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:

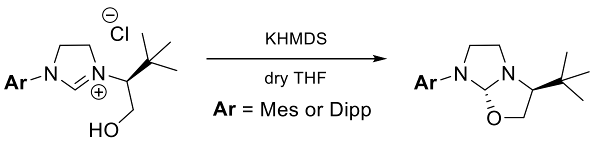
Unless indicated otherwise, all reactions were performed under inert atmosphere using Schlenk line techniques. Reactions at elevated temperature were maintained by thermostatically controlled oil-bath. Tetrahydrofuran, toluene, dichloromethane and diethyl ether were purified using MBraun MB-SPS-5 Solvent 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 **L1a**H·Cl and **L1b**H·Cl were synthesized according to literature procedure.[1] Solution of *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 $KMnO_4$. ^{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 ($CDCl_3$ = 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 $CFCl_3$ (δ = 0.0 ppm) as the internal standard; ^{31}P chemical shifts are reported with H_3PO_4 (δ = 0.0 ppm) as the internal standard; ^{11}B chemical shifts are reported with $BF_3.Et_2O$ (δ = 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 = oublet 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] a) M. Nakamura, T. Hatakeyama, K. Hara, E. Nakamura, *J. Am. Chem. Soc.* **2003**, *125*, 6362-6363; b) H. Clavier, L. Coutable, L. Toupet, J.-C. Guillemin, M. Mauduit, *J. Organomet. Chem.* **2005**, *690*, 5237-5254; c) T. Jennequin, J. Wencel-Delord, D. Rix, J. Daubignard, C. Crévisy, M. Mauduit, *Synlett* **2010**, *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, *Chem. Eur. J.* **2015**, *21*, 993-997.

[2] *Titration of n-Butyllithium :*https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Aldrich/Datasheet/1/689327dat.pdf

Physiques de l'Ouest (CRMPO), Université de Rennes 1. Data for oxazolidines **2a** and **2b** were acquired on a Bruker Maxis 4G device while gold (AuCl-**1a** and AuCl-**1b)** and copper complexes (CuBr-**1a** and CuBr-**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 (λ=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:



General procedure:

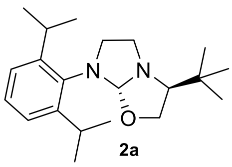
In a round bottom flask, the imidazolinium salt (1.0 equiv) and the base (3.0 or 1.0 equiv) were dissolved in dry THF over 1 h. Then, the mixture was filtrated through celite pad and the solvent was removed under vacuum to afford the pure oxazolidine.

Optimization Table:

Entry	Base (equiv)	scale (mmol)	NMR conv. (isolated yield) (%)	dr (2a) evaluated by NMR
1	KHMDS (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	KHMDS (1.0)	1.36	100 (95)	100/0

(3*S*,7a*S*)-3-(*tert*-butyl)-7-(2,6-diisopropylphenyl)hexahydroimidazo[2,1-*b*]oxazole (2a):

Imidazolinium salt **L1a**H·Cl (499 mg, 1.36 mmol), KHMDS (272 mg, 1.36 mmol) and THF (10 mL). White solid (427 mg, 95% yield).

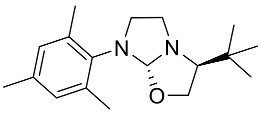


2a

Chemical Formula: $C_{21}H_{34}N_2O$
Molecular Weight: 330,52

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 – 7.26 (m, 1H), 7.20 – 7.18 (m, 2H), 5.35 (s, 1H, N-C<u>**H**</u>(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). **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 150.7, 148.4, 140.0, 127.4, 124.8, 123.4, 110.8 (N-<u>**C**</u>H(O)-N), 73.8, 64.2, 55.8, 54.1, 33.9, 28.0, 27.1, 26.2, 25.3, 24.6, 24.5. **HRMS** (ESI, CH_3OH, positive mode) calcd for $C_{21}H_{35}N_2O$ $[M+H]^+$: 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) : Imidazolinium salt **L1b**H·Cl (500 mg, 1.54 mmol), KHMDS (310 mg, 1.55 mmol), THF (25 mL). Colourless oil (444 mg, 99% yield).

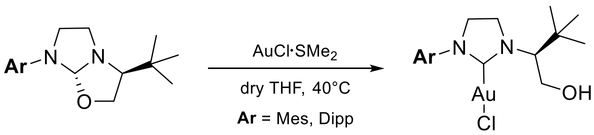


2b

Chemical Formula: $C_{18}H_{28}N_2O$
Molecular Weight: 288,44

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.89 (s, 2H), 5.39 (s, 1H, N-C<u>**H**</u>(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). **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 139.9, 136.0, 129.4, 109.8 (N-<u>**C**</u>H(O)-N), 74.1, 64.2, 56.0, 51.2, 34.0, 26.2, 21.0, 18.3. **HRMS** (ESI, CH_3OH, positive mode) calcd for $C_{18}H_{29}N_2O$ $[M+H]^+$: m/z 289.2274, found: 289.2278 (1 ppm).

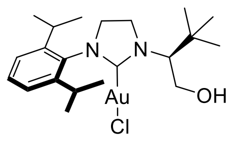
1.3. Representative procedure for the synthesis of gold complexes from the oxazolidine derivatives:



General procedure:

In a round bottom flask under argon atmosphere, the oxazolidine (1.0 equiv) and AuCl·SMe_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.

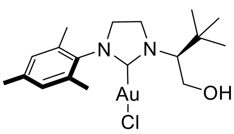
AuCl-1a complex: Oxazolidine **2a** (83 mg, 0.25 mmol), AuCl·SMe_2 (81 mg, 0.27 mmol), THF (5.0 mL). white/grey solid (118.1 mg, 84% yield).



AuCl-1a
Chemical Formula: $C_{21}H_{34}AuClN_2O$
Molecular Weight: 562,94

^{1}H NMR ($CDCl_3$, 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). **^{13}C NMR** ($CDCl_3$, 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, CH_2Cl_2, negative mode) calcd for $C_{21}H_{34}N_2OCl_2Au$ $[M+Cl]^-$: m/z 597.1719, found: 597.1720 (0 ppm).

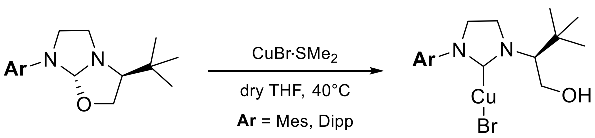
AuCl-1b complex: Oxazolidine **2b** (80 mg, 0.28 mmol), AuCl·SMe_2 (89.6 mg, 0.30 mmol), THF (4.0 mL). white/grey solid (57.4 mg, 40% yield).



AuCl-1b
Chemical Formula: $C_{18}H_{28}AuClN_2O$
Molecular Weight: 520,86

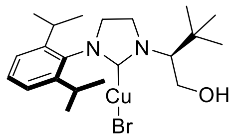
^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.90 – 6.87 (m, 2H), 4.62 (s, 1H), 4.04 – 3.93 (m, 2H), 3.91 – 3.72 (m, 5H), 2.27 (s, 3H), 2.21 (s, 3H), 2.20 (s, 3H), 1.09 (s, 9H). **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 195.8 ($C_{carbene}$), 138.6, 135.8, 135.6, 134.9, 129.6, 129.5, 70.4, 57.9, 50.6, 33.9, 28.3, 21.1, 18.0. **HRMS** (ESI, CH_2Cl_2, negative mode) calcd for $C_{18}H_{28}N_2OCl_2Au$ $[M+Cl]^-$: 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·SMe_2 (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.

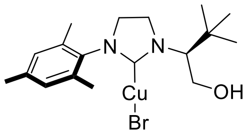
CuBr-1a complex: Oxazolidine **2a** (83.2 mg, 0.25 mmol), $CuBr{\cdot}SMe_2$ (56.5 mg, 0.275 mmol), THF (5.0 mL). white/greenish powder (64.1 mg, 54% yield). Relatively unstable in solution.



CuBr-1a
Chemical Formula: $C_{21}H_{34}BrCuN_2O$
Molecular Weight: 473,97

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 – 7.31 (m, 1H), 7.19 (d, *J* = 7.8 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 NMR** ($CDCl_3$, 101 MHz): δ 204.0 ($C_{carbene}$), 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_2Cl_2, negative mode) calcd for $C_{21}H_{34}N_2OBr_2Cu$ $[M+Br]^-$: m/z 551.0339, found: 551.0343 (1 ppm).

CuBr-1b complex: Oxazolidine **2b** (70 mg, 0.24 mmol), $CuBr{\cdot}SMe_2$ (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).

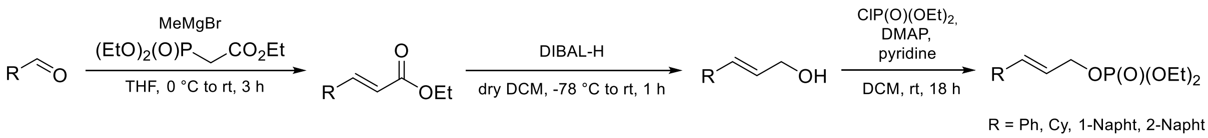


CuBr-1b
Chemical Formula: $C_{18}H_{28}BrCuN_2O$
Molecular Weight: 431,89

^{1}H NMR (500 MHz, CD_2Cl_2) δ 6.96 (s, 2H), 4.07 (s, 1H), 4.03 – 3.71 (m, 7H), 2.29 (s, 3H), 2.23 (d, *J* = 8.4 Hz, 6H), 1.08 (s, 9H). **^{13}C NMR** (126 MHz, CD_2Cl_2) δ 203.9 ($C_{carbene}$), 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_2Cl_2, negative mode) calcd for $C_{18}H_{28}N_2OBr_2Cu$ $[M+Br]^-$: 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:

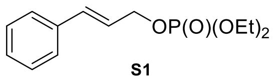


The (*E*)-Allylic phosphates were synthesized from the corresponding allylic alcohols using known procedure.[3] The allylic alcohols were synthesized from the corresponding aldehyde by two-step Horner-Wadsworth-Emmons olefination[4]/dibal-H reduction[5] sequence. Only the

[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).

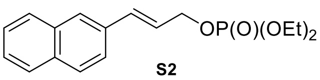
Cinnamyl diethyl phosphate (S1): colourless oil (3.99 g, 99% global yield).



S1
Chemical Formula: $C_{13}H_{19}O_4P$
Molecular Weight: 270,26

^{1}H 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 (dt, *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). **^{13}C 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). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ -0.75.

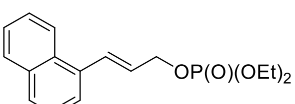
(*E*)-diethyl (3-(naphthalen-2-yl)allyl) phosphate (S2): colourless oil (3.91 g, 47% global yield).



S2
Chemical Formula: $C_{17}H_{21}O_4P$
Molecular Weight: 320,32

^{1}H 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). **^{13}C 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). **^{31}P 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)



S3
Chemical Formula: $C_{17}H_{21}O_4P$
Molecular Weight: 320,32

^{1}H 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). **^{13}C 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). **^{31}P NMR** ($CDCl_3$, 162 MHz) δ -0.65.

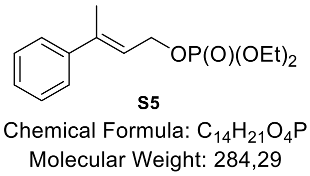
(*E*)-3-cyclohexylallyl diethyl phosphate (S4): colourless oil (2.004 g, 26% global yield)

S4
Chemical Formula: $C_{13}H_{25}O_4P$
Molecular Weight: 276,31

^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.86 – 5.67 (m, 1H), 5.54 (dtd, *J* = 15.5, 6.4, 1.3 Hz, 1H), 4.47 (dddd, *J* = 8.3, 6.4, 1.2, 0.8 Hz, 2H), 4.10

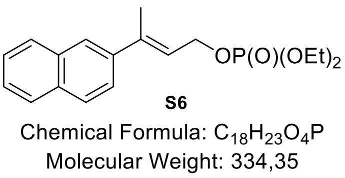
(dq, *J* = 7.9, 7.1 Hz, 4H), 1.98 (ddd, *J* = 14.1, 11.0, 2.5 Hz, 1H), 1.83 – 1.63 (m, 6H), 1.33 (td, *J* = 7.1, 1.0 Hz, 6H), 1.29 – 0.94 (m, 4H). ^{13}**C NMR** ($CDCl_3$, 101 MHz): δ 142.20, 122.07 (d, *J* = 6.6 Hz), 68.54 (d, *J* = 5.6 Hz), 63.76 (d, *J* = 5.8 Hz), 40.39, 32.62, 26.22, 26.06, 16.28 (d, *J* = 6.8 Hz). ^{31}**P NMR** ($CDCl_3$, 162 MHz) δ -0.77.

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



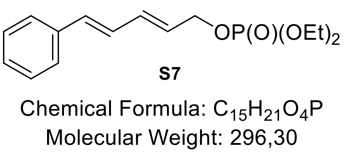
^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.36 – 7.31 (m, 2H), 7.29 – 7.16 (m, 3H), 5.88 (tq, *J* = 6.9, 1.4 Hz, 1H), 4.69 (ddd, *J* = 8.4, 6.9, 0.8 Hz, 2H), 4.06 (dq, *J* = 8.0, 7.1 Hz, 4H), 2.04 (dd, *J* = 1.4, 0.7 Hz, 3H), 1.27 (td, *J* = 7.1, 1.0 Hz, 6H). ^{13}**C NMR** (101 MHz, $CDCl_3$): δ 142.5, 140.5, 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) δ – 0.50

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



^{1}**H NMR** (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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) δ – 0.48.

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



^{1}**H NMR** (400 MHz, $CDCl_3$) δ 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 (ddtd, *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, $CDCl_3$) δ 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) δ – 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_2Zn (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 S_N2/S_N2' 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 $MgSO_4$, 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_2Zn (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 S_N2/S_N2' 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 $MgSO_4$, 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:

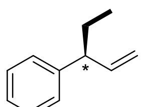
In a flame-dried Schlenk tube under Argon, Cu complex (0.005 mmol, 1.0 mol%) was dissolved in dry THF (0.5 mL). Then, the reaction was cooled down to 0 °C and Et_2Zn (1M in hexane, 1.5 mmol, 3.0 equiv) was added dropwise. The resulting mixture was stirred at 0 °C for 10 min. After this time, the reaction 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 ^1H 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.

1.5.3. 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 Et_2Zn (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 SN_2/SN_2' 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 $MgSO_4$, 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.

1.5.4. Characterization of catalysis products:

(pent-1-en-3-yl)benzene (γ-P1):



γ-P1

Chemical Formula: $C_{11}H_{14}$
Molecular Weight: 146,23

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 – 7.27 (m, 2H), 7.24 – 7.14 (m, 3H), 6.03 – 5.87 (m, 1H), 5.07 – 5.03 (m, 1H), 5.03 – 4.98 (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): δ 144.6, 142.4, 128.5, 127.8, 126.2, 114.2, 51.9, 28.5, 12.3. **$[\alpha]_D^{25}$** (c = 0.16, $CHCl_3$) = + 25 (89% ee). Analytical data for this compound were consistent with the previously reported data.[6]

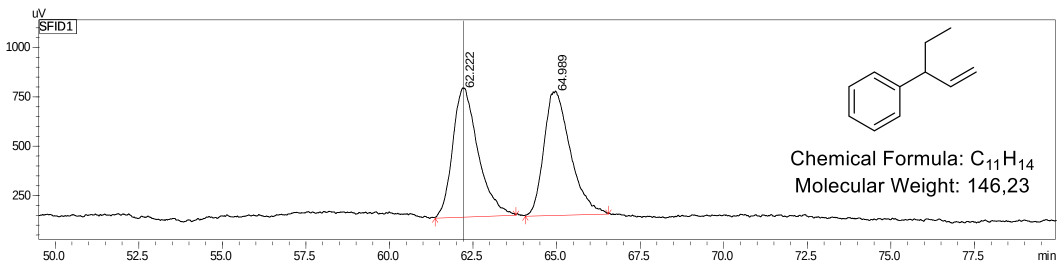
Entry	Catalytic system (mol%)	Time (h)	Conv. (yield) (%)	γ/α ratio	ee (%)
1	**L1a**H·PF_6/$(CuOTf)_2$.toluene (1.2/1)	0.5	>99 (62)	>99:1	90
2	**2a**/$(CuOTf)_2$.toluene (1.2/1)	0.5	>99 (92)	>99:1	89
3	**2a**/CuBr·SMe_2 (1.2/1)	0.5	>99 (97)	>99:1	88
4	**CuBr-1a** (1)	0.5	>99 (99)	>99:1	89
5	**2a** (5)	12	>99 (98)	>99:1	90
6	**2a** (1)	23	87 (76)[a]	97:3	91
7	**CuBr-1b** (1)	0.5	>99 (88)	>99:1	87
8	**2b** (5)	12	Nr	Nd	Nd
9	**CuBr-1a** (1) with EtMgBr	0.5	>99 (92)	>99:1	90
10	**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.

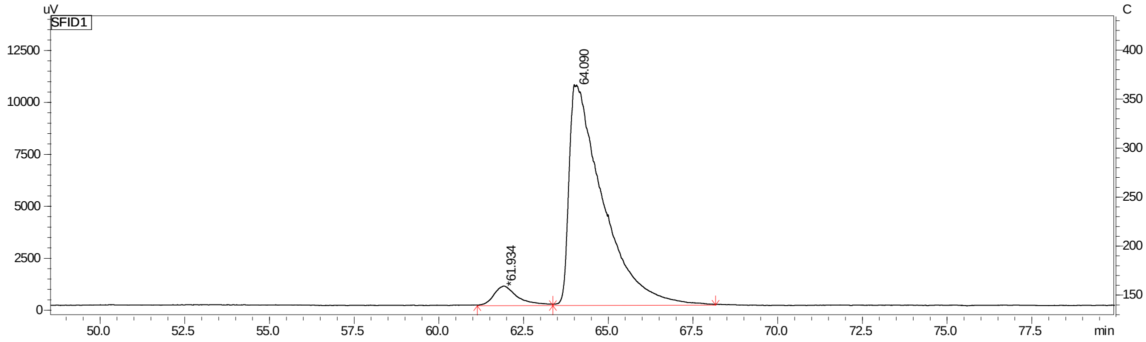
- Racemic mixture:



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

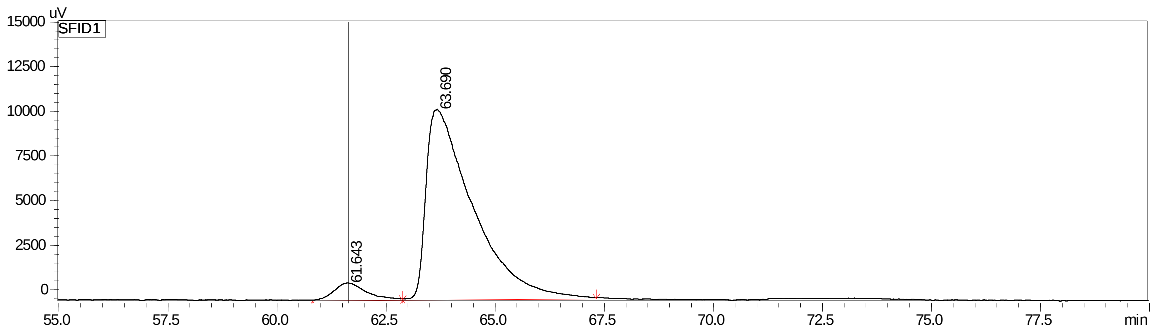
[6] M. A. Kacprzynski, A. H. Hoveyda, *J. Am. Chem. Soc.* **2004**, *126*, 10676-10681.

