Supporting Information

Chiral Oxazolidines Acting as Transient Hydroxyalkyl-Functionalized N-Heterocyclic Carbenes: An Efficient Route to Air Stable Copper and Gold Complexes for Asymmetric Catalysis†

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1.1. General information:

Unless indicated otherwise, all reactions were performed under inert atmosphere using Schlenk line techniques. Reactions at elevated temperature were maintained by thermostatically controlled oil-bath. Tetrahydrofuran, toluene, dichloromethane and diethyl ether were purified using MBraun MB-SPS-5 Solvent Purification System. Other solvents were distilled over Sodium/Benzophenone or Calcium hydride. (L)-leucine was purchased from Fluorochem, potassium hexafluorophosphate was purchased from Alfa Aesar, Copper (II) triflate was purchased from Strem and Copper (I) triflate.toluene complex was purchased from Sigma Aldrich. Other chemicals were used as received unless otherwise noted. (L)-tert-leucinol and alkoxy-imidazolinium salts \textbf{L1aHCl} and \textbf{L1bHCl} were synthesized according to literature procedure.\(^1\) Solution of \textit{n}-butyllithium was titrated using a solution of 1,10 phenanthridine in dry propanol and dry toluene according to Sigma Aldrich procedure.\(^2\) Silica gel chromatography was performed with Sigma-Aldrich’s silica gel high-purity grade, pore size 60 Å, 230-400 mesh particle size, 40-63 μm particle size. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F254) using UV light as visualizing agent and by staining with KMnO\textsubscript{4}. \(^1\)H (400 MHz), \(^13\)C (101 MHz), \(^19\)F (376 MHz), \(^{31}\)P (162 MHz) NMR spectra were acquired on 400 MHz Bruker instruments with complete proton decoupling for nucleus other than \(^1\)H. Chemicals shifts were reported relative to residual solvent peaks (CDCl\textsubscript{3} = 7.26 ppm for \(^1\)H and 77.16 ppm for \(^13\)C; THF-\(d_8\) = 3.58 and 1.73 ppm for \(^1\)H and 67.57 and 25.37 ppm for \(^13\)C); \(^19\)F chemical shifts are reported with CFC\textsubscript{3} (\(\delta = 0.0\) ppm) as the internal standard; \(^{31}\)P chemical shifts are reported with H\textsubscript{3}PO\textsubscript{4} (\(\delta = 0.0\) ppm) as the internal standard; \(^{11}\)B chemical shifts are reported with BF\textsubscript{3}.Et\textsubscript{2}O (\(\delta = 0.0\) ppm) as the internal standard. Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentuplet, quint = quintet, h = heptet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dddd = doublet of doublets of doublets of doublets dt = doublet of triplet, dq = doublet of quartet, td = triplet of doublet, dtd = doublet of triplet of doublet, pd = pentuplet of doublet, qd = quartet of doublet, br = broad. Mass spectrometric analyses were performed at Centre Régional de Mesures

\(^1\)M. Nakamura, T. Hatakeyama, K. Har, E. Nakamura, \textit{J. Am. Chem. Soc.} \textbf{2003}, \textit{125}, 6362-6363; \textit{b) H. Clavier, L. Coutable, L. Toupet, J.-C. Guillemin, M. Mauduit, \textit{J. Organomet. Chem.} \textbf{2005}, \textit{690}, 5237-5254; c) T. Jennequin, J. Wencel-Delord, D. Rix, J. Daubignard, C. Crévisy, M. Mauduit, \textit{Synlett} \textbf{2010}, \textit{2010}, 1661-1665; d) C. Jahier-Diallo, M. S. T. Morin, P. Queval, M. Rouen, I. Artur, P. Querard, L. Toupet, C. Crévisy, O. Baslé, M. Mauduit, \textit{Chem. Eur. J.} \textbf{2015}, \textit{21}, 993-997.

\(^2\)Titration of \textit{n}-Butyllithium ;https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Datasheet/1/689327dat.pdf

S2
Physiques de l’Ouest (CRMPO), Université de Rennes 1. Data for oxazolidines \( \text{2a} \) and \( \text{2b} \) were acquired on a Bruker Maxis 4G device while gold (AuCl\( \text{-1a} \) and AuCl\( \text{-1b} \)) and copper complexes (CuBr\( \text{-1a} \) and CuBr\( \text{-1b} \)) were analyzed on a Thermo Fisher Q-Exactive apparatus. Optical rotations were recorded on a JASCO P=2000 polarimeter using a 1 mL cell with 1 dm path length. All samples were carried out in CHCl\(_3\) in 2 or 5 mL volumetric flask (concentration in g/100mL). Specific rotations are reported in deg.dm\(^{-1}\).cm\(^3\).g\(^{-1}\) for a wave length related to sodium line spectrum (\( \lambda = 589 \) nm). Melting points were determined on a Stuart® SMP 10 melting point apparatus and are uncorrected. Enantiomeric excesses were determined by GC analysis (Gas Chromatography) with a Shimadzu 2014 chromatograph or HPLC analysis (High Performance Liquid Chromatography) on Alliance e2695 Waters® HPLC with a UV/visible detector 2489 Waters® at 254nm.

1.2. Representative procedure for the preparation of oxazolidine derivatives:

![Chemical structure](image)

**General procedure:**

In a round bottom flask, the imidazolinium salt (1.0 equiv) and the base (3.0 or 1.0 equiv) were dissolved in dry THF over 1 h. Then, the mixture was filtrated through celite pad and the solvent was removed under vacuum to afford the pure oxazolidine.

**Optimization Table:**

| Entry | Base (equiv) | scale (mmol) | NMR conv. (isolated yield) (%) | dr (2a) evaluated by NMR |
|-------|-------------|--------------|--------------------------------|--------------------------|
| 1     | KHMD (1.0)  | 0.021        | 100                            | 100/0                    |
| 2     | KH (2.0)    | 0.027        | 100 (quant.)                   | 100/0                    |
| 3     | KH (2.0)    | 0.82         | 100 (96)                       | 100/0                    |
| 4     | KHMD (1.0)  | 1.36         | 100 (95)                       | 100/0                    |
(3S,7aS)-3-(tert-butyl)-7-(2,6-diisopropylphenyl)hexahydroimidazo[2,1-b]oxazole (2a):
Imidazolium salt L1aHCl (499 mg, 1.36 mmol), KHMD (272 mg, 1.36 mmol) and THF (10 mL). White solid (427 mg, 95% yield).

\[ \text{Imidazolinium salt L1aH} \]  

\[ \text{Cl} \] (499 mg, 1.36 mmol), KHMDS (272 mg, 1.36 mmol) and THF (10 mL). White solid (427 mg, 95% yield).

\[ \text{1H NMR (CDCl}_3, 400 MHz): \delta 7.30 – 7.26 (m, 1H), 7.20 – 7.18 (m, 2H), 5.35 (s, 1H, N-CH(O)-N), 4.11 (t, J = 8.3 Hz, 1H), 3.88 – 3.82 (m, 1H), 3.69 – 3.50 (m, 3H), 3.36 – 3.31 (m, 2H), 3.28 – 3.21 (m, 1H), 2.79 (t, J = 7.3 Hz, 1H), 1.35 – 1.21 (m, 12H), 0.99 (s, 9H). \]

\[ \text{13C NMR (CDCl}_3, 101 MHz): \delta 150.7, 148.4, 140.0, 127.4, 124.8, 123.4, 110.8 (N-CH(O)-N), 73.8, 64.2, 55.8, 54.1, 33.9, 28.0, 27.1, 26.2, 25.3, 24.6, 24.5. \]

\[ \text{HRMS (ESI, CH}_3\text{OH, positive mode) calcd for C}_{21}\text{H}_{35}\text{N}_2\text{O} [M+H]^+: m/z 331.2743, found: 331.2743 (0 ppm). \]

mp: 48-52 °C.

(3S,7aS)-3-(tert-butyl)-7-mesitylhexahydroimidazo[2,1-b]oxazole (2b): Imidazolium salt L1bHCl (500 mg, 1.54 mmol), KHMD (310 mg, 1.55 mmol), THF (25 mL). Colourless oil (444 mg, 99% yield).

\[ \text{1H NMR (CDCl}_3, 400 MHz): \delta 6.89 (s, 2H), 5.39 (s, 1H, N-CH(O)-N), 4.11 – 4.02 (m, 1H), 3.60 – 3.52 (m, 2H), 3.46 (m, 1H), 3.26 (q, J = 7.7, 7.0 Hz, 1H), 3.17 (q, J = 8.3 Hz, 1H), 2.76 (t, J = 7.2 Hz, 1H), 2.36 (s, 6H), 2.28 (s, 3H), 0.96 (s, 9H). \]

\[ \text{13C NMR (CDCl}_3, 101 MHz): \delta 139.9, 136.0, 129.4, 109.8 (N-CH(O)-N), 74.1, 64.2, 56.0, 51.2, 34.0, 26.2, 21.0, 18.3. \]

\[ \text{HRMS (ESI, CH}_3\text{OH, positive mode) calcd for C}_{18}\text{H}_{29}\text{N}_2\text{O} [M+H]^+: m/z 289.2274, found: 289.2278 (1 ppm). \]

1.3. Representative procedure for the synthesis of gold complexes from the oxazolidine derivatives:

\[ \text{AuCl·SMe}_2 \] (dry THF, 40°C, Ar = Mes, Dipp)

General procedure:
In a round bottom flask under argon atmosphere, the oxazolidine (1.0 equiv) and AuCl·SMe\textsubscript{2} (1.1 equiv) were dissolved in dry THF. The reaction mixture was stirred at 40 °C over 2 h. Then, the reaction mixture was filtered on celite pad to remove the purple precipitate and the solvent was removed under reduced pressure. The crude was purified on silica gel with an
eluent gradient (100% DCM to 9:1 DCM/acetone) to afford the corresponding gold chloride complex as a white/grey solid.

**AuCl-1a complex:** Oxazolidine 2a (83 mg, 0.25 mmol), AuCl·SMe2 (81 mg, 0.27 mmol), THF (5.0 mL). white/grey solid (118.1 mg, 84% yield).

**1H NMR** (CDCl₃, 400 MHz): δ 7.35 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 7.8 Hz, 2H), 4.65 (brs, 1H), 4.05 – 3.97 (m, 2H), 3.91 – 3.78 (m, 5H), 2.98 (p, J = 6.9 Hz, 1H), 2.88 (p, J = 6.8 Hz, 1H), 1.33 (dd, J = 16.3, 6.8 Hz, 6H), 1.22 (dd, J = 12.1, 6.9 Hz, 6H), 1.09 (s, 9H).

**13C NMR** (CDCl₃, 101 MHz): δ 196.4 (C carbene), 146.9, 149.9, 134.5, 129.8, 124.6, 124.5, 70.5, 58.0, 53.5, 34.0, 28.7, 28.4, 28.3, 25.1, 25.06, 24.4, 24.37. **HRMS** (ESI, CH₂Cl₂, negative mode) calcd for C₂₁H₃₄N₂OCl₂Au [M+Cl]⁻: m/z 597.1719, found: 597.1720 (0 ppm).

**AuCl-1b complex:** Oxazolidine 2b (80 mg, 0.28 mmol), AuCl·SMe2 (89.6 mg, 0.30 mmol), THF (4.0 mL). white/grey solid (57.4 mg, 40% yield).

**1H NMR** (CDCl₃, 400 MHz): δ 6.90 – 6.87 (m, 2H), 4.62 (s, 1H), 4.04 – 3.93 (m, 2H), 3.91 – 3.72 (m, 5H), 2.27 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.09 (s, 9H). **13C NMR** (CDCl₃, 101 MHz): δ 195.8 (C carbene), 138.6, 135.8, 135.6, 134.9, 129.6, 129.5, 70.4, 57.9, 50.6, 33.9, 28.3, 21.1, 18.0. **HRMS** (ESI, CH₂Cl₂, negative mode) calcd for C₁₈H₂₈N₂OCl₂Au [M+Cl]⁻: m/z 555.1249, found: 555.1252 (0 ppm).

### 1.4. Representative procedure for the synthesis of copper complexes from the oxazolidine derivatives:

In a round bottom flask under argon, the oxazolidine (1.0 equiv) and CuBr·SMe₂ (1.1 equiv) were dissolved in dry THF. The reaction mixture was stirred at 40 °C over 1 h. Then, the reaction mixture was filtered on celite pad to remove the precipitate and the solvent was removed under reduced pressure. The crude was purified on silica gel with an eluent gradient (100% DCM to 9:1 DCM/acetone) to afford the corresponding copper complex as a white/greenish solid.
**CuBr-1a complex:** Oxazolidine 2a (83.2 mg, 0.25 mmol), CuBr-SMe\(_2\) (56.5 mg, 0.275 mmol), THF (5.0 mL). white/greenish powder (64.1 mg, 54% yield). Relatively unstable in solution.

\[ ^1H\text{NMR} \quad (\text{CDCl}_3, 400 \text{ MHz}): \delta 7.41 – 7.31 (m, 1H), 7.19 (d, J = 7.8 \text{ Hz}, 2H), 4.17 (brs, 1H), 4.08 – 3.82 (m, 7H), 2.95 (m, 2H), 1.36 – 1.21 (m, 12H), 1.10 (s, 9H). \]

\[ ^{13}C\text{NMR} \quad (\text{CDCl}_3, 101 \text{ MHz}): \delta 204.0 \text{ (C carbene)}, 146.9, 146.8, 134.8, 129.6, 124.5, 124.4, 70.8, 58.7, 53.2, 34.3, 28.6, 28.4, 28.2, 25.3, 24.0. \]

**HRMS** (ESI, CH\(_2\)Cl\(_2\), negative mode) calcd for C\(_{21}\)H\(_{34}\)N\(_2\)OBr\(_2\)Cu [M+Br]\(^-\): m/z 551.0339, found: 551.0343 (1 ppm).

**CuBr-1b complex:** Oxazolidine 2b (70 mg, 0.24 mmol), CuBr-SMe\(_2\) (55 mg, 0.27 mmol), THF (4.0 mL). yellow/greenish powder (56.6 mg, 55% yield). Relatively unstable in solution (during the \(^{13}C\) spectrum acquisition, a signal appears at 160 ppm that could be the oxidation of the carbene species, longer the \(^{13}C\) acquisition is, more this signal is intense).

\[ ^1H\text{NMR} \quad (500 \text{ MHz, CD}_2\text{Cl}_2) \delta 6.96 (s, 2H), 4.07 (s, 1H), 4.03 – 3.71 (m, 7H), 2.29 (s, 3H), 2.23 (d, J = 8.4 \text{ Hz}, 6H), 1.08 (s, 9H). \]

\[ ^{13}C\text{NMR} \quad (126 \text{ MHz, CD}_2\text{Cl}_2) \delta 203.9 \text{ (C carbene)}, 138.8, 136.3, 136.2, 135.9, 129.8, 129.7, 71.2, 50.8, 34.4, 28.3, 21.2, 18.2, 18.1. \]

**HRMS** (ESI, CH\(_2\)Cl\(_2\), negative mode) calcd for C\(_{18}\)H\(_{26}\)N\(_2\)OBr\(_2\)Cu [M+Br]\(^-\): m/z 508.9869, found: 508.9869 (0 ppm).

1.5. Asymmetric Allylic Alkylation of zinc reagents to allyl phosphates:

1.5.1. **Representative procedure for allyl phosphate preparation:**

The (E)-Allyl phosphates were synthesized from the corresponding allylic alcohols using known procedure.\(^3\) The allylic alcohols were synthesized from the corresponding aldehyde by two-step Horner-Wadsworth-Emmons olefination\(^4\)/dibal-H reduction\(^5\) sequence. Only the

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\(^3\) C. A. Luchaco-Cullis, H. Mizutani, K. E. Murphy, A. H. Hoveyda, *Angew. Chem. Int. Ed.* 2001, 40, 1456-1460.

\(^4\) K.-s. Lee, A. H. Hoveyda, *J. Org. Chem.* 2009, 74, 4455-4462.

\(^5\) D. L. J. Clive, E. J. L. Stoffman, *Chem. Commun.* 2007, 2151-2153.
phosphate S1 was synthesized from the commercially available cinnamyl alcohol (98% purity, purchased from Sigma Aldrich).

**Cinnamyl diethyl phosphate (S1):** colourless oil (3.99 g, 99% global yield).

\[
\text{Chemical Formula: } C_{13}H_{18}O_4P \\
\text{Molecular Weight: 270.26}
\]

**\(^1H\) NMR** (CDCl\(_3\), 400 MHz): δ 7.41 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 6.68 (dtd, \(J = 15.7, 1.5\) Hz, 1H), 6.31 (dt, \(J = 15.9, 6.2\) Hz, 1H), 4.70 (ddd, \(J = 8.4, 6.2, 1.4\) Hz, 2H), 4.14 (dq, \(J = 8.0, 7.1\) Hz, 4H), 1.35 (td, \(J = 7.1, 1.0\) Hz, 6H).  \(^13C\) NMR (CDCl\(_3\), 101 MHz): δ 136.2, 134.0, 128.8, 128.3, 126.8, 123.8 (d, \(J = 6.7\) Hz), 68.1 (d, \(J = 5.5\) Hz), 64.0 (d, \(J = 5.8\) Hz), 16.3 (d, \(J = 6.7\) Hz).  \(^31P\) NMR (CDCl\(_3\), 162 MHz) δ -0.75.

\((E)\)-diethyl (3-(naphthalen-2-yl)allyl) phosphate (S2): colourless oil (3.91 g, 47% global yield).

\[
\text{Chemical Formula: } C_{17}H_{24}O_4P \\
\text{Molecular Weight: 320.32}
\]

**\(^1H\) NMR** (CDCl\(_3\), 400 MHz): δ 7.87 – 7.71 (m, 4H), 7.59 (dd, \(J = 8.6, 1.8\) Hz, 1H), 7.52 – 7.36 (m, 2H), 6.90 – 6.76 (m, 1H), 6.43 (dt, \(J = 15.8, 6.2\) Hz, 1H), 4.75 (ddd, \(J = 8.5, 6.2, 1.4\) Hz, 2H), 4.15 (dq, \(J = 8.0, 7.1\) Hz, 4H), 1.35 (td, \(J = 7.1, 1.0\) Hz, 6H).  \(^13C\) NMR (CDCl\(_3\), 101 MHz): δ 134.0, 133.6, 133.5, 133.3, 128.4, 128.1, 127.7, 127.1, 126.5, 126.2, 124.0 (d, \(J = 6.8\) Hz), 123.5, 68.0 (d, \(J = 5.4\) Hz), 63.9 (d, \(J = 5.8\) Hz), 16.2 (d, \(J = 6.7\) Hz).  \(^31P\) NMR (CDCl\(_3\), 162 MHz) δ -0.70.

\((E)\)-diethyl (3-(naphthalen-1-yl)allyl) phosphate (S3): pale yellow oil (3.857 g, 44% global yield).

\[
\text{Chemical Formula: } C_{17}H_{24}O_4P \\
\text{Molecular Weight: 320.32}
\]

**\(^1H\) NMR** (CDCl\(_3\), 400 MHz): δ 8.14 – 8.05 (m, 1H), 7.93 – 7.75 (m, 2H), 7.60 (dt, \(J = 7.3, 1.0\) Hz, 1H), 7.56 – 7.49 (m, 2H), 7.49 – 7.42 (m, 2H), 6.35 (dt, \(J = 15.6, 6.1\) Hz, 1H), 4.82 (ddd, \(J = 8.6, 6.1, 1.5\) Hz, 2H), 4.23 – 4.11 (m, 4H), 1.37 (td, \(J = 7.1, 1.0\) Hz, 6H).  \(^13C\) NMR (CDCl\(_3\), 101 MHz): δ 134.0, 133.7, 131.3, 131.2, 128.7, 128.6, 127.0 (d, \(J = 6.5\) Hz), 126.4, 126.0, 125.7, 124.3, 123.8, 68.1 (d, \(J = 5.5\) Hz), 64.0 (d, \(J = 5.8\) Hz), 16.3 (d, \(J = 6.8\) Hz).  \(^31P\) NMR (CDCl\(_3\), 162 MHz) δ -0.65.

\((E)\)-3-cyclohexylallyl diethyl phosphate (S4): colourless oil (2.004 g, 26% global yield).

\[
\text{Chemical Formula: } C_{13}H_{26}O_4P \\
\text{Molecular Weight: 278.31}
\]

**\(^1H\) NMR** (CDCl\(_3\), 400 MHz): δ 5.86 – 5.67 (m, 1H), 5.54 (ddd, \(J = 15.5, 6.4, 1.3\) Hz, 1H), 4.47 (ddd, \(J = 8.3, 6.4, 1.2, 0.8\) Hz, 2H), 4.10
(dq, $J = 7.9, 7.1$ Hz, 4H), 1.98 (ddd, $J = 14.1, 11.0, 2.5$ Hz, 1H), 1.83 – 1.63 (m, 6H), 1.33 (td, $J = 7.1, 1.0$ Hz, 6H), 1.29 – 0.94 (m, 4H). $^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 142.20, 122.07 (d, $J = 6.6$ Hz), 68.54 (d, $J = 5.6$ Hz), 63.76 (d, $J = 5.8$ Hz), 40.39, 32.62, 26.22, 26.06, 16.28 (d, $J = 6.8$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz) $\delta$ -0.77.

