Gold(I)-Catalysed Direct Thioetherifications Using Allylic Alcohols: an Experimental and Computational Study

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# Table of contents

**Experimental Supporting Information:**  Pages 3-72

1. General Experimental Section  
   pg 3
2. Representative Optimisation Studies  
   pg 4
3. Experimental Procedures  
   pg 7
4. $^1$H NMR and $^{13}$C NMR Spectra of Synthesised Compounds  
   pg 37
5. References for Experimental Section  
   pg 72

**Computational Supporting Information:**  Pages 73 -188

1. Computational Details and References  
   pg 73
2. Reactions of Substrate 4'  
   pg 75
3. Reactions of Substrate 24  
   pg 103
4. Reactions of Substrate 4' with PhSH at [(Johnphos)Au(NCMe)]+, 5.  
   pg 127
5. Reactions of 9, 10 and 11 with PhSH  
   pg 149
6. Reactions of Substrate 17  
   pg 162
1) General Experimental Section

$^1$H NMR spectra was recorded on Bruker AV 300 and AV 400 spectrometers at 300 and 400 MHz respectively and referenced to residual solvent. $^{13}$C NMR spectra were recorded using the same spectrometers at 75 and 100 MHz respectively. Chemical shift data are quoted in parts per million (ppm) and are referenced to tetramethylsilane (TMS) or to residual solvent peaks (CDCl$_3$ at $\delta$$_H$ 7.26). $J$ values are given in Hz and s, d, dd, dt, t, q and m abbreviations correspond to singlet, doublet, doublet of doublet, doublet of triplet, triplet, quartet and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea and APCI represents atmospheric pressure chemical ionisation. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat to a diamond/ZnSe plate. Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 pre-coated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic KMnO$_4$ or aqueous acidic ammonium molybdate as appropriate. Petrol ether refers to petroleum ether (40-60 °C). Chemicals were purchased from Sigma-Aldrich, Acros, Fisher and Apollo chemical companies and used without further purification. Tetrahydrofuran was dried by distillation from sodium – benzophenone under nitrogen or using an MBRAUN SPS-800 solvent purification system. High performance liquid chromatography (HPLC) was done on Agilent Technologies 1120 Compact LC.

Gold catalyst 5 was purchased from Sigma-Aldrich and used without further purification. All thiophenols and thiols were purchased from Sigma-Aldrich, Fisher or Apollo and used without further purification. Scavenger QuadraPure(TM) MPA (100-400 mum particle size, extent of labeling: 1.5 mmol/g loading, 1% cross-linked with divinylbenzene) was purchased from Sigma-Aldrich.

The gold(I)-catalysed reactions were carried out in screw cap 1 dram vials unless otherwise indicated. No special precautions to exclude air or moisture were taken unless otherwise indicated.
2) Representative Optimization Studies

Below are representative screens that were carried out in order to optimise the reaction conditions.

**General procedure for optimization studies**

The catalyst 5 was added to a solution of allylic alcohol 4 and thiol 2a in solvent at the required temperature, the vial was sealed and the resulting mixture was stirred for the required time. The solution was filtered through a plug of silica with diethyl ether followed by concentration under reduced pressure. The crude mixture was analysed by $^1$H NMR to give the following results:

**Temperature Screen:**

| Entry | Temperature | Conversion to 3a |
|-------|-------------|------------------|
| 1     | 30 °C       | 46%              |
| 2     | 40 °C       | 88%              |

**Reaction Time Screen:**

| Entry | Time       | Conversion to 3a |
|-------|------------|------------------|
| 1     | 8 hours    | 67%              |
| 2     | 16 hours   | 81%              |
| 3     | 2 days     | 82%              |
| 4     | 3 days     | 88%              |
Concentration Screen:

| Entry | Concentration (mol L\(^{-1}\)) | Conversion to 3a | Conversion to unidentified side products |
|-------|---------------------------------|------------------|------------------------------------------|
| 1     | 0.621                           | 72%              | 24%                                      |
| 2     | 0.386                           | 72%              | 15%                                      |
| 3     | 0.199                           | 74%              | 16%                                      |
| 4     | 0.0996                          | 78%              | 11%                                      |
| 5     | 0.0498                          | 65%              | 24%                                      |

Solvent Screen:

| Entry | Solvent             | Conversion to 3a |
|-------|---------------------|------------------|
| 1     | Toluene             | 72%              |
| 2     | CHCl\(_3\)          | 92%              |
| 3     | 1,2-dichloroethane  | 90%              |

CHCl\(_3\) was therefore used as the optimal solvent, as the solvent had changed another temperature screen was carried out.
Temperature Screen:

| Entry | Temperature | Conversion to 3a |
|-------|-------------|------------------|
| 1     | 30 °C       | 79%              |
| 2     | 35 °C       | 91%              |
| 3     | 40 °C       | 92%              |

35 °C was therefore deemed sufficient for good conversion.
3) Experimental procedures

Synthesis of starting materials

Allylic alcohol 16 and 24 were purchased from Sigma-Aldrich. All other allylic alcohol substrates were prepared following known literature procedures. Allylic alcohols 4, 8, 9, 10, 11, 12, 17 were obtained following known literature procedure using vinyl Grignard addition to ketones/aldehydes. 13-15, 19, 20, 21 were prepared by nBuLi, tBuLi or CyLi addition to the corresponding enone or enal as appropriate. 18 was prepared by PhMgBr addition to the crotonaldehyde. 22 and 23 were prepared by partial reduction of the corresponding alkynes. 26 was prepared from reduction of the corresponding enone.

Characterization for 13-15 is given below.

4-Butyl-oct-2-ene-4-ol (13)

To a solution of ethyl-trans-2-butenoate (1.09 mL, 8.76 mmol) in diethyl ether (16 mL) n-BuLi (14.6 mL, 23.4 mmol) was added dropwise at 0 °C over 30 minutes. After stirring at 0 °C for 3 h the reaction mixture was quenched with saturated NH₄Cl (35 mL) and allowed to warm to room temperature. The layers were separated and the water layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL) and dried over Na₂SO₄. The crude was purified through flash column chromatography in hexane:diethyl ether (5:1) to yield the titled compound 13 as a colourless oil (1.02 g, 3.50 mmol, 40 %). ν max / cm⁻¹ 3453 (br), 2956, 2929, 2861, 1467, 1456, 1377, 1253, 1141, 1027, 999, 970, 903, 799, 730. ¹H NMR (300 MHz, CDCl₃) δ 5.51 (dq, J = 15.5, 6.3 Hz, 1H, CH₃CH=), 5.35 (dq, J = 15.5, 1.4 Hz, 1H, CH₃CH=), 1.62 (dd, J = 6.3, 1.4 Hz, 3H, CH₃CH=), 1.57 – 1.12 (m, 12H, CH₂), 0.81 (t, J = 6.8 Hz, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 137.3 (CH), 122.7 (CH), 74.8 (C), 40.8 (CH₂), 25.8 (CH₂), 23.3 (CH₂), 17.7 (CH₃), 14.1 (CH₃). Found (ASAP): [M]⁺ 183.741. C₁₂H₂₃O₁ requires 183.1743.
(E)-2,2,3-Trimethylhex-4-en-3-ol (14)

A solution of tBuLi (8.13 mL of a 1.9 M solution in hexanes, 15.45 mmol) was added dropwise to a stirred solution of (E)-3-penten-2-one (1 g, 1.16 mL, 11.89 mmol) in THF (10 mL) at 0 °C under Ar. The resulting solution was stirred at 0 °C for 30 min then warmed to rt. Then, a saturated solution of NH₄Cl (aq) (15 mL) was added, and the two layers were separated. The aqueous layer was extracted with Et₂O (3 × 20 mL). The combined organic layers were dried (MgSO₄) and evaporated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with 9:1 petrol-Et₂O as eluent gave trimethylhexenol 14 (143 mg, 8%) as a colourless oil. ν_max/cm⁻¹ 3456 (br), 2957, 2926, 2871, 1463, 1375, 1215, 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δH 5.69 (1H, dq, J = 15.6, 0.8 Hz, =CHC), 5.60 (1H, dq, J = 15.6, 5.9 Hz, MeCH), 1.70 (3H, dd, J = 5.9, 0.8 Hz, =CHMe), 1.34 (1H, br s, OH), 1.21 (3H, s, Me), 0.91 (9H, s, CMe₃); ¹³C NMR (75 MHz, CDCl₃) δC 136.2 (HC), 123.2 (HC), 77.0 (C), 37.5 (C), 25.5 (CH₃), 23.6 (CH₃), 17.9 (CH₃); Found (APCI): [M – H]+ 141.1271, C₉H₁₇O requires 141.1274.

2-Methyl-3-butyl-hept-1-en-3-ol (15)

To a solution of methylmetacrylate (1.1 mL, 9.98 mmol) in dry diethyl ether (20 mL) n-BuLi (15 mL, 23.97 mmol) was added dropwise at 0 °C over 0.5 h. After stirring at 0 °C for a further 18 h the reaction mixture was quenched with saturated NH₄Cl (aq.) (20 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. The solution was concentrated under reduced pressure and purified with flash column chromatography (hexane: diethyl ether 10:1) to yield the titled compound 15 as a colourless oil (132.3 mg, 0.72 mmol, 7 %). ν_max / cm⁻¹ 3484 (br), 2956, 2936, 2861, 1643, 1457, 1378, 1257, 1143, 1044, 989, 897, 793, 731. ¹H NMR (300 MHz, CDCl₃) δ 4.89 (s, 1H, =CHH), 4.82 (s, 1H, =CHH), 1.62 (s, 3H, CH₃C=CH₂), 1.53 – 1.01 (m, 12H, CH₂), 0.83 (t, J = 6.9 Hz, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃) δ 148.6 (C), 110.4 (CH₂), 77.7 (C), 39.2 (CH₂), 25.3 (CH₂), 23.1 (CH₂), 19.7 (CH₃), 14.1 (CH₃). Found (ASAP): [M]+ 184.1821. C₁₂H₂₄O₁ requires 184.1822.
General procedure A for 3a-3i (thiophenol nucleophiles):

Thiophenol 2 (1.1 equiv.) and 5 (5 mol%) were added to a solution of allylic alcohol 4 (1 equiv.) in chloroform (0.386 M) in a 1 dram vial. The reaction mixture was allowed to stir at 35 °C for 24 hours. The mixture was then filtered through a plug of silica with diethyl ether. The filtrate was concentrated under reduced pressure. Purification of the crude material was carried out by flash column chromatography.

3-Hexanon-2-en-1-yl phenyl sulfide (3a):

General procedure A. Purification of the crude product by column chromatography (pure petrol ether) yielded the title compound 3a (17.3 mg, 0.054 mmol, 70%) as a pale yellow liquid.

$\nu_{\text{max}}/\text{cm}^{-1}$ 3060, 2960, 2853, 1580, 1439, 1024, 688; $\delta_{\text{H}}$ (300 MHz, CDCl$_3$) 7.46 – 7.04 (5H, m, Ar-H), 5.20 (1H, t, $J = 7.7$ Hz, C=CH), 3.49 (2H, d, $J = 7.7$ Hz, SCH$_2$), 1.95 – 1.84 (4H, m, C=CCH$_2$), 1.32 – 1.10 (16H, m, Alkyl-H), 0.86 – 0.76 (6H, m, Alkyl-CH$_3$); $\delta_{\text{c}}$ (75 MHz, CDCl$_3$) 144.8 (C), 137.1 (C), 129.8 (CH), 128.8 (CH), 126.1 (CH), 119.1 (CH), 36.9 (CH$_2$), 32.2 (CH$_2$), 31.9 (CH$_2$), 30.2 (CH$_2$), 29.6 (CH$_2$), 29.2 (CH$_2$), 28.6 (CH$_2$), 28.1 (CH$_2$), 22.8 (2CH$_2$), 14.3 (2CH$_3$); Found (APCI): [M + H]$^+$ 319.2454, C$_{21}$H$_{35}$S requires 319.2454.
3-Hexanon-2-en-1-yl 2-methylphenyl sulfide (3b):

General procedure A. Purification of the crude product by column chromatography (pure petrol ether) yielded the title compound 3b (15.2 mg, 0.046 mmol, 62%) as a colourless liquid.

\[ \nu_{\text{max}}/\text{cm}^{-1} \] 2955, 2925-2855, 1589, 1466, 1065, 740; \[ \delta_{\text{H}} \] (300 MHz, CDCl\(_3\)) 7.20 – 7.04 (4H, m, Ar-H), 5.22 (1H, t, \( J = 7.7 \) Hz, C=CH), 3.45 (2H, d, \( J = 7.7 \) Hz, SCH\(_2\)), 2.29 (3H, s, Aryl-CH\(_3\)), 1.98-1.85 (4H, m, CH\(_2\)=CH(CH\(_2\)Alkyl)), 1.33-1.10 (16H, m, Alkyl-H); \[ \delta_{\text{c}} \] (75 MHz, CDCl\(_3\)) 145.1 (C), 137.7 (C), 136.6 (C), 130.1 (CH), 128.7 (CH), 126.4 (CH), 125.8 (CH), 118.8 (CH), 36.9 (CH\(_2\)), 31.9 (CH\(_2\)), 31.3 (CH\(_2\)), 30.3 (CH\(_2\)), 29.9 (CH\(_2\)), 29.6 (CH\(_2\)), 29.3 (CH\(_2\)), 29.1 (CH\(_2\)), 28.6 (CH\(_2\)), 28.1 (CH\(_2\)), 22.8 (CH\(_2\)), 20.5 (CH\(_3\)), 14.3 (2CH\(_3\)); Found (APCI): [M + H]\(^+\) 333.2608, C\(_{22}\)H\(_{37}\)S requires 333.2610.

3-Hexanon-2-en-1-yl 3-methylphenyl sulfide (3c):

General procedure A. Purification of the crude product by column chromatography (pure petrol ether) yielded the title compound 3c (17.2 mg, 0.052 mmol, 76%) as a colourless liquid.

\[ \nu_{\text{max}}/\text{cm}^{-1} \] 2955, 2925, 2855, 1592, 1466, 1081, 770, 688; \[ \delta_{\text{H}} \] (300 MHz, CDCl\(_3\)) 7.10 – 6.87 (4H, m, Ar-H), 5.20 (1H, t, \( J = 7.6 \) Hz, C=CH), 3.4 (2H, d, \( J = 7.6 \) Hz, SCH\(_2\)), 2.24 (3H, s, Aryl-CH\(_3\)), 1.91 (4H, t, \( J = 7.2 \) Hz, CH\(_2\)=CH(CH\(_2\)Alkyl)), 1.43 – 1.23 (16H, m, Alkyl-H); \[ \delta_{\text{c}} \] (75 MHz, CDCl\(_3\)) 144.7 (C), 138.6 (C), 136.7 (C), 130.4 (CH), 128.7 (CH), 126.9 (CH), 126.7 (CH), 119.2 (CH), 36.9 (CH\(_2\)), 32.1 (CH\(_2\)), 31.9 (2CH\(_2\)), 30.2 (CH\(_2\)), 29.6 (CH\(_2\)), 29.2 (CH\(_2\)), 28.6 (CH\(_2\)), 28.2 (CH\(_2\)), 22.8 (2CH\(_2\)), 21.5 (CH\(_3\)), 14.3 (2CH\(_3\)); Found (APCI): [M + H]\(^+\) 333.2608, C\(_{22}\)H\(_{37}\)S requires 333.2610.
3-Hexanon-2-en-1-yl 4-methylphenyl sulfide (3d):

General procedure A. Purification of the crude product by column chromatography (pure petrol ether) yielded the title compound 3d (19.4 mg, 0.058 mmol, 71%) as a pale yellow liquid.

ν_{max}/cm⁻¹ 2955, 2926, 2856, 1491, 1092, 802; δ_{H} (300 MHz, CDCl₃) 7.29 (2H, d, J = 7.8 Hz, Ar-H), 7.11 (2H, d, J = 7.8 Hz, Ar-H), 5.19 (1H, t, J = 7.7 Hz, C=CH), 3.44 (2H, d, J = 7.7 Hz, SCH₂), 2.24 (3H, s, Aryl-CH₃), 1.94-1.82 (4H, m, CH₂=CH(CH₂Alkyl), 1.32-1.08 (16H, m, Alkyl-H), 0.81 (6H, t, J = 6.7, Alkyl-CH₃); δ_{C} (75 MHz, CDCl₃) 144.5 (C), 136.3 (C), 133.2 (C), 130.73 (CH), 129.9 (CH), 129.6 (CH), 128.7 (CH), 119.4 (CH), 36.9 (CH₂), 32.9 (CH₂), 31.9 (2CH₂), 30.2 (CH₂), 29.6 (CH₂), 29.2 (CH₂), 28.6 (CH₂), 28.2 (CH₂), 22.8 (2CH₂), 21.2 (CH₃), 14.3 (2CH₃); Found (APCI): [M]⁺ 332.2530, C₂₂H₃₆S requires 332.2532.

1-[(3-Hexanon-2-en-1-yl)sulfanyl]-2-methoxybenzene (3e):

General procedure A. Purification of the crude product by column chromatography (pure petrol ether to 100:1 petrol ether-diethyl ether) yielded the title compound 3e (15.7 mg, 0.045 mmol, 66%) as a colourless liquid.

ν_{max}/cm⁻¹ 2955, 2925, 2855, 1577, 1463, 1243, 1044, 743; δ_{H} (300 MHz, CDCl₃) 7.21 (1H, td, J = 7.9, 1.6 Hz, Ar-H), 7.11 (1H, td, J = 7.9, 1.6 Hz, Ar-H), 6.83 (1H, td, J = 7.5, 1.6 Hz, Ar-H), 6.76 (1H, dd, J = 9.7, 5.7 Hz, Ar-H), 5.20 (1H, t, J = 7.7 Hz, C=CH), 3.82 (3H, s, OCH₃), 3.47 (2H, d, J = 7.7 Hz, SCH₂), 1.96-1.85 (4H, m, CH₂=CH(CH₂Alkyl), 1.31-1.11 (16H, m, Alkyl-H), 0.85-0.77 (6H, m, Alkyl-CH₃); δ_{C} (75 MHz, CDCl₃) 157.6 (C), 144.9 (C), 130.3 (CH), 127.2 (CH), 125.2 (C), 121.0 (CH), 119.1 (CH), 110.4 (CH), 55.9 (CH₂), 36.9 (CH₂), 31.9 (2CH₂), 30.4 (CH₂), 30.2 (CH₂), 29.7 (CH₂), 29.2 (CH₂), 28.7 (CH₂), 28.8 (CH₂), 22.81 (CH₂), 22.77 (CH₂), 14.3 (2CH₃); Found (APCI): [M + H]⁺ 349.2558, C₂₂H₃₇OS requires 349.2560.
1-[(3-Hexanon-2-en-1-yl)sulfanyl]-4-methoxybenzene (3f):

General procedure A. Purification of the crude product by column chromatography (pure petrol ether to 100:1 petrol ether-diethyl ether) yielded the title compound 3f (15.3 mg, 0.044 mmol, 64%) as a colourless liquid.

\[ \nu_{\text{max}}/\text{cm}^{-1} \ 2955, 2927, 2856, 1592, 1493, 1245, 1036, 825; \ \delta_{\text{H}} \ (300 \text{ MHz, CDCl}_3) \ 7.28 (2H, d, J = 8.8 \text{ Hz, Aryl-H}), 6.75 (2H, d, J = 8.8 \text{ Hz, Aryl-H}), 5.17 (1H, t, J = 7.8 \text{ Hz, C=CH}), 3.72 (3H, s, OCH}_3), 3.38 (2H, d, J = 7.8 \text{ Hz, SCHR}_2), 1.92 – 1.84 (2H, m, C=CCH}_2), 1.84 – 1.75 (2H, m, C=CCH}_2), 1.32 – 1.08 (16H, m, Alkyl-H), 0.87 – 0.75 (6H, m, Alkyl-CH}_3); \ \delta_{\text{C}} \ (100 \text{ MHz, CDCl}_3) \ 159.1 (C), 144.3 (C), 134.1 (CH), 126.8 (C), 119.8 (CH), 114.5 (CH), 55.5 (CH), 36.9 (CH), 34.3 (CH), 31.94 (CH), 31.91(CH), 30.1 (CH), 29.6 (CH), 29.2 (CH), 28.6 (CH), 28.2 (CH), 22.8 (2CH), 14.27 (CH), 14.26 (CH); \text{Found (APCI): [M + H]^+} 349.2551, \text{C}_{22}H_{37}OS \text{ requires 349.2560.}

3-Hexanon-2-en-1-yl 4-nitrophenyl sulfide (3g):

General procedure A. Purification of the crude product by column chromatography (pure petrol ether to 100:1 petrol ether-diethyl ether) yielded the title compound 3g (18.3 mg, 0.050 mmol, 68%) as a yellow liquid.

\[ \nu_{\text{max}}/\text{cm}^{-1} \ 2956, 2928, 2857, 1579, 1514, 1337, 853; \ \delta_{\text{H}} \ (300 \text{ MHz, CDCl}_3) \ 8.04 (2H, d, J = 9.0 \text{ Hz Ar-H}), 7.25 (2H, d, J = 9.0 \text{ Hz, Ar-H}), 5.20 (1H, t, J = 7.5 \text{ Hz, C=CH}), 3.60 (2H, d, J = 7.5 \text{ Hz, SCHR}_2), 2.07 – 1.90 (4H, m, CH=CH(CH}_2Alkyl)), 1.38-1.12 (16H, m, Alkyl-H), 0.90-0.72 (6H, m, Alkyl-CH}_3); \ \delta_{\text{C}} \ (75 \text{ MHz, CDCl}_3) \ 148.4 (C), 146.7 (C), 145.1 (C), 126.5 (CH), 124.0 (CH), 117.3 (CH), 36.9 (CH), 31.90 (CH), 31.86 (CH), 30.5 (CH), 30.4 (CH), 29.6 (CH), 29.1 (CH), 28.6 (CH), 28.0 (CH), 22.8 (2CH), 14.2 (2CH); \text{Found (APCI): [M + H]^+} 364.2301, \text{C}_{21}H_{34}O_2NS \text{ requires 364.2305.}
**1-Bromo-4-[(3-hexanon-2-en-1-yl)sulfanyl]benzene (3h):**

General procedure A. Purification of the crude product by column chromatography (pure petrol ether) yielded the title compound \(3h\) (20.2 mg, 0.051 mmol, 73%) as a colourless liquid.

\[\nu_{\text{max}}/\text{cm}^{-1} 2955, 2925, 2855, 1472, 1069, 740; \delta_{\text{H}} (300 \text{ MHz, CDCl}_3) 7.31 (2\text{H, d, } J = 8.5 \text{ Hz, Ar-H}), 7.12 (2\text{H, d, } J = 8.5 \text{ Hz, Ar-H}), 5.17 (1\text{H, t, } J = 7.7 \text{ Hz, C=CH}), 3.46 (2\text{H, d, } J = 7.7 \text{ Hz, SCH}_2), 1.84-1.86 (4\text{H, m, CH}_2=\text{CH(CH}_2\text{Alkyl}), 1.30-1.13 (16\text{H, m, Alkyl-H}), 0.81 (6\text{H, t, } J = 5.4, \text{ Alkyl-CH}_3); \delta_{\text{C}} (75 \text{ MHz, CDCl}_3) 145.2 (\text{C}), 136.3 (\text{C}), 131.9 (\text{CH}), 131.4 (\text{CH}), 120.0 (\text{CH}), 118.8 (\text{CH}), 36.9 (\text{CH}_2), 32.3 (\text{CH}_2), 31.9 (\text{CH}_2), 30.3 (\text{CH}_2), 29.6 (\text{CH}_2), 29.2 (\text{CH}_2), 28.6 (\text{CH}_2), 28.1 (\text{CH}_2), 22.8 (\text{CH}_2), 14.3 (\text{CH}_3); \text{Found (APCI): [M + H]+ 397.1555, C}_{21}\text{H}_{34}\text{BrS requires 397.1559.}

**4-[(3-Hexanon-2-en-1-yl)sulfanyl]phenol (3i):**

General procedure A. Purification of the crude product by column chromatography (pure hexane to 5:1 hexane-diethyl ether) yielded the title compound \(3i\) (11.8 mg, 0.035 mmol, 49%) as a pale yellow liquid.

\[\nu_{\text{max}}/\text{cm}^{-1} 3363, 2955, 2926, 2856, 1493, 1215, 828; \delta_{\text{H}} (300 \text{ MHz, CDCl}_3) 7.28 - 7.15 (2\text{H, d, } J = 8.6 \text{ Hz, Ar-H}), 6.73 - 6.62 (2\text{H, d, } J = 8.6 \text{ Hz, Ar-H}), 5.16 (1\text{H, t, } J = 7.8 \text{ Hz, C=CH}), 4.59 (1\text{H, s, OH}), 3.37 (2\text{H, d, } J = 7.8 \text{ Hz, SCH}_2), 1.93 - 1.74 (4\text{H, m, CH}_2=\text{CH(CH}_2\text{Alkyl}), 1.31 - 1.09 (16\text{H, m, Alkyl-H}), 0.88 - 0.74 (6\text{H, m, Alkyl-CH}_3); \delta_{\text{C}} (75 \text{ MHz, CDCl}_3) 155.0 (\text{C}), 144.4 (\text{C}), 134.3 (\text{CH}), 127.1 (\text{C}), 119.7 (\text{CH}), 115.9 (\text{CH}), 36.9 (\text{CH}_2), 34.3 (\text{CH}_2), 31.93 (\text{CH}_2), 31.90 (\text{CH}_2), 30.1 (\text{CH}_2), 29.6 (\text{CH}_2), 29.2 (\text{CH}_2), 28.6 (\text{CH}_2), 28.2 (\text{CH}_2), 22.8 (\text{CH}_2), 14.3 (\text{CH}_3); \text{Found (APCI): [M + H]+ 335.2403, C}_{21}\text{H}_{35}\text{OS requires 335.2398.}
Benzyl 3-hexan-2-en-1-yl sulfone (7j):

A solution of benzyl mercaptan 2j (8.9 µL, 0.0688 mmol) and catalyst 5 (2.6 mg, 0.0033 mmol) in CHCl₃ (0.16 mL), was added to a solution of 3-hexyl-1-nonen-3-ol 4 (15.5 mg, 0.068 mmol) at 50 °C and stirred for 3 days. The solution was then filtered through a silica plug with diethyl ether and concentrated under reduced pressure. Purification of the crude product by column chromatography (pure petrol ether to 5:1 petrol ether:diethyl ether) yielded the title compound 7j (10.5 mg, 0.029 mmol, 42%) as a colourless liquid.

ν max/cm⁻¹ 2927, 2857, 1655, 1456, 1313, 1117, 698; δH (300 MHz, CDCl₃) 7.32 (5H, m, Ar-H), 5.21 (1H, t, J = 7.6 Hz, C=CH), 4.10 (2H, s, SCH₂Ar), 3.53 (2H, d, J = 7.6 Hz, SCH₂CH), 2.06-1.85 (4H, m, CH₂=CH(CH₂Alkyl)), 1.30-1.09 (16H, m, Alkyl-H), 0.89-0.73 (6H, m, Alkyl-CH₃); δc (75 MHz, CDCl₃) 150.9 (C), 130.8 (CH), 129.17 (CH), 129.10 (CH), 128.0 (C), 109.7 (CH), 58.2 (CH₂), 51.6 (CH₂), 37.2 (CH₂), 31.9 (CH₂), 31.8 (CH₂), 30.9 (CH₂), 29.5 (CH₂), 29.2 (CH₂), 28.3 (CH₂), 22.0 (CH₂), 22.79 (CH₂), 22.74 (CH₂), 14.2 (2CH₃); Found (APCI): [M + H]⁺ 365.2507, C₂₂H₃₇O₂S requires 365.2509.
General procedure B for 3j-3o (alkyl thiols as nucleophiles):

4-Nitrothiophenol (1.1 equiv.) and 5 (5 mol%) were added to a solution of allylic alcohol (1 equiv.) in chloroform (0.386 M) in a 1 dram vial. The vial was capped and the solution allowed to stir for 72 h (for temperatures see below), after which it was allowed to cool down to room temperature. Scavenger Reaxa QuadraPure™ MPA (0.5 equiv.) was added and the mixture was stirred gently for 3 h. The reaction mixture was then filtered through a plug of cotton wool with diethyl ether. The filtrate was concentrated under reduced pressure. Purification of the crude material was carried out by flash column chromatography.

Benzyl 3-hexanoyl-2-en-1-yl sulfide (3j):

\[
\begin{align*}
\text{Benzyl 3-hexanoyl-2-en-1-yl sulfide (3j):} & \\
\text{The reaction was carried out at 50 °C following general procedure B. The product was purified using flash column chromatography using neat hexane. Product 3j was obtained as colourless liquid (12.3 mg, 37.0 µmol, 56%).} & \\
\text{ν max/cm}^{-1} & 2955, 2925, 2855, 1603, 1494, 1454, 1378, 1232, 1071, 767, 717, 697; \delta_H (300 MHz, CDCl}_3) 7.34-7.19 (5 H, m, Ar-H), 5.21 (1 H, t, J = 7.6 Hz, C=CH), 3.69 (2 H, s, SCH}_2Ph), 3.07 (2 H, d, J = 7.6 Hz, C=CHCH}_2), 2.09-1.83 (4 H, m, HC=CHCH}_2), 1.46-1.11 (16 H, m, alkyl CH}_2), 0.99-0.71 (6 H, m, CH}_3); \delta_C (75 MHz, CDCl}_3) 144.2 (C), 138.8 (C), 129.0 (CH), 128.6 (CH), 127.0 (CH), 120.0 (CH), 37.0 (CH}_2), 35.9 (CH}_2), 31.9 (CH}_2), 31.9 (CH}_2), 30.3 (CH}_2), 29.6 (CH}_2), 29.3 (CH}_2), 29.1 (CH}_2), 28.7 (CH}_2), 28.3 (CH}_2), 22.81 (CH}_2), 22.79 (CH}_2), 14.3 (2x CH}_3); \text{Found (APCI): } [\text{M+H}]^+ 333.2607, \text{C}_{22}\text{H}_{37}\text{S requires 333.2610.}
\end{align*}
\]
Butyl(3-hexylnon-2-en-1-yl)sulfide (3k)

The reaction was carried out at 60 °C following general procedure B. The product was purified using flash column chromatography using neat hexane. Product 3k was obtained as colourless liquid (9.40 mg, 31.5 µmol, 47 %).

\[ \nu_{\text{max/cm}^{-1}} \text{2956, 2925, 2856, 1465, 1378, 1221, 724; } \delta_{\text{H}} \text{(300 MHz, CDCl}_3\text{) 5.20 (1 H, t, } J = 7.7 \text{ Hz, C=CH), 3.15 (2 H, d, } J = 7.7 \text{ Hz, C=CHCH}_3\text{), 2.46 (2 H, m, SCH}_2\text{-alkyl), 2.09-1.92 (4 H, m, HC=CHCH}_2\text{), 1.63-1.18 (20 H, m, alkyl CH}_2\text{), 0.97-0.81 (9 H, m, CH}_3\text{); } \delta_{\text{C}} \text{(75 MHz, CDCl}_3\text{) 143.5 (C), 120.7 (CH), 36.9 (CH}_2\text{), 32.1 (CH}_2\text{), 31.9 (2x CH}_2\text{), 31.1 (CH}_2\text{), 30.2 (CH}_2\text{), 29.6 (CH}_2\text{), 29.4 (CH}_2\text{), 29.3 (CH}_2\text{), 28.8 (CH}_2\text{), 28.3 (CH}_2\text{), 22.8 (2x CH}_2\text{), 22.3 (CH}_2\text{), 14.3 (2x CH}_3\text{), 13.9 (CH}_3\text{); Found (APCI): [M+H]^+ 299.2761, C\text{_{19}H\text{39}S} \text{ requires 299.2767.} \]

Cyclohexyl(3-hexylnon-2-en-1-yl)sulfide (3l)

The reaction was carried out at 60 °C following general procedure B. The product was purified using flash column chromatography using neat hexane. Product 3l was obtained as colourless liquid (12.0 mg, 36.4 µmol, 56 %).

\[ \nu_{\text{max/cm}^{-1}} \text{2925, 2853, 1448, 1378, 1262, 1199, 998, 886, 724; } \delta_{\text{H}} \text{(300 MHz, CDCl}_3\text{) 5.21 (1 H, t, } J = 7.7 \text{ Hz, C=CH), 3.17 (2 H, d, } J = 7.7 \text{ Hz, C=CHCH}_3\text{), 2.76-2.50 (1 H, m, SCH), 2.12-1.86 (4 H, m, HC=CHCH}_2\text{), 1.85-1.10 (26 H, m, alkyl CH}_2\text{), 0.75-0.95 (6 H, m, CH}_3\text{); } \delta_{\text{C}} \text{(75 MHz, CDCl}_3\text{) 143.1 (C), 121.0 (CH), 43.0 (CH), 36.9 (CH}_2\text{), 33.9 (CH}_2\text{), 31.9 (2x CH}_2\text{), 31.8 (CH}_2\text{), 30.1 (CH}_2\text{), 29.7 (CH}_2\text{), 29.2 (CH}_2\text{), 28.7 (CH}_2\text{), 28.2 (CH}_2\text{), 27.9 (CH}_2\text{), 26.4 (CH}_2\text{), 26.1 (CH}_2\text{), 22.8 (2x CH}_2\text{), 14.3 (2x CH}_3\text{); Found (APCI): [M+H]^+ 325.2919, C\text{_{21}H\text{41}S} \text{ requires 325.2923.} \]
2-((3-Hexylnon-2-en-1-yl)thio)ethanol (3n)

The reaction was carried out at 50 °C following general procedure B. The product was purified using flash column chromatography using a gradient eluent system of neat hexane to 5:1 hexane:diethyl ether. Product 3n was obtained as yellow liquid (8.50 mg, 29.7 µmol, 45%).

\[ \nu_{\text{max}}/\text{cm}^{-1} \quad 3366, 2955, 2924, 2856, 1655, 1465, 1378, 1221, 1045, 1013, 724; \]
\[ \delta_{\text{H}} (300 \text{ MHz, CDCl}_3) 5.20 \ (1 \ H, t, J = 7.7 \text{ Hz, C}=\text{CH}), \ 3.70 \ (2 \ H, t, J = 5.8 \text{ Hz, CH}_2\text{OH}), \ 3.16 \ (2 \ H, d, J = 7.7 \text{ Hz, C}=\text{CHCH}_2), \ 2.69 \ (2 \ H, t, J = 5.8 \text{ Hz, SCH}_2\text{CH}_2), \ 2.13 \ (1 \ H, s, \text{OH}), \ 2.06-1.92 \ (4 \ H, m, \text{HC} = \text{CCH}_2), \]
\[ 1.46-1.13 \ (16 \ H, m, \text{alkyl CH}_2), \ 0.98-0.75 \ (6 \ H, \text{m, CH}_3); \]
\[ \delta_{\text{C}} (75 \text{ MHz, CDCl}_3) 144.4 \ (\text{C}), \ 120.0 \ (\text{CH}), \ 60.4 \ (\text{CH}_2), \ 36.9 \ (\text{CH}_2), \ 34.6 \ (\text{CH}_2), \ 31.9 \ (2 \times \text{CH}_2), \ 30.3 \ (\text{CH}_2), \ 29.6 \ (\text{CH}_2), \ 29.3 \ (\text{CH}_2), \ 28.8 \ (\text{CH}_2), \ 28.7 \ (\text{CH}_2), \ 28.2 \ (\text{CH}_2), \ 22.8 \ (2 \times \text{CH}_2), \ 14.3 \ (2 \times \text{CH}_2); \]
\[ \text{Found (APCI): } [\text{M+H}]^+ 287.2404, \ C_{17}\text{H}_{35}\text{OS} \text{ requires 287.2403}. \]

3-(3-Hexylnon-2-enylthio)propanoic acid (3o)

The reaction was carried out at 45 °C following general procedure B. The product was purified using flash column chromatography using a gradient eluent system of neat hexane to 1:1 hexane:diethyl ether. Product 3o was obtained as colourless liquid (18.5 mg, 58.8 µmol, 89%).

\[ \nu_{\text{max}}/\text{cm}^{-1} \quad 3035, 2955, 2925, 2856, 1709, 1430, 1264, 1197, 927, 724; \]
\[ \delta_{\text{H}} (300 \text{ MHz, CDCl}_3) 5.20 \ (1 \ H, t, J = 7.7 \text{ Hz, C}=\text{CH}), \ 3.19 \ (2 \ H, d, J = 7.7 \text{ Hz, C}=\text{CHCH}_2), \ 2.80-2.59 \ (4 \ H, m, \text{SCH}_2\text{CH}_2), \ 2.10-1.90 \ (4 \ H, m, HC = \text{CCH}_2), \ 1.48-1.14 \ (16 \ H, m, \text{alkyl CH}_2), \ 0.95-0.76 \ (6 \ H, \text{m, CH}_3); \]
\[ \delta_{\text{C}} (75 \text{ MHz, CDCl}_3) 177.7 \ (\text{C}), \ 144.4 \ (\text{C}), \ 120.0 \ (\text{CH}), \ 36.9 \ (\text{CH}_2), \ 34.8 \ (\text{CH}_2), \ 31.9 \ (2 \times \text{CH}_2), \ 30.2 \ (\text{CH}_2), \ 29.6 \ (\text{CH}_2), \ 29.5 \ (\text{CH}_2), \ 29.3 \ (\text{CH}_2), \ 28.7 \ (\text{CH}_2), \ 28.2 \ (\text{CH}_2), \ 25.9 \ (\text{CH}_2), \ 22.8 \ (2 \times \text{CH}_2), \ 14.3 \ (2 \times \text{CH}_2); \]
\[ \text{Found (APCI): } [\text{M+H}]^+ 315.2356, \ C_{18}\text{H}_{35}\text{O}_2\text{S requires 315.2352}. \]
General procedure C for 3p-3w:
4-Nitrothiophenol 2g (1.1 equiv.) and 5 (5 mol%) were added to a solution of allylic alcohol substrate (1 equiv.) in chloroform (0.386 M) in a 1 dram vial. The vial was capped and the solution allowed to stir at 35 °C for 24 h. The mixture was then filtered through a plug of silica with diethyl ether. The filtrate was concentrated under reduced pressure. Purification of the crude material was carried out by flash column chromatography.

(3,3-Dicyclohexylallyl)(4-nitrophenyl)sulfane (3p)

General procedure C. Purified using flash column chromatography using a gradient eluent system of neat hexane to 50:1 hexane:diethyl ether. Product 3p was obtained as yellow solid (20.8 mg, 57.9 µmol, 86%).