- Table 1, entry 1



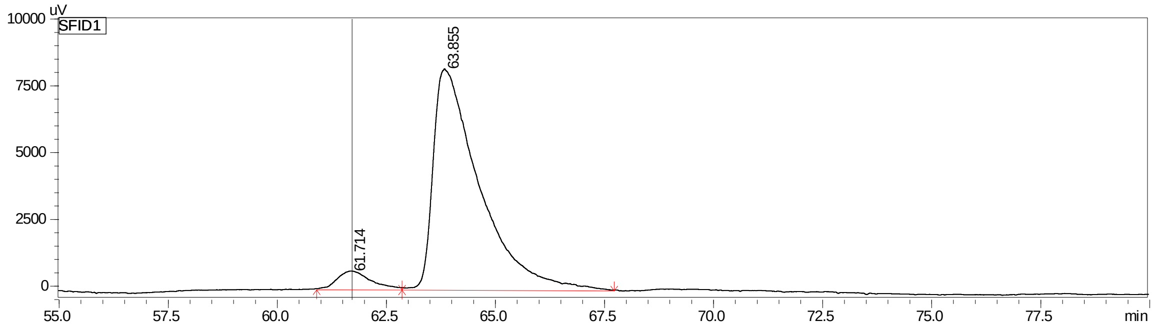
Peak	Retention time	Area	Height	% Area
1	61.934	41834	905	5.425
2	64.080	729249	10559	94.575

- Table 1, entry 2



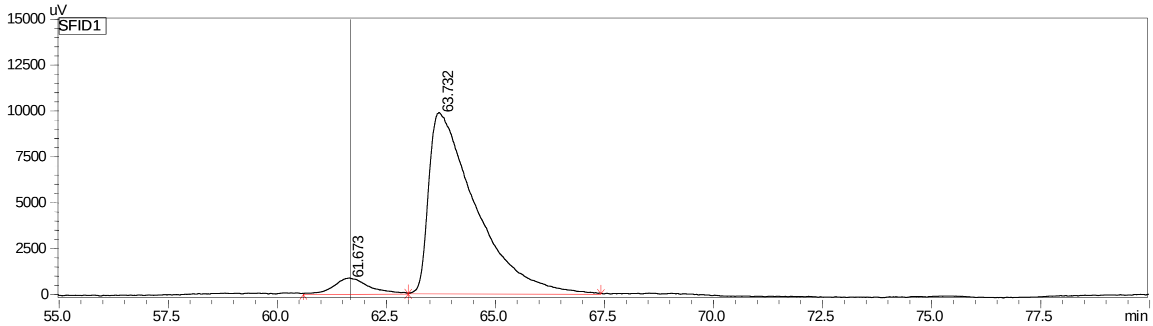
Peak	Retention time	Area	Height	% Area
1	61.643	46601	947	5.586
2	63.690	787629	10622	94.414

- Table 1, entry 3



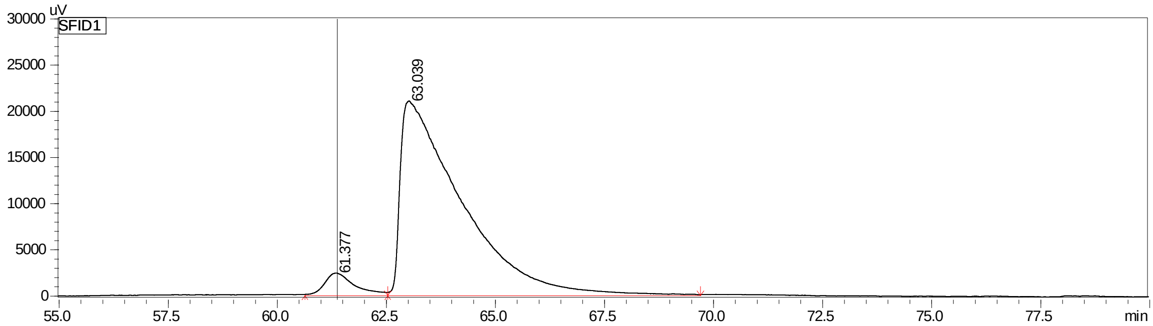
Peak	Retention time	Area	Height	% Area
1	61.714	34737	668	5.440
2	63.855	603760	8247	94.560

- Table 1, entry 4



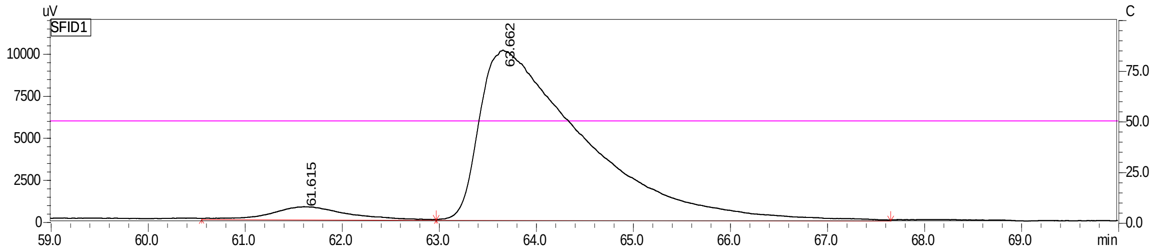
Peak	Retention time	Area	Height	% Area
1	61.673	42820	834	5.542
2	63.732	729892	9840	94.458

- Table 1, entry 5



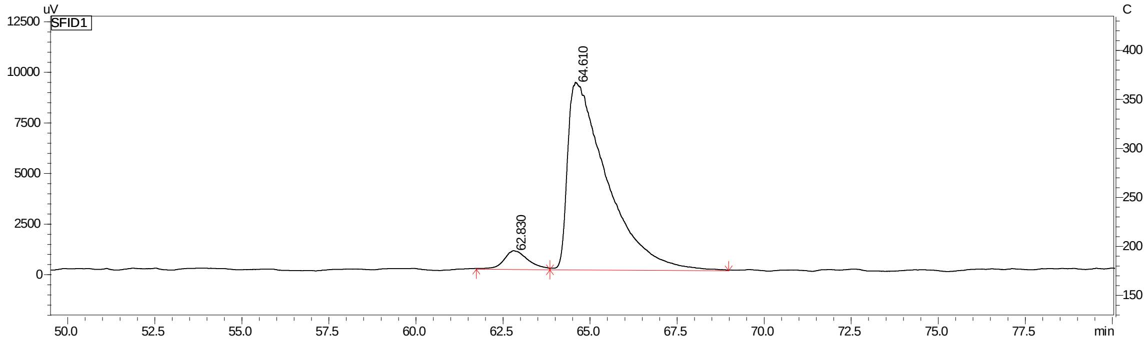
Peak	Retention time	Area	Height	% Area
1	61.377	107512	2356	5.047
2	63.039	2022556	20974	94.953

- Table 1, entry 6



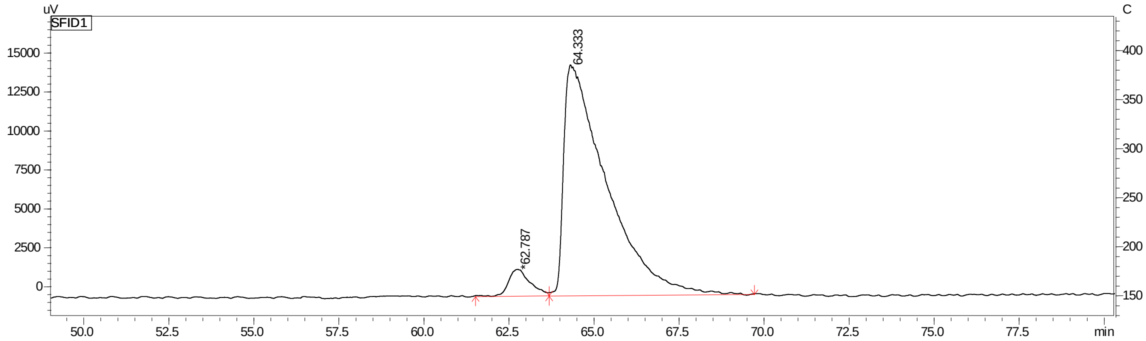
Peak	Retention time	Area	Height	% Area
1	61.615	36178	729	4.629
2	63.662	745358	10052	95.371

- Table 1, entry 7:



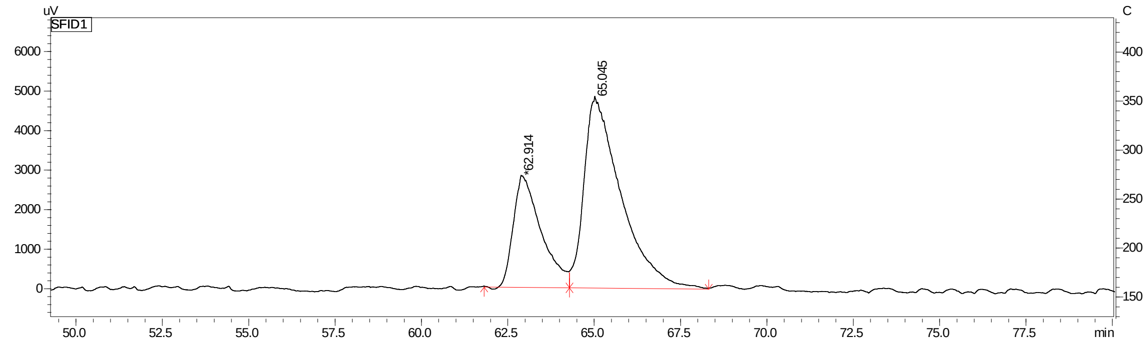
Peak	Retention time	Area	Height	% Area
1	62.830	40600	888	5.338
2	64.610	760638	9231	95.662

- Table 1, entry 9:



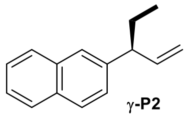
Peak	Retention time	Area	Height	% Area
1	62.787	71732	1683	5.290
2	64.333	1284306	14768	94.710

- 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):



γ-P2

Chemical Formula: $C_{15}H_{16}$
Molecular Weight: 196,29

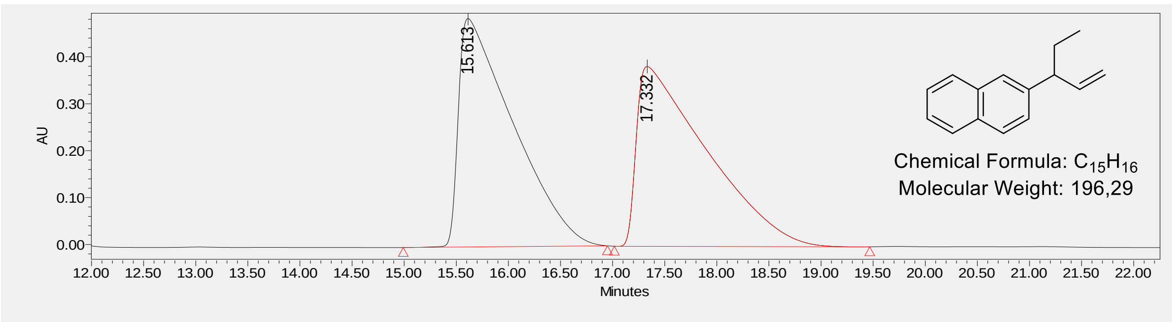
Entry	Catalytic system (mol%)	Time (h)	Conv. (yield) (%)	γ/α ratio	ee (%)
1	**CuBr-1a**	0.5	>99 (96)	>99:1	89
2	**2a**	12	>99 (84)	>99:1	89

^{1}H NMR ($CDCl_3$, 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). **^{13}C NMR** ($CDCl_3$, 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. **$[\alpha]_D^{25}$** (c = 0.5, $CHCl_3$) = + 5 (89% ee). Analytical data for this compound were consistent with the previously reported data.[6]

Analytical parameters:

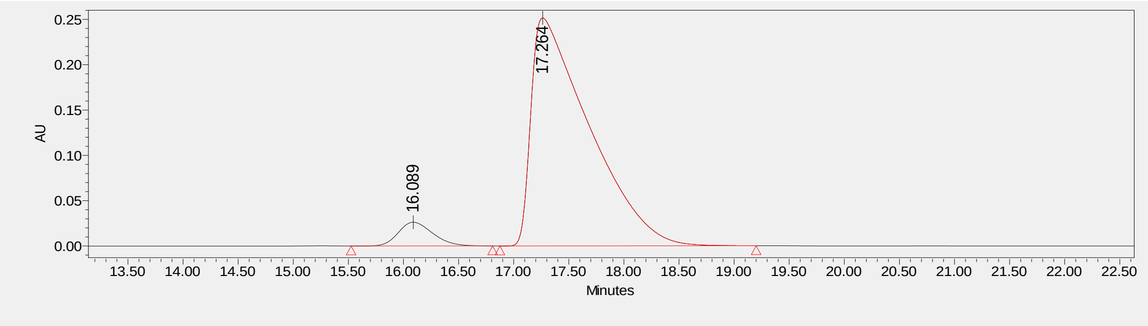
HPLC method 1: OJ-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane (100%) at 1.0 mL/min as mobile phase at 25°C and λ = 254 nm.

- Racemic mixture:



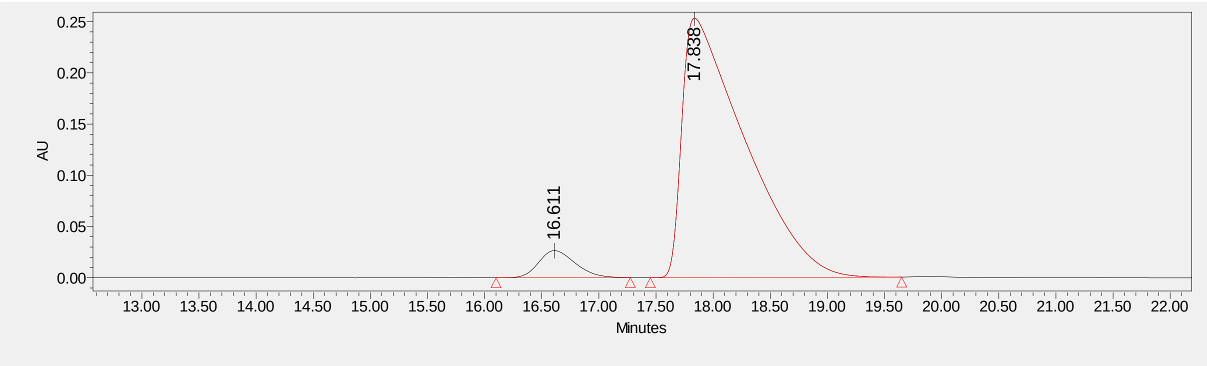
Peak	Retention time	Area	Height	% Area
1	15.613	17761103	487161	49.77
2	17.332	17926199	383228	50.23

- With **CuBr-1a**:



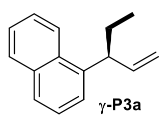
Peak	Retention time	Area	Height	% Area
1	16.089	569810	26240	5.81
2	17.264	9229969	251652	94.19

- 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 (γ-P3a):



Chemical Formula: $C_{15}H_{16}$
Molecular Weight: 196,29

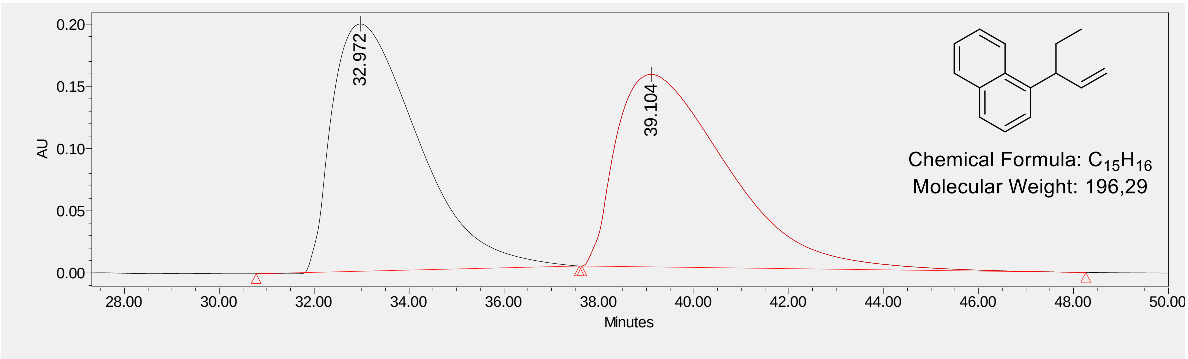
Entry	Catalytic system (mol%)	Time (h)	Conv. (yield) (%)	γ/α ratio	ee (%)
1	**CuBr-1a**	0.5	>99 (68)	>99:1	94
2	**2a**	12	>99 (79)	>99:1	94

^{1}H NMR ($CDCl_3$, 400 MHz): δ 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** ($CDCl_3$, 101 MHz): δ 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. **[α]$_D^{25}$** (c = 0.52, $CHCl_3$) = – 21 (94% ee). Analytical data for this compound were consistent with the previously reported data.[7]

Analytical parameters:

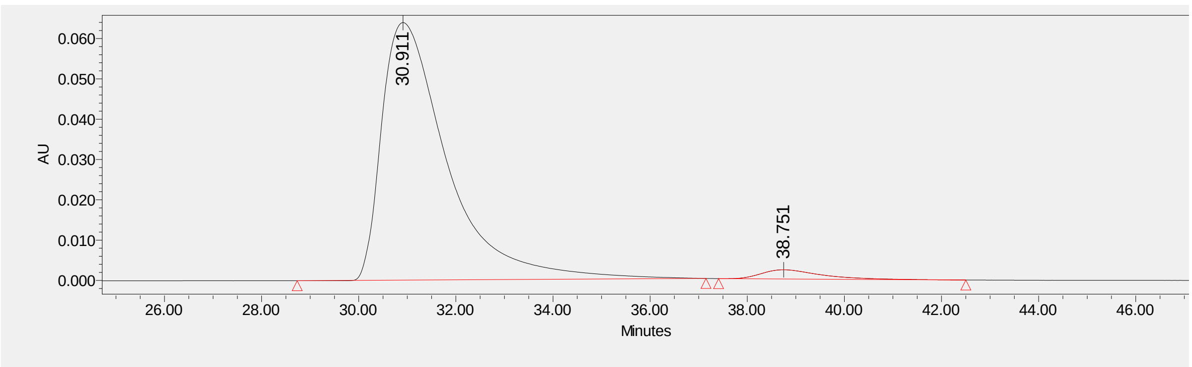
HPLC method 2: OD-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane (100%) at 1.0 mL/min as mobile phase at 25°C and λ = 254 nm.

- Racemic mixture:



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

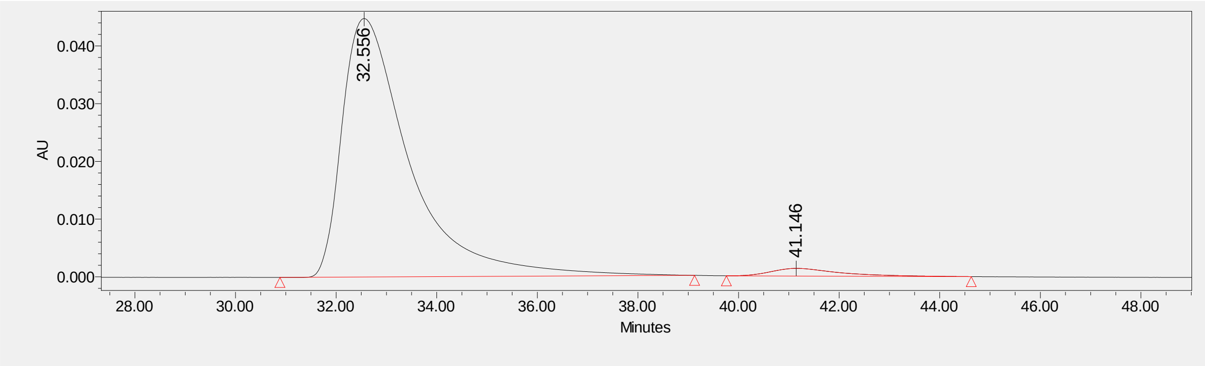
- With **CuBr-1a**:



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

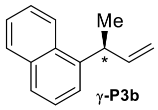
[7] M. Magrez, Y. Le Guen, O. Baslé, C. Crévisy, M. Mauduit, *Chem. Eur. J.* **2013**, *19*, 1199-1203.

- 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):



Chemical Formula: $C_{14}H_{14}$
Molecular Weight: 182,27

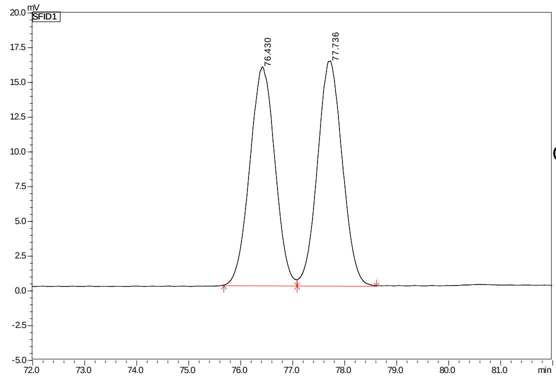
Entry	Catalytic system (mol%)	Time (h)	Conv. (yield) (%)	γ/α ratio	ee (%)
1	**CuBr-1a**	0.5	>99 (99)	>99:1	96
2	**2a**	12	>99 (68)	>99:1	96

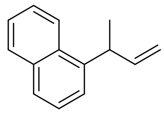
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (ddd, *J* = 8.4, 1.5, 0.7 Hz, 1H), 8.01 – 7.86 (m, 1H), 7.78 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.62 – 7.34 (m, 4H), 6.32 – 6.14 (m, 1H), 5.25 – 5.08 (m, 2H), 4.36 (qd, *J* = 7.0, 5.4 Hz, 1H), 1.58 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 143.3, 141.9, 134.4, 131.9, 129.3, 127.2, 126.2, 126.1, 125.8, 124.1, 123.9, 114.1, 38.3, 20.7. **$[\alpha]_D^{25}$** (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:

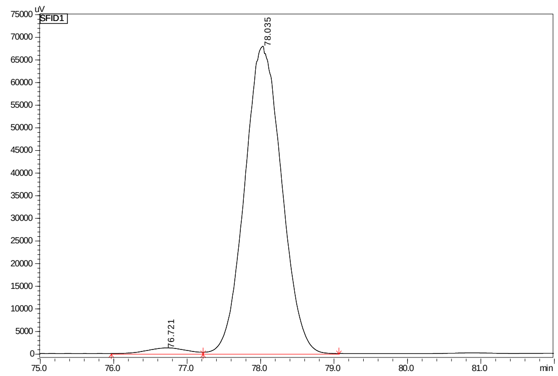




Chemical Formula: $C_{14}H_{14}$
Molecular Weight: 182,27

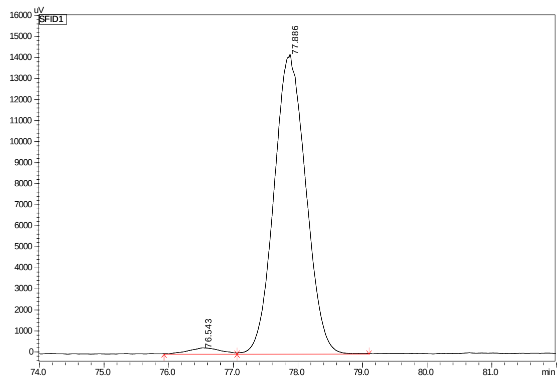
Peak	Retention time	Area	Height	% Area
1	76.430	528674	15722	49.644
2	77.736	536266	16155	50.356

- With **CuBr-1a**:



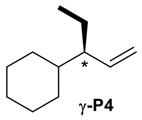
Peak	Retention time	Area	Height	% Area
1	76.721	8750	276	1.778
2	77.886	483409	14492	98.222

- With 2**a**:



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):



γ-**P4**

Chemical Formula: $C_{11}H_{20}$
Molecular Weight: 152,28

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

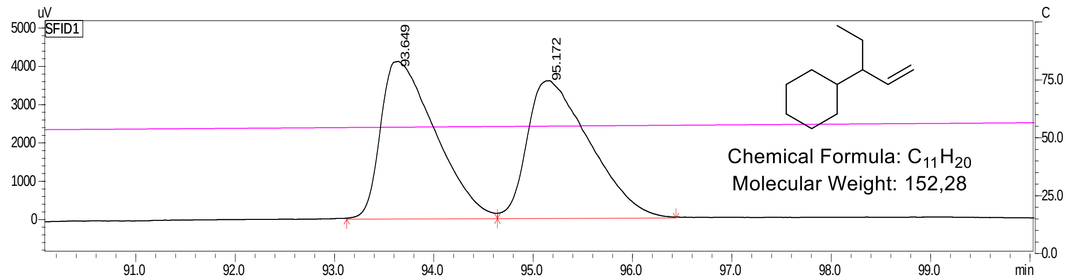
[a] The conversion and yield were determined by ^{1}H NMR using mesitylene as external standard (0.33 equiv regarding the substrate **S4**).