$(E)$-diethyl (3-phenylbut-2-en-1-yl) phosphate (S5):

![Chemical Structure](attachment:structure_s5.png)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36 – 7.31 (m, 2H), 7.29 – 7.16 (m, 3H), 5.88 (tq, $J = 6.9, 1.4$ Hz, 1H), 4.69 (ddd, $J = 8.4, 6.9, 0.8$ Hz, 2H), 4.06 (dq, $J = 8.0, 7.1$ Hz, 4H), 2.04 (dd, $J = 1.4, 0.7$ Hz, 3H), 1.27 (td, $J = 7.1, 1.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 142.5, 140.5, 128.4, 127.8, 126.0, 122.0 (d, $J = 6.9$ Hz), 64.4 (d, $J = 5.4$ Hz), 63.9 (d, $J = 5.9$ Hz), 16.3 (d, $J = 2.7$ Hz), 16.2. $^{31}$P NMR (CDCl$_3$, 162 MHz) $\delta$ –0.50

$(E)$-diethyl (3-(naphthalen-2-yl)but-2-en-1-yl) phosphate (S6):

![Chemical Structure](attachment:structure_s6.png)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.92 – 7.72 (m, 4H), 7.58 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.52 – 7.41 (m, 2H), 6.11 (tq, $J = 6.9, 1.4$ Hz, 1H), 4.83 (ddq, $J = 8.4, 7.0, 0.8$ Hz, 2H), 4.15 (dq, $J = 7.9, 7.1$ Hz, 4H), 2.22 (dd, $J = 1.4, 0.7$ Hz, 3H), 1.36 (td, $J = 7.1, 1.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 140.3, 139.7, 133.4, 133.0, 128.3, 128.0, 127.7, 126.4, 126.2, 124.9, 124.2, 122.6 (d, $J = 6.8$ Hz), 64.5 (d, $J = 5.4$ Hz), 63.9 (d, $J = 5.8$ Hz), 16.4 (d, $J = 2.6$ Hz), 16.3. $^{31}$P NMR (CDCl$_3$, 162 MHz) $\delta$ –0.48

diethyl ((2E,4E)-5-phenylpenta-2,4-dien-1-yl) phosphate (S7):

![Chemical Structure](attachment:structure_s7.png)

$^{1}$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 – 7.36 (m, 2H), 7.36 – 7.28 (m, 2H), 7.28 – 7.20 (m, 1H), 6.77 (ddd, $J = 15.7, 10.4, 0.8$ Hz, 1H), 6.60 (d, $J = 15.6$ Hz, 1H), 6.48 (dtd, $J = 15.2, 10.4, 1.3, 0.6$ Hz, 1H), 5.90 (ddd, $J = 15.2, 6.8, 6.0$ Hz, 1H), 4.63 (ddd, $J = 8.0, 6.4, 1.3$ Hz, 2H), 4.13 (dq, $J = 8.0, 7.1$ Hz, 4H), 1.35 (td, $J = 7.1, 1.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 136.9, 134.4, 134.3, 128.8, 128.0, 127.6, 127.3 (d, $J = 6.6$ Hz), 126.6, 67.7 (d, $J = 5.5$ Hz), 63.9 (d, $J = 5.8$ Hz), 16.3 (d, $J = 6.6$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz) $\delta$ –0.52.
1.5.2. **Representative procedure for copper-catalysed allylic alkylation of zinc reagents to allyl phosphates:**

1.5.2.1. **General procedure 1 using imidazolium salt in situ:**

In a flame-dried Schlenk tube under Argon, (CuOTf)$_2$toluene complex (0.0025 mmol, 0.5 mol%) and imidazolium salt (0.0055 mmol, 1.1 mol%) were dissolved in dry THF (0.5 mL) and the mixture was stirred for 10 min. The mixture was cooled down to 0 °C and n-BuLi (2.5M in hexane, 2.5 mol%) was added dropwise. The mixture was stirred for 10 min at 0 °C, then, allowed to warm up to room temperature and stirred 10 min at room temperature. Then, the reaction was cooled down to 0 °C and Et$_2$Zn (1M in hexane, 1.5 mmol, 3.0 equiv) was added dropwise. The resulting mixture was stirred at 0 °C for 10 min. After this time, the reaction was allowed to warm up to room temperature, stirred over 10 min and a solution of phosphate (0.5 mmol, 1.0 equiv) in dry THF (0.5 mL) was added dropwise. The reaction mixture was stirred at room temperature over 0.5 h (completion of the reaction followed by TLC analysis (eluent: pentane/EtOAc, 8/2). The reaction was quenched at 0 °C with HCl (1.0 mL, 1N). The SN$_2$/SN$_2^+$ ratio was determined by $^1$H NMR of the crude mixture. The reaction was then, extracted with diethyl ether (3x5 mL). Organic layers were gathered, dried over anhydrous MgSO$_4$, filtered and the solvent was carefully removed under reduced pressure. The crude was filtered on silica gel with pentane as eluent to afford the corresponding product as a colourless oil.

1.5.2.2. **General procedure 2 using oxazolidine ligand in situ:**

In a flame-dried Schlenk tube under Argon, the oxazolidine (0.006 mmol, 1.2 mol%) and Copper salt (0.005 mmol, 1.0 mol%) were dissolved in dry THF (0.5 mL). Then, the reaction was cooled down to 0 °C and Et$_2$Zn (1M in hexane, 1.5 mmol, 3.0 equiv) was added dropwise. The resulting mixture was stirred at 0 °C for 10 min. After this time, the reaction was allowed to warm up to room temperature and a solution of phosphate (0.5 mmol, 1.0 equiv) in dry THF (0.5 mL) was added dropwise. The reaction mixture was stirred at room temperature over 0.5 h (completion of the reaction followed by TLC analysis (eluent: pentane/EtOAc, 8/2). The reaction was quenched at 0 °C with HCl (1.0 mL, 1N). The SN$_2$/SN$_2^+$ ratio was determined by $^1$H NMR of the crude mixture. The reaction was then, extracted with diethyl ether (3x5 mL). Organic layers were gathered, dried over anhydrous MgSO$_4$, filtered and the solvent was carefully removed under reduced pressure. The crude was filtered on silica gel with pentane as eluent to afford the corresponding product as a colourless oil.
1.5.2.3. General procedure 3 for AAA with isolated Cu complex:

In a flame-dried Schlenk tube under Argon, Cu complex (0.005 mmol, 1.0 mol%) was dissolved in dry THF (0.5 mL). Then, the reaction was cooled down to 0 °C and Et₂Zn (1M in hexane, 1.5 mmol, 3.0 equiv) was added dropwise. The resulting mixture was stirred at 0 °C for 10 min. After this time, the reaction was allowed to warm up to room temperature and a solution of phosphate (0.5 mmol, 1.0 equiv) in dry THF (0.5 mL) was added dropwise. The reaction mixture was stirred at room temperature over 0.5 h (completion of the reaction followed by TLC analysis (eluent: pentane/EtOAc, 8/2). The reaction was quenched at 0 °C with HCl (1.0 mL, 1N). The SN₂/SN₂’ ratio was determined by ¹H NMR of the crude mixture. The reaction was then extracted with diethyl ether (3x5 mL). Organic layers were gathered, dried over anhydrous MgSO₄, filtered and the solvent was carefully removed under reduced pressure. The crude was filtered on silica gel with pentane as eluent to afford the corresponding product as a colourless oil.

1.5.3. Representative procedure for Copper-free allylic alkylation using zinc reagents to allyl phosphates:

In a flame-dried Schlenk tube under Argon, the oxazolidine (0.025 mmol, 5.0 mol%) was dissolved in dry THF (0.5 mL). Then, the reaction was cooled down to 0 °C and Et₂Zn (1M in hexane, 1.5 mmol, 3.0 equiv) was added dropwise. The resulting mixture was stirred at 0 °C for 10 min. After this time, the reaction was allowed to warm up to room temperature and a solution of phosphate (0.5 mmol, 1.0 equiv) in dry THF (0.5 mL) was added dropwise. The reaction mixture was stirred at room temperature over 12 h. The reaction was quenched at 0 °C with HCl (1.0 mL, 1N). The SN₂/SN₂’ ratio was determined by ¹H NMR of the crude mixture. The reaction was then extracted with diethyl ether (3x5 mL). Organic layers were gathered, dried over anhydrous MgSO₄, filtered and the solvent was carefully removed under reduced pressure. The crude was filtered on silica gel with pentane as eluent to afford the corresponding product as a colourless oil.

1.5.4. Characterization of catalysis products:

(pent-1-en-3-yl)benzene (γ-P1):

\[
\begin{align*}
\text{Chemical Formula: } & \text{C}_{11}\text{H}_{14} \\
\text{Molecular Weight: } & 146.23
\end{align*}
\]

¹H NMR (CDCl₃, 400 MHz): \(\delta 7.36 - 7.27 \text{ (m, 2H), 7.24 - 7.14 \text{ (m, 3H), 6.03 - 5.87 \text{ (m, 1H), 5.07 - 5.03 \text{ (m, 1H), 5.03 - 4.98 \text{ (m, 1H), 3.14 (q, J = 7.5 Hz, 1H), 1.74 (pd, J = 7.4, 4.1 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H).} \)
$^{13}$C NMR (CDCl$_3$, 101 MHz): $\delta$ 144.6, 142.4, 128.5, 127.8, 126.2, 114.2, 51.9, 28.5, 12.3. [$\alpha$]$^{25}_D$ ($c = 0.16$, CHCl$_3$) = +25 (89% ee). Analytical data for this compound were consistent with the previously reported data.$^6$

| Entry | Catalytic system (mol%) | Time (h) | Conv. (yield) (%) | $\gamma/\alpha$ ratio | ee (%) |
|-------|------------------------|----------|-------------------|----------------------|--------|
| 1     | L1aHPF$_6$/CuOTf$_2$.toluene (1.2/1) | 0.5      | >99 (62)         | >99:1               | 90     |
| 2     | 2a/CuOTf$_2$.toluene (1.2/1) | 0.5      | >99 (92)         | >99:1               | 89     |
| 3     | 2a/CuBr·SMe$_2$ (1.2/1) | 0.5      | >99 (97)         | >99:1               | 88     |
| 4     | CuBr·1a (1) | 0.5      | >99 (99)         | >99:1               | 89     |
| 5     | 2a (5) | 12       | >99 (98)         | >99:1               | 89     |
| 6     | CuBr·1b (1) | 23      | 87 (76)$^a$     | 97:3                | 91     |
| 7     | 2b (5) | 12       | Nr                | Nd                  |        |
| 8     | CuBr·1a (1) with EtMgBr | 0.5      | >99 (92)         | >99:1               | 90     |
| 9     | 2a (5) with EtMgBr | 0.5      | >99 (Nd)         | 21:79               | 39     |

$^a$ Conversions and yields were determined by $^1$H NMR spectroscopy using mesitylene as external standard (0.33 equiv regarding the substrate S1).

**Analytical parameters:**

**GC method 1:** capillary column: GTA: 30 m x 0.25 mm x 0.12 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (40 cm/sec), 20.0 split ratio, temperature program (Rate - Temperature - Hold Time): 50 °C - 80 min; 10 °C/min – 160 °C – 10 min.

- Racemic mixture:

![Graph](image_url)

| Peak | Retention time | Area | Height | % Area |
|------|----------------|------|--------|--------|
| 1    | 62.222         | 34005| 650    | 49.908 |
| 2    | 64.989         | 34130| 625    | 50.092 |

$^6$ M. A. Kacprzynski, A. H. Hoveyda, J. Am. Chem. Soc. 2004, 126, 10676-10681.
- **Table 1, entry 1**

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 61.934         | 41834 | 905    | 5.425  |
| 2    | 64.080         | 729249| 10559  | 94.575 |

- **Table 1, entry 2**

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 61.643         | 46601 | 947    | 5.586  |
| 2    | 63.690         | 787629| 10622  | 94.414 |

- **Table 1, entry 3**

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 61.714         | 34737 | 668    | 5.440  |
| 2    | 63.855         | 603760| 8247   | 94.560 |
Table 1, entry 4

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 61.673         | 42820 | 834    | 5.542  |
| 2    | 63.732         | 729892| 9840   | 94.458 |

Table 1, entry 5

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 61.377         | 107512| 2356   | 5.047  |
| 2    | 63.039         | 2022556| 20974 | 94.953 |

Table 1, entry 6

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 61.615         | 36178 | 729    | 4.629  |
| 2    | 63.662         | 745358| 10052  | 95.371 |
- Table 1, entry 7:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 62.830         | 40600 | 888    | 5.338  |
| 2    | 64.610         | 760638| 9231   | 95.662 |

- Table 1, entry 9:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 62.787         | 71732 | 1683   | 5.290  |
| 2    | 64.333         | 1284306| 14768  | 94.710 |

- Table 1, entry 10:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 62.914         | 155391| 2811   | 30.403 |
| 2    | 65.045         | 355713| 4822   | 69.597 |
2-(pent-1-en-3-yl)naphthalene (γ-P2):

| Entry | Catalytic system | Time (h) | Conv. (yield) (%) | γ/α ratio | ee (%) |
|-------|------------------|----------|------------------|-----------|--------|
| 1     | CuBr-1a          | 0.5      | >99 (96)         | >99:1     | 89     |
| 2     | 2a               | 12       | >99 (84)         | >99:1     | 89     |

^1H NMR (CDCl₃, 400 MHz): δ 7.87 (ddd, J = 8.2, 4.2, 2.7 Hz, 3H), 7.71 (d, J = 1.7 Hz, 1H), 7.59 – 7.48 (m, 2H), 7.42 (dd, J = 8.5, 1.8 Hz, 1H), 6.18 – 6.04 (m, 1H), 5.22 – 5.16 (m, 1H), 5.14 (d, J = 1.1 Hz, 1H), 3.39 (q, J = 7.4 Hz, 1H), 1.92 (pd, J = 7.4, 1.3 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H). ^13C NMR (CDCl₃, 101 MHz): δ 142.3, 142.0, 133.8, 132.4, 128.1, 127.8, 127.7, 126.5, 126.1, 126.0, 125.4, 114.4, 51.9, 28.3, 12.4. [α]D²⁵ (c = 0.5, CHCl₃) = + 5 (89% ee).

Analytical data for this compound were consistent with the previously reported data.⁶

Analytical parameters:

**HPLC method 1:** OJ-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane (100%) at 1.0 mL/min as mobile phase at 25°C and λ = 254 nm.

- Racemic mixture:

| Peak | Retention time | Area  | Height | % Area |
|------|---------------|-------|--------|--------|
| 1    | 15.613        | 17761103 | 487161 | 49.77  |
| 2    | 17.332        | 17926199 | 383228 | 50.23  |

- With CuBr-1a:
| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 16.089         | 569810| 26240  | 5.81   |
| 2    | 17.264         | 922969| 251652 | 94.19  |

- With 2a:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 16.611         | 587751| 26408  | 5.68   |
| 2    | 17.838         | 9758712| 253482| 94.32  |

1-(pent-1-en-3-yl)naphthalene ($\gamma$-P3a):

- **Entry**:  
  - **Catalytic system**: CuBr-1a, 2a  
  - **Time (h)**: 0.5, 12  
  - **Conv. (yield) (%)**: >99 (68), >99 (79)  
  - **$\gamma/\alpha$ ratio**: >99:1, >99:1  
  - **ee (%)**: 94, 94

$^1$H NMR (CDCl₃, 400 MHz): $\delta$ 8.18 (ddd, $J = 8.8$, 1.5, 0.7 Hz, 1H), 7.95 – 7.83 (m, 1H), 7.77 (ddd, $J = 8.1$, 1.5, 0.8 Hz, 1H), 7.66 – 7.35 (m, 4H), 6.22 – 5.99 (m, 1H), 5.22 – 5.09 (m, 2H), 4.06 (q, $J = 7.2$ Hz, 1H), 2.05 – 1.89 (m, 2H), 1.01 (td, $J = 7.4$, 0.5 Hz, 3H). $^{13}$C NMR (CDCl₃, 101 MHz): $\delta$ 141.9, 140.6, 134.2, 132.0, 129.1, 126.8, 125.8, 125.7, 125.4, 124.1, 123.6, 114.8,
46.2, 28.2, 12.5. \([\alpha]_D^{25} \text{ (c = 0.52, CHCl}_3) = \text{ – 21 (94% ee).}\) Analytical data for this compound were consistent with the previously reported data.\(^7\)

**Analytical parameters:**

**HPLC method 2:** OD-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane (100\%) at 1.0 mL/min as mobile phase at 25°C and \(\lambda = 254\) nm.

- **Racemic mixture:**

| Peak | Retention time | Area     | Height  | % Area |
|------|----------------|----------|---------|--------|
| 1    | 32.972         | 25124711 | 198738  | 49.77  |
| 2    | 39.104         | 25359233 | 154668  | 50.23  |

- **With CuBr-1a:**

| Peak | Retention time | Area     | Height  | % Area |
|------|----------------|----------|---------|--------|
| 1    | 30.911         | 6008318  | 63900   | 96.86  |
| 2    | 38.751         | 194856   | 2297    | 3.14   |

\(^7\) M. Magrez, Y. Le Guen, O. Baslé, C. Crévisy, M. Mauduit, *Chem. Eur. J.* 2013, **19**, 1199-1203.
• With 2a:

| Peak | Retention time | Area | Height | % Area |
|------|----------------|------|--------|--------|
| 1    | 32.556         | 4182405 | 44782 | 97.13  |
| 2    | 41.146         | 123590  | 1320  | 2.87   |

1-(but-3-en-2-yl)naphthalene (γ-P3b):

| Entry | Catalytic system (mol%) | Time (h) | Conv. (yield) (%) | γ/α ratio | ee (%) |
|-------|-------------------------|----------|-------------------|-----------|--------|
| 1     | CuBr-1a                 | 0.5      | >99 (99)          | >99:1     | 96     |
| 2     | 2a                      | 12       | >99 (68)          | >99:1     | 96     |

$^1$H NMR (CDCl$_3$, 400 MHz): δ 8.19 (ddd, $J = 8.4$, 1.5, 0.7 Hz, 1H), 8.01 – 7.86 (m, 1H), 7.78 (dt, $J = 8.0$, 1.1 Hz, 1H), 7.62 – 7.34 (m, 4H), 6.32 – 6.14 (m, 1H), 5.25 – 5.08 (m, 2H), 4.36 (qd, $J = 7.0$, 5.4 Hz, 1H), 1.58 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz): δ 143.3, 141.9, 134.4, 131.9, 129.3, 127.2, 126.2, 126.1, 125.8, 124.1, 123.9, 114.1, 38.3, 20.7. [α]$_D^{25}$ (c = 0.31, CHCl$_3$) = – 22 (96% ee). Analytical data for this compound were consistent with the previously reported data.⁷

**Analytical parameters:**

**GC method 2:** capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (40 cm/sec), 5.0 split ratio, temperature program (Rate - Temperature - Hold Time): 120 °C - 95 min; 10 °C/min – 170 °C – 10 min.
• Racemic mixture:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 76.430         | 528674| 15722  | 49.644 |
| 2    | 77.736         | 536266| 16155  | 50.356 |

• With CuBr-1a:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 76.721         | 8750  | 276    | 1.778  |
| 2    | 77.886         | 483409| 14492  | 98.222 |

• With 2a:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 76.543         | 46205 | 1267   | 1.906  |
| 2    | 78.035         | 2378539| 67807  | 98.094 |
(pent-1-en-3-yl)cyclohexane (γ-P4):

| Entry | Catalytic system (mol%) | Time (h) | Conv. (yield) (%) | γ/α ratio | ee (%) |
|-------|-------------------------|----------|------------------|-------------|--------|
| 1     | CuBr-1a                 | 0.5      | >99 (71)         | >99:1       | 82     |
| 2*    | 2a                      | 24       | 64 (25)          | >99:1       | 81     |

*The conversion and yield were determined by 1H NMR using mesitylene as external standard (0.33 equiv regarding the substrate S4).

1H NMR (CDCl₃, 400 MHz): δ 5.55 (ddd, J = 17.0, 10.2, 9.3 Hz, 1H), 5.08 – 4.80 (m, 2H), 1.77 – 1.60 (m, 6H), 1.54 – 1.46 (m, 1H), 1.31 – 1.08 (m, 5H), 1.07 – 0.87 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). 13C NMR (CDCl₃, 101 MHz): δ 141.6, 115.1, 52.2, 41.6, 31.3, 29.9, 27.0, 26.9, 26.8, 24.5, 12.2. [α]D₂₅ (c = 0.36, CHCl₃) = +6 (82% ee). Analytical data for this compound were consistent with the previously reported data.⁷

Analytical parameters:

GC method 3: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (40 cm/sec), 5.0 split ratio, temperature program (Rate - Temperature - Hold Time): 50 °C - 80 min; 0.3 °C/min – 65 °C – 0 min; 10 °C/min – 180 °C – 10 min.

- Racemic mixture:

| Peak | Retention time | Area   | Height | % Area  |
|------|----------------|--------|--------|---------|
| 1    | 93.649         | 156103 | 4092   | 50.045  |
| 2    | 95.172         | 155824 | 3573   | 49.955  |

- With CuBr-1a:
### Table 1: 

| Peak | Retention time | Area | Height | % Area |
|------|----------------|------|--------|--------|
| 1    | 92.494         | 18126| 605    | 9.959  |
| 2    | 93.457         | 163886| 3717  | 90.0441|

- With 2a:

(3-methylpent-1-en-3-yl)benzene (γ-P5):

![Chemical Structure](image)

The general procedure 3 for Cu-AAA reactions was followed using S5 (142.3 mg, 0.5 mmol, 1.0 equiv), Et₂Zn (1 M in hexane, 1.5 mL, 1.5 mmol, 3.0 equiv) and a stock solution of the complex CuBr-1a (2.37 mg, 0.005 mmol, 1.0 mol%). The desired product γ-P5 was obtained as a colourless oil (63.3 mg, 89% yield).

