.484096000	3.021889000	-0.596662000
1	-5.489850000	3.368649000	-0.355711000
1	-3.773100000	3.389476000	0.149707000
1	-4.182482000	3.396809000	-1.578713000
8	-4.551956000	1.604643000	-0.583174000
6	-3.392366000	0.970159000	-0.901509000
8	-2.389974000	1.608861000	-1.199522000
6	-3.468440000	-0.474273000	-0.783941000
16	-5.015095000	-1.283736000	-0.809634000

16	-2.041744000	-1.389819000	-1.291120000
6	-2.072070000	-1.222782000	-3.101618000
1	-2.983772000	-1.662593000	-3.514701000
1	-1.203583000	-1.753038000	-3.502897000
1	-2.008063000	-0.167432000	-3.376074000

P_F

HF = -2571.8457698 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.669584 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy = 0.597868

Sum of electronic and thermal Free Energies = -2571.247902 hartrees

Single Point Energy (wB97xd/cc-pVDZ in chloroform)

HF = -2571.976438 hartrees

Coordinates:

6	-3.680010000	0.754464000	-1.618256000
6	-4.751596000	0.211939000	-2.195223000
6	-5.189402000	-1.149524000	-1.735335000
6	-2.868883000	0.045506000	-0.558559000
6	-1.762627000	0.925834000	-0.042495000
6	-0.545968000	0.437911000	0.263334000
7	0.507620000	1.133563000	0.775331000
6	1.752694000	0.504372000	1.187750000
6	2.299238000	1.477324000	2.249993000
6	1.665663000	2.838503000	1.925609000
6	0.329553000	2.486944000	1.268772000
1	-3.344275000	1.747669000	-1.906366000
1	-6.177875000	-1.414231000	-2.121159000
1	-1.998219000	1.977375000	0.098770000
1	-0.347937000	-0.614527000	0.104430000
1	1.523078000	-0.468131000	1.635695000
1	3.390759000	1.521689000	2.260008000
1	1.974830000	1.134908000	3.237958000
1	2.293450000	3.398395000	1.228927000
1	1.529485000	3.449624000	2.821064000
1	0.080518000	3.171827000	0.448208000
1	-0.506777000	2.508084000	1.985062000
6	2.712254000	0.221054000	-0.021636000
8	2.003158000	-0.597746000	-0.942831000
14	1.715697000	-2.250921000	-1.014176000
6	3.208604000	-3.233571000	-1.586169000
1	2.889090000	-4.246312000	-1.862290000
1	3.967172000	-3.319071000	-0.801822000
1	3.678893000	-2.776755000	-2.463293000
6	0.353782000	-2.360528000	-2.301269000
1	-0.458817000	-1.659731000	-2.079272000

1	-0.067140000	-3.371455000	-2.350356000
1	0.740220000	-2.108521000	-3.294929000
6	1.143767000	-2.973979000	0.627956000
1	0.895288000	-4.031910000	0.475145000
1	0.258225000	-2.485506000	1.048850000
1	1.941875000	-2.932464000	1.377338000
6	3.996214000	-0.506704000	0.394735000
6	5.009918000	-0.657749000	-0.559459000
6	4.169911000	-1.109527000	1.641624000
6	6.160067000	-1.382556000	-0.278036000
1	4.885961000	-0.203990000	-1.538135000
6	5.320791000	-1.844000000	1.926886000
1	3.413020000	-1.019004000	2.413368000
6	6.319288000	-1.982962000	0.970004000
1	6.930980000	-1.484826000	-1.035932000
1	5.432887000	-2.304539000	2.903804000
1	7.216865000	-2.551647000	1.193708000
6	3.006838000	1.541247000	-0.734211000
6	4.114351000	2.326330000	-0.404483000
6	2.093694000	2.031622000	-1.671126000
6	4.301509000	3.576283000	-0.989198000
1	4.841256000	1.964839000	0.316394000
6	2.278140000	3.281039000	-2.255124000
1	1.233080000	1.427671000	-1.934600000
6	3.381342000	4.060434000	-1.914403000
1	5.170374000	4.169882000	-0.719996000
1	1.556264000	3.646001000	-2.980197000
1	3.525891000	5.034770000	-2.371898000
1	-2.427591000	-0.844759000	-1.025704000
1	-4.488433000	-1.925862000	-2.062239000
6	-5.572483000	0.893675000	-3.251072000
1	-5.153926000	1.869924000	-3.511720000
1	-6.602976000	1.041227000	-2.903980000
1	-5.625146000	0.287262000	-4.163862000
6	-4.831256000	2.794577000	1.857126000
1	-5.240685000	3.557316000	1.196729000
1	-5.552812000	2.532575000	2.633646000
1	-3.906705000	3.145665000	2.321548000
8	-4.568254000	1.667338000	1.018399000
6	-4.043252000	0.605255000	1.625345000
8	-3.819176000	0.551944000	2.812824000
6	-3.745637000	-0.526521000	0.633305000
16	-5.355083000	-1.244025000	0.087749000