^{1}H NMR ($CDCl_3$, 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). **^{13}C NMR** ($CDCl_3$, 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. **$[\alpha]_D^{25}$** (c = 0.36, $CHCl_3$) = +6 (82% ee). Analytical data for this compound were consistent with the previously reported data.[7]

Analytical parameters:

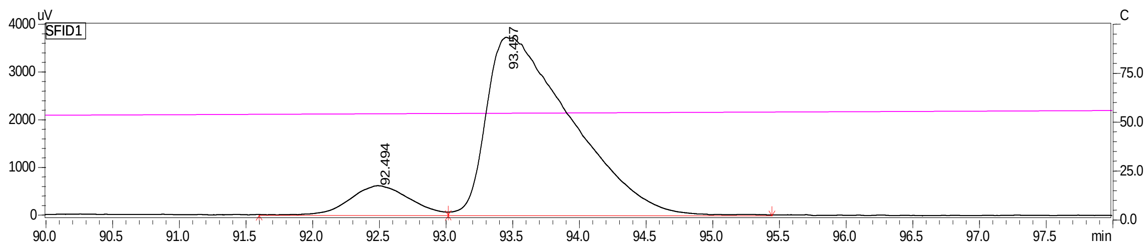
GC method 3: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 µm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1µL. Helium as carrier gas (40 cm/sec), 5.0 split ratio, temperature program (Rate - Temperature - Hold Time): 50 °C - 80 min; 0.3 °C/min – 65 °C – 0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

- Racemic mixture:



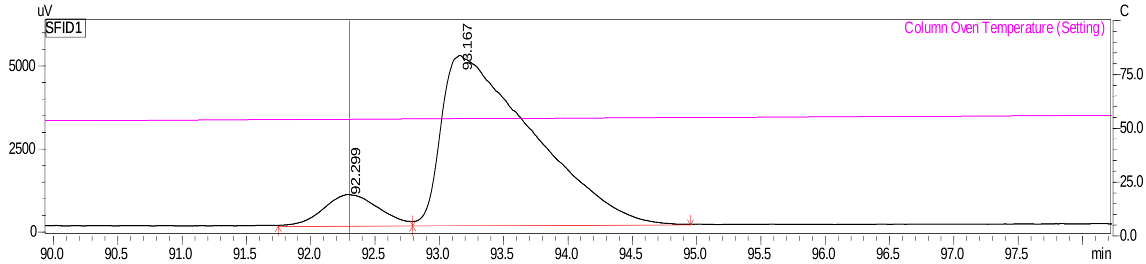
Peak	Retention time	Area	Height	% Area
1	93.649	156103	4092	50.045
2	95.172	155824	3573	49.955

- With **CuBr-1a**:



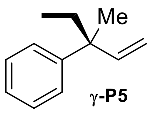
Peak	Retention time	Area	Height	% Area
1	92.494	18126	605	9.959
2	93.457	163886	3717	90.0441

- With 2**a**:



Peak	Retention time	Area	Height	% Area
1	92.299	26856	922	9.655
2	93.167	251304	5103	90.345

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



Chemical Formula: $C_{12}H_{16}$
Molecular Weight: 160,26

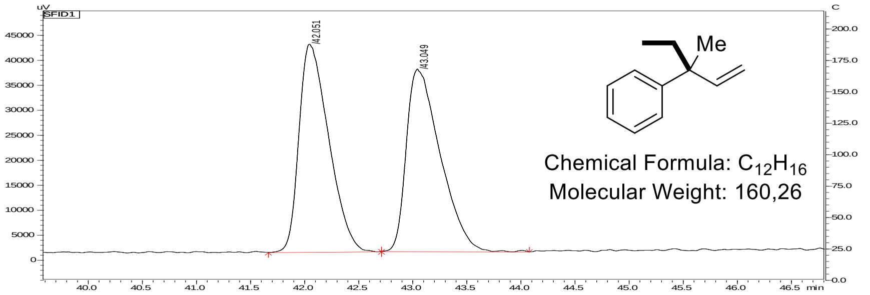
The general procedure 3 for Cu-AAA reactions was followed using **S5** (142.3 mg, 0.5 mmol, 1.0 equiv), Et_2Zn (1 M in hexane, 1.5 mL, 1.5 mmol, 3.0 equiv) and a stock solution of the complex **CuBr-1a** (2.37 mg, 0.005 mmol, 1.0 mol%). The desired product **γ-P5** was obtained as a colourless oil (63.3 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) 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). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 147.1, 128.2, 126.9, 125.8, 111.9, 44.7, 33.6, 24.5, 9.1. **$[\alpha]_D^{25}$** (c = 0.16, $CHCl_3$) = +10 (85% ee). Analytical data for this compound were consistent with the previously reported data.[7]

Analytical parameters:

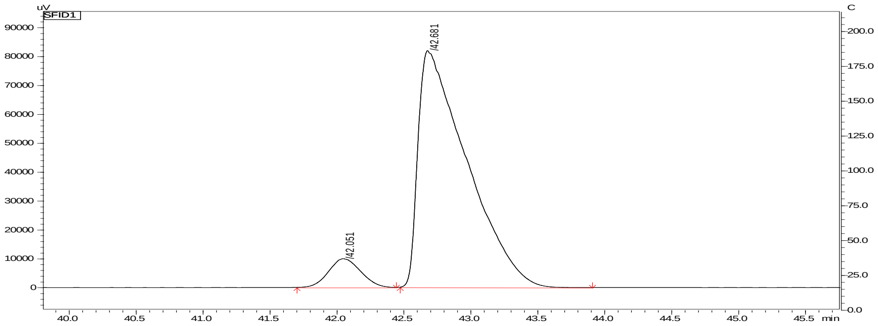
GC method 4: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 µm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1µL. Helium as carrier gas (30 cm/sec), 10 split ratio, temperature program (Rate - Temperature - Hold Time): 80 °C - 55 min; 10 °C/min – 160 °C – 10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

- Racemic mixture:



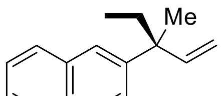
Peak	Retention time	Area	Height	% Area
1	42.051	793030	41563	49.942
2	43.049	794871	36502	50.058

- 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):



γ-P6

Chemical Formula: $C_{16}H_{18}$
Molecular Weight: 210,32

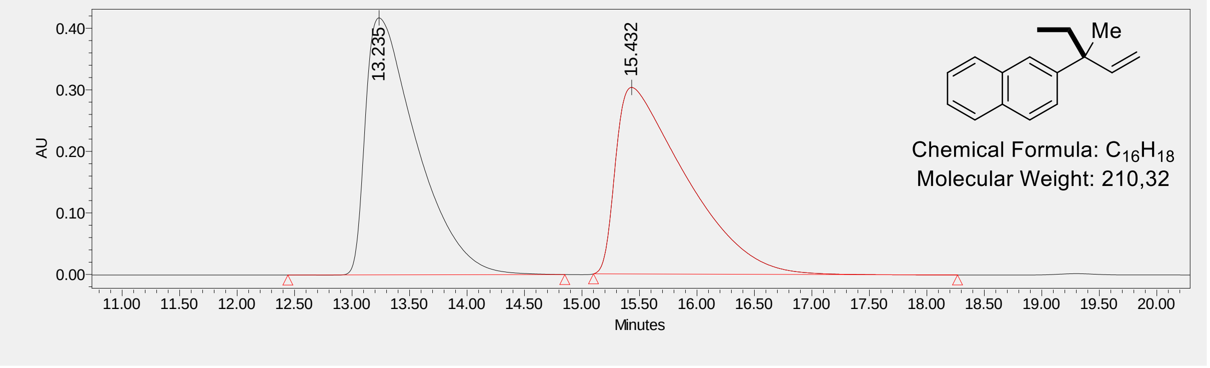
The general procedure 3 for Cu-AAA reactions was followed using **S6** (134.0 mg, 0.4 mmol, 1.0 equiv), Et_2Zn (1 M in hexane, 1.2 mL, 1.2 mmol, 3.0 equiv) and a stock solution of the complex **CuBr-1a** (1.90 mg, 0.004 mmol, 1.0 mol%). The desired product **γ-P6** was obtained as a colourless oil (79.9 mg, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) 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, $CDCl_3$) 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. **[α]$_D^{25}$** (c = 0.2, $CHCl_3$) = +17 (84% ee). Analytical data for this compound were consistent with the previously reported data.[8]

Analytical parameters:

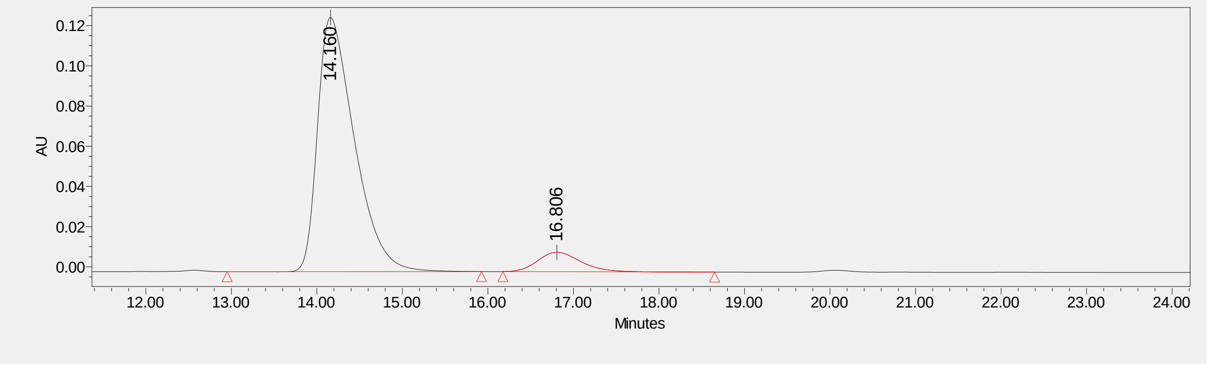
HPLC method 2: OJ-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane (100%) at 1.0 mL/min as mobile phase at 25°C and λ = 254 nm.

- Racemic mixture:



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

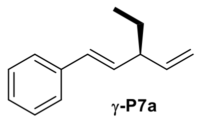
- With **CuBr-1a**:



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 (γ-P7a):



γ-P7a

Chemical Formula: $C_{13}H_{16}$

Molecular Weight: 172,27

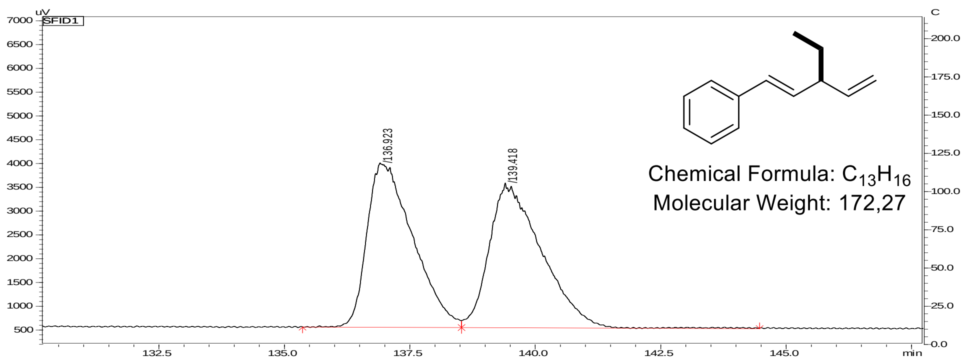
The general procedure 3 for Cu-AAA reactions was followed using **S7** (148.5 mg, 0.5 mmol, 1.0 equiv), Et_2Zn (1 M in hexane, 1.5 mL, 1.5 mmol, 3.0 equiv) and a stock solution of the complex **CuBr-1a** (2.37 mg, 0.005 mmol, 1.0 mol%). The desired product **γ-P7a** was obtained as a colourless oil (77.5 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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:

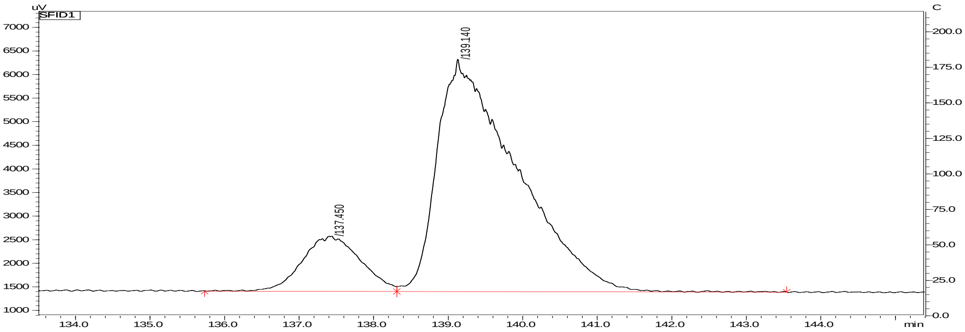
GC method 5: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 µm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1µL. Helium as carrier gas (39.1 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 80 °C - 175 min; 10 °C/min – 160 °C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

- Racemic mixture:



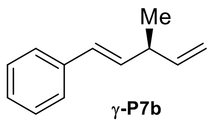
Peak	Retention time	Area	Height	% Area
1	136.923	217633	3444	50.086
2	139.418	216890	3029	49.914

- 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-methylpenta-1,4-dien-1-yl)benzene (γ-P7b):



Chemical Formula: $C_{12}H_{14}$
Molecular Weight: 158,24

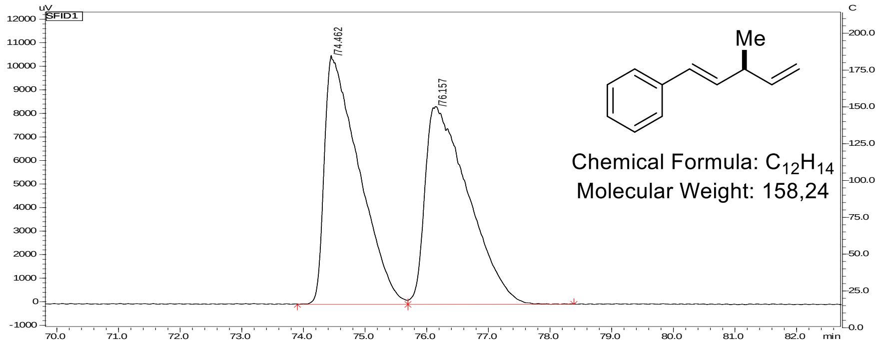
The general procedure 3 for Cu-AAA reactions was followed using **S7** (148.3 mg, 0.5 mmol, 1.0 equiv), Me_2Zn (1.2 M in Toluene, 1.3 mL, 1.56 mmol, 3.1 equiv) and a stock solution of the complex **CuBr-1a** (2.37 mg, 0.005 mmol, 1.0 mol%). The desired product **γ-P7b** was obtained as a colourless oil (68.1 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 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 (ddddd, *J* = 13.7, 8.2, 6.8, 5.4, 1.3 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 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:

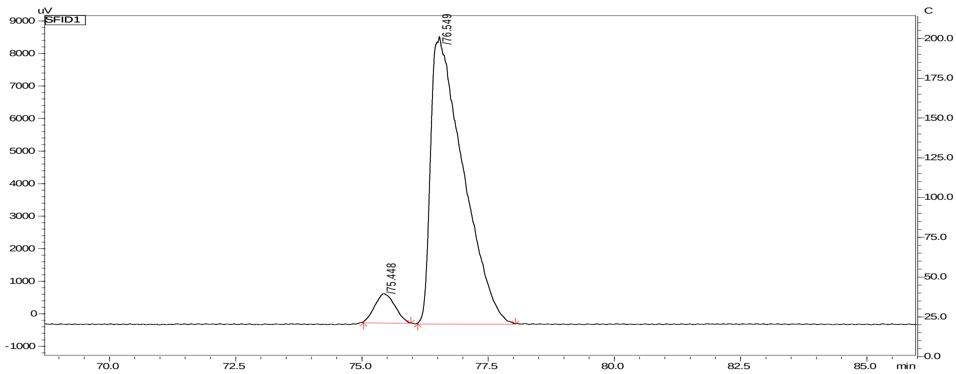
GC method 6: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (39.1 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 80 °C - 100 min; 10 °C/min – 160 °C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

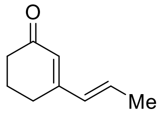
1.6. Asymmetric Conjugated Addition:

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):

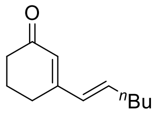


S10

Chemical Formula: $C_9H_{12}O$
Molecular Weight: 136,19

^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.24 – 6.18 (m, 2H, 2C**H**$_{Alkene}$), 5.86 (s, 1H, C**H**$_{Alkene}$), 2.44 (td, *J* = 6.1, 1.3 Hz, 2H, C**H$_2$**), 2.43 – 2.35 (m, 2H, C**H$_2$**), 2.10 – 1.95 (m, 2H, C**H$_2$**), 1.88 (dd, *J* = 5.2, 0.6 Hz, 3H, C**H$_3$**). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.71, 157.75, 134.01, 132.89, 126.34, 37.79, 25.15, 22.47, 19.00. 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):



S11

Chemical Formula: $C_{12}H_{18}O$
Molecular Weight: 178,28

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 – 6.12 (m, 2H), 5.88 – 5.83 (m, 1H), 2.45 (td, *J* = 6.1, 1.4 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 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.4, 157.7, 139.3, 131.4, 126.4, 37.8, 33.0, 31.1, 25.1, 22.4, 22.3, 13.9. 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_2Zn (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. Wencel-Delord, A. Alexakis, C. Crévisy, M. Mauduit, *Org. Lett.* **2010**, *12*, 4335-4337.

was purified by silica gel chromatography (pentane/Et_2O: 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, $(CuOTf)_2$·toluene complex (0.005 mmol, 0.5 mol%) or CuBr·SMe_2 (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_2Zn (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 was purified by silica gel chromatography (pentane/Et_2O: 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_2Zn (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 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 was purified by silica gel chromatography (pentane/Et_2O: 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 Et_2O (1.3 mL) was added and the mixture was cooled down to 0 °C in an ethanol cold bath. The EtMgBr (3M in Et_2O, 1.2 equiv) was added dropwise to the solution for 5 minutes. A solution of the 3-methyl-2-cyclohexenone (0.5 mmol) in Et_2O (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 $MgSO_4$, filtrated and concentrated in vacuo to give an oily residue. That crude was purified by flash chromatography on a silica gel (pentane/Et_2O: 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, R_2Zn (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 NH_4Cl 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_2O: 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 $CuBr{\cdot}SMe_2$ (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_2Zn (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_4Cl 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_2O: 85/15) to afford the desired compound as colourless oil.

1.6.3.3. General procedure 3 using isolated complex:

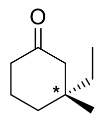
A flame-dried Schlenk tube under argon was charged with the copper complex (0.011 mmol, 2.0 mol%) and dry THF (0.5 mL). Then, the solution was stirred 10 min and R_2Zn (3.0 equiv) was added dropwise to the Schlenk. The reaction mixture was stirred 10 min at room temperature and 10 min at 0 °C. A solution 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_4Cl 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_2O: 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_4Cl (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. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 85/15) to afford the desired compound as colourless oil.