**1H NMR** (400 MHz, CDCl₃) δ 7.35 – 7.28 (m, 4H), 7.22 – 7.16 (m, 1H), 6.04 (ddd, J = 17.5, 10.8, 1.6 Hz, 1H), 5.17 – 5.00 (m, 2H), 1.93 – 1.70 (m, 2H), 1.36 (s, 3H), 0.78 (td, J = 7.4, 1.6 Hz, 3H). **13C NMR** (101 MHz, CDCl₃) δ 147.6, 147.1, 128.2, 126.9, 125.8, 111.9, 44.7, 33.6, 24.5, 9.1. [α]D²⁵ (c = 0.16, CHCl₃) = +10 (85% ee). Analytical data for this compound were consistent with the previously reported data.⁷

**Analytical parameters:**

**GC method 4:** capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (30 cm/sec), 10 split ratio, temperature program (Rate - Temperature - Hold Time): 80 °C - 55 min; 10 °C/min – 160 °C – 10 min.
• Racemic mixture:

| Peak | Retention time | Area    | Height  | % Area |
|------|----------------|---------|---------|--------|
| 1    | 42.051         | 793030  | 41563   | 49.942 |
| 2    | 43.049         | 794871  | 36502   | 50.058 |

• With CuBr-1a:

| Peak | Retention time | Area    | Height  | % Area |
|------|----------------|---------|---------|--------|
| 1    | 42.051         | 164547  | 9928    | 7.356  |
| 2    | 42.681         | 2072413 | 81894   | 92.644 |

(S)-2-(3-methylpent-1-en-3-yl)naphthalene (γ-P6):

The general procedure 3 for Cu-AAA reactions was followed using S6 (134.0 mg, 0.4 mmol, 1.0 equiv), Et₂Zn (1 M in hexane, 1.2 mL, 1.2 mmol, 3.0 equiv) and a stock solution of the complex CuBr-1a (1.90 mg, 0.004 mmol, 1.0 mol%). The desired product γ-P6 was obtained as a colourless oil (79.9 mg, 95% yield).

$^1$H NMR (400 MHz, CDCl₃) δ 7.90 – 7.74 (m, 4H), 7.58 – 7.39 (m, 3H), 6.16 (ddd, J = 17.5, 10.6, 2.1 Hz, 1H), 5.25 – 5.09 (m, 2H), 2.05 – 1.84 (m, 2H), 1.51 (s, 3H), 0.85 (td, J = 7.6, 2.6 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl₃) δ 147.0, 145.0, 133.5, 132.0, 128.1, 127.7, 127.5,
125.94, 125.9, 125.5, 125.0, 112.3, 44.9, 33.4, 24.5, 9.1. \([\alpha]D^25\) (c = 0.2, CHCl$_3$) = +17 (84% ee). Analytical data for this compound were consistent with the previously reported data.\(^8\)

**Analytical parameters:**

**HPLC method 2:** OJ-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane (100%) at 1.0 mL/min as mobile phase at 25°C and \(\lambda = 254\) nm.

- **Racemic mixture:**

  ![Racemic mixture graph](image)

  | Peak | Retention time | Area    | Height   | % Area  |
  |------|----------------|---------|----------|---------|
  | 1    | 13.235         | 12971188| 417622   | 50.16   |
  | 2    | 15.432         | 12889462| 303250   | 49.84   |

- **With CuBr-1a:**

  ![CuBr-1a graph](image)

  | Peak | Retention time | Area    | Height   | % Area  |
  |------|----------------|---------|----------|---------|
  | 1    | 14.160         | 3788473 | 126433   | 91.76   |
  | 2    | 16.806         | 340047  | 9689     | 8.24    |

\(^8\) W. Xiong, G. Xu, X. Yu, W. Tang, *Organometallics* 2019, 38, 4003-4013.
(S,E)-(3-ethylpenta-1,4-dien-1-yl)benzene ($\gamma$-P7a):

The general procedure 3 for Cu-AAA reactions was followed using S7 (148.5 mg, 0.5 mmol, 1.0 equiv), Et$_2$Zn (1 M in hexane, 1.5 mL, 1.5 mmol, 3.0 equiv) and a stock solution of the complex CuBr-1a (2.37 mg, 0.005 mmol, 1.0 mol%). The desired product $\gamma$-P7a was obtained as a colourless oil (77.5 mg, 90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.42 (m, 2H), 7.39 – 7.34 (m, 2H), 7.30 – 7.24 (m, 1H), 6.51 – 6.39 (m, 1H), 6.20 (dd, $J = 15.9$, 7.7 Hz, 1H), 5.88 (ddd, $J = 17.5$, 10.3, 7.3 Hz, 1H), 5.18 – 5.11 (m, 2H), 2.90 – 2.80 (m, 1H), 1.62 (p, $J = 7.3$ Hz, 2H), 1.02 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 141.3, 137.8, 133.2, 129.8, 128.6, 127.1, 126.2, 114.5, 49.0, 27.8, 11.9. $[\alpha]_D^{25}$ (c = 0.22, CHCl$_3$) = +61 (71% ee). Analytical data for this compound were consistent with the previously reported data.$^6$

Analytical parameters:

**GC method 5:** capillary column: $\beta$-dex 325: 30 m x 0.25 mm x 0.25 $\mu$m, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1 $\mu$L. Helium as carrier gas (39.1 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 80 °C - 175 min; 10 °C/min – 160 °C – 10 min.

- Racemic mixture:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 136.923        | 217633| 3444   | 50.086 |
| 2    | 139.418        | 216890| 3029   | 49.914 |
With CuBr-1a:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 137.450        | 61864 | 1159   | 14.598 |
| 2    | 139.140        | 361919| 4912   | 85.402 |

\((E)-(3\text{-}\text{methylpent-1,4-dien-1-yl})\text{benzene (γ-P7b)}:\)

\[CH_{12}H_{14}\]

\[\text{Molecular Weight: 158.24}\]

The general procedure 3 for Cu-AAA reactions was followed using S7 (148.3 mg, 0.5 mmol, 1.0 equiv), Me\(_2\)Zn (1.2 M in Toluene, 1.3 mL, 1.56 mmol, 3.1 equiv) and a stock solution of the complex CuBr-1a (2.37 mg, 0.005 mmol, 1.0 mol%). The desired product γ-P7b was obtained as a colourless oil (68.1 mg, 86% yield).

\(^1H\text{ NMR}\ (400 \text{ MHz, } CDCl_3) \delta 7.49 – 7.41 (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.22 (m, 1H), 6.46 (dd, J = 16.0, 1.2 Hz, 1H), 6.25 (dd, J = 15.9, 7.0 Hz, 1H), 5.95 (ddd, J = 17.0, 10.2, 6.5 Hz, 1H), 5.20 – 5.05 (m, 2H), 3.11 (dddd, J = 13.7, 8.2, 6.8, 5.4, 1.3 Hz, 1H), 1.28 (d, J = 6.8 Hz, 3H). \(^13C\text{ NMR}\ (101 \text{ MHz, } CDCl_3) \delta 142.6, 137.8, 134.4, 128.8, 128.6, 127.1, 126.2, 113.5, 40.8, 19.9. [\alpha]D^{25} (c = 0.17, CHCl_3) = +47 (88% ee).\] Analytical data for this compound were consistent with the previously reported data.\(^7\)

**Analytical parameters:**

**GC method 6:** capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (39.1 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 80 °C - 100 min; 10 °C/min – 160 °C – 10 min.
• Racemic mixture:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 74.462         | 409871| 12257  | 49.941 |
| 2    | 76.157         | 409531| 11843  | 50.059 |

• With CuBr-1a:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 75.448         | 24325 | 888    | 5.819  |
| 2    | 76.549         | 393720| 8815   | 94.181 |

1.6. Asymmetric Conjugated Addition:

1.6.1. Data of substrates:

3-Methyl-2-cyclohexenone S8 and cyclohexenone S9 were purchased from Alfa Aesar and used without further purification. (E)-3-(prop-1-enyl)cyclohex-2-enone S10 and (E)-3-(hex-1-en-1-yl)cyclohex-2-en-1-one S11 were prepared using known procedures.9

9 H. Hénon, M. Mauduit, A. Alexakis, Angew. Chem. Int. Ed. 2008, 47, 9122-9124.
(E)-3-(prop-1-enyl)cyclohex-2-enone (S10):

\[ \text{Chemical Formula: } C_{9}H_{12}O \]

\[ \text{Molecular Weight: 136.19} \]

\[ ^{1}H \text{ NMR (CDCl}_{3} \text{, 400 MHz): } \delta 6.24 - 6.18 \text{ (m, 2H, } 2\text{CCH}_{\text{Alkene}}), 5.86 \text{ (s, 1H, } \text{CH}_{\text{Alkene}}), 2.44 \text{ (td, } J = 6.1, 1.3 \text{ Hz, 2H, } \text{CH}_{2}), 2.43 - 2.35 \text{ (m, 2H, } \text{CH}_{2}), 2.10 - 1.95 \text{ (m, 2H, } \text{CH}_{2}), 1.88 \text{ (dd, } J = 5.2, 0.6 \text{ Hz, 3H, } \text{CH}_{3}). \]

\[ ^{13}C \text{ NMR (101 MHz, CDCl}_{3} \text{): } \delta 200.71, 157.75, 134.01, 132.89, 126.34, 37.79, 25.15, 22.47, 19.00. \text{ Analytical data for this compound were consistent with the previously reported data.}^{9} \]

(E)-3-(hex-1-en-1-yl)cyclohex-2-en-1-one (S11):

\[ \text{Chemical Formula: } C_{9}H_{12}O \]

\[ \text{Molecular Weight: 178.28} \]

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_{3} \text{): } \delta 6.27 - 6.12 \text{ (m, 2H), 5.88 - 5.83 (m, 1H), 2.45 (td, } J = 6.1, 1.4 \text{ Hz, 2H), 2.41 - 2.35 (m, 2H), 2.22 - 2.15 (m, 2H), 2.06 - 1.97 (m, 2H), 1.46 - 1.36 (m, 2H), 1.36 - 1.28 (m, 2H), 0.90 (t, } J = 7.2 \text{ Hz, 3H). }^{13}C \text{ NMR (101 MHz, CDCl}_{3} \text{): } \delta 200.4, 157.7, 139.3, 131.4, 126.4, 37.8, 33.0, 31.1, 25.1, 22.4, 22.3, 13.9. \text{ Analytical data for this compound were consistent with the previously reported data.}^{10} \]

1.6.2. General procedure for 1,4-addition:

1.6.2.1. General procedure 1 using imidazolium salt in situ:

In a flame-dried Schlenk tube under Argon, (CuOTf)$_2$toluene complex (0.005 mmol, 0.5 mol%) and imidazolium salt (0.012 mmol, 1.2 mol%) were dissolved in dry EtOAc (0.5 mL) and the mixture was stirred for 10 min. The mixture was cooled down to 0 °C and n-BuLi (2.5M in hexane, 2.5 mol%) was added dropwise. The mixture was stirred for 10 min at 0 °C, then, allowed to warm up to room temperature and stirred 10 min at room temperature. Then, Et$_2$Zn (1M in hexane, 3.0 mL, 3.0 mmol, 3.0 equiv) was added dropwise and the reaction mixture was stirred 10 min at room temperature. The reaction mixture was cooled down to 0 °C and a solution of 3-methylcyclohexenone (115 µL, 1.0 mmol, 1.0 equiv) in EtOAc (0.5 mL, 0.2 mL and 0.3 mL to rince) was added dropwise. As soon as the addition of the substrate was completed, the ice bath was removed. The reaction mixture was stirred at room temperature over 16 h. Upon completion of the reaction (TLC monitoring), HCl (1N, 1.0 mL) was added at 0 °C and the compound was extracted with diethylether (3x5.0 mL). The combined organic layers were then washed with saturated NaHCO$_3$ aqueous solution (15 mL), brine (15 mL), and dried over MgSO$_4$. The solvents were carefully removed under vacuum. The crude product

\[ ^{10} J. \text{ Wencel-Delord, A. Alexakis, C. Crévisy, M. Mauduit, } \text{Org. Lett. 2010, 12, 4335-4337.} \]
was purified by silica gel chromatography (pentane/Et<sub>2</sub>O: 5/1) to isolate the corresponding product as a colourless oil.

1.6.2.2. **General procedure 2 using oxazolidine in situ:**

In a flame-dried Schlenk tube under Argon, (CuOTf)<sub>2</sub>-toluene complex (0.005 mmol, 0.5 mol%) or CuBr·SMe<sub>2</sub> (0.01 mmol, 1.0 mol%) and the oxazolidine (0.012 mmol, 1.2 mol%) were dissolved in dry EtOAc (0.5 mL) and the mixture was stirred for 10 min. Then, Et<sub>2</sub>Zn (1M in hexane, 3.0 mL, 3.0 mmol, 3.0 equiv) was added dropwise and the reaction mixture was stirred 10 min at room temperature. The reaction mixture was cooled down to 0 °C and a solution of 3-methylcyclohexenone (115 µL, 1.0 mmol, 1.0 equiv) in EtOAc (0.5 mL, 0.2 mL and 0.3 mL to rinse) was added dropwise. As soon as the addition of the substrate was completed, the ice bath was removed. The reaction mixture was stirred at room temperature over 16 h. Upon completion of the reaction (TLC monitoring), HCl (1N, 1.0 mL) was added at 0 °C and the compound was extracted with diethylether (3x5.0 mL). The combined organic layers were then washed with saturated NaHCO<sub>3</sub> aqueous solution (15 mL), brine (15 mL), and dried over MgSO<sub>4</sub>. The solvents were carefully removed under vacuum. The crude product was purified by silica gel chromatography (pentane/Et<sub>2</sub>O: 5/1) to isolate the corresponding product as a colourless oil.

1.6.2.3. **General procedure 3 using isolated complex:**

In a flame-dried Schlenk tube under Argon, copper complex (0.01 mmol, 1.0 mol%) was dissolved in dry EtOAc (0.5 mL) and the mixture was stirred for 10 min. Then, R<sub>2</sub>Zn (3.0 or 6.0 equiv) was added dropwise and the reaction mixture was stirred 10 min at room temperature. The reaction mixture was cooled down to 0 °C and a solution of enone (1.0 mmol, 1.0 equiv) in EtOAc (0.5 mL, 0.2 mL and 0.3 mL to rinse) was added dropwise. As soon as the addition of the substrate was completed, the ice bath was removed. The reaction mixture was stirred at room temperature over 16 h. Upon completion of the reaction (TLC monitoring), HCl (1N, 1.0 mL) was added at 0 °C and the compound was extracted with diethylether (3x5.0 mL). The combined organic layers were then washed with saturated NaHCO<sub>3</sub> aqueous solution (15 mL), brine (15 mL), and dried over MgSO<sub>4</sub>. The solvents were carefully removed under vacuum. The crude product was purified by silica gel chromatography (pentane/Et<sub>2</sub>O: 5/1) to isolate the corresponding product as a colourless oil.
1.6.2.4. General procedure 4 using Grignard reagent:

A flame-dried Schlenk tube was charged with copper complex (3.0 mol%). The system was again dried in vacuo at rt. for 15 minutes. Then, dry Et₂O (1.3 mL) was added and the mixture was cooled down to 0 °C in an ethanol cold bath. The EtMgBr (3M in Et₂O, 1.2 equiv) was added dropwise to the solution for 5 minutes. A solution of the 3-methyl-2-cyclohexenone (0.5 mmol) in Et₂O (5.0 mL) was then added dropwise to the solution at 0 °C over 15 minutes with a syringe pump, then the solution was stirred for 30 minutes at 0 °C. The reaction was hydrolyzed at 0 °C by addition of HCl 1M (1.0 mL) and the aqueous layer was separated and extracted further with diethyl ether (3x10 mL). The combined organic layers were dried on MgSO₄, filtrated and concentrated in vacuo to give an oily residue. That crude was purified by flash chromatography on a silica gel (pentane/Et₂O: 5/1) to give the pure product as a colourless oil.

1.6.3. General procedure for 1,6-addition:

1.6.3.1. General procedure 1 using imidazolium salt in situ:

A flame-dried Schlenk tube was charged with Cu(OTf)₂ (0.022 mmol, 4.0 mol%), and the imidazolium salt (0.03 mmol, 6.0 mol%). The system was flushed with argon, and dry THF (1.0 mL) was added. The solution was stirred for 10 min and n-BuLi (2.5M in hexane, 0.08 mmol, 16 mol%) was added and stirred again for 10 min. 0.5 mL of this solution was transferred to a flame-dried Schlenk tube. Then, R₂Zn (1.5 mmol, 3.0 equiv) was added dropwise to the Schlenk and the reaction mixture was stirred 10 min at room temperature and 10 min at 0 °C. A solution of dienone (70.0 mg, 0.51 mmol, 1.0 equiv) in dry THF (0.5 mL) was added to the reaction at 0 °C and the solution was stirred at room temperature for 1.5 h. The reaction was quenched with NH₄Cl solid (500 mg). The solution was stirred for 1 h and then dry DCM (4.0 mL) and DBU (110 µL, 0.74 mmol, 1.44 equiv) was added to the solution. The reaction was stirred for 5 h and then filtered on a small pad of silica, washed with ethyl acetate, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (pentane/Et₂O: 85/15) to afford the desired compound as colourless oil.

1.6.3.2. General procedure 2 using oxazolidine in situ:

A flame-dried Schlenk tube under argon was charged with Cu(OTf)₂ or CuBr·SMe₂ (0.011 mmol, 2.0mol%), and the oxazolidine (0.015 mmol, 3.0mol%) and dry THF (0.5 mL).
Then, the solution was stirred 10 min and R$_2$Zn (1.5 mmol, 3.0 equiv) was added dropwise to the Schlenk. The reaction mixture was stirred 10 min at room temperature and 10 min at 0 °C. A solution of dienone (70.0 mg, 0.51 mmol, 1.0 equiv) in dry THF (0.5 mL) was added to the reaction at 0 °C and the solution was stirred at room temperature for 1.5 h. The reaction was quenched with NH$_4$Cl solid (500 mg). The solution was stirred for 1 h and then dry DCM (4.0 mL) and DBU (110 µL, 0.74 mmol, 1.44 equiv) was added to the solution. The reaction was stirred for 5 h and then filtered on a small pad of silica, washed with ethyl acetate, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (pentane/Et$_2$O: 85/15) to afford the desired compound as colourless oil.

1.6.3.3. **General procedure 3 using isolated complex:**

A flame-dried Schlenk tube under argon was charged with the copper complex (0.011 mmol, 2.0 mol%) and dry THF (0.5 mL). Then, the solution was stirred 10 min and R$_2$Zn (3.0 equiv) was added dropwise to the Schlenk. The reaction mixture was stirred 10 min at room temperature and 10 min at 0 °C. A solution of dienone (70.0 mg, 0.51 mmol, 1.0 equiv) in dry THF (0.5 mL) was added to the reaction at 0 °C and the solution was stirred at room temperature for 1.5 h. The reaction was quenched with NH$_4$Cl solid (500 mg). The solution was stirred for 1 h and then dry DCM (4.0 mL) and DBU (110 µL, 0.74 mmol, 1.44 equiv) was added to the solution. The reaction was stirred for 5 h and then filtered on a small pad of silica, washed with ethyl acetate, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel (pentane/Et$_2$O: 85/15) to afford the desired compound as colourless oil.

1.6.3.4. **General procedure 4 using Grignard reagent:**

A flame-dried Schlenk tube was charged with copper complex (3.0 mol%). The system was again dried in vacuo at rt. for 15 minutes. Then, dry DCM (1.5 mL) was added and the mixture was cooled down to 0 °C in an ethanol cold bath. The Grignard reagent (1.2 equiv) was added dropwise to the solution for 5 minutes. A solution of the dienone (0.5 mmol) in DCM (5.0 mL) was then added dropwise to the solution at -10 °C over 15 minutes with a syringe pump, then the solution was stirred for 1 h at -10 °C. The reaction was hydrolysed at -10 °C with a saturated solution of NH$_4$Cl (0.5 mL). The solution was stirred for 1 h and then dry DCM (4.0 mL) and DBU (110 µL, 0.74 mmol, 1.44 equiv) was added to the solution. The reaction was stirred for 5 h and then filtered on a small pad of silica, washed with ethyl acetate, and concentrated under vacuum.
vacuum. The crude product was purified by flash chromatography on silica gel (pentane/Et<sub>2</sub>O: 85/15) to afford the desired compound as colourless oil.