M.p. 102-104 °C; \( \nu_{\text{max}}/\text{cm}^{-1} \) 2926, 2851, 1659, 1573, 1503, 1344, 1092, 906, 851, 740; \( \delta_{\text{H}} \) (300 MHz, CDCl₃) 8.11 (2 H, d, \( J = 9.0 \) Hz, Ar-H), 7.33 (2 H, d, \( J = 9.0 \) Hz, Ar-H), 5.24 (1 H, t, \( J = 7.6 \) Hz, C=CH), 3.72 (2H, d, \( J = 7.6 \) Hz, C=CHCH₂), 2.43 (1 H, m, cyclohexyl CH), 1.92 (1 H, m, cyclohexyl CH'), 1.83-0.93 (20 H, m, cyclohexyl CH₂); \( \delta_{\text{C}} \) (75 MHz, CDCl₃) 156.8 (C), 148.5 (C), 145.1 (C), 126.8 (CH), 123.9 (CH), 115.4 (CH), 41.2 (CH), 40.5 (CH), 35.0 (CH₂), 31.0 (CH₂), 30.3 (CH₂), 27.2 (CH₂), 26.6 (CH₂), 26.3 (CH₂), 26.2 (CH₂); Found (APCI): [M+H]⁺ 360.1984, C₂₁H₂₉NO₂S requires 360.1992.
(E)-(4-Nitrophenyl)(3,4,4-trimethylpent-2-enyl)sulfane (3q)

General procedure C. Purified using flash column chromatography; using a gradient eluent system of neat hexane to 20:1 hexane:diethyl ether. Product obtained as yellow liquid (18.3 mg, 69.0 µmol, 59%). $\nu_{\text{max}}/\text{cm}^{-1}$ 2963, 2870, 1646, 1594, 1577, 1509, 1478, 1333, 1092, 852, 836, 741; $\delta_{\text{H}}$ (300 MHz, CDCl$_3$) 8.11 (2 H, d, $J = 9.0$ Hz, Ar-H), 7.31 (2 H, d, $J = 9.0$ Hz, Ar-H), 5.36 (1 H, t, $J = 7.4$ Hz, C=CH), 3.67 (2 H, d, $J = 7.4$ Hz, C=CHCH$_2$), 1.73 (3 H, s, C=CC(CH$_3$)$_3$); $\delta_{\text{C}}$ (75 MHz, CDCl$_3$) 150.0 (C), 148.4 (C), 145.1 (C), 126.7 (CH), 123.9 (CH), 114.6 (CH), 36.7 (C), 31.0 (CH$_2$), 29.0 (CH$_3$), 13.2 (CH$_3$); Found (APCI): [M+H]$^+$ 266.1207, C$_{14}$H$_{20}$NO$_2$S requires 266.1209.

(E)-(4-Nitrophenyl)(3-phenylbut-2-enyl)sulfane (3r)

General procedure C. 1H NMR analysis of crude reaction mixture showed that $E$:Z ratio was 9:1. Purified using flash column chromatography; using a gradient eluent system of neat petroleum ether to 50:1 petroleum ether:diethyl ether. Product 3r ($E$ isomer only) was obtained as a yellow oil (17.0 mg, 59.6 µmol, 59%). $\nu_{\text{max}}/\text{cm}^{-1}$ 2919, 1682, 1594, 1577, 1509, 1478, 1334, 1089, 852, 837, 740; $\delta_{\text{H}}$ (300 MHz, CDCl$_3$) 8.13 (2 H, d, $J = 9.0$ Hz, SAr-H), 7.37 (2 H, d, $J = 9.0$ Hz, SAr-H), 7.42-7.23 (5 H, m, Ar-H), 5.89 (1 H, t, $J = 7.6$ Hz, C=CH), 3.86 (2 H, d, $J = 7.6$ Hz, C=CHCH$_2$), 2.14 (3 H, s, CH$_3$); $\delta_{\text{C}}$ (75 MHz, CDCl$_3$) 147.7 (C), 145.3 (C), 142.6 (C), 140.4 (C), 128.5 (CH), 127.7 (CH), 126.9 (CH), 125.9 (CH), 124.1 (CH), 120.9 (CH), 31.2 (CH$_2$), 16.3 (CH$_3$); Found (APCI): [M+H]$^+$ 286.0891, C$_{16}$H$_{20}$NO$_2$S requires 286.0896.
(E)-(3-Cyclohexylbut-2-enyl)(4-nitrophenyl)sulfane (3s)

![Chemical Structure](image)

General procedure C. ¹H NMR analysis of crude reaction mixture showed that E:Z ratio was approximately 6:1. Purified using flash column chromatography; using a gradient eluent system of neat hexane to 50:1 hexane:diethyl ether. Product 3s was obtained as yellow liquid (20.7 mg, 71.0 µmol, 73%) as a 6:1 mixture of E and Z isomers. Characterisation of the major E isomer is given below.

ν<sub>max/cm</sub><sup>-1</sup> 2924, 2851, 1655, 1593, 1577, 1508, 1332, 1090, 852, 836, 741; δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 8.10 (2 H, d, J = 9.0 Hz, Ar-H), 7.31 (2 H, d, J = 9.0 Hz, Ar-H), 5.33-5.19 (1 H, m, J = 7.4 Hz, C=CH), 3.72-3.62 (2 H, m, J = 7.4 Hz, C=CHCH<sub>2</sub>), 1.95-1.02 (11 H, cyclohexyl CH, cyclohexyl CH<sub>2</sub>), 1.69 (3 H, s, CH<sub>3</sub>);

δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 148.4 (C), 147.2 (C), 145.1 (C), 126.6 (CH), 124.0 (CH), 115.8 (CH), 47.4 (CH), 31.8 (CH<sub>2</sub>), 31.2 (CH<sub>2</sub>), 30.6 (CH<sub>2</sub>), 29.8 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>), 26.4 (CH<sub>2</sub>), 14.9 (CH<sub>3</sub>); Found (APCI): [M+H]<sup>+</sup> 292.1364, C<sub>16</sub>H<sub>22</sub>NO<sub>2</sub>S requires 292.1366.

(2-Cyclohexylideneethyl)(4-nitrophenyl)sulfane (3t)

![Chemical Structure](image)

General procedure C. Purified using flash column chromatography; using a gradient eluent system of neat hexane to 50:1 hexane:diethyl ether. Product 3t was obtained as a yellow oil (17.3 mg, 65.7 µmol, 55%). ν<sub>max/cm</sub><sup>-1</sup> 2927, 2853, 1661, 1593, 1577, 1508, 1332, 1090, 852, 835, 740; δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 8.10 (2 H, d, J = 9.0 Hz, Ar-H), 7.32 (2 H, d, J = 9.0 Hz, Ar-H), 5.24 (1 H, t, J = 7.6 Hz, C=CH), 3.67 (2 H, d, J = 7.6 Hz, C=CHCH<sub>2</sub>S), 2.26-2.02 (4 H, m, C=CCH<sub>2</sub>CH<sub>2</sub>), 1.61-1.47 (6 H, m, CH<sub>2</sub>); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 148.3 (C), 146.2 (C), 145.1 (C), 126.6 (CH), 124.0 (CH), 114.3 (CH), 37.1 (CH<sub>2</sub>), 29.9 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 28.5 (CH<sub>2</sub>), 27.9 (CH<sub>2</sub>), 26.7 (CH<sub>2</sub>); Found (APCI): [M+H]<sup>+</sup> 264.1051, C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>S requires 264.1053.
(4-Butyloct-3-en-2-yl)(4-nitrophenyl)sulfane (3u)

General procedure C. Purified using flash column chromatography; using a gradient eluent system of neat hexane to 50:1 hexane:diethyl ether. Product 3u was obtained as yellow liquid (13.0 mg, 40.4 µmol, 50%).

ν max/cm⁻¹ 2956, 2929, 2860, 1653, 1577, 1512, 1335, 1091, 852, 742; δ H (300 MHz, CDCl₃) 8.09 (2 H, d, J = 9.0 Hz, Ar-H), 7.38 (2 H, d, J = 9.0 Hz, Ar-H), 5.09 (1 H, d, J = 9.8 Hz, C=C), 4.26 (1 H, dq, J = 9.8, 6.7 Hz, C=C), 2.21-1.86 (4 H, m, HC=CCH₂), 1.40 (3 H, d, J = 6.7 Hz, SCH₃), 1.36-1.08 (8 H, m, alkyl CH₂), 0.95-0.78 (6 H, m, alkyl CH₃); δ C (75 MHz, CDCl₃) 147.0 (C), 145.6 (C), 143.3 (C), 129.4 (CH), 126.0 (CH), 123.8 (CH), 40.6 (CH), 36.3 (CH₂), 30.8 (CH₂), 30.4 (CH₂), 30.3 (CH₂), 23.1 (CH₂), 22.5 (CH₂), 21.9 (CH₃), 14.2 (CH₃), 14.1 (CH₃); Found (APCI): [M+H]+ 322.1831, C₁₈H₂₈NO₂S requires 322.1835.

(E)-(4-Nitrophenyl)(4,5,5-trimethylhex-3-en-2-yl)sulfane (3v)

General procedure C. Purified using flash column chromatography using eluent system 19:1 hexane-Et₂O. Product 3v was obtained a colourless oil (21 mg, 75 µmol, 72%).

ν max/cm⁻¹ 2961, 2924, 2868, 1594, 1577, 1513, 1477, 1361, 1260, 1110, 1084, 1010, 852 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ H 8.09 (2H, d, J = 9.0 Hz, ArH), 7.36 (2H, d, J = 9.0 Hz, ArH), 5.16 (1H, dq, J = 9.4, 1.3 Hz, C=C), 4.23 (1H, dq, J = 9.4, 6.7 Hz, SCH), 1.66 (3H, d, J = 1.3 Hz, =CCH₃), 1.41 (3H, d, J = 6.7 Hz, SCHCH₃), 0.99 (9H, s, CMe₃); ¹³C NMR (75 MHz, CDCl₃) δ C 147.1 (C), 146.7 (C), 145.6 (C), 129.4 (CH), 123.7 (CH), 123.3 (CH), 41.1 (CH), 36.4 (C), 29.0 (CH₃), 21.4 (CH₃), 13.3 (CH₃); Found (APCI): [M+H]⁺ 280.1369, C₁₅H₂₂NO₂S requires 280.1366. 
(3-Butyl-2-methylhept-2-enyl)(4-nitrophenyl)sulfane (3w)

General procedure C. Purified using flash column chromatography; using a gradient eluent system of neat hexane to 50:1 hexane:diethyl ether. Product 3w was obtained as yellow liquid (16.0 mg, 49.8 µmol, 61%).

$\nu_{\text{max}}$/cm$^{-1}$ 2956, 2929, 2860, 1578, 1511, 1334, 1091, 852, 837, 742; $\delta_{\text{H}}$ (300 MHz, CDCl$_3$) 8.11 (2 H, d, $J = 9.0$ Hz, Ar-H), 7.33 (2 H, d, $J = 9.0$ Hz, Ar-H), 3.69 (2 H, s, SCH$_2$), 2.09-1.97 (4 H, m, C=CCH$_2$ alkyl), 1.79 (3 H, s, C=CCH$_3$), 1.42-1.21 (8 H, m, alkyl CH$_2$), 0.96-0.84 (6 H, m, alkyl CH$_3$); $\delta_{\text{C}}$ (75 MHz, CDCl$_3$) 149.2 (C), 145.1 (C), 141.1 (C), 126.8 (CH), 123.9 (CH), 121.5 (C), 37.4 (CH$_2$), 32.5 (CH$_2$), 32.4 (CH$_2$), 31.5 (CH$_2$), 30.8 (CH$_2$), 23.2 (CH$_2$), 23.0 (CH$_2$), 18.2 (CH$_3$), 14.2 (2x CH$_3$); Found (APCI): [M+H]$^+$ 322.1831, C$_{18}$H$_{26}$NO$_2$S requires 322.1835.
General procedure D for 3x-3aa, 24 and 25 (secondary or primary allylic alcohol substrates):

4-Nitrothiophenol 2g (1.1 equiv.) and 5 (5 mol%) were added to a solution of allylic alcohol (1 equiv.) in chloroform (0.386 M) in a 1 dram vial. The vial was capped and solution allowed to stir at 45 °C for 72 h. The mixture was then filtered through a plug of silica with diethyl ether. The filtrate was concentrated under reduced pressure. Purification of the crude material was done by flash column chromatography.

Cyclohex-2-enyl(4-nitrophenyl)sulfane (3x)

General procedure D. Purified using flash column chromatography using a gradient eluent system of neat hexane to 100:1 hexane:diethyl ether. Product 3x was obtained as yellow liquid (32.2 mg, 137 µmol, 89%).

$\nu_{\text{max}}/\text{cm}^{-1}$ 2927, 2834, 1645, 1593, 1575, 1505, 1478, 1331, 1084, 852, 836, 741; $\delta_{\text{H}}$ (300 MHz, CDCl$_3$) 8.12 (2 H, d, $J = 9.0$ Hz, Ar-H), 7.38 (2 H, d, $J = 9.0$ Hz, Ar-H), 5.93 (1 H, m, C=CH), 5.75 (1 H, m, C=CH), 4.07 (1 H, m, SCH), 2.17-1.59 (6 H, m, CH$_2$); $\delta_{\text{C}}$ (75 MHz, CDCl$_3$) 147.4 (C), 145.3 (C), 132.1 (CH), 127.4 (CH), 125.3 (CH), 124.1 (CH), 42.2 (CH), 28.6 (CH$_2$), 24.9 (CH$_2$), 19.5 (CH$_2$); Found (APCI): [M+H]$^+$ 236.0739, C$_{12}$H$_{14}$NO$_2$S requires 236.0740.
Cinnamyl(4-nitrophenyl)sulfane (3y)

General procedure D. Purified using flash column chromatography using a gradient eluent system of neat hexane to 50:1 hexane:diethyl ether. Product 3y was obtained as yellow solid (19.4 mg, 71.5 µmol, 64%). M.p. 90-92 °C; \(\nu_{\text{max}}/\text{cm}^{-1}\) 2923, 2853, 1674, 1573, 1507, 1477, 1330, 1090, 1078, 968, 851, 835, 760, 739, 692, 681; \(\delta_{\text{H}}\) (300 MHz, CDCl\(_3\)) 8.13 (2 H, d, \(J = 9.0\) Hz, SAr-H), 7.38 (2 H, d, \(J = 9.0\) Hz, SAr-H), 7.37-7.20 (5 H, m, Ar-H), 6.63 (1 H, d, \(J = 15.7\) Hz, HC=CHPh), 6.24 (1 H, dt, \(J = 15.7, 6.9\) Hz, HC=CHPh), 3.86 (2 H, d, \(J = 6.9\) Hz, SCH\(_2\)); \(\delta_{\text{C}}\) (75 MHz, CDCl\(_3\)) 147.0 (C), 145.4 (C), 136.3 (C), 134.2 (CH), 128.8 (CH), 128.2 (CH), 127.1 (CH), 126.6 (CH), 124.1 (CH), 123.2 (CH), 35.2 (CH\(_2\)); Found (APCI): [M+H]\(^+\) 272.0740, C\(_{15}\)H\(_{14}\)NO\(_2\)S requires 272.0735.

\((E)-(4-Nitrophenyl)(4-phenylbut-3-en-2-yl)sulfane (33z)\)

General procedure D. Purified using flash column chromatography using a gradient eluent system of neat hexane to 100:1 hexane:diethyl ether. Product 3z was obtained as yellow oil (20.7 mg, 72.5 µmol, 72%). \(\nu_{\text{max}}/\text{cm}^{-1}\) 3026, 2968, 2924, 1576, 1507, 1333, 1082, 963, 852, 836, 741, 692; \(\delta_{\text{H}}\) (300 MHz, CDCl\(_3\)) 8.10 (2 H, d, \(J = 9.0\) Hz, SAr-H), 7.43 (2 H, d, \(J = 9.0\) Hz, SAr-H), 7.34-7.06 (5 H, m, C=CH-Ar-H), 6.48 (1 H, d, \(J = 15.8\) Hz, Ph-CH), 6.17 (1 H, dd, \(J = 15.8, 8.2\) Hz, Ph-CH=CH), 4.16 (1 H, dq, \(J = 8.2, 6.9\) Hz, S-CH), 1.57 (3 H, d, \(J = 6.9\) Hz, CH\(_3\)); \(\delta_{\text{C}}\) (75 MHz, CDCl\(_3\)) 146.1 (C), 145.8 (C), 136.3 (C), 131.3 (CH), 130.4 (CH), 129.3 (CH), 128.8 (CH), 128.1 (CH), 126.5 (CH), 123.9 (CH), 45.0 (CH), 20.8 (CH\(_3\)); Found (APCI): [M+NH\(_4\)]\(^+\) 303.1158, C\(_{16}\)H\(_{15}\)NO\(_2\)SNH\(_4\) requires 303.1162.
(4-Nitrophenyl)(oct-3-en-2-yl)sulfane (3aa)

General procedure D. Purified using flash column chromatography using 99:1 hexane-Et₂O as eluent. Product 3aa (as an inseparable mixture of ~3:2 E:Z and 8:1 S₈₂':S₈₂) was obtained as a colourless oil (20 mg, 75.4 µmol, 65%). The spectrum for this mixture is shown below, with the CHS peak of each integrated.
(75 MHz, CDCl$_3$; E/Z isomers of 3aa) $\delta$ C 146.9 (C), 146.8 (C), 145.6 (C), 145.5 (C), 133.1 (CH), 131.0 (CH), 130.7 (CH), 129.0 (CH), 128.8 (CH), 128.4 (CH), 123.8 (2 × CH), 50.0 (CH), 44.5 (CH), 34.6 (CH$_2$), 31.9 (CH$_2$), 31.4 (CH$_2$), 29.4 (CH$_2$), 22.5 (CH$_2$), 22.1 (CH$_2$), 20.9 (CH$_3$), 17.8 (CH$_3$), 14.1 (CH$_3$), 14.0 (CH$_3$).
(E)-(4-cyclohexylbut-3-en-2-yl)(4-nitrophenyl)sulfane (3ab)

General procedure D. Purified using flash column chromatography using 19:1 hexane-Et₂O as eluent. Product 3aa (>20:1 E:Z) was obtained as a colourless oil (24 mg, 82 µmol, 85%), as an inseparable mixture of 2:1 S_N2':S_N2 products. The spectrum for this mixture is shown below, with the CHS peak of each integrated.
Found (APCI): [M+H]$^+$ 292.1362, C$_{16}$H$_{22}$NO$_2$S requires 292.1366.
(E)-(5,5-Dimethylhex-3-en-2-yl)(4-nitrophenyl)sulfane (3ac)

General procedure D. Purified using flash column chromatography using 19:1 hexane-Et₂O as eluent. Product 3ac (4:1 E:Z ratio) was obtained as a colourless oil (22 mg, 83 µmol, 71%).

ν_max/cm⁻¹ 2960, 2866, 1577, 1476, 1336, 1180, 1088, 971, 852, 838, 742 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) (4:1 mixture of E,Z alkene isomers) δ_H 8.12-8.05 (2.5 H, m, ArH), 7.41-7.34 (2.5 H, m, ArH), 5.56 (1 H, dd, J = 15.6, 0.8 Hz, EtBuCH=), 5.46-5.41 (0.5 H, m, Z' BuCH= and 'BuCH=CH), 5.27 (1 H, dd, J = 15.5, 8.4 Hz, EtBuCH=CH), 3.99-3.89 (1 H, m, E SCH), 3.54-3.50 (0.25 H, m, Z SCH), 1.63-1.61 (0.75 H, m, E SCHMe), 1.44 (1 H, d, J = 8.4 Hz, E SCHMe), 1.07 (2.25 H, s, Z CMe₃), 0.92 (9 H, s, E CMe₃); ¹³C NMR (75 MHz, CDCl₃) (mixture of alkene isomers) δ_C 146.6 (C⁻E), 145.8 (C⁻Z), 144.0 (CH × 2, E+Z), 129.7 (CH × 2, E+Z), 129.0 (C⁻E), 128.6 (C⁻Z), 125.8 (CH × 2, E+Z), 123.7 (CH⁻E), 123.6 (CH⁻Z), 45.2 (CH × 2, E+Z), 35.2 (C⁻Z), 33.1 (C⁻E), 29.6 (CH₃ × 2, E+Z), 28.1 (CH₃⁻Z), 21.1 (CH₃⁻E); Found (APCI): [M+H⁺] 266.1208, C₁₄H₁₉NO₂S requires 266.1209.

(3-Methylbut-2-enyl)(4-nitrophenyl)sulfane (25)

General procedure D. Purified using flash column chromatography using a gradient eluent system of neat hexane to 150:1 hexane:diethyl ether. Product 25 was obtained as colourless liquid (22.8 mg, 102 µmol, 59%).

ν_max/cm⁻¹ 2972, 2915, 1667, 1593, 1577, 1507, 1331, 1090, 852, 835, 740; δ_H (300 MHz, CDCl₃) 8.11 (2 H, d, J = 9.0 Hz, Ar-H), 7.31 (2 H, d, J = 9.0 Hz, Ar-H), 5.30 (1 H, t, J = 7.5 Hz, C=CH), 3.65 (2 H, d, J = 7.5 Hz, CH₂), 1.75 (3 H, s, CH₃), 1.73 (3 H, s, CH₃); δ_C (75 MHz, CDCl₃) 148.3 (C), 145.1 (C), 138.3 (C), 126.5 (CH), 124.0 (CH), 117.7 (CH), 30.6 (CH₂), 25.8 (CH₂), 18.1 (CH₃); Found (APCI): [M+H⁺] 224.0740, C₁₁H₁₄NO₂S requires 224.0740.
(4-Methylpent-3-en-2-yl)(4-nitrophenyl)sulfane (27)

General procedure D. Purified using flash column chromatography using a gradient eluent system of neat hexane to 100:1 hexane:diethyl ether. Product 27 was obtained as yellow liquid (30.9 mg, 130 µmol, 87%).

ν<sub>max</sub>/cm<sup>-1</sup> 2970, 2924, 2866, 1576, 1508, 1333, 1092, 1061, 852, 835, 741; δ<sub>H</sub> (300 MHz, CDCl<sub>3</sub>) 8.09 (2 H, d, J = 9.0 Hz, Ar-H), 7.36 (2 H, d, J = 9.0 Hz, Ar-H), 5.11 (1 H, dsept, J = 9.6, 1.3 Hz, C=CH), 4.22 (1 H, dq, J = 9.6, 6.7 Hz, SCH), 1.69 (3 H, d, J = 1.3 Hz, HC=CCH<sub>3</sub>), 1.66 (3 H, d, J = 1.3 Hz, HC=CCH<sub>3</sub>), 1.39 (3 H, d, J = 6.7 Hz, SCHCH<sub>3</sub>); δ<sub>C</sub> (75 MHz, CDCl<sub>3</sub>) 147.1 (C), 145.6 (C), 135.1 (C), 129.1 (CH), 126.3 (CH), 123.8 (CH), 40.8 (CH), 25.7 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 18.3 (CH<sub>3</sub>); Found (APCI): [M+H]<sup>+</sup> 238.0899, C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub>S requires 238.0896.
The following 4 procedures describe the 4 steps towards enantioenriched \( (R,E)-(4\text{-cyclohexylbut-3-en-2-yl})(4\text{-nitrophenyl})\)sulfane 3ab using a general procedure by Gais\textsuperscript{14}:

### 4-Cyclohexylbut-3-yn-2-ol

\[
\text{4-Cyclohexylbut-3-yn-2-ol}
\]

\[\text{BuLi (15.01 mL of a 1.6 M solution, 24.02 mmol) was added dropwise to a stirred solution of cyclohexylacetylene (2.0 g, 2.41 mL, 18.5 mmol) in THF (20 mL) at } -78 \degree \text{C under Ar. The resulting solution was stirred at } -78 \degree \text{C for 10 minutes, and acetaldehyde (1.06 g, 1.36 mL, 24.0 mmol) was added dropwise. The resulting solution was stirred at } -78 \degree \text{C for 10 minutes then allowed to warm to rt. Saturated NH}_3\text{Cl (aq) (20 mL) was added and the layers were separated, extracting the aqueous with Et}_2\text{O (3 } \times 20 \text{ mL). The combined organic layers were dried (MgSO}_4\text{) and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with 9:1 pentane:Et}_2\text{O as eluent gave 4-cyclohexylbut-3-yn-2-ol (2.41 g, 86%) as a colourless oil.} \]

### \( (E)\)-4-Cyclohexylbut-3-en-2-ol

\[
\text{\( (E)\)-4-Cyclohexylbut-3-en-2-ol}
\]

\(\text{A solution of 4-cyclohexylbut-3-yn-2-ol (1.8 g, 11.8 mmol) in THF (10 mL) was added dropwise to a stirred suspension of LiAlH}_4\text{ (897 mg, 23.6 mmol) in THF (10 mL) at RT under Ar. The resulting solution was stirred at RT for 4 h. A 1 M solution of NaOH (aq.) was added dropwise until a white precipitate was observed. The solids were filtered off over Celite\textsuperscript{\textregistered}, washing with Et}_2\text{O (50 mL). The filtrate was concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with 9:1 pentane:Et}_2\text{O as eluent gave (E)-4-cyclohexylbut-3-en-2-ol}}
\]
(1.43 g, 78%) as a colourless oil. \( R_F 0.1 \) (9:1 pentane:Et\(_2\)O); \( \nu_{\text{max}}/\text{cm}^{-1} \) 3331 (br), 2969, 2921, 2850, 1448, 1367, 1130, 1057, 966, 941, 891, 864, 842, 569; \( \delta_H \) (300 MHz, CDCl\(_3\)) 5.54 (1H, dd, \( J = 15.7, 6.3 \) Hz, =CH), 5.42 (1H, ddd, \( J = 15.7, 6.2, 0.7 \) Hz, =CH), 4.21 (1H, dq, \( J = 6.3, 6.3 \) Hz, OCH), 1.97-1.81 (1H, m, =CHCH), 1.83 (1H, br s, OH), 1.75-1.58 (4H, m, Cy-H), 1.33-0.94 (6H, m, Cy-H), 1.21 (3H, d, \( J = 6.3 \) Hz, OCH\(_2\)), \( \delta_C \) (75 MHz, CDCl\(_3\)) 136.8 (CH), 131.7 (CH), 69.1 (CH), 40.2 (CH), 32.9 (CH\(_2\)), 26.2 (CH\(_2\)), 26.1 (CH\(_2\)), 23.5 (CH\(_3\)). Data Consistent with that reported in the literature.[16]

\( (E)-O-4\text{-cyclohexylbut-3-en-2-yl propylcarbamothioate} \)

A solution of \( (E)-4\text{-cyclohexylbut-3-en-2-ol} \) (500 mg, 3.24 mmol) in THF (2 mL) was added dropwise to a stirred suspension of NaH (145 mg of a 60% dispersion in mineral oil, 3.60 mmol) in THF (2 mL) at 0 °C under Ar. The resulting solution was stirred at 0 °C for 1 h. Then, a solution of \( n\text{propylisothiocyanate} \) (329 mg, 336 \( \mu \text{L}, \) 3.25 mmol) in THF (1 mL) was added. The resulting solution was stirred at 0 °C for 1 h. Then, a saturated solution of NaH\(_2\)CO\(_3\) (aq.) (3 mL) was added and the layers were separated, extracting the aqueous with EtOAc (3 \( \times 10 \) mL). The combined organic layers were dried (MgSO\(_4\)) and concentrated under reduced pressure to give the crude product. Purification by flash column chromatography on silica with 9:1 pentane:Et\(_2\)O as eluent gave \( (E)-O-4\text{-cyclohexylbut-3-en-2-yl propylcarbamothioate} \) (587 mg, 71%) as a colourless oil, \( R_F 0.2 \) (9:1 pentane:Et\(_2\)O); \( \nu_{\text{max}}/\text{cm}^{-1} \) 3290, 2964, 2924, 2852, 1657, 1514, 1448, 1400, 1378, 1354, 1263, 1193 (C=S), 1129, 1038, 964, 928, 892, 809, 736, 703, 606; \( \delta_H \) (300 MHz, CDCl\(_3\)) (4:1 mixture of rotamers) 6.69 (0.3H, br s, N-H), 6.26 (1H, br s, N-H), 5.97-5.84 (0.3H, m, =CH), 5.75-5.24 (2.3H, m, =CH), 3.96-3.83 (1H, m, OCH), 3.53-3.43 (0.3H, m, OCH), 3.32-3.09 (2.6H, m, NCH\(_2\)), 1.86-1.41 (13H, m, Cy-H + \( n\text{Pr-H} \)), 1.39-0.80 (10.4H, m, Cy-H + \( n\text{Pr-H} \)); \( \delta_C \) (75 MHz, CDCl\(_3\)) (mixture of rotamers) 166.9 (2 \( \times C \)), 139.2 (CH), 1302. (CH), 127.3 (CH), 126.8 (CH), 53.7 (2 \( \times C \)), 46.3 (CH\(_2\)), 44.8 (CH\(_2\)), 43.1 (2 \( \times C\)), 42.6 (CH), 40.3 (CH), 32.7 (CH\(_2\)), 30.9 (CH\(_2\)), 30.3 (CH\(_2\)), 26.4 (CH\(_2\)), 26.4 (CH\(_2\)), 26.2 (CH\(_2\)), 26.1 (CH\(_2\)), 23.1 (CH\(_2\)), 22.6 (CH\(_2\)), 17.9 (2 \( \times C\)), 11.4 (CH\(_3\)), 11.4 (CH\(_3\)); Found (NSI): [M+H]\(^+\) 256.1730, \( C_{14}H_{25}NOS \) requires 256.1730.
(R,E)-(4-cyclohexylbut-3-en-2-yl)(4-nitrophenyl)sulfane (3ab) [+] rac-29

\[
\begin{array}{c}
\text{O=S} \\
\text{O=S} \\
\text{C6H5} \\
\text{C6H5} \\
\text{Me} \\
\text{Me} \\
\text{(R-3ab)} \\
\text{80:20 er} \\
\text{Me} \\
\text{(rac-29)} \\
\text{50:50 er} \\
\end{array}
\]

Pd$_2$(dba)$_3$ (45 mg, 0.044 mmol, 7.5 mol%) and (R,R)-DACH-phenyl Trost ligand (73 mg, 0.105 mmol) were stirred in CH$_2$Cl$_2$ (4 mL) in a Schlenk tube at rt under Ar until a colour change from red to orange was observed. Then, (E)-O-4-cyclohexylbut-3-en-2-yl propyl carbamothioate (300 mg, 1.17 mmol) in CH$_2$Cl$_2$ (2 mL) was added. The resulting solution was stirred at RT under Ar for 6 days.

Then, a saturated solution of NH$_4$Cl(aq) (10 mL) was added. The resulting solution was stirred at RT for 30 min. The layers were separated, extracting the aqueous with CH$_2$Cl$_2$ (3 × 20 mL). The combined organic layers were dried (MgSO$_4$) and concentrated under reduced pressure. The residue was passed over a plug of silica, using 9:1 pentane:Et$_2$O as eluent, to give 183 mg of a yellow oil. 27 mg of this residue was taken up in dioxane (1 mL) at rt under Ar. Then, 1-iodo-4-nitrobenzene (26 mg, 0.106 mmol), Pd(OAc)$_2$ (3 mg, 0.011 mmol), triphenylphosphine (9 mg, 0.032 mmol), $^5$Bu$_4$NI (39 mg, 0.106 mmol) and K$_2$CO$_3$ (19 mg, 0.137 mmol) were added. The resulting solution was stirred at reflux under Ar for 4 h. Then, hexane (6 mL) was added, and the solution allowed to cool to rt. The resulting suspension was filtered over Celite®, washing with Et$_2$O (20 mL). The filtrate was washed with H$_2$O (10 mL), dried (MgSO$_4$) and evaporated under reduced pressure to give the crude product.

Purification by flash column chromatography on silica with 19:1 pentane:Et$_2$O as eluent 2:1 mixture of (R)-3ab and 29, 80:20 er ((R)-3ab), 50:50 er (29) (combined yield 24 mg, 54%) as a colourless oil.

**HPLC trace of 3ab (80:20 er)**

HPLC conditions: Daicel CHIRALPAK® IA 99:1 hexane:IPA, 1 mL/min, 25 °C.
HPLC trace of 29 (racemic)

HPLC conditions: Daicel CHIRALPAK® IA, 99.4:0.6 hexane:IPA, 1mL/min, 25 °C.
Resubjection of enantioenriched 3ab (+29)

A 2:1 mixture of (R)-3ab and 29, 80:20 er (3ab), 50:50 er (29) (12 mg, 0.041 mmol) from the previous reaction, p-nitrothiophenol (0.6 mg, 0.004 mmol) and catalyst 5 (2 mg, 0.002 mmol, 5 mol%) were stirred in CHCl₃ (107 μL) at 45 °C under air for 3 days. The resulting solution was filtered over a plug of silica, washing with 9:1 pentane:Et₂O. The filtrate was concentrated under reduced pressure to give the crude product. Purification by flash column chromatography gave a 4:1 mixture of 3ab:29 (10 mg, 83%, both 50:50 er).
HPLC trace of product (3ab) - racemic

HPLC conditions: Daicel CHIRALPAK® IA 99:1 hexane:IPA, 1 mL/min, 25 °C.

HPLC trace of product (29) - racemic

HPLC conditions: Daicel CHIRALPAK® IA 99.4:0.6 hexane:IPA, 1 mL/min, 25 °C.
4) $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of synthesised compounds

$^1\text{H}$ NMR, 300 MHz, CDCl3

$^{13}\text{C}$ NMR, 75 MHz, CDCl3
3a

$\text{CH}_3(\text{CH}_2)_5$ $\text{H}_3\text{C}(\text{H}_2\text{C})_5$ $\text{S}$

**1H 300 MHz Job 20876 Green Samantha I. A06I CDCl$_3$ 24.9°C**

**13C 75.5 MHz Job 20876 Green Samantha I. A06I CDCl$_3$ 24.9°C 3 hours 1 min**
$\text{CH}_3(\text{CH}_2)_5$  
$\text{H}_3\text{C}(\text{H}_2\text{C})_5$  
$\text{S}$  

3b

1H 300.1MHz Job 22858 Green Samantha L  C129 CDCl3  24.9°C

13C 75.5MHz Job 22900 Green Samantha L  C129 CDCl3  25.1°C  3 hours  1 min
**$	ext{CH}_3\text{CH}(\text{CH}_2)_5$**

**$	ext{H}_2\text{C}(\text{CH}_2)_5$**

**$\text{SOMe}$**

---

1H 300.1MHz Job 23437 Green Samantha L. CI47 CDCl3 25.1°C

---

13C 75.5MHz Job 23451 Green Samantha L. CI47 CDCl3 25.0°C 3 hours 1 min

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(E)-4-cyclohexylbut-3-en-2-ol
(E)-O-(4-cyclohexylbut-3-en-2-yl) propylcarbamothioate
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Computational Supporting Information for:

Gold(I)-Catalysed Direct Thioetherifications using Allylic Alcohols – an Experimental and Computational Study

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Table of Contents

1. Computational Details and References pg 73
2. Reactions of Substrate 4’ pg 75
3. Reactions of Substrate 24 pg 103
4. Reactions of Substrate 4’ with PhSH at [(Johnphos)Au(NCMe)]+, 5. pg 127
5. Reactions of 9, 10 and 11 with PhSH pg 149
6. Reactions of Substrate 17 pg 162
1. Computational Details and References.

Calculations were run with Gaussian 03 Revision D.01 with PCM solvent corrections run with Gaussian 09, Revision A.02. Geometry optimisations were performed using the BP86 functional with Au, P and S centres described with the Stuttgart RECPs and associated basis sets (with added d-orbital polarisation on P ($\zeta = 0.387$) and S ($\zeta = 0.503$) and 6-31G** basis sets for all other atoms. All stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue) and IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. Frequency calculations also provided a free energy in the gas-phase, computed at 298.15 K and 1 atm. Energies reported in the text are based on the gas-phase free energies and incorporate a correction for dispersion effects using Grimme’s D3 parameter set (i.e. BP86-D3) as well as solvation (PCM approach) in CHCl$_3$.

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2. Reactions of Model Substrate 4'

Figure S1. First $S_N2'$ step via *anti* attack of PhSH. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl$_3$) in red. All energies are in kcal/mol and are quoted relative to $5'$ and the separated reactants set to zero.