1.6.4. Catalysis products:

3-ethyl-3-methylcyclohexanone (P8a):



P8a
Chemical Formula: $C_9H_{16}O$
Molecular Weight: 140,23

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.21 (t, *J* = 6.8 Hz, 2H, C**H₂**), 2.12 (d, *J* = 13.5 Hz, 1H, C**H₂**), 2.04 (d, *J* = 13.5 Hz, 1H, C**H₂**), 1.85 – 1.76 (m, 2H, C**H₂**), 1.61 – 1.53 (m, 1H, C**H₂**), 1.53 – 1.43 (m, 1H, C**H₂**), 1.31 – 1.21 (m, 2H, C**H₂**), 0.83 (s, 3H, C**H₃**), 0.78 (t, *J* = 7.5 Hz, 3H, C**H₃**). **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 211.72 (**C**O), 52.52 (**C**H_2), 40.19 (**C**H_2), 37.81 (**C**$_{quat}$), 34.51 (**C**H_2), 33.08 (**C**H_2), 23.56 (**C**H_2), 21.26 (**C**H_3), 6.88 (**C**H_3). **$[\alpha]_D^{25}$** (c = 0.53, $CHCl_3$) = +5.4 (99% ee). Analytical data for this compound were consistent with the previously reported data.[11]

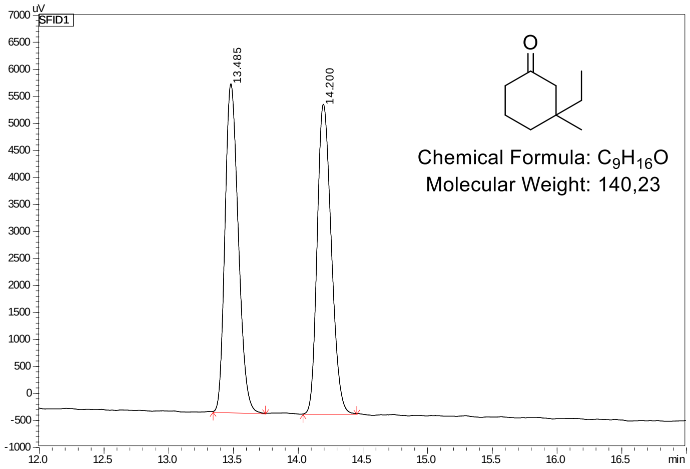
Entry	Catalytic system (mol%)	Conv. (yield) (%)	ee (%)
1	**L1b**H·PF_6/$(CuOTf)_2$.toluene (1.2/1)	>99 (80)	99
2	**2b**/$(CuOTf)_2$.toluene (1.2/1)	35 (23)	97
3	**2b**/CuBr·SMe_2 (1.2/1)	>99 (97)	>99
4	**CuBr-1b** (1)	>99 (67)	99
5	**2b** (5)	Nr	Nd
6	**CuBr-1a** (1)	>99 (84)*	85
7	**2a** (5)	Nr	Nd
8	**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.

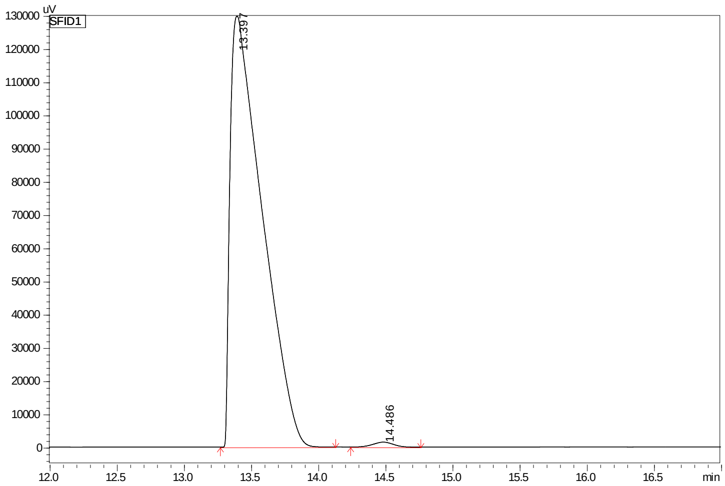
[11] C. Jahier-Diallo, M. S. T. Morin, P. Queval, M. Rouen, I. Artur, P. Querard, L. Toupet, C. Crévisy, O. Baslé, M. Mauduit, *Chem. Eur. J.* **2015**, *21*, 993-997.

- Racemic mixture:



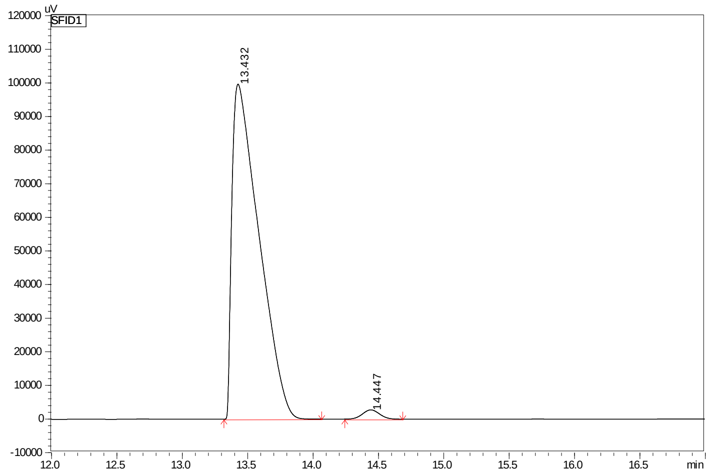
Peak	Retention time	Area	Height	% Area
1	13.485	43482	6076	50.008
2	14.200	43468	5728	49.992

- Table 2, entry 1:



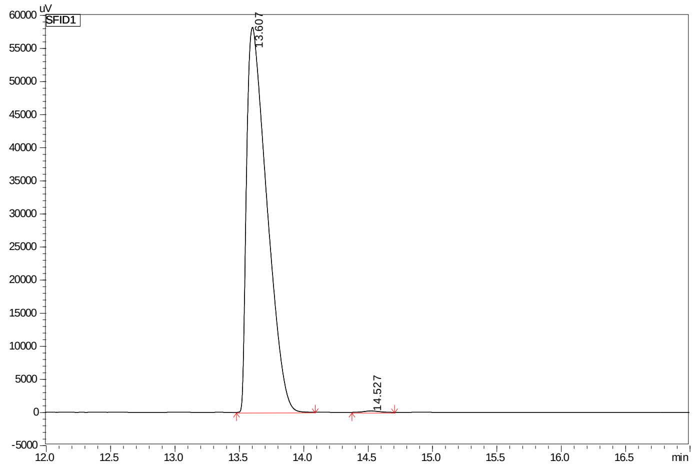
Peak	Retention time	Area	Height	% Area
1	13.397	2147649	129741	99.297
2	14.486	15207	1465	0.703

- Table 2, entry 2:



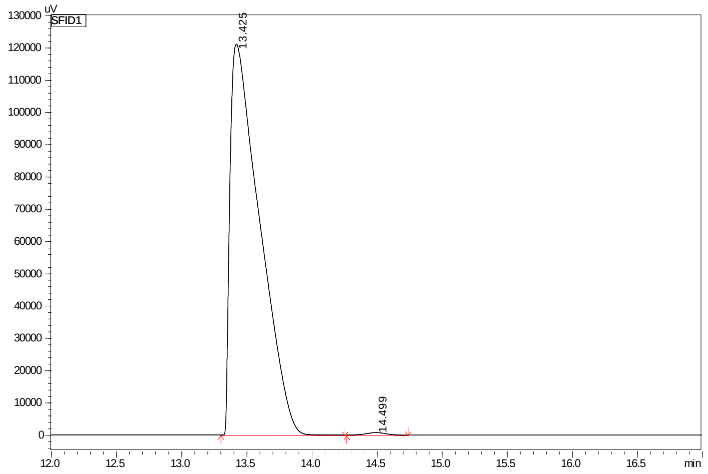
Peak	Retention time	Area	Height	% Area
1	13.432	1430946	99648	98.274
2	14.447	25134	2750	3.197

- Table 2, entry 3:



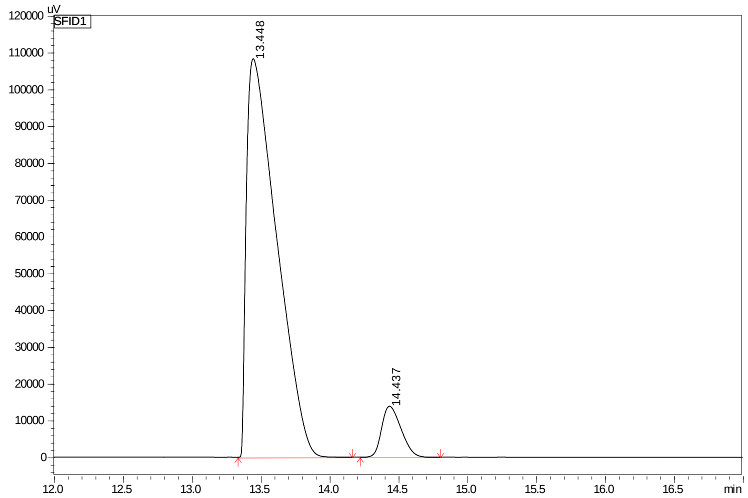
Peak	Retention time	Area	Height	% Area
1	13.607	635263	58140	99.738
2	14.527	1671	206	3.555

- Table 2, entry 4:



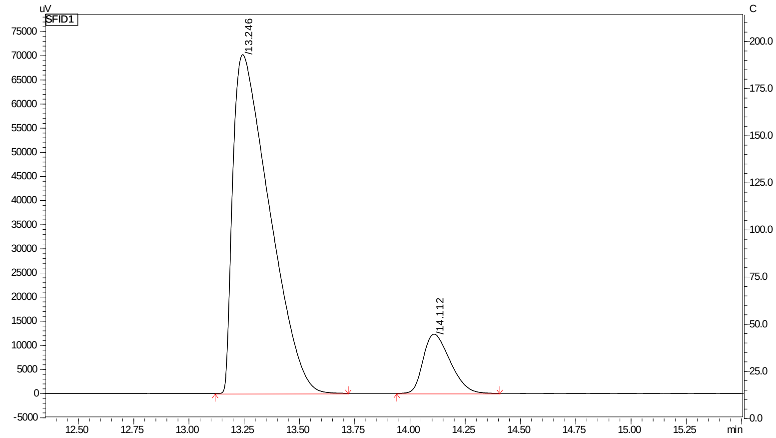
Peak	Retention time	Area	Height	% Area
1	13.425	1916278	121105	99.598
2	14.499	7725	768	0.402

- Table 2, entry 6:



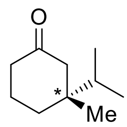
Peak	Retention time	Area	Height	% Area
1	13.448	1648519	108262	92.419
2	14.437	135230	13821	2.924

- Table 2, entry 8:



Peak	Retention time	Area	Height	% Area
1	13.246	806223	70149	88.611
2	14.112	103621	12245	11.389

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



P8b
Chemical Formula: $C_{10}H_{18}O$
Molecular Weight: 154,25

The general procedure 3 for 1,4-ACA reactions was followed using **S8** (115 µL, 1.0 mmol, 1.0 equiv), $^{i}Pr_2Zn$ (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).

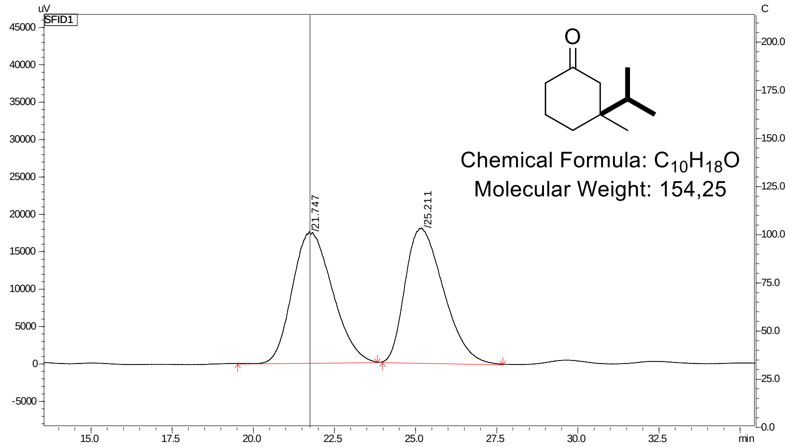
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 – 2.18 (m, 3H), 2.08 (dt, *J* = 13.5, 1.7 Hz, 1H), 1.96 – 1.74 (m, 2H), 1.68 – 1.46 (m, 3H), 0.85 (d, *J* = 6.8 Hz, 6H), 0.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 213.1, 52.0, 41.3, 41.2, 36.4, 34.2, 22.1, 19.9, 17.1, 16.9. **$[\alpha]_D^{25}$** (c = 0.29, $CHCl_3$) = +16 (93% ee). Analytical data for this compound were consistent with the previously reported data.[12]

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.

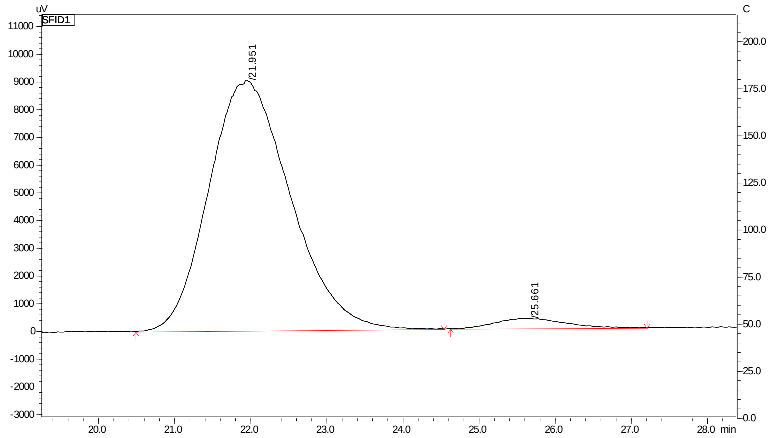
[12] S. Kehrli, D. Martin, D. Rix, M. Mauduit, A. Alexakis, *Chem. Eur. J.* **2010**, *16*, 9890-9904.

- Racemic mixture:



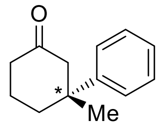
Peak	Retention time	Area	Height	% Area
1	21.747	1493570	17519	50.259
2	25.211	1478185	18024	49.741

- With **CuBr-1b**:



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):



P8c
Chemical Formula: $C_{13}H_{16}O$
Molecular Weight: 188,27

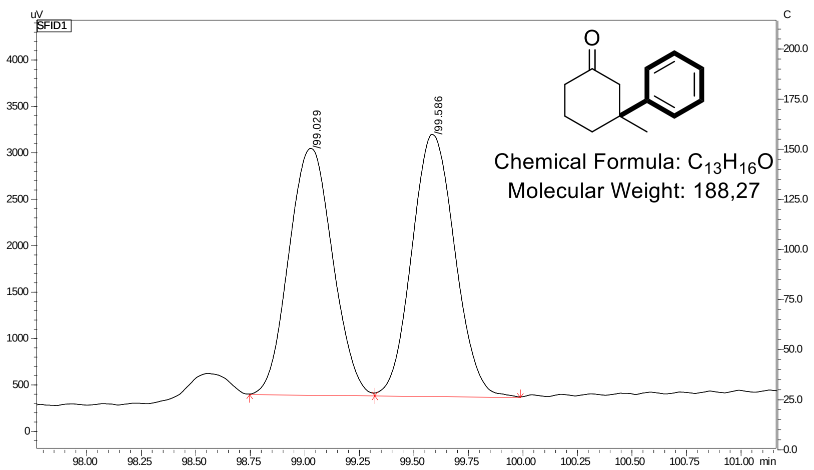
The general procedure 3 for 1,4-ACA reactions was followed using **S8** (29 µL, 0.25 mmol, 1.0 equiv), a solution of Ph_2Zn (330 mg, 1.5 mmol, 6.0 equiv) in Toluene (3.0 mL) and a stock solution of the complex **CuBr-1b** (1.08 mg, 0.0025 mmol, 1.0 mol%). The desired product **P8c** was obtained as a 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:

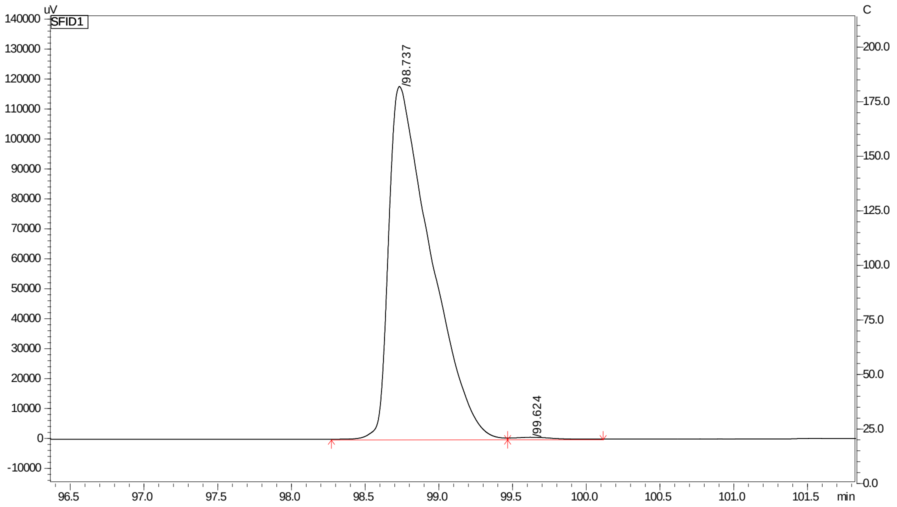
GC method 9: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 µm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1µL. Helium as carrier gas (30 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 120 °C - 90 min; 3.0 °C/min – 170 °C –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

- Racemic mixture:



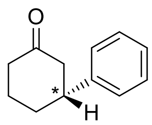
Peak	Retention time	Area	Height	% Area
1	99.029	37004	2652	48.923
2	99.586	38634	2818	51.077

- With **CuBr-1b**:



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):



P9

Chemical Formula: $C_{12}H_{14}O$
Molecular Weight: 174,24

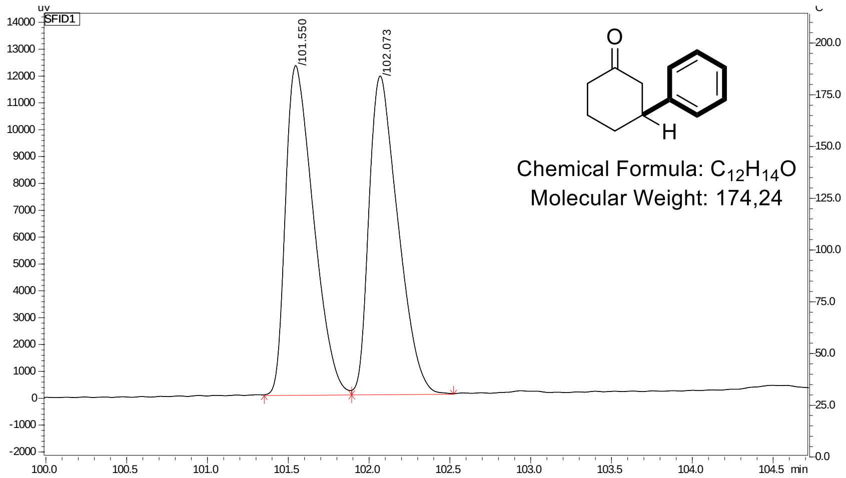
The general procedure 3 for 1,4-ACA reactions was followed using **S9** (24.0 mg, 0.25 mmol, 1.0 equiv), a solution of Ph_2Zn (165 mg, 0.75 mmol, 3.0 equiv) in Toluene (1.5 mL) and a stock solution of the complex **CuBr-1b** (1.08 mg, 0.0025 mmol, 1.0 mol%). The desired product **P9** was obtained as a colourless oil (30.9 mg, 71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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:

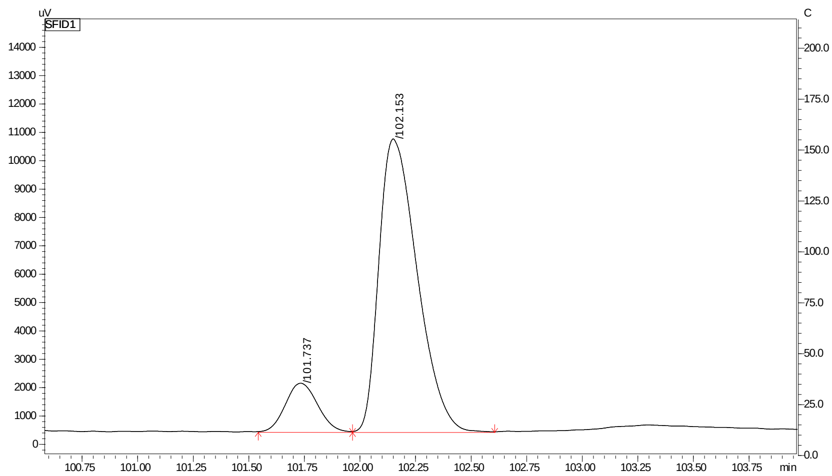
GC method 10: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (30 cm/sec), 2.5 split ratio, temperature program (Rate - Temperature - Hold Time): 120 °C - 90 min; 3.0 °C/min – 160 °C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

- Racemic mixture:



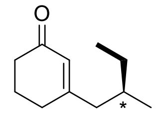
Peak	Retention time	Area	Height	% Area
1	101.550	147379	12257	49.941
2	102.073	147728	11843	50.059

- 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):