### 1.6.4. Catalysis products:

3-ethyl-3-methylcyclohexanone (P8a):

![Chemical structure of P8a](image)

**Chemical Formula:** C<sub>10</sub>H<sub>16</sub>O  
**Molecular Weight:** 140.23

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ 2.21 (t, <i>J</i> = 6.8 Hz, 2H, <CH<sub>2</sub>/>), 2.12 (d, <i>J</i> = 13.5 Hz, 1H, <CH<sub>2</sub>/>), 2.04 (d, <i>J</i> = 13.5 Hz, 1H, <CH<sub>2</sub>/>), 1.85 – 1.76 (m, 2H, <CH<sub>2</sub>/>), 1.61 – 1.53 (m, 1H, <CH<sub>2</sub>/>), 1.53 – 1.43 (m, 1H, <CH<sub>2</sub>/>), 1.31 – 1.21 (m, 2H, <CH<sub>2</sub>/>), 0.83 (s, 3H, <CH<sub>3</sub>/>), 0.78 (t, <i>J</i> = 7.5 Hz, 3H, <CH<sub>3</sub>/>).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ 211.72 (C=O), 52.52 (C<sub>H</sub>.), 40.19 (C<sub>quat</sub>), 37.81 (C<sub>H</sub>.), 33.08 (C<sub>H</sub>.), 23.56 (C<sub>H</sub>.), 21.26 (C<sub>H</sub>.), 6.88 (C<sub>H</sub>.).

<sup>25</sup>αD<sub>25</sub> (c = 0.53, CHCl<sub>3</sub>) = +5.4 (99% ee). Analytical data for this compound were consistent with the previously reported data.\textsuperscript{11}

| Entry | Catalytic system (mol%) | Conv. (yield) (%) | ee (%) |
|-------|-------------------------|-------------------|--------|
| 1     | L1bOPFP<sub>6</sub>/CuOTf<sub>2</sub>·toluene (1.2/1) | >99 (80) | 99 |
| 2     | 2b/CuOTf<sub>2</sub>·toluene (1.2/1) | 35 (23) | 97 |
| 3     | 2b/CuBr·SMe<sub>2</sub> (1.2/1) | >99 (97) | >99 |
| 4     | CuBr-1b (1) | >99 (67) | 99 |
| 5     | 2b (5) | Nr | Nd |
| 6     | CuBr-1a (1) | >99 (84)* | 85 |
| 7     | 2a (5) | Nr | Nd |
| 8     | CuBr-1b (1) with EtMgBr | >99 (86) | 77 |
| 9     | 2b (5) with EtMgBr | >99 (Mr) | Nd |

**Analytical parameters:**

**GC method 7:** capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (40 cm/sec), 5.0 split ratio, temperature program (Rate - Temperature - Hold Time): 100 °C - 20 min; 3.0 °C/min – 125 °C – 0 min; 20 °C/min – 160 °C – 10 min.

\textsuperscript{11} C. Jahier-Diallo, M. S. T. Morin, P. Queval, M. Rouen, I. Artur, P. Querard, L. Toupet, C. Crévisy, O. Baslé, M. Mauduit, *Chem. Eur. J.* 2015, 21, 993-997.
• Racemic mixture:

![Graph of racemic mixture](image_url)

| Peak | Retention time | Area   | Height  | % Area |
|------|----------------|--------|---------|--------|
| 1    | 13.485         | 43482  | 6076    | 50.008 |
| 2    | 14.200         | 43468  | 5728    | 49.992 |

• Table 2, entry 1:

![Graph of Table 2, entry 1](image_url)

| Peak | Retention time | Area   | Height  | % Area |
|------|----------------|--------|---------|--------|
| 1    | 13.397         | 2147649| 129741  | 99.297 |
| 2    | 14.486         | 15207  | 1465    | 0.703  |
- Table 2, entry 2:

| Peak | Retention time | Area   | Height | % Area  |
|------|----------------|--------|--------|---------|
| 1    | 13.432         | 1430946| 99648  | 98.274  |
| 2    | 14.447         | 25134  | 2750   | 3.197   |

- Table 2, entry 3:

| Peak | Retention time | Area   | Height | % Area  |
|------|----------------|--------|--------|---------|
| 1    | 13.607         | 635263 | 58140  | 99.738  |
| 2    | 14.527         | 1671   | 206    | 3.555   |
- Table 2, entry 4:

| Peak | Retention time | Area    | Height  | % Area |
|------|---------------|---------|---------|--------|
| 1    | 13.425        | 1916278 | 121105  | 99.598 |
| 2    | 14.499        | 7725    | 768     | 0.402  |

- Table 2, entry 6:

| Peak | Retention time | Area    | Height  | % Area |
|------|---------------|---------|---------|--------|
| 1    | 13.448        | 1648519 | 108262  | 92.419 |
| 2    | 14.437        | 135230  | 13821   | 2.924  |
Table 2, entry 8:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 13.246         | 80623 | 70149  | 88.611 |
| 2    | 14.112         | 103621| 12245  | 11.389 |

3-isopropyl-3-methylcyclohexan-1-one (P8b):

The general procedure 3 for 1,4-ACA reactions was followed using S8 (115 μL, 1.0 mmol, 1.0 equiv), tPr2Zn (1M in Toluene, 3.0 mL, 3.0 mmol, 3.0 equiv) and a stock solution of the complex CuBr-1b (4.31 mg, 0.01 mmol, 1.0 mol%). The desired product P8b was obtained as a colourless oil (112.6 mg, 73% yield).

$^1$H NMR (400 MHz, CDCl₃) δ 2.33 – 2.18 (m, 3H), 2.08 (dt, $J = 13.5, 1.7$ Hz, 1H), 1.96 – 1.74 (m, 2H), 1.68 – 1.46 (m, 3H), 0.85 (d, $J = 6.8$ Hz, 6H), 0.79 (s, 3H). $^{13}$C NMR (101 MHz, CDCl₃) δ 213.1, 52.0, 41.3, 41.2, 36.4, 34.2, 22.1, 19.9, 17.1, 16.9. [α]D$^{25}$ (c = 0.29, CHCl₃) = +16 (93% ee). Analytical data for this compound were consistent with the previously reported data.

Analytical parameters:

GC method 8: capillary column: Lipodex E: 25 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (90 cm/sec), 40.0 split ratio, temperature program (Rate - Temperature - Hold Time): 60 °C - 0 min; 1.0 °C/min – 130 °C – 0 min; 10 °C/min – 160 °C – 10 min.

12 S. Kehrli, D. Martin, D. Rix, M. Mauduit, A. Alexakis, Chem. Eur. J. 2010, 16, 9890-9904.
• Racemic mixture:

![Graph of racemic mixture with retention times and areas]

| Peak | Retention time | Area    | Height | % Area |
|------|---------------|---------|--------|--------|
| 1    | 21.747        | 1493570 | 17519  | 50.259 |
| 2    | 25.211        | 1478185 | 18024  | 49.741 |

• With CuBr-1b:

![Graph of compound with CuBr-1b with retention times and areas]

| Peak | Retention time | Area    | Height | % Area |
|------|---------------|---------|--------|--------|
| 1    | 21.951        | 671311  | 9031   | 96.834 |
| 2    | 25.661        | 21945   | 357    | 3.166  |
3-methyl-3-phenylcyclohexan-1-one (P8c):

The general procedure 3 for 1,4-ACA reactions was followed using S8 (29 μL, 0.25 mmol, 1.0 equiv), a solution of Ph₂Zn (330 mg, 1.5 mmol, 6.0 equiv) in Toluene (3.0 mL) and a stock solution of the complex CuBr-1b (1.08 mg, 0.0025 mmol, 1.0 mol%). The desired product P8c was obtained as a colourless oil (36.7 mg, 78% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.32 (s, 4H), 7.24 – 7.17 (m, 1H), 2.88 (dt, \(J = 14.4, 1.1\) Hz, 1H), 2.44 (dq, \(J = 14.1, 0.8\) Hz, 1H), 2.32 (ddt, \(J = 7.3, 6.5, 0.8\) Hz, 2H), 2.19 (dddd, \(J = 13.6, 8.0, 3.6, 1.6\) Hz, 1H), 1.98 – 1.82 (m, 2H), 1.72 – 1.61 (m, 1H), 1.33 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 211.6, 147.6, 128.6, 126.3, 125.7, 53.2, 42.9, 40.9, 38.1, 29.9, 22.1. [\(\alpha\)]\(_D\)\(^{25}\) (c = 0.51, CHCl\(_3\)) = –37 (99% ee). Analytical data for this compound were consistent with the previously reported data.\(^{11}\)

**Analytical parameters:**

**GC method 9:** capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (30 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 120 °C - 90 min; 3.0 °C/min – 170 °C – 10 min.

- Racemic mixture:

| Peak | Retention time | Area   | Height | % Area |
|------|---------------|--------|--------|--------|
| 1    | 99.029        | 37004  | 2652   | 48.923 |
| 2    | 99.586        | 38634  | 2818   | 51.077 |
• With CuBr-1b:

![Graph](image)

| Peak | Retention time | Area   | Height | % Area |
|------|----------------|--------|--------|--------|
| 1    | 98.737         | 2335431| 117739 | 99.568 |
| 2    | 99.624         | 10124  | 627    | 0.432  |

3-phenylcyclohexan-1-one (P9):

![Structure](image)

Chemical Formula: C12H14O  
Molecular Weight: 174.24

The general procedure 3 for 1,4-ACA reactions was followed using S9 (24.0 mg, 0.25 mmol, 1.0 equiv), a solution of Ph2Zn (165 mg, 0.75 mmol, 3.0 equiv) in Toluene (1.5 mL) and a stock solution of the complex CuBr-1b (1.08 mg, 0.0025 mmol, 1.0 mol%). The desired product P9 was obtained as a colourless oil (30.9 mg, 71% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.23 (m, 2H), 7.22 – 7.09 (m, 3H), 2.94 (tt, \(J = 11.6, 4.0\) Hz, 1H), 2.57 – 2.25 (m, 4H), 2.13 – 1.97 (m, 2H), 1.85 – 1.64 (m, 2H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 211.1, 144.3, 128.7, 126.7, 126.6, 47.0, 44.8, 41.2, 32.8, 25.6. \([\alpha]_D^{25}\) (c = 0.16, CHCl\(_3\)) = + 4.7 (76% ee). Analytical data for this compound were consistent with the previously reported data.\(^{11}\)

**Analytical parameters:**

**GC method 10:** capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (30 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 120 °C - 90 min; 3.0 °C/min – 160 °C – 10 min.
• Racemic mixture:

| Peak | Retention time | Area     | Height  | % Area  |
|------|----------------|----------|---------|---------|
| 1    | 101.550        | 147379   | 12257   | 49.941  |
| 2    | 102.073        | 147728   | 11843   | 50.059  |

Chemical Formula: C₃₂H₆₄O
Molecular Weight: 174.24

• With CuBr-1b:

| Peak | Retention time | Area     | Height  | % Area  |
|------|----------------|----------|---------|---------|
| 1    | 101.737        | 17151    | 1710    | 12.178  |
| 2    | 102.153        | 123682   | 10324   | 87.822  |
3-(2-methylbutyl)cyclohex-2-enone (1,6-P10a):

\[ \text{1H NMR (CDCl}_3, 400 \text{ MHz): } \delta 5.85 (\text{h}, J = 1.2 \text{ Hz}, 1\text{H}), 2.42 – 2.32 \text{ (m, 2H)}, 2.32 – 2.17 \text{ (m, 3H)}, 2.03 – 1.92 \text{ (m, 3H)}, 1.72 – 1.58 \text{ (m, 1H)}, 1.43 – 1.28 \text{ (m, 1H)}, 1.22 – 1.13 \text{ (m, 1H)}, 0.96 – 0.81 \text{ (m, 6H)}. \]

\[ \text{13C NMR (CDCl}_3, 101 \text{ MHz): } \delta 199.9, 165.9, 127.1, 45.8, 37.5, 32.8, 29.8, 29.6, 22.9, 19.2, 11.4. \]

[\( \alpha \)D]25 (c = 0.26, CHCl3) = +8.8 (65% ee).

Analytical data for this compound were consistent with the previously reported data.\(^{11}\)

| Entry | Catalytic system (mol%) | Conv. (yield) (%) | Selectivity \(1,6/1,4\) | ee (%) |
|-------|------------------------|------------------|---------------------|--------|
| 1     | Li1bHPF6/(CuOTf)2 (3/2) | Mr               | Nd                  | Nd     |
| 2     | 2b/(CuOTf)2 (3/2)       | >99 (Nd)         | 100/0               | 53     |
| 3     | 2a/CuBr·SMes2 (3/2)     | >99 (Nd)         | 100/0               | 74     |
| 4     | CuBr-1b (2)            | >99 (68)         | 100/0               | 85     |
| 5     | CuBr-1a (2)            | >99 (90)         | 100/0               | 65     |
| 6     | 2b (5)                 | Nr               | Nd                  | Nd     |
| 7     | 2a (5)                 | Nr               | Nd                  | Nd     |
| 8     | CuBr-1b (3) with EtMgBr| >99 (84)         | 0/100               | 95     |

Analytical parameters:

**GC method 11:** capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (40 cm/sec), 20.0 split ratio, temperature program (Rate - Temperature - Hold Time): 100 °C - 45 min; 1.0 °C/min – 150 °C – 5.0 min; 10 °C/min – 170 °C – 10 min.

- Racemic mixture:
| Peak | Retention time | Area   | Height | % Area |
|------|----------------|--------|--------|--------|
| 1    | 86.592         | 249993 | 6276   | 49.949 |
| 2    | 88.319         | 250505 | 5206   | 50.051 |

- **Table 3, entry 2:**

- **Table 3, entry 3:**
| Peak | Retention time | Area   | Height | % Area |
|------|---------------|--------|--------|--------|
| 1    | 87.202        | 68844  | 1782   | 87.108 |
| 2    | 89.080        | 10189  | 247    | 12.892 |

- Table 3, entry 4:

| Peak | Retention time | Area   | Height | % Area |
|------|---------------|--------|--------|--------|
| 1    | 86.383        | 428678 | 8806   | 92.684 |
| 2    | 88.804        | 33838  | 734    | 7.316  |

- Table 3, entry 5:

| Peak | Retention time | Area   | Height | % Area |
|------|---------------|--------|--------|--------|
| 1    | 86.781        | 205340 | 5033   | 82.222 |
| 2    | 88.826        | 44397  | 1006   | 17.778 |
(E)-3-ethyl-3-(prop-1-en-1-yl)cyclohexan-1-one (1,4-P10a):

The general procedure 4 for 1,6-ACA reactions was followed using S10 (68.1 mg, 0.5 mmol, 1.0 equiv), EtMgBr (3M in diethyl ether, 0.2 mL, 0.6 mmol, 1.2 equiv) and the complex CuBr-1b (6.5 mg, 0.015 mmol, 3.0 mol%). The desired product 1,4-P10a was obtained as a colourless oil (69.8 mg, 84% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.39 – 5.28 (m, 1H), 5.15 (dq, $J$ = 15.8, 1.6 Hz, 1H), 2.45 (dt, $J$ = 14.1, 1.7 Hz, 1H), 2.32 – 2.14 (m, 2H), 2.11 (dd, $J$ = 14.1, 1.3 Hz, 1H), 1.83 – 1.78 (m, 1H), 1.71 – 1.56 (m, 6H), 1.36 (q, $J$ = 7.5 Hz, 2H), 0.77 (td, $J$ = 7.5, 0.7 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 212.1, 136.7, 125.4, 49.9, 44.3, 41.5, 35.3, 34.3, 21.9, 18.4, 8.0. $[^{\alpha}]D^{25}$ (c = 0.72, CHCl$_3$) = + 3.3 (95% ee). Analytical data for this compound were consistent with the previously reported data. The enantiomeric excess has been determined on the hydrogenated compound following reported procedure.

Analytical parameters:

GC method 12: capillary column: G-TA: 30 m x 0.25 mm x 0.12 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (30 cm/sec), 50.0 split ratio, temperature program (Rate - Temperature - Hold Time): 85 °C - 70 min; 1.0 °C/min – 100 °C – 0 min; 5 °C/min – 160 °C – 10 min.

- Racemic mixture:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 93.334         | 202034| 19830  | 48.395 |
| 2    | 93.902         | 215437| 20295  | 51.605 |
• With CuBr-1b:

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 93.382         | 13899 | 1783   | 2.683  |
| 2    | 93.843         | 504157| 41242  | 97.317 |

(E)-3-(but-3-en-1-yl)-3-(prop-1-en-1-yl)cyclohexan-1-one (1,4-P10b):

The general procedure 4 for 1,6-ACA reactions was followed using S10 (68.1 mg, 0.5 mmol, 1.0 equiv), but-3-en-1-ylMgBr (1M in diethyl ether, 0.6 mL, 0.6 mmol, 1.2 equiv) and the complex CuBr-1b (6.5 mg, 0.015 mmol, 3.0 mol%). The desired product 1,4-P10b was obtained as a colourless oil (23.0 mg, 24% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 5.77 (ddt, $J$ = 16.8, 10.2, 6.5 Hz, 1H), 5.35 (dq, $J$ = 15.8, 6.3 Hz, 1H), 5.17 (dq, $J$ = 15.8, 1.7 Hz, 1H), 5.02 – 4.88 (m, 2H), 2.48 (dt, $J$ = 14.1, 1.8 Hz, 1H), 2.33 – 2.17 (m, 2H), 2.14 (dd, $J$ = 14.4, 1.1 Hz, 1H), 2.00 – 1.90 (m, 2H), 1.85 – 1.76 (m, 2H), 1.71 – 1.58 (m, 5H), 1.47 – 1.37 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 212.0, 139.3, 136.9, 126.0, 114.8, 50.6, 44.4, 41.6, 41.4, 36.1, 28.4, 22.1, 18.7. $[^{[\alpha]}]_D^{25}$ (c = 0.1, CHCl$_3$) = +83 (97% ee). Analytical data for this compound were consistent with the previously reported data. The enantiomeric excess has been determined on the hydrogenated compound following reported procedure.

Analytical parameters:

GC method 13: capillary column: G-TA: 30 m x 0.25 mm x 0.12 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (30 cm/sec), 20.0 split ratio, temperature program (Rate - Temperature - Hold Time): 105 °C - 80 min; 5 °C/min – 160 °C – 10 min.
• Racemic mixture:

![Racemic mixture](image)

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 82.926         | 544967| 13125  | 49.508 |
| 2    | 84.642         | 555793| 14948  | 50.492 |

• With CuBr-1b:

![CuBr-1b](image)

| Peak | Retention time | Area  | Height | % Area |
|------|----------------|-------|--------|--------|
| 1    | 83.076         | 504847| 11707  | 99.144 |
| 2    | 84.861         | 4361  | 162    | 1.917  |

3-(2-phenylhexyl)cyclohex-2-en-1-one (1,6-P11a):

![3-(2-phenylhexyl)cyclohex-2-en-1-one](image)

The general procedure 3 for 1,6-ACA reactions was followed using S11 (45 mg, 0.25 mmol, 1.0 equiv), Ph₃Zn (164.7 mg, 0.75 mmol, 3.0 equiv) in Toluene (2.0 mL) and a stock solution of the complex CuBr-1b (2.16 mg, 0.005 mmol, 2.0 mol%). The desired product 1,6-P11a was obtained as a colourless oil (45.0 mg, 70% yield).
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 7.13 – 7.09 (m, 2H), 5.76 (t, $J$ = 1.3 Hz, 1H), 2.78 (tt, $J$ = 9.0, 6.1 Hz, 1H), 2.55 (dd, $J$ = 13.8, 6.4 Hz, 1H), 2.43 (dd, $J$ = 13.8, 8.8 Hz, 1H), 2.31 – 2.22 (m, 2H), 2.22 – 2.13 (m, 1H), 2.12 – 2.02 (m, 1H), 1.90 – 1.81 (m, 2H), 1.69 – 1.53 (m, 2H), 1.34 – 1.04 (m, 4H), 0.82 (t, $J$ = 7.2 Hz, 3H).  

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 199.9, 164.9, 144.3, 128.6, 127.6, 127.5, 126.5, 45.8, 44.5, 37.4, 36.4, 30.0, 29.8, 22.8, 22.7, 14.1.  

[α]$_D^{25}$ (c = 0.24, CHCl$_3$) = – 62 (90% ee). Analytical data for this compound were consistent with the previously reported data.$^{11}$

Analytical parameters:

**HPLC method 3:** OJ-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane/iPrOH (95/5) at 0.5 mL/min as mobile phase at 25°C and λ = 254 nm.

- Racemic mixture:

| Peak | Retention time | Area    | Height | % Area |
|------|----------------|---------|--------|--------|
| 1    | 29.316         | 4419989 | 90669  | 51.43  |
| 2    | 40.937         | 4174334 | 55900  | 48.57  |

- With CuBr-1b:
| Peak | Retention time | Area    | Height | % Area |
|------|----------------|---------|--------|--------|
| 1    | 29.595         | 457885  | 9609   | 5.78   |
| 2    | 41.216         | 7459072 | 98969  | 94.22  |

3-(2-isopropylhexyl)cyclohex-2-en-1-one (1,6-P11b):

The general procedure 3 for 1,6-ACA reactions was followed using S11 (90 mg, 0.5 mmol, 1.0 equiv), iPr₂Zn (1 M in Toluene, 1.5 mL, 1.5 mmol, 3.0 equiv) and a stock solution of the complex CuBr-1b (4.32 mg, 0.01 mmol, 2.0 mol%). The desired product 1,6-P11b was obtained as a colourless oil (82.3 mg, 74% yield).