Figure S2. First $S_N2'$ step via *syn* attack of PhSH. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl$_3$) in red. All energies are in kcal/mol and are quoted relative to $5'$ and the separated reactants set to zero.
Figure S3. Second S$_{N}$2' step to form the formal S$_{N}$2 product 28 via syn attack of PhSH. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl$_3$) in red. All energies are in kcal/mol and are quoted relative to 5' and the separated reactants set to zero.
Table S1. Computed relative energies (kcal/mol) for the reactions 4' with PhSH. Energies are reported as $\Delta E$ (gas-phase SCF energies), $\Delta H_{298}$ (zero-point energy corrected energies at 298.15 K), $\Delta G$ (free energies at 298.15 K and 1 atm), $\Delta G_{\text{disp}}$ (including a correction for dispersion effects using Grimme’s D3 parameter set) and $\Delta G_{\text{CHCl3+disp}}$ including an additional correction for CHCl$_3$ solvent via the PCM approach.

|                  | $\Delta E$ | $\Delta H_{298}$ | $\Delta G$ | $\Delta G_{\text{disp}}$ | $\Delta G_{\text{CHCl3+disp}}$ |
|------------------|------------|------------------|------------|--------------------------|-------------------------------|
| 5'               | 0.0        | 0.0              | 0.0        | 0.0                      | 0.0                           |
| *IntI4' (anti)   | +7.2       | +7.1             | +7.5       | +3.5                     | +0.9                          |
| *IntI4' (syn)    | +2.1       | +2.1             | +2.7       | -1.2                     | -2.4                          |
| IntI4' (anti)    | +2.6       | +4.5             | +14.2      | +3.7                     | +2.3                          |
| IntI4' (syn)     | -4.6       | -2.6             | +8.1       | -5.4                     | -2.5                          |
| TS(I-II)4' (anti)| +3.6       | +4.9             | +17.2      | +5.5                     | +9.1                          |
| TS(I-II)4' (syn) | +13.6      | +14.4            | +26.5      | +14.6                    | +19.2                         |
| Int(I-II)4' (syn)| +4.3       | +6.1             | +19.3      | +6.3                     | +9.9                          |
| TS(I-II)$_{B}$4' | +6.9       | +8.9             | +21.3      | +7.9                     | +11.1                         |
| IntII4' (anti)   | -10.2      | -7.0             | +3.8       | -6.5                     | -3.9                          |
| IntII4' (syn)    | -13.9      | -10.7            | +0.5       | -12.1                    | -8.9                          |
| *IntII4' (anti)  | -1.5       | -0.4             | +0.4       | -5.4                     | -6.7                          |
| *IntII4' (syn)   | -1.5       | -0.4             | -0.2       | -6.5                     | -6.8                          |
| IntIII4' (anti)  | -4.4       | -1.5             | +8.3       | -5.0                     | -3.6                          |
| TS(III-IV)$_{A}$ | +3.2       | +5.2             | +19.3      | +0.4                     | +5.0                          |
| Int(III-IV)4'    | +2.3       | +4.3             | +19.3      | +0.1                     | +6.5                          |
| TS(III-IV)$_{A}$ | +4.7       | +6.5             | +21.0      | +2.7                     | +7.7                          |
| IntIV4' (anti)   | -1.0       | +1.8             | +10.1      | -4.4                     | -2.1                          |
| *IntIV4' (anti)  | +2.6       | +3.5             | +5.0       | -3.0                     | -3.0                          |
| [(Me$_3$P)Au(SHPh)]$^+$ | +3.0 | +3.2 | +3.5 | +0.8 | +0.3 |

*Complex computed in the absence of PhSH nucleophile
4'

16

C  -0.99096 -0.15998 -0.68191
C  -2.17978 -0.01659 -0.07576
C   0.35717  0.00249  0.01047
O   0.20519  0.14049  1.43509
C   1.03076  1.30972 -0.45019
C   1.25736 -1.21481 -0.30513
H   2.22975 -1.10254  0.20221
H   1.43651 -1.31724 -1.38957
H   0.78570 -2.15082  0.04411
H   1.16932  1.31718 -1.54380
H   2.01740  1.41503  0.03148
H   0.40537  2.17124 -0.16821
H  -0.22765 -0.68029  1.74234
H  -2.23746  0.25721  0.98320
H  -3.12229 -0.14623 -0.61626
H  -0.94546 -0.41252 -1.75106

SCF(BP86) = -271.747350648
H 0K = -271.610487
H 298K = -271.602862
G 298K = -271.641019
Solvent Correction(CHCl3) = -0.00299837
BP86-D3 Correction = -0.01360767
Lowest frequencies = 114.4346 cm⁻¹, 221.6111 cm⁻¹
**Acetonitrile**

6

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -0.27724  | 0.00001   | 0.00000   |
| N       | -1.45073  | -0.00001  | -0.00000  |
| C       | 1.18521   | -0.00000  | -0.00000  |
| H       | 1.56908   | -0.75455  | -0.70605  |
| H       | 1.56909   | -0.23420  | 1.00648   |
| H       | 1.56911   | 0.98872   | -0.30042  |

SCF (BP86) = -132.751073663
H 0K = -132.706992
H 298K = -132.703349
G 298K = -132.731053
Solvent Correction (CH3Cl) = -0.00550907
BP86-D3 Correction = -0.00127441
Lowest frequencies = 373.9768 cm⁻¹, 373.9955 cm⁻¹
2a

13

S  -2.30589  -0.08411  -0.00001
C  -0.50937   0.00314  -0.00001
H  -2.52407   1.25935   0.00017
C   2.31065   0.00157  -0.00001
C   1.60229   1.21347   0.00000
C  0.19915   1.22104   0.00000
C  0.19915  -1.21626   0.00001
C  1.60116  -1.21052   0.00001
H  3.40497   0.00149  -0.00001
H  2.14160   2.16667   0.00001
H  -0.34123   2.17370  -0.00002
H  -0.34553  -2.16639  0.00003
H  2.14038  -2.16366   0.00001

SCF(BP86) = -242.466521945
H 0K = -242.370169
H 298K = -242.363647
G 298K = -242.401071
Solvent Correction(CHCl3) = -0.00332263
BP86-D3 Correction = -0.00877366
Lowest frequencies = 95.0392 cm⁻¹, 178.2693 cm⁻¹
C  -2.16709  0.60438 -0.17525
C  -1.37907  1.66760  0.51651
S   0.18249  2.17621 -0.41776
C  -2.33255 -0.68389  0.21555
C   1.17361  0.67743 -0.25689
C  -1.73770 -1.29090  1.46500
C  -2.33255 -0.68389  0.21555
H  -4.01542 -2.03642 -0.02447
H  -2.57355 -2.50909 -0.93569
H  -3.57922 -1.14705 -1.51285
H  -1.09235 -2.15014  1.20379
H  -2.53297 -1.68554  2.12551
H  -1.12806 -0.58548  2.04853
H  -1.93699  2.61994  0.55964
H  -1.08109  1.40184  1.54148
H  -2.63601  0.91759 -1.11834
C   2.77000  1.63199 -0.02612
C   2.93508 -0.57000  0.87853
C   2.13900  0.88100  0.76698
C   1.01646 -0.38677 -1.16911
C   1.81079 -1.53863 -1.04808
H   3.39273 -2.52858  0.06134
H   3.68607 -0.63610  1.67305
H   2.25997  1.41365  1.46719
H   0.27505 -0.29967 -1.96800
H   1.68555 -2.36129 -1.76038

SCF (BP86) = -437.80402827
H 0K = -437.591476
H 298K = -437.578329
G 298K = -437.632829
Solvent Correction (CHCl3) = -0.00345369
BP86-D3 Correction = -0.02579540
Lowest frequencies = 24.0999 cm\(^{-1}\), 37.3450 cm\(^{-1}\)
|   |   |   |   |
|---|---|---|---|
| C | 1.83749 | 1.37291 | -0.15835 |
| C | 1.38694 | 2.34833 | 0.65188 |
| C | 1.93154 | -0.09594 | 0.16767 |
| S | 0.72440 | -1.02266 | -1.00338 |
| C | 1.62145 | -0.44487 | 1.62664 |
| C | 3.30955 | -0.64785 | -0.25394 |
| H | 3.35762 | -1.74061 | -0.11044 |
| H | 4.09713 | -0.18044 | 0.36243 |
| H | 3.52729 | -0.42509 | -1.31240 |
| H | 2.32493 | 0.07962 | 2.29855 |
| H | 1.72673 | -1.52936 | 1.79043 |
| H | 0.59622 | -0.15415 | 1.90682 |
| C | -0.49811 | -0.46442 | -0.45291 |
| H | 1.03371 | 2.15172 | 1.66881 |
| H | 1.35732 | 3.38978 | 0.31690 |
| H | 2.17315 | 1.63194 | -1.17248 |
| C | -3.48689 | 0.33057 | 0.32829 |
| C | -2.93943 | -0.86425 | 0.82366 |
| C | -1.64953 | -1.26170 | 0.43715 |
| C | -1.45503 | 0.73213 | -0.95233 |
| C | -2.74336 | 1.12657 | -0.55867 |
| H | -4.49422 | 0.63806 | 0.62825 |
| H | -3.51750 | -1.49097 | 1.51110 |
| H | -1.21652 | -2.19345 | 0.81391 |
| H | -0.87435 | 1.34108 | -1.65027 |
| H | -3.16967 | 2.05564 | -0.95197 |

SCF (BP86) = -437.796345583
H 0K = -437.588363
H 298K = -437.571076
G 298K = -437.623488
Solvent Correction (CHCl3) = -0.00327463
BP86-D3 Correction = -0.02890771
Lowest frequencies = 30.5930 cm⁻¹, 62.5830 cm⁻¹
| Element | X   | Y    | Z   |
|---------|-----|------|-----|
| Au      | 0.00000 | 0.00000 | 0.27882 |
| P       | 0.00000 | 0.00000 | -2.01876 |
| C       | 0.00002 | 1.70667 | -2.73020 |
| H       | -0.89591 | 2.24702 | -2.38882 |
| H       | -0.89598 | 2.24699 | -2.38883 |
| C       | -1.47803 | -0.85332 | -2.73020 |
| H       | -1.42910 | -0.82507 | -3.83091 |
| H       | -1.49802 | -1.89939 | -2.38882 |
| H       | -2.39394 | -0.34756 | -2.38883 |
| C       | 1.47801 | -0.85335 | -2.73020 |
| H       | 1.42908 | -0.82510 | -3.83091 |
| H       | 2.39393 | -0.34763 | -2.38882 |
| H       | 1.49796 | -1.89943 | -2.38883 |
| N       | 0.00000 | 0.00000 | 2.34123 |
| C       | 0.00000 | 0.00000 | 3.50951 |
| C       | 0.00000 | 0.00000 | 4.96207 |
| H       | 0.00002 | 1.65017 | -3.83091 |
| H       | -0.79509 | 0.66685 | 5.33517 |
| H       | 0.97506 | 0.35514 | 5.33517 |
| H       | -0.17997 | -1.02200 | 5.33517 |

SCF(BP86) = -394.816760183
H 0K = -394.658816
H 298K = -394.645144
G 298K = -394.701058
Solvent Correction(CHCl3) = -0.05231851
BP86-D3 Correction = -0.01603484
Lowest frequencies = 14.6238 cm⁻¹, 37.9964 cm⁻¹
*IntI4' (anti)

30

P  -2.38553  0.39539  0.03669
C  -2.61981  1.77228  1.25112
C  -2.98787  1.04302 -1.58944
C  -3.58805 -0.92231  0.03669
Au -0.18921 -0.42411 -0.05359
C   2.13004 -0.59200 -0.54573
C   1.65623 -1.70250  0.14346
C   2.97359  0.55663  0.02488
H  -3.67524  2.08986  1.25560
H  -1.98209  2.62441  0.97111
H  -2.33606  1.42724  2.25700
H  -3.54842 -1.74829 -0.19501
H  -4.60747 -0.50412  0.55807
H  -3.32304 -1.30823  1.52739
H  -4.02909  1.39042 -1.48920
H  -2.93810  0.24331 -2.34396
H  -2.35091  1.88039 -1.91245
O  4.30846  0.14845 -0.34949
C   2.96534  0.63856  1.55409
C   2.60379  1.89832 -0.62370
H  3.32689  2.67106 -0.31612
H  1.59601  2.28393 -0.31760
H  2.61427  1.82819 -1.72688
H  1.94971  0.83132  1.93965
H  3.62149  1.46171  1.87563
H  3.35342 -0.28925  2.00295
H  4.48308  0.45840 -1.26069
H  1.81333 -1.80573  1.22339
H  1.37898 -2.61448 -0.39935
H  2.11635 -0.63019 -1.64621

SCF(BP86)  = -533.80159362
H 0K  = -533.551183
H 298K = -533.533388
G 298K  = -533.599102
Solvent Correction(CHCl3)  = -0.05404296
BP86-D3 Correction = -0.03463755
Lowest frequencies = 9.3216 cm⁻¹, 36.9935 cm⁻¹
*IntI₄⁻ (syn)*

30

P  -2.36256  0.37978  0.04411
C  -2.95662  1.11438 -1.54786
C  -3.57013 -0.96003  0.46082
C  -2.60012  1.69007  1.32916
Au -0.16563 -0.42041 -0.06584
C   2.15513 -0.62043 -0.58531
C   1.68152 -1.70422  0.13830
C   2.88651  0.55953  0.03127
H   -3.99815  1.45688 -1.43479
H   -2.90258  0.35646 -2.34400
H   -2.31740  1.96735 -1.82180
H   -2.32145  1.28918  2.31556
H   -3.65379  2.01295  1.34575
H   -1.95465  2.55143  1.09972
H   -4.58923  -0.54250  0.50460
H   -3.31053  -1.30889  1.43618
H   -3.52710  -1.74602  -0.30834
O   2.47393  0.59799  1.40674
C   2.52964  1.87532  -0.69009
C   4.40599  0.26438  -0.07686
H   4.97124  1.11490  0.34298
H   4.72759  0.14029  -1.12382
H   4.66456  -0.64581  0.48618
H   2.80167  1.83813 -1.75843
H   3.08010  2.71555  -0.23424
H   1.44978  2.08442  -0.60620
H   3.01751  1.26930  1.86191
H   1.83336  -1.74102  1.22316
H   1.38964  -2.62910  -0.37291
H   2.17974  -0.67551 -1.68229

SCF(BP86) = -533.809627303
H 0K =  -533.559084
H 298K = -533.541282
G 298K =  -533.606765
Solvent Correction(CHCl3) = -0.05168875
BP86-D3 Correction = -0.03461175
Lowest frequencies = 10.8845 cm⁻¹, 37.5183 cm⁻¹
IntI₄' (anti)

SCF(BP86) = -776.275343906
H 0K = -775.927161
H 298K = -775.901166
G 298K = -775.989486
Solvent Correction(CHCl₃) = -0.05535675
BP86-D3 Correction = -0.05392868
Lowest frequencies = 6.6475 cm⁻¹, 9.2485 cm⁻¹
IntI₁· (syn)

P  -2.61653 -1.48207  0.13651
C  -2.26076 -3.18549 -0.50037
C  -2.85611 -1.69235  1.96182
C  -4.29183 -1.05569 -0.53315
Au -0.91314  0.02842 -0.43884
C  -0.21221  2.25303 -0.96721
C   0.69090  1.29385 -1.40328
S   1.25962  -0.08569  1.40801
C  -0.04509  3.09290  0.28825
H  -3.06558 -3.87629 -0.20090
H  -1.30231 -3.53450 -0.08719
H  -2.18822 -3.16009 -1.59837
H  -4.60759 -0.79794 -0.13196
H  -5.02426 -1.82696 -0.24190
H  -4.23956 -0.99007 -1.62875
H  -3.63732 -2.44513  2.15635
H  -3.15472 -0.73168  2.40836
H  -1.90875 -2.01929  2.41723
C  2.87293 -1.07622  0.60274
H   1.20433  0.25298  1.67391
O   0.85864  2.37521  1.16120
C   0.59798  4.43618 -0.14137
C  -1.39646  3.32818  0.99062
H  -2.10983  3.84146  0.32408
H  -1.25649  3.96350  1.88178
H  -1.83799  2.36967  1.30971
H   0.71621  5.08734  0.74279
H  -0.03311  4.97680 -0.86546
H   1.58787  4.26481 -0.59199
H   1.06394  2.96833  1.90955
H   0.64377  0.92970 -2.43703
H   1.61164  1.09168 -0.84551
H  -1.00159  2.59698 -1.64823
C   5.38831  1.17046 -0.64611
C   4.60443 -2.33223 -0.54739
C   3.34724 -2.29292  0.07370
C   3.65331  0.09427  0.50994
C   4.90941  0.03777 -0.11681
H   6.36924 -1.20892 -1.12853
H   4.97261 -3.27998 -0.95241
H   2.74535 -3.20429  0.15278
H   3.28662  1.03775  0.92798
H   5.51614  0.94658 -0.18250

SCF(BP86) = -776.286893066
H 0K = -775.938492
H 298K = -775.912506
G 298K = -775.999131

Solvent Correction(CHCl₃) = -0.04861740
BP86-D3 Correction = -0.05865049
Lowest frequencies = 15.5028 cm⁻¹, 16.0381 cm⁻¹
TS(I-II)$_{4'}$ (syn)

P  -2.80862 -1.61166  0.34082
C  -2.16429 -3.28119 -0.92947
C  -3.07187 -1.70484  2.17303
C  -4.50936 -1.51671 -0.38973
Au -1.40441  0.14163 -0.30252
C  -0.14375  1.86244  0.92947
C   1.00788  1.30340 -1.53696
S   1.71095  0.69863 -0.14968
C   0.04790  2.87291  0.21937
H  -2.84856 -4.06982  0.21297
H  -1.16888 -3.42816  0.30615
H  -2.07429 -3.33532 -1.23574
H  -4.98748 -0.57465 -0.08085
H  -5.13909 -2.36882 -0.04767
H  -4.43590 -1.53361 -1.48781
H  -3.73089 -2.55305  2.42016
H  -3.53110 -0.76838  2.52466
H  -2.10083 -1.83449  2.67476
C   3.48699 -0.90738  0.05756
H   1.52960  0.28311  0.78949
O   0.78770  2.12132  1.23286
C   0.88145  4.09336 -0.22412
C  -1.30188  3.32327  0.79546
H  -1.89934  3.66030  0.03248
H  -1.14841  4.03040  1.63678
H  -1.88411  2.46825  1.15966
H   1.02319  4.79109  0.62026
H   1.37200  4.64903 -1.02874
H   1.87696  3.79257 -0.58854
H   0.69133  2.72796  1.97709
H   0.92119  0.77714  2.49293
H   2.01439  1.64481 -1.27820
H   0.93693  2.12418 -1.65915
C   6.25375 -1.28611  0.27962
C   5.48884 -2.15513 -0.51573
C   4.10286 -1.97252 -0.63208
C   4.24928 -0.06260  0.85234
C   5.63286 -0.22590  0.96137
H   7.33372 -1.43569  0.36944
H   5.96849 -2.98295 -1.04601
H   3.50573 -2.65512 -1.24583
H   3.76612  0.80225  1.38041
H   6.22677  0.45159  1.58264

SCF(BP86) = -776.257851827
H 0K = -775.910311
H 298K = -775.885327
G 298K = -775.969884
Solvent Correction(CHCl3) = -0.04588647
BP86-D3 Correction = -0.05602818
Lowest frequencies = -134.4843 cm$^{-1}$, 11.1992 cm$^{-1}$
TS(I-II)$_{(anti)}$

$$P \quad -3.70942 \quad -0.92471 \quad 0.29568$$

$$C \quad -3.65999 \quad -2.12435 \quad 1.70806$$

$$C \quad -4.99335 \quad 0.32550 \quad 0.76958$$

$$C \quad -4.45292 \quad -1.86699 \quad -1.11681$$

$$Au \quad -1.63046 \quad 0.03454 \quad -0.21831$$

$$C \quad 0.22368 \quad 1.10549 \quad -0.72420$$

$$C \quad 0.86713 \quad -0.14912 \quad -0.93666$$

$$S \quad 3.22569 \quad 0.28112 \quad -1.70107$$

$$H \quad -4.66671 \quad -2.53244 \quad 1.89462$$

$$H \quad -3.29856 \quad -1.61088 \quad 2.61205$$

$$H \quad -2.96917 \quad -2.94629 \quad 1.46596$$

$$H \quad -4.58417 \quad -1.19291 \quad -1.97697$$

$$H \quad -5.43023 \quad -2.28305 \quad -0.82257$$

$$H \quad -3.77701 \quad -2.68578 \quad -1.40695$$

$$H \quad -5.94990 \quad -0.17686 \quad 0.98988$$

$$H \quad -5.13308 \quad 1.03860 \quad -0.05720$$

$$H \quad -4.65772 \quad 0.87618 \quad 1.66159$$

$$C \quad 4.30624 \quad -0.47692 \quad -0.47995$$

$$H \quad 2.94862 \quad 1.45092 \quad -1.00665$$

$$O \quad 1.95362 \quad 2.68420 \quad -0.07434$$

$$C \quad 1.03621 \quad 1.39432 \quad 1.70708$$

$$C \quad -0.33544 \quad 3.20639 \quad 0.58569$$

$$H \quad 0.06125 \quad 3.96064 \quad 1.28436$$

$$H \quad -1.27705 \quad 2.80782 \quad 1.00024$$

$$H \quad -0.58054 \quad 3.70430 \quad -0.37058$$

$$H \quad 0.15606 \quad 0.86771 \quad 2.11215$$

$$H \quad 1.36312 \quad 2.14879 \quad 2.43952$$

$$H \quad 1.85613 \quad 0.66780 \quad 1.58716$$

$$H \quad 1.73213 \quad 4.02420 \quad -0.70117$$

$$H \quad 1.26528 \quad -0.72935 \quad -0.09879$$

$$H \quad 0.66398 \quad -0.71322 \quad -1.85137$$

$$H \quad -0.06789 \quad 1.63409 \quad 1.64902$$

$$C \quad 6.02382 \quad -1.73326 \quad 1.34580$$

$$C \quad 5.57974 \quad -0.42220 \quad 1.58468$$

$$C \quad 4.71985 \quad 0.21473 \quad 0.67718$$

$$C \quad 4.74947 \quad -1.79166 \quad -0.72925$$

$$C \quad 5.60849 \quad -2.41320 \quad 0.18890$$

$$H \quad 6.69762 \quad -2.22138 \quad 2.05610$$

$$H \quad 5.90841 \quad 0.11581 \quad 2.47937$$

$$H \quad 4.38583 \quad 1.24102 \quad 0.85861$$

$$H \quad 4.43448 \quad -2.32056 \quad -1.63481$$

$$H \quad 5.95740 \quad -3.43191 \quad -0.00615$$

SCF(BP86) = -776.27388003

H 298K = -775.925124

G 298K = -775.900556

Solvent Correction(CHCl3) = -0.04746359

BP86-D3 Correction = -0.05570422

Lowest frequencies = -99.9387 cm$^{-1}$, 3.1439 cm$^{-1}$
Int(I-II)₄⁺ (syn)

| Atom | X    | Y    | Z    |
|------|------|------|------|
| P    | -3.41031 | -1.05216 | 0.31517 |
| C    | -3.32654 | -2.86044 | -0.09873 |
| C    | -3.81282 | -1.01735 | 2.12802 |
| C    | -4.96727 | -0.46625 | -0.51038 |
| Au   | -1.47758 | 0.15878 | -0.28993 |
| C    | 0.25840  | 1.21534 | -0.93402 |
| C    | 1.39283  | 0.24185 | -1.28195 |
| S    | 1.80047  | -0.78010 | 0.25950 |
| C    | 0.67746  | 2.38281 | -0.02636 |
| H    | -4.25475 | -3.37118 | 0.20503 |
| H    | -2.46976 | -3.13866 | 0.42295 |
| H    | -3.18112 | -2.97853 | -1.18353 |
| H    | -5.14754 | 0.58663 | -0.24417 |
| H    | -5.82802 | -1.07755 | -0.19401 |
| H    | -4.84825 | -0.53715 | -1.60249 |
| H    | -4.72158 | -1.60556 | 2.33506 |
| H    | -3.97068 | 0.02457 | 2.44851 |
| H    | -2.96779 | -1.43561 | 2.69625 |
| C    | 3.60501  | -0.93614 | 0.19892 |
| H    | 1.40241  | 0.71347 | 1.15878 |
| O    | 0.91650  | 1.70096 | 1.38712 |
| C    | 2.00278  | 3.07319 | -0.37554 |
| C    | -0.43918 | 3.39107 | 0.21792 |
| H    | -0.65815 | 3.91716 | -0.72653 |
| H    | -0.14604 | 4.15070 | 0.96213 |
| H    | -1.35629 | 2.88230 | 0.55250 |
| H    | 2.22735  | 3.89643 | 0.32601 |
| H    | 1.91975  | 3.52160 | -1.37948 |
| H    | 2.85907  | 2.38007 | -0.38912 |
| H    | 1.52796  | 2.25776 | 1.91985 |
| H    | 1.07719  | -0.46680 | -2.06141 |
| H    | 2.34361  | 0.70806 | -1.59633 |
| H    | -0.07028 | 1.68564 | -1.88272 |
| C    | 6.38786  | -1.26640 | 0.11097 |
| C    | 5.55666  | -2.11061 | -0.64365 |
| C    | 4.16253  | -1.95640 | -0.59668 |
| C    | 4.43467  | -0.09191 | 0.96264 |
| H    | 5.82716  | -0.26204 | 0.91649 |
| H    | 7.47372  | -1.39618 | 0.07747 |
| H    | 5.99170  | -2.89995 | -1.26417 |
| H    | 3.51184  | -2.62524 | -1.16866 |
| H    | 4.00010  | 0.68568 | 1.59932 |
| H    | 6.47244  | 0.39007 | 1.51312 |

SCF(BP86) = -776.27276943
H 0K = -775.922795
H 298K = -775.898535
G 298K = -775.981265
Solvent Correction(CHCl3) = -0.04741320
BP86-D3 Correction = -0.05791403
Lowest frequencies = 5.6008 cm⁻¹, 14.7306 cm⁻¹
TS(IIIB)₄⁺ (syn)

P  -3.32714 -1.11009  0.30878
C  -3.15344 -2.90343 -0.13090
C  -3.68312 -1.10305  2.12939
C  -4.91820 -0.58082 -0.48526
Au  -1.46818  0.17792 -0.30475
C  -0.27436  1.28679 -0.96121
C  -1.40583  0.32540  1.33158
S  1.76583 -0.78325  0.14908
C  0.62026  2.43522 -0.10959
H  -4.04669 -3.46512  0.18743
H  -2.26188 -3.31536  0.36606
H  -3.02681  3.00034 -1.22002
H  -5.13970  0.45954 -0.20198
H  -5.74401 -1.23399 -0.16145
H  -4.81425 -0.63465 -1.57976
H  -4.56095 -1.73125  2.35188
H  -3.87632 -0.70888  2.49444
H  -2.80718 -1.48982 -2.67235
C  3.57086 -0.91965  0.12553
H  1.00486  0.75184  1.43114
O  0.51231  1.60750  1.67753
C  2.05515  2.90992 -0.00243
C  -0.41612  3.52219  0.03411
H  -0.26807  4.24807 -0.78783
H  -0.29563  4.07953  0.97600
H  -1.43897  3.12225 -0.02494
H  -2.17807  3.69668  0.75921
H  -2.32190  3.36331 -0.97686
H  -2.77497  2.09895  0.18403
H  -1.09503  2.07414  2.31573
H  -1.09928 -0.32301 -2.16519
H  -2.35870  0.81275 -1.60265
H  -0.22290  1.00008 -1.86553
C  6.36355 -1.21468  0.14604
C  5.62157 -1.61648 -0.97744
C  4.22446 -1.48639 -0.98756
C  4.31184 -0.51600  1.25412
C  5.70734 -0.67349  1.26272
H  7.45156 -1.32994  0.15315
H  6.12874 -2.05002 -1.84505
H  3.64533 -1.83229 -1.84945
H  3.80088 -0.90501  2.12422
H  6.28052 -0.36526  2.14272

SCF(BP86) = -776.268523852
H 0K = -775.918748
H 298K = -775.894168
G 298K = -775.978096
Solvent Correction(CHCl3) = -0.04805956
BP86-D3 Correction = -0.05855697
Lowest frequencies = -201.7304 cm⁻¹, 6.6371 cm⁻¹
IntII₄* (anti)

\[
\begin{align*}
P & \quad -3.73735 \quad -0.91805 \quad 0.22963 \\
C & \quad -3.74926 \quad -2.09233 \quad 1.66126 \\
C & \quad -5.11296 \quad 0.27884 \quad 0.55325 \\
C & \quad -4.27872 \quad -1.91279 \quad -1.23565 \\
Au & \quad -1.66783 \quad 0.12516 \quad -0.10587 \\
C & \quad 0.37540 \quad 0.78274 \quad -0.82265 \\
C & \quad 1.33418 \quad -0.38453 \quad -0.82643 \\
S & \quad 2.97704 \quad 0.21204 \quad -1.56012 \\
C & \quad 0.15022 \quad 1.66343 \quad 0.25320 \\
H & \quad -4.74497 \quad -2.55443 \quad 2.58512 \\
H & \quad -2.99444 \quad -2.87660 \quad 1.49838 \\
H & \quad -4.35927 \quad -1.25647 \quad -2.11549 \\
H & \quad -5.25710 \quad -2.37768 \quad -1.03214 \\
H & \quad -3.53496 \quad -2.69729 \quad -1.44232 \\
H & \quad -6.06065 \quad -0.26715 \quad 0.68966 \\
H & \quad -5.20566 \quad 0.96979 \quad -0.29841 \\
H & \quad -4.88905 \quad 0.85903 \quad 1.46130 \\
C & \quad 4.17484 \quad -0.37586 \quad -0.45706 \\
H & \quad 3.06170 \quad 2.38179 \quad -0.53682 \\
O & \quad 0.94116 \quad 3.08984 \quad 0.13914 \\
C & \quad 0.70534 \quad 1.43844 \quad 1.63569 \\
C & \quad -0.38832 \quad 3.04903 \quad -0.01194 \\
H & \quad 0.49425 \quad 3.18889 \quad 0.02012 \\
H & \quad -1.09099 \quad 3.38339 \quad 0.76840 \\
H & \quad -0.85991 \quad 3.14518 \quad -1.00233 \\
H & \quad 0.02133 \quad 1.82468 \quad 2.40882 \\
H & \quad 1.64101 \quad 2.03068 \quad 1.68977 \\
H & \quad 0.94500 \quad 0.38785 \quad 1.85632 \\
H & \quad 3.67555 \quad 3.71071 \quad -0.01803 \\
H & \quad 1.55617 \quad -0.76745 \quad 0.17932 \\
H & \quad 0.97372 \quad -1.20921 \quad -1.45972 \\
H & \quad 0.12380 \quad 1.17315 \quad -1.82155 \\
C & \quad 6.10015 \quad -1.77649 \quad 1.18886 \\
C & \quad 5.63554 \quad -0.48326 \quad 1.48158 \\
C & \quad 4.67235 \quad 0.12460 \quad 0.66124 \\
C & \quad 4.64564 \quad -1.86950 \quad -0.76076 \\
C & \quad 5.60705 \quad -2.46703 \quad 0.06909 \\
H & \quad 6.85406 \quad -2.24405 \quad 1.82987 \\
H & \quad 6.02797 \quad 0.05864 \quad 2.34800 \\
H & \quad 4.30859 \quad 1.13634 \quad 0.87248 \\
H & \quad 4.26860 \quad -2.39275 \quad -1.64495 \\
H & \quad 5.97695 \quad -3.47002 \quad -0.16578 \\
\end{align*}
\]

\[\text{SCF(BP86)} = -776.29580923\]
\[\text{H 0K} = -775.945849\]
\[\text{H 298K} = -775.919443\]
\[\text{G 298K} = -776.006059\]
\[\text{Solvent Correction(CHCl3)} = -0.04908504\]
\[\text{BP86-D3 Correction} = -0.05346922\]
\[\text{Lowest frequencies} = 15.1505 \text{ cm}^{-1}, 18.8582 \text{ cm}^{-1}\]
IntII\textsubscript{4} - (syn)

P  -2.65898  -1.59693  -0.05565
C  -2.01567  -2.85410  -1.24640
C  -2.63823  -2.40879   1.60232
C  -4.44318  -1.33471  -0.47875
Au -1.39788   0.37412  -0.10215
C   0.17430   2.01032  -0.42460
C   1.53307   1.50892   0.00575
S   2.03648   0.20267  -1.01497
H  -0.77465   2.62684   0.40455
H  -2.63720  -3.76326  -1.20168
H  -0.98257  -3.07831  -0.93690
H  -2.02525  -2.44632  -2.26834
H  -4.89682  -0.63985   0.24424
H  -4.97885  -2.29750  -0.44695
H  -4.52306  -0.90414  -1.48851
H  -3.18883  -3.51338   1.57238
H  -3.05321  -1.73712   2.35776
H  -1.56133  -2.60666   1.83881
C   3.69052  -0.26671  -0.38699
H   1.02397  -1.71177   0.15843
O   0.60672  -2.38360   0.75357
C  -0.62068   2.74333   1.90482
C  -1.86835   3.48195  -0.20362
H  -1.61603   4.54535  -0.02866
H  -2.84267   3.30586   0.28153
H  -1.97102   3.33133  -1.28920
H  -1.59846   2.66826   2.40811
H  -0.21872   3.74736   2.14069
H   0.06085   1.99796   2.33960
H   1.19864  -3.15637   0.69534
H   2.28374   2.29505  -0.19502
H   1.57915   1.24567   1.02265
H   0.06964   2.18804  -1.50609
C   6.29057  -0.73711   0.54544
C   6.09269  -0.02758  -0.65037
C   4.79218   0.21214  -1.12254
C   3.88398  -0.99017   0.80758
C   5.18835  -1.21767   1.27254
H   7.30616  -0.92128   0.90906
H   6.95142   0.34011  -1.22058
H   4.62900   0.76021  -2.05568
H   3.03824  -1.37739   1.35615
H   5.34335  -1.77717   2.20048

SCF\textsubscript{(BP86)} = -776.301666871
H DK = -775.951726
H 298K = -775.925364
G 298K = -776.011234
Solvent Correction\textsubscript{(CHCl\textsubscript{3})} = -0.04793618
BP86-D3 Correction = -0.05730587
Lowest frequencies = 11.1702 cm\textsuperscript{-1}, 30.5728 cm\textsuperscript{-1}
*IntII₄ (anti)*

P 3.27725 -1.13717 -0.06390
C 4.83835 -0.15424 0.10148
C 3.36543 -2.43969 1.24879
C 3.42496 -2.03788 -1.67496
Au 1.34575 0.18055 0.08479
C -0.82149 0.91213 0.06022
C -1.45535 0.63916 -1.27909
S -3.22402 1.25576 -1.22530
C -0.07662 2.05114 0.41760
H 5.71088 -0.82356 0.02678
H 4.84967 0.35660 1.07625
H 4.88418 0.59998 -0.69874
H 2.55776 -2.70300 -1.80514
H 4.35125 -2.63507 1.68698
H 3.44528 -1.31114 -2.50128
H 4.29136 -3.02647 1.13437
H 2.49431 -3.10691 1.16285
H 3.35248 -1.96241 2.24046
C -4.04351 -0.11123 -0.37405
C 0.30772 3.12768 -0.57340
C 0.06745 2.43235 1.87762
H 0.62784 3.26839 2.08654
H 1.08091 2.79839 2.11143
H 0.18552 1.60519 2.55894
H 1.27460 3.58673 -0.31015
H 0.45251 3.93139 -0.52401
H 0.35374 2.77736 -1.61481
H 0.97857 1.17921 -2.10822
H -1.47983 -0.43384 1.52093
H -1.24932 0.32897 0.89987
C -5.42052 -2.18843 0.92159
C -4.98062 -2.35627 -0.40297
C -4.30251 -1.31762 -1.05809
C -4.48825 0.06023 0.95256
C -5.18000 -0.97992 1.59485
H -5.96101 -2.99643 1.42434
H -5.18456 -3.29078 -0.93537
H -3.99899 -1.43000 -2.10139
H -4.30307 1.00788 1.46785
H -5.53218 -0.84292 2.62217

SCF(BP86) = -699.864008888
H 0K = -699.538119
H 298K = -699.514645
G 298K = -699.595954
Solvent Correction(CHCl3) = -0.05030723
BP86-D3 Correction = -0.04641935
Lowest frequencies = 12.8400 cm⁻¹, 15.6727 cm⁻¹
95

*IntII₄* (syn)

40

P -2.45782 -1.76917 0.07319
C -1.69391 -3.02897 -1.04621
C -2.39898 -2.50495 1.77068
C -4.24999 -1.70010 -0.38596
Au -1.34118 0.27753 -0.08079
C 0.15087 1.95741 -0.57046
C -1.69391 1.53510 -1.0669
S 1.83300 -0.22865 -0.63989
C -0.82629 2.61068 0.19489
H -2.20327 -3.99869 -0.92414
H -0.62695 -3.13417 -0.79720
H -1.78351 -2.69341 -2.09056
H -4.77758 -1.01398 0.29386
H -4.69506 -2.70577 -0.31234
H -4.34940 -1.32848 -1.41712
H -2.90583 -3.48371 1.77281
H -2.89867 -1.83051 2.48251
H -1.34899 -2.63298 2.07463
C 3.57893 -0.41919 -0.20306
C -0.68001 2.88845 1.67468
C -1.96059 3.34114 -0.49322
H -1.75991 4.43081 -0.43094
H -2.92583 3.17328 0.01143
H -2.05503 3.07708 -1.55700
H -1.65238 2.80837 2.18775
H -0.33785 3.93273 1.80626
H 0.04273 2.23096 2.17889
H 2.27696 2.17665 -0.59901
H 1.65237 1.61525 0.98252
H 0.02731 1.99809 -1.66357
C 6.28651 -0.77498 0.43594
C 5.91585 -0.42188 -0.87192
C 4.56187 -0.24329 -1.19780
C 3.94722 -0.78516 1.10725
C 5.30378 -0.95637 1.42356
H 7.34295 -0.91480 0.68512
H 6.80480 -0.28734 -1.64341
H 4.26390 0.02570 -2.21598
H 3.17471 -0.94024 1.86732
H 5.59219 -1.23938 2.44085

SCF(BP86) = -699.864072054
H 0K = -699.538288
H 298K = -699.514708
G 298K = -699.596959
Solvent Correction(CHCl₃) = -0.04872543
BP86-D3 Correction = -0.04717095
Lowest frequencies = 7.7748 cm⁻¹, 14.7668 cm⁻¹
IntIII₄ (anti)

|    | 4.490712 | 0.178740 | 0.093389 |
|----|----------|----------|----------|
| P  | 5.026624 | 0.788416 | 1.757543 |
| C  | 5.467477 | -1.364632| -0.212322|
| C  | 5.130910 | 1.420263 | -1.122370|
| Au | 2.180732 | -0.139717| -0.081018|
| C  | -0.029874| -0.012470| -0.508187|
| C  | -0.555575| 1.315101 | 0.014514 |
| S  | -2.396844| 1.354517 | -0.405641|
| C  | 0.018706 | -1.204775| 0.241844 |
| H  | 6.120038 | 0.926292 | 1.773123 |
| C  | 4.737145 | 0.056640 | 2.526990 |
| C  | 4.531800 | 1.747559 | 1.973296 |
| H  | 4.904641 | 1.982671 | -2.145210|
| H  | 6.220942 | 1.532698 | 0.004238 |
| H  | 4.640438 | 2.390311 | -0.949767|
| H  | 6.545168 | -1.148542| -0.130101|
| H  | 5.244510 | -1.745971| -1.220383|
| C  | 5.188245 | -2.128855| 0.528866 |
| C  | -2.738127| 3.121491 | -0.251058|
| C  | -3.937492| -0.453626| 1.172138 |
| S  | -4.083014| -1.629330| 1.852439 |
| C  | -0.270355| -1.261072| 1.719524 |
| C  | 0.117609 | -2.538123| -0.462059|
| H  | -0.872468 | -3.031579| -0.399472|
| H  | 0.836966 | -3.211031| 0.034091 |
| H  | 0.382083 | -2.438384| -1.525971|
| H  | 0.345017 | -2.028010| 2.217650 |
| H  | -1.332405| -1.559834| 1.853835 |
| H  | -0.133624| -0.298566| 2.233849 |
| C  | -3.743914| -2.710851| 0.452942 |
| C  | -0.407415| 1.469541 | 1.064773 |
| H  | -0.101763| 2.151795 | -0.567443|
| H  | -0.049711| -0.131577| -1.602634|
| C  | -3.358308| 5.849919 | 0.038731 |
| C  | -3.308367| 5.050558 | 1.115780 |
| C  | -3.003358| 3.684592 | 1.014442 |
| C  | -2.792091| 3.921111 | -1.411182|
| C  | -3.103737| 5.285286 | -1.299464|
| C  | -3.604561| 6.913161 | 0.043899 |
| H  | -3.518063| 5.487863 | 2.097066 |
| H  | -2.982149| 3.051976 | 1.907414 |
| H  | -2.601355| 3.469532 | -2.389642|
| H  | -3.152719| 5.305453 | -2.200071|
| C  | -3.224998| -4.506186| -1.662947|
| C  | -3.113463| -4.932474| -0.325762|
| C  | -3.362706| -4.040997| 0.729962 |
| C  | -3.872459| -2.848464| -0.885496|
| C  | -3.604824| -3.181098| -1.932394|
| H  | -3.031452| -5.204285| -2.480309|
| H  | -2.830569| -5.965851| -0.09969 |
| H  | -3.257177| -4.378818| 1.767471 |
| H  | -4.195615| -1.263053| -1.109731|
| H  | -3.713099| -2.841501| -2.967849|

SCF(BP86) = -942.335190669
H 0K = -941.912104
H 298K = -941.880130
G 298K = -941.984512
Solvent Correction(CHCl3) = -0.04929878
BP86-D3 Correction = -0.06699874
Lowest frequencies = 11.0747 cm⁻¹, 12.3887 cm⁻¹
TS(III-IV)₄⁺ (anti)

53

P  -4.372496  -0.404963  -0.057398
C  -4.906877  -2.180546  -0.046621
C  -5.246250  0.365093  1.386117
C  -5.184714  0.329486  -1.553505
Au  -2.050923  -0.115748  -0.038941
C  0.123505  0.143556  -0.218214
C  0.580734  -1.069794  -1.025388
S  2.380324  -1.049261  -1.645740
C  0.518887  0.348160  1.161910
H  -6.006786  -2.247884  -0.069060
H  -4.527048  -2.671240  0.862474
H  -4.489509  -2.692647  -0.927007
H  -4.977407  1.409935  -1.588029
H  -6.273788  0.164117  -1.516431
H  -4.772221  -0.139239  -2.459980
H  -6.332886  0.198307  1.306590
H  -5.041099  1.446378  1.402613
H  -4.873856  -0.082043  2.320435
C  3.169895  -2.381480  -0.709831
S  2.900377  1.155302  0.995262
C  0.840806  -0.835521  2.052313
C  0.022008  1.591330  1.876038
H  0.672628  1.849661  2.726566
H  -0.986604  1.398493  2.287463
H  -0.048354  2.457432  1.199109
H  -0.106683  -1.336013  2.332234
H  1.327816  -0.513441  2.985153
H  1.477907  -1.585617  1.558890
C  2.717071  2.751997  0.201765
H  0.471416  -2.014931  -0.473340
H  -0.008157  -1.149376  -1.950711
H  0.136250  1.082770  -1.601216
C  4.509782  -4.449953  0.643352
C  5.089899  -3.175027  0.556848
C  4.422011  -2.135110  -0.111186
C  2.598239  -3.669717  -0.651211
C  3.264638  -4.693532  0.039251
H  5.030812  -5.255559  1.169236
H  6.064558  -2.980278  1.015055
H  4.879972  -1.142888  -0.174127
H  1.652636  -3.880807  -1.160979
H  2.818229  -5.692049  0.082988
C  2.424708  5.304363  -0.932984
C  2.574497  5.165668  0.457247
C  2.721655  3.894644  1.030716
C  2.571764  2.885331  -1.195890
C  2.427717  4.164925  -1.754128
H  2.317896  6.298935  -1.376099
H  2.586382  6.050824  1.100662
H  2.855640  3.789913  2.112355
H  2.599160  2.003957  -1.843460
H  2.327399  4.268468  -2.839170