16	-2.815407000	-1.776333000	1.627636000
6	-2.574237000	-3.082729000	0.399082000
1	-3.525398000	-3.365811000	-0.060637000
1	-2.178898000	-3.941887000	0.946528000
1	-1.850541000	-2.808149000	-0.373745000

P_{DF}

HF = -2571.8437234 hartrees

Imaginary Frequencies: none found

Zero-point correction = 0.668329 (Hartree/Particle)

Temperature: 298.150 Kelvin. Pressure: 1.00000 Atm.

Thermal correction to Gibbs Free Energy = 0.595615

Sum of electronic and thermal Free Energies = -2571.248108 hartrees

Single Point Energy (wB97xd/cc-pVDZ in chloroform)

HF = -2571.974803 hartrees

Coordinates:

6	-4.094276000	-0.203597000	-1.913861000
6	-5.295910000	0.367063000	-1.990399000
6	-5.597572000	1.517029000	-1.072468000
6	-2.993637000	0.272951000	-0.988859000
6	-1.826617000	-0.674741000	-1.046371000
6	-0.559972000	-0.328280000	-1.348848000
7	0.467100000	-1.217311000	-1.502011000
6	1.859810000	-0.859506000	-1.699873000
6	2.476170000	-2.169012000	-2.223496000
6	1.579405000	-3.306835000	-1.703633000
6	0.238447000	-2.642591000	-1.361042000
1	-3.851719000	-1.053036000	-2.547972000
1	-6.661191000	1.771977000	-1.070866000
1	-2.073019000	-1.719647000	-0.881979000
1	-0.280929000	0.711566000	-1.497695000
1	1.907781000	-0.070091000	-2.456930000
1	3.517606000	-2.291014000	-1.917760000
1	2.462401000	-2.144212000	-3.317324000
1	2.010911000	-3.766633000	-0.813220000
1	1.458126000	-4.092204000	-2.453926000
1	-0.089000000	-2.885719000	-0.339367000
1	-0.565360000	-2.948854000	-2.045308000
6	2.538171000	-0.240188000	-0.420371000
8	1.939621000	1.044664000	-0.323104000
14	2.406770000	2.446059000	0.482032000
6	2.720243000	2.151246000	2.310405000
1	2.884010000	3.114245000	2.809743000
1	3.603698000	1.530924000	2.489205000
1	1.862544000	1.664341000	2.785669000
6	0.900645000	3.534817000	0.262242000
1	0.026217000	3.027548000	0.680145000

1	0.703148000	3.731800000	-0.797417000
1	1.020821000	4.497344000	0.772163000
6	3.896696000	3.275958000	-0.307112000
1	4.009523000	4.282181000	0.116218000
1	3.759924000	3.381951000	-1.388826000
1	4.829615000	2.730543000	-0.136139000
6	4.051683000	-0.056508000	-0.607975000
6	4.929327000	-0.081348000	0.480111000
6	4.576327000	0.279675000	-1.861537000
6	6.281838000	0.210720000	0.323657000
1	4.555558000	-0.331120000	1.467095000
6	5.927241000	0.565003000	-2.024822000
1	3.929304000	0.330548000	-2.730612000
6	6.788391000	0.533434000	-0.930965000
1	6.938672000	0.185068000	1.188145000
1	6.306597000	0.818531000	-3.010278000
1	7.843226000	0.757750000	-1.057066000
6	2.159003000	-1.098370000	0.788654000
6	2.872092000	-2.253977000	1.120739000
6	0.992016000	-0.811613000	1.500519000
6	2.436533000	-3.094405000	2.141743000
1	3.776126000	-2.509356000	0.575154000
6	0.547788000	-1.653129000	2.515847000
1	0.407577000	0.063564000	1.238966000
6	1.270118000	-2.798326000	2.841865000
1	3.009074000	-3.985235000	2.384121000
1	-0.377491000	-1.416783000	3.031633000
1	0.925628000	-3.457701000	3.633305000
1	-2.667386000	1.261409000	-1.337857000
1	-5.041988000	2.417485000	-1.357752000
6	-6.387830000	-0.097214000	-2.910190000
1	-6.057497000	-0.933779000	-3.532584000
1	-6.718449000	0.713429000	-3.571451000
1	-7.265516000	-0.419907000	-2.335816000
6	-3.969762000	-3.084324000	1.279580000
1	-4.552622000	-3.748799000	0.644020000
1	-2.926450000	-3.407004000	1.321671000
1	-4.384506000	-3.058793000	2.289397000
8	-4.063559000	-1.794281000	0.669092000
6	-3.387241000	-0.822421000	1.277260000
8	-2.772376000	-0.976930000	2.307558000
6	-3.472263000	0.503206000	0.508182000
16	-5.207385000	1.110817000	0.668502000