$^1$H NMR (400 MHz, CDCl₃) $\delta$ 5.86 (p, $J$ = 1.3 Hz, 1H), 2.38 – 2.31 (m, 2H), 2.29 – 2.21 (m, 2H), 2.17 (ddd, $J$ = 13.9, 6.6, 1.1 Hz, 1H), 2.04 (ddd, $J$ = 13.9, 7.8, 1.1 Hz, 1H), 1.96 (dq, $J$ = 7.9, 6.2 Hz, 2H), 1.69 (hd, $J$ = 6.8, 3.6 Hz, 1H), 1.51 – 1.38 (m, 1H), 1.31 – 1.17 (m, 5H), 1.17 – 1.05 (m, 1H), 0.92 – 0.78 (m, 9H). $^{13}$C NMR (101 MHz, CDCl₃) $\delta$ 199.9, 166.9, 127.3, 41.7, 40.1, 37.5, 29.9, 29.8, 29.7, 29.0, 23.1, 22.9, 18.9, 18.8, 14.2. $[\alpha]_D^{25}$ (c = 0.52, CHCl₃) = −4.5 (66% ee). Analytical data for this compound were consistent with the previously reported data.¹¹

Analytical parameters:

GC method 14: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (40 cm/sec), 30.0 split ratio, temperature program (Rate - Temperature - Hold Time): 100 °C – 80 min; 0.20 °C/min – 120 °C – 15.0 min; 5 °C/min – 160 °C – 10 min.
• Racemic mixture:

| Peak | Retention time | Area   | Height | % Area   |
|------|----------------|--------|--------|----------|
| 1    | 206.205        | 17500  | 1629   | 49.326   |
| 2    | 206.890        | 17978  | 1641   | 50.674   |

• With CuBr-1b:

| Peak | Retention time | Area   | Height | % Area   |
|------|----------------|--------|--------|----------|
| 1    | 206.213        | 6639   | 608    | 16.849   |
| 2    | 206.896        | 32763  | 3033   | 83.151   |
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1.7. NMR spectra:

$^1$H NMR (CDCl$_3$, 400 MHz) of 2a:

Chemical Formula: C$_{21}$H$_{34}$N$_2$O  
Molecular Weight: 330.52

$^{13}$C NMR (CDCl$_3$, 101 MHz) of 2a:

Chemical Formula: C$_{21}$H$_{34}$N$_2$O  
Molecular Weight: 330.52

S50
\(^1\)H NMR (CDCl\(_3\), 400 MHz) of 2b:

**Chemical Formula:** C\(_{19}\)H\(_{29}\)N\(_2\)O  
**Molecular Weight:** 288.44

\(^{13}\)C NMR (CDCl\(_3\), 101 MHz) of 2b:

**Chemical Formula:** C\(_{19}\)H\(_{29}\)N\(_2\)O  
**Molecular Weight:** 288.44
$^1$H NMR (CDCl$_3$, 400 MHz) of AuCl-1a:

Chemical Formula: C$_3$H$_5$AuClN$_2$O
Molecular Weight: 562.94

$^{13}$C NMR (CDCl$_3$, 101 MHz) of AuCl-1a:

Chemical Formula: C$_3$H$_5$AuClN$_2$O
Molecular Weight: 562.94
$^1$H NMR (CDCl$_3$, 400 MHz) of AuCl-1b:

![NMR spectrum of AuCl-1b](image)

AuCl-1b
Chemical Formula: C$_{18}$H$_{28}$AuCIN$_3$O
Molecular Weight: 520.86

$^{13}$C NMR (CDCl$_3$, 101 MHz) of AuCl-1b:

![NMR spectrum of AuCl-1b](image)

AuCl-1b
Chemical Formula: C$_{18}$H$_{28}$AuCIN$_3$O
Molecular Weight: 520.86
$^1$H NMR (CDCl$_3$, 400 MHz) of CuBr-1a:

![1H NMR spectrum of CuBr-1a](image)

Chemical Formula: C$_{21}$H$_{34}$BrCuN$_2$O  
Molecular Weight: 473.97

$^{13}$C NMR (CDCl$_3$, 101 MHz) of CuBr-1a:

![13C NMR spectrum of CuBr-1a](image)

Chemical Formula: C$_{21}$H$_{34}$BrCuN$_2$O  
Molecular Weight: 473.97
$^1$H NMR (CD$_2$Cl$_2$, 500 MHz) of CuBr-1b:

![NMR spectrum of CuBr-1b](image)

Chemical Formula: C$_{19}$H$_{27}$BrCuN$_2$O
Molecular Weight: 431.89

$^{13}$C NMR (CD$_2$Cl$_2$, 126 MHz) of CuBr-1b:

![NMR spectrum of CuBr-1b](image)

Chemical Formula: C$_{19}$H$_{27}$BrCuN$_2$O
Molecular Weight: 431.89
$^1$H NMR (CDCl$_3$, 400 MHz) of $\gamma$-P1:

Chemical Formula: C$_{11}$H$_{14}$
Molecular Weight: 146.23

$^{13}$C NMR (CDCl$_3$, 101 MHz) of $\gamma$-P1:

Chemical Formula: C$_{11}$H$_{14}$
Molecular Weight: 146.23
$^1$H NMR (CDCl$_3$, 400 MHz) of $\gamma$-P2:

Chemical Formula: C$_{10}$H$_{16}$
Molecular Weight: 196.29

$^{13}$C NMR (CDCl$_3$, 101 MHz) of $\gamma$-P2:

Chemical Formula: C$_{10}$H$_{16}$
Molecular Weight: 196.29
$^{1}$H NMR (CDCl$_3$, 400 MHz) of $\gamma$-P3a:

Chemical Formula: C$_{16}$H$_{16}$
Molecular Weight: 196.29

$^{13}$C NMR (CDCl$_3$, 101 MHz) of $\gamma$-P3a:

Chemical Formula: C$_{16}$H$_{16}$
Molecular Weight: 196.29
$^1$H NMR (CDCl$_3$, 400 MHz) of $\gamma$-P3b:

Chemical Formula: C$_{14}$H$_{14}$
Molecular Weight: 182.27

$^{13}$C NMR (CDCl$_3$, 101 MHz) of $\gamma$-P3b:

Chemical Formula: C$_{14}$H$_{14}$
Molecular Weight: 182.27
$^1$H NMR (CDCl$_3$, 400 MHz) of γ-P4:

\[ \text{Chemical Formula: } C_{11}H_{20} \]
\[ \text{Molecular Weight: 152.28} \]

$^{13}$C NMR (CDCl$_3$, 101 MHz) of γ-P4:

\[ \text{Chemical Formula: } C_{11}H_{20} \]
\[ \text{Molecular Weight: 152.28} \]
$^1$H NMR (CDCl$_3$, 400 MHz) of γ-P5:

Chemical Formula: C$_{12}$H$_{16}$
Molecular Weight: 160.26

$^{13}$C NMR (CDCl$_3$, 101 MHz) of γ-P5:

Chemical Formula: C$_{12}$H$_{16}$
Molecular Weight: 160.26
$^{1}$H NMR (CDCl$_3$, 400 MHz) of $\gamma$-P6:

Chemical Formula: C$_{16}$H$_{18}$
Molecular Weight: 210.32

$^{13}$C NMR (CDCl$_3$, 101 MHz) of $\gamma$-P6:

Chemical Formula: C$_{16}$H$_{18}$
Molecular Weight: 210.32
$^1$H NMR (CDCl$_3$, 400 MHz) of $\gamma$-P7a:

Chemical Formula: C$_{13}$H$_{16}$
Molecular Weight: 172.27

$^{13}$C NMR (CDCl$_3$, 101 MHz) of $\gamma$-P7a:

Chemical Formula: C$_{13}$H$_{16}$
Molecular Weight: 172.27
$^1$H NMR (CDCl$_3$, 400 MHz) of $\gamma$-P7b:

Chemical Formula: C$_{12}$H$_{14}$
Molecular Weight: 158.24

$^{13}$C NMR (CDCl$_3$, 101 MHz) of $\gamma$-P7b:

Chemical Formula: C$_{12}$H$_{14}$
Molecular Weight: 158.24
$^1$H NMR (CDCl$_3$, 400 MHz) of P8a:

Chemical Formula: C$_9$H$_{16}$O
Molecular Weight: 140.23

$^{13}$C NMR (CDCl$_3$, 101 MHz) of P8a:

Chemical Formula: C$_9$H$_{16}$O
Molecular Weight: 140.23
$^1$H NMR (CDCl$_3$, 400 MHz) of P8b:

![NMR spectrum](image)

Chemical Formula: C$_{10}$H$_{18}$O
Molecular Weight: 154.25

$^{13}$C NMR (CDCl$_3$, 101 MHz) of P8b:

![NMR spectrum](image)

Chemical Formula: C$_{10}$H$_{18}$O
Molecular Weight: 154.25
$^1$H NMR (CDCl$_3$, 400 MHz) of P8c:

![NMR spectrum of P8c]  
Chemical Formula: C$_{13}$H$_{18}$O  
Molecular Weight: 188.27

$^{13}$C NMR (CDCl$_3$, 101 MHz) of P8c:

![NMR spectrum of P8c]  
Chemical Formula: C$_{13}$H$_{18}$O  
Molecular Weight: 188.27
$^1$H NMR (CDCl$_3$, 400 MHz) of P9:

![NMR spectrum image]

Chemical Formula: C$_{12}$H$_{14}$O  
Molecular Weight: 174.24

$^{13}$C NMR (CDCl$_3$, 101 MHz) of P9:

![NMR spectrum image]

Chemical Formula: C$_{12}$H$_{14}$O  
Molecular Weight: 174.24
$^1$H NMR (CDCl$_3$, 400 MHz) of 1,6-P10a:

Chemical Formula: C$_{11}$H$_{19}$O  
Molecular Weight: 166.26

$^{13}$C NMR (CDCl$_3$, 101 MHz) of 1,6-P10a:

Chemical Formula: C$_{11}$H$_{19}$O  
Molecular Weight: 166.26
$^1$H NMR (CDCl$_3$, 400 MHz) of 1,4-P10a:

Chemical Formula: C$_{11}$H$_{18}$O
Molecular Weight: 166.26

$^{13}$C NMR (CDCl$_3$, 101 MHz) of 1,4-P10a:

Chemical Formula: C$_{11}$H$_{18}$O
Molecular Weight: 166.26
$^1\text{H NMR (CDCl}_3, 400\text{ MHz)}$ of $1,4$-P10b:

$^{13}\text{C NMR (CDCl}_3, 101\text{ MHz)}$ of $1,4$-P10b:
$^1$H NMR (CDCl$_3$, 400 MHz) of 1,6-P11a:

![1H NMR spectrum](image)

Chemical Formula: C$_{13}$H$_{23}$O
Molecular Weight: 256.39

$^{13}$C NMR (CDCl$_3$, 101 MHz) of 1,6-P11a:

![$^{13}$C NMR spectrum](image)

Chemical Formula: C$_{13}$H$_{23}$O
Molecular Weight: 256.39
$^1$H NMR (CDCl$_3$, 400 MHz) of 1,6-P11b:

1,6-P11b
Chemical Formula: C$_{15}$H$_{26}$O
Molecular Weight: 222.37

$^{13}$C NMR (CDCl$_3$, 101 MHz) of 1,6-P11b:

1,6-P11b
Chemical Formula: C$_{15}$H$_{26}$O
Molecular Weight: 222.37
1.8. X-Ray crystallography:

Data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector using MoKα radiation (0.71073 Å) at $T = 150$ K.

All the structures were solved by dual-space algorithm using the SHELXT program\cite{1}, and then refined with full-matrix least-squares methods based on $F^2$ (SHELXL).\cite{2} All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters.

The CIF files of (S,S)-2a, AuCl-1a and AuCl-1b have been deposited with CCDC numbers: (S,S)-2a (2090324), AuCl-1a (2090326), AuCl-1b (2090325).

\cite{1} Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. Acta Crystallogr. Sect. Found. Adv. 71, 3–8 (2015).

\cite{2} Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Crystallogr. Sect. C Struct. Chem. 71, 3–8 (2015)

- X-Ray structure of oxazolidine (S,S)-2a:
Bond precision: C-C = 0.0030 Å  Wavelength=0.7107 Å

Cell: a=6.1890(4)  b=12.3978(9)  c=26.4025(15)
    alpha=90  beta=90  gamma=90

Temperature: 150 K

Calculated  Reported
Volume  2025.9(2)  2025.9(2)
Space group  P 21 21 21  P 2ac 2ac
Hall group  P 2ac 2ac  P 2ac 2ac

Moiety formula  C21 H34 N2 O  C21 H34 N2 O
Sum formula  C21 H34 N2 O  C21 H34 N2 O
M  330.50  330.50

Dx,g cm-3  1.084  1.084
Z  4  4

Mu (mm-1)  0.066  0.066
F000  728.0  728.0
F000’  728.25

h,k,lmax  8,16,34  8,16,33

Nref  4616[ 2667]  4572

Tmin,Tmax  0.981,0.989  0.838,0.989
Tmin’  0.962

Correction method= # Reported T Limits: Tmin=0.838 Tmax=0.989
AbsCorr = MULTI-SCAN

Data completeness= 1.71/0.99  Theta(max)= 27.466

R(reflections)= 0.0406( 4348)  wR2(reflections)= 0.1051( 4572)

S = 1.067  Npar= 226

- X-Ray structure of complex AuCl-1a:
Bond precision: C-C = 0.0322 Å  Wavelength=0.71073

| Cell |          |          |          |
|------|----------|----------|----------|
| a    | 9.7764(12) | b        | 14.6129(18) |
| alpha | 90       | beta    | 90       |
| c    | 16.587(2)  |          |          |
| gamma | 90       |          |          |

Temperature: 150 K

| Calculated | Reported |
|------------|----------|
| Volume     | 2369.6(5) | 2369.7(5) |
| Space group| P 21 21 21 | P 21 21 21 |
| Hall group | P 2ac 2ab  | P 2ac 2ab  |
| Moiety formula | C21 H34 Au Cl N2 O | C21 H34 Au Cl N2 O |
| Sum formula | C21 H34 Au Cl N2 O | C21 H34 Au Cl N2 O |
| Mr         | 562.92    | 562.92    |
| DX, g cm-3 | 1.578     | 1.578     |
| Z          | 4         | 4         |
| Mu (mm-1)  | 6.332     | 6.332     |
| P000       | 1112.0    | 1112.0    |
| P000’      | 1105.21   |           |
| h,k,lmax   | 12,19,21  | 12,18,21  |
| Nref       | 5472[ 3085] | 5320    |
| Tmin,Tmax  | 0.510,0.827 | 0.530,0.827 |
| Tmin’      | 0.057     |           |

Correction method= # Reported T Limits: Tmin=0.530 Tmax=0.827
AbsCorr = MULTI-SCAN

Data completeness= 1.72/0.97  Theta(max)= 27.548
R(reflections)= 0.0544( 4340)  wR2(reflections)= 0.1361( 5320)
S = 1.025  Npar= 231
• X-Ray structure of complex AuCl-1b:

Bond precision: \( \text{C-C} = 0.0140 \text{ Å} \)  \( \text{Wavelength}=0.71073 \)

Cell:
- \( a=28.311(3) \)  \( b=9.3672(9) \)  \( c=15.1782(16) \)
- \( \alpha=90 \)  \( \beta=102.115(4) \)  \( \gamma=90 \)

Temperature: 150 K

| Calculated | Reported |
|------------|----------|
| Volume | 3935.5(7) | 3935.6(7) |
| Space group | C 2 | C 2 |
| Hall group | C 2y | C 2y |
| Moiety formula | C18 H28 Au Cl N2 O | C18 H28 Au Cl N2 O |
| Sum formula | C18 H28 Au Cl N2 O | C18 H28 Au Cl N2 O |
| Mr | 520.84 | 520.84 |
| Density, g cm\(^{-3}\) | 1.758 | 1.758 |
| Z | 8 | 8 |
| \( \mu (\text{mm}^{-1}) \) | 7.618 | 7.617 |
| F(000) | 2032.0 | 2032.0 |
| F(000') | 2018.47 | |
| h,k,lmax | 36,12,19 | 36,12,19 |
| Nref | 9072 [4814] | 8916 |
| Tmin, Tmax | 0.381, 0.766 | 0.536, 0.766 |
| Tmin' | 0.180 | |

Correction method = # Reported T Limits: Tmin=0.536 Tmax=0.766
AbsCorr = MULTI-SCAN

Data completeness = 1.85/0.98  \( \Theta_{\text{max}} = 27.527 \)

R(reflections) = 0.0290 (8163)  \( \text{WR2(reflections)} = 0.0619 \) (8916)

\( S = 1.024 \)  \( \text{Npar} = 428 \)
1.9. DFT Calculations

- Computational details

Geometries were optimized with the Gaussian09 [D. J. Gaussian 16 Rev. B.01, Wallingford, CT, 2016] package using the B3LYP functional. [Physical Review A 1988, 38 (6), 3098-3100][ Physical Review B 1986, 33 (12), 8822-8824] The electronic configuration of the system was described with the split-valence SVP basis set [The Journal of Chemical Physics 1992, 97 (4), 2571-2577] for main group atoms (C, H, S, N and O) and the relativistic Stuttgart-Dresden effective core potential with the associated valence triple-ζ basis set for Au. All geometries were confirmed as minimum or transition state through frequency calculations. The reported free energies were built through single point energy calculations on the B3LYP geometries using the B3LYP-D3 [The Journal of Chemical Physics 2010, 132 (15), 154104][ Journal of Computational Chemistry 2004, 25 (12), 1463-1473] functional and the triple-ζ TZVP basis set [The Journal of Chemical Physics 2003, 119 (24), 12753-12762] for main group atoms. Solvent effects were included with the PCM model using 1,4-dioxane as the solvent, [The Journal of Physical Chemistry A 1998, 102 (11), 1995-2001] To this B3LYP/SVP electronic energy in solvent, zero point and thermal corrections were added from the gas-phase frequency calculations at the B3LYP-D3/TZVP level.

- Cartesian coordinates of species reported in the context with solvent energies (in a.u.).

| 2a-(S,S) | H   | 1.425792 | -2.345002 | 0.676593 |
|----------|-----|----------|-----------|----------|
| E=       | C   | 3.424514 | -3.009760 | 1.106748 |
| C        |     | 1.787351 | 0.157793  | 0.114400 |
| C        |     | 2.740682 | -0.871423 | -0.094903|
| C        |     | 4.007689 | -0.523443 | -0.585343|
| H        |     | 4.751361 | -1.305332 | -0.758410|
| C        |     | 4.334153 | 0.803268  | -0.860751|
| H        |     | 5.327064 | 1.055355  | -1.243020|
| C        |     | 3.392077 | 1.808585  | -0.649838|
| H        |     | 3.657608 | 2.845700  | -0.871217|
| C        |     | 2.111059 | 1.511658  | -0.161654|
| C        |     | 2.404061 | -2.334106 | 0.175788 |
| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | 1.653655 | 3.861957 | -1.704991 |
| H    | -0.002317 | 4.129101 | -1.114570 |
| H    | 0.393162 | 2.651898 | -2.029964 |
| C    | 1.599125 | 3.653685 | 1.103777 |
| H    | 1.817554 | 3.156891 | 2.062241 |
| H    | 0.834714 | 4.426650 | 1.287624 |
| H    | 2.519136 | 4.167343 | 0.780044 |
| N    | 0.498478 | -0.194687 | 0.619538 |
| C    | 0.135286 | -0.013655 | 2.020058 |
| H    | 0.295968 | 1.029317 | 2.358061 |
| H    | 0.721294 | -0.668693 | 2.687697 |
| C    | -1.348921 | -0.384109 | 2.025311 |
| H    | -1.471376 | -1.466985 | 2.228120 |
| H    | -1.917838 | 0.168023 | 2.789668 |
| N    | -1.795821 | -0.036475 | 0.668248 |
| C    | -0.651183 | -0.276223 | -0.203093 |
| H    | -0.618226 | 0.436855 | -1.052385 |
| O    | -0.872121 | -1.584399 | -0.766511 |
| C    | -2.256367 | -1.621016 | -1.038008 |
| H    | -2.583564 | -2.669906 | -1.072852 |
| H    | -2.479846 | -1.160155 | -2.019875 |
| C    | -2.918804 | -0.818954 | 0.127222 |
| H    | -3.244506 | -1.540337 | 0.898836 |
| C    | -4.169297 | 0.027391 | -0.244779 |
| C    | -3.822706 | 1.147525 | -1.242156 |
| H    | -3.479879 | 0.753874 | -2.211978 |
| H    | -3.032042 | 1.796395 | -0.835935 |
| H    | -4.708818 | 1.772326 | -1.439892 |
| C    | -4.719422 | 0.665862 | 1.043947 |
| H    | -3.968257 | 1.327390 | 1.502130 |