SCF(BP86) = -942.323020106
H 0K = -941.899615
H 298K = -941.869452
G 298K = -941.966890
Solvent Correction(CHCl3) = -0.04410199
BP86-D3 Correction = -0.07614278
Lowest frequencies = -84.1086 cm⁻¹, 8.0984 cm⁻¹
Int(III-IV), \text{(anti)}

| Atm  | X      | Y      | Z      |
|------|--------|--------|--------|
| P    | -4.354402 | -0.457534 | -0.045515 |
| C    | -4.870386 | -2.240990 | -0.052479 |
| C    | -5.218403 | 0.265453  | 1.430459  |
| C    | -5.234757 | 0.282856  | -1.502564 |
| Au   | -2.027570 | -0.121476 | -0.074629 |
| C    | 0.101863  | 0.201119  | -0.0207045 |
| C    | 0.617129  | -1.014182 | -1.540111 |
| C    | 0.657596  | 0.498042  | 1.656712  |
| H    | -5.969334 | -3.24915 | -0.045766 |
| H    | -4.458351 | -2.743327 | 0.836132  |
| H    | -4.470411 | -2.732101 | -0.952804 |
| H    | -5.051534 | 1.368054  | -1.525610 |
| H    | -6.318556 | 0.093779  | -1.436104 |
| H    | -4.846020 | -0.160522 | -2.429840 |
| H    | -6.302747 | 0.076389  | 1.373561  |
| H    | -5.036212 | 1.350703  | 1.463440  |
| H    | -4.815106 | -0.188773 | 2.348544  |
| C    | 3.240019  | -2.343759 | -0.668821 |
| H    | 2.768915  | 0.245056  | -0.206553 |
| S    | 2.606797  | 1.127899  | 1.015311  |
| C    | 0.838891  | -0.714711 | 2.090861  |
| C    | -0.026933 | 1.670376  | 1.875639  |
| H    | 0.523138  | 1.968895  | 2.784415  |
| H    | -1.042155 | 1.360902  | 2.180017  |
| H    | -0.125306 | 2.546405  | 1.214453  |
| H    | -0.151561 | -1.177055 | 2.252103  |
| H    | 1.241315  | -0.416814 | 3.072486  |
| H    | 1.502246  | -1.485587 | 1.664832  |
| C    | 2.553708  | 2.729000  | 0.194389  |
| H    | 0.550144  | -1.952066 | -0.394474 |
| H    | 0.075599  | -1.140906 | -1.913226 |
| H    | 0.153482  | 1.111910  | -0.168113 |
| C    | 4.522965  | -4.493475 | 0.598959  |
| C    | 5.076851  | -3.205449 | 0.669175  |
| C    | 4.437805  | -2.123691 | 0.040910  |
| C    | 2.692408  | -3.638781 | -0.763274 |
| C    | 3.332953  | -4.706980 | -0.013631 |
| C    | 5.023220  | -5.332240 | 1.092069  |
| H    | 6.008815  | -3.034924 | 1.216465  |
| H    | 4.877098  | -1.122480 | 0.093879  |
| H    | 1.785842  | -3.816807 | -1.350340 |
| C    | 2.907398  | -5.712896 | -0.190138 |
| C    | 2.530913  | 5.277549  | -0.968700 |
| C    | 2.667555  | 5.144046  | 0.423128  |
| C    | 2.682785  | 3.871150  | 1.011809  |
| C    | 2.424547  | 2.854651  | -1.204359 |
| C    | 2.414111  | 4.135606  | -1.777397 |
| H    | 2.525923  | 6.272322  | -1.42228 |
| H    | 2.770856  | 6.031526  | 1.054688  |
| H    | 2.804078  | 3.762610  | 2.094089  |
| H    | 2.355270  | 1.970947  | -1.844140 |
| H    | 2.321992  | 4.237403  | -2.863664 |

SCF(BP86) = -942.324574194  
H 0K = -941.900928  
H 298K = -941.870780  
G 298K = -941.966986  
Solvent Correction(CHCl3) = -0.04143085  
BP86-D3 Correction = -0.07643137  
Lowest frequencies = 9.6317 cm⁻¹, 18.3463 cm⁻¹
Ts(III-IV)\textsuperscript{4'} (anti)

P \quad -4.289409 \quad -0.645725 \quad -0.031448
C \quad -4.748839 \quad -2.070952 \quad 1.062642
C \quad -5.289773 \quad 0.781612 \quad 0.601624
C \quad -5.032422 \quad -1.051300 \quad -1.681667
Au \quad -1.986666 \quad -0.204095 \quad -0.116918
C \quad 0.140709 \quad 0.358120 \quad -0.186299
C \quad 0.487724 \quad -0.860245 \quad -0.877301
S \quad 2.759818 \quad -0.943864 \quad -1.531867
C \quad 0.680557 \quad 0.690922 \quad 1.206889
H \quad -5.841158 \quad -2.218219 \quad 1.059681
H \quad -4.408766 \quad -1.867609 \quad 2.089744
H \quad -4.253735 \quad -2.984591 \quad 0.699817
H \quad -4.868012 \quad -0.210113 \quad -2.372275
H \quad -6.113975 \quad -1.236548 \quad -1.577983
H \quad -4.543484 \quad -1.947909 \quad -2.092206
H \quad -6.360822 \quad 0.522019 \quad 0.613057
H \quad -5.130408 \quad 1.655818 \quad -0.047983
H \quad -4.962623 \quad 1.034096 \quad 1.621856
C \quad 3.426457 \quad -2.353983 \quad -0.633161
H \quad 2.911315 \quad 0.038560 \quad -0.505024
S \quad 2.497833 \quad 1.352059 \quad 1.042938
C \quad 0.846265 \quad -0.533415 \quad 2.122334
C \quad -0.149972 \quad 1.786308 \quad 1.889295
H \quad 0.306527 \quad 2.086026 \quad 2.846854
H \quad -1.166871 \quad 1.402824 \quad 2.095951
H \quad -0.247661 \quad 2.680958 \quad 1.253044
H \quad -0.133091 \quad -1.030028 \quad 2.249079
H \quad 1.205330 \quad -0.227106 \quad 3.118477
H \quad 1.555938 \quad -1.276409 \quad 1.721460
C \quad 2.345531 \quad 2.939382 \quad 0.197107
H \quad 0.580778 \quad -1.797913 \quad -0.318057
H \quad 0.14055 \quad -0.975095 \quad -1.909311
H \quad 0.099017 \quad 1.250491 \quad -0.033133
C \quad 4.477132 \quad -4.603512 \quad 0.666083
C \quad 4.767304 \quad -3.317111 \quad 1.145009
C \quad 4.247557 \quad -2.183911 \quad 0.500547
C \quad 3.135226 \quad -3.642816 \quad -1.124061
C \quad 3.664833 \quad -4.764735 \quad -0.468318
H \quad 4.890402 \quad -5.483162 \quad 1.171497
H \quad 5.409412 \quad -3.187329 \quad 2.021736
H \quad 4.492850 \quad -1.181962 \quad 0.865297
H \quad 2.511200 \quad -3.768286 \quad -2.015100
C \quad 3.443562 \quad -5.765722 \quad -0.851572
C \quad 2.219547 \quad 5.454534 \quad -1.054027
C \quad 2.245889 \quad 4.284586 \quad -1.830863
C \quad 2.313782 \quad 3.026829 \quad -1.211151
C \quad 2.330765 \quad 4.115832 \quad 0.976088
C \quad 2.266111 \quad 5.368827 \quad 0.347116
H \quad 2.174324 \quad 6.433307 \quad -1.543161
H \quad 2.226308 \quad 4.348842 \quad -2.923364
H \quad 2.361735 \quad 2.122022 \quad -1.824555
H \quad 2.37936 \quad 4.043560 \quad 2.066747
H \quad 2.258918 \quad 6.278986 \quad 0.954881

SCF(BP86) = -942.320597146
H 0K = -941.897246
H 298K = -941.867302
G 298K = -941.964176
Solvent Correction(CHCl3) = -0.04361495
BP86-D3 Correction = -0.07516386
Lowest frequencies = -134.7252 cm\textsuperscript{-1}, 8.1177 cm\textsuperscript{-1}
IntIV₄ (anti)

P  -2.47560  -2.95185  0.13673
C  -3.29745  -3.30943  -1.48445
C  -1.61238  -4.52206  0.60963
C  -3.85667  -2.76674  1.35715
Au  -1.06974  -1.07875  0.09426
C   1.08538  -0.17834  -0.06546
C  -0.08873  -0.04028  -0.16738
S  -2.21492  3.47905  2.53546
C   1.79484  -0.01404  -1.37383
H  -3.95765  -4.18671  -1.38827
H  -2.53104  -3.50852  -2.24890
H  -3.89055  -2.43556  -1.79439
H  -3.43800  -2.62101  2.36458
H  -4.49143  -3.66765  1.34817
H  -4.46325  -1.88684  1.09394
H  -2.33288  -5.35595  0.63068
H  -1.15775  -4.40348  1.60491
H  -0.81909  -4.74009  -0.12135
C  -2.09419  3.70335  0.75566
H  -1.29234  4.41941  2.87677
S  3.22344  1.23737  -0.07753
C  1.04665  0.81993  -2.60045
C  2.30294  -1.44294  -1.57836
H  2.94431  -1.50021  -2.47251
H  1.44063  -2.11861  -1.72977
H  2.87895  -1.80642  -0.71285
H  0.11201  -0.05242  -2.74565
H  1.66583  0.40210  -3.50299
H  0.78135  1.58536  -2.50230
C  4.40287  0.37818  -0.02006
H  -0.55661  1.48883  -0.63405
H  -0.32170  1.23527  1.18847
H  1.61810  -0.23553  0.80301
C  -1.96724  3.89511  -2.05793
C  -0.97962  4.49753  -1.25958
C  -1.03321  4.39881  0.14048
C  -3.09639  3.11101  -0.04225
C  -3.02526  3.20460  -1.44135
H  -1.92696  3.98533  -3.14760
H  -0.16189  5.05807  -1.72442
H  -0.25289  4.86801  0.74871
H  -3.94227  2.60131  0.43137
H  -3.81831  2.75762  -2.05015
C  6.34826  -0.82478  1.61291
C  5.35769  -0.01018  2.18670
C  4.38660  0.59602  1.37478
C  5.40858  -0.42729  -0.59733
H  6.37484  -1.02924  0.22321
H  7.10815  -1.29034  2.24815
H  5.34634  0.16355  3.26732
H  3.62871  1.25356  1.81214
H  5.43665  -0.56571  -1.68215
H  7.15593  -1.65017  -0.22648

SCF(BP86) = -942.329758986
H 0K = -941.90690
H 298K = -941.874851
G 298K = -941.981637
Solvent Correction(CHCl₃) = -0.04793721
BP86-D3 Correction = -0.06889157
Lowest frequencies = 4.3216 cm⁻¹, 6.8323 cm⁻¹
*IntIV₄ (anti)*

\[
\begin{array}{ccc}
P & -3.534725 & 0.807865 & 0.405949 \\
C & -4.475792 & -0.264810 & 1.586615 \\
C & -3.237253 & 2.398222 & 1.309254 \\
C & -4.733389 & 1.225847 & -0.942668 \\
Au & -1.587367 & -0.198902 & -0.422788 \\
C & 0.906204 & -0.693604 & -0.598948 \\
C & 0.000883 & -1.312626 & -1.474922 \\
C & -5.389245 & 0.253244 & 1.921196 \\
H & -3.843986 & -0.495126 & 2.457905 \\
H & -4.749990 & -1.206242 & 1.085657 \\
H & -4.260773 & 1.924211 & -1.650035 \\
H & -5.636073 & 1.690431 & -0.513719 \\
H & -5.013445 & 0.308151 & -1.482051 \\
H & -4.196640 & 2.821758 & 1.648611 \\
H & -2.736935 & 3.112592 & 0.637956 \\
H & -2.589882 & 2.211850 & 2.179487 \\
S & 3.233048 & -1.624364 & -0.111732 \\
C & 0.954808 & 2.623797 & 1.077673 \\
C & 1.560376 & -0.263449 & 1.807882 \\
H & 2.157563 & -0.607010 & 2.639409 \\
H & 0.535858 & -0.078046 & 2.179972 \\
H & 1.997908 & 0.700311 & 1.503858 \\
H & -0.113376 & -2.535648 & 1.347051 \\
H & 1.501076 & -2.995304 & 1.959542 \\
H & 1.044637 & -3.386572 & 0.283154 \\
C & 4.122227 & -0.058994 & -0.704446 \\
H & -0.253966 & -2.371069 & -1.342980 \\
H & -0.081643 & -0.930751 & -2.500808 \\
H & 1.282537 & 0.303407 & -0.868770 \\
C & 5.659529 & 2.291597 & -0.064233 \\
C & 4.962598 & 1.912658 & -1.225147 \\
C & 4.196222 & 0.737172 & -1.234090 \\
C & 4.836413 & 0.313178 & 1.089468 \\
C & 5.598774 & 1.491089 & 1.087630 \\
H & 6.261698 & 3.205385 & -0.064444 \\
H & 5.023816 & 2.526709 & -2.129061 \\
H & 3.673418 & 0.421927 & -2.142518 \\
H & 4.804069 & -0.326130 & 1.976531 \\
H & 6.155272 & 1.776824 & 1.985622 \\
\end{array}
\]

SCF (BP86) = -699.857546383
H 0K = -699.531619
H 298K = -699.508456
G 298K = -699.588660
Solvent Correction (CHCl3) = -0.04815896
BP86-D3 Correction = -0.04991336
Lowest frequencies = 6.2402 cm⁻¹, 17.2375 cm⁻¹
[ (Me₃P)Au(SHPh) ]⁺

P  -2.704648  0.609773  0.162628
C  -2.972175  1.282798  1.865295
C  -2.942733  2.036522  -0.991416
Au -0.638153  -0.426568  -0.076165
S   1.462838  -1.586863  -0.242029
H   1.495078  -1.775867  -1.594527
C  -4.115635  -0.543542  -0.162612
C  -4.066302  -1.386958  0.548318
H  -5.071185  -0.009613  -1.384390
H  -2.859665  1.685451  -2.031213
H  -2.165356  2.792976  -0.804943
H  -3.937446  2.483877  -0.832553
H  -2.193501  2.026564  2.092782
H  -2.908716  0.463208  2.597109
H  -3.965197  1.756996  1.927762
C   2.773154  -0.323710  -0.106827
C   4.829320  1.527636  0.214783
C   3.852007  1.730389  -0.775560
C   2.806882  0.808766  -0.939430
C   3.742743  -0.546642  0.884737
C   4.773157  0.396274  1.042808
H   5.638136  2.253870  0.337647
H   3.898577  2.610850  -1.423485
H   2.040135  0.968155  -1.703893
H   3.704264  -1.440049  1.515305
H   5.536174  0.233924  1.809715

SCF(BP86) = -504.527406283
H 0K = -504.316802
H 298K = -504.300275
G 298K = -504.365534
Solvent Correction(CH3Cl) = -0.051002
BP86-D3 Correction = -0.02773234
Lowest frequencies = 10.3816 cm⁻¹, 15.8397 cm⁻¹
3. Reactions of Substrate 24

**Figure S4.** First SN2' step to form 28 via *anti* attack of PhSH. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl₃) in red. All energies are in kcal/mol and are quoted relative to 5' and the separated reactants set to zero.

**Figure S5.** Second SN2' step to form 3a' via *anti* attack of PhSH. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl₃) in red. All energies are in kcal/mol and are quoted relative to 5' and the separated reactants set to zero.
Figure S6. Alternative routes to the formation of 3a' via either C–O bond cleavage and formation of an allylic cation or direct SN2 attack at an O-bound form of 24. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl3) in red. All energies are in kcal/mol and are quoted relative to 5' and the separated reactants set to zero.
Table S2. Computed relative energies (kcal/mol) for the reactions 24 with PhSH. Energies are reported as $\Delta E$ (gas-phase SCF energies), $\Delta H_{298}$ (zero-point energy corrected energies at 298.15 K), $\Delta G$ (free energies at 298.15 K and 1 atm), $\Delta G_{\text{disp}}$ (including a correction for dispersion effects using Grimme’s D3 parameter set) and $\Delta G_{\text{CHCl}_3+\text{disp}}$ including an additional correction for CHCl$_3$ solvent via the PCM approach.

|                  | $\Delta E$ | $\Delta H_{298}$ | $\Delta G$ | $\Delta G_{\text{disp}}$ | $\Delta G_{\text{CHCl}_3+\text{disp}}$ |
|------------------|------------|------------------|------------|--------------------------|----------------------------------|
| 5'               | 0.0        | 0.0              | 0.0        | 0.0                      | 0.0                              |
| *IntI$_{24}$ (anti) | +5.5       | +5.2             | +5.3       | +0.6                     | -0.7                            |
| IntI$_{24}$ (anti)   | +0.6       | +2.2             | +12.5      | -0.5                     | +0.2                            |
| IntV$_{24}$        | +4.8       | +4.9             | +4.9       | +1.8                     | +0.5                            |
| IntVII$_{24}$      | +60.3      | +56.0            | +44.6      | +46.9                    | +28.5                           |
| $^1$TS(V-VI)$_{24}$ | +19.3      | +19.5            | +28.2      | +22.0                    | +26.3                           |
| $^2$TS(V-VI)$_{24}$ | +11.8      | +13.6            | +31.5      | +18.1                    | +26.3                           |
| IntVI$_{24}$       | +4.0       | +5.2             | +4.7       | +0.9                     | -5.8                            |
| TS(I-II$^\Lambda$)$_{24}$ (anti) | +4.2   | +5.3             | +18.7      | +3.7                     | +8.0                            |
| Int(I-II)$_{24}$ (anti) | +3.4       | +4.9             | +19.7      | +4.4                     | +9.9                            |
| TS(I-I-I)$_{24}$ (anti) | +4.4       | +5.7             | +21.2      | +5.8                     | +9.3                            |
| IntIV$_{24}$ (anti) | -5.9       | -3.5             | +6.6       | -6.3                     | -3.0                            |
| *IntII$_{24}$ (anti) | +2.4       | +2.8             | +5.4       | -4.4                     | -4.3                            |
| IntIII$_{24}$ (anti) | -1.2       | +1.1             | +10.4      | -5.8                     | -3.4                            |
| TS(III-IV)$_{24}$ (anti) | +4.6    | +5.8             | +21.3      | +1.2                     | +6.4                            |
| Int(III-IV)$_{24}$ (anti) | +2.1       | +3.6             | +19.6      | -1.4                     | +5.2                            |
| TS(III-IV$^b$)$_{24}$ (anti) | +3.1    | +4.4             | +19.6      | -1.1                     | +3.7                            |
| IntIV$_{24}$ (anti) | -4.6       | -2.2             | +8.6       | -6.5                     | -4.8                            |
| *IntIV$_{24}$ (anti) | -1.6       | -1.1             | +0.7       | -6.9                     | -8.0                            |

*Complex computed in the absence of PhSH nucleophile

$^1$Denotes the presence of one PhSH nucleophile in the calculations

$^2$Denotes the presence of two PhSH nucleophiles in the calculations
C  -0.28617  -0.52100  -0.30302  
C   0.95468   -0.04520  -0.04044  
C  -1.57041   0.25049  -0.44988  
O  -2.59701  -0.25016   0.42604  
H  -2.20451  -0.25250   1.31983  
C  1.30218   1.41799   0.12424  
C   2.12973   -0.98954   0.09457  
H  -0.43044  -1.60890  -0.40531  
H  -1.41253   1.34016  -0.30715  
H   2.91139  -0.76297  -0.65554  
H   1.82999  -2.04226  -0.03197  
H   2.61278  -0.88383   1.08490  
H   0.42661  -2.08156   0.10214  
H   1.98994   1.74741  -0.67757  
H   1.83757   1.58591   1.07771  
H  -1.98270   0.12023  -1.46819  

SCF(BP86) = -271.74708883  
H 0K = -271.609674  
H 298K = -271.601733  
G 298K = -271.641506  
Solvent Correction(CH3Cl) = -0.00331222  
BP86-D3 Correction = -0.01074018  
Lowest frequencies = 68.3286 cm⁻¹, 140.9430 cm⁻¹
*IntI_{24} (anti)*

\[
\begin{array}{ccc}
P & 2.397271 & -0.120167 & 0.105000 \\
C & 3.268823 & 1.428639 & -0.414521 \\
C & 2.950736 & -0.453221 & 1.839812 \\
Au & 0.069643 & 0.008993 & -0.123911 \\
C & -2.105691 & -0.311215 & -0.575839 \\
C & -2.182981 & 0.936414 & 0.064925 \\
C & -2.586292 & -1.614186 & 0.048178 \\
O & -4.011037 & -1.551989 & -0.014827 \\
H & -4.359729 & -2.459073 & 0.073384 \\
C & -2.533939 & 1.093095 & 1.523300 \\
C & -2.156595 & 2.212357 & -0.744479 \\
H & -2.118335 & -0.292631 & -1.676159 \\
C & 3.126611 & -1.474793 & -0.923545 \\
H & -2.220944 & -1.721283 & 1.092157 \\
H & -2.175962 & -2.463092 & -0.533768 \\
H & -3.184235 & 2.623696 & -0.763077 \\
H & -1.838274 & 2.050362 & -1.785550 \\
H & -1.520157 & 2.983733 & -0.279487 \\
H & -3.592180 & 1.410585 & 1.583346 \\
H & -1.936056 & 1.889452 & 1.996525 \\
H & -2.434611 & 0.164845 & 2.102728 \\
H & 4.050595 & -0.515012 & 1.876207 \\
H & 2.517612 & -1.403503 & 2.187271 \\
H & 2.892219 & -1.299948 & -1.984161 \\
H & 3.032033 & 1.647874 & -1.466750 \\
H & 4.357661 & 1.300228 & -0.301284 \\
H & 2.951214 & 2.268766 & 0.211166 \\
H & 2.606407 & 0.358551 & 2.498426 \\
H & 2.701800 & -2.441714 & -0.616537 \\
H & 4.222312 & -1.496389 & -0.788874 \\
\end{array}
\]

SCF(BP86) = -533.804016643
H 0K = -533.553574
H 298K = -533.535182
G 298K = -533.603079
Solvent Correction(CH3Cl) = -0.05218225
BP86-D3 Correction = -0.03300075
Lowest frequencies = 6.2137 cm\(^{-1}\), 36.7849 cm\(^{-1}\)
IntI\textsubscript{24} (anti)

|     | SCF(BP86) | H 0K  | H 298K | G 298K |
|-----|-----------|-------|--------|--------|
| P   | -776.278347859 | -775.929987 | -775.903601 | -775.992594 |
| C   | 4.673302 | -0.410739 | 1.629477 | 0.131871 |
| C   | 4.921331 | -0.233053 | -1.305142 | 4.328284 |
| C   | 2.188701 | 0.271634 | 0.385565 | 0.131871 |
| Au  | 1.641307 | -0.038928 | -0.111251 | -0.228276 |
| C   | -0.423857 | -0.665639 | -0.711500 | 0.051926 |
| C   | -0.749731 | 0.456123 | 0.131871 | -4.424821 |
| S   | -0.484004 | 1.004546 | 1.004546 | -1.747551 |
| H   | 5.750398 | 1.680482 | 1.574252 | -0.847617 |
| C   | 4.530752 | 1.574252 | 2.535340 | -0.030655 |
| H   | 3.970056 | -0.626822 | 0.368591 | 2.713864 |
| H   | 5.417643 | 0.368591 | 1.155737 | 2.325695 |
| H   | 3.825069 | 1.155737 | 1.155737 | 2.608727 |
| H   | 5.988771 | 1.148103 | 1.185103 | -0.008056 |
| H   | 4.574652 | 2.228276 | 2.228276 | 0.255828 |
| H   | 4.786362 | -1.404064 | -1.404064 | -1.320882 |
| H   | -3.530078 | 0.095375 | 0.095375 | -2.244127 |
| O   | -1.834073 | -1.232837 | -1.232837 | -2.493315 |
| H   | -1.835094 | -1.634913 | -1.634913 | -3.382867 |
| C   | -0.967424 | 1.793639 | 1.793639 | -0.600546 |
| C   | -1.118771 | 0.367753 | 0.367753 | 1.512269 |
| H   | -0.558783 | -1.662449 | -1.662449 | -1.28059 |
| H   | 0.229963 | -1.628563 | -1.628563 | -2.504214 |
| H   | -2.213274 | 0.522081 | 0.522081 | 1.590358 |
| H   | -0.883857 | -0.612637 | -0.612637 | 1.953141 |
| H   | -0.641422 | 1.166394 | 1.166394 | 2.104500 |
| H   | -2.060334 | 1.897288 | 1.897288 | -0.782477 |
| H   | -0.664209 | 2.619980 | 2.619980 | 0.061884 |
| H   | -0.466000 | 1.902153 | 1.902153 | -1.573050 |
| C   | -4.576571 | 0.239711 | 0.239711 | -0.122981 |
| C   | -4.888580 | -0.873145 | -0.873145 | 2.449874 |
| C   | -5.198938 | 0.478152 | 0.478152 | 2.220849 |
| C   | -5.040014 | 1.038895 | 1.038895 | 0.943382 |
| C   | -4.274786 | -1.120209 | -1.120209 | 0.100672 |
| C   | -4.427062 | 1.665817 | 1.665817 | 1.385420 |
| H   | -5.016795 | -1.306999 | -1.306999 | 3.446165 |
| H   | -5.567730 | 1.104342 | 1.104342 | 3.09753 |
| H   | -5.277655 | 2.094348 | 2.094348 | 0.773429 |
| H   | -3.925539 | -1.745782 | -1.745782 | -0.726219 |
| H   | -4.198507 | -2.724566 | -2.724566 | 1.548454 |
| H   | -0.204468 | 0.097592 | 0.097592 | -2.684889 |

SCF(BP86) = -776.278347859
H 0K = -775.929987
H 298K = -775.903601
G 298K = -775.992594
Solvent Correction(CH3Cl) = -0.05227167
BP86-D3 Correction = -0.05513402
Lowest frequencies = 5.4116 cm\(^{-1}\), 16.7055 cm\(^{-1}\)
IntV24

-2.245853  0.700910  0.008037
-2.742409  1.181946  1.722992
-2.056045  2.280042  -0.934776
-0.372108  -0.595194  -0.008037
-2.742409  1.181946  1.722992
-2.056045  2.280042  -0.934776
-0.372108  -0.595194  -0.008037
-2.742409  1.181946  1.722992
-2.056045  2.280042  -0.934776
-0.372108  -0.595194  -0.008037
-2.742409  1.181946  1.722992
-2.056045  2.280042  -0.934776
-0.372108  -0.595194  -0.008037

SCF(BP86) = -533.805135892
H 0K = -533.553730
H 298K = -533.535652
G 298K = -533.603627
Solvent Correction(CH3Cl) = -0.05229451
BP86-D3 Correction = -0.03049079
Lowest frequencies = 12.2397 cm⁻¹, 15.6594 cm⁻¹
### IntVII\(_{24}\)

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| P       | 1.503761  | -0.000061 | -0.000004 |
| C       | 2.302151  | -0.838280 | -1.456704 |
| C       | 2.269239  | 1.694470  | -0.003594 |
| C       | 2.302211  | -0.832060 | 1.460236  |
| Au      | 0.765869  | -0.002113 | 0.000006  |
| O       | 2.764469  | -0.108785 | 0.000076  |
| H       | 3.097160  | 0.810694  | -0.000444 |
| H       | 1.977592  | -1.889851 | 1.466154  |
| H       | 3.01791   | -0.791769 | 1.388904  |
| H       | 1.965591  | -0.345201 | 2.381494  |
| H       | 1.977852  | -1.883551 | 1.494086  |
| H       | 1.965531  | -0.335151 | 2.382926  |
| H       | 3.401851  | -0.785619 | 1.392266  |
| H       | 1.929338  | 2.242769  | 0.888326  |
| H       | 1.929048  | 2.239099  | 0.897654  |
| H       | 3.369989  | 1.631971  | -0.003654 |

SCF(BP86) = -338.074767856
H 0K = -337.950612
H 298K = -337.939568
G 298K = -337.988751
Solvent Correction(CH3Cl) = -0.01518402
BP86-D3 Correction = -0.01355728
Lowest frequencies = 42.6019 cm\(^{-1}\), 91.7081 cm\(^{-1}\)

| 110 |
Cationic Organic fragment of IntVII$_{24}$

\[
\begin{array}{cccc}
C & 0.851058 & -0.696785 & -0.013964 \\
C & -0.410020 & -0.013885 & -0.009865 \\
C & 2.066693 & -0.065162 & 0.011590 \\
C & -0.557563 & 1.457139 & 0.000333 \\
C & -1.642364 & -0.834554 & -0.003551 \\
H & 0.824315 & -1.792322 & -0.043729 \\
H & 2.174088 & 1.024062 & 0.039452 \\
H & -1.002729 & 1.755043 & -0.973797 \\
H & 0.363422 & 2.031507 & 0.157616 \\
H & -1.321374 & 1.752785 & 0.745193 \\
H & -1.529296 & -1.774497 & -0.569974 \\
H & -2.539833 & -0.280688 & -0.316216 \\
H & -1.810257 & -1.149757 & 1.053312 \\
H & 2.994840 & -0.646648 & 0.000881 \\
\end{array}
\]

SCF(BP86) = -195.641962192
H 0K = -195.521346
H 298K = -195.514690
G 298K = -195.551649
Solvent Correction(CH3Cl) = -0.06433655
BP86-D3 Correction = -0.00830891
Lowest frequencies = 78.1467 cm$^{-1}$, 108.6905 cm$^{-1}$
|  |  |  |  |
|---|---|---|---|
| P  | -3.799690 | -0.918414 | 0.432955 |
| C  | -3.582143 | -1.816938 | 2.042044 |
| Au | -1.905767 | 0.049607  | -0.385517 |
| C  | 2.157451  | 2.620610  | -0.594288 |
| C  | 1.926719  | 3.661421  | 0.269712  |
| C  | 2.068377  | 1.208830  | -0.277031 |
| O  | -0.207925 | 0.848481  | -1.182939 |
| H  | -0.445654 | 1.741770  | -1.502560 |
| C  | 1.549723  | 3.492289  | 1.716885  |
| H  | 2.027505  | 5.082749  | -0.215961 |
| H  | 2.440584  | 2.866456  | 1.626008  |
| C  | -4.548371 | -2.179367 | -0.702967 |
| H  | 2.020637  | 0.487517  | 1.093094  |
| H  | 2.283004  | 4.007368  | 2.364219  |
| H  | 1.478041  | 2.444740  | 2.042411  |
| H  | 0.576556  | 3.978720  | 1.912750  |
| H  | 2.301968  | 5.147645  | 1.279798  |
| H  | 2.775221  | 5.643870  | 0.375006  |
| H  | 1.067341  | 5.611323  | -0.069128 |
| H  | -3.217961 | -1.112190 | 2.804992  |
| H  | -4.538453 | -2.255197 | 2.371142  |
| H  | -2.836498 | -2.616383 | 1.913731  |
| H  | -6.063393 | -0.236867 | 1.137477  |
| H  | -4.835219 | 1.028419  | 1.498930  |
| H  | -5.421735 | 0.811506  | -0.176666 |
| H  | -3.819141 | -2.983993 | 0.882774  |
| H  | -5.465236 | -2.602682 | 0.261298  |
| H  | -4.788123 | -1.701599 | -1.665102 |
| S  | 4.150569  | 0.673999  | 0.398573  |
| C  | 4.365277  | -1.098040 | 0.156860  |
| H  | 4.717101  | 1.097294  | -0.765892 |
| C  | 4.622188  | -3.866963 | -0.081519 |
| C  | 4.591014  | -3.275200 | 1.191566  |
| C  | 4.464646  | -1.883897 | 1.321536  |
| C  | 4.385605  | -1.679117 | -1.125959 |
| C  | 4.523424  | -3.070059 | 1.235301  |
| H  | 4.729577  | -4.951464 | -0.176643 |
| H  | 4.677468  | -3.893658 | 2.089808  |
| H  | 4.461778  | -1.417025 | 2.315567  |
| H  | 4.303300  | -1.061598 | -2.026173 |
| H  | 4.553157  | -3.530424 | -2.227336 |

SCF(BP86) = -776.248466267
H 0K = -775.902639
H 298K = -775.876167
G 298K = -775.967703
Solvent Correction(CH3Cl) = -0.04657893
BP86-D3 Correction = -0.04413852
Lowest frequencies = -133.7005 cm⁻¹, 7.4236 cm⁻¹
\[
\begin{align*}
\text{SCF(BP86) } & = -1261.20309496 \\
\end{align*}
\]
H 0K = -1260.662270
H 298K = -1260.619397
G 298K = -1260.754490
Solvent Correction(CH3Cl) = -0.04399081
BP86-D3 Correction = -0.08945173
Lowest frequencies = -191.5982 cm⁻¹, 6.2344 cm⁻¹
IntVI$_{24}$

17

P  1.56824 -0.00018  0.00384
C  2.25994  1.50957 -0.80440
C  2.27024 -0.05866  1.71099
Au -0.70889  0.00025 -0.00110
O  -2.90139 -0.00067 -0.07673
H  -3.32762 -0.78829  0.31684
C  2.25924 -1.45168 -0.90541
H  1.91920 -2.38277 -0.42747
H  3.36050 -1.40654 -0.88367
H  1.92882 -0.97325  2.21883
H  1.92898  0.81918  2.28011
H  3.37118 -0.05683  1.65448
H  1.92150  2.40604 -0.26332
H  1.90910  1.56295 -1.84608
H  3.36118  1.46190 -0.78723
H  -3.32881  0.78359  0.32220

SCF(BP86) = -338.468872417
H 0K = -338.332280
H 298K = -338.320605
G 298K = -338.320605
Solvent Correction(CHCl$_3$) = -0.06056610
BP86-D3 Correction = -0.01455309
Lowest frequencies = 9.8094 cm$^{-1}$, 85.9645 cm$^{-1}$
TS(I-II\textsuperscript{a})_{24} (anti)

|   |   |   |
|---|---|---|
| P | -3.716318 | 0.694155 | -0.075301 |
| C | -4.728902 | -0.213478 | -1.356018 |
| C | -4.659440 | 0.521424 | 1.511073 |
| C | -3.868102 | 2.484285 | -0.532696 |
| Au | -1.501925 | -0.043162 | 0.091021 |
| C | 0.566074 | -0.679132 | 0.441391 |
| C | 0.962913 | -1.102395 | 0.881471 |
| S | 3.527912 | 1.527089 | -0.592725 |
| C | 0.926588 | 0.162375 | 1.608130 |
| H | -4.750390 | -1.84894 | 1.084870 |
| H | -4.272797 | -0.090099 | -2.350119 |
| H | -3.351101 | 3.092866 | 0.220444 |
| H | -4.929747 | 2.776576 | -0.580627 |
| H | -3.395768 | 2.652988 | -1.512458 |
| H | -5.690951 | 0.887634 | 1.382081 |
| H | -4.158685 | 1.104111 | 2.239261 |
| H | -4.680332 | -0.537468 | 1.810779 |
| H | 0.597339 | -1.918652 | 0.659033 |
| O | 1.887461 | -1.947253 | 2.030214 |
| H | 1.860852 | -2.593332 | 2.761742 |
| C | 0.688445 | -2.507311 | -1.374134 |
| C | 1.151806 | -0.048887 | -1.953750 |
| H | 1.013921 | 0.289590 | 0.728806 |
| H | -0.027289 | -1.209940 | 2.451761 |
| H | 1.800322 | -0.414291 | -2.764608 |
| H | 1.571699 | 0.883363 | -1.549399 |
| H | 0.171356 | 0.192046 | -2.407145 |
| H | 1.304445 | -2.747547 | -2.256299 |
| H | -0.372109 | -2.575298 | -1.685211 |
| H | 0.854492 | -3.275814 | -0.604026 |
| C | 4.114558 | 0.105905 | -0.141238 |
| C | 5.048726 | 2.685901 | 0.448611 |
| C | 5.214576 | 2.154842 | -0.844748 |
| C | 4.751676 | 0.865935 | -1.145391 |
| C | 3.943053 | 0.631806 | 1.157321 |
| C | 4.416818 | 1.922283 | 1.440849 |
| H | 5.420540 | 3.688459 | 0.677138 |
| H | 5.715842 | 2.741050 | -1.621083 |
| H | 4.898069 | 0.447038 | -2.146423 |
| H | 3.457263 | 0.031636 | 1.932530 |
| H | 4.296494 | 2.327402 | 2.450663 |
| H | 0.006329 | -2.597757 | 1.326265 |

SCF(BP86) = -776.272652256
H 0K = -775.923762
H 298K = -775.898798
G 298K = -775.982831
Solvent Correction(CH3Cl) = -0.04655497
BP86-D3 Correction = -0.05811568
Lowest frequencies = -59.1187 cm\(^{-1}\), 6.2128 cm\(^{-1}\)
### Int(I-II)$_{24}$ (anti)

| Symbol | $x$     | $y$     | $z$     |
|--------|---------|---------|---------|
| P      | -3.717196 | 0.675698 | -0.069349 |
| C      | -4.781974 | -0.421285 | -0.123722 |
| C      | -4.616466 | 0.773365  | 1.551533  |
| C      | -3.918046 | 2.365878  | -0.810608 |
| Au     | -1.483567 | -0.31193 | 0.133188  |
| C      | 0.560154  | -0.637407 | -1.163861 |
| C      | 1.167236  | -1.004747 | -0.916063 |
| S      | 3.193040  | -1.447410 | -0.635704 |
| C      | -5.551013 | -1.698419 | 1.508438  |
| H      | -4.788491 | -1.437569 | -0.699775 |
| H      | -4.566291 | -0.465164 | -2.141106 |
| H      | -3.379688 | 3.100555  | -0.192411 |
| H      | -4.984305 | 2.639987  | -0.862620 |
| H      | -3.487556 | 2.374329  | -1.823711 |
| H      | -5.653822 | 1.112098  | 1.397084  |
| H      | -4.094617 | 1.479585  | 2.215377  |
| H      | -4.621600 | -0.219711 | 2.026416  |
| H      | 2.823767  | -1.916511 | 0.677272  |
| O      | 1.948742  | -1.990030 | 1.941045  |
| H      | 1.957863  | -2.835484 | 2.448223  |
| C      | 0.709415  | -2.330329 | -1.535135 |
| C      | 1.202943  | 0.138890  | -1.928853 |
| H      | 1.035319  | 0.286661  | 0.798953  |
| H      | 0.017518  | -1.331879 | 2.398426  |
| H      | 1.796764  | -0.125484 | -2.819962 |
| H      | 1.610525  | 1.062627  | -1.487544 |
| H      | 0.171352  | 0.351036  | -2.260402 |
| H      | 1.229157  | -2.535068 | -2.484740 |
| H      | -0.372704 | -2.257446 | -1.744607 |
| H      | 0.856781  | -3.195768 | -0.67536 |
| C      | 0.983397  | 0.095082  | -0.150815 |
| C      | 5.273254  | 2.490374  | 0.492884  |
| C      | 5.312657  | 2.007593  | -0.825966 |
| C      | 4.671477  | 0.804886  | -1.156240 |
| C      | 3.940922  | 0.567020  | 1.177195  |
| C      | 4.593207  | 1.769938  | 1.488914  |
| H      | 5.782433  | 3.424883  | 0.746891  |
| H      | 5.851881  | 2.561550  | -1.600159 |
| H      | 4.714678  | 0.416895  | -2.178787 |
| H      | 3.420879  | -0.003241 | 1.951843  |
| H      | 4.573410  | 2.139914  | 2.518592  |
| H      | 0.081215  | -2.638306 | 1.174366  |