***1,6*-P10a**

Chemical Formula: $C_{11}H_{18}O$

Molecular Weight: 166,26

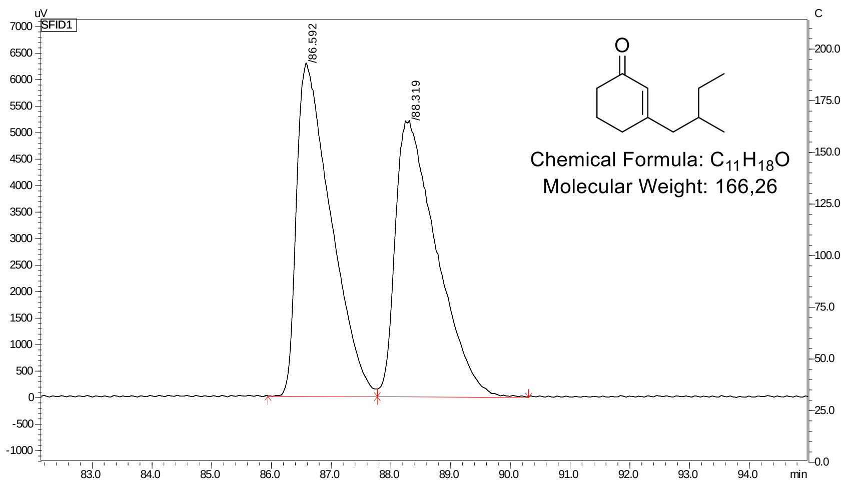
^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.85 (h, *J* = 1.2 Hz, 1H), 2.42 – 2.32 (m, 2H), 2.32 – 2.17 (m, 3H), 2.03 – 1.92 (m, 3H), 1.72 – 1.58 (m, 1H), 1.43 – 1.28 (m, 1H), 1.22 – 1.13 (m, 1H), 0.96 – 0.81 (m, 6H). **^{13}C NMR** ($CDCl_3$, 101 MHz): δ 199.9, 165.9, 127.1, 45.8, 37.5, 32.8, 29.8, 29.6, 22.9, 19.2, 11.4. **$[\alpha]_D^{25}$** (c = 0.26, $CHCl_3$) = + 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	**L1b**H·PF_6/$(CuOTf)_2$ (3/2)	Mr	Nd	Nd
2	**2b**/$(CuOTf)_2$ (3/2)	>99 (Nd)	100/0	53
3	**2a**/CuBr·SMe_2 (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:

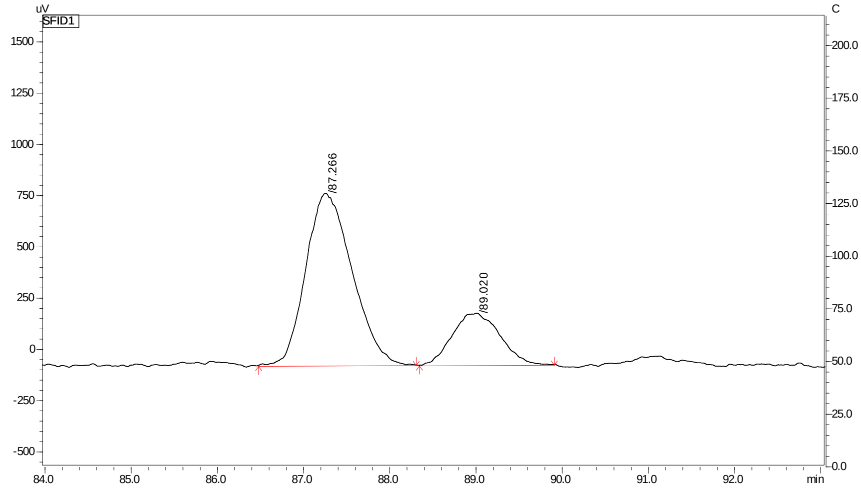
GC method 11: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 µm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1µL. Helium as carrier gas (40 cm/sec), 20.0 split ratio, temperature program (Rate - Temperature - Hold Time): 100 °C - 45 min; 1.0 °C/min – 150 °C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

- Racemic mixture:



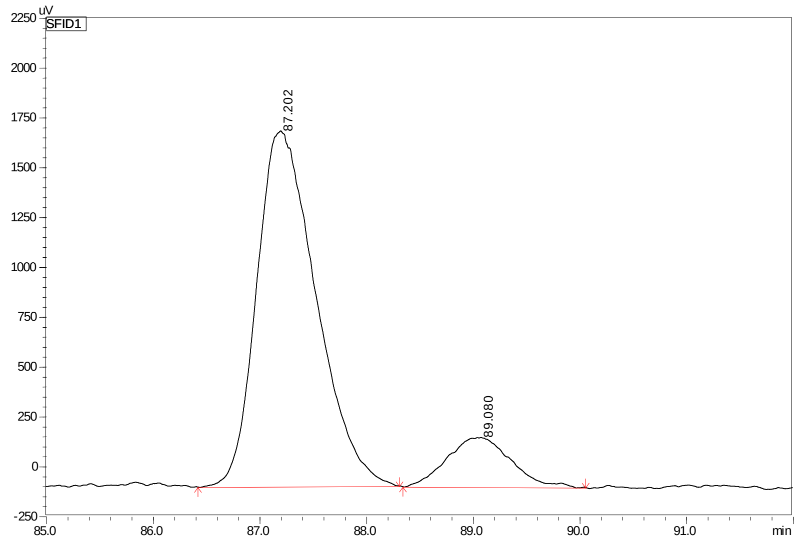
Peak	Retention time	Area	Height	% Area
1	86.592	249993	6276	49.949
2	88.319	250505	5206	50.051

- Table 3, entry 2:



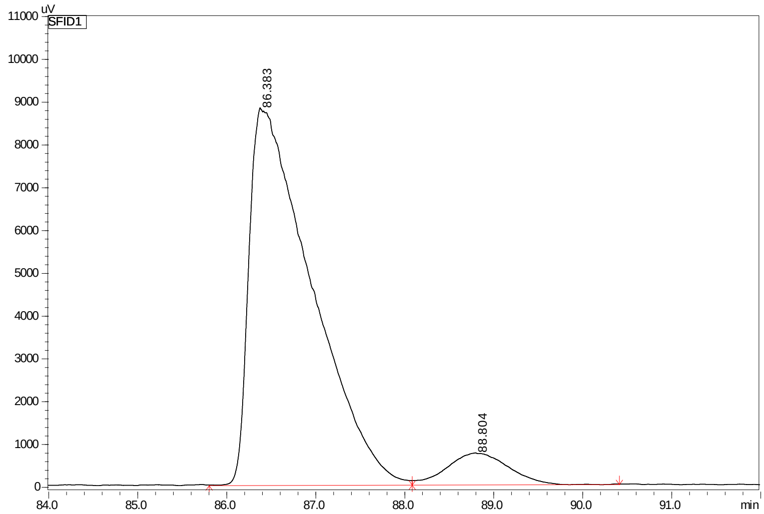
Peak	Retention time	Area	Height	% Area
1	87.266	31290	839	76.507
2	89.020	9608	252	23.493

- Table 3, entry 3:



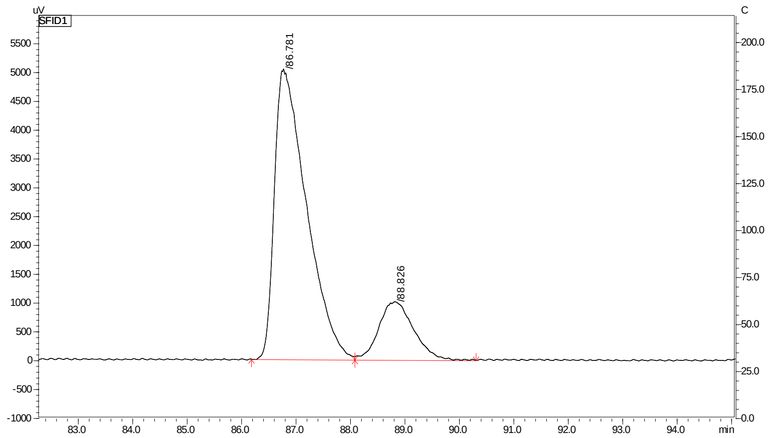
Peak	Retention time	Area	Height	% Area
1	87.202	68844	1782	87.108
2	89.080	10189	247	12.892

- Table 3, entry 4:



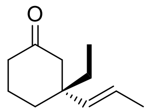
Peak	Retention time	Area	Height	% Area
1	86.383	428678	8806	92.684
2	88.804	33838	734	7.316

- 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):



***1,4*-P10a**
Chemical Formula: $C_{11}H_{18}O$
Molecular Weight: 166,26

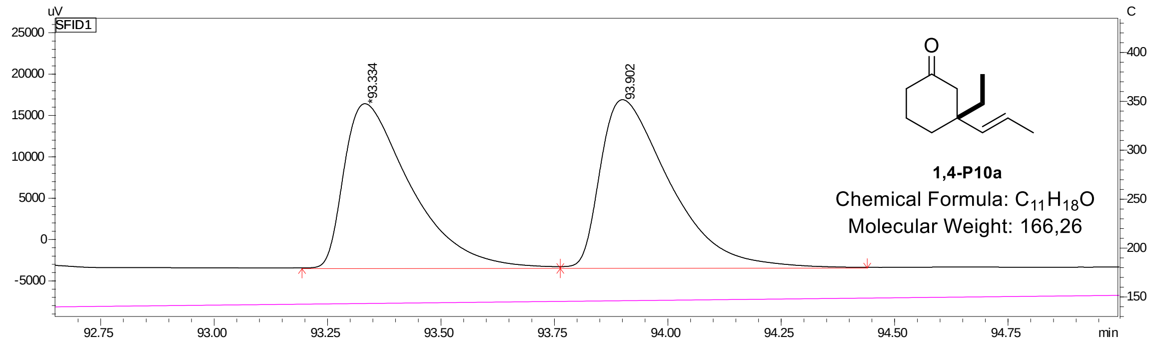
The general procedure 4 for 1,6-ACA reactions was followed using **S10** (68.1 mg, 0.5 mmol, 1.0 equiv), EtMgBr (3M in diethyl ether, 0.2 mL, 0.6 mmol, 1.2 equiv) and the complex **CuBr-1b** (6.5 mg, 0.015 mmol, 3.0 mol%). The desired product ***1,4*-P10a** was obtained as a colourless oil (69.8 mg,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

^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.[9] The enantiomeric excess has been determined on the hydrogenated compound following reported procedure.[9]

Analytical parameters:

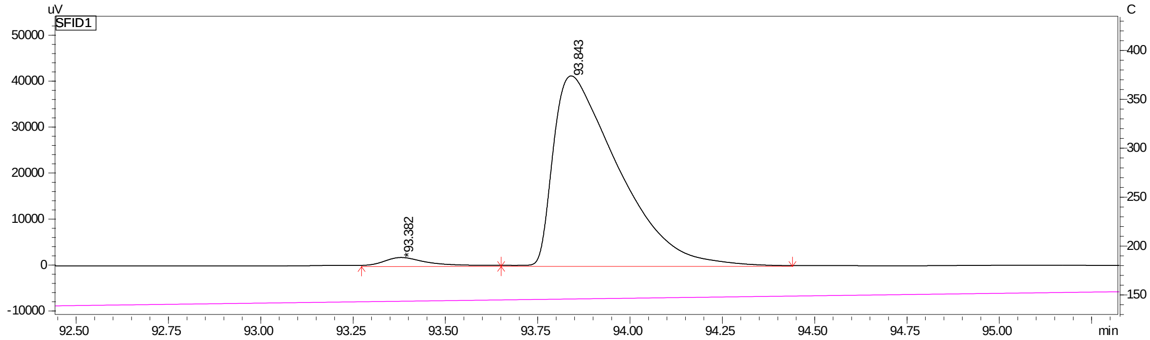
GC method 12: capillary column: G-TA: 30 m x 0.25 mm x 0.12 µm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1µL. Helium as carrier gas (30 cm/sec), 50.0 split ratio, temperature program (Rate - Temperature - Hold Time): 85 °C - 70 min; 1.0 °C/min – 100 °C – 0 min;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

- Racemic mixture:



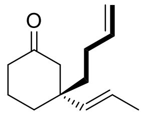
Peak	Retention time	Area	Height	% Area
1	93.334	202034	19830	48.395
2	93.902	215437	20295	51.605

- 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):



***1,4*-P10b**
Chemical Formula: $C_{13}H_{20}O$
Molecular Weight: 192,30

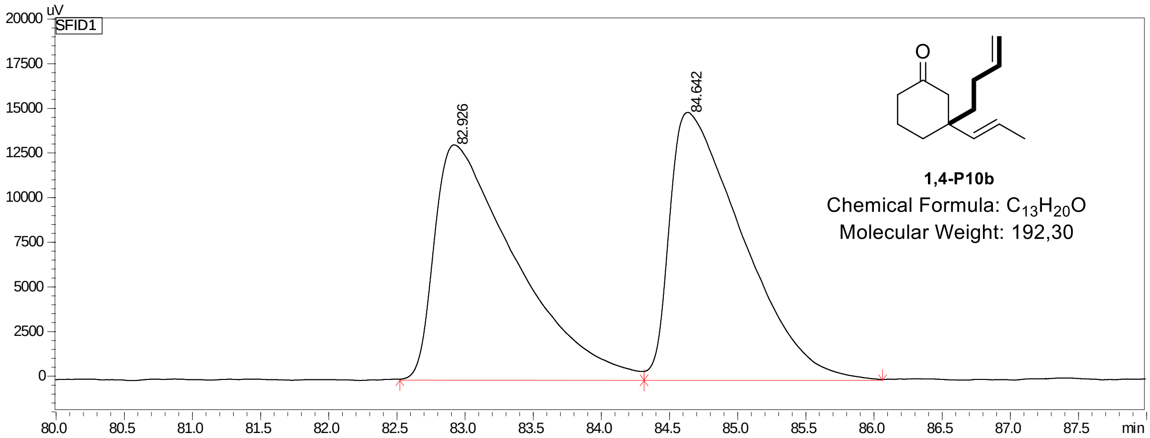
The general procedure 4 for 1,6-ACA reactions was followed using **S10** (68.1 mg, 0.5 mmol, 1.0 equiv), but-3-en-1-ylMgBr (1M in diethyl ether, 0.6 mL, 0.6 mmol, 1.2 equiv) and the complex **CuBr-1b** (6.5 mg, 0.015 mmol, 3.0 mol%). The desired product ***1,4*-P10b** was obtained as a colourless oil (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.[9] The enantiomeric excess has been determined on the hydrogenated compound following reported procedure.[9]

Analytical parameters:

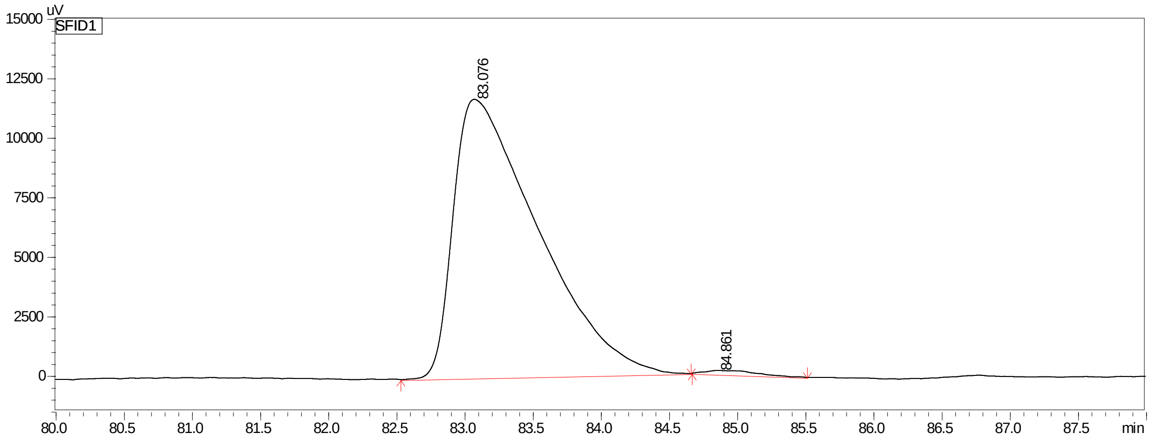
GC method 13: capillary column: G-TA: 30 m x 0.25 mm x 0.12 µm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1µL. Helium as carrier gas (30 cm/sec), 20.0 split ratio, temperature program (Rate - Temperature - Hold Time): 105 °C - 80 min; 5 °C/min – 160 °C – 10 min.

- Racemic mixture:



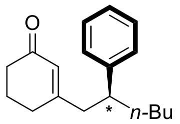
Peak	Retention time	Area	Height	% Area
1	82.926	544967	13125	49.508
2	84.642	555793	14948	50.492

- With **CuBr-1b**:



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):



***1,6*-P11a**
Chemical Formula: $C_{18}H_{24}O$
Molecular Weight: 256,39

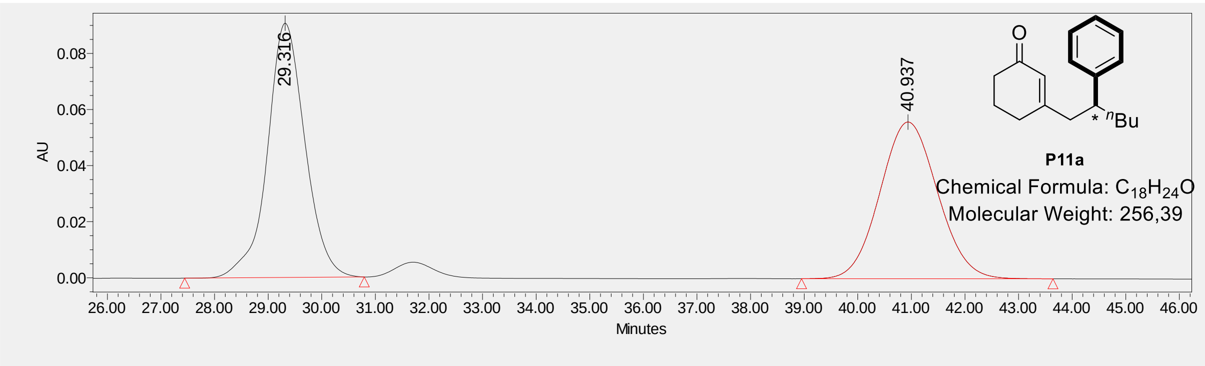
The general procedure 3 for 1,6-ACA reactions was followed using **S11** (45 mg, 0.25 mmol, 1.0 equiv), Ph_2Zn (164.7 mg, 0.75 mmol, 3.0 equiv) in Toluene (2.0 mL) and a stock solution of the complex **CuBr-1b** (2.16 mg, 0.005 mmol, 2.0 mol%). The desired product ***1,6*-P11a** was obtained as a colourless 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. **$[\alpha]_D^{25}$** (c = 0.24, $CHCl_3$) = – 62 (90% ee). Analytical data for this compound were consistent with the previously reported data.[11]

Analytical parameters:

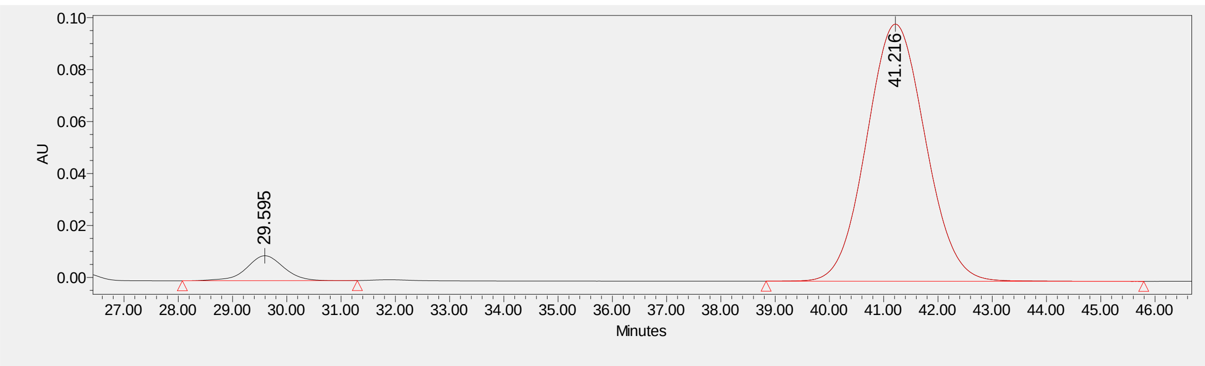
HPLC method 3: OJ-H column (0.46 cm x 25 cm) as stationary chiral phase and with hexane/iPrOH (95/5) at 0.5 mL/min as mobile phase at 25°C and λ = 254 nm.