**TS1-({S,S})**

E = -1005.85251466 A.U.
|   |   |   |   |
|---|---|---|---|
| C | 0.958437 | 3.288830 | -1.241180 |
| H | 1.797386 | 3.609568 | -1.880210 |
| H | 0.324522 | 4.170429 | -1.051550 |
| H | 0.364911 | 2.558155 | -1.811975 |
| C | 2.232302 | 3.730092 | 0.913764 |
| H | 2.582515 | 3.308335 | 1.869331 |
| H | 1.586400 | 2.558155 | -1.811975 |
| H | 0.364911 | 2.558155 | -1.811975 |
| C | 2.232302 | 3.730092 | 0.913764 |
| H | 2.582515 | 3.308335 | 1.869331 |
| H | 1.586400 | 2.558155 | -1.811975 |
| H | 0.364911 | 2.558155 | -1.811975 |
| N | 0.496846 | -0.001511 | 0.748703 |
| C | 0.234295 | -0.024559 | 2.200193 |
| H | 0.450084 | 0.965578 | 2.638040 |
| H | 0.872758 | -0.763636 | 2.706670 |
| C | -1.268956 | -0.377724 | 2.259246 |
| H | -1.437354 | -1.426514 | 2.558945 |
| H | -1.831866 | 0.270311 | 2.947210 |
| N | -1.707924 | -0.189889 | 0.865865 |
| C | -0.652558 | -0.055663 | 0.064875 |
| H | -0.824432 | -0.317794 | -1.016572 |
| O | -1.637805 | -1.652701 | -1.521160 |
| C | -2.589394 | -1.938523 | -0.612358 |
| H | -2.308457 | -2.768298 | 0.100418 |
| H | -3.558194 | -2.280351 | -1.054988 |
| C | -2.974562 | -0.724534 | 0.334761 |
| H | -3.516347 | -1.126039 | 1.208631 |
| C | -3.893917 | 0.384592 | -0.274431 |
| C | -3.299255 | 1.010852 | -1.551021 |
| H | -3.021093 | 0.234166 | -2.276636 |
| H | -2.391657 | 1.594982 | -1.328125 |
| H | -4.026025 | 1.703514 | -2.007650 |
| C | -4.124599 | 1.487421 | 0.778322 |

**Carbene C**

E = -1005.86847669 A.U.
|   |   |   |   |   | C  | -4.011140 | 1.259355 | 1.167684 |
|---|---|---|---|---|---|---------|---------|---------|
|   |   |   |   |   | H  | -3.042361 | 1.717607 | 1.419848 |
|   |   |   |   |   | H  | -4.375576 | 0.710077 | 2.052658 |
|   |   |   |   |   | H  | -4.719911 | 2.080513 | 0.973824 |
| H  | 0.413200 | 2.310991 | 0.531893 |   | C  | -5.303498 | -0.206040 | -0.389993 |
|   |   |   |   |   | H  | -6.019607 | 0.623821 | -0.501992 |
| H  | 0.336368 | 2.306169 | -1.944704 |   | H  | -5.679541 | -0.860236 | 0.415470 |
| H  | 1.661579 | 3.495252 | -2.008702 |   | H  | -5.317684 | -0.778111 | -1.329547 |
| H  | 0.093081 | 3.950930 | -1.297288 |   | N  | 0.525735 | -0.083095 | 0.664483 |
| N  | 0.525735 | -0.083095 | 0.664483 |   | C  | 0.232200 | -0.027342 | 2.116083 |
| H  | 0.371060 | 0.999931 | 2.496673 |   | C  | -2.148073 | 1.085665 | 0.395359 |
| H  | 0.907068 | -0.686840 | 2.683331 |   | C  | -2.755397 | 1.633526 | -0.766107 |
| C  | -1.235767 | -0.477897 | 2.157445 |   | C  | -4.083347 | 1.279798 | -1.047011 |
| H  | -1.349396 | -1.504515 | 2.550741 |   | H  | -4.571175 | 1.686503 | -1.935770 |
| H  | -1.869265 | 0.185106 | 2.764294 |   | C  | -4.799161 | 0.430832 | -0.204483 |
| N  | -1.612973 | -0.440449 | 0.726458 |   | H  | -5.834708 | 0.171173 | -0.440450 |
| C  | -0.563141 | -0.285483 | -0.100567 |   | C  | -4.196363 | -0.075258 | 0.944326 |
| H  | -1.370802 | -1.029873 | -1.693870 |   | C  | -2.148073 | 1.085665 | 0.395359 |
| O  | -2.169301 | -1.533529 | -1.992752 |   | C  | -2.867633 | 0.238433 | 1.271497 |
| C  | -2.799876 | -1.949847 | -0.814803 |   | C  | -2.050485 | 2.643827 | -1.672157 |
| H  | -2.255291 | -2.793390 | -0.335136 |   | H  | -0.977152 | 2.623968 | -1.441236 |
| H  | -3.796501 | -2.338560 | -1.078113 |   | C  | -2.554654 | 4.073384 | -1.390472 |
| C  | -2.948706 | -0.857289 | 0.269533 |   | H  | -2.007060 | 4.807510 | -2.004058 |
| H  | -3.411481 | -1.367064 | 1.134267 |   | H  | -3.627220 | 4.170013 | -1.626492 |
| C  | -3.899623 | 0.345026 | -0.069291 |   | H  | -2.425559 | 4.352003 | -0.332826 |
| C  | -3.402360 | 1.185266 | -1.260961 |   | C  | -2.179212 | 2.313738 | -3.168247 |
| H  | -3.338905 | 0.583100 | -2.176353 |   | H  | -1.836618 | 1.291480 | -3.386585 |
| H  | -2.401050 | 1.599355 | -1.068034 |   | H  | -3.217208 | 2.406644 | -3.526609 |
| H  | -4.090052 | 2.030093 | -1.433756 |   | H  | -1.562283 | 3.005388 | -3.763233 |

**TS2**

\[E = -2080.06204983 \text{ A.U.}\]
C  -2.262832 -0.304304  2.561321  C  3.985624  2.359241  1.730882
H  -1.175127 -0.157701  2.513165  H  3.234223  2.001425  2.44981
C  -2.483143 -1.815943  2.732172  H  3.840440  3.440501  1.568508
H  -3.544305 -2.067506  2.896359  H  4.971786  2.229179  2.204330
H  -1.911411 -2.180578  3.598606  C  5.127477  2.025068  -0.453948
H  -2.123886 -2.370077  1.852113  H  6.066253  1.919877  0.112486
C  -2.798491  0.464849  3.785010  H  5.032329  3.085210  -0.744385
H  -2.618938  1.548738  3.701730  H  5.238523  1.430001  -1.372663
H  -2.308102  0.110477  4.706202  Au  0.596848  -1.635185  0.003495
H  -3.885493  0.320866  3.905678  S  0.310083  -2.625385  -2.16208
N  -0.794475  1.461023  0.704535  Cl  1.128044  -1.656026  2.332909
C  -0.493814  2.583755  1.617063  C  -0.554377  -1.457792  -3.265093
H  -0.503921  2.235333  2.663543  C  -0.982147  -3.898199  -1.953334
H  -1.233489  3.390447  1.514311  H  -0.748018  -1.951717  -4.228462
C  0.910888  2.981426  1.163222  H  -1.492979  -1.115791  -2.807673
H  0.906927  3.856766  0.485938  H  0.123322  -0.604489  -3.407889
H  1.568901  3.210449  2.007786  H  -1.194805  -4.357405  -2.929787
N  1.352872  1.783361  0.407659  H  -0.576708  -4.653235  -1.267245
C  0.304248  0.993776  0.080292  H  -1.894082  -3.461834  -1.523937
O  1.331258  1.298543  -2.422389  H  0.608557  0.999205  -1.826722
C  2.494156  1.024263  -1.672876  
H  3.353901  1.265003  -2.312483  
H  2.557632  -0.050237  -1.426224  
C  2.605919  1.857649  -0.377151  
H  2.668894  2.917342  -0.694093  
C  3.935680  1.561166  0.413485  
C  4.101906  0.069400  0.759214  
H  4.218383  -0.558934  -0.136995  
H  3.249376  -0.316815  1.337145  
H  5.010302  -0.069985  1.368105  

AuCl·1a

E= -1602.01926817 A.U.
C  -2.064151   -0.800069    0.478797   H   1.776805   -3.071854    1.430411
C   -2.564503   -0.116849    1.611479   H   1.277185   -3.311968   -0.270497
C   -3.909788    0.277882    1.596259   N   1.487087   -1.284267    0.280893
H    -4.321573    0.815048    2.453961   C   2.821625   -0.880085   -0.183093
C   -4.728431    0.006882    0.501534   H   2.643359    0.043102   -0.754613
H    -5.773235    0.327968    0.508540   C   3.361157   -1.908072   -1.186258
C   -4.214039   -0.664993   -0.605962   H   4.274294   -1.495837   -1.646868
H   -4.862253   -0.860290   -1.463371   H   3.650167   -2.848172   -0.674961
C   -2.877071   -1.085073   -0.642914   O   2.358507   -2.144998   -2.156064
C   -1.695511    0.216196    2.820909   H   2.738340   -2.661762   -2.877323
H   -0.684976   -0.171646    2.624766   C   3.818254   -0.497481    0.968489
C   -1.557040    1.737154    3.014512   C   4.153957   -1.675214    1.905325
H   -2.527245    2.203719    3.250307   H   3.277743   -1.999242    2.487515
H   -1.161485    2.219822    2.107676   H   4.921802   -1.365623    2.632282
H   -0.870755    1.957854    3.848407   H   4.553161   -2.548656    1.365621
C   -2.209439   -0.468123    4.100762   C   5.125593    0.027869    0.336253
H   -3.210297   -0.102145    4.381663   H   5.770053    0.464250    1.115480
H   -1.533670   -0.263022    4.947071   H   4.924199    0.816691   -0.406749
H   -2.280485   -1.561147    3.978585   H   5.707473   -0.767251   -0.155657
C   -2.336969   -1.786105   -1.886315   C   3.199235    0.637336    1.806693
H   -1.313032   -2.121296   -1.664371   H   3.900719    0.951501    2.596157
C   -2.236549   -0.807961   -3.071832   H   2.266624    0.318120    2.294901
H   -1.605186    0.058406   -2.821252   H   2.963719    1.517528    1.188696
H   -3.229598   -0.428183   -3.363110
H   -1.796989   -1.309436   -3.949603
C   -3.156384   -3.034611   -2.255977
H   -4.186328   -2.777196   -2.551544
H   -3.220081   -3.744197   -1.415083
H   -2.693474   -3.557631   -3.108527
C   1.146082   -2.679719    0.622530
AuCl·SMe$_2$

E= -1074.18126143 A.U.

|   | C    | H    |   |
|---|------|------|---|
| Au | -0.094150 | -0.087889 | 1.856794 |
| H  | -0.639844  | -0.880685  | 2.386597  |
| S  | -0.303570  | 0.870121  | 2.358855  |
| Cl | -1.924984  | 0.108197  | 0.040251  |
| C  | -2.486473  | 1.399038  | -0.090043 |
| C  | -3.834616  | 1.475163  | -0.467138 |
| H  | -4.305432  | 2.453257  | -0.585855 |
| H  | -4.586100  | 0.323377  | -0.695026 |
| H  | -5.635560  | 0.408406  | -0.986699 |
| H  | -4.005586  | -0.936163 | -0.554165 |
| H  | -4.609355  | -1.827228 | -0.738723 |
| H  | -2.661651  | -1.078583 | -0.181433 |
| H  | -1.690483  | 2.681499  | 0.140267  |
| H  | -0.680228  | 2.402255  | 0.480962  |
| C  | -1.517965  | 3.477314  | -1.167217 |
| C  | -4.077778  | 2.872937  | -1.953426 |
| C  | -0.897190  | 4.371045  | -0.996725 |
| C  | -2.310748  | 3.553938  | 1.246825  |
| H  | -3.308858  | 3.921806  | 0.961972  |
| H  | -1.678981  | 4.435199  | 1.439537  |
| H  | -2.419559  | 2.998019  | 2.191396  |
| H  | -2.056203  | -2.473280 | -0.040414 |
| H  | -1.003204  | -2.365062 | 0.263828  |
| H  | -2.051460  | -3.224756 | -1.384789 |
| H  | -1.515833  | -2.660192 | -2.164387 |
| C  | -3.074089  | -3.407461 | -1.750790 |
| H  | -1.558789  | -4.203749 | -1.275801 |

SMe$_2$

E= -478.080470814 A.U.

|   | C    | H    |   |
|---|------|------|---|
| S  | 0.000000  | 0.660509  | 0.000015  |
| C  | 1.391435  | -0.512103 | 0.000014  |
| C  | -1.391435 | -0.512103 | 0.000014  |
| H  | 1.384995  | -1.148085 | 0.899641  |
| H  | 1.384016  | -1.148829 | -0.899085 |
| H  | 2.314591  | 0.085455  | -0.000760 |
| H  | -1.385017 | -1.148059 | 0.899660  |
| H  | -2.314591 | 0.085455  | -0.000799 |
| H  | -1.383994 | -1.148855 | -0.899066 |
| C  | -2.056203 | -2.473280 | -0.040414 |
| C  | -1.003204 | -2.365062 | 0.263828  |
| C  | -2.051460 | -3.224756 | -1.384789 |
| H  | -1.515833 | -2.660192 | -2.164387 |
| H  | -3.074089 | -3.407461 | -1.750790 |
| H  | -1.558789 | -4.203749 | -1.275801 |

L1aH

E= -1006.35203589 A.U.

|   | C    | H    |   |
|---|------|------|---|
| C  | 0.507484  | -0.030590 | -0.344450 |
| N  | -0.543574 | -0.012579 | 0.449191  |
| H  | -3.817399 | -3.485875 | 0.799649  |
|    |  X         |  Y         |  Z         |    |    |  X         |  Y         |  Z         |
|----|------------|------------|------------|----|----|------------|------------|------------|
| H  | -2.749737  | -2.773679  | 2.026834   | C  | 1.488592  | -0.375943  | 1.716583   |
| H  | -2.271076  | -4.269132  | 1.183014   | H  | 2.034146  | 0.279974   | 2.342353   |
| H  | -0.808505  | -0.324604  | 1.068899   | N  | 1.670084  | -0.136554  | 0.272293   |
| C  | 2.933314   | -0.443124  | -0.437020  | C  | 3.386923  | -1.854997  | -0.040261  |
| H  | 2.034146   | 0.279974   | 2.342353   | C  | 3.806397  | -1.861495  | 0.984243   |
| H  | -1.424541  | -1.424541  | 1.944275   | C  | 4.192465  | -2.164884  | -0.725383  |
| N  | 1.670084   | -0.136554  | 0.272293   | H  | 5.662512  | 0.532203   | -0.642098  |
| C  | 1.888789   | -0.017519  | 0.065929   | C  | 2.718435  | -1.140810  | -0.157229  |
| H  | 1.659351   | -1.424541  | 1.944275   | C  | 4.080670  | -0.916756  | -0.405069  |
| H  | 1.670084   | -0.136554  | 0.272293   | H  | 4.743817  | -1.767757  | -0.579576  |
| C  | 2.933314   | -0.443124  | -0.437020  | C  | 4.598263  | 0.375837   | -0.446855  |
| H  | 5.169351   | -1.424541  | 1.944275   | C  | 3.757195  | 1.471667   | -0.256959  |
| H  | 1.670084   | -0.136554  | 0.272293   | H  | 4.173035  | 2.479402   | -0.313260  |
| C  | 2.535300   | -3.618111  | -0.050108  | C  | 0.193061  | 0.684182   | -0.344791  |
| C  | 4.013061   | 0.684182   | -0.344791  | H  | 2.535300  | -1.424541  | 1.944275   |
| H  | 4.468922   | 0.976185   | 1.098591   | H  | 3.806397  | -1.861495  | 0.984243   |
| C  | 2.798928   | -3.433001  | 0.939920   | H  | 6.207563  | -2.697139  | -0.146474  |
| H  | 3.757195   | 1.471667   | -0.256959  | C  | 2.176871  | -2.568421  | -0.171138  |
| H  | 2.535300   | -3.618111  | -0.050108  | C  | 1.094345  | -2.519260  | 0.014734   |
| C  | 4.013061   | 0.684182   | -0.344791  | H  | 4.822128  | -0.074892  | 1.623236   |
| C  | 4.468922   | 0.976185   | 1.098591   | H  | 2.535300  | -1.424541  | 1.944275   |
| H  | 5.307571   | -0.146474  | 1.082953   | C  | 3.806397  | -1.861495  | 0.984243   |
| H  | 4.822128   | 0.074892   | 1.623236   | H  | 6.207563  | -2.697139  | -0.146474  |
| C  | 1.888789   | -0.017519  | 0.065929   | C  | 3.386923  | -1.854997  | -0.040261  |
| H  | 5.940184   | -0.146474  | 1.082953   | C  | 2.535300  | -1.424541  | 1.944275   |
| C  | 1.888789   | -0.017519  | 0.065929   | H  | 2.535300  | -1.424541  | 1.944275   |
| C  | 4.013061   | 0.684182   | -0.344791  | H  | 4.822128  | -0.074892  | 1.623236   |
| C  | 4.468922   | 0.976185   | 1.098591   | H  | 2.535300  | -1.424541  | 1.944275   |
| H  | 5.307571   | 1.688908   | 1.082953   | C  | 3.806397  | -1.861495  | 0.984243   |
| H  | 4.822128   | 0.074892   | 1.623236   | H  | 6.207563  | -2.697139  | -0.146474  |
| C  | 1.904014   | 1.091447   | -1.273506  | H  | 3.386923  | -1.854997  | -0.040261  |
| C  | 4.948537   | -0.050932  | -2.201936  | C  | 3.757195  | 1.471667   | -0.256959  |
| H  | 5.787563   | -0.581964  | -0.718782  | C  | 2.535300  | -1.424541  | 1.944275   |
| C  | 3.427557   | 1.970689   | -0.957877  | C  | 2.535300  | -1.424541  | 1.944275   |
| H  | 4.172932   | 2.779837   | -0.931058  | C  | 1.888789  | -0.017519  | 0.065929   |
| H  | 2.542858   | 2.323316   | -0.404605  | C  | 2.535300  | -1.424541  | 1.944275   |
| H  | 3.139755   | 1.822825   | -2.011946  | C  | 2.535300  | -1.424541  | 1.944275   |
| H  | 0.415557   | 0.034175   | -1.430653  | C  | 2.535300  | -1.424541  | 1.944275   |

**TS1-(R,S)**

E= -1005.84221194 A.U.
|   |       |       |       | 2a-(R,S) |
|---|-------|-------|-------|----------|
| H | 2.564796 | 3.337841 | 1.944918 | E= -1005.88006165 A.U. |
| N | 0.503403 | -0.224870 | 0.386142 |  |
| C | 0.027159 | -0.624058 | 1.722929 | C -1.851186 | 0.076101 | 0.109304 |
| H | 0.455743 | 0.017954 | 2.505908 | C -2.387160 | 1.370464 | -0.117287 |
| H | 0.315300 | -1.667316 | 1.942004 | C -3.749604 | 1.486322 | -0.430222 |
| C | -1.496910 | -0.465037 | 1.577968 | H -4.179342 | 2.475100 | -0.611633 |
| H | -2.051490 | -1.269978 | 2.078773 | C -4.567436 | 0.360917 | -0.517439 |
| H | -1.839251 | 0.501306 | 1.986134 | H -5.626856 | 0.472321 | -0.764092 |
| N | -1.682839 | -0.483950 | 0.112008 | C -4.032076 | -0.906407 | -0.293302 |
| C | -0.514854 | -0.180718 | -0.484086 | H -4.680349 | -1.783066 | -0.370012 |
| H | -0.674932 | 0.589793 | -1.374415 | C -2.676294 | -1.074467 | 0.023682 |
| C | -2.648518 | 1.573649 | -0.823535 | C -1.527385 | 2.630946 | -0.041690 |
| H | -3.473285 | 1.903307 | -1.496258 | H -0.500380 | 2.324357 | 0.202585 |
| H | -2.836285 | 2.087718 | 0.154297 | C -1.997359 | 3.579452 | 1.076162 |
| C | -2.865321 | 0.026425 | -0.614640 | H -1.324801 | 4.449516 | 1.155660 |
| H | -2.753305 | -0.408207 | -1.621786 | H -3.013255 | 3.962294 | 0.884469 |
| C | -4.248409 | -0.473720 | -0.106416 | H -2.013578 | 3.072768 | 2.054042 |
| C | -4.704864 | 0.160908 | 1.225253 | C -1.467246 | 3.362977 | -1.394982 |
| H | -4.708111 | 1.26003 | 1.171685 | H -1.109056 | 2.697857 | -2.196477 |
| H | -4.078655 | -0.133376 | 2.079501 | H -2.457431 | 3.741766 | -1.971112 |
| H | -5.732917 | -0.161744 | 1.457889 | H -0.784065 | 4.226404 | -1.339290 |
| C | -4.219398 | -2.009623 | 0.032686 | C -2.110560 | -2.474055 | 0.240349 |
| H | -5.213760 | -2.390529 | 0.317960 | H -1.087926 | -2.344105 | 0.621630 |
| H | -3.502880 | -2.346860 | 0.796591 | C -1.988301 | -3.234998 | -1.092226 |
| H | -3.936902 | -2.487745 | -0.919279 | H -2.969758 | -3.356923 | -1.581007 |
| C | -5.300752 | -0.118481 | -1.181574 | H -1.569228 | -4.241374 | -0.924456 |
| H | -6.278173 | -0.549651 | -0.911505 | H -1.316221 | -2.703060 | -1.781305 |
| H | -5.018418 | -0.520206 | -2.168217 | C -2.909760 | -3.279053 | 1.278287 |
| H | -5.433831 | 0.968157 | -1.286613 | H -2.995768 | -2.736558 | 2.233568 |
| O | -1.414893 | 1.836756 | -1.338524 | H -2.414322 | -4.243097 | 1.479777 |
| Element | X          | Y          | Z          | Alcoholate |
|---------|------------|------------|------------|------------|
| H       | -3.931644  | -3.505858  | 0.931526   | E = -1005.84132451 A.U. |
| N       | -0.472891  | -0.092840  | 0.439993   |
| C       | 0.039168   | 0.130500   | 1.784526   |
| H       | -0.348655  | -0.607235  | 2.508410   |
| H       | -0.221046  | 1.137776   | 2.166745   |
| C       | 1.548886   | -0.014169  | 1.581056   |
| H       | 2.123790   | 0.593528   | 2.294840   |
| H       | 1.844135   | -1.072094  | 1.712760   |
| N       | 1.738022   | 0.464164   | 0.198974   |
| C       | 0.569466   | -0.004706  | -0.519329  |
| H       | 0.300561   | 0.646382   | -1.370898  |
| C       | 2.347058   | -1.445885  | -1.040839  |
| H       | 2.740948   | -1.743031  | -2.027122  |
| H       | 2.616980   | -2.239309  | -0.317805  |
| C       | 2.858904   | -0.049637  | -0.605557  |
| H       | 2.845197   | 0.574963   | -1.517607  |
| C       | 4.304407   | 0.090613   | -0.057855  |
| C       | 4.629244   | -0.791565  | 1.166280   |
| H       | 4.392319   | -1.852194  | 0.989470   |
| H       | 4.100997   | -0.470919  | 2.073797   |
| H       | 5.707868   | -0.731377  | 1.384460   |
| C       | 5.552389   | 1.568756   | 0.299432   |
| H       | 5.589627   | 1.716543   | 0.642093   |
| H       | 3.875943   | 1.911314   | 1.096452   |
| H       | 4.388875   | 2.221424   | -0.573461  |
| C       | 5.263071   | -0.314881  | -1.199663  |
| H       | 6.309532   | -0.143725  | -0.901051  |
| H       | 5.075363   | 0.272615   | -2.113195  |
| H       | 5.164908   | -1.381481  | -1.457745  |
| O       | 0.940171   | -1.293018  | -1.106612  |

S87
Alternative reaction pathways investigated.