SCF(BP86) = -776.273864487
H 0K = -775.923994
H 298K = -775.899299
G 298K = -775.981250
Solvent Correction(CH3Cl) = -0.04467395
BP86-D3 Correction = -0.05863422
Lowest frequencies = 9.6369 cm$^{-1}$, 19.7427 cm$^{-1}$
TS(I-II)\textsubscript{24} (anti)

|       |  P   |  C   |  Au  |  C   |  S   |  C   |  H   |  C   |  H   |  C   |  H   |  C   |  H   |  C   |  H   |  C   |  H   |  C   |  H   |  C   |  H   |  C   |  H   |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| \text{p} | 3.695474 | 0.697884 | 0.049061 | 4.618561 | -0.041516 | 1.478814 | 4.757455 | 0.340388 | -1.429837 | 3.837367 | 2.531223 | 0.296138 | 1.478814 | -0.055092 | -0.167182 | -0.591449 | -0.652987 | 0.368852 | -3.142026 | -1.404027 | 0.699749 | -0.457794 | -1.755745 | -1.331249 |
| \text{c} | 5.645055 | 0.357587 | 1.520378 | 4.654827 | -1.135660 | 1.363814 | 4.093981 | 0.198823 | 2.416256 | 3.381027 | 3.050876 | -0.560251 | 4.895611 | 2.826265 | 0.384206 | 3.298647 | 2.819420 | 1.211818 | 5.778440 | 0.723475 | -1.269985 | 4.319958 | 0.821395 | -2.518030 | -2.599498 | -2.084455 | -0.937915 |
| \text{c} | -2.011318 | -2.293669 | -1.821108 | -2.011893 | -3.266519 | -1.957047 | -0.719431 | -2.200587 | 1.694706 | -1.212363 | 0.275555 | 1.915074 | -1.046749 | 0.238330 | -0.838148 | -0.068251 | -1.479175 | -2.316886 | -1.774709 | 0.085200 | 2.843824 | -1.630676 | 1.171772 | 1.429055 | -0.163408 | 0.494330 | 2.185240 | -1.215033 | -2.343084 | 2.668119 |
| \text{c} | 0.364944 | -2.084552 | 1.870600 | -0.866890 | -3.124995 | 1.109261 | -3.929590 | 0.128403 | 0.159330 | -5.251423 | 2.484810 | -3.004861 | -5.218666 | 2.110217 | 0.748321 | -4.555902 | 0.931868 | 1.135354 | -3.978624 | 0.496088 | -1.201954 | -4.638817 | 1.676841 | -1.576804 | -5.790339 | 3.400672 | -0.903744 | -5.700331 | 2.730587 | 1.506016 |
| \text{c} | -4.535714 | 0.627519 | 2.186113 | -3.522304 | -0.140254 | -1.956811 | -4.682024 | 1.958683 | -2.633480 | -0.026380 | -2.691892 | -0.552687 |

SCF(BP86) = -776.272353426
H 0K = -775.922103
H 298K = -775.898032
G 298K = -775.978815
Solvent Correction(CH3Cl) = -0.04788165
BP86-D3 Correction = -0.05879518
Lowest frequencies = -178.4263 cm\textsuperscript{-1}, 8.4192 cm\textsuperscript{-1}

118
### IntII₂₄ (anti)

|  |  |  |  |
|---|---|---|---|
| P | 3.601087 | 0.461874 | 0.838389 |
| C | 4.034874 | -0.793258 | 2.130702 |
| C | 5.103544 | 0.590390 | -0.238389 |
| C | 3.504223 | 2.079516 | 1.737100 |
| Au | 1.673990 | -0.055436 | -0.389553 |
| C | -0.799311 | -0.417689 | -0.779557 |
| C | -1.414217 | -1.487735 | 0.068975 |
| S | -3.138770 | -1.429681 | -0.786977 |
| C | 0.103128 | -0.578735 | 1.842369 |
| H | 4.961857 | -0.497864 | 2.648634 |
| H | 4.17751 | -1.774807 | 1.653615 |
| H | 3.214474 | -0.867480 | 2.660596 |
| H | 3.324686 | 2.888843 | 1.013108 |
| H | 4.446612 | 2.269768 | 2.276132 |
| H | 2.669410 | 2.051529 | 2.453797 |
| H | 5.986466 | 0.838793 | 0.372943 |
| H | 4.946616 | 1.374865 | -0.994041 |
| H | 5.269678 | -0.369153 | -0.751170 |
| H | -2.037534 | 1.752936 | -3.369478 |
| O | -1.529442 | 2.114208 | -2.620032 |
| H | -1.577949 | 3.079006 | -2.749287 |
| C | -0.877043 | -2.903121 | -0.163936 |
| C | -1.490279 | -1.123563 | 1.552260 |
| H | -1.166971 | 0.600266 | -0.593684 |
| H | 0.173399 | 0.243974 | -2.565464 |
| H | -2.124467 | -1.841901 | 2.086149 |
| H | -1.896692 | -0.112407 | 1.709809 |
| H | -0.474624 | -1.162328 | 1.987117 |
| H | -1.433627 | -3.626404 | 0.451366 |
| H | 0.189248 | -2.951837 | 0.124172 |
| H | -0.961787 | -3.219164 | -1.216838 |
| C | -4.065600 | -0.161891 | 0.095048 |
| C | -5.657617 | 1.744123 | 1.404443 |
| C | -5.720194 | 0.395439 | 1.791415 |
| C | -4.924609 | -0.560726 | 1.141891 |
| C | -4.009851 | 1.190955 | -0.305398 |
| C | -4.803033 | 2.338462 | 0.361088 |
| H | -6.280624 | 2.487508 | 1.911494 |
| H | -6.391209 | 0.084033 | 2.597995 |
| H | -4.973491 | -1.614883 | 1.431625 |
| H | -3.349180 | 1.497874 | -1.124788 |
| H | -4.761673 | 3.189082 | 0.955781 |
| H | 0.359903 | -1.580885 | -2.206757 |

SCF(BP86) = -776.288770059
H OK = -775.939895
H 298K = -775.912779
G 298K = -776.002068
Solvent Correction(CH3Cl) = -0.04810439
BP86-D3 Correction = -0.05487416
Lowest frequencies = 12.7900 cm⁻¹, 16.0278 cm⁻¹
*IntII* (anti)

SCF(BP86) = -699.857560117
H 0K = -699.531650
H 298K = -699.504842
G 298K = -699.588500
Solvent Correction(CH3Cl) = -0.04827478
BP86-D3 Correction = -0.04993104
Lowest frequencies = 8.0078 cm^-1, 17.0987 cm^-1
IntIII$_{24}$ (anti)

53

P  -2.47560 -2.95185  0.13673
C  -3.29745 -3.30943 -1.48445
C  -1.61238 -4.52206  0.60963
C  -3.85667 -2.76674  1.35715
Au -1.06974 -1.07875  0.09426
C   1.08538  0.17834 -0.06546
C  -0.08873  0.90428  0.16738
S  -2.21492  3.47905  2.53546
C   1.79884 -0.01404 -1.37833
H  -3.95765 -4.18671 -1.38827
H  -2.53104 -3.50852 -2.24890
H  -3.89055 -2.43556 -1.79439
H  -3.43800 -2.62101  2.36458
H  -4.49143 -3.66765  1.34817
H  -4.46325 -1.88684  1.09394
H  -2.33288  5.35995  0.63068
H  -1.15775  4.40348  1.60491
H  -0.81909  -4.74009  -0.12135
C   -2.09419  3.70335  0.75566
H  -1.29234  4.41941  2.87677
S   3.22344  1.23737  -1.07753
C   1.04665  0.51993  -2.60045
C  -2.30294  -1.44294  -1.57836
H  -2.94431  -1.00021  -2.47251
H  -1.44063  -2.11861  -1.72977
H  -2.87895  -1.80642  -0.71285
H   0.11201  -0.05242  -2.74565
H  -1.66583  -0.40210  -3.50299
H   0.78135  1.58536  -2.50230
C   4.40287  0.37818  -0.02066
H  -0.55681  1.48883  -0.63405
H  -0.32170  1.23527  1.18847
H  -1.61810  -0.23553  -0.80301
C   -1.96724  3.89511  -2.05793
C  -0.97962  4.49753  -1.25958
H  -1.03321  4.39881  0.14048
C  -3.09639  3.11101  -0.04225
C  -3.02526  3.20460  -1.44135
H  -1.92696  3.98533  -3.14760
H  -0.16189  5.05807  -1.72442
H  -0.25289  4.86801  0.74871
H   -3.94227  2.60131  0.43137
H  -3.81831  2.75762  -2.05015
C   6.34826  -0.82478  1.61291
C  -5.35769  -0.01018  2.18670
C  -4.38660  0.59602  1.37478
C  -5.40858  -0.42729  -0.59733
C  -6.37484  -1.02924  0.22321
H  -7.10815  -1.29034  2.24815
H   5.34634  0.16355  3.26732
H   3.62871  1.25356  1.81214
H   5.43665  -0.56571  -1.68215
H   7.15593  -1.65017  -0.22648

SCF(BP86) = -942.329758986
H 0K = -941.906907
H 298K = -941.874851
G 298K = -941.981637
Solvent Correction(CHCl3) = -0.04793721
BP86-D3 Correction = -0.06889157
Lowest frequencies = 4.3216 cm$^{-1}$, 6.8323 cm$^{-1}$
TS(III-IV)_{24} (anti)

P  -4.289409  -0.645725  -0.031448
C  -4.748839  -2.070986  1.062798
C  -5.289773  0.781612  0.601624
C  -5.032422  -1.051300  -1.681667
Au  -1.986666  -0.204095  -0.116918
C  0.140709  0.358120  -0.186299
C  0.487724  -0.860245  -0.877301
S  2.759818  -0.943864  -1.531867
C  0.680557  0.690922  1.206889
H  -5.841158  -2.218219  1.059681
H  -4.408766  -1.867609  2.089744
H  -4.253735  -2.984581  0.699817
H  -4.868012  -0.210113  -2.372275
H  -6.113975  -1.236548  -1.577983
H  -4.543484  -1.947909  -2.092206
H  -6.360822  0.522019  0.613057
H  -5.130408  1.655818  -0.047983
H  -4.962623  1.034036  1.621856
C  3.426457  -2.353983  -0.633161
H  2.911315  0.038560  -0.500524
C  2.497833  1.352059  1.042937
C  0.846265  -0.533415  2.122934
C  -0.149972  1.786308  1.889295
H  0.306527  2.086026  2.846854
H  -1.166871  1.402824  2.095951
H  -0.247661  2.680958  1.253044
H  -0.133091  -1.030028  2.249079
H  1.205330  -0.227106  3.118467
H  1.555938  -1.276409  1.721460
C  2.345531  2.939382  0.197107
H  0.580778  -1.797913  -0.319571
H  0.144055  -0.975095  -1.909711
H  0.099517  2.150491  -0.834313
C  4.477132  -4.605312  0.666083
C  4.767304  -3.317111  1.145009
C  4.247557  -2.183911  0.500547
C  3.135226  -3.642816  -1.124061
C  3.664838  -4.764735  -0.463918
C  4.890402  -5.483162  1.171497
H  5.409412  -3.187329  2.021736
H  4.492850  -1.181962  0.865297
H  2.511200  -3.768286  -2.015100
C  3.443662  -5.765721  -0.851572
C  2.19547  5.454534  -1.054027
C  2.245889  4.284586  -1.830863
C  2.313782  3.026829  -1.211151
C  2.350765  4.115852  0.976088
C  2.266111  5.368827  0.347126
H  2.174324  6.433307  -1.541361
H  2.226308  4.348842  -2.923364
H  2.361735  2.122022  -1.824555
H  2.379936  4.043560  2.066747
H  2.258918  6.278986  0.954881

SCF(BP86) = -942.320597146
H 0K = -941.897246
H 298K = -941.867302
G 298K = -941.964176
Solvent Correction(CHCl3) = -0.04361495
BP86-D3 Correction = -0.07516386
Lowest frequencies = -134.7252 cm^{-1}, 8.1177 cm^{-1}
Int(III-IV)$_{24}$ (anti)

| SCF(BP86) = -942.324574194 |
| H 0K = -941.900928 |
| H 298K = -941.870730 |
| G 298K = -941.966986 |
| SCF(BP86) = -942.324574194 |
| H 0K = -941.900928 |
| H 298K = -941.870730 |
| G 298K = -941.966986 |

Solvent Correction(CHCl3) = -0.04143085
BP86-D3 Correction = -0.07643137
Lowest frequencies = 9.6317 cm$^{-1}$, 18.3463 cm$^{-1}$

P  -4.354402  -0.457534  -0.045515
C   -4.870386  -2.240980  -0.052479
C   -5.218403  0.265453  1.430459
C   -5.234757  0.282856  -1.502564
Au  -2.027570  -0.121476  -0.074629
C    0.101863  0.201119  -0.207045
C    0.617129  -1.014182  -0.965553
S    2.470233  -0.958180  -1.541011
C    0.657596  0.498042  1.168471
C    -5.969334  -3.243915  -0.045766
H    -4.458351  -2.743327  0.836132
H    -4.470411  -2.732101  -0.952804
H    -5.051534  1.368054  -1.436104
H    -4.840620  -0.160522  -2.429840
H    -6.302747  0.076389  1.373561
H    -5.036821  1.350703  1.463440
H    -4.815106  -0.188773  2.348544
C    3.240019  -2.437359  -0.668921
S    2.606797  1.127989  1.015311
C    0.838991  -0.714711  2.090861
C   -0.026933  1.670376  1.875639
H    0.523138  1.968995  2.784415
H   -1.042155  1.360902  2.180017
H    -0.125306  2.546405  1.214453
H   -0.151561  -1.177055  2.252103
H    1.243115  -0.416814  3.072468
H    1.502246  -1.485587  1.664832
C    2.553708  2.729000  0.194389
H    0.550144  -1.952066  -0.394474
H    0.075599  -1.140906  -1.913226
H    0.153482  1.119110  -0.034113
C    4.522965  -4.493475  0.598959
C    5.076581  -3.205449  0.669175
C    4.437805  -2.123691  0.040910
C    2.692408  -3.638781  -0.763274
C    3.332953  -4.706980  -3.116631
H    5.023220  -5.332240  1.092069
H    6.008815  -3.034924  1.216465
H    4.877098  -1.122480  0.093879
H    1.785842  -3.816807  -1.350340
H    2.907398  -5.712896  -0.190118
C    2.530913  5.277549  -0.968700
C    2.667555  5.144046  0.423128
C    2.682785  3.871150  1.011809
C    2.424547  2.854651  -1.204359
C    2.414111  4.135606  -1.777997
H    2.525923  6.272322  -1.422288
H    2.770369  6.031526  1.054688
H    2.804078  3.762610  2.094089
H    2.355270  1.970947  -1.844140
H    2.321992  4.237403  -2.863664
TS(III-IVB)_{24} (anti)

53

|   |   |   |
|---|---|---|
| P | -4.372496 | -0.404963 | -0.057398 |
| C | -4.906877 | -2.180546 | -0.046621 |
| C | -5.246250 | 0.365093 | 1.386117 |
| C | -5.184714 | 0.329486 | -1.553505 |
| Au | -2.050923 | -0.115748 | -0.038941 |
| C | 0.135055 | 0.143556 | -0.218214 |
| C | 0.580734 | -1.069794 | 1.402613 |
| S | 2.380324 | -1.082043 | 2.320435 |
| C | 3.168985 | 0.164117 | -0.709831 |
| H | 2.910180 | 0.363472 | -0.177359 |
| S | 2.900377 | 1.155302 | 0.995262 |
| C | 0.840866 | -0.835521 | 2.052313 |
| C | 0.022008 | 1.591330 | 1.876038 |
| H | 0.672628 | 1.849661 | 2.726566 |
| H | -0.986604 | 1.398493 | 2.287463 |
| H | -0.048354 | 2.457432 | 1.059010 |
| H | -0.106635 | -1.336013 | 2.352234 |
| H | 1.327816 | -0.513441 | 2.985153 |
| H | 1.477907 | -1.585617 | 1.558890 |
| C | 2.717071 | 2.751997 | 0.201765 |
| H | 0.471416 | -2.014931 | -0.473340 |
| H | -0.008157 | -1.149376 | -1.950711 |
| H | 0.136250 | 1.082770 | -0.601210 |
| C | 4.509782 | -4.449953 | 0.643352 |
| C | 5.089899 | -3.175027 | 0.556848 |
| C | 4.422011 | -2.135110 | -0.11186 |
| C | 2.598239 | -3.669717 | -0.651211 |
| C | 3.264638 | -4.693532 | 0.039251 |
| H | 5.030812 | -5.255559 | 1.169236 |
| H | 6.604558 | -2.980278 | 1.015055 |
| H | 4.879972 | -1.142888 | -0.174127 |
| H | 1.652636 | -3.880807 | -1.160979 |
| H | 2.818229 | -5.692049 | 0.882988 |
| C | 2.424708 | 5.304363 | -0.932984 |
| C | 2.574497 | 5.165668 | 0.457247 |
| C | 2.721695 | 3.894644 | 1.030716 |
| C | 2.571764 | 2.885331 | -1.19890 |
| C | 2.427717 | 4.164925 | -1.754128 |
| H | 2.317896 | 6.298935 | -1.376099 |
| H | 2.586382 | 6.050824 | 1.100662 |
| H | 2.855640 | 3.789913 | 2.112355 |
| H | 2.599160 | 2.003957 | -1.843460 |
| C | 2.327399 | 4.268468 | -2.839170 |

SCF(BP86) = -942.323020106
H 0K = -941.899615
H 298K = -941.869452
G 298K = -941.966890
Solvent Correction(CHCl3) = -0.04410199
BP86-D3 Correction = -0.07614278
Lowest frequencies = -84.1086 cm⁻¹, 8.0984 cm⁻¹
|  |  |  |
|---|---|---|
| P | 4.490712 | 0.178740 | 0.093389 |
| C | 5.026624 | 0.788416 | 1.757543 |
| C | 5.467477 | -1.364632 | -0.212322 |
| C | 5.130910 | 1.420263 | -1.122370 |
| Au | 2.180732 | -0.139717 | -0.081018 |
| C | -0.029874 | -0.012470 | -0.508187 |
| C | -0.555575 | 1.315101 | -1.204859 |
| C | -2.396844 | 1.354157 | -0.405641 |
| C | 0.018706 | -1.204775 | 0.241944 |
| H | 6.120038 | 0.926292 | 1.773123 |
| H | 4.737145 | 0.056640 | 2.526990 |
| H | 4.531800 | 1.747559 | 1.973296 |
| H | 4.904641 | 1.082671 | -2.145210 |
| H | 6.220942 | 1.532698 | -1.004238 |
| H | 4.640438 | 2.390311 | -0.949767 |
| H | 6.545168 | -1.148542 | -0.130101 |
| H | 5.244510 | -1.745971 | -1.220383 |
| H | 5.188245 | -2.128855 | 0.528806 |
| C | -2.738127 | 3.121491 | -0.251058 |
| H | -3.937492 | -0.453626 | 1.172138 |
| S | -4.083014 | -1.629330 | 1.852439 |
| C | -0.270355 | -1.261072 | 1.719524 |
| C | 0.117609 | -2.538123 | -0.462059 |
| C | -0.872468 | -3.031579 | -0.399472 |
| H | 0.836966 | -3.211031 | 0.034091 |
| H | 0.382083 | -2.438384 | -1.525971 |
| H | 0.345017 | -2.028010 | 2.217650 |
| H | -0.133624 | -2.985666 | 2.233849 |
| C | -3.743914 | -2.710851 | 0.452942 |
| H | -0.407415 | 1.469541 | 1.064773 |
| H | -0.101763 | 2.151795 | -0.567443 |
| H | -0.049711 | -0.131577 | -1.602634 |
| C | -3.358508 | 5.849919 | -0.038731 |
| H | -3.308367 | 5.050558 | 1.115780 |
| C | -3.003358 | 3.684592 | 1.014442 |
| C | -2.792091 | 3.921111 | -1.411182 |
| C | -3.103737 | 5.285286 | -1.299464 |
| H | -3.604561 | 6.913161 | 0.043899 |
| H | -3.518063 | 5.487863 | 2.097066 |
| H | -2.982149 | 3.051976 | 1.907414 |
| H | -2.601355 | 3.469532 | -2.389642 |
| H | -3.152719 | 5.905453 | -2.200071 |
| C | -3.224998 | -4.506186 | -1.660294 |
| C | -3.113463 | -4.932474 | -0.325762 |
| C | -3.362706 | -4.040997 | 0.729962 |
| C | -3.872459 | -2.844646 | -0.885496 |
| C | -3.604824 | -3.181098 | -1.932394 |
| H | -3.031452 | -5.204285 | -2.480309 |
| H | -2.830569 | -5.965851 | -0.099969 |
| H | -3.267177 | -4.378818 | 1.767471 |
| H | -4.195615 | -1.263053 | -1.109731 |
| H | -3.713099 | -2.841501 | -2.967849 |

SCF(BP86) = -942.335190669
H 0K = -941.912104
H 298K = -941.980100
G 298K = -941.984512
Solvent Correction(CHCl3) = -0.04929878
BP86-D3 Correction = -0.06699874
Lowest frequencies = 11.0747 cm⁻¹, 12.3887 cm⁻¹
*IntIV\textsubscript{24} (anti)

\begin{verbatim}

P  3.27725  -1.13717  -0.06390
C  4.83835   -0.15424   0.10148
C  3.36543  -2.43969   1.24879
C  3.42496  -2.03788  -1.67496
Au 1.34575   0.18055   0.08479
C  -0.82149   0.91213   0.06022
C  -1.45535   0.63916  -1.27909
S  -3.22402   1.25576  -1.22530
C  -0.07662   2.05114   0.41760
H  5.71088  -0.82356   0.02678
H  4.84967   0.35660   1.07625
H  4.88418   0.59998  -0.69874
H  2.55776  -2.70300  -1.80514
H  4.35125  -2.63507  -1.68698
H  3.44528  -1.31114  -2.50128
H  4.29136  -3.02647   1.13437
H  2.49431  -3.10691   1.16285
H  3.35248  -1.96241   2.24046
C  -4.04351  -0.11123  -0.37405
C  -0.07662   2.05114   0.41760
H  -0.62784   3.26839   2.08654
H   1.08901   2.79839   2.11143
H  -0.18552   1.60519   2.55894
H   1.27460   3.58673  -0.31015
H  -0.45251   3.93139  -0.52401
H   0.35374   2.77736  -1.61481
H  -0.97857   1.17921  -2.11082
H  -1.47983  -0.43384  -1.52093
H  -1.24932   0.32897   0.88987
C  -5.42052  -2.18843   0.92159
C  -4.90802  -2.35627  -0.40297
C  -4.30251  -1.31762  -1.05809
C  -4.88825   0.06023   0.95256
C  -5.18000  -0.97992   1.59485
H  -5.96101  -2.99643   1.42434
H  -5.18456  -3.29078  -0.93537
H  -3.98989  -1.43000  -2.10139
H  -4.30307   1.00788   1.46785
H  -5.53218  -0.84292   2.62217

SCF(BP86) = -699.864008888
H 0K = -699.864008888
H 298K = -699.538119
G 298K = -699.595954
Solvent Correction(CHCl3) = -0.05030723
BP86-D3 Correction = -0.0441935
Lowest frequencies = 12.8400 cm\textsuperscript{-1}, 15.6727 cm\textsuperscript{-1}
\end{verbatim}
4. Reactions of Substrate 4' with PhSH at [(Johnphos)Au(NCMe)]⁺, 5.

Figure S7. First S_N2' step to form 3a' via *anti* attack of PhSH using the full experimental catalyst. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl₃) in red. All energies are in kcal/mol and are quoted relative to 5 and the separated reactants set to zero.

Figure S8. Second S_N2' step to form 28 via *anti* attack of PhSH using the full experimental catalyst. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl₃) in red. All energies are in kcal/mol and are quoted relative to 5 and the separated reactants set to zero.
Table S3. Computed relative energies (kcal/mol) for the reactions 4' with PhSH at the full experimental catalyst, [(Johnphos)Au(NCMe)]⁺, 5. Energies are reported as ΔE (gas-phase SCF energies), ΔH₂⁹⁸ (zero-point energy corrected energies at 298.15 K), ΔG (free energies at 298.15 K and 1 atm), ΔG_{disp} (including a correction for dispersion effects using Grimme’s D3 parameter set) and ΔG_{CHCl₃+disp} including an additional correction for CHCl₃ solvent via the PCM approach.

|                  | ΔE  | ΔH₂⁹⁸ | ΔG   | ΔG_{disp} | ΔG_{CHCl₃+disp} |
|------------------|-----|-------|------|-----------|-----------------|
| **5**            | 0.0 | 0.0   | 0.0  | 0.0       | 0.0             |
| *IntI₄' (anti)   | +5.8| +5.8  | +8.4 | +1.1      | -1.2            |
| IntI₄' (anti)    | +2.7| +4.5  | +15.5| +1.3      | +1.1            |
| TS(I-II)₄' (anti)| +6.9| +8.0  | +23.0| +7.5      | +10.0           |
| IntII₄' (anti)   | -10.1| -6.9 | +4.8 | -9.6      | -7.7            |
| *IntII₄' (anti)  | -0.7| +0.5  | +2.7 | -6.8      | -8.7            |
| IntIII₄' (anti)  | -4.5| -1.5  | +10.3| -11.0     | -10.6           |
| TS(III-IV)₄' (anti)| +8.4| +9.8 | +26.9| +3.6      | +6.6            |
| IntIV₄' (anti)   | -0.1| +2.7  | +12.9| -4.2      | -3.4            |
| *IntIV₄' (anti)  | +2.9| +3.9  | +8.0 | +3.8      | -4.9            |
| [(Johnphos)Au(SHPh)]⁺ | -0.1| 0.0  | +2.8 | -3.4      | -3.4            |

*Complex computed in the absence of PhSH nucleophile
5

55

P  -1.27163  -0.65909   0.03615
C  -1.89274  -1.56822  -1.56789
C  -1.82140  -1.46815   1.70650
Au  1.04556  -0.69156  -0.03819
N   3.09801  -0.93359  -0.13331
C  -1.37656  -2.94693  1.70152
C  -3.33605  -1.37026  2.81282
C  -3.63722   -2.02985  -1.51025
C   -0.98853  -2.80063  -1.80725
C  -1.69159  -0.56455  -2.72614
C   4.25692  -1.07043  -0.18607
C  -1.96717   1.06891  -0.00569
C  -3.20804   3.60818  -0.24587
C  -3.99639  -3.54029
C  -3.76555   1.20013  -0.07920
C  -1.16474  -2.24673  -0.04235
C  -1.81463  -3.49739  -0.17019
H  -3.64310  -0.90742
C  -6.00033   2.75900   -2.05240
C  -0.39551   2.00203   2.05254
C  -2.84099   4.30818   2.04023
H  -0.64931  -0.20337  -2.77899
C  -2.35920  -3.07511   -2.64611
C  -1.91409  -1.07766   -3.67870
C  -4.07285  -1.19828  -1.37990
C  -3.53936  -2.77782  -1.72056
C  -3.61219  -2.51186   -2.74289
C  -1.26443  -3.27964  -2.75418
C  -1.07427  -3.55611   -1.01123
C   0.07405  -3.51799  -1.90113
C  -1.96593  -3.35933  -1.00002
C  -1.53330  -3.36631   3.71147
C  -0.30640  -3.05856   1.45480
C  -0.03279  -0.77822   2.69423
C  -1.32901  -1.13461  -3.79281
C  -1.33962  -0.36722   2.83611
C  -3.54245  -1.88473   2.94043
C  -3.95033  -1.86035   1.21370
C  -3.67069  -0.32758   2.09851
C   5.69810  -1.25387  -0.25207
H   6.16022  -0.94029   0.69845
H   6.11611  -0.64865  -1.07324
H   5.93224  -2.31599  -0.43281

SCF(BP86) = -1053.45861377
H 0K = -1053.005853
H 298K = -1052.975617
G 298K = -1053.069791
Solvent Correction(CH3Cl) = -0.04347255
BP86-D3 Correction = -0.09110686
Lowest frequencies = 17.6703 cm⁻¹, 18.8994 cm⁻¹
*IntI₄* (anti)

SCF(BP86) = -1192.44559865
H 0K = -1191.900055
H 298K = -1191.865950
G 298K = -1191.964443
Solvent Correction(CH₃Cl) = -0.04452049
BP86-D3 Correction = -0.11504354
Lowest frequencies = 11.5954 cm$^{-1}$, 23.7161 cm$^{-1}$
IntI₁⁺ (anti)

P  2.39266 -0.92570  0.32330
C  2.08797 -1.86546  2.00133
C  3.15321 -2.00362 -1.09698
Au -1.69112  0.23371 -1.56888
C  -1.84470  0.71236 -2.75111
S  -4.95869  1.81895 -0.28738
C  -2.36971 -1.02112 -2.13658
C   4.61298 -2.44150 -0.85604
C   3.10417 -2.78931  2.43981
C   0.79680 -2.70458  1.85820
C   1.8512 -0.76314  3.05990
C  -5.71109  0.60019  0.80212
O  -3.62684 -0.45777 -2.61062
C  -2.65172 -2.11859 -1.09917
C  -0.75489 -1.56735 -3.32842
H  -2.10369 -2.40604 -3.80445
H  -0.58329 -1.94952 -3.00215
H  -1.40168 -0.78224 -4.08545
H  -1.71723 -2.50532 -0.65708
H  -3.16868 -2.96170 -1.58759
H  -3.30656 -1.75116 -0.29315
H  -3.97017 -1.04095 -3.31474
H  -2.36520  0.13617  0.49636
H  -1.60715  1.75622 -0.03984
H  -1.35302  0.94256 -2.33769
C  -6.91097 -1.22643  2.58078
C  -6.61170 -1.61332  1.26473
C  -6.01675 -0.70760  0.37214
C  -6.00999  0.99243  2.12296
C  -6.60992  0.07917  3.00252
H  -7.38171 -1.93378  3.27002
H  -6.85181 -2.62507  0.92114
H  -5.79778 -1.00886 -0.65738
H  -5.77910  2.08054  2.46019
H  -6.84438  0.39437  4.02443
C  -3.59821  0.44971  0.68887
C  -5.49507  2.39406  1.51226
C  -5.80031  1.03128  1.62852
C  -4.85112  0.70825  1.22486
C  -3.29395  1.83661  0.55298
C  -4.25875  2.77994  0.98179
C   6.21589  3.15486  1.82693
C   6.76235  0.70576  2.03546
C  -5.10918 -0.97747  1.33805
C  -2.04228  2.43042 -0.02302
C  -4.02281  3.84329  0.87332
C  -0.12176  3.89248 -1.12702
C  -0.10225  3.90028  0.26089
C  -1.17909  3.18193  0.80727
C  -1.80233  2.42388 -1.41792
C  -0.73121  3.15219 -1.96418
C  -0.94224  4.47712 -1.55490
C  -0.54713  4.48722  0.91849
C   1.36991  3.21732  1.88507
C   2.49089  1.88944 -2.07985
C   0.58349  3.16500 -3.04923
C   1.04270 -0.07521  2.76542
C   2.76186 -0.16876  3.25248
C   1.55536 -1.24350  4.00839
C   4.18630 -2.24826  2.60750
C   3.42140 -3.61009  1.72679
C   2.96685 -3.25378  3.40373
C   0.57479 -3.17409  2.83340
C   0.49110 -3.51273  1.11656
C  -0.06903 -2.07886  1.58086
C   2.34787 -3.96486 -0.46821
C   2.57700 -3.76759 -2.21820
C   1.19392 -2.97711 -1.41590
C   2.07321 -0.80954 -2.61322
|   |   |   |   |
|---|---|---|---|
| H | 3.50769 | -1.68650 | -3.21569 |
| H | 3.72159 | -0.20732 | -2.24817 |
| H | 4.92663 | -3.07227 | -1.70734 |
| H | 4.73854 | -3.04370 | 0.05705 |
| H | 5.30194 | -1.58397 | -0.81603 |
| H | -4.70679 | 0.96387 | -1.32262 |

SCF(BP86) = -1434.91707953
H 0K = -1434.274253
H 298K = -1434.231582
G 298K = -1434.356058
Solvent Correction(CH3Cl) = -0.04458081
BP86-D3 Correction = -0.13456028
Lowest frequencies = 5.4610 cm⁻¹, 7.3449 cm⁻¹
TS(I-II)\_4\,, (anti)

P  -2.34849 -1.00042 -0.16416
C  -2.03983 -2.23570 -1.64069
C  -3.15880 -1.81709  1.39520
Au -0.23494 -0.12274  0.45739
C   1.71809  0.60055  1.05922
C   2.36095  0.59126 -0.25424
S   4.36219  1.49711 -0.16838
C   2.34876 -0.20621  2.20865
C  -2.25453 -2.98264  1.85191
C  -4.60406 -2.31874  1.19770
C  -3.16316 -0.71198  2.47696
C  -3.17266 -3.24685 -1.91307
C  -0.73913 -3.01827 -1.34052
C  -1.80987 -1.34913 -2.88613
C   5.47543  0.29821 -0.91600
O   3.62023  0.51791  2.52156
C   2.69343 -1.65912  1.84744
H  -0.06078 -3.36331 -0.54112
C  -1.36294  0.50820 -0.25424
C   1.71809  0.60055  1.05922
H   1.99603 -0.61994  4.32705
H   0.52594 -0.65782  3.31509
C   1.27287  0.91013  3.74415
C   1.77788 -2.21830  1.59485
C  -3.17232 -2.16764  2.70349
C   3.38205 -1.72080  0.98882
H   4.11189 -0.00298  3.18849
H   2.67547 -0.37002 -0.68012
C   0.93297  1.27272 -0.99798
C   1.48120  1.62474  1.39787
C   7.20937 -1.51602 -2.16063
C   6.92438 -1.64401 -0.79102
C   6.05495 -0.74137 -0.16109
C   5.76085  0.43769 -2.28884
C   6.62762 -0.47685 -2.90548
C   7.88997 -2.22206 -2.64551
C   7.38316 -2.44695 -0.20580
C   5.83764 -0.83606  0.90704
C   5.31917  1.25630 -2.86625
C   6.85394  0.36960 -3.97065
C  -3.56964  0.26841 -0.79169
C  -5.46999  2.04068 -1.93968
C  -5.75222  0.67004 -1.86412
C  -4.80845 -0.19696 -1.29945
C  -3.29080  1.66497 -0.85314
C  -4.25482  2.52096 -1.43799
C  -6.19188  2.73456 -2.83134
C  -6.69778  0.27180 -2.24465
C  -5.04609 -1.26173 -1.25894
C  -2.06120  2.35699 -0.33831
C  -4.03460  3.59244 -1.48116
C   0.06260  3.99886  0.56879
C  -0.06164  3.69448 -0.79790
C  -1.11913  2.88722 -1.24908
C  -1.92349  2.66689  1.03402
C  -0.87168  3.48246  1.48264
C   0.86635  4.65645  0.91569
C   0.64570  4.11532 -1.52073
C  -1.23570  2.68237 -2.31870
C  -2.66894  2.29849  1.74557
C  -0.79735  3.73353  2.54580
C  -1.01399 -0.60303 -2.71363
C  -2.72323 -0.81698 -3.19489
C   1.48974 -1.99190 -3.72601
C  -1.42562 -2.76640 -2.18197
C  -3.34351 -3.92706 -1.06318
C  -2.87914 -3.87438 -2.77445
C  -0.50249 -3.65558 -2.21207
C  -0.43212 -3.67786 -0.46364
C   0.13346 -2.33855 -1.66996
C  -2.30384 -3.84373  1.16549
H   2.59592 -3.33417  2.84239
H  -1.19971 -2.67106  1.94878
H  -2.14623 -0.33933  2.69008
H -3.57906 -1.12743  3.41279
H -3.79501  0.14321  2.18324
H -4.94258 -2.78124  2.14273
H -4.69161 -3.08459  0.41161
H -5.30003 -1.49625  0.97124
H  4.35021  1.00593  1.16525

SCF(BP86) = -1434.91043321
H 0K = -1434.266759
H 298K = -1434.226088
G 298K = -1434.344195
Solvent Correction(CH3Cl) = -0.04032521
BP86-D3 Correction = -0.13691659
Lowest frequencies = -96.1449 cm⁻¹, 5.2745 cm⁻¹
IntII$_4^-$ (anti)

P  -2.39319 -1.00273 -0.11540
C  -2.03855 -2.30064 -1.52319
C  -3.27937 -1.72106  1.45120
Au -0.29163 -0.14786  0.54575
C   1.77292  0.72170  0.79081
C   2.57080  0.52805 -0.47649
S   4.23757  1.40731 -0.27361
C   1.72332 -0.17543  1.87312
C  -2.43392 -2.89486  1.99075
C  -4.73078 -2.18281  1.20447
C  -3.29298 -0.57066  2.48384
C  -3.19357 -3.28317 -1.80798
C  -0.78127 -3.10952 -1.12533
C  -1.72079 -1.47068 -2.78797
C   5.37635  0.20319 -0.99956
O   4.70064  0.32726  2.85135
C   2.34740 -1.54863  1.84445
C   1.34836  0.32893  3.24729
H   2.30351  0.46111  3.79298
H   0.74074 -0.39954  3.80865
H   0.82724  1.29800  3.21513
C   1.76311 -2.26250  2.44772
C   3.34605 -1.44984  3.14210
C   2.47711 -1.95799  0.83196
C   5.51173  0.64502  3.28785
C   2.79534 -0.52559 -0.69356
C   2.06911  0.98155 -1.34418
C   1.50609  1.76753  1.00997
C   7.20030 -1.60628 -2.12410
C   6.93463 -1.64372 -0.74508
C   6.02361 -0.74041 -0.17528
C   5.64818  0.25108 -2.38189
C   6.55894 -0.65946 -2.94015
C   7.91416 -2.31072 -2.56249
C   7.44189 -2.37488 -0.10741
C   5.81340 -0.75306  0.90011
C   5.15646  1.00267 -3.00725
C   6.77338 -0.62238 -4.01293
C   3.52034  0.29020 -0.84475
C  -5.28259  2.08000 -2.16465
C  -5.62911  0.72774 -2.40004
C  -4.75215 -0.14990 -1.39094
C  -3.17582  1.66011 -0.95374
C  -4.07307  2.53384 -1.62589
C  -5.95121  2.78135 -2.67310
C  -6.57222  0.35182 -2.44795
C  -5.03430 -1.20149 -1.31453
C  -1.94555  2.34071 -0.40400
C  -3.80643  3.59243 -1.70648
C  0.13550  4.01307  0.54144
C  0.06871  3.66793 -0.81958
C  -0.96817  2.84492 -1.28978
C  -1.86283  2.68407  0.96655
C  -0.83090  3.51557  1.43312
H   0.92234  4.68429  0.90036
H  0.08820  4.06431 -1.52294
H  -1.04251  2.61332 -2.35769
H  -2.63868  2.33935  1.65708
H  -0.80124  3.79927  2.49031
H  -0.90832 -0.74441 -2.60768
H  -2.59982 -0.92286 -3.16188
H  -1.38251 -2.15671 -3.58505
H  -4.13556 -2.78151 -2.33890
H  -3.42531 -3.92323 -0.94168
H  -2.88331 -3.95298 -2.63030
H  -0.52799 -3.79384 -1.95511
H  -0.93480 -3.72383 -0.22473
H  0.08809 -2.45254 -0.94984
H  -2.48321 -3.78117  1.33764
H  -2.83048 -3.19430  2.97747
H  -1.37447 -2.61515  2.12515
H  -2.27494 -0.22298  2.73058
H  -3.76340 -0.93427  3.41513
H  -3.88346  0.29051  2.12847
H  -5.12654 -2.59303  2.15110
H  -4.80864 -2.97895  0.44809
H  -5.38680 -1.34820  0.91279
H   4.65720  0.83503  2.00643