16	-2.327677000	1.633389000	1.413950000
6	-2.670955000	3.201339000	0.577238000
1	-2.306763000	3.216754000	-0.453743000
1	-2.136234000	3.969392000	1.140940000
1	-3.740394000	3.426630000	0.605003000

6. ^1H AND ^{13}C NMR SPECTRA

Compound 2a – ^1H NMR

Compound 2a-¹³C NMR

Compound 2c-1H NMR

Compound 2c-¹³C NMR

Compound 2d-1H NMR

Compound 2d - ¹³C NMR

Compound 2e - ¹H NMR

Compound 2e - ¹³C NMR

Compound 2f - ¹H NMR

Compound 2f - ¹³C NMR

Compound 4a-1H NMR

Compound 4a-¹³C NMR **4a**

Compound 4b-1H NMR

Compound 4b-¹³C NMR **4b**

Compound 4c-1H NMR

4c

Compound 4c-¹³C NMR

Compound 4d-1H NMR

Compound 4d-¹³C NMR

Compound 4e-1H NMR

Compound 4e-¹³C NMR

Compound 4f-1H NMR

Compound 4f-¹³C NMR

Compound 4g-1H NMR

Compound 4g-¹³C NMR

Compound 4h-1H NMR

Compound 4h-¹³C NMR

Compound 4i-1H NMR

Compound 4i-13C NMR

Compound 4j-1H NMR

Compound 4j-¹³C NMR

Compound 4k-1H NMR

Compound 4k-13C NMR

Compound 4I-1H NMR

Compound 4I-13C NMR

Compound 4m-¹H NMR

Compound 4m-¹³C NMR

Compound 4n-1H NMR

Compound 4n-¹³C NMR

Compound 4o-1H NMR

Compound 4o-¹³C NMR

Compound 4p-1H NMR

Compound 4p-¹³C NMR

Compound 4q-1H NMR

4q

Compound 4q-13C NMR

Compound 4r-1H NMR

Compound 4r-¹³C NMR

Compound 5a_H1 NMR

Compound 5b-1H NMR

Compound 5b-13C NMR

Compound 6-¹H NMR

Compound 6-13C NMR

Compound 7 - ¹H NMR

Compound 7-13C NMR

Compound 8 - ¹H NMR

8

Compound 8-C13 NMR

7. UPC² and HPLC traces

	Retention Time (min)	% Area
1	4.635	96.14
2	7.655	3.86

	Retention Time (min)	% Area
1	3.960	96.74
2	5.286	3.26

	Retention Time (min)	% Area
1	5.170	96.53
2	10.142	3.47

	Retention Time (min)	% Area
1	2.632	92.36
2	8.501	7.64

	Retention Time (min)	% Area
1	12.380	96.11
2	14.285	3.89

	Retention Time (min)	% Area
1	4.070	95.25
2	4.280	4.75

	Retention Time (min)	% Area
1	3.635	95.50
2	3.825	4.50

	Retention Time (min)	% Area
1	2.869	92.41
2	4.900	7.59

	Retention Time (min)	% Area
1	5.901	92.13
2	7.734	7.87

	Retention Time (min)	% Area
1	9.437	92.89
2	12.811	7.11

	Retention Time (min)	% Area
1	2.360	97.05
2	3.651	2.95

	Retention Time (min)	% Area
1	1.022	18.84
2	1.273	33.50
3	1.507	30.02
4	1.651	17.64

	Retention Time (min)	% Area
1	2.953	96.95
2	4.474	3.05

	Retention Time (min)	% Area
1	17.406	2.33
2	3.413	97.67

	Retention Time (min)	% Area
1	3.663	5.14
2	4.067	94.86

	Retention Time (min)	% Area
1	1.451	8.53
2	3.198	91.47

	Retention Time (min)	% Area
1	3.308	95.93
2	4.039	4.07