Alternative reaction pathways for the formation of AuCl-1a have been investigated and reported in Figure S1 (see below).

1) The concerted pathway A that requires an unaffordable energy barrier of 47.6 kcal/mol;

2) The stepwise mechanism B assisted by gold coordination to the carbon atom that involves a very energy demanding H transfer step with a barrier of 50 kcal/mol.

3) The stepwise mechanisms C and D assisted by gold coordination to the oxygen atom occurring with a determining energy barrier around 33 kcal/mol.

All these alternative pathways are unfavorable with respect to the one reported in Figure 5 and thus ruled out.
Figure S1
A1-B1

E= -2080.00535731 A.U.

H  4.514995  0.746107  -3.286344
N  1.282640  1.467597  -0.085237
C  1.414494  2.895352  -0.413707
H  2.208452  3.048494  -1.155793
H  1.666115  3.474155  0.493022
C  0.014891  3.220787  -0.952495
H  -0.344015  4.207798  -0.629351
H  -0.011810  3.195973  -2.054826
N  -0.844508  2.155588  -0.397513
C  -0.022627  1.172207  0.105259
H  -0.385180  0.293869  0.791848
O  -0.671114  1.388045  1.994376
C  -1.981021  1.692328  1.702385
H  -2.421281  2.327296  2.496444
H  -2.621637  0.786931  1.632771
C  -2.058208  2.502652  0.363235
H  -1.947599  3.572829  0.616796
C  -3.389630  2.384779  -0.436732
C  -3.633326  0.961739  -0.967774
H  -3.709605  0.220721  -0.158590
H  -2.825268  0.638925  -1.642469
H  -4.575622  0.926052  -1.538149
C  -3.343655  3.354342  -1.634041
C  -3.291521  4.395318  -1.308736
H  -4.298288  3.336615  -2.184178
H  -4.546727  2.801256  0.493350
C  -5.497682  2.815009  -0.062713
H  -4.389375  3.811542  0.907450
H  -4.669315  2.105317  1.337297
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Au      | -0.557414 | -0.989710 | -0.570342 |
| S       | -2.072744  | -2.281628  | 2.022164  |
| Cl      | -0.878912  | -2.905413  | -1.854512 |
| C       | -0.764215  | -3.533479  | 2.224861  |
| C       | -3.284017  | -3.253570  | 1.069738  |
| H       | -1.124085  | -4.381609  | 2.827139  |
| H       | -0.412505  | -3.885927  | 1.243861  |
| H       | 0.067807   | -3.046521  | 2.753063  |
| H       | -3.620070  | -4.129349  | 1.645686  |
| H       | -4.146689  | -2.597398  | 0.884801  |
| H       | -2.854744  | -3.564506  | 0.105437  |

**B2**

\[ E = -2080.03932883 \text{ A.U.} \]

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -2.462228 | 0.275927 | 0.371436 |
| C       | -3.348571 | 1.127626 | -0.340148|
| C       | -4.589738 | 0.615577 | -0.748108|
| H       | -5.276230 | 1.257521 | -1.305637|
| C       | -4.970690 | -0.688532| -0.446373|
| H       | -5.941056 | -1.068497| -0.776857|
| C       | -4.117315 | -1.501395| 0.295934  |
| C       | -4.434921 | -2.514721| 0.551683  |
| C       | -2.863643 | -1.042463| 0.723156  |
| C       | -3.041497 | 2.595735 | -0.627462 |
| H       | -2.029005 | 2.798422 | -0.260666 |
| C       | -4.011317 | 3.524315 | 0.127658  |
| H       | -3.734757 | 4.580592 | -0.027251 |
| H       | -5.050209 | 3.400620 | -0.219696 |
| H       | -4.000439 | 3.326476 | 1.211635  |
| C       | -3.033492 | 2.905043 | -2.133700 |

\( H -2.301341 \quad 2.273725 \quad -2.657266 \)
\( H -4.022358 \quad 2.740254 \quad -2.592300 \)
\( H -2.762684 \quad 3.959907 \quad -2.308240 \)
\( C -2.010936 \quad -1.949788 \quad 1.605909 \)
\( H -1.012581 \quad -1.490894 \quad 1.667827 \)
\( C -1.839240 \quad -3.366027 \quad 1.031571 \)
\( H -2.797844 \quad -3.906719 \quad 0.981335 \)
\( H -1.171593 \quad -3.961054 \quad 1.676328 \)
\( H -1.402951 \quad -3.349105 \quad 0.021783 \)
\( C -2.583435 \quad -2.011794 \quad 3.036627 \)
\( H -2.691213 \quad -1.009638 \quad 3.480786 \)
\( H -1.928867 \quad -2.607266 \quad 3.695020 \)
\( H -3.580274 \quad -2.482644 \quad 3.043954 \)
\( N -1.179723 \quad 0.752076 \quad 0.803301 \)
\( C -1.023222 \quad 1.471061 \quad 2.063124 \)
\( H -1.528829 \quad 0.943949 \quad 2.887011 \)
\( H -1.441463 \quad 2.498345 \quad 2.020738 \)
\( C \quad 0.500999 \quad 1.487840 \quad 2.219839 \)
\( C \quad 0.863658 \quad 2.371327 \quad 2.759757 \)
\( H \quad 0.850017 \quad 0.594052 \quad 2.765605 \)
\( N \quad 1.012851 \quad 1.468548 \quad 0.846423 \)
\( C \quad -0.008555 \quad 0.877823 \quad -0.004347 \)
\( C \quad -0.583111 \quad 0.770269 \quad 1.772589 \)
\( O \quad -0.138366 \quad 1.749152 \quad -1.113142 \)
\( C \quad 1.048105 \quad 2.510285 \quad -1.219946 \)
\( C \quad 0.811377 \quad 3.445969 \quad -1.743853 \)
\( H \quad 1.808907 \quad 1.960086 \quad -1.804033 \)
\( C \quad 1.489721 \quad 2.719907 \quad 0.236336 \)
\( H \quad 0.914068 \quad 3.578374 \quad 0.645189 \)
\( C \quad 2.997290 \quad 3.063631 \quad 0.439139 \)
| Element | X-coord | Y-coord | Z-coord |
|---------|---------|---------|---------|
| C       | 3.91529 | 1.90915 | 0.00729 |
| H       | 3.80304 | 1.66050 | -1.05956 |
| H       | 3.69638 | 1.00805 | 0.59681 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| C       | 3.27694 | 3.37812 | 1.92168 |
| H       | 3.14226 | 2.49173 | 2.55962 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| C       | 3.27694 | 3.37812 | 1.92168 |
| H       | 3.14226 | 2.49173 | 2.55962 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| C       | 3.27694 | 3.37812 | 1.92168 |
| H       | 3.14226 | 2.49173 | 2.55962 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| Au      | 0.60140 | -1.03543 | -0.79062 |
| S       | 2.52051 | -1.54871 | 0.91749 |
| Cl      | 1.15427 | -3.18916 | -1.89164 |
| C       | 3.92293 | -1.96366 | -0.17485 |
| C       | 2.09505 | -3.22770 | 1.48867 |
| H       | 4.72161 | -2.41778 | 0.42880 |
| H       | 3.56960 | -2.64377 | -0.96335 |
| H       | 4.28301 | -1.02601 | -0.61730 |
| H       | 2.50809 | -3.64824 | 2.03591 |
| C       | 1.23615 | -3.13317 | 2.16612 |
| H       | 1.82578 | -3.84330 | 0.61831 |
| C       | 3.00804 | -1.18634 | 3.68753 |
| H       | 2.54112 | -1.26239 | 4.68343 |
| N       | 0.88063 | -1.49578 | 0.50630 |
| C       | 2.16103 | -0.88037 | 0.28718 |
| C       | 2.80920 | -0.99295 | -0.96933 |
| C       | 4.03862 | -0.33860 | -1.14694 |
| H       | 4.54031 | -0.40113 | -2.11523 |

**B2-C2**

E= -2080.00477573 A.U.

| Element | X-coord | Y-coord | Z-coord |
|---------|---------|---------|---------|
| N       | 0.88063 | -1.49578 | 0.50630 |
| C       | 3.91525 | 1.90915 | 0.00729 |
| H       | 3.80304 | 1.66050 | -1.05956 |
| H       | 3.69638 | 1.00805 | 0.59681 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| C       | 3.27694 | 3.37812 | 1.92168 |
| H       | 3.14226 | 2.49173 | 2.55962 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| C       | 3.27694 | 3.37812 | 1.92168 |
| H       | 3.14226 | 2.49173 | 2.55962 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| C       | 3.27694 | 3.37812 | 1.92168 |
| H       | 3.14226 | 2.49173 | 2.55962 |
| H       | 4.97074 | 2.17925 | 0.17253 |
| Au      | 0.60140 | -1.03543 | -0.79062 |
| S       | 2.52051 | -1.54871 | 0.91749 |
| Cl      | 1.15427 | -3.18916 | -1.89164 |
| C       | 3.92293 | -1.96366 | -0.17485 |
| C       | 2.09505 | -3.22770 | 1.48867 |
| H       | 4.72161 | -2.41778 | 0.42880 |
| H       | 3.56960 | -2.64377 | -0.96335 |
| H       | 4.28301 | -1.02601 | -0.61730 |
| H       | 2.50809 | -3.64824 | 2.03591 |
| C       | 1.23615 | -3.13317 | 2.16612 |
| H       | 1.82578 | -3.84330 | 0.61831 |
| C       | 3.00804 | -1.18634 | 3.68753 |
| H       | 2.54112 | -1.26239 | 4.68343 |
| N       | 0.88063 | -1.49578 | 0.50630 |
| C       | 2.16103 | -0.88037 | 0.28718 |
| C       | 2.80920 | -0.99295 | -0.96933 |
| C       | 4.03862 | -0.33860 | -1.14694 |
| H       | 4.54031 | -0.40113 | -2.11523 |

S92
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -1.217194 | -3.548400 | 1.892716 |
| H    | -0.605803 | -2.176115 | 2.842182 |
| N    | -1.338491 | -1.664070 | 0.906773 |
| C    | -0.354490 | -1.057215 | 0.078217 |
| H    | -0.548302 | -0.327087 | -1.840045 |
| O    | -0.831070 | -1.825538 | -1.432076 |
| C    | -2.223428 | -1.937400 | -1.309826 |
| H    | -2.587606 | -2.795493 | -1.897870 |
| H    | -2.729384 | -1.030803 | -1.696913 |
| C    | -2.534883 | -2.140847 | 0.199314 |
| H    | -2.606847 | -3.228467 | 0.380461 |
| C    | -3.879817 | -1.538869 | 0.706060 |
| C    | -3.881946 | -0.002166 | 0.645236 |
| H    | -3.773751 | 0.378730  | -0.381529 |
| H    | -3.056446 | 0.404893  | 1.248241 |
| H    | -4.828545 | 0.394574  | 1.047352 |
| C    | -4.089713 | -1.973420 | 2.169316 |
| H    | -3.289707 | -1.582927 | 2.817548 |
| H    | -4.103268 | -3.072187 | 2.266447 |
| H    | -5.049493 | -1.593963 | 2.556123 |
| C    | -5.027139 | -2.104328 | -0.153034 |
| H    | -6.001895 | -1.767550 | 0.234950 |
| H    | -5.030738 | -3.207528 | -0.144979 |
| H    | -4.960761 | -1.774338 | -1.201759 |
| Au   | -0.502732 | 0.861947  | -0.760062 |
| S    | -0.529592 | 2.689775  | 1.321659 |
| Cl   | -0.752483 | 2.732242  | -2.248204 |
| C    | -2.036886 | 3.647023  | 0.956352 |
| C    | 0.736041  | 3.876679  | 0.759516 |
| H    | -2.047921 | 4.564229  | 1.562760 |

\[E = -2080.06298648 \text{ A.U.}\]

A1-B3

-2.441310 -0.904133 -0.117254
-2.187513 -2.064711 -0.887914
-2.555024 -3.308265 -0.355293
-2.369922 -4.217485 -0.932696
-3.151141 -3.404700 0.900894
-3.425885 -4.383629 1.302807
-3.398263 -2.252638 1.643900
-3.866082 -2.339589 2.627292
-3.059494 -0.982986 1.154198
-1.555866 -1.992570 -2.275580
-1.243488 -0.950899 -2.436337
-2.569517 -2.363358 -3.374726
-2.121498 -2.242170 -4.374915
-2.898341 -3.411724 -3.282141
-3.471817 -1.732615 -3.328320
-0.288590 -2.856149 -2.384541
0.452525 -2.561495 -1.624314
-0.507021 -3.928818 -2.254458
0.179128 -2.730332 -3.374722
-3.392992 0.249851 1.991357
-2.989417 1.131892 1.472594
-2.735149 0.202933 3.381884

S93
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -3.149569 | -0.614587 | 3.995052 |
| H    | -2.923554  | 1.145065  | 3.923172 |
| H    | -1.647456  | 0.054428  | 3.301479 |
| C    | -4.917063  | 0.449956  | 2.102518 |
| H    | -5.396816  | 0.512179  | 1.112184 |
| H    | -5.146444  | 1.378417  | 2.650901 |
| H    | -5.392244  | -0.382720 | 2.646649 |
| N    | -2.115600  | 0.376358  | -0.680420 |
| C    | -3.092548  | 1.118066  | -1.480065 |
| H    | -4.014914  | 1.281531  | -0.894011 |
| H    | -3.370276  | 0.580305  | -2.400178 |
| C    | -2.353277  | 2.426380  | -1.767889 |
| H    | -1.881172  | 2.394292  | -2.768273 |
| H    | -3.010467  | 3.307924  | -1.731368 |
| N    | -1.330385  | 2.489800  | -0.706011 |
| C    | -1.071153  | 1.173831  | -0.304129 |
| H    | -0.602954  | 0.951957  | 0.662416  |
| O    | 0.403727   | 0.901032  | -1.228281 |
| C    | 0.799260   | 2.163410  | -1.727277 |
| H    | 0.665766   | 2.184978  | -2.825475 |
| H    | 1.860123   | 2.361624  | -1.517899 |
| C    | -0.119248  | 3.237558  | -1.057270 |
| H    | -0.419522  | 3.973041  | -1.819983 |
| C    | 0.510387   | 4.080061  | 0.096175  |
| C    | 1.171602   | 3.224658  | 1.190029  |
| H    | 1.984588   | 2.597415  | 0.793044  |
| H    | 0.471051   | 2.550092  | 1.700918  |
| H    | 1.612751   | 3.879771  | 1.959105  |
| C    | -0.594043  | 4.952038  | 0.722463  |
| H    | -1.375316  | 4.332434  | 1.185389  |

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -1.075940 | 5.596079 | -0.033068 |
| H    | -0.170934  | 5.609269  | 1.498935 |
| C    | 1.574070   | 5.006669  | -0.529089 |
| H    | 2.016944   | 5.654672  | 0.243631 |
| H    | 1.138224   | 5.660636  | -1.303261 |
| H    | 2.399505   | 4.440692  | -0.990087 |
| H    | -0.424246  | -0.320320 |
| N    | 3.633856   | -1.892479 | 0.283309 |
| Cl   | 0.831844   | -0.356127 | 2.254703 |
| C    | 2.720412   | -3.212295 | 1.160173 |
| C    | 4.346975   | -1.031315 | 1.730424 |
| C    | 3.447741   | -3.855044 | 1.676588 |
| H    | 2.011129   | -2.739557 | 1.856848 |
| H    | 2.180424   | -3.793801 | 0.401224 |
| C    | 5.026850   | -1.723519 | 2.247817 |
| H    | 4.912297   | -0.170063 | 1.350264 |
| H    | 3.522873   | -0.696501 | 2.378906 |
| C    | 0.799260   | 2.163410  | -1.727277 |
| H    | 0.665766   | 2.184978  | -2.825475 |
| H    | 1.860123   | 2.361624  | -1.517899 |
| C    | -0.119248  | 3.237558  | -1.057270 |
| H    | -0.419522  | 3.973041  | -1.819983 |
| C    | 0.510387   | 4.080061  | 0.096175  |
| C    | 1.171602   | 3.224658  | 1.190029  |
| H    | 1.984588   | 2.597415  | 0.793044  |
| H    | 0.471051   | 2.550092  | 1.700918  |
| H    | 1.612751   | 3.879771  | 1.959105  |
| C    | -0.594043  | 4.952038  | 0.722463  |
| H    | -1.375316  | 4.332434  | 1.185389  |

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -3.149569 | -0.614587 | 3.995052 |
| H    | -2.923554  | 1.145065  | 3.923172 |
| H    | -1.647456  | 0.054428  | 3.301479 |
| C    | -4.917063  | 0.449956  | 2.102518 |
| H    | -5.396816  | 0.512179  | 1.112184 |
| H    | -5.146444  | 1.378417  | 2.650901 |
| H    | -5.392244  | -0.382720 | 2.646649 |
| N    | -2.115600  | 0.376358  | -0.680420 |
| C    | -3.092548  | 1.118066  | -1.480065 |
| H    | -4.014914  | 1.281531  | -0.894011 |
| H    | -3.370276  | 0.580305  | -2.400178 |
| C    | -2.353277  | 2.426380  | -1.767889 |
| H    | -1.881172  | 2.394292  | -2.768273 |
| H    | -3.010467  | 3.307924  | -1.731368 |
| N    | -1.330385  | 2.489800  | -0.706011 |
| C    | -1.071153  | 1.173831  | -0.304129 |
| H    | -0.602954  | 0.951957  | 0.662416  |
| O    | 0.403727   | 0.901032  | -1.228281 |
| C    | 0.799260   | 2.163410  | -1.727277 |

B3

E= -2080.07363201 A.U.
| Element | X   | Y   | Z   | Element | X   | Y   | Z   |
|---------|-----|-----|-----|---------|-----|-----|-----|
| H       | -1.392434 | -0.920966 | -2.329437 | C      | 1.296547  | 2.012296  | -1.847337 |
| C       | -2.538938  | -2.392028  | -3.390324  | H      | 1.105811  | 2.188348  | -2.930566  |
| H       | -1.854762  | -2.401347  | -4.254326  | H      | 2.336256  | 2.346029  | -1.669088  |
| H       | -2.937928  | -3.413133  | -3.274925  | C      | 0.340970  | 2.992908  | -1.064025  |
| H       | -3.387625  | -1.732880  | -3.636949  | H      | 0.136855  | 3.845186  | -1.732085  |
| C       | -0.590213  | -2.819958  | -1.807128  | C      | 0.883681  | 3.652234  | 0.250384   |
| H       | -0.079559  | -2.466365  | -0.898698  | C      | 1.542812  | 2.664167  | 1.228024   |
| H       | -0.897326  | -3.866801  | -1.645433  | H      | 2.410001  | 2.162344  | 0.770992   |
| H       | 0.131152   | -2.801025  | -2.639641  | H      | 0.869686  | 1.873435  | 1.591715   |
| C       | -3.867678  | 0.737566   | 1.774032   | H      | 1.909363  | 3.215066  | 2.110355   |
| H       | -3.350917  | 1.547888   | 1.236753   | C      | -0.267499 | 4.387918  | 0.964624   |
| C       | -3.180017  | 0.602245   | 3.146538   | H      | -1.020689 | 3.687954  | 1.355582   |
| H       | -3.687561  | -0.153354  | 3.769007   | H      | -0.776448 | 5.098108  | 0.290388   |
| H       | -3.219222  | 1.561074   | 3.689995   | H      | 0.122801  | 4.964282  | 1.818563   |
| H       | -2.127535  | 0.296309   | 3.035262   | C      | 1.934200  | 4.701947  | -0.173694  |
| C       | -5.340128  | 1.161634   | 1.916608   | H      | 2.349411  | 5.204506  | 0.714024   |
| H       | -5.829487  | 1.282112   | 0.936214   | H      | 1.495149  | 5.478900  | -0.822358  |
| H       | -5.412675  | 2.120924   | 2.454496   | H      | 2.777020  | 4.246045  | -0.716154  |
| H       | -5.922937  | 0.421514   | 2.488225   | Au     | 2.292747  | -0.490546 | -0.389871  |
| N       | -2.314467  | 0.588316   | -0.724494  | S      | 3.681600  | -1.894704 | 0.876527   |
| C       | -3.037270  | 1.463804   | -1.662688  | Cl     | 0.205768  | -0.761633 | 1.968231   |
| H       | -3.953107  | 1.846038   | -1.181583  | C      | 2.598676  | -3.316704 | 1.265346   |
| H       | -3.333660  | 0.907428   | -2.564099  | C      | 3.701422  | -1.092398 | 2.519775   |
| C       | -2.004877  | 2.571656   | -1.943060  | H      | 3.118601  | -3.959213 | 1.990632   |
| H       | -1.565662  | 2.481805   | -2.951217  | H      | 1.646699  | -2.927743 | 1.659995   |
| H       | -2.420608  | 3.584775   | -1.838150  | H      | 2.436397  | -3.866604 | 0.328909   |
| N       | -0.961779  | 2.328848   | -0.929709  | H      | 4.186538  | -1.775841 | 3.231850   |
| C       | -1.157528  | 1.139517   | -0.364780  | H      | 4.295018  | -0.173697 | 2.422907   |
| H       | -0.518819  | 0.651909   | 0.395575   | H      | 2.662537  | -0.859736 | 2.804070   |
| O       | 1.062811   | 0.688409   | -1.547739  |
B3-C3