SCF(BP86) = -1434.93757839
H  0K = -1434.292793
H 298K = -1434.249845
G 298K = -1434.373104
Solvent Correction(CH3Cl) = -0.04117649
BP86-D3 Correction = -0.13531985
Lowest frequencies = 7.1499 cm⁻¹, 12.6539 cm⁻¹
*IntII\(4\)· (anti)

75

P  2.31105 -0.52148  0.67634
C  1.89209 -0.98317  2.52130
C  3.60212 -1.68457 -0.18301
Au  0.27936 -0.65596 -0.51925
C  -1.82761 -0.56641 -1.32924
C  -2.79148 -1.79821 -1.84427
P  -0.52027 -1.13816 -0.07863
C  -0.50293 -1.58053  0.39434
C  -3.63384 -1.24833 -1.66569
C  -3.10935 -1.37792  3.38242
C  -0.88713 -2.15914  2.50644
C  -1.19715  0.26180  3.11858
C  -5.49493  0.13280  0.48179
C  -1.72561 -3.12906 -1.21124
C  -0.80678 -1.87395 -3.24026
H  -1.56902 -2.31298 -3.91231
H  -0.07171 -2.53934 -3.28333
H  -0.53253 -0.88371 -3.63418
H  -0.87242 -3.82485 -1.27267
H  -2.55479 -3.58885 -1.78144
H  -2.04645 -3.04783 -0.16314
H  -2.68216 -1.16010  0.60121
H  -2.68065  0.60352  0.27232
H  -1.74561  0.30418 -1.99812
C  -7.07458  1.09778  2.59435
C  -7.22947 -0.26305  2.54336
C  -5.94323 -0.75016  1.48567
C  -5.84683  1.49720  0.53105
C  -6.63590  1.97534  1.58895
C  -7.69363  1.47291  3.41524
C  -7.08113 -0.95006  3.31772
H  -5.68637 -1.81251  1.42649
H  -5.51170  2.17017 -0.26432
H  -6.91477  3.03341  1.62287
C  -0.30787  1.19430  0.70059
C  4.17115  3.77533  1.02471
C  4.75436  2.67393  1.66575
C  4.18653  1.40423  1.50439
C  2.45562  2.31060  0.03187
C  3.04028  3.58603  0.22199
H  4.59582  4.77695  1.14238
H  5.64234  2.79703  2.93001
H  4.64785  0.56179  2.02284
C  1.27586  2.29259 -0.89747
C  2.59218  4.40490 -0.29432
H  -0.61355  2.69277 -2.77221
C  -0.96702  3.11743 -1.44108
C  -0.07056  2.92630 -0.51362
C  -1.41255  1.85617 -2.23732
C  -0.37800  2.05912 -3.16622
H  -1.60819  2.87489 -3.50272
H  -1.88513  3.62599 -1.12995
H  -0.03589  3.29661  0.51158
H  2.35567  1.40621 -2.56228
H  0.53804  1.75045 -4.20751
H  0.33225  0.88054  2.51003
H  1.88363  1.11659  3.22132
H  0.81894  0.00612  4.12453
H  3.85256 -0.57115  3.47500
H  3.61148 -2.28588  3.01154
H  2.75317 -1.60060  4.40428
H  0.58852 -2.37763  3.54757
H  1.31354 -3.08187  2.08368
H  -0.02506 -1.90814  1.93789
H  3.15386 -3.53115  0.94915
H  3.72700 -3.78321  0.71270
H  2.05173 -2.39386 -0.43224
H  2.64433 -1.34025 -2.14604
H  4.33957 -1.89902 -2.21277
H  3.96551 -0.20907 -1.77908
H  5.67163 -2.29899 -0.14627
H  5.08325 -1.83782  1.46331
H  5.46440 -0.58023  0.24568

SCF(BP86) = -1358.50460683
H 0K = -1357.883625
H 298K = -1357.843728
G 298K = -1357.961072
Solvent Correction(CH3Cl) = -0.04237948
BP86-D3 Correction = -0.12740843
Lowest frequencies = 5.7573 cm⁻¹, 12.9741 cm⁻¹
|   | P   | C   | Au  | C   | S   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   | C   |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 3.29594 | 0.18656 | 0.27448 | 4.09250 | 1.51735 | -0.90564 | 3.88716 | 0.27596 | 2.12053 | 0.96160 | 0.58404 | 0.25125 | -1.26275 | 0.94461 | -0.02152 | -1.55792 | 1.11817 | -1.49085 | -3.40522 | 1.23829 | -1.79120 | -0.90609 | 1.96064 | 0.88376 | 3.63339 | 1.70603 | 2.64336 | 5.36570 | -0.10677 | 2.34139 | 2.99666 | -0.72613 | 2.89052 | 5.60917 | 1.72492 | -0.71547 | 3.36991 | 2.86493 | -0.67590 | 3.79672 | 1.02947 | -2.34230 | -3.76476 | 2.88303 | -1.13697 | -4.34347 | -0.97021 | 1.45446 | -0.62106 | 3.39105 | -0.04831 | -1.09295 | 1.73728 | 2.37158 | -1.98135 | 2.31082 | 2.69821 | 2.11889 | 2.95591 | 0.67874 | 2.62103 | 3.80539 | 1.07351 | -1.51392 | 4.00394 | 0.71025 | -0.39487 | 3.51256 | -0.58485 | -3.90672 | 0.51405 | 0.86532 | -1.07312 | 1.99485 | -1.94573 | -1.26771 | 0.21928 | -2.05794 | -1.68081 | 0.02513 | 0.41604 | -4.34475 | 5.44762 | -0.14432 | -3.74100 | 5.30238 | -1.40588 | -3.45824 | 4.02340 | -1.90862 | -4.38664 | 3.02644 | 0.12015 | -4.67550 | 3.31608 | 0.61202 | -4.57318 | 6.44637 | 0.24077 | -3.50462 | 6.18626 | -2.00692 | -3.01126 | 3.90236 | -2.90075 | -4.65866 | 2.13910 | -0.70220 | -5.16655 | 4.42052 | 1.58429 | 3.80296 | -1.47751 | -0.39571 | 4.79148 | -3.84643 | -1.60733 | 5.68925 | -2.90571 | -1.08481 | 5.13329 | -1.73726 | -0.49381 | 2.88731 | -2.44398 | -0.90790 | 3.41554 | -3.60995 | -1.51486 | 5.15758 | -4.76412 | -2.07775 | 6.76936 | -3.07178 | -1.13891 | 5.90988 | -1.01015 | -0.10866 | 1.39102 | -2.38341 | -0.85568 | 2.71052 | -4.35294 | -1.90078 | -1.42651 | -2.71664 | -0.82624 | -0.74296 | -2.57186 | -2.04623 | 0.65241 | -2.41143 | -2.06182 | 0.68933 | -2.51362 | 0.36825 | -0.70620 | -2.68377 | 0.37971 | -2.51022 | -2.87245 | -0.81078 | -1.29292 | -2.61340 | -2.99242 | 1.18477 | -2.33443 | -3.01595 | 1.24941 | -2.95174 | -1.30764 | -1.23201 | -2.81194 | 1.33107 | 2.71793 | 0.85410 | -2.50208 | 4.33947 | 0.10409 | -2.59030 | 4.13563 | 1.81235 | -3.05378 | 6.19587 | 0.81573 | -0.91539 | 5.86017 | 2.10021 | 0.28955 | 5.94802 | 2.48794 | -1.43943 | 3.75995 | 3.59990 | -1.40299 | 3.53911 | 3.27479 | 0.33180 | 2.28152 | 2.77537 | -0.83426 | 4.32339 | 2.44266 | 2.03939 | 3.79223 | 1.71866 | 3.73631 | 2.59584 | 2.03786 | 2.45259 | 1.92494 | -0.47445 | 2.80964 |
H   3.27193 -0.69820  3.96025  
H   3.14485 -1.76076  2.53777  
H   5.59480  0.01553  3.41544  
H   6.06658  0.53496  1.78538  
H   5.56425 -1.15873  2.08520  
C  -6.17869 -4.96892  0.05496  
C  -5.77896 -4.77874  1.38791  
C  -6.1564 -5.92148 -0.25901  
H  -6.61564 -5.58374  2.11943  
C  -4.91118 -3.41996  2.83933  
C  -5.36803 -1.88067 -1.19639  
H  -6.33764 -4.05672 -1.90915  
H  -4.26345 -0.34783  0.23703

SCF(BP86) = -1600.97726954
H 0K = -1600.258705
H 298K = -1600.210524
G 298K = -1600.350035
Solvent Correction(CH3Cl) = -0.04197091
BP86-D3 Correction = -0.15491520
Lowest frequencies = 3.4136 cm⁻¹, 9.8228 cm⁻¹
TS(III-IV)\_4: (anti)

\begin{align*}
P &\quad -2.99309 \quad 0.29247 \quad -0.79215 \\
C &\quad -3.24435 \quad 2.16600 \quad -1.27289 \\
C &\quad -3.51106 \quad 0.95811 \quad -2.18245 \\
Au &\quad -0.67647 \quad -0.01454 \quad -0.37423 \\
C &\quad 1.48329 \quad -0.29215 \quad -0.12871 \\
C &\quad 1.67657 \quad 0.86165 \quad 0.75310 \\
S &\quad 3.70044 \quad 1.03958 \quad 1.58274 \\
C &\quad 2.20432 \quad -0.38421 \quad -1.47179 \\
C &\quad -2.72923 \quad -0.9806 \quad 3.44670 \\
C &\quad -5.02061 \quad -1.02128 \quad -2.49451 \\
C &\quad -3.05627 \quad -2.34519 \quad -1.67078 \\
C &\quad -4.55690 \quad 2.48901 \quad -2.01567 \\
C &\quad -2.05134 \quad 2.59579 \quad -2.15882 \\
C &\quad -3.18181 \quad 2.94970 \quad 0.05830 \\
P &\quad 4.29607 \quad 2.62208 \quad 0.95693 \\
S &\quad 4.10837 \quad -0.79172 \quad -1.19263 \\
C &\quad 2.28011 \quad 0.94183 \quad -2.24667 \\
H &\quad 1.64966 \quad -1.51214 \quad -2.34398 \\
H &\quad 2.24832 \quad -1.63281 \quad -2.26753 \\
H &\quad 0.61253 \quad -1.26506 \quad -2.63903 \\
H &\quad 1.63069 \quad -2.47471 \quad -1.81275 \\
H &\quad 1.25337 \quad 1.98229 \quad -2.44320 \\
H &\quad 2.78911 \quad 0.80305 \quad -3.21418 \\
H &\quad 2.81420 \quad 1.73220 \quad -1.69260 \\
H &\quad 4.15617 \quad -2.48256 \quad -0.56613 \\
H &\quad 1.64855 \quad 1.86379 \quad 0.30688 \\
H &\quad 1.51750 \quad -1.25464 \quad 0.41063 \\
C &\quad 5.22675 \quad 1.15266 \quad 0.07693 \\
C &\quad 4.16488 \quad 5.04604 \quad 0.99358 \\
C &\quad 3.69525 \quad 3.80139 \quad 1.44070 \\
C &\quad 5.36702 \quad 2.68192 \quad 0.44211 \\
C &\quad 5.82552 \quad 3.93510 \quad -0.39347 \\
H &\quad 5.9256 \quad 0.88814 \quad -0.26463 \\
H &\quad 3.70225 \quad 5.96323 \quad 1.37100 \\
H &\quad 2.87698 \quad 3.74843 \quad 2.16630 \\
H &\quad 5.84604 \quad 1.76581 \quad -0.31577 \\
H &\quad 6.65956 \quad 3.98455 \quad -1.10036 \\
C &\quad -4.13395 \quad -0.01295 \quad 0.65958 \\
C &\quad -5.99715 \quad -0.19525 \quad 2.79902 \\
C &\quad -6.44175 \quad 0.14732 \quad 1.51514 \\
C &\quad -5.51572 \quad 0.23948 \quad 0.46860 \\
C &\quad -3.68847 \quad -0.38157 \quad 1.96243 \\
C &\quad -4.63801 \quad -0.45367 \quad 3.00821 \\
H &\quad -6.70256 \quad -0.26803 \quad 3.63253 \\
H &\quad -7.50029 \quad 0.34850 \quad 1.32419 \\
H &\quad -5.88159 \quad 0.52330 \quad -0.51913 \\
C &\quad -2.28371 \quad -0.72970 \quad 2.36406 \\
H &\quad -4.28732 \quad -0.74095 \quad 4.00465 \\
C &\quad 0.20805 \quad -1.53914 \quad 3.44440 \\
C &\quad -0.37354 \quad -0.32321 \quad 3.84357 \\
C &\quad -1.61209 \quad 0.07387 \quad 3.31323 \\
C &\quad -1.68285 \quad -1.94481 \quad 1.96225 \\
C &\quad -0.44969 \quad -2.34742 \quad 2.50191 \\
H &\quad 1.15483 \quad -1.86630 \quad 3.88633 \\
H &\quad 0.12355 \quad 0.30321 \quad 4.59339 \\
H &\quad -2.07898 \quad 3.00556 \quad 3.65012 \\
H &\quad -2.20946 \quad -2.99662 \quad 1.26132 \\
H &\quad -0.01604 \quad -3.30664 \quad 2.20081 \\
H &\quad -2.25881 \quad 2.72426 \quad 0.62139 \\
H &\quad -4.04535 \quad 2.73873 \quad 0.70837 \\
H &\quad -3.18122 \quad 4.03163 \quad -0.16633 \\
H &\quad -5.45452 \quad 2.26431 \quad -1.41990 \\
H &\quad -4.63148 \quad 1.96980 \quad -2.98475 \\
H &\quad -4.57943 \quad 3.57358 \quad -2.22802 \\
H &\quad -2.13104 \quad 3.68059 \quad -2.39518 \\
H &\quad -2.03740 \quad 2.08325 \quad -3.13324 \\
H &\quad -1.00819 \quad 2.40805 \quad -1.65736 \\
H &\quad -3.10098 \quad 0.32764 \quad -3.93365 \\
H &\quad -2.85575 \quad -1.41180 \quad -4.20151 \\
H &\quad -1.64850 \quad -0.48312 \quad -3.27127 \\
H &\quad -1.97030 \quad -2.37685 \quad -1.47485
\end{align*}
H  -3.28764 -3.10474 -2.43956  
H  -3.58893 -2.63421 -0.74873  
H  -5.17201 -1.73945 -3.32093  
H  -5.43517 -0.05601 -2.82465  
H  -5.60663 -1.38579 -1.63686  
C   4.35804 -5.13863  0.33456  
C   4.53286 -4.84392 -1.02752  
C   4.43543 -3.51965 -1.48127  
C   3.99119 -2.77696  0.80396  
C   4.09041 -4.10530  1.24739  
H   4.44145 -6.17145  0.68652  
H   4.75299 -5.64462 -1.74040  
H   4.58363 -3.28315 -2.53929  
H   3.80532 -1.97715  1.52652  
H   3.97105 -4.33012  2.31205  
H   4.10762  0.20817  0.41940  

SCF(BP86) = -1600.95663792  
H 0K = -1600.238612  
H 298K = -1600.192471  
G 298K = -1600.323635  
Solvent Correction(CH3Cl) = -0.03793615  
BP86-D3 Correction = -0.15806278  
Lowest frequencies = -143.7779 cm⁻¹, 6.9881 cm⁻¹
IntIV₄ (anti)

88

P  -2.75292 -0.67575  0.87894
C  -2.80292 -2.62254  0.84809
C  -2.93595  0.11621  2.63955
Au -0.65575 -0.06024 -0.02529
C   1.60231  0.94213 -0.20914
S   2.59231 -3.61964 -1.90711
C  -2.7754  0.79457  0.99258
C  -1.89528 -0.49831  3.5944
C  -4.30111 -0.05090  3.27928
C  -2.66791  1.54246  2.44311
C  -3.88685 -3.25460  1.74513
C  -1.42582 -3.14805  1.28677
C  -3.03997 -3.01118 -0.62936
C   4.20332 -3.69568 -1.08907
C   4.12880  1.46663  0.37646
C   3.89753  3.25223  0.47905
H   1.63483 -1.00432 -1.18854
H   0.86154  0.37957 -2.15185
H   1.33124  1.95928 -0.37191
C   6.64198 -3.71354  0.31480
C   6.48849 -2.90693 -0.82501
C   5.27016 -2.88315 -1.52238
C   4.35612 -4.51522  0.04648
C   5.57198 -4.51237  0.74835
H   7.59317 -3.72594  0.85529
H   7.31930 -2.28688 -1.17696
H   5.15486 -2.23943 -2.40606
H   3.53656 -5.16727  0.36565
H   5.68636 -5.15889  1.62663
C  -4.19903 -0.91090 -0.14648
C  -6.50669  0.51477 -1.68621
C  -6.63529 -0.21451 -0.49652
C  -5.49161 -0.51343  0.25420
C  -4.06987  0.66594 -1.34834
C  -5.29321  0.94309 -2.09699
H   7.38695  0.75432 -2.29056
H  -7.61613 -0.55677 -0.15300
H  -5.61247 -1.09628  1.16880
C  -2.80433  1.23213 -1.92207
H  -5.13527  1.52644 -3.01740
C  -0.64684  2.51590 -3.23750
C  -1.24668  1.37979 -3.87488
C  -2.32124  0.74843 -3.15958
H  -2.18644  2.37127 -1.35352
H  -1.1932  3.00927 -2.00877
H   0.16827  3.02715 -3.75957
H  -0.69556  0.39787 -4.71260
H  -2.80741 -0.11692 -3.62222
H  -2.57812  2.78587 -0.41946
H  -0.67721  3.91018 -1.57058
H  -2.28570 -2.56014 -1.29386
H  -4.04068 -2.71899 -0.98433
H  -2.95218 -4.10835 -0.72367
H  -4.90799 -2.96343  1.45585
H  -3.73753 -3.02571  2.81255
H  -3.82705 -4.35288  1.63888
H  -4.14323 -4.24908  1.93331
H  -1.17747 -2.90469  2.33368
H   0.60767 -2.75462  0.64624
H  -2.08301 -1.54456  3.82354
H   1.82610  0.07673  4.50225
H   0.85379 -0.45928  3.10578
H  -1.65049  1.80844  2.03144
H  -2.72350  2.13019  3.42327
H   3.40187  2.09367  1.77738
H  -4.30342  0.40787  4.28430
H  -4.62159 -1.10443  3.41172
H  -5.1433  0.46726  2.70634
C   3.70302  6.05729  0.58671
C   3.43149  5.38055 -0.61421
C   3.53003  3.98144  -0.67267
C   4.18711  3.93643  1.67958
C   4.08305  5.33521  1.73021
H   3.63223  7.14874  0.62764
H   3.15496  5.94364 -1.51148
H   3.34601  3.44902 -1.61109
H   4.50451  3.37094  2.56067
H   4.31168  5.86193  2.66213
H   3.04394 -3.39239 -3.15582
C   2.81367 -0.76702  1.26277
C   1.95899  1.41613  2.24549
H   2.68461  1.32322  3.06953
H   1.00978  0.94820  2.56526
H   1.77119  2.48680  2.06574
H   3.48546 -0.84836  2.13122
H   3.30496 -1.25648  0.40591
H   1.88553 -1.32287  1.48869

SCF(BP86) = -1600.97012527
H 0K = -1600.252288
H 298K = -1600.203850
G 298K = -1600.345853
Solvent Correction(CH3Cl) = -0.04138690
BP86-D3 Correction = -0.14828263
Lowest frequencies = 4.3131 cm⁻¹, 8.1708 cm⁻¹
\*IntIV\*₄· (anti)
H  3.24468 -3.32141 -1.84501
H  2.80930 -2.00977 -2.96905
H  1.57330 -2.68731 -1.86744

SCF(BP86) = -1358.49894062
H 0K = -1357.877748
H 298K = -1357.838321
G 298K = -1357.952691
Solvent Correction(CH3Cl) = -0.04115673
BP86-D3 Correction = -0.13085220
Lowest frequencies = 7.6803 cm⁻¹, 14.9137 cm⁻¹
| Element | Atomic Number | X Position | Y Position | Z Position |
|---------|---------------|------------|------------|------------|
| P       | 15            | -4.90510   | -0.11051   |            |
| C       | 6             | -2.17069   | 1.45771    |            |
| C       | 6             | -1.58902   | -1.054416  |            |
| Au      | 79            | -0.25777   | -0.60197   |            |
| C       | 6             | -2.86860   | -2.043037  |            |
| C       | 6             | -1.87788   | -1.405373  |            |
| C       | 6             | -0.91087   | -2.670533  |            |
| C       | 6             | -3.02576   | 1.704880   |            |
| C       | 6             | -3.10587   | 1.152978   |            |
| C       | 6             | -1.32786   | 2.710956   |            |
| C       | 6             | 0.30057    | -1.325826  |            |
| C       | 6             | 1.64269    | -1.050408  |            |
| C       | 6             | 0.54069    | 0.604745   |            |
| C       | 6             | 2.58179    | 1.730883   |            |
| C       | 6             | 1.26817    | 1.663144   |            |
| C       | 6             | 0.26601    | 1.109230   |            |
| C       | 6             | 1.88019    | 0.660409   |            |
| C       | 6             | 2.87340    | 1.234889   |            |
| C       | 6             | 3.73860    | 2.163604   |            |
| C       | 6             | 1.01813    | 2.041950   |            |
| C       | 6             | -0.75341   | 1.076421   |            |
| C       | 6             | 2.38306    | 0.152726   |            |
| C       | 6             | 3.90174    | 1.274405   |            |
| C       | 6             | 3.71356    | -0.746143  |            |
| C       | 6             | 3.46182    | 0.626295   |            |
| C       | 6             | 2.80938    | 1.071322   |            |
| C       | 6             | 2.65989    | -1.225533  |            |
| C       | 6             | 3.30271    | 1.669863   |            |
| C       | 6             | 4.27031    | -1.087497  |            |
| C       | 6             | 3.80373    | 1.353940   |            |
| C       | 6             | 2.64987    | 2.142512   |            |
| C       | 6             | 2.35749    | -1.944369  |            |
| C       | 6             | 3.52027    | 2.735758   |            |
| C       | 6             | -0.68973   | 2.553026   |            |
| C       | 6             | -0.68606   | 3.017369   |            |
| C       | 6             | -2.01327   | 3.546839   |            |
| C       | 6             | -2.42540   | 1.965031   |            |
| C       | 6             | -3.67103   | 0.846207   |            |
| C       | 6             | -3.69197   | 2.563825   |            |
| C       | 6             | -3.78079   | 2.015872   |            |
| C       | 6             | -3.73495   | 0.264809   |            |
| C       | 6             | -2.54034   | 1.004424   |            |
| C       | 6             | -3.71583   | 1.964930   |            |
| C       | 6             | -3.16809   | -3.035321  |            |
| C       | 6             | -2.70807   | -2.138238  |            |
| C       | 6             | -0.27425   | -2.880629  |            |
| C       | 6             | -0.84193   | -3.608642  |            |
| C       | 6             | 0.44643    | -2.380607  |            |
| C       | 6             | -2.28265   | -2.354977  |            |
| C       | 6             | -2.62729   | -0.624881  |            |
| C       | 6             | -0.96461   | -1.179381  |            |
| C       | 6             | -0.18737   | -0.012387  |            |
| C       | 6             | -0.99126   | 1.901852   |            |
| C       | 6             | -0.32553   | 2.300431   |            |
| C       | 6             | 0.07470    | 1.345511   |            |
| C       | 6             | -0.85006   | -0.427290  |            |
| C       | 6             | -1.25575   | 0.543645   |            |
| C       | 6             | -1.30562   | 2.635052   |            |
| C       | 6             | -0.12044   | 3.359795   |            |
| C       | 6             | 0.58211    | 1.647999   |            |
| C       | 6             | -1.04175   | -1.488907  |            |
| C       | 6             | -1.77243   | 0.230774   |            |

SCF(BP86) = -1163.17418434
H 0K = -1162.668675
H 298K = -1162.635907
G 298K = -1162.735298
Solvent Correction(CH3Cl) = -0.041320
BP86-D3 Correction = -0.10851633
Lowest frequencies = 12.9479 cm⁻¹, 15.1736 cm⁻¹
5. Reactions of 9, 10 and 11 with PhSH

\begin{align*}
\text{Bu}^+ & \quad + \quad \text{PhSH} & \quad \rightarrow & \quad \text{Bu}^+ & \quad \text{PhSH} & \quad + & \quad \text{H}_2\text{O} \\
\text{9} & \quad \text{2a} & \quad \text{(E)-30} & \quad \text{31} \\
\text{Ph}^+ & \quad + \quad \text{PhSH} & \quad \rightarrow & \quad \text{Ph}^+ & \quad \text{PhSH} & \quad + & \quad \text{H}_2\text{O} \\
\text{10} & \quad \text{2a} & \quad \text{(E)-32} & \quad \text{33} \\
\text{Cy}^+ & \quad + \quad \text{PhSH} & \quad \rightarrow & \quad \text{Cy}^+ & \quad \text{PhSH} & \quad + & \quad \text{H}_2\text{O} \\
\text{11} & \quad \text{2a} & \quad \text{(E)-34} & \quad \text{35}
\end{align*}

Figure S9. Reactions of 9, 10 and 11 to form formal SN2 and SN2' products.

Table S4. Computed relative energies (kcal/mol) for the reactions of 9, 10, and 11 with PhSH. Energies are reported as $\Delta E$ (gas-phase SCF energies), $\Delta H_{298}$ (zero-point energy corrected energies at 298.15 K), $\Delta G$ (free energies at 298.15 K and 1 atm), $\Delta G_{\text{disp}}$ (including a correction for dispersion effects using Grimme’s D3 parameter set) and $\Delta G_{\text{CHCl}_3+\text{disp}}$ including an additional correction for CHCl$_3$ solvent via the PCM approach.

|       | $\Delta E$ | $\Delta H_{298}$ | $\Delta G$ | $\Delta G_{\text{disp}}$ | $\Delta G_{\text{CHCl}_3+\text{disp}}$ |
|-------|------------|------------------|------------|--------------------------|----------------------------------|
| From 9 |            |                  |            |                          |                                   |
| (E)-30 | -4.8       | -3.4             | -3.9       | -3.0                     | -4.9                             |
| (Z)-30 | -0.7       | +0.7             | +1.0       | +0.9                     | -0.9                             |
| 31    | +2.8       | +3.8             | +5.0       | +0.3                     | -1.1                             |
| From 10 |            |                  |            |                          |                                   |
| (E)-32 | -7.6       | -6.3             | -6.0       | -8.7                     | -10.1                            |
| (Z)-32 | -7.4       | -6.1             | -5.9       | -7.0                     | -8.4                             |
| 33    | +0.9       | +1.8             | +3.1       | -1.6                     | -2.8                             |
| From 11 |            |                  |            |                          |                                   |
| (E)-34 | -5.1       | -3.6             | -4.6       | -3.8                     | -5.6                             |
| (Z)-34 | -4.7       | -3.2             | -4.1       | -3.8                     | -5.6                             |
| 35    | +1.3       | +2.3             | +3.7       | -1.0                     | -2.3                             |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| O       | -0.722183 | 0.615017  | -1.433114 |
| C       | -0.425258 | 0.488609  | -0.027184 |
| C       | -0.339115 | 1.307179  | 0.589808  |
| H       | -0.055632 | 1.885642  | 1.655331  |
| H       | 0.386931  | 2.527414  | 0.042429  |
| H       | -1.326980 | 2.398293  | 0.527290  |
| C       | 0.952084  | -0.296871 | 0.031077  |
| C       | -1.537862 | -0.266367 | 0.693180  |
| C       | 0.809558  | -1.634733 | -0.732592 |
| C       | 2.066318  | 0.539020  | -0.643483 |
| C       | 1.360388  | -0.599897 | 1.491001  |
| H       | 2.984492  | -0.067477 | -0.734299 |
| H       | 1.760621  | 0.856346  | -1.653086 |
| H       | 2.326082  | 1.437767  | -0.058276 |
| H       | 2.337659  | -1.113559 | 1.500875  |
| H       | 1.468101  | 0.316308  | 2.097195  |
| H       | 0.636132  | -1.263630 | 1.993103  |
| H       | 1.761304  | -2.193037 | -0.690491 |
| H       | 0.021773  | -2.267554 | -0.291547 |
| H       | 0.554542  | -1.460014 | -1.789089 |
| H       | -1.494974 | -0.243893 | 1.790571  |
| C       | -2.560085 | -0.889783 | 0.084468  |
| H       | -3.351442 | -1.386951 | 0.653875  |
| H       | -2.621083 | -0.932484 | -1.008185 |
| H       | -1.566229 | 1.103756  | -1.488432 |

SCF(BP86) = -389.680346065
H 0K = -389.461263
H 298K = -389.449626
G 298K = -389.496665
Solvent Correction(CH3Cl) = -0.00244022
BP86-D3 Correction = -0.02995967
Lowest frequencies = 57.7975 cm⁻¹, 108.0369 cm⁻¹
|   | S    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | C    | H    | H    | H    | H    | H    | H    | H    | H    | H    | H    | H    | H    | H    | H    | H    |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | -1.008660 | -0.792300 | -0.288734 | 1.383658 | 0.241239 | 0.666926 | 2.436602 | 0.381417 | -0.152898 | -2.714533 | -0.271562 | -0.082541 | -3.706447 | -1.260217 | -0.277532 | -5.063186 | -0.931540 | -0.164713 | -5.455829 | 0.379587 | 0.156569 | -4.472868 | 1.360180 | 0.355320 | -3.109248 | 1.045567 | 0.231579 | -3.408072 | -2.288533 | -0.509814 | -5.818329 | -1.709926 | -0.318649 | -6.516582 | 0.631896 | 0.251835 | -4.763184 | 2.386999 | 0.603363 | -2.362784 | 1.831849 | 0.374093 | -0.096459 | 1.488807 | -0.200703 | -0.504733 | 0.855555 | 1.424842 | 1.529685 | -0.466878 | 1.565174 | 3.852468 | -0.146134 | 0.162240 | 2.286193 | 1.197182 | -1.424738 | 4.242080 | -1.226980 | -0.884578 | 4.871267 | 1.023162 | 0.086794 | 3.956513 | -0.783935 | 1.564982 | 2.903996 | 0.789637 | -2.242433 | 1.247177 | 1.218689 | -1.786672 | 2.614149 | 2.242812 | -1.275365 | 5.887733 | 0.654999 | 0.311229 | 4.899927 | 1.484513 | -0.914246 | 4.626449 | 1.811550 | 0.819849 | 5.257643 | -1.607969 | -0.676234 | 3.541770 | -2.078729 | -0.849988 | 4.244024 | -0.831022 | -1.913974 | 4.955616 | -1.106809 | 1.749454 | 3.679288 | -0.069768 | 2.359371 | 3.313804 | -1.675724 | 1.661685 |

SCF(BP86) = -555.736680141
H 0K = -555.441540
H 298K = -555.424369
G 298K = -555.488472
Solvent Correction(CH3Cl) = -0.00379926
BP86-D3 Correction = -0.03732698
Lowest frequencies = 12.9665 cm⁻¹, 28.0636 cm⁻¹
\begin{center}
\begin{tabular}{ccc}
$\text{Z}$ & -30 \\
\hline
S & $-0.891602$ & $-0.997868$ & $0.457832$ \\
C & $0.210005$ & $-0.085038$ & $-0.745995$ \\
C & $1.469972$ & $-0.880339$ & $-0.934037$ \\
C & $2.738951$ & $-0.638870$ & $-0.510517$ \\
C & $-2.512594$ & $-0.288107$ & $0.153913$ \\
C & $-3.624785$ & $-1.020008$ & $0.629369$ \\
C & $-4.922460$ & $-0.518893$ & $0.464888$ \\
C & $-5.136452$ & $0.707578$ & $-0.107851$ \\
C & $-4.034265$ & $1.432157$ & $-0.066230$ \\
C & $-2.727209$ & $0.947631$ & $-0.491470$ \\
H & $-3.467179$ & $-1.987095$ & $1.119441$ \\
H & $-5.773047$ & $-1.098938$ & $0.838775$ \\
H & $-6.152108$ & $1.092364$ & $-0.323193$ \\
H & $-4.385403$ & $2.391449$ & $-1.172307$ \\
H & $-1.883151$ & $1.540980$ & $-0.852756$ \\
H & $-0.350129$ & $-0.082456$ & $-0.569641$ \\
H & $0.380662$ & $0.364324$ & $-0.573599$ \\
H & $1.309984$ & $-1.804784$ & $-1.505892$ \\
C & $3.193107$ & $0.596521$ & $0.314489$ \\
C & $3.801122$ & $-1.643718$ & $-0.917936$ \\
C & $4.685308$ & $0.503913$ & $0.728830$ \\
C & $3.041345$ & $1.823638$ & $-0.547385$ \\
C & $2.375954$ & $0.717720$ & $1.628889$ \\
H & $4.310208$ & $-2.085580$ & $-0.042603$ \\
H & $3.364045$ & $-2.467136$ & $-1.504649$ \\
H & $4.592309$ & $-1.176696$ & $-1.533250$ \\
H & $3.396670$ & $2.763182$ & $0.021284$ \\
H & $3.639802$ & $1.810246$ & $-1.468526$ \\
H & $1.997072$ & $2.071500$ & $-0.839412$ \\
H & $4.956119$ & $1.402365$ & $1.309947$ \\
H & $4.885011$ & $-0.372745$ & $1.367969$ \\
H & $5.362930$ & $0.458036$ & $-0.140006$ \\
H & $2.717234$ & $1.596799$ & $2.204882$ \\
H & $1.293272$ & $0.823181$ & $1.463919$ \\
H & $2.522454$ & $-0.176224$ & $2.259131$ \\
\hline
SCF (BP86) = $-555.73003848$
H 0K = $-555.434828$
H 298K = $-555.417817$
G 298K = $-555.480716$
Solvent Correction (CH3Cl) = $-0.00372069$
BP86-D3 Correction = $-0.03889275$
Lowest frequencies = 18.1250 cm$^{-1}$, 29.7730 cm$^{-1}$
\end{tabular}
\end{center}
| Atom | X       | Y       | Z      |
|------|---------|---------|--------|
| S    | -0.032168 | -0.821173 | -0.976984 |
| C    | -1.133996  | 0.203532  | 0.245051   |
| C    | -0.936197  | 1.646460  | -0.155858   |
| C    | 1.642399   | -0.439104  | -0.435708   |
| C    | 2.337144   | -1.347346  | 0.392368    |
| C    | 3.670389   | -1.096682  | 0.753203    |
| C    | 4.318590   | 0.062559   | 0.295977    |
| C    | 3.631946   | 0.969060   | -0.528453   |
| C    | 2.300823   | 0.720429   | -0.898600   |
| H    | 1.824764   | -2.248722  | 0.742466    |
| H    | 4.203052   | -1.809541  | 1.391706    |
| H    | 5.359375   | 0.255874   | 0.576432    |
| H    | 4.136210   | 1.870429   | -0.893057   |
| H    | 1.764225   | 1.415193   | -1.549783   |
| C    | -2.633423  | -0.271966  | -0.018847   |
| C    | -0.667226  | -0.085214  | 1.678323    |
| H    | -1.273943  | 1.895430   | -1.169569   |
| C    | -0.370321  | 2.619454   | 0.583914    |
| H    | -0.260523  | 3.633016   | 0.185285    |
| H    | 0.001648   | 2.452983   | 1.599208    |
| H    | -1.279835  | 0.470530   | 2.409385    |
| H    | -0.732753  | -1.157806  | 1.910997    |
| H    | 0.380959   | 0.221365   | 1.817197    |
| C    | -3.592106  | 0.653096   | 0.774565    |
| C    | -3.020244  | -0.185532  | -1.517784   |
| C    | -2.858606  | -1.730562  | 0.448723    |
| H    | -4.636028  | 0.338745   | 0.599885    |
| H    | -3.410800  | 0.603946   | 1.861327    |
| H    | -3.494745  | 1.705784   | 0.461461    |
| H    | -3.873100  | -2.056597  | 0.160420    |
| H    | -2.134709  | -2.422662  | -0.013067   |
| H    | -2.782836  | -1.831519  | 1.543902    |
| H    | -4.078915  | -0.475549  | -1.635697   |
| H    | -2.914384  | 0.833581   | -1.924365   |
| H    | -2.418019  | -0.864815  | -2.143758   |

SCF(BP86) = -555.724456545
H 0K = -555.429971
H 298K = -555.412956
G 298K = -555.474283
Solvent Correction(CH3Cl) = -0.00303443
BP86-D3 Correction = -0.04622588
Lowest frequencies = 22.3311 cm⁻¹, 49.5870 cm⁻¹
|  |  |  |  |
|---|---|---|---|
| C | -1.931813 | -0.874825 | -0.529896 |
| C | -3.035342 | -0.615444 | 1.249192 |
| O | -1.649392 | 1.487788 | -0.09011 |
| H | -1.543472 | 1.585664 | -0.976913 |
| H | -3.482085 | 0.384210 | -1.261625 |
| H | -3.534130 | -1.396398 | -1.830918 |
| H | -1.518127 | -1.890912 | -0.518604 |
| C | 0.339437 | 0.042086 | 0.089112 |
| C | -1.517541 | -0.024240 | 1.804808 |
| H | -2.602030 | 0.091868 | 1.959898 |
| H | -0.981055 | 0.732467 | 2.400034 |
| H | -1.211096 | -1.024075 | 2.150803 |
| C | 3.144063 | -0.144513 | -0.271723 |
| C | 2.495433 | 1.093969 | -0.387013 |
| C | 1.105841 | 1.185649 | -0.204850 |
| C | 1.003596 | -1.196627 | 0.214827 |
| C | 2.391775 | -1.290126 | 0.035895 |
| H | 4.227271 | -0.217768 | -0.414328 |
| H | 3.071942 | 1.996970 | -0.615769 |
| H | 0.601154 | 2.154002 | -0.270282 |
| H | 0.438804 | -2.102161 | 0.463966 |
| H | 2.886863 | -2.261988 | 0.137022 |

SCF(BP86) = -463.476951711
H 0K = -463.288465
H 298K = -463.277754
G 298K = -463.324429
Solvent Correction(CH3Cl) = -0.00382334
BP86-D3 Correction = -0.02252316
Lowest frequencies = 48.9435 cm⁻¹, 82.5660 cm⁻¹
### Geometry (E) -32

| Atom | Coordinates | Cartesian Coordinates |
|------|-------------|-----------------------|
| C    | 0.351457    | -1.691910 0.216827   |
| C    | -0.953826   | -2.322545 0.566810   |
| C    | 0.947106    | -0.626582 0.823849   |
| H    | -0.887436   | -3.424672 0.533990   |
| H    | -1.343055   | -2.032123 1.553463   |
| H    | 0.842096    | -2.123694 -0.664491  |
| C    | 2.270897    | -0.138034 0.340957   |
| C    | 0.521421    | 0.130942 1.977424    |
| H    | 1.054368    | 0.299809 2.785331    |
| H    | -0.546432   | -0.393312 2.402689   |
| H    | -0.037849   | 1.123220 1.648532    |
| C    | 4.785735    | 0.811231 -0.593743   |
| C    | 3.874653    | 1.692030 0.009203    |
| C    | 2.638122    | 1.222744 0.476053    |
| C    | 3.212822    | -1.014537 -0.252213  |
| C    | 4.448049    | -0.547000 -0.718153  |
| H    | 5.753986    | 1.175750 -0.952172   |
| H    | 4.126023    | 2.752618 0.118077    |
| H    | 1.940263    | 1.928968 0.936154    |
| H    | 2.982405    | -2.082783 -0.318187  |
| H    | 5.158246    | -1.250507 -1.165908  |
| S    | -2.309681   | -1.982259 -0.706663  |
| C    | -2.548489   | -0.208576 -0.479154  |
| C    | -2.963851   | 2.556705 -0.147315   |
| C    | -3.792639   | 1.063985 0.516708    |
| C    | -3.585763   | 0.257904 0.355098    |
| C    | -1.725716   | 0.716651 -1.154675   |
| C    | -1.932080   | 2.095143 -0.981824   |
| H    | -3.126605   | 3.632213 -0.020386   |
| H    | -4.602437   | 1.992838 1.162567    |
| H    | -4.224478   | -0.466691 0.870063   |
| H    | -0.931602   | 0.348369 -1.809770   |
| H    | -1.289991   | 2.809231 -1.508453   |

SCF(BP86) = -629.537694444
H 0K = -629.273281
H 298K = -629.257084
G 298K = -629.319655
Solvent Correction(CH3Cl) = -0.00448839
BP86-D3 Correction = -0.03546523
Lowest frequencies = 17.7798 cm⁻¹, 25.7603 cm⁻¹
### (Z) -32

| Atom | x  | y  | z  |
|------|----|----|----|
| C    | 1.015877 | 1.849819 | 0.488038 |
| C    | -0.124956 | 0.901686 | 0.704260 |
| C    | 2.310286 | 1.527886 | 0.223459 |
| H    | 0.223246 | -0.132475 | 0.851000 |
| H    | -0.734293 | 1.215686 | 1.569339 |
| H    | 0.762135 | 2.914169 | 0.578679 |
| C    | 2.791441 | 0.128134 | 0.026235 |
| C    | 3.353974 | 2.622915 | 0.122961 |
| H    | 4.138590 | 2.510438 | 0.893396 |
| H    | 2.902784 | 3.620198 | 0.248000 |
| H    | 3.868826 | 2.589396 | -0.853998 |
| C    | 3.740170 | -2.517809 | -0.370320 |
| C    | 2.585018 | -2.073416 | -1.032821 |
| C    | 2.116529 | -0.764984 | -0.840018 |
| C    | 3.962377 | -0.331268 | 0.674744 |
| C    | 4.426805 | -1.640329 | 0.484926 |
| H    | 4.106933 | -3.538126 | -0.523587 |
| H    | 2.048025 | -2.743968 | -1.712194 |
| H    | 1.227578 | -0.419980 | -1.380003 |
| H    | 4.504906 | 0.337388 | 1.351433 |
| H    | 5.329254 | -1.976123 | 1.006979 |
| S    | -1.250888 | 0.969723 | -0.785938 |
| C    | -2.757288 | 0.185910 | -0.201750 |
| C    | -5.203666 | -1.015888 | 0.543660 |
| C    | -4.043161 | -1.240463 | 1.299221 |
| C    | -2.821764 | -0.653028 | 0.930104 |
| C    | -3.928420 | 0.417170 | -0.958668 |
| C    | -5.137154 | -0.187494 | -0.589979 |
| H    | -6.151430 | -1.479465 | 0.834855 |
| H    | -4.079225 | -1.886595 | 2.183089 |
| H    | -1.925353 | -0.860021 | 1.521211 |
| H    | -3.888332 | 1.079184 | -1.830648 |
| H    | -6.035851 | 0.001691 | -1.186865 |

SCF(BP86) = -629.537381861
H 0K = -629.273004
H 298K = -629.256796
G 298K = -629.319517
Solvent Correction(CH3Cl) = -0.00442160
BP86-D3 Correction = -0.03293397
Lowest frequencies = 15.2644 cm⁻¹, 26.3728 cm⁻¹
|  | 0.342074 | -0.794976 | -0.881663 |
|---|---|---|---|
| C | -0.616451 | 0.367411 | 0.336215 |
| C | -0.263367 | 1.769168 | -0.093529 |
| C | 2.066802 | -0.508201 | -0.445737 |
| C | 2.720325 | -1.378935 | 0.453366 |
| C | 4.082408 | -1.202170 | 0.743366 |
| C | 4.801619 | -0.157242 | 0.140408 |
| C | 4.157054 | 0.709980 | -0.757114 |
| C | 2.795654 | 0.537288 | -1.052204 |
| H | 2.154326 | -2.195544 | 0.912040 |
| H | 4.582544 | -1.884681 | 1.438987 |
| H | 5.865059 | -0.022894 | 0.364367 |
| H | 4.716888 | 1.521492 | -1.234612 |
| H | 2.289144 | 1.202364 | -1.756772 |
| C | -2.097713 | 0.040308 | 0.089454 |
| C | -0.229183 | 0.038253 | 1.786866 |
| H | -0.584334 | 2.022446 | -1.112638 |
| C | 0.420667 | 2.678682 | 0.624944 |
| H | 0.653934 | 3.663045 | 0.207457 |
| H | 0.773358 | 2.483102 | 1.642038 |
| C | -3.047151 | 1.072942 | -0.057021 |
| C | -4.410762 | 0.780244 | -0.219961 |
| C | -4.851045 | -0.551422 | -0.240159 |
| C | -3.916708 | -1.588710 | -0.086793 |
| C | -2.555551 | -1.296078 | 0.080112 |
| H | -2.716773 | 2.116050 | -0.026750 |
| H | -5.129454 | 1.599358 | -0.330422 |
| H | -5.913815 | -0.780292 | -0.371487 |
| H | -4.247464 | -2.632760 | -0.097536 |
| H | -1.834684 | -2.112453 | 0.195151 |
| H | -0.768282 | 0.711266 | 2.476920 |
| H | -0.506925 | -0.998023 | 2.032787 |
| H | 0.853909 | 0.158020 | 1.951761 |

SCF(BP86) = -629.524159434
H 0K = -629.260450
G 298K = -629.305107
Solvent Correction(CH3Cl) = -0.00416506
BP86-D3 Correction = -0.03879392
Lowest frequencies = 24.4972 cm⁻¹, 37.0578 cm⁻¹
From 11
11

SCF(BP86) = -467.106351444
H 0K = -466.850026
H 298K = -466.837967
G 298K = -466.887013
Solvent Correction(CH3Cl) = -0.00259353
BP86-D3 Correction = -0.03423157
Lowest frequencies = 59.6954 cm⁻¹, 96.4352 cm⁻¹
S  -1.811013  0.807775  0.177585
C  -0.874902  -0.739545  -0.295435
C   0.546955  -0.361311  -0.591298
C   1.624757  -0.528913  0.215067
H  -0.959777  -1.474976  0.519289
H  -1.368294  -1.146314  -1.194429
C  -3.531406   0.321046   0.012739
C  -3.974098  -1.017375  -0.034606
C  -5.345337  -1.300816  -0.145377
H  -6.289861  -0.264742  -0.194335
C  -5.850010   1.069245  -0.137312
C  -4.484045   1.364301  -0.042602
C  -3.258825  -1.842645   0.022201
C  -5.673222  -2.345417  -0.185275
H  -7.357227  -0.492309  -0.277608
H  -6.574502   1.889701  -0.179496
H  -4.147368   2.406626  -0.005200
C   0.702072   0.122334  -1.565229
C   2.997705  -0.078892  -0.274027
C   1.550523  -1.153415   1.591641
H   2.060157  -0.521296   2.340236
C   0.516697  -1.300656   1.938090
H   2.058404  -2.135339   1.614300
C   4.042569  -1.225781  -0.288742
H   2.873780   0.261997  -1.322599
C   5.396179  -0.751357  -0.852908
H   4.194398  -1.597817   0.743725
C   3.654432  -2.076716  -0.878547
C   5.938533   0.461328  -0.072730
H   6.126318  -1.581178  -0.833196
H   5.268366  -0.472237  -1.917930
C   4.907806   1.605620  -0.033946
H   6.174771   0.149544   0.964506
H   6.887372   0.812612  -0.517823
C   3.552966   1.130276   0.527297
H   5.290742   2.449991   0.568036
H   4.758233   1.996026  -1.060436
C   3.684549   0.841680   1.588860
H   2.816330   1.953976   0.511734

SCF(BP86) = -633.163016803
H 0K = -632.830815
H 298K = -632.813080
G 298K = -632.879911
Solvent Correction(CH3Cl) = -0.00384975
BP86-D3 Correction = -0.04178062
Lowest frequencies = 12.1429 cm^{-1}, 20.8390 cm^{-1}
(Z) -34

|   | 1.530377 | 0.915083 | 0.703003 |
|---|----------|----------|----------|
| C | 0.504141 | 0.821947 | -0.856480 |
| C | -0.630931 | 1.796798 | -0.732210 |
| C | -1.917651 | 1.525275 | -0.396663 |
| H | 1.168617 | 1.098977 | -1.692197 |
| H | 0.164611 | -0.215193 | -1.001125 |
| C | 3.063550 | 0.100872 | 0.244519 |
| C | 4.174576 | 0.315151 | 1.092288 |
| C | 5.398466 | -0.311273 | 0.824743 |
| C | 5.542464 | -1.147074 | -0.296382 |
| C | 4.428686 | -1.355709 | -1.141967 |
| C | 3.206196 | -0.745042 | -0.875182 |
| H | 4.075881 | 0.981905 | 1.956010 |
| H | 6.249066 | -0.134074 | 1.491750 |
| H | 6.502424 | -1.628359 | -0.508044 |
| H | 4.538862 | -2.006779 | -2.017786 |
| H | 2.358258 | -0.938736 | -1.538048 |
| H | -0.356411 | 2.844644 | -0.914075 |
| C | -2.427998 | 0.121983 | -0.093959 |
| C | -2.920227 | 2.659087 | -0.328953 |
| H | -3.802011 | 2.464470 | -0.966570 |
| H | -3.302766 | 2.799663 | 0.698564 |
| H | -2.471006 | 3.611323 | -0.653396 |
| C | -3.346424 | -0.425874 | -1.221821 |
| H | -1.557110 | -0.559080 | -0.030552 |
| C | -3.809470 | -1.866016 | -0.925386 |
| H | -4.235427 | 0.227651 | -1.321803 |
| H | -2.813576 | -0.382084 | -2.189327 |
| C | -4.506884 | -1.967468 | 0.444478 |
| H | -4.481777 | -2.219590 | -1.728608 |
| H | -2.929002 | -2.539339 | -0.935543 |
| C | -3.609745 | -1.416713 | 1.569277 |
| H | -5.450675 | -1.381665 | 0.415593 |
| H | -4.790128 | -3.014951 | 0.654943 |
| C | -3.156255 | 0.026002 | 1.273188 |
| H | -4.139804 | -1.45197 | 2.538564 |
| H | -2.716908 | -2.064565 | 1.675875 |
| H | -4.045316 | 0.686640 | 1.265145 |
| H | -2.491882 | 0.395337 | 2.075687 |

SCF(BP86) = -633.162463067
H 0K = -632.830091
H 298K = -632.812488
G 298K = -632.879104
Solvent Correction(CH3Cl) = -0.00383330
BP86-D3 Correction = -0.04255061
Lowest frequencies = 10.8615 cm⁻¹, 18.5658 cm⁻¹
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| S       | 0.577784 | -0.882930 | -0.881576 |
| C       | -0.443375 | 0.365481 | 0.184458 |
| C       | -0.042449 | 1.732992 | -0.309911 |
| C       | 2.279184 | -0.544453 | -0.398326 |
| C       | 2.892656 | -1.321404 | 0.608360 |
| C       | 4.239151 | -1.107740 | 0.943586 |
| C       | 4.983455 | -0.120511 | 0.277020 |
| C       | 4.379111 | 0.652401 | -0.728071 |
| C       | 3.032954 | 0.443822 | -1.066928 |
| H       | 2.307882 | -2.095419 | 1.114795 |
| H       | 4.707841 | -1.717519 | 1.723371 |
| H       | 6.05043 | 0.041820 | 0.556043 |
| H       | 4.958111 | 1.418742 | -1.254491 |
| H       | 2.557778 | 1.036504 | -1.853115 |
| C       | -1.930012 | 0.080342 | -0.223370 |
| C       | -0.154563 | 0.130663 | 1.670443 |
| H       | -0.340238 | 1.938297 | -1.348340 |
| C       | 0.637841 | 2.673900 | 0.371302 |
| C       | 0.890571 | 3.631966 | -0.093512 |
| H       | 0.967821 | 2.530291 | 1.404643 |
| H       | -0.714457 | 0.851480 | 2.292413 |
| H       | -0.441557 | -0.888153 | 1.972080 |
| C       | 0.917680 | 0.256863 | 1.889772 |
| C       | 2.899742 | 1.125379 | 0.385607 |
| H       | -1.969973 | 0.205643 | -1.327332 |
| C       | -4.337542 | 0.929198 | -0.133308 |
| H       | -2.896335 | 1.023598 | 1.488994 |
| H       | -2.546379 | 2.148238 | 0.164788 |
| C       | 4.848768 | -0.498404 | 0.133227 |
| H       | -5.010229 | 1.674601 | 0.327359 |
| H       | -4.356997 | 1.124578 | -1.226194 |
| C       | -3.877642 | -1.550287 | -0.434387 |
| H       | -4.947482 | -0.648876 | 1.226628 |
| H       | -5.859239 | -0.633710 | -0.294257 |
| C       | 2.443267 | -1.344004 | 0.094099 |
| C       | -4.225581 | -2.569892 | -0.187205 |
| H       | -3.869967 | -1.482255 | -1.540650 |
| H       | -2.441535 | -1.498993 | 1.190942 |
| H       | -1.766961 | -2.105177 | -0.332721 |

**SCF (BP86)** = -633.152937312
H OK = -632.821165
H 298K = -632.803730
G 298K = -632.866767
Solvent Correction(CH3Cl) = -0.00306479
BP86-D3 Correction = -0.05047592
Lowest frequencies = 23.0520 cm⁻¹, 47.2347 cm⁻¹
5. Reactions of Substrate 17

**Figure S10.** First $S_N2'$ step via *anti* attack of PhSH to give $E$-36. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl₃) in red. All energies are in kcal/mol and are quoted relative to 5' and the separated reactants set to zero.

**Figure S10.** Second $S_N2'$ step via *anti* attack of PhSH to give 37. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl₃) in red. All energies are in kcal/mol and are quoted relative to 5' and the separated reactants set to zero.
Figure S11. Alternative routes to the formation of 37 via either C–O bond cleavage and formation of an allylic cation or direct SN2 attack at a O-bound form of 17. Gas phase SCF energies (BP86) are shown in black with free energies at the BP86-D3(CHCl3) in red. All energies are in kcal/mol and are quoted relative to 5' and the separated reactants set to zero.
Table S5. Computed relative energies (kcal/mol) for the reactions 17 with PhSH. Energies are reported as $\Delta E$ (gas-phase SCF energies), $\Delta H_{298}$ (zero-point energy corrected energies at 298.15 K), $\Delta G$ (free energies at 298.15 K and 1 atm), $\Delta G_{\text{disp}}$ (including a correction for dispersion effects using Grimme’s D3 parameter set) and $\Delta G_{\text{CHCl3+disp}}$ including an additional correction for CHCl3 solvent via the PCM approach.

|                  | $\Delta E$ | $\Delta H_{298}$ | $\Delta G$ | $\Delta G_{\text{disp}}$ | $\Delta G_{\text{CHCl3+disp}}$ |
|------------------|------------|------------------|------------|--------------------------|-------------------------------|
| 5'               | 0.0        | 0.0              | 0.0        | 0.0                      | 0.0                           |
| *IntI$_{17}$ (anti, pro-$E$) | +4.3       | +4.3             | +5.4       | -1.6                     | -2.4                          |
| *IntI$_{17}$ (anti, pro-$Z$) | +5.8       | +5.7             | +6.7       | +1.4                     | +0.1                          |
| IntI$_{17}$ (anti, pro-$E$) | -0.2       | +1.7             | +11.6      | -2.1                     | -0.7                          |
| IntI$_{17}$ (anti, pro-$Z$) | +1.2       | +3.2             | +14.1      | +0.4                     | +2.4                          |
| IntV$_{17}$ (pro-$E$) | +4.0       | +4.1             | +4.6       | +1.3                     | +2.0                          |
| #IntVII$_{17}$ (pro-$E$) | +20.9      | +19.9            | +18.5      | +18.3                    | +21.8                         |
| IntVII$_{17}$ (pro-$E$) | +45.1      | +42.3            | +31.9      | +35.3                    | +23.9                         |
| IntVI$_{17}$ (pro-$E$) | -0.7       | +0.8             | +0.2       | -1.6                     | -8.6                          |
| TS(I-II)$_{17}$ (anti, pro-$E$) | +0.8       | +2.2             | +14.6      | +2.6                     | +7.7                          |
| TS(I-II)$_{17}$ (anti, pro-$Z$) | +1.9       | +3.4             | +17.2      | +3.0                     | +7.8                          |
| Int(I-II)$_{17}$ (anti, pro-$E$) | -0.5       | +0.9             | +14.2      | +2.3                     | +8.0                          |
| TS(I-II)$_{17}$ (anti, pro-$E$) | -0.5       | +0.0             | +14.6      | +2.8                     | +8.5                          |
| IntII$_{17}$ (anti, pro-$E$) | -16.4      | -13.0            | -2.2       | -12.1                    | -8.4                          |
| IntII$_{17}$ (anti, pro-$Z$) | -11.9      | -8.5             | +0.8       | -10.4                    | -6.9                          |
| *IntII$_{17}$ (anti, pro-$E$) | -6.6       | -5.5             | -4.1       | -10.2                    | -10.2                         |
| *IntII$_{17}$ (anti, pro-$Z$) | -3.6       | -2.4             | -1.2       | -8.2                     | -7.9                          |
| IntIII$_{17}$ (anti, pro-$S$) | -11.2      | -8.2             | +0.6       | -13.8                    | -10.9                         |
| TS(III-IV)$_{17}$ (anti, pro-$S$) | +0.3       | +2.2             | +15.7      | -2.2                     | +3.1                          |
| IntIV$_{17}$ (anti, pro-$S$) | -6.2       | -3.5             | +6.2       | -11.6                    | -9.0                          |
| *IntIV$_{17}$ (anti, pro-$S$) | -2.4       | -1.6             | +0.4       | -8.4                     | -8.0                          |

*Complex computed in the absence of PhSH nucleophile
#Computed as an ion pair
| Element | X     | Y     | Z     |
|---------|-------|-------|-------|
| C       | 2.155265 | -0.341177 | 0.626776 |
| C       | 3.103817  | -1.258699  | 0.372373  |
| C       | 1.134803  | 0.350882   | -0.442226  |
| O       | 1.586302  | 1.766145   | -0.419523  |
| H       | 2.556493  | 1.866001   | -0.399103  |
| H       | 3.327303  | -1.579550  | -0.652502  |
| H       | 3.685290  | -1.728255  | 1.172164   |
| H       | 1.936926  | -0.027614  | 1.656630   |
| C       | -0.158987 | 0.125043   | -0.227481  |
| H       | 1.615676  | -0.079134  | -1.430525  |
| C       | -2.908577 | -0.350321  | 0.192935   |
| C       | -2.369707 | 0.926825   | 0.411625   |
| C       | -1.000759 | 1.165444   | 0.204539   |
| C       | -0.704423 | -1.155785  | -0.445407  |
| C       | -2.070197 | -1.393284  | -0.237227  |
| H       | -3.976212 | -0.533713  | 0.353981   |
| H       | -3.017514 | 1.745416   | 0.743876   |
| H       | -0.573685 | 2.158755   | 0.364089   |
| H       | -0.050335 | -1.971521  | -0.775495  |
| H       | -2.481772 | -2.393108  | -0.412384  |

SCF(BP86) = -424.161108345
H 0K = -423.999863
H 298K = -423.990369
G 298K = -424.034907
Solvent Correction(CH3Cl) = -0.00398490
BP86-D3 Correction = -0.01648625
Lowest frequencies = 20.1171 cm⁻¹, 82.9163 cm⁻¹
(E) -36

30

C  0.309555  -1.812563  0.277514
C  -1.018706  -2.268910  0.778544
C  1.004854  -0.786196  0.826487
H  -1.067731  -3.367089  0.886627
H  -1.284300  -1.809283  1.743940
H  0.695573  -2.342016  -0.603114
C  2.307845  -0.255009  0.399898
H  -0.282016  1.698675
C  4.819759  0.850481  -0.332255
C  5.116555  1.364845  0.768256
C  2.877261  0.817792  1.127657
C  3.052387  -0.761139  -0.708142
C  4.269510  -0.215215  -1.067591
H  5.788354  1.274309  -0.616759
H  4.533660  2.194496  1.348910
H  2.331270  1.223480  1.987482
H  2.622546  -1.590577  -1.293795
H  4.810905  -0.623036  -1.927983
S  -2.423764  -1.925496  -0.435380
C  -2.553648  -0.130526  -0.302332
C  -2.823817  2.666472  -0.126978
C  -3.645136  1.831226  0.648577
C  -3.511087  0.436442  0.564705
C  -1.734562  0.710119  -1.038347
C  -1.869584  2.104762  -0.990735
H  -2.930541  3.754363  -0.061136
H  -4.393715  2.265323  1.319947
H  -4.146972  -0.222863  1.163975
H  -1.00177  0.264733  -1.760390
H  -1.229385  2.752562  -1.598843

SCF(BP86) = -590.225603601
H 0K = -589.988650
H 298K = -589.973872
G 298K = -590.034045
Solvent Correction(CH3Cl) = -0.00471764
BP86-D3 Correction = -0.02828956
Lowest frequencies = 17.9078 cm^-1, 19.5598 cm^-1
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| S    | -1.095522 | 0.967493 | -0.802086 |
| C    | -0.061284  | 1.104330  | 0.748228  |
| C    | 1.042468   | 2.092421   | 0.513630   |
| C    | -2.590095  | 0.154421   | -0.226204  |
| C    | -3.724760  | 0.248121   | -1.063651  |
| C    | -4.919611  | -0.389486  | -0.705228  |
| C    | -5.009068  | -1.113709  | 0.496091   |
| C    | -3.885075  | -1.201190  | 1.330964   |
| C    | -2.676648  | -0.580075  | 0.974444   |
| H    | -3.668225  | 0.829258   | -1.990605  |
| H    | -5.790234  | -0.307645  | -1.364729  |
| H    | -5.946657  | -1.602829  | 0.779191   |
| H    | -3.939254  | -1.765014  | 2.268559   |
| H    | -1.807251  | -0.680029  | 1.630219   |
| H    | -0.735495  | 1.459460   | 1.545696   |
| C    | 0.332660   | 0.109917   | 1.012459   |
| H    | 0.756577   | 3.147203   | 0.606336   |
| C    | 2.341813   | 1.815101   | 0.235322   |
| C    | 2.995212   | 0.507354   | 0.040536   |
| C    | 4.352422   | 0.365777   | 0.421570   |
| C    | 5.022970   | -0.854879  | 0.273329   |
| C    | 4.356320   | -1.961578  | -0.278944  |
| C    | 3.019737   | -1.830339  | -0.690534  |
| C    | 2.344576   | -0.610785  | -0.538423  |
| H    | 4.876804   | 1.227152   | 0.851488   |
| H    | 6.069605   | -0.941964  | 0.583825   |
| H    | 4.880275   | -2.915039  | -0.402859  |
| C    | 2.501061   | -2.676687  | -1.147854  |
| H    | 1.320693   | -0.509108  | -0.914568  |
| H    | 3.023931   | 2.675550   | 0.190443   |

SCF(BP86) = -590.221484159
H 0K = -589.983933
H 298K = -589.969433
G 298K = -590.028306
Solvent Correction(CH3Cl) = -0.004457122
BP86-D3 Correction = -0.02859682
Lowest frequencies = 16.7045 cm⁻¹, 27.1694 cm⁻¹
S    -0.288165   -1.718587   -0.944034
C    1.080509   -1.219495   0.284008
C    2.251612   -2.119787   -0.020522
C    -1.647957   -0.654722   -0.413370
C    -1.815879   0.629796   -0.970299
C    -2.902215   1.427768   -0.577630
C    -3.825944   0.950095   0.366346
C    -3.663110   -0.330463   0.920614
C    -2.578112   -1.132515   0.533520
H    -1.091476   0.994712   -1.703670
H    -3.027442   2.424770   -1.013212
H    -4.674545   1.573551   0.667109
H    -4.384178   -0.708653   1.653177
H    -2.446024   -2.134589   0.953910
C    1.430184   0.255695   0.203841
H    0.684641   -1.454315   1.286146
H    2.787136   -1.914111   -0.956700
C    2.660040   -3.120675   0.777764
H    3.522032   -3.743037   0.518816
H    2.148441   -3.350024   1.719623
C    1.288785   1.069253   1.344903
C    1.639993   2.428676   1.307331
C    2.139689   2.993414   0.124509
C    2.280324   2.191601   -1.022073
C    1.924909   0.836468   -0.984081
H    0.901759   0.631124   2.272154
H    1.520415   3.045444   2.204383
H    2.414792   4.052820   0.092396
H    2.665203   2.625870   -1.951051
H    2.012905   0.223177   -1.887710

SCF(BP86) = -590.212291942
H 0K = -589.976037
H 298K = -589.961059
G 298K = -590.021123
Solvent Correction(CH3Cl) = -0.004775303
BP86-D3 Correction = -0.03207694
Lowest frequencies = 15.1620 cm⁻¹, 29.8354 cm⁻¹
*IntI\\(_{17}\) (anti, pro-E)*

| Atomic Number | X     | Y     | Z     |
|---------------|-------|-------|-------|
| P             | 2.339069 | 0.732656 | -0.054819 |
| C             | 1.931289 | 2.214435 | -1.084726 |
| C             | 2.766705 | 1.380427 | 1.624687 |
| Au            | 0.584370 | -0.815855 | 0.025877 |
| C             | -1.492816 | -1.854335 | -0.340688 |
| C             | -0.597362 | -2.745427 | 0.228440 |
| C             | -2.566277 | -1.082749 | 0.420009 |
| O             | -3.777382 | -1.582069 | -0.143459 |
| H             | -4.513310 | -1.035495 | 0.200434 |
| H             | -0.016744 | -3.433190 | -0.397407 |
| H             | -0.618421 | -2.953737 | 1.305189 |
| H             | -1.598987 | -1.813584 | -1.434360 |
| C             | 3.909903 | 0.041170 | -0.746382 |
| C             | -2.396566 | 0.427146 | -0.240806 |
| C             | -2.480635 | -1.326943 | 1.501941 |
| C             | -2.106034 | 3.212608 | -0.089728 |
| C             | -2.612098 | 2.426295 | -1.140790 |
| C             | -2.753614 | 1.040590 | -0.977486 |
| C             | -1.893599 | 1.220654 | 1.293549 |
| C             | -1.750167 | 2.609144 | 1.128985 |
| H             | -2.015444 | 4.296690 | -0.211684 |
| H             | -2.909996 | 2.897231 | -2.082922 |
| H             | -3.188505 | 0.430263 | -1.779477 |
| H             | -1.650308 | 0.754577 | 2.256243 |
| H             | -1.393165 | 3.222956 | 1.962479 |
| H             | 1.004405 | 2.673526 | -0.707577 |
| H             | 4.691752 | 0.818053 | -0.747862 |
| H             | 3.883115 | 1.869357 | 2.061647 |
| H             | 3.509760 | 2.108130 | 1.546193 |
| H             | 3.735370 | -0.307523 | -1.775560 |
| H             | 1.775340 | 1.900806 | -2.128112 |
| H             | 2.757705 | 2.942200 | -1.037644 |
| H             | 4.238712 | -0.810354 | -0.131426 |
| H             | 3.073744 | 0.546551 | 2.274071 |

SCF(BP86) = -686.219883815
H 0K = -685.945093
H 298K = -685.925361
G 298K = -685.996881
Solvent Correction(CH3Cl) = -0.05196535
BP86-D3 Correction = -0.04247116
Lowest frequencies = 12.0370 cm⁻¹, 21.6263 cm⁻¹
**IntI**$_{17}$ (anti, pro-Z)

34

|   | C          | Au       | C          | C          | Au       | C          | C          | H          | H          | C          | C          | H          | H          | C          | C          | H          | P          | H          | H          | H          | H          | H          | H          | H          | H          |
|---|------------|----------|------------|------------|----------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
|   | 2.801723   | 0.765232 | -1.128573  | -0.960013  | -2.110902 | -3.661323  | -1.5313346 | -0.439558  | -0.711880  | 4.254653   | -2.720397  | -1.546720  | -3.813215  | -4.344339  | -3.802631  | -2.203906  | -2.744897  | -4.243246  | -5.188555  | -4.227201  | -1.394213  | -2.349827  | 2.736441   | 3.745470   | 1.949973   | 4.208377   | 2.128507   | 2.740336   | 5.151238   | 2.999919   |
|   | 2.286949   | -0.513606| -1.866959  | -1.527318  | -1.207621 | -2.252731  | -1.969513  | -2.207176  | -2.814848  | -0.250967  | 0.095643   | -0.998438  | 2.510984   | 1.280245   | 0.076222   | 1.332838   | 2.537090   | 3.448148   | 1.258218   | -0.886212  | 1.352559   | 3.494351   | 0.683201   | 2.809285   | 2.916864   | -0.483350  | 1.736140   | 1.666889   | 2.091872   | 0.355667   |
|   | -0.744798  | -0.239356 | 0.014548   | -1.317836  | 0.987706  | 1.191012   | 1.912297   | -2.002684  | 0.383680   | -0.319601  | 0.490679   | 1.926266   | -0.466721  | -0.889439  | -0.412809  | 0.924547   | 0.444999   | -0.833360  | -1.585337  | -0.716739  | 1.665539   | 0.799991   | 0.176296   | -0.518282  | -0.446834  | -1.394417  | 2.303627   | 2.090088   | -1.826262  | -0.112450  |
|   |            |          |            |            |          |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |            |
| SCF(BP86) = | -686.217594299 |
| H 0K = | -685.942761 |
| H 298K = | -685.923099 |
| G 298K = | -685.994804 |
| Solvent Correction(CH3Cl) = | -0.05285743 |
| BP86-D3 Correction = | -0.03978676 |
| Lowest frequencies = 11.2424 cm$^{-1}$, 14.1264 cm$^{-1}$ |
IntI1\(_7\) (anti, pro-\(E\))

P  3.066819   -1.567464   0.366417
C  4.391552   -0.276043   0.462206
C  2.860653   -2.212691   2.088933
Au  1.083675   -0.724548   -0.552846
C  -0.547057   0.654095   -1.430575
C  -1.013582   -0.651659   -1.485191
S  -4.358424   -0.086529   -1.792239
C  -0.978628   1.658901   -0.366069
C  1.316389   -0.458672   -0.053469
O  -1.935911   2.483644   -1.060969
H  -2.013378   3.321908   -0.562950
H  -0.882087   -1.258323   -2.398446
H  -1.692683   -1.040523   -0.716796
H  -0.048680   1.090542   -2.307829
C  -4.304881   -1.268453   2.650338
C  -4.148244   0.087089   2.316144
C  -4.159817   0.497331   0.973267
C  -4.470623   -1.821135   0.280558
C  -4.471317   -2.216811   1.627577
H  -4.311237   -1.580834   3.698888
H  -4.037841   0.838319   3.105485
H  -4.067303   1.558337   0.719631
H  -4.600098   -2.567211   -0.910815
H  -4.605523   -3.274805   1.875281
C  3.789132   -2.963449   -0.610900
H  -3.728366   1.196190   -1.643441
C  0.202626   2.454876   0.172573
H  -1.470216   1.112047   0.464162
C  2.393540   3.919903   1.175844
C  1.926073   4.155770   -0.129360
C  0.835965   3.428546   -0.629968
C  0.670900   2.228419   1.483827
C  1.763566   2.957911   1.983444
C  3.234762   4.499492   1.568773
H  2.405009   4.916356   -0.753914
H  0.456646   3.630044   -1.637121
H  0.157632   1.500059   2.123231
H  2.103137   2.795924   3.011349
H  4.019433   0.580461   1.046275
H  4.725089   -3.305525   -0.140000
H  2.498341   -1.404336   2.741802
H  3.825677   -2.587618   2.470704
H  3.995855   -2.623806   -1.637159
H  4.636469   0.067333   -0.553865
H  5.289942   -0.695031   0.939409
H  3.070388   -3.796138   -0.648328
H  2.123331   -3.029834   2.089062

SCF(BP86) = -928.693686455
H 0K = -928.321215
H 298K = -928.293090
G 298K = -928.388035
Solvent Correction(CH3Cl) = -0.05184365
BP86-D3 Correction = -0.06194841
Lowest frequencies = 8.9278 cm\(^{-1}\), 10.1876 cm\(^{-1}\)
### IntI\(_{17}\) (anti, pro-Z)

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 4.340368 | -1.137542 | -1.262051 |
| C    | 3.935877 | -2.118460 | 1.491639  |
| Au   | 1.086430 | -0.717202 | -0.010531 |
| C    | -0.820960 | 0.381084  | 0.576107  |
| C    | -0.868881 | 0.268028  | -0.810946 |
| S    | -3.738166 | 1.310318  | -1.382761 |
| C    | -0.527381 | 1.696020  | 1.310613  |
| C    | -4.372775 | -0.099963 | -0.463565 |
| H    | -1.827702 | 2.318907  | 1.380983  |
| C    | -1.743344 | 3.114354  | 1.946845  |
| H    | -0.510539 | 1.072450  | -1.462848 |
| H    | -1.364055 | -0.584348 | -1.285672 |
| C    | -1.375295 | -0.395979 | 1.169804  |
| C    | -5.386617 | -2.361889 | 0.870187  |
| C    | -5.442291 | -2.283068 | -0.531848 |
| C    | -4.932070 | -1.159675 | -1.202959 |
| C    | -4.316342 | -0.170575 | 0.944336  |
| C    | -4.824880 | -1.303478 | 1.601442  |
| H    | -5.788878 | -3.237350 | 1.389540  |
| C    | -5.887338 | -3.098442 | -1.110002 |
| H    | -4.992886 | -1.102223 | -2.295338 |
| H    | -3.891397 | 0.658596  | 1.519084  |
| C    | -4.791473 | -1.347852 | 2.695173  |
| C    | 2.855607  | -3.649699 | -0.787527 |
| C    | 0.521722  | 2.583352  | 0.652572  |
| H    | -0.176381 | 1.434325  | 2.330851  |
| C    | 2.501048  | 4.179411  | -0.572620 |
| C    | 1.166148  | 4.255873  | -1.003572 |
| C    | 0.179580  | 3.465212  | -0.392078 |
| C    | 1.860493  | 2.526834  | 1.093928  |
| C    | 2.846479  | 3.318087  | 0.482481  |
| H    | 3.265512  | 4.806326  | -1.041923 |
| H    | 0.888929  | 4.942355  | -1.807636 |
| H    | -0.866240 | 3.548850  | -0.704896 |
| H    | 2.123884  | 1.883561  | 1.943154  |
| H    | 3.877892  | 3.284618  | 0.848120  |
| H    | -3.258063 | 1.989469  | -0.299661 |
| P    | 3.090931  | -1.924445 | 0.143151  |
| H    | 5.263331  | -1.739724 | -1.278526 |
| H    | 4.565585  | -0.123006 | -0.900232 |
| H    | 2.170007  | -4.192938 | -0.123417 |
| H    | 2.416896  | -3.602691 | -1.798041 |
| H    | 4.177411  | -1.126016 | 1.901251  |
| H    | 4.863712  | -2.700067 | 1.366602  |
| H    | 3.927965  | -1.068112 | -2.280146 |
| H    | 3.825312  | -4.167188 | -0.829272 |
| H    | 3.266296  | -2.641491 | 2.191249  |

SCF(BP86) = -928.691354497
H 0K = -928.318529
H 298K = -928.290667
g 298K = -928.384166
Solvent Correction(CH3Cl) = -0.05087661
BP86-D3 Correction = -0.06179849
Lowest frequencies = 6.4290 cm\(^{-1}\), 12.2773 cm\(^{-1}\)
IntV17 (pro-E)

P  3.32077 -0.08337  0.03621
C  3.96889  0.61386  1.62237
C  4.16039 -1.71573 -0.18501
C  3.96920  1.01106 -1.30589
Au  1.05044 -0.25645  0.00348
C  -1.66301  1.79600 -0.61201
C  -1.18782  2.96794 -0.15208
C  -2.03040  0.65638  0.9215
O  -1.09300 -0.48334 -0.07949
H  -1.45001 -1.30811  0.31424
H  -1.02620  3.14371  0.91795
H  -1.85023  1.64868 -1.68286
C  -3.44292  0.14012  0.15160
H  -1.81961  0.91996  1.34333
H  3.54773  1.61928  1.77892
H  5.06671  0.67480  1.58176
H  3.66413 -0.03482  2.45818
H  3.54936  2.02170 -1.19009
H  3.66755  0.60828 -2.28459
H  5.06893  1.05891 -1.24873
H  3.86119 -2.15390 -1.14915
H  3.85998 -2.39605  0.62612
H  5.25374 -1.57733 -0.16526
C  -6.08429 -0.80698 -0.07253
C  -5.24516 -0.79160 -1.20070
C  -3.93135 -0.31703 -1.09375
C  -4.28744  0.11256  1.28085
C  -5.60541 -0.35402  1.16722
H  -7.11181 -1.17286 -0.16124
H  -5.61819 -1.14593 -2.16646
H  -3.28245 -0.30824 -1.97606
H  -3.91413  0.46743  2.24851
H  -6.25629 -0.36604  2.04662
H  -0.97462  3.80217 -0.82670