E= -2080.03913353 A.U.

|   |   |   |   |   |
|---|---|---|---|---|
| C | -2.796790 | -1.284940 | 0.023986 |   |   |
| C | -2.683371 | -2.395462 | -0.842794 |   |   |
| C | -2.938962 | -3.669119 | -0.317812 |   |   |
| H | -2.850044 | -4.544062 | -0.966052 |   |   |
| C | -3.277685 | -3.840867 | 1.022332 |   |   |
| H | -3.466546 | -4.843437 | 1.414854 |   |   |
| C | -3.352175 | -2.736412 | 1.868097 |   |   |
| H | -3.590264 | -2.885910 | 2.923613 |   |   |
| C | -3.116996 | -1.438815 | 1.392288 |   |   |
| C | -2.233174 | -2.258533 | -2.293939 |   |   |
| H | -2.077395 | -1.187717 | -2.493538 |   |   |
| C | -3.292511 | -2.766061 | -3.288003 |   |   |
| H | -2.956824 | -2.608848 | -4.326367 |   |   |
| H | -3.479256 | -3.845186 | -3.163176 |   |   |
| H | -4.258215 | -2.249206 | -3.161080 |   |   |
| C | -0.874394 | -2.951836 | -2.510754 |   |   |
| H | -0.136245 | -2.615986 | -1.765165 |   |   |
| H | -0.967767 | -4.046785 | -2.418688 |   |   |
| H | -0.491165 | -2.736657 | -3.522645 |   |   |
| C | -3.139499 | -0.264381 | 2.364751 |   |   |
| H | -3.097071 | 0.662980 | 1.774375 |   |   |
| C | -1.882218 | -0.290833 | 3.256052 |   |   |
| H | -1.905057 | -1.156516 | 3.938626 |   |   |
| H | -1.822524 | 0.621775 | 3.872516 |   |   |
| H | -0.966102 | -0.375103 | 2.651878 |   |   |
| C | -4.426757 | -0.201780 | 3.203530 |   |   |
| H | -5.326476 | -0.168866 | 2.567811 |   |   |
| H | -4.425969 | 0.699173 | 3.838732 |   |   |

H -4.524400 -1.070683 3.874042
N -2.633227 0.035563 -0.524788
C -3.758058 0.702268 -1.224871
H -4.572997 0.902920 -0.507481
H -4.159997 0.062900 -2.023349
C -3.103792 1.991992 -1.745525
H -2.869373 1.938813 -2.824555
H -3.723325 2.882967 -1.577164
N -1.852482 2.027571 -0.962193
C -1.595421 0.856857 -0.353209
H -0.148889 0.950080 -0.028237
O 0.823994 1.512605 -0.161165
C 0.559570 2.386541 -1.241143
H 0.562770 1.835838 -2.202633
C 1.352404 3.146392 -1.302427
C -0.823359 3.070975 -1.101522
H -1.011517 3.557574 -2.075776
C -0.926928 4.208631 -0.023733
C -0.637609 3.702302 1.401573
H 0.389212 3.326470 1.501353
C -1.315735 2.882304 1.683589
C -0.784156 4.521349 2.124908
C -2.346508 4.810979 -0.056707
H -3.105809 4.083095 0.267713
H -2.617337 5.171811 -1.063612
H -2.409092 5.671061 0.628744
C 0.073897 5.324948 -0.383921
H -0.061872 6.185728 0.289641
H -0.072028 5.686781 -1.416161
H 1.118901 4.996257 -0.282377
Au     2.544487     0.196266     -0.014611
S      4.659489     -0.890103     0.097196
Cl     1.098883     -1.978731     0.700115
C      4.324569     -2.392633     -0.891006
C      4.563831     -1.625867     1.769616
H      5.131967     -3.117707     -0.712700
H      3.337600     -2.786087     -0.600991
H      4.321501     -2.090823     -1.946924
H      5.371555     -2.364539     1.875386
H      4.706983     -0.810437     2.491121
H      3.567325     -2.077173     1.893841
C      3.551068     -0.392886     0.097420
C      3.608021     -1.669829     0.702494
C      4.384315     -2.657487     0.079009
H      4.437220     -3.656160     0.518540
C      5.080918     -2.390846     -1.098092
H      5.677119     -3.176293     -1.569581
C      5.012207     -1.125483     -1.678575
H      5.555386     -0.931784     -2.606373
C      4.252016     -0.101417     -1.095981
C      2.829484     -2.009169     1.970445
H      2.379489     -1.077328     2.344630
C      3.739135     -2.555193     3.084974
H      3.159465     -2.717889     4.007935
H      4.189966     -3.521772     2.808303
H      4.561744     -1.859539     3.316849
C      1.669730     -2.977429     1.669678

C3

E= -2080.04623564 A.U.

C      3.551068     -0.392886     0.097420
C      3.608021     -1.669829     0.702494
C      4.384315     -2.657487     0.079009
H      4.437220     -3.656160     0.518540
C      5.080918     -2.390846     -1.098092
C      5.677119     -3.176293     -1.569581
C      5.012207     -1.125483     -1.678575
H      5.555386     -0.931784     -2.606373
C      4.252016     -0.101417     -1.095981
C      2.829484     -2.009169     1.970445
H      2.379489     -1.077328     2.344630
C      3.739135     -2.555193     3.084974
H      3.159465     -2.717889     4.007935
H      4.189966     -3.521772     2.808303
H      4.561744     -1.859539     3.316849
C      1.669730     -2.977429     1.669678
|       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| C     | -0.464612 | 3.250484 | -1.253620 | C     | 3.538515 | -3.372625 | -0.616708 |       |       |       |       |       |       |       |       |       |
| H     | -1.229735 | 2.507416 | -1.515319 | H     | 4.028505 | -4.250614 | -1.045244 |       |       |       |       |       |       |       |       |       |
| H     | 0.517746 | 2.817529 | -1.498605 | C     | 3.847250 | -2.100092 | -1.090215 |       |       |       |       |       |       |       |       |       |
| H     | -0.607837 | 4.135786 | -1.894613 | H     | 4.584286 | -1.991298 | -1.889257 |       |       |       |       |       |       |       |       |       |
| C     | 0.477899 | 4.782935 | 0.489151  | C     | 3.235516 | -0.955484 | -0.558327 |       |       |       |       |       |       |       |       |       |
| H     | 1.500544 | 4.468195 | 0.229277  | C     | 0.924723 | -2.642436 | 2.073324  |       |       |       |       |       |       |       |       |       |
| H     | 0.470103 | 5.109343 | 1.542964  | H     | 0.401138 | -1.688385 | 2.238908  |       |       |       |       |       |       |       |       |       |
| H     | 0.242206 | 5.663691 | -0.128688 | C     | 1.614975 | -3.048136 | 3.391123  |       |       |       |       |       |       |       |       |       |
| C     | -1.956416 | 4.221437 | 0.524491  | H     | 0.877023 | -3.141885 | 4.204793  |       |       |       |       |       |       |       |       |       |
| H     | -2.143579 | 5.116237 | -0.089922 | H     | 2.119258 | -4.022641 | 3.286201  |       |       |       |       |       |       |       |       |       |
| H     | -2.058082 | 4.520664 | 1.581642  | H     | 2.380357 | -2.321108 | 3.707673  |       |       |       |       |       |       |       |       |       |
| H     | -2.753790 | 3.497587 | 0.299780  | C     | -0.149078 | -3.676157 | 1.690458  |       |       |       |       |       |       |       |       |       |
| Au    | -1.963625 | -1.361988 | -0.376406 | H     | -0.638572 | -3.421290 | 0.739160  |       |       |       |       |       |       |       |       |       |
| S     | -5.189378 | 1.413751 | 0.237556  | H     | 0.276945 | -4.688401 | 1.596262  |       |       |       |       |       |       |       |       |       |
| Cl    | -3.046632 | -3.349455 | -0.738485 | H     | -0.922119 | -3.723074 | 2.475197  |       |       |       |       |       |       |       |       |       |
| C     | -5.635577 | -0.125388 | 1.106787  | C     | 3.634930 | 0.413592  | -1.103436 |       |       |       |       |       |       |       |       |       |
| C     | -5.208575 | 0.815779 | -1.484053 | H     | 3.127927 | 1.179026  | -0.499136 |       |       |       |       |       |       |       |       |       |
| H     | -6.646558 | -0.456238 | 0.822679  | C     | 3.159917 | 0.600710  | -2.555688 |       |       |       |       |       |       |       |       |       |
| H     | -4.910224 | -0.925932 | 0.896207  | H     | 3.646046 | -0.120921 | -3.232260 |       |       |       |       |       |       |       |       |       |
| H     | -5.626500 | 0.098145 | 2.183394  | H     | 3.403187 | 1.613380  | -2.917727 |       |       |       |       |       |       |       |       |       |
| H     | -6.216107 | 0.476922 | -1.770795 | H     | 2.072342 | 0.455604  | -2.640552 |       |       |       |       |       |       |       |       |       |
| H     | -4.923815 | 1.663891 | -2.123162 | C     | 5.147325 | 0.670160  | -0.973833 |       |       |       |       |       |       |       |       |       |
| H     | -4.485869 | -0.002139 | -1.626937 | H     | 5.489635 | 0.554420  | 0.066999  |       |       |       |       |       |       |       |       |       |
| H     | 5.392452 | 1.693722 | -1.301447 | H     | 5.736701 | -0.022384 | -1.595953 |       |       |       |       |       |       |       |       |       |

**C3-D3**

E= -2080.03028049 A.U.

|       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| C     | 2.269384 | -1.131036 | 0.462849 | C     | 2.063535 | 0.542412 | 2.359710 |       |       |       |       |       |       |       |       |
| C     | 1.945406 | -2.418009 | 0.959659 | H     | 3.095305 | 0.931319 | 2.279542 |       |       |       |       |       |       |       |       |
| C     | 2.601654 | -3.524159 | 0.402876 | H     | 2.053055 | -0.238840 | 3.129506 |       |       |       |       |       |       |       |       |
| H     | 2.362284 | -4.526159 | 0.765120 | C     | 1.041892 | 1.651868 | 2.607081 |       |       |       |       |       |       |       |       |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 0.204453 | 1.314364 | 3.245337 |
| H    | 1.481860 | 2.546427 | 3.063222 |
| N    | 0.546190 | 1.903351 | 1.235411 |
| C    | 0.817355 | 0.877077 | 0.400285 |
| H    | -0.129683 | 1.681146 | -1.067478 |
| O    | -1.050441 | 1.997901 | -1.228829 |
| C    | -1.496462 | 2.554507 | 0.018226 |
| H    | -2.094186 | 1.806822 | 0.565065 |
| C    | -0.351873 | 3.029574 | 0.927184 |
| H    | -0.843604 | 3.290791 | 1.881471 |
| C    | 0.397591  | 4.337396 | 0.464963 |
| C    | 1.082305  | 4.182152 | -0.906244 |
| H    | 0.356464  | 4.018212 | -1.714617 |
| C    | 1.791712  | 3.339627 | -0.910382 |
| H    | 1.654289  | 5.094131 | -1.142887 |
| C    | 1.471329  | 4.720900 | 1.503441 |
| H    | 2.283557  | 3.979663 | 1.547542 |
| H    | 1.044918  | 4.835297 | 2.514014 |
| H    | 1.928736  | 5.684872 | 1.230355 |
| C    | -0.623410 | 5.491729 | 0.395124 |
| H    | -0.105265 | 6.440632 | 0.185384 |
| H    | -1.165058 | 5.614446 | 1.348308 |
| H    | -1.366909 | 5.347252 | -0.402848 |
| Au   | -1.165247 | -0.426318 | -1.152381 |
| S    | -4.265281 | -0.051449 | 1.310725 |
| Cl   | -1.920919 | -2.590717 | -1.540005 |
| C    | -4.086474 | -1.831758 | 1.655191 |
| C    | -5.123046 | -0.137829 | -0.295166 |
| H    | -5.073382 | -2.307750 | 1.766362 |

A1-B4

E = -2080.06341895 A.U.
| Atom | X  | Y  | Z  |
|------|----|----|----|
| H    | 2.269210 | 2.579100 | 3.534824 |
| H    | 3.477862 | 1.326415 | 3.180572 |
| H    | 1.746375 | 1.005327 | 2.897707 |
| C    | 3.797941 | 3.374476 | 1.324767 |
| H    | 3.934803 | 3.747978 | 0.297691 |
| H    | 4.758650 | 2.953887 | 1.664419 |
| H    | 3.570890 | 4.242061 | 1.965371 |
| N    | 1.335668 | 1.172714 | -1.010006 |
| C    | 2.375553 | 1.385669 | -2.018959 |
| H    | 3.163850 | 2.062454 | -1.637176 |
| H    | 1.972849 | 1.830897 | -2.942922 |
| C    | 2.908011 | -0.025906 | -2.253298 |
| H    | 2.350544 | -0.517850 | -3.074426 |
| H    | 3.977242 | -0.036838 | -2.513926 |
| N    | 2.666864 | -0.694787 | -0.965191 |
| C    | 1.461702 | -0.104297 | -0.428020 |
| H    | 1.427143 | -0.090202 | 0.674402 |
| O    | 0.396065 | -1.062452 | -0.824896 |
| C    | 0.988527 | -2.349565 | -0.661436 |
| H    | 0.477029 | -3.051203 | -1.333695 |
| H    | 0.855463 | -2.702526 | 0.376126 |
| C    | 2.492462 | -2.154144 | -1.012223 |
| H    | 2.651259 | -2.483543 | -2.053847 |
| C    | 3.502712 | -2.950823 | -0.137480 |
| C    | 3.469468 | -2.495557 | 1.332278 |
| H    | 2.492441 | -2.676412 | 1.807698 |
| H    | 3.697738 | -1.422014 | 1.414733 |
| H    | 4.221815 | -3.046938 | 1.918895 |
| C    | 4.916379 | -2.709808 | -0.698500 |
| H    | 5.176287 | -1.640814 | -0.658093 |

**B4**

E = -2080.06848479 A.U.

| Atom | X  | Y  | Z  |
|------|----|----|----|
| H    | 4.994391 | -3.042535 | -1.747212 |
| H    | 5.669342 | -3.264631 | -0.115784 |
| C    | 3.166853 | -4.451128 | -0.234338 |
| H    | 3.909735 | -5.050283 | 0.316182 |
| H    | 3.171221 | -4.797926 | -1.281303 |
| H    | 2.178393 | -4.684103 | 0.193634 |
| Au   | -1.938022 | -1.146749 | -0.132803 |
| S    | -1.079618 | -0.375125 | 2.385115 |
| Cl   | -4.145249 | -1.716350 | -0.656387 |
| H    | -2.093285 | -1.545502 | 3.348023 |
| C    | -2.060271 | 1.147219 | 2.589266 |
| H    | -2.139863 | -1.228768 | 4.400462 |
| H    | -3.101948 | -1.622164 | 2.917750 |
| H    | -1.601195 | -2.525816 | 3.285090 |
| H    | -2.100738 | 1.427100 | 3.652291 |
| H    | -1.549884 | 1.938460 | 2.023564 |
| H    | -3.073876 | 1.005750 | 2.188027 |
| C    | -0.184391 | 2.354609 | -0.156533 |
| C    | -1.506382 | 2.564469 | -0.626964 |
| C    | -2.377097 | 3.333770 | 0.158347 |
| H    | -3.400756 | 3.500714 | -0.182747 |
| C    | -1.963237 | 3.884658 | 1.369363 |
| H    | -2.661591 | 4.472683 | 1.970704 |
| C    | -0.653280 | 3.697122 | 1.805115 |
| H    | -0.331091 | 4.153245 | 2.744411 |
| C    | 0.264754 | 2.950166 | 1.051361 |
| C    | -1.978620 | 2.033051 | -1.977243 |
|  |  |  |  |  |  |
|---|---|---|---|---|---|
| **B4-C3** | **H** | -5.196179 | -0.138100 | 3.989214 |
| **E= -2080.03954687 A.U.** | **N** | -2.905727 | 0.800533 | -0.214804 |
| **C** | **C** | -3.593480 | 2.065283 | -0.546719 |
| -3.625083 | -0.402137 | 0.108811 | **H** | -4.142665 | 2.441399 | 0.333344 |
| -3.993892 | -1.277845 | -0.938538 | **H** | -4.320276 | 1.914924 | -1.358747 |
| -4.706221 | -2.437384 | -0.601436 | **C** | -2.419281 | 2.979613 | -0.940150 |
| -4.994205 | -3.139519 | -1.386981 | **C** | -2.356207 | 3.145184 | -2.030204 |
| -5.043278 | -2.717034 | 0.721844 | **H** | -2.486468 | 3.958714 | -0.451134 |
| -5.595394 | -3.628948 | 0.963007 | **C** | -1.581957 | 0.946076 | -0.169979 |
| -4.670793 | -1.839805 | 1.738524 | **H** | -0.382382 | 0.177913 | -0.274043 |
| -4.933037 | -2.076026 | 2.772393 | **C** | -3.958078 | -0.665106 | 1.457377 |
| -3.598149 | -1.023849 | -2.390448 | **C** | -0.726667 | 0.190623 | -0.584555 |
| -3.203684 | 0.001458 | -2.454999 | **C** | 1.095807 | 1.489244 | -0.144797 |
| -4.795074 | -1.110810 | -3.352549 | **H** | 2.131807 | 1.674880 | -0.449094 |
| -4.485701 | -0.835933 | -4.373771 | **H** | 1.061358 | 1.548829 | 0.959683 |
| -5.209328 | -2.130551 | -3.402303 | **C** | 0.172323 | 2.573419 | -0.747981 |
| -5.610724 | -0.434731 | -3.049632 | **H** | 0.309788 | 2.543263 | -1.846855 |
| -2.460267 | -1.968110 | -2.823044 | **C** | 0.566886 | 4.023000 | -0.272716 |
| -1.578288 | -1.862407 | -2.172980 | **C** | 0.070198 | 4.301441 | 1.158855 |
| -2.780939 | -3.021755 | -2.782541 | **H** | 0.478240 | 3.577202 | 1.880419 |
| -2.147747 | -1.751018 | -3.857448 | **H** | -1.027010 | 4.264446 | 1.237134 |
| -3.536797 | 0.256060 | 2.599155 | **C** | 0.390939 | 5.304723 | 1.482059 |
| -3.095064 | 1.161114 | 2.156582 | **C** | 0.010399 | 5.090591 | -1.243202 |
| -2.441562 | -0.399194 | 3.460958 | **H** | -1.085272 | 5.150814 | -1.257726 |
| -2.812178 | -1.315464 | 3.948573 | **H** | 0.351268 | 4.901585 | -2.274151 |
| -2.106044 | 0.289803 | 4.253259 | **H** | 0.379519 | 6.086912 | -0.952684 |
| -1.566018 | -0.675140 | 2.853503 | **C** | 2.104893 | 4.177450 | -0.304806 |
| -4.731309 | 0.707429 | 3.457383 | **H** | 2.371855 | 5.227750 | -0.110121 |
| -5.513081 | 1.185528 | 2.845589 | **H** | 2.519813 | 3.910018 | -1.290216 |
| -4.404289 | 1.432887 | 4.219736 | **H** | 2.614853 | 3.565008 | 0.451376 |
| Element | X  | Y  | Z   |
|---------|----|----|-----|
| Au      | 1.989531 | -1.437374 | -0.117440 |
| S       | 5.155533 | 1.027213  | 0.284946  |
| Cl      | 3.389881 | -3.194288 | 0.378890  |
| C       | 5.824044 | -0.143011 | -0.942560 |
| C       | 5.361607 | 0.031763  | 1.798122  |
| H       | 6.898751 | -0.316380 | -0.775405 |
| H       | 5.278005 | -1.097447 | -0.904329 |
| H       | 5.687897 | 0.313409  | -1.933613 |
| H       | 6.428174 | -0.140528 | 2.012027  |
| H       | 4.923101 | 0.606926  | 2.626503  |
| H       | 4.835381 | -0.930153 | 1.704126  |