SCF(BP86) = -686.220467543
H 0K = -685.945490
H 298K = -685.925679
G 298K = -685.998241
Solvent Correction(CH3Cl) = -0.04966730
BP86-D3 Correction = -0.03644421
Lowest frequencies = 10.4876 cm⁻¹, 17.6315 cm⁻¹
IntVII_{17} (pro-E)

\begin{tabular}{llll}
  P & 1.503762 & -0.000059 & -0.000004 \\
  C & 2.302146 & -0.838285 & -1.456703 \\
  C & 2.269239 & 1.694473 & -0.003590 \\
  C & 2.302214 & -0.832063 & 1.460237 \\
  Au & -0.765870 & -0.002114 & 0.000005 \\
  O & -2.764466 & -0.108781 & 0.000081 \\
  H & -3.097163 & 0.810697 & -0.000439 \\
  H & 1.977590 & -1.889847 & 1.486148 \\
  H & 3.401788 & -0.791769 & -1.388900 \\
  H & 1.965590 & -0.345199 & -2.381494 \\
  H & 1.977845 & -1.883549 & 1.494086 \\
  H & 1.965531 & -0.335153 & 2.382933 \\
  H & 3.401848 & -0.785616 & 1.392275 \\
  H & 1.929337 & 2.242775 & 0.888335 \\
  H & 1.929046 & 2.239099 & -0.897654 \\
  H & 3.369991 & 1.631970 & 0.003649 \\
\end{tabular}

\texttt{SCF(BP86) = -338.074767856}
\texttt{H 0K = -337.950612}
\texttt{H 298K = -337.939568}
\texttt{G 298K = -337.988751}
\texttt{Solvent Correction(CH3Cl) = -0.01252181}
\texttt{BP86-D3 Correction = -0.01355728}
\texttt{Lowest frequencies = 42.5807 cm^{-1}, 91.7053 cm^{-1}}
Organic cation fragment for IntVII\textsubscript{17} (pro-E)

C  2.49797  0.41886  0.00004
C  3.78763 -0.04226  0.00000
C  1.40966 -0.50074 -0.00003
H  4.01156 -1.11524 -0.00006
H  2.31116  1.49741  0.00012
C  0.02620 -0.20749 -0.00005
H  1.68125 -1.56629 -0.00010
C  -2.74955  0.24487  0.00007
C  -1.86266  1.34868  0.00000
C  -0.49080  1.13446 -0.00006
C  -0.89634 -1.31113 -0.00003
C  -2.26755 -1.08279  0.00004
H  -3.82952  0.42522  0.00013
H  -2.26129  2.36679  0.00000
H   0.19181  1.98832 -0.00013
H  -0.50356 -2.33335 -0.00005
H  -2.96914 -1.92123  0.00008
H   4.64027  0.64365  0.00005

SCF(BP86) = -348.080138071
H 0K = -347.933245
H 298K = -347.925183
G 298K = -347.965992
Solvent Correction(CH3Cl) = -0.05637435
BP86-D3 Correction = -0.01218360
Lowest frequencies = 83.9377 cm\textsuperscript{-1}, 140.5147 cm\textsuperscript{-1}
**IntVII**

34

P  -3.418014  -0.252883  0.468360
C  -3.721168  -1.880252  1.305563
C  -3.916135  1.016169  1.726734
Au -1.306931  0.002338  -0.348860
C  3.528543  2.623868  0.316143
C  2.609023  3.621237  0.141032
O  3.164367  1.281311  -0.004053
H  0.605240  0.243068  -2.023868
C  3.164367  2.623868  0.316143
C  4.526994  2.866316  0.697216
C  -4.727993  -0.149989  -0.839817
C  3.978626  0.126624  0.106692
H  2.131611  1.100343  -0.388514
C  5.443512  -2.263527  0.256132
C  6.055199  -1.045088  0.640969
C  5.337474  0.141732  0.570005
C  3.375539  -1.120739  -0.279053
C  4.110706  -2.301775  -0.201499
H  7.091011  -1.044003  0.991733
H  5.809903  1.082750  0.865946
H  2.331160  -1.091113  -0.626706
H  3.659506  -3.254393  -0.493130
H  -3.846999  2.018558  1.277477
H  -3.230431  0.965457  2.586279
H  -4.948385  0.835377  2.068285
H  -4.593059  -0.934988  -1.591205
H  -4.670471  0.831124  -1.355262
H  -5.727617  -0.281258  -0.394591
H  -3.526381  -2.695843  0.592633
H  -4.762081  -1.942329  1.662680
H  -3.032566  -1.984748  2.157900
H  6.020623  -3.192329  0.316598

SCF(BP86) = -686.193546456
H 0K = -685.921244
H 298K = -685.900422
G 298K = -685.976058
Solvent Correction(CH3Cl) = -0.04522441
BP86-D3 Correction = -0.03145088
Lowest frequencies = 12.4695 cm⁻¹, 12.9890 cm⁻¹
TS(I-II\textsuperscript{a})\textsubscript{17} (anti, pro-E)

P    3.177007   -1.890514   0.348117
C    4.723270   -0.902911   0.087376
C    3.209452   -2.375501   2.137177
Au   1.245020   -0.729861   -0.292091
C    -0.437215   0.505347   -0.955106
C    -1.320251   -0.614040   -0.929661
S    -3.583290   0.087350   -1.707998
C    -0.669497   1.666861   0.011875
C    -4.642576   -0.289541   -0.304929
O    -1.769364   2.429947   -0.568679
H    -1.823565   3.285246   -0.097557
H    -1.255162   -1.377882   -1.710196
H    -1.774543   -0.932541   0.015432
H    -0.103874   0.837018   -1.952032
C    -6.312478   -0.965423   1.841850
C    -5.473504   0.158063   1.930270
C    -4.631293   0.500750   0.862336
C    -5.482560   -1.416670   -0.403527
C    -6.314002   -1.749156   0.676197
H    -6.969096   -1.225314   2.677382
H    -5.476016   0.776700   2.833243
H    -3.980794   1.379082   0.924386
H    -5.496261   -2.019420   -1.317456
H    -6.971608   -2.620428   0.599624
C    3.449351   -3.469458   -0.584488
H    -3.131321   1.311138   -1.263456
C    0.557641   2.543160   0.209576
H    -0.982975   1.256170   0.995066
C    2.840942   4.157478   0.577479
C    2.162161   4.166017   -0.653792
C    1.025090   3.365549   -0.837759
C    1.235075   2.550065   1.445801
C    2.374466   3.350925   1.628418
H    3.722214   4.790415   0.721333
H    2.514832   4.805038   -1.469524
H    0.484061   3.390273   -1.789913
H    0.858256   1.935953   2.272871
H    2.884914   3.360336   2.596895
H    4.659795   0.032018   0.664511
H    4.380230   -3.954252   -0.247898
H    3.128394   -1.472626   2.761339
H    4.819744   -0.652821   -0.980221
H    3.917405   -1.250064   -1.660924
H    4.148874   -2.902022   2.371824
H    5.604232   -1.480249   0.411714
H    2.598833   -4.146725   0.413141
H    2.354836   -3.034686   2.352992

SCF(BP86) = -928.692034331
H 0K = -928.319017
H 298K = -928.293207
G 298K = -928.383250
Solvent Correction(CH3Cl) = -0.04609117
BP86-D3 Correction = -0.05916102
Lowest frequencies = -81.8427 cm\textsuperscript{-1}, 3.9282 cm\textsuperscript{-1}
Int(I-II)$_{17}$ (anti, pro-$E$)

\begin{align*}
\text{SCF(BP86)} &= -928.694185176 \\
H \text{OK} &= -928.321164 \\
H \text{298K} &= -928.294456 \\
G \text{298K} &= -928.384022 \\
\text{Solvent Correction(CH3Cl)} &= -0.04501049 \\
\text{BP86-D3 Correction} &= -0.0588583 \\
\text{Lowest frequencies} &= 12.4946 \text{ cm}^{-1}, 17.1369 \text{ cm}^{-1}
\end{align*}
TS(I-II)$_{17}$ (anti, pro-E)

P  3.220561  -1.903055  0.323128
C  4.745926  -0.848352  0.401526
C  3.162056  -2.753092  1.972835
Au 1.272911  -0.715842  -0.236938
C  -0.471949  0.373266  -0.816477
C  -1.620588  -0.603848  -0.787327
S  -3.300715  0.195315  -1.470258
C  -4.563221  -0.283697  -0.274128
O  -1.810328  2.393698  -0.495845
H  -2.040517  3.124187  0.116618
H  -1.474311  -1.474116  -1.441184
H  -1.908766  -0.932336  0.223523
H  -0.247175  0.699535  -1.849652
C  -0.647625  1.590850  0.082262
C  -4.563221  -0.283697  -0.274128
O  -1.810328  2.393698  -0.495845
H  -2.040517  3.124187  0.116618
H  -1.474311  -1.474116  -1.441184
H  -1.908766  -0.932336  0.223523
H  -0.247175  0.699535  -1.849652
C  -6.555653  -1.083655  1.516264
C  -5.636553  -0.883511  1.890472
C  -6.472498  -1.278177  -0.60152
C  -5.481948  -1.753666  0.245166
C  -7.337263  -1.393921  2.216060
C  -5.702548  0.378868  2.877772
C  -3.923094  1.099039  1.283719
C  -5.423448  -1.729389  -1.65533
C  -7.197336  -2.447578  -0.04896
C  -3.654131  -3.253052  -0.87506
C  -2.793102  1.493907  -0.890711
C  0.536432  2.525972  0.187265
C  -0.961469  1.269338  -1.094008
C  2.728730  4.284833  0.411134
C  2.153323  4.031235  -0.846783
C  2.13276  3.158670  -0.960074
C  1.108272  2.797313  1.446533
C  2.204531  3.668073  1.558285
C  3.577182  4.970945  0.496635
C  2.552101  4.521206  -1.740612
C  0.606938  2.978900  -1.939585
C  0.695661  2.320566  2.343781
C  2.639610  3.873356  2.541478
C  4.602782  -0.058317  0.114389
C  4.579515  -3.764417  -0.536768
C  2.994822  2.004352  2.762183
C  4.903202  -0.373792  -0.578187
C  3.793600  -2.818393  -3.176749
C  4.106813  -3.286524  2.166894
C  5.625073  -1.457605  0.667246
C  2.828981  -3.980374  -0.918511
C  2.326773  -3.469993  1.983476

SCF(BP86) = -928.694165327
H 0K = -928.321714
H 298K = -928.295734
G 298K = -928.383248
Solvent Correction(CH3Cl) = -0.04512896
BP86-D3 Correction = -0.0580550
Lowest frequencies = -77.1164 cm$^{-1}$, 10.4952 cm$^{-1}$
### TS(I-II)$_{17}$ (anti, pro-Z)

| Atom | SCF(BP86) | OK | 298K | H 298K | G 298K | Solvent Corr(CH3Cl) | BP86-D3 Corr | Lowest Frequencies |
|------|-----------|----|------|--------|-------|----------------------|---------------|------------------|
|      |           |    |      |        |       |                      |               |                  |
| C    | 4.383862  | -1.021164 | -1.349764 |        |       |                      |               |                  |
| C    | 4.157417  | -2.036669 | 1.400409  |        |       |                      |               |                  |
| Au   | 1.172019  | -0.729626 | 0.081646  |        |       |                      |               |                  |
| C    | -0.746416 | 0.254742  | 0.505778  |        |       |                      |               |                  |
| C    | -1.027779 | 0.243732  | -0.887282 |        |       |                      |               |                  |
| S    | -3.376558 | 1.127484  | -1.248820 |        |       |                      |               |                  |
| C    | -0.558804 | 1.577664  | 1.266371  |        |       |                      |               |                  |
| C    | -4.309234 | -0.189051 | -0.455492 |        |       |                      |               |                  |
| O    | -1.906487 | 2.056169  | 1.433242  |        |       |                      |               |                  |
| H    | -1.833746 | 2.966173  | 1.891586  |        |       |                      |               |                  |
| H    | -0.629256 | 1.028002  | -1.540022 |        |       |                      |               |                  |
| H    | -1.334885 | -0.686496 | 1.372943  |        |       |                      |               |                  |
| C    | -1.281992 | -0.500812 | 1.101263  |        |       |                      |               |                  |
| C    | -5.768576 | -2.294924 | 0.679626  |        |       |                      |               |                  |
| C    | -5.704455 | -2.156683 | -0.717255 |        |       |                      |               |                  |
| C    | -4.977591 | -1.104896 | -1.293181 |        |       |                      |               |                  |
| C    | -4.365644 | -0.318390 | 0.947425  |        |       |                      |               |                  |
| C    | -5.102079 | -1.375418 | 1.505532  |        |       |                      |               |                  |
| C    | -6.346235 | -3.112558 | 1.122970  |        |       |                      |               |                  |
| C    | -6.230233 | -2.864644 | -1.365277 |        |       |                      |               |                  |
| C    | -4.941377 | -0.990064 | -2.381584 |        |       |                      |               |                  |
| C    |-3.851699  | 0.404096  | 1.588926  |        |       |                      |               |                  |
| C    | -5.158487 | -1.472763 | 2.594384  |        |       |                      |               |                  |
| C    | 0.023778  | -3.579912 | -0.827832 |        |       |                      |               |                  |
| C    | 0.374035  | 2.583924  | 0.603950  |        |       |                      |               |                  |
| C    | -0.151796 | 1.328161  | 2.266631  |        |       |                      |               |                  |
| C    | 2.156950  | 4.400428  | -0.623858 |        |       |                      |               |                  |
| C    | 0.805569  | 4.372639  | -1.003537 |        |       |                      |               |                  |
| C    | -0.081968 | 3.472573  | -0.390576 |        |       |                      |               |                  |
| C    | 1.728841  | 2.634649  | 0.993992  |        |       |                      |               |                  |
| C    | 2.616326  | 3.533248  | 0.381394  |        |       |                      |               |                  |
| C    | 2.844927  | 5.109407  | -1.094602 |        |       |                      |               |                  |
| C    | 3.436827  | 5.050780  | -1.770478 |        |       |                      |               |                  |
| C    | -1.141266 | 3.480769  | -0.668442 |        |       |                      |               |                  |
| C    | 2.082486  | 1.980702  | 1.800788  |        |       |                      |               |                  |
| C    | 3.660961  | 3.574868  | 0.707031  |        |       |                      |               |                  |
| C    | -3.039457 | 1.812746  | -0.103083 |        |       |                      |               |                  |
| C    | 3.211889  | -1.853441 | -0.179642 |        |       |                      |               |                  |
| C    | 5.323043  | -1.593844 | -1.419127 |        |       |                      |               |                  |
| C    | 4.597302  | -0.003230 | -0.990125 |        |       |                      |               |                  |
| C    | 2.394348  | -4.162339 | -0.137858 |        |       |                      |               |                  |
| C    | 2.535210  | -3.548873 | -1.813624 |        |       |                      |               |                  |
| C    | 4.381988  | -1.040697 | 1.815158  |        |       |                      |               |                  |
| C    | 5.099107  | -2.579880 | 1.223045  |        |       |                      |               |                  |
| C    | 3.919144  | -0.954343 | -2.345279 |        |       |                      |               |                  |
| C    | 4.011132  | -4.060761 | -0.921224 |        |       |                      |               |                  |
| C    | 3.547269  | -2.592427 | 2.132391  |        |       |                      |               |                  |

SCF(BP86) = -928.690246737
H 0K = -928.316838
H 298K = -928.290338
G 298K = -928.379133
Solvent Correction(CH3Cl) = -0.04642200
BP86-D3 Correction = -0.06268799
Lowest frequencies = -98.2618 cm⁻¹, 8.7392 cm⁻¹
**IntII\textsubscript{17} (anti, pro-E)**

\[
\begin{array}{ccc}
\text{P} & 2.748141 & -2.441788 & 0.063024 \\
\text{C} & 4.499637 & -1.976895 & -0.317411 \\
\text{C} & 2.779880 & -3.168810 & 1.765671 \\
\text{Au} & 1.246210 & -0.664670 & -0.143230 \\
\text{C} & -0.447272 & 0.734119 & -0.722509 \\
\text{C} & -1.748654 & 0.034303 & -0.413962 \\
\text{S} & -3.107594 & 1.343791 & -0.463654 \\
\text{C} & 0.254902 & 1.447040 & 0.266267 \\
\text{C} & -4.566250 & 0.298659 & -0.252481 \\
\text{O} & -1.949693 & 1.063408 & 2.562305 \\
\text{H} & -2.253281 & 1.493108 & 3.382498 \\
\text{H} & -1.994466 & -0.726135 & -1.16920 \\
\text{H} & -1.754699 & -0.409345 & 0.593066 \\
\text{H} & -0.269233 & 0.969080 & -1.781346 \\
\text{C} & -6.881076 & -1.247347 & 0.077465 \\
\text{C} & -5.993683 & -1.074516 & 1.154001 \\
\text{C} & -4.838291 & -0.294805 & 0.999168 \\
\text{C} & -5.449644 & 0.123668 & -1.335866 \\
\text{C} & -6.611176 & -0.645942 & -1.162561 \\
\text{H} & -7.786416 & -1.848470 & 0.207364 \\
\text{H} & -6.208171 & -1.537447 & 2.122556 \\
\text{H} & -4.146762 & -0.139234 & 1.833808 \\
\text{H} & -5.227399 & 0.591604 & -2.299831 \\
\text{H} & -7.303635 & -0.776940 & -2.000011 \\
\text{C} & 2.349381 & -3.849742 & -1.071899 \\
\text{H} & -2.477395 & 1.491515 & 1.847134 \\
\text{C} & 1.296029 & 2.466385 & 0.072707 \\
\text{H} & -0.122023 & 1.335744 & 1.298658 \\
\text{C} & 3.267596 & 4.474885 & -0.152109 \\
\text{C} & 2.702404 & 3.907097 & -1.310971 \\
\text{C} & 1.725893 & 2.912964 & -1.203746 \\
\text{C} & 1.871113 & 3.049936 & 1.230363 \\
\text{C} & 2.848570 & 4.046370 & 1.118237 \\
\text{H} & 4.027523 & 5.257104 & -0.243239 \\
\text{H} & 3.019979 & 4.252343 & -2.299538 \\
\text{H} & 1.283528 & 2.494143 & -2.113405 \\
\text{H} & 1.533631 & 2.718720 & 2.218747 \\
\text{H} & 3.278632 & 4.493311 & 2.019537 \\
\text{H} & 4.825097 & -1.182833 & 0.371632 \\
\text{H} & 3.081607 & -4.661924 & -0.934165 \\
\text{H} & 3.082196 & -2.395707 & 2.488307 \\
\text{H} & 4.561679 & -1.599999 & -1.349398 \\
\text{H} & 2.379594 & -3.499928 & -2.113488 \\
\text{H} & 3.493062 & -4.008317 & 1.803224 \\
\text{H} & 5.155570 & -2.855522 & -0.205261 \\
\text{H} & 1.338308 & -4.223690 & -0.850176 \\
\text{H} & 1.773184 & -3.527589 & 2.028591 \\
\end{array}
\]

\[\text{SCF(BP86)} = -928.719400637\]
\[\text{H 0K} = -928.344798\]
\[\text{H 298K} = -928.316511\]
\[\text{G 298K} = -928.410083\]

\[\text{Solvent Correction(CH3Cl)} = -0.04818937\]
\[\text{BP86-D3 Correction} = -0.05585878\]

\[\text{Lowest frequencies} = 5.9327 \text{ cm}^{-1}, 19.7828 \text{ cm}^{-1}\]

181
IntII_{17} (anti, pro-Z)

C 4.225307  -1.494969  -1.570871
C 4.264352  -2.163767  1.303036
Au 1.306045  -0.642385  0.193601
C  -0.798862  0.246579  0.283120
C  -1.464836  0.179453  -1.063538
S  -3.115169  1.091613  -0.998900
C  -4.223461  -0.226361  -0.440178
O  -2.519488  1.998950  2.218962
H  -3.091535  2.630548  2.692506
H  -0.885285  0.641035  -1.875422
H  -1.697669  -0.857869  -1.346392
H  -1.267980  -0.391913  1.044392
C  -6.008953  -2.225849  0.379825
C  -5.760654  -2.027406  -0.98831
C  -4.869695  -1.026229  -1.405155
C  -4.76796  -0.413394  0.934540
C  -5.369350  -1.420359  1.336605
H  -6.708812  -3.004040  0.700209
H  -6.267551  -2.646328  -1.735880
H  -4.680554  -0.854576  -2.469510
H  -3.978741  0.227989  1.671436
H  -5.570106  -1.563737  2.402446
C  2.656888  -3.781839  -0.564609
C  0.641798  2.458285  0.225435
H  0.179484  1.181935  1.898008
C  1.875854  4.838154  -0.685214
C  0.895548  4.206552  -1.467686
C  0.282245  3.029724  -1.023297
C  1.620315  3.124073  1.012118
C  2.237137  4.295188  0.560409
H  2.351231  5.759472  -1.039225
H  0.59804  4.641686  -2.425877
H  -0.502861  2.583789  -1.636628
H  1.886499  2.711046  1.991733
H  2.987060  4.792101  1.183165
H  -2.799068  2.078413  1.280098
P  3.146052  -2.040047  -0.168182
H  5.070071  -2.192769  -1.690265
H  4.608253  -0.483685  -1.365954
H  2.065847  -4.194332  0.263779
H  2.042631  -3.791627  -1.47783
H  4.654974  -1.165306  1.551534
H  5.103484  -2.843116  1.081307
H  3.634271  -1.470271  -2.499016
H  3.559865  -4.399035  -0.719211
H  3.696150  -2.548992  2.163338

SCF(BP86) = -928.712248158
H 0K = -928.337751
H 298K = -928.309319
G 298K = -928.405301
Solvent Correction(CH3Cl) = -0.04858689
BP86-D3 Correction = -0.05778748
Lowest frequencies = 2.7321 cm^{-1}, 7.0480 cm^{-1}

182
*IntII17 (anti, pro-E)

P  -2.888131  -2.002796  0.423231
C  -4.202983  -1.215783  1.462792
C  -3.772748  -2.759154  -1.016692
Au  -1.201620  -0.514483  -0.213590
C   0.863269   0.449563  -0.591473
C   1.664249  -0.399105  -1.541371
S   3.327535   0.427983  -1.787799
C  -0.099661  -1.381305  -0.104947
C   4.259575  -0.230589  -0.388677
H   1.850045  -1.415261  -1.163552
H   1.201187  -0.463029  -2.539511
H   1.284250   0.538695   0.419480
C   5.812203   -1.203232  1.740774
C   5.435479  -2.064237   0.695250
C   4.670738  -1.580309  -0.376400
C   4.639640   0.634761   0.657263
C   5.420568   0.144901   1.716999
H   6.420690  -1.581807  2.567927
H   5.756593  -3.110731   0.702534
H   4.408418  -2.237957  -1.211694
H   4.332908   1.685003   0.629396
H   5.722252   0.819676   2.524404
C  -2.251128  -3.427245   1.420815
C  -0.632943   2.536796  -0.271691
H  -0.363174   1.361562  -2.083752
C  -1.693936   4.089331   1.026894
C  -0.757689   3.990448   1.687270
C  -0.229648   2.864856   1.047666
C  -1.574611   3.370577  -0.925006
C  -2.099056   4.498432  -0.281437
H  -2.098450   5.692418   1.530826
H  -0.432291   4.240325   2.701702
H   0.510039   2.248590   1.568800
H  -1.882578   3.132901  -1.949689
H  -2.817713   5.138122  -0.802313
H  -4.675325  -0.397636   0.898116
H  -3.083860  -4.095559   1.694242
H  -4.240341  -1.965010  -1.618391
H  -3.748564  -0.802160   2.375799
H  -1.768210  -3.048427   2.334364
H  -4.548991  -3.454420  -0.657745
H  -4.967555  -1.964202   1.735511
H  -1.509529  -3.986082   0.830095
H  -3.051737  -3.304557  -1.644387

SCF(BP86) = -852.285955458
H 0K = -851.935504
H 298K = -851.910337
G 298K = -851.997672
Solvent Correction(CH3Cl) = -0.04914679
BP86-D3 Correction = -0.04974030
Lowest frequencies = 10.0600 cm⁻¹, 13.0386 cm⁻¹
*IntII_{17} \text{(anti, pro-Z)}*

C  -4.109950  -1.389343  1.555711
C  -4.046588  -2.352792  -1.233992
Au  -1.181000  -0.606393  -0.215918
C  0.930900  0.318931  -0.339696
C  1.552343  0.343906  1.028683
S  3.181981  1.275738  0.955917
C  0.055555  1.246350  -0.940370
C  4.281658  0.004077  0.295022
H  0.940054  1.246350  -0.940370
H  1.775933  -0.673824  1.385224
H  1.420641  -0.372430  -1.040196
C  6.079999  -1.903541  -0.710326
C  5.643196  -1.984937  0.623199
C  4.752733  -1.028289  1.133166
C  4.722821  0.090350  -1.041008
C  5.624979  -0.864381  -1.530711
H  6.784103  -2.644962  -1.100623
H  6.011073  -2.784285  1.274319
H  4.434457  -1.067205  2.180020
H  4.367748  0.907128  -1.676943
H  5.972925  -0.793365  -2.573476
C  -2.428911  -3.704123  0.832899
C  -0.565785  2.485813  -0.439819
H  -0.082161  1.101484  -2.022727
C  -1.840783  4.893840  0.325470
C  -0.774173  4.384778  1.086807
C  -0.141037  3.192575  0.714546
C  -1.626278  3.030242  -1.213384
C  -2.263090  4.215016  -0.830821
H  -2.328622  5.827226  0.622576
H  -0.423122  4.928090  1.969297
H  0.715112  2.846020  1.295899
H  -1.943023  2.511461  -2.128673
H  -3.077889  4.617954  -1.439812
P  -2.972622  -2.034404  0.244836
H  -4.931388  -2.104141  1.726339
H  -4.523985  -0.420740  1.236871
H  -1.797341  -4.175634  0.064733
H  -1.843880  -3.594673  1.758665
H  -4.460397  -1.401691  -1.595262
H  -4.860543  -3.038273  -0.964294
H  -3.546920  -1.245546  2.490422
H  -3.303998  -4.338240  1.026516
H  -3.433502  -2.802246  -2.034434

SCF(BP86) = -852.2811788
H 0K = -851.930427
H 298K = -851.905323
G 298K = -851.992951
Solvent Correction(CH3Cl) = -0.04875727
BP86-D3 Correction = -0.05115393
Lowest frequencies = 7.6783 cm\(^{-1}\), 12.3048 cm\(^{-1}\)
**IntIII\textsubscript{17} (anti, pro-S)**

|      |      |      |      |      |
|------|------|------|------|------|
| P    | -2.575055 | -2.141000 | -1.782040 |
| C    | -2.510949  | -3.974219  | -1.527762  |
| C    | -4.324588  | -1.651946  | -1.481119  |
| C    | -2.355908  | -1.883207  | -3.601974  |
| Au   | -1.018803  | -0.982588  | -0.479860  |
| C    | 0.954900   | -0.169228  | 0.398254   |
| C    | 1.674397   | 0.661022   | -0.629270  |
| S    | 3.273829   | 1.267231   | 0.131704   |
| C    | -0.082804  | 0.326303   | 1.205036   |
| C    | 4.331474   | -0.183762  | -0.065865  |
| H    | -2.076542  | 4.549678   | 1.899666   |
| S    | -2.505663  | 3.765222   | 0.873195   |
| C    | -1.063894  | 3.993310   | -0.183239  |
| H    | 1.115617   | 1.568727   | -0.910253  |
| H    | 1.478803   | -1.085241  | 0.705750   |
| C    | -0.572069  | -0.229512  | 2.481003   |
| H    | -0.471208  | 1.326095   | 0.954414   |
| H    | -1.509878  | -4.346050  | -1.794165  |
| H    | -3.267764  | -4.469208  | -2.157826  |
| H    | -2.705714  | -4.202932  | -0.468928  |
| H    | -1.354416  | -2.226900  | -3.902384  |
| H    | -2.448857  | -0.811224  | -3.831014  |
| H    | -3.121605  | -2.448347  | -4.157919  |
| H    | -4.453437  | -0.576832  | -1.614870  |
| H    | -4.545678  | -1.848723  | -0.358108  |
| H    | -5.016079  | -2.229033  | -2.053496  |
| C    | -1.584218  | -1.176153  | 4.941286   |
| C    | -0.489826  | -1.820232  | 4.332572   |
| C    | 0.014581   | -1.354355  | 3.114280   |
| C    | -1.669871  | 0.413372   | 3.106200   |
| C    | -2.170529  | -0.057444  | 4.326832   |
| H    | -1.970462  | -1.542479  | 5.897483   |
| H    | -0.023149  | -2.682384  | 4.818877   |
| H    | 0.878371   | -1.854143  | 2.664145   |
| H    | -2.117315  | 1.290461   | 2.623075   |
| H    | -3.014723  | 0.451430   | 4.802195   |
| H    | 1.929884   | 0.094166   | -1.537008  |
| C    | 1.127288   | 4.286716   | -1.934304  |
| C    | 1.265001   | 4.590802   | -0.569097  |
| C    | 0.180919   | 4.435585   | 0.310350   |
| C    | -1.207751  | 3.691984   | -1.554202  |
| C    | -0.111334  | 3.833778   | -2.420277  |
| H    | 1.971822   | 4.417371   | -2.614703  |
| H    | 2.221264   | 4.955186   | -0.180767  |
| H    | 0.303466   | 4.671675   | 1.372505   |
| H    | -2.182866  | 3.385378   | -1.947440  |
| H    | -0.237262  | 3.614994   | -3.486186  |
| C    | 6.070857   | -2.375525  | -0.333414  |
| C    | 5.654140   | -1.665049  | -1.473370  |
| C    | 4.796084   | -0.563036  | -1.342993  |
| C    | 4.750902   | -0.894409  | 1.077126   |
| C    | 5.625032   | -1.985296  | 0.938714   |
| C    | 6.751362   | -3.226511  | -0.439001  |
| C    | 6.015495   | -1.956176  | -2.464917  |
| H    | 4.499751   | 0.015380   | -2.224377  |
| H    | 4.399653   | -0.582996  | 2.065894   |
| H    | 5.956188   | -2.530331  | 1.828479   |

SCF(BP86) = -1094.75982937
H 0K = -1094.312313
H 298K = -1094.278303
G 298K = -1094.391185
Solvent Correction(CH3Cl) = -0.04791583
BP86-D3 Correction = -0.07179615
Lowest frequencies = 5.3215 cm\(^{-1}\), 8.1185 cm\(^{-1}\)
| Element | X  | Y  | Z   |
|---------|----|----|-----|
| P       | 4.277278 | 0.207173 | -0.369105 |
| C       | 5.175602  | 1.702468  | -0.998156 |
| C       | 5.031655  | -0.144327  | 1.287333 |
| Au      | 4.840264  | -1.184821  | -1.456550 |
| C       | 1.950843  | 0.444033  | -0.279064 |
| C       | -0.227827  | 0.582007  | -0.050003 |
| S       | -2.621141  | 2.223471  | -1.520640 |
| C       | -0.808167  | -0.828540  | -0.103906 |
| H       | -0.0335642  | 1.038108  | -2.190116 |
| C       | -0.317927  | 1.073640  | 0.933128 |
| C       | -0.079770  | -1.856097  | 0.738503 |
| H       | -0.852581  | -1.173059  | -1.151038 |
| C       | 4.835738  | 1.929011  | -2.020236 |
| H       | 6.262767  | 1.520983  | -1.002939 |
| H       | 4.948999  | 2.562822  | -0.350135 |
| H       | 4.497745  | -1.004549  | -2.486948 |
| H       | 4.399633  | -2.126669  | -1.958787 |
| C       | 5.939678  | -1.261283  | -1.441917 |
| C       | 4.590685  | -1.065361  | 1.697949 |
| H       | 4.811565  | 0.689000  | 1.972003 |
| H       | 6.123064  | -0.265412  | 1.193285 |
| C       | 1.279104  | -3.805953  | 2.271049 |
| C       | 0.888942  | -2.589168  | 2.859663 |
| C       | 0.211693  | -1.623325  | 2.102163 |
| C       | 0.308359  | -3.082542  | 0.159984 |
| C       | 0.984879  | -4.051257  | 0.920659 |
| H       | 1.79712  | -4.563080  | 2.867606 |
| H       | 1.100385  | -2.398388  | 3.916959 |
| H       | -0.112121  | -0.692069  | 2.579766 |
| H       | 0.074785  | -3.280523  | -0.892409 |
| H       | 1.271626  | -5.001299  | 0.458447 |
| H       | -0.007180  | 2.488666  | -1.906797 |
| C       | -4.549080  | -4.542068  | -2.127924 |
| C       | -4.347982  | -3.438338  | -2.094269 |
| C       | -3.760608  | -2.265951  | -1.595919 |
| C       | -3.564997  | -3.310925  | 0.607794 |
| H       | -4.160345  | -4.476571  | 0.099858 |
| H       | -5.015408  | -5.451662  | -1.638316 |
| H       | -4.660054  | -3.548512  | -3.142381 |
| H       | -3.621517  | -1.398680  | -2.249350 |
| H       | -3.260790  | -3.250362  | 1.656675 |
| H       | -4.320981  | -5.335379  | 0.761397 |
| C       | -3.042325  | 5.335179  | 1.841368 |
| C       | -2.561745  | 5.700251  | 0.573288 |
| C       | -2.437134  | 4.739539  | -0.440636 |
| C       | -3.289050  | 3.027787  | 1.092075 |
| C       | -3.408151  | 4.003308  | 2.094857 |
| H       | -3.145083  | 6.089787  | 2.627045 |
| H       | -2.287703  | 6.739290  | 0.366178 |
| H       | -2.047811  | 5.028955  | -1.432822 |
| H       | -3.592250  | 1.995681  | 1.290405 |
| H       | -3.796295  | 3.715671  | 3.077060 |

SCF(BP86) = -1094.74138322
H 0K = -1094.293811
H 298K = -1094.261642
G 298K = -1094.367133
Solvent Correction(CH3Cl) = -0.04396925
BP86-D3 Correction = -0.07737049
Lowest frequencies = -120.1802 cm\(^{-1}\), 6.1675 cm\(^{-1}\)
IntIV17 (anti, pro-S)

57

P
C 3.805270  -0.043374  -1.095864
C 4.479224  0.841909  -2.576656
C 4.628227  0.738835  0.367483
C 4.493281  -1.760035  -1.190342
Au 1.468658  0.000891  -0.982576
C -0.691161  -0.142998  0.034101
C -0.743859  0.039773  -1.350654
C -0.843669  -1.468231  -0.710831
C -2.199740  3.388379  0.693343
H -4.376011  2.897476  1.498899
S -2.663930  -1.402757  1.277518
C -3.528208  -1.736894  -0.267153
H -0.943839  -0.809223  -2.015638
H -0.695664  0.747064  0.678430
C 0.049222  -1.722325  1.904428
H -0.776857  -2.299457  -0.009405
H 4.083501  0.377550  -3.492756
H 5.579879  0.785191  -2.581220
H 4.164977  1.896292  -2.547935
H 4.096829  -2.264281  -2.084782
H 4.185694  -2.324216  -0.296812
H 5.593500  -1.724264  -1.244942
H 4.316740  0.213838  1.283122
H 4.320733  1.792995  0.438634
H 5.723615  0.680059  0.260044
C 1.691291  -2.281577  4.134324
C 1.080571  -1.023055  4.005085
C 0.264877  -0.742006  2.897906
C 0.663622  -2.958171  2.045065
C 1.481037  -3.262696  3.151120
H 2.320883  -2.499813  5.002512
H 1.231598  -0.259353  4.774658
H -0.212269  0.240878  2.817342
H 0.489636  -3.757792  1.287117
H 1.945106  -4.249104  3.249801
H -0.922984  1.041820  -1.757008
C -4.968047  -2.276411  -2.616259
C -4.886026  -0.961384  -2.130832
C -4.163916  -0.683360  -0.958241
C -3.619148  -3.061464  -0.748169
C -4.333715  -3.324644  -1.925862
H -5.534672  -2.488405  -3.528368
H -5.387697  -0.146553  -2.662648
H -4.099089  0.339926  -0.572496
H -3.149905  -3.876632  -0.187830
H -4.410550  -4.352069  -2.295540
C 0.945224  3.742482  1.263836
C 0.051738  3.986537  -0.030040
C -1.310919  3.812800  -0.319050
C -1.705762  3.138476  1.992102
C -0.341182  3.321580  2.270312
H 1.601407  3.911495  1.494894
H 0.723176  4.345656  -0.817281
H -1.690486  4.037800  -1.321685
H -2.386712  2.824746  2.790026
H 0.022731  3.154367  3.289576

SCF(BP86) = -1094.75178487
H 0K = -1094.304624
H 298K = -1094.270666
G 298K = -1094.382295
Solvent Correction(CH3Cl) = -0.04839041
BP86-D3 Correction = -0.07712229
Lowest frequencies = 6.8348 cm^-1, 8.4793 cm^-1
*IntIV17 (anti, pro-S)

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| P    | 3.478075 | -0.935311 | 0.292803 |
| C    | 4.181991 | -2.634329 | 0.509827 |
| C    | 4.507670 | -0.131226 | -1.019456 |
| C    | 3.865871 | -0.028603 | 1.859532 |
| Au   | 1.194081 | -0.955863 | -0.221116 |
| C    | -0.919060 | -0.040706 | -0.895433 |
| C    | -0.964956 | -1.412241 | -0.627807 |
| C    | -1.355578 | 1.021976  | 0.061780  |
| S    | -3.097522 | 1.430558  | -0.592647 |
| C    | -4.038030 | -0.004260 | -0.046438 |
| H    | -1.374867 | -1.774032 | 0.322920  |
| H    | -0.699250 | 0.292324  | -1.912228 |
| C    | -0.513940 | 2.279417  | 0.079375  |
| H    | -1.483615 | 0.621187  | 1.079954  |
| H    | 3.654855  | -3.149298 | 1.326338  |
| H    | 5.255969  | -2.568067 | 0.747328  |
| H    | 4.046298  | -3.208341 | -0.420415 |
| H    | 3.344342  | -0.511524 | 2.699926  |
| H    | 3.517185  | 1.011629  | 1.772849  |
| H    | 4.952411  | -0.041929 | 2.043927  |
| H    | 4.182210  | 0.911899  | -1.150524 |
| H    | 4.374782  | -0.669270 | -1.970351 |
| C    | 5.570705  | -0.153203 | -0.729035 |
| C    | 0.589806  | 4.137098  | -1.058707 |
| C    | -0.183470 | 2.967371  | -1.108944 |
| C    | -0.061736 | 2.788839  | 1.314683  |
| C    | 0.714174  | 3.957518  | 1.362323  |
| H    | 1.638605  | 5.550234  | 0.212540  |
| H    | 0.829039  | 4.668228  | -1.985252 |
| H    | -0.548289 | 2.606859  | -2.077444 |
| H    | -0.330785 | 2.273237  | 2.243937  |
| H    | 1.050266  | 4.347160  | 2.328435  |
| H    | -0.925592 | -2.135560 | -1.450873 |
| C    | -5.613467 | -2.180777 | 0.770665  |
| C    | -5.286698 | -2.023314 | -0.585847 |
| C    | -4.493569 | -0.940502 | -0.999270 |
| C    | -4.379038 | -0.154249 | 1.315570  |
| C    | -5.157919 | -1.248199 | 1.719687  |
| H    | -6.232912 | -3.024912 | 1.089122  |
| H    | -5.650435 | -2.742341 | -1.326573 |
| H    | -4.239770 | -0.806579 | -2.055305 |
| H    | -4.054127 | 0.595578  | 2.044177  |
| H    | -5.427388 | -1.361576 | 2.774481  |

SCF(BP86) = -852.279305431
H 0K = -851.929175
H 298K = -851.904052
G 298K = -851.990535
Solvent Correction(CH3Cl) = -0.048577231
BP86-D3 Correction = -0.05401734
Lowest frequencies = 8.1690 cm⁻¹, 16.4009 cm⁻¹