- Racemic mixture:



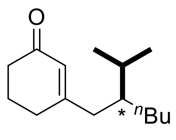
Peak	Retention time	Area	Height	% Area
1	29.316	4419989	90669	51.43
2	40.937	4174334	55900	48.57

- 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):



***1,6*-P11b**
Chemical Formula: $C_{15}H_{26}O$
Molecular Weight: 222,37

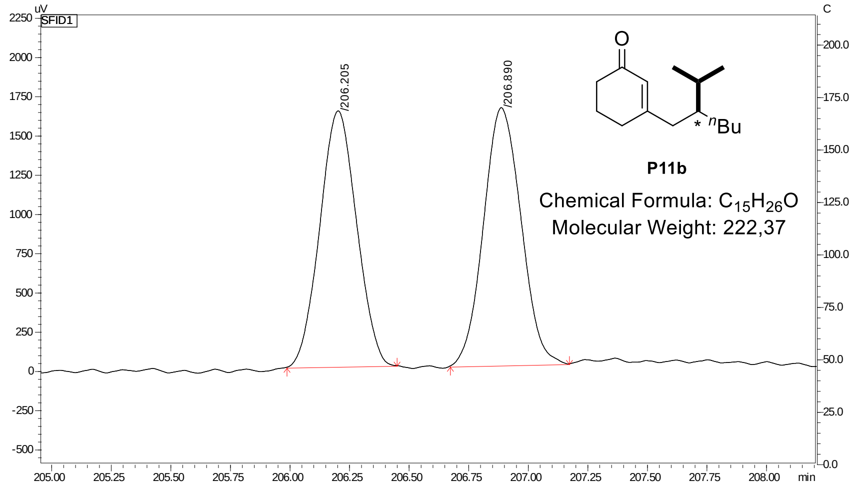
The general procedure 3 for 1,6-ACA reactions was followed using **S11** (90 mg, 0.5 mmol, 1.0 equiv), $^{i}Pr_2Zn$ (1 M in Toluene, 1.5 mL, 1.5 mmol, 3.0 equiv) and a stock solution of the complex **CuBr-1b** (4.32 mg, 0.01 mmol, 2.0 mol%). The desired product ***1,6*-P11b** was obtained as a colourless oil (82.3 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CHCl_3$) = – 4.5 (66% ee). Analytical data for this compound were consistent with the previously reported data.[11]

Analytical parameters:

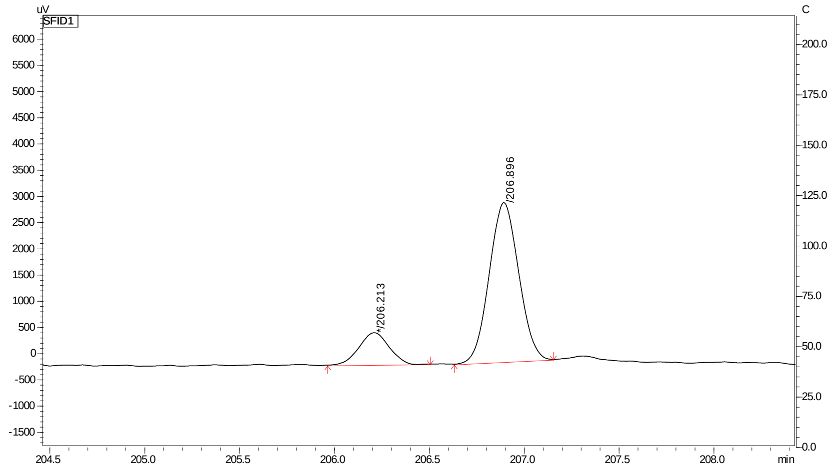
GC method 14: capillary column: β-dex 325: 30 m x 0.25 mm x 0.25 μm, injector temperature: 250 °C, detector (FID) temperature: 250 °C, injection volume: 1μL. Helium as carrier gas (40 cm/sec), 30.0 split ratio, temperature program (Rate - Temperature - Hold Time): 100 °C – 80 min; 0.20 °C/min – 120 °C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

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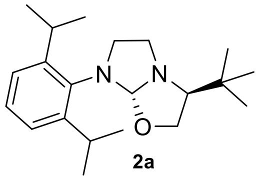
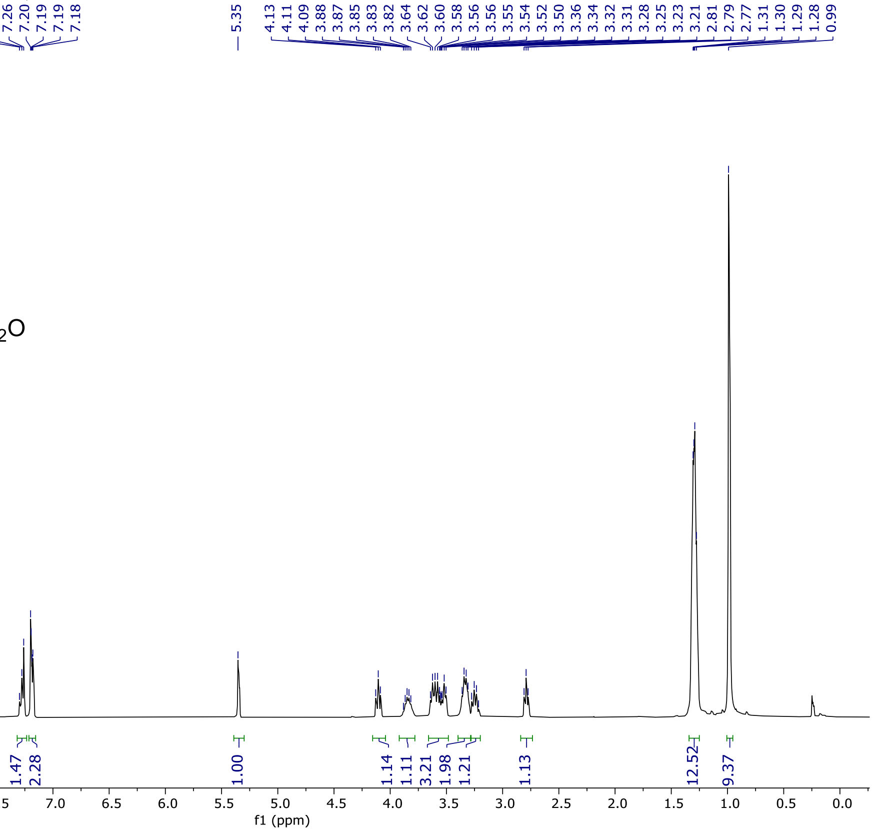
1.7. NMR spectra:

[1]H NMR ($CDCl_3$, 400 MHz) of 2a:

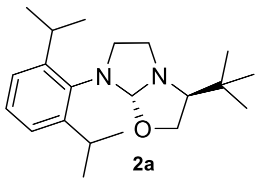


2a

Chemical Formula: $C_{21}H_{34}N_2O$
Molecular Weight: 330,52

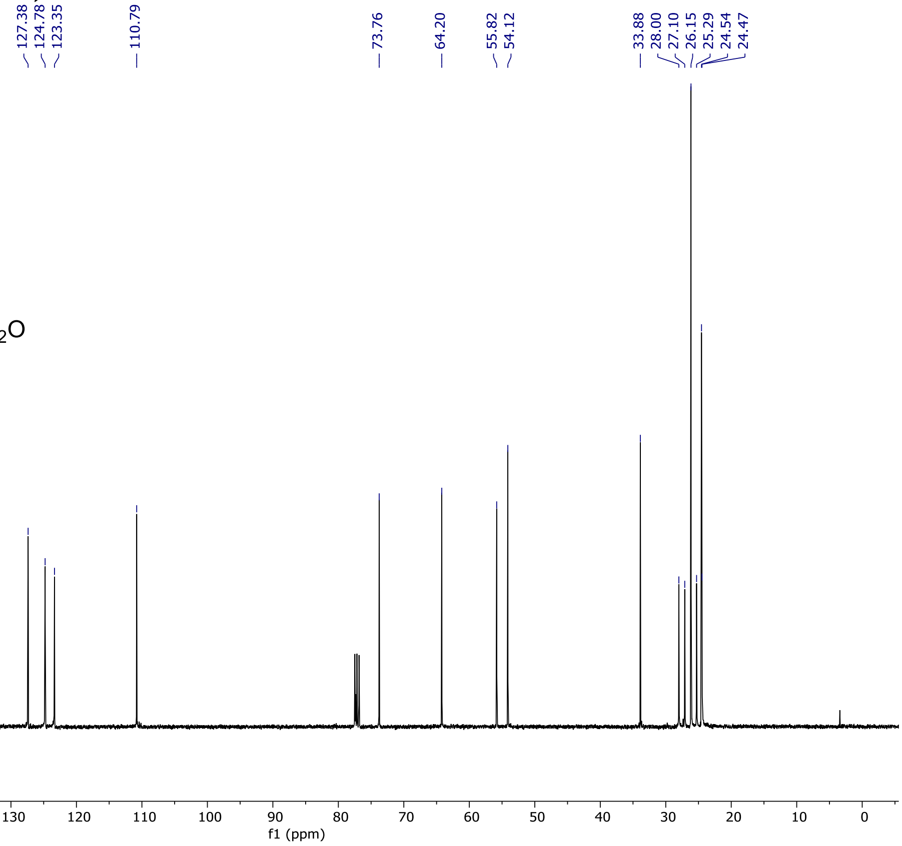


[13]C NMR ($CDCl_3$, 101 MHz) of 2a:

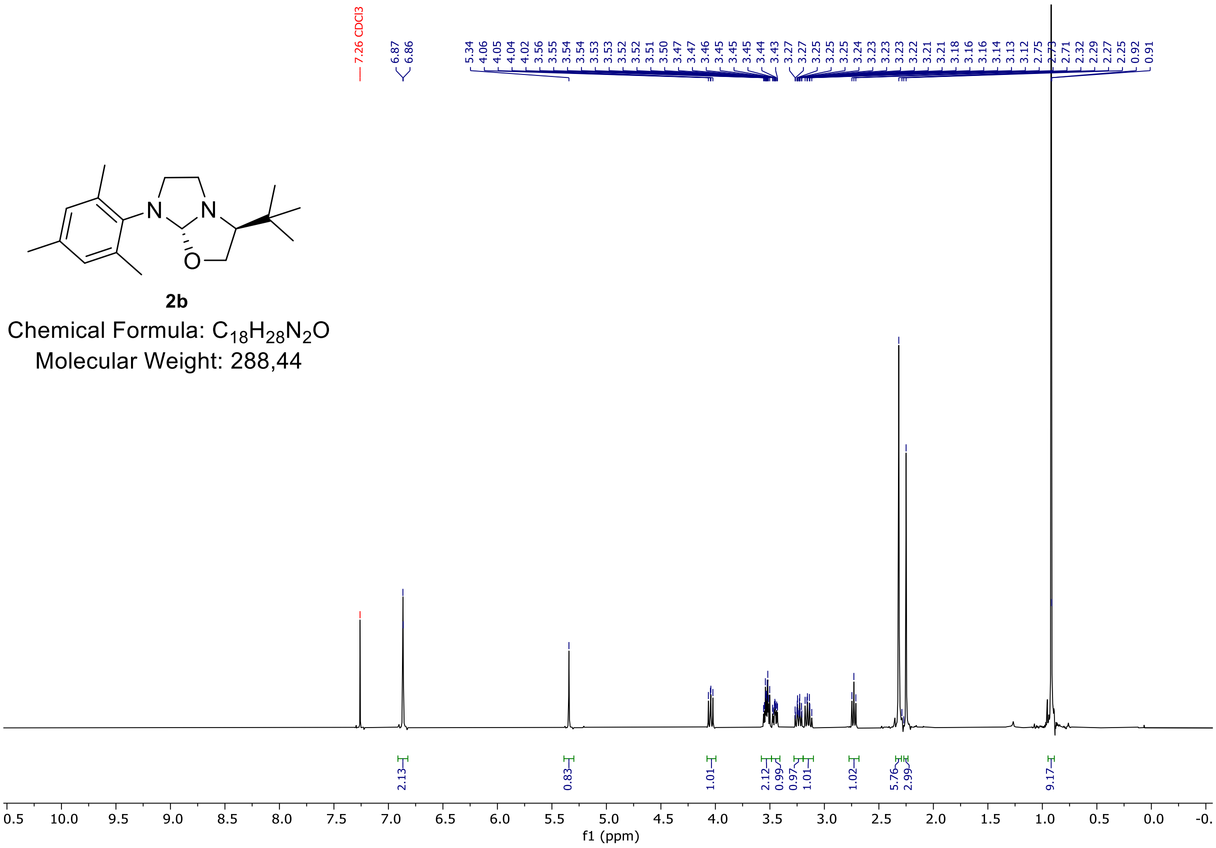


2a

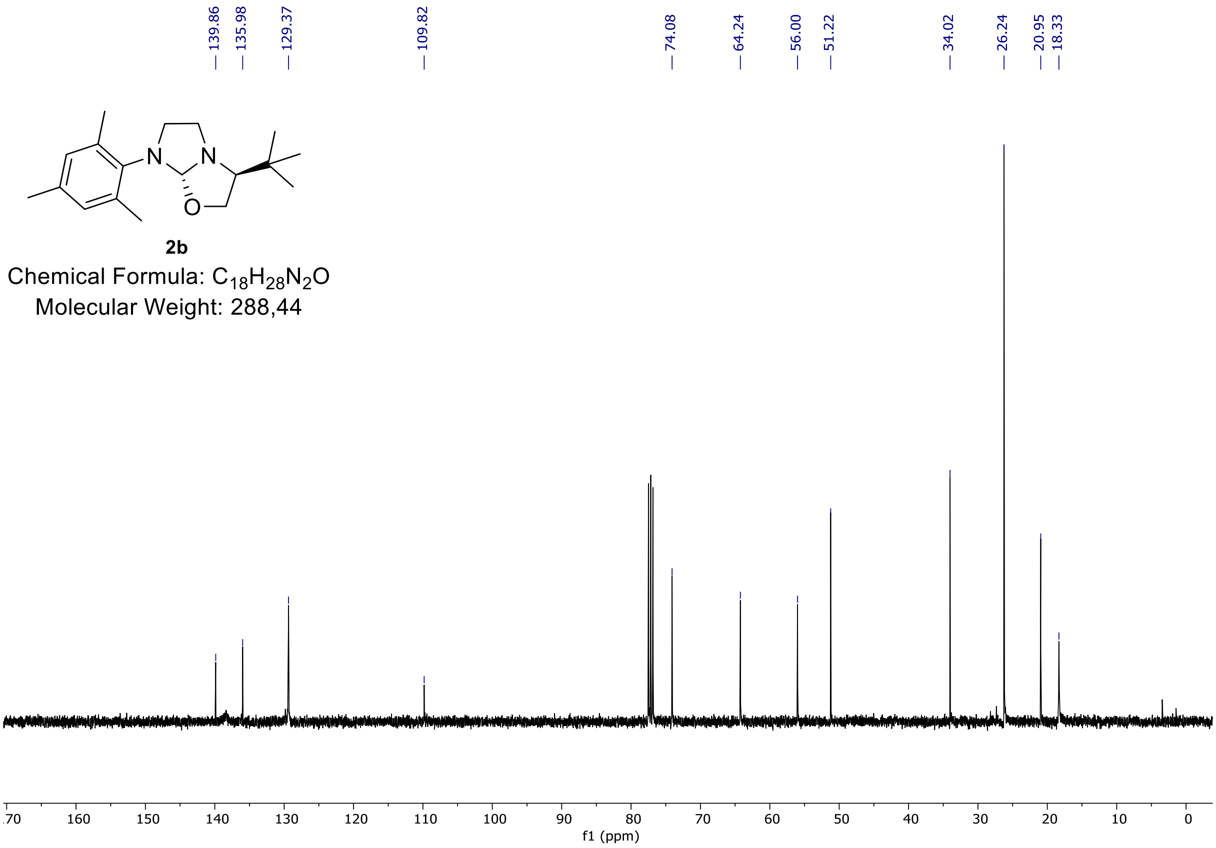
Chemical Formula: $C_{21}H_{34}N_2O$
Molecular Weight: 330,52



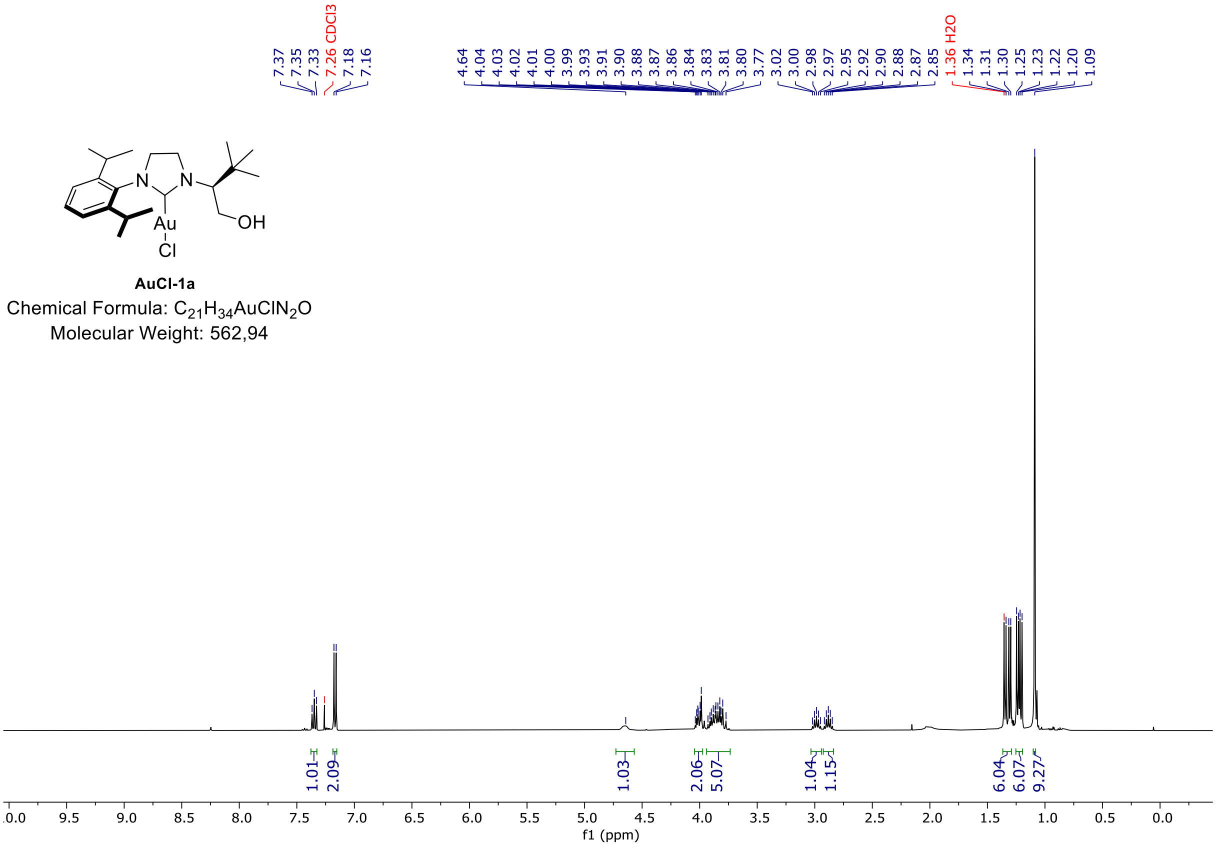
^{1}H NMR ($CDCl_3$, 400 MHz) of 2b:



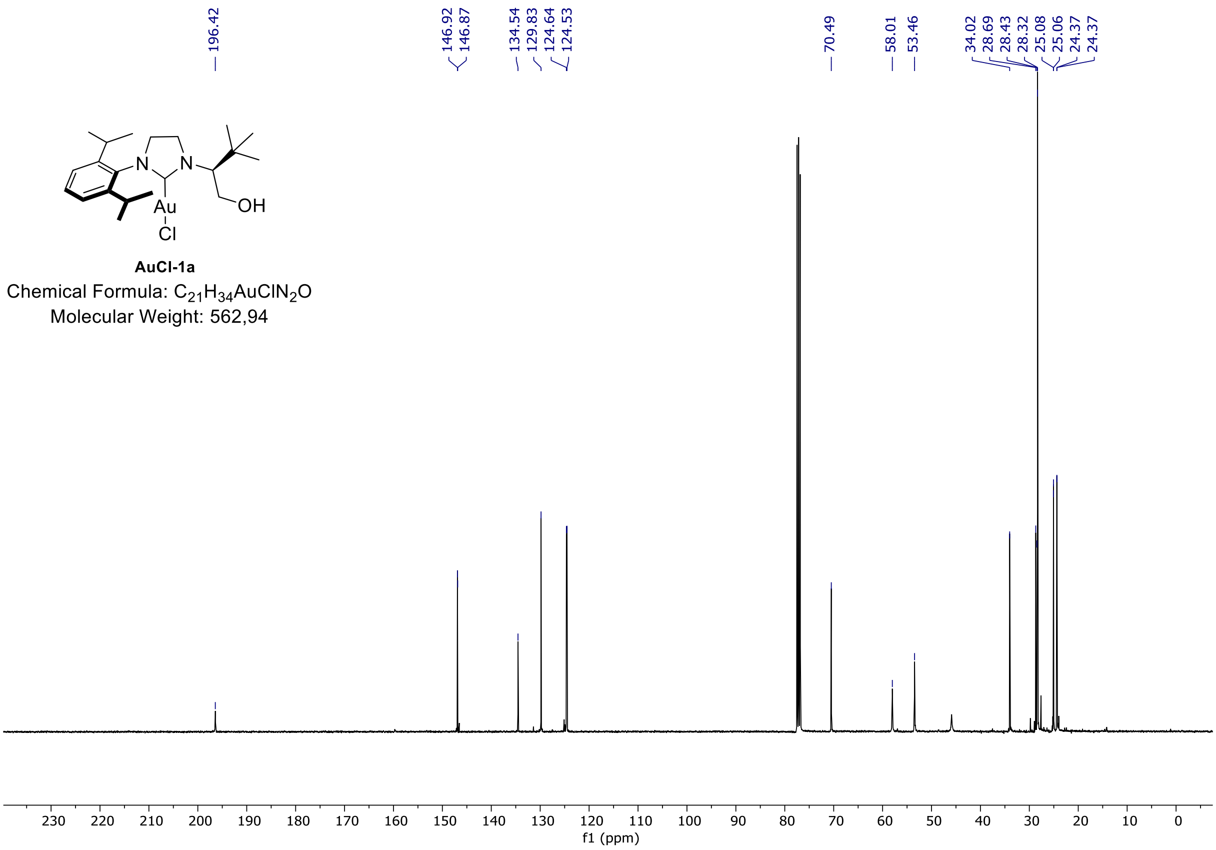
^{13}C NMR ($CDCl_3$, 101 MHz) of 2b:



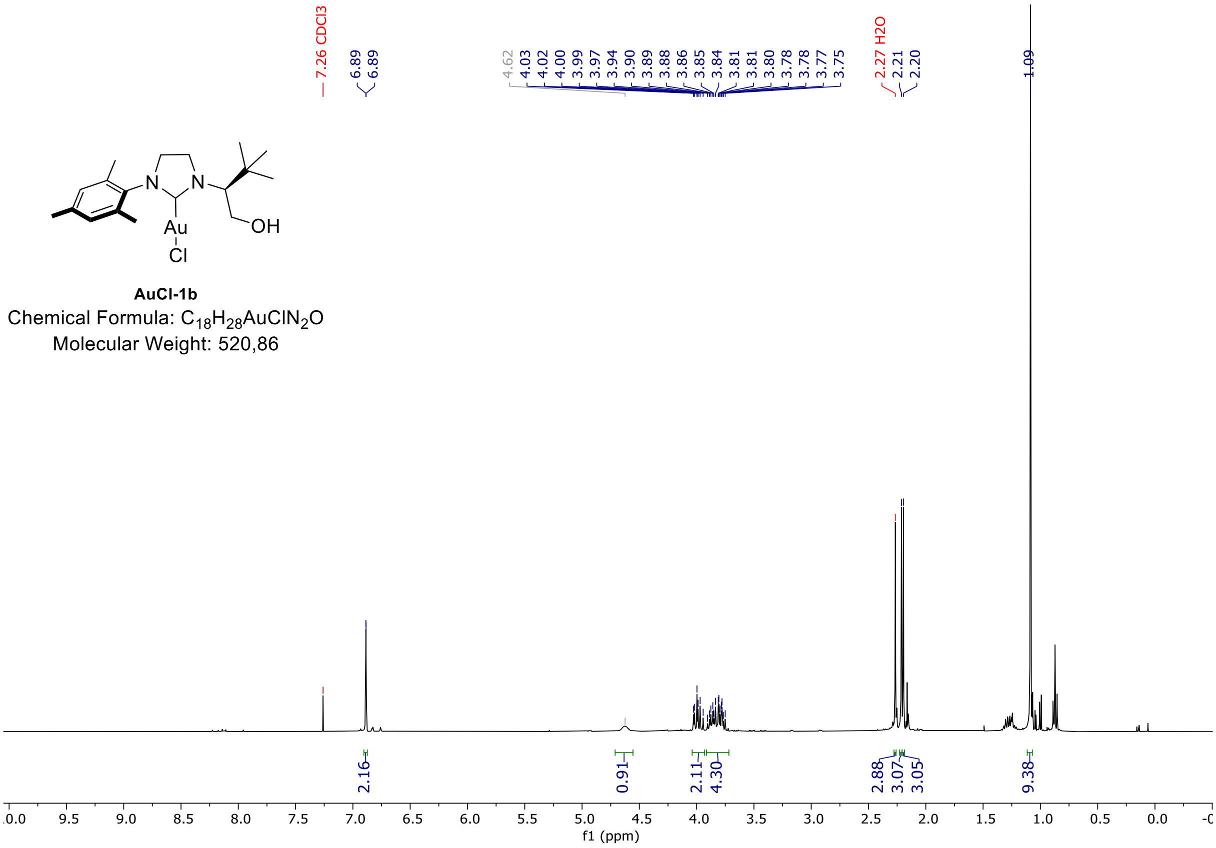
^{1}H NMR ($CDCl_3$, 400 MHz) of AuCl-1a:



^{13}C NMR ($CDCl_3$, 101 MHz) of AuCl-1a:

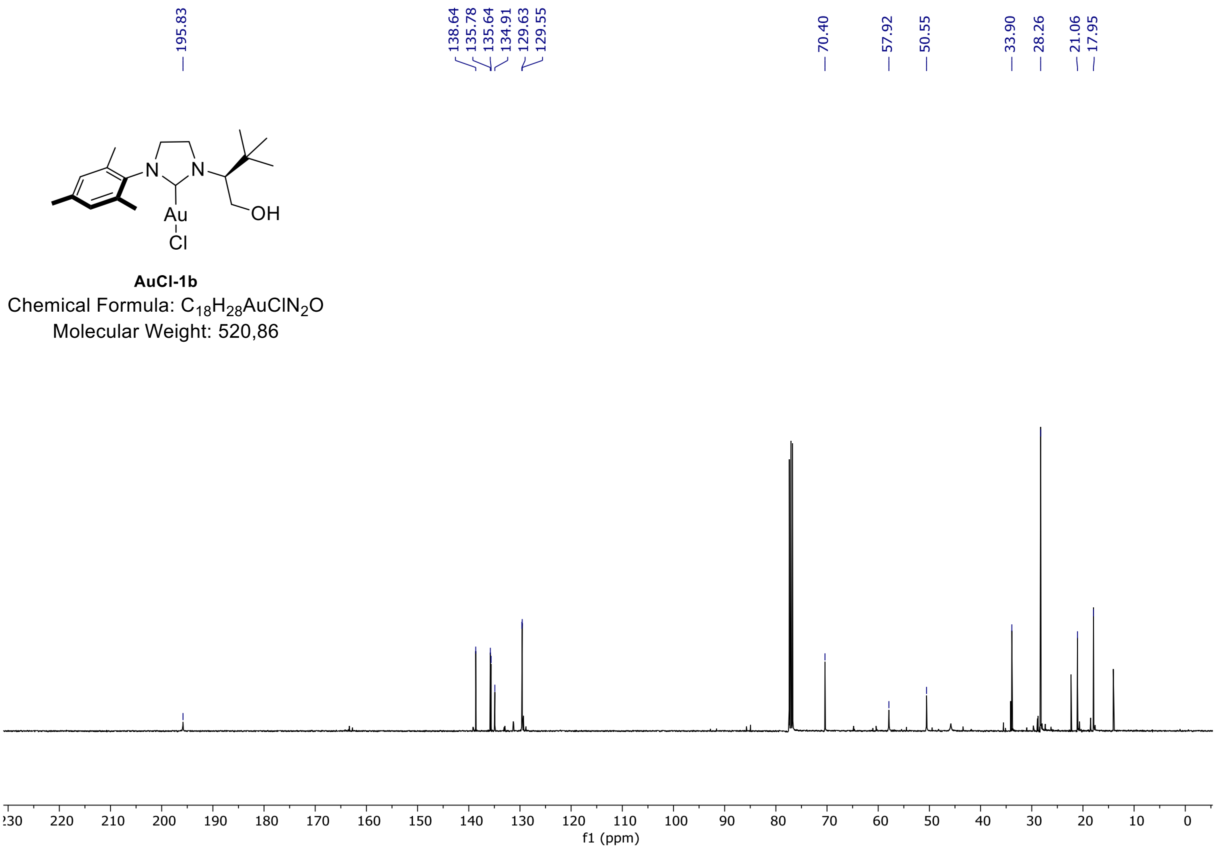


[1]H NMR ($CDCl_3$, 400 MHz) of AuCl-1b:



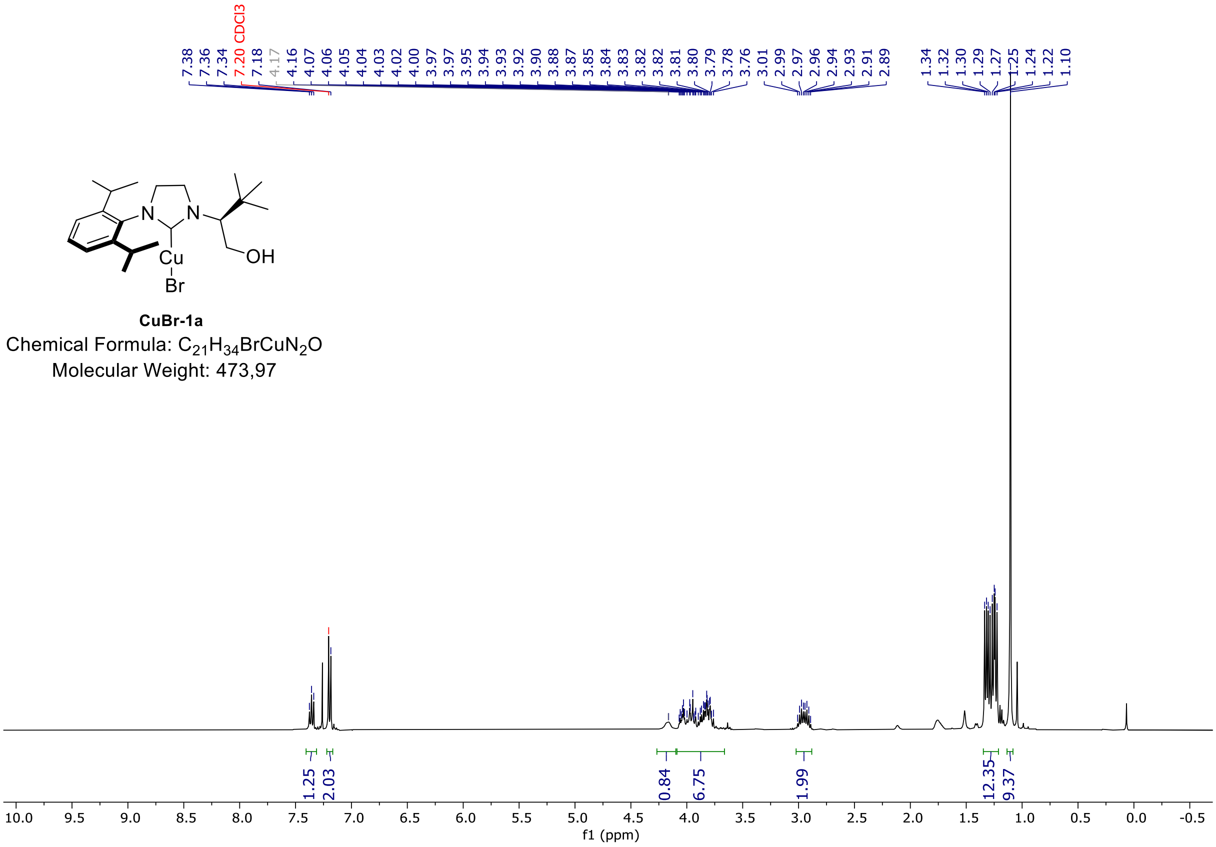
AuCl-1b
Chemical Formula: $C_{18}H_{28}AuClN_2O$
Molecular Weight: 520,86

[13]C NMR ($CDCl_3$, 101 MHz) of AuCl-1b:

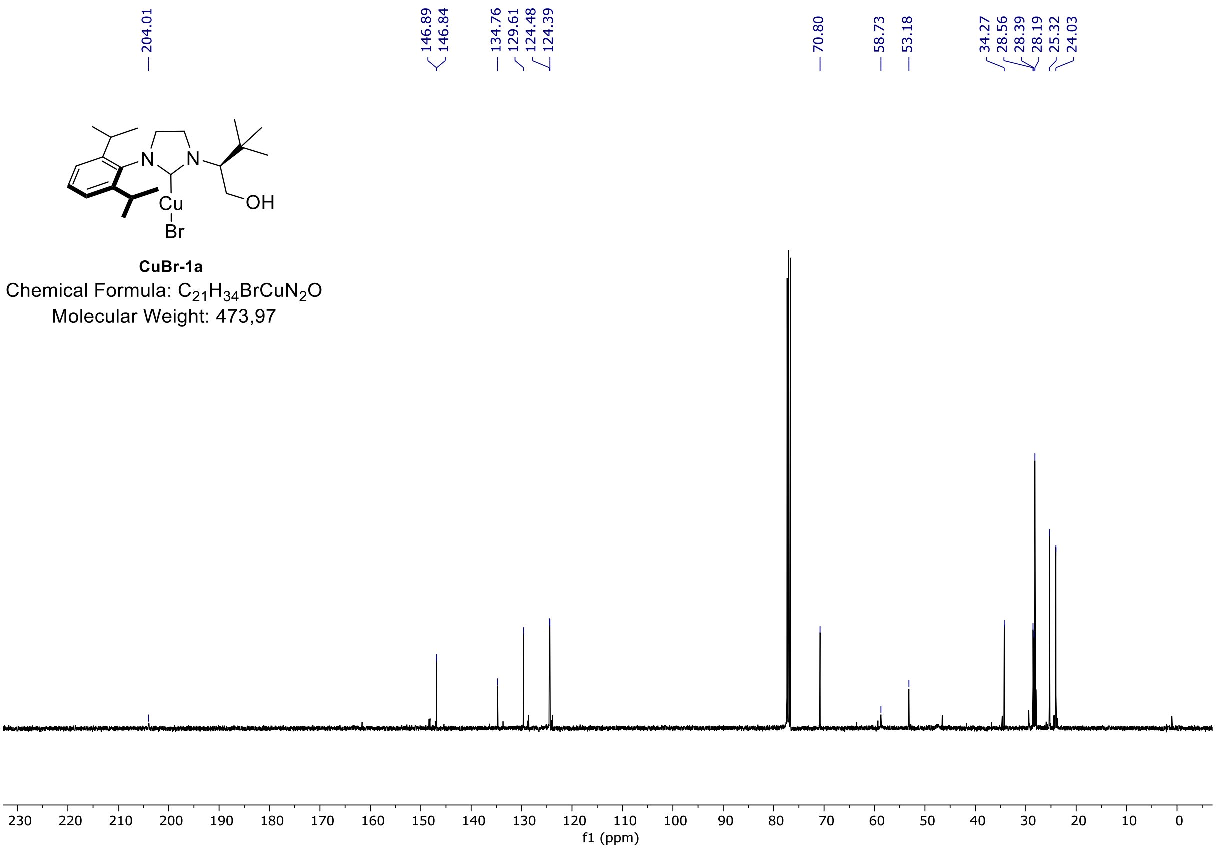


AuCl-1b
Chemical Formula: $C_{18}H_{28}AuClN_2O$
Molecular Weight: 520,86

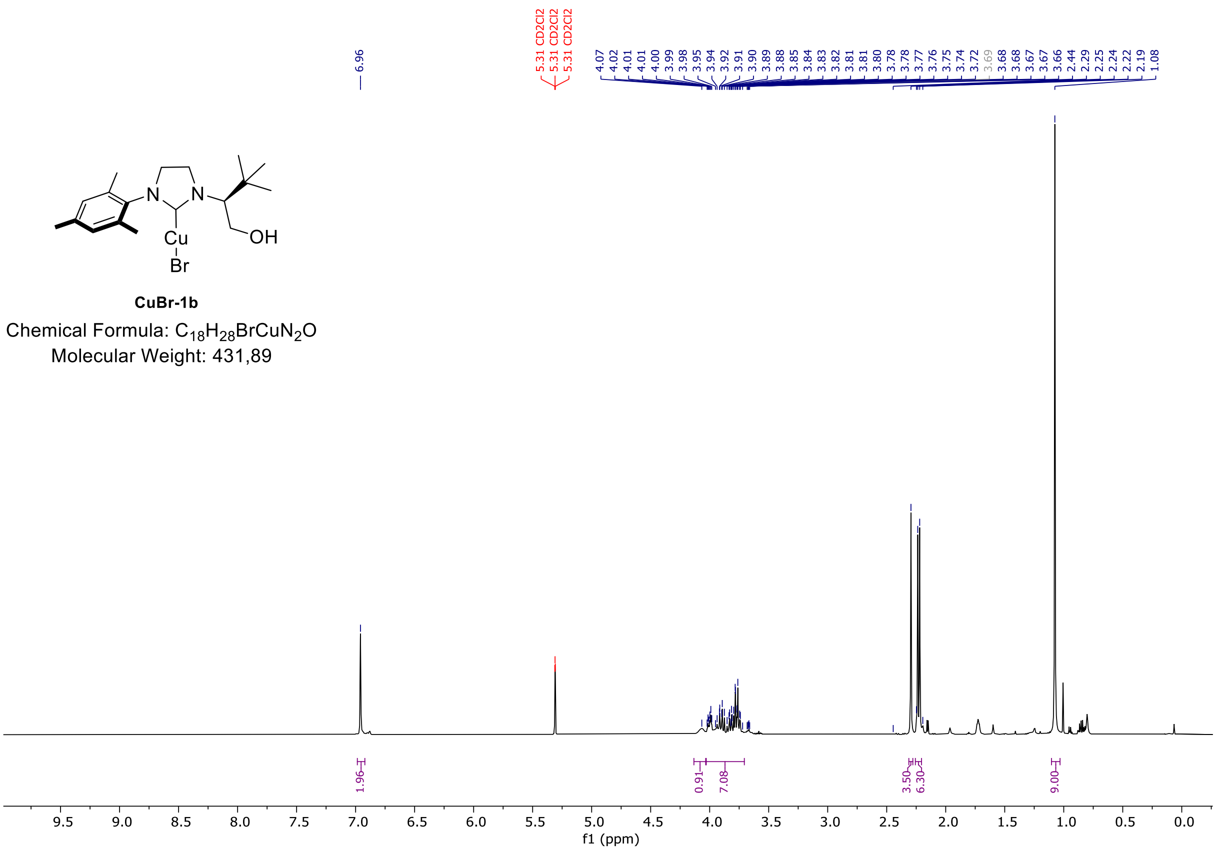
^{1}H NMR ($CDCl_3$, 400 MHz) of CuBr-1a:



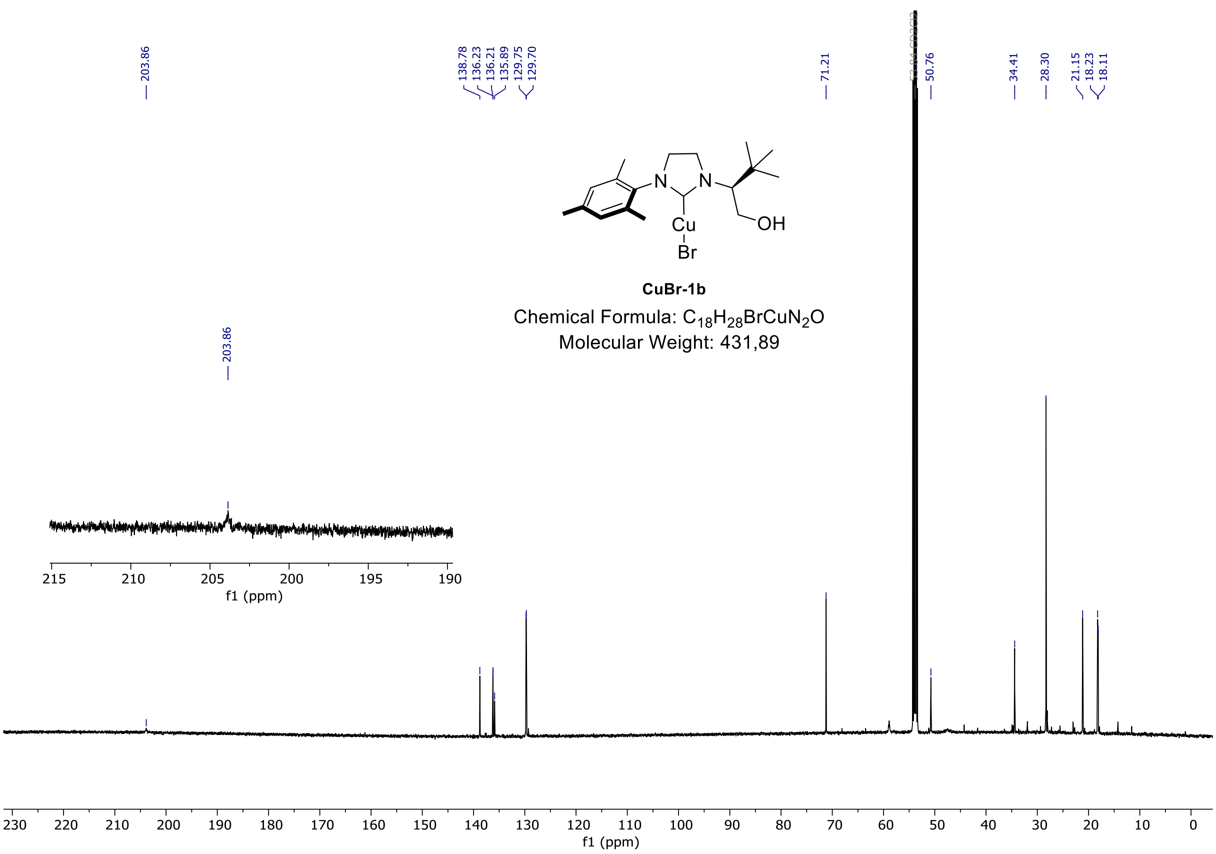
^{13}C NMR ($CDCl_3$, 101 MHz) of CuBr-1a:



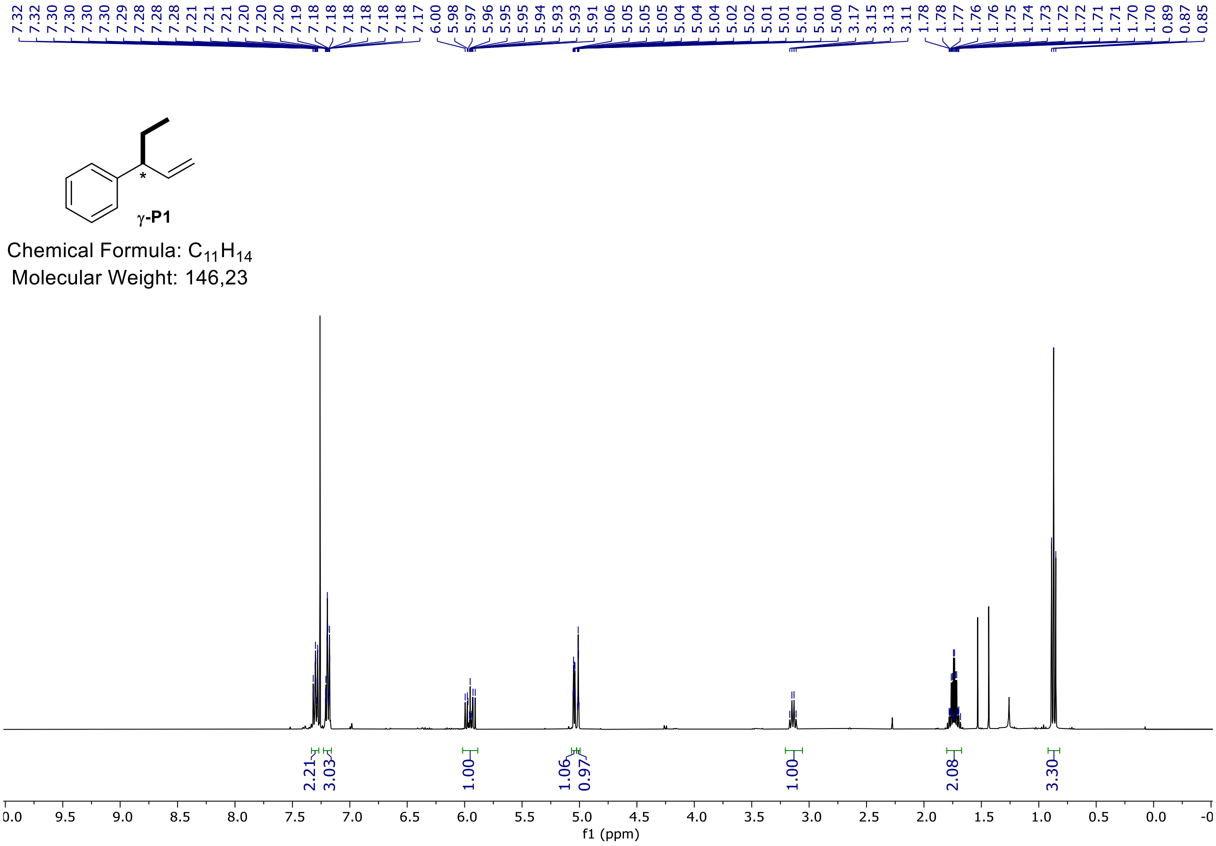
^{1}H NMR (CD_2Cl_2, 500 MHz) of CuBr-1b:



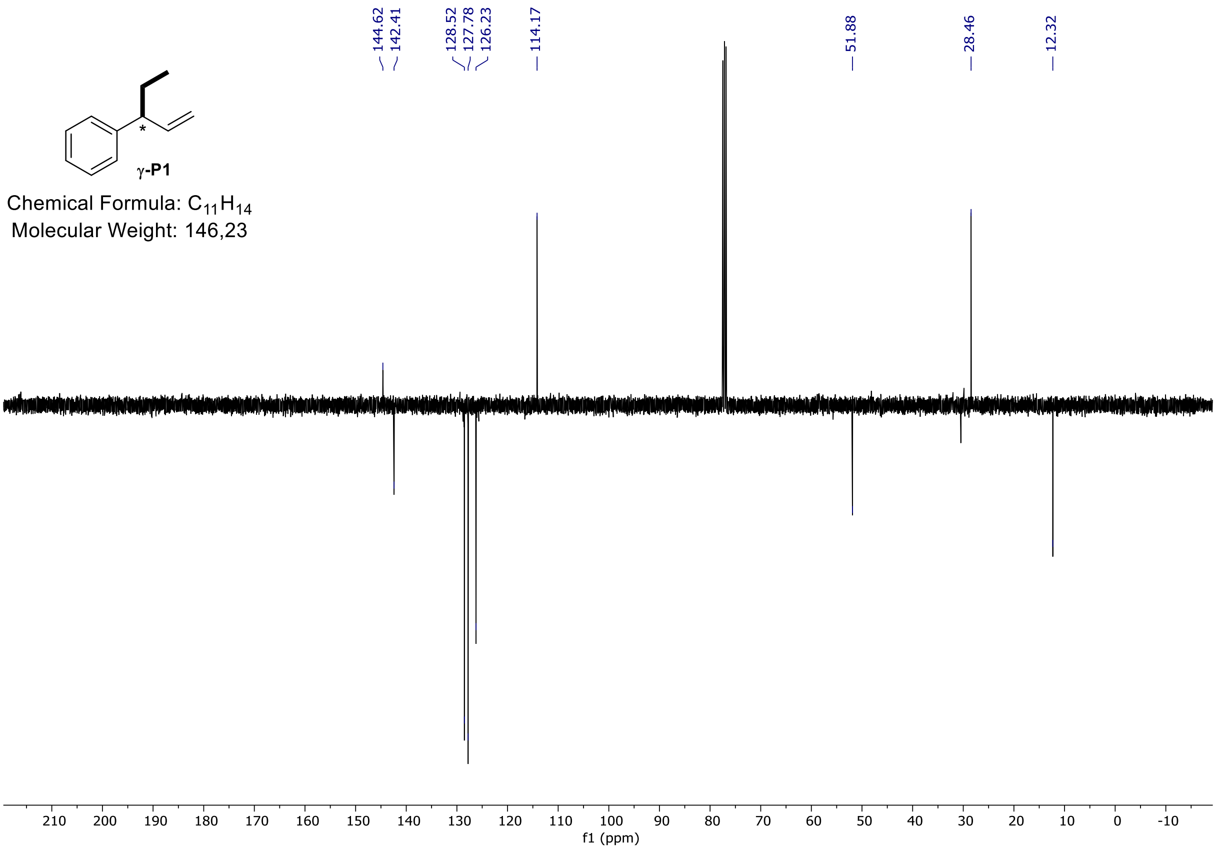
^{13}C NMR (CD_2Cl_2, 126 MHz) of CuBr-1b:



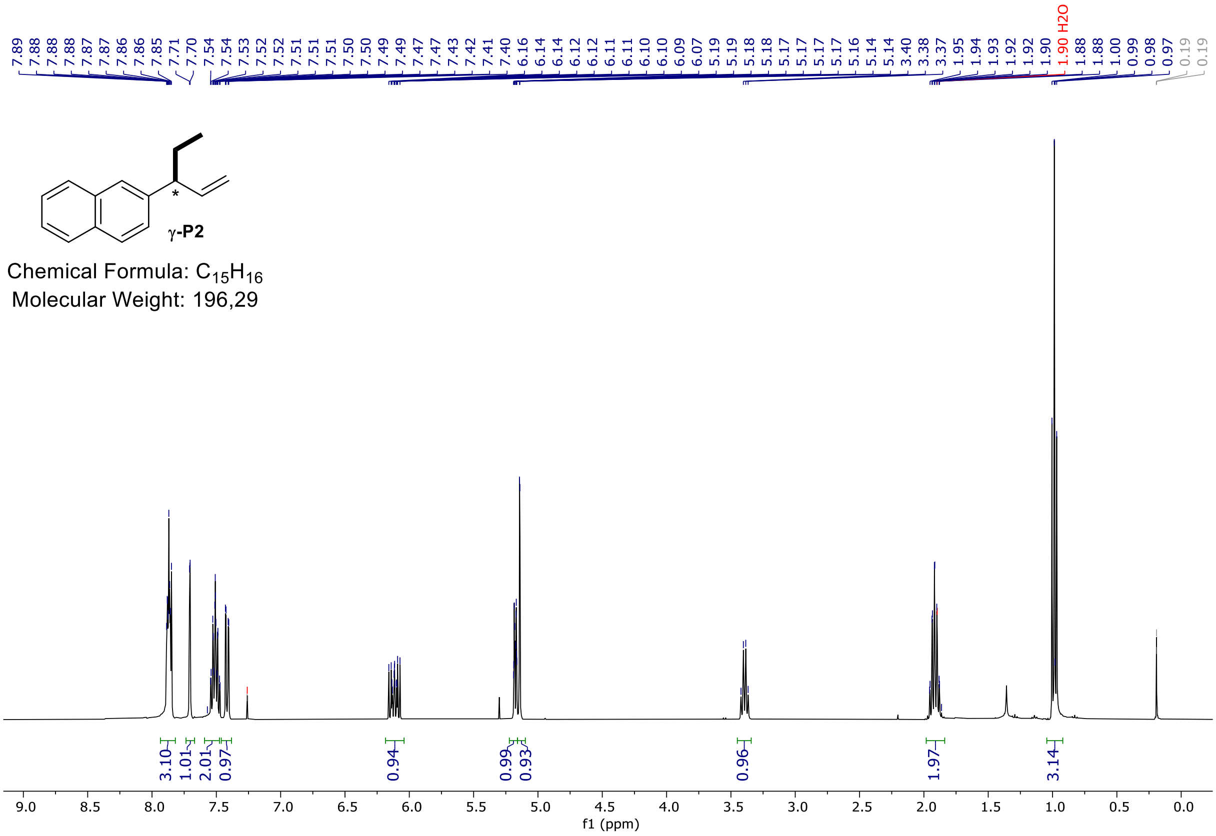
^{1}H NMR ($CDCl_3$, 400 MHz) of γ-P1:



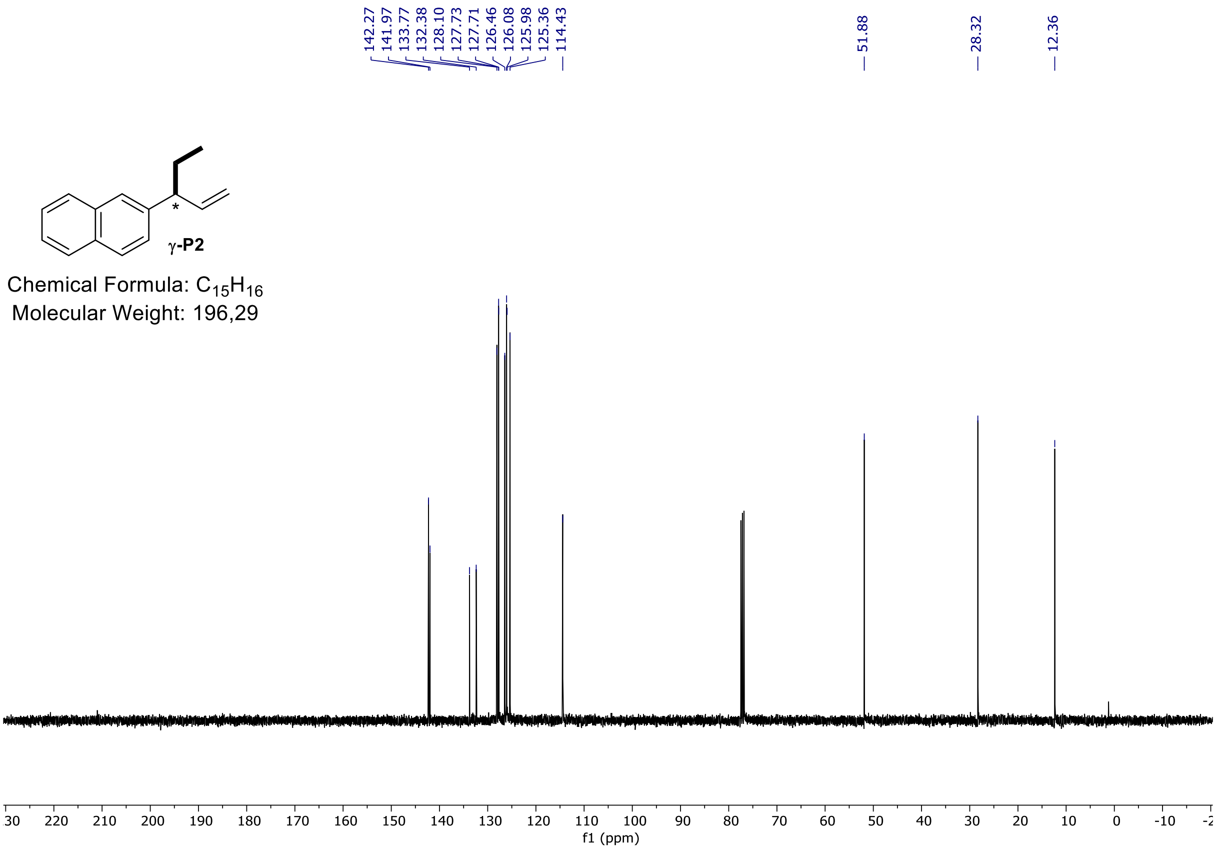
^{13}C NMR ($CDCl_3$, 101 MHz) of γ-P1:



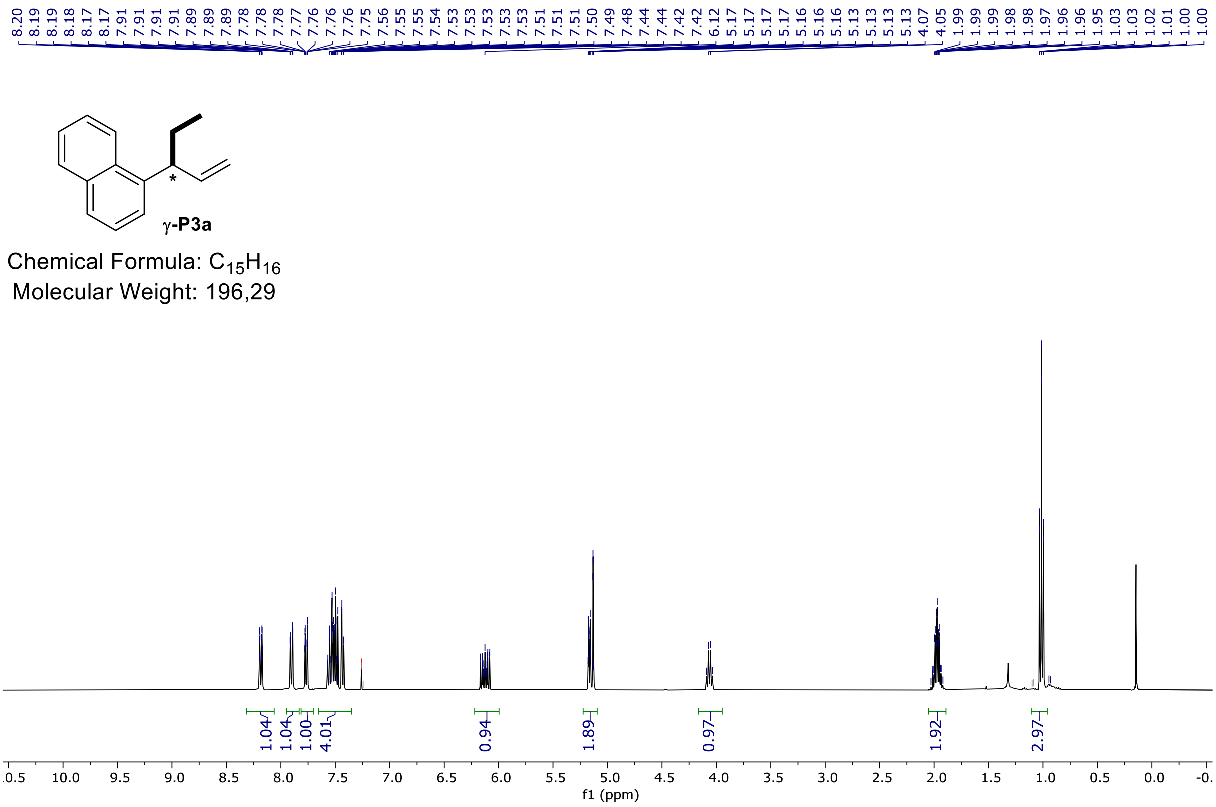
[1]H NMR ($CDCl_3$, 400 MHz) of γ-P2:



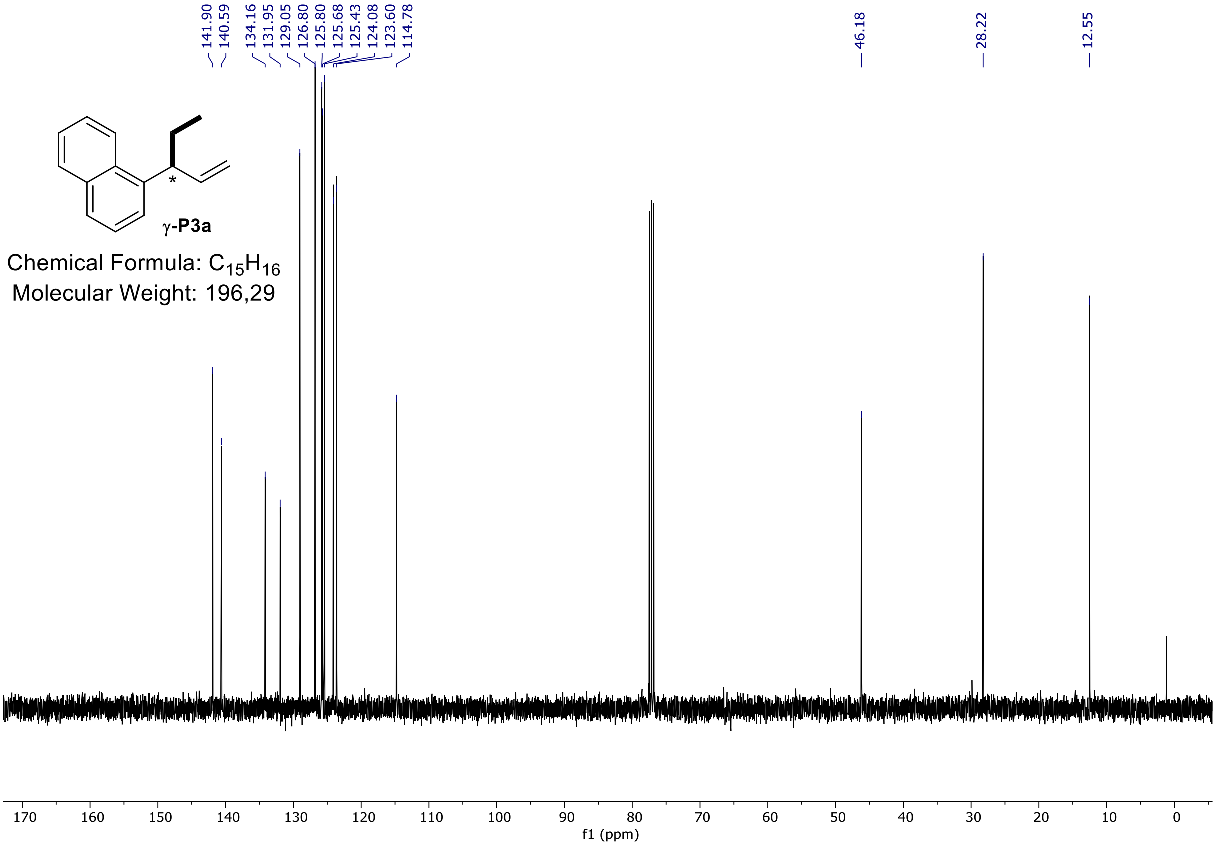
[13]C NMR ($CDCl_3$, 101 MHz) of γ-P2:



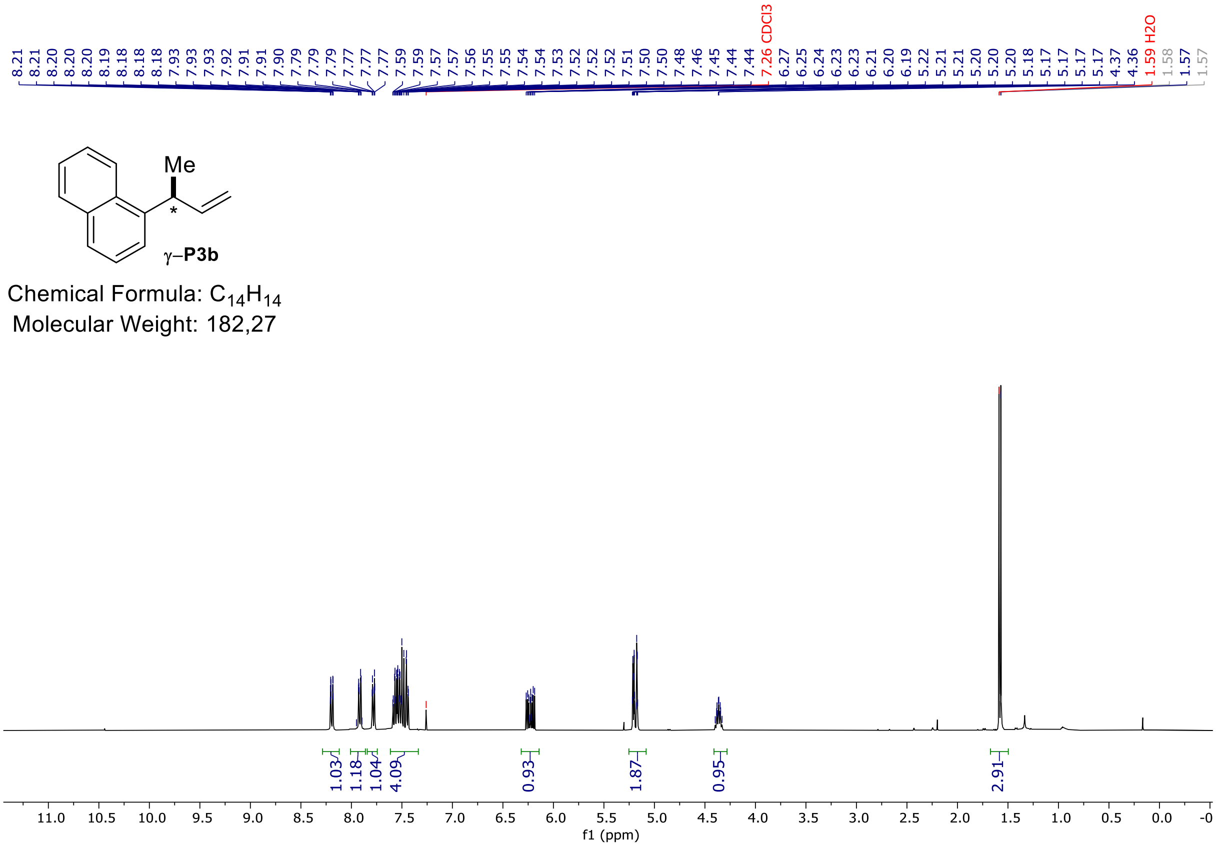
^{1}H NMR ($CDCl_3$, 400 MHz) of γ-P3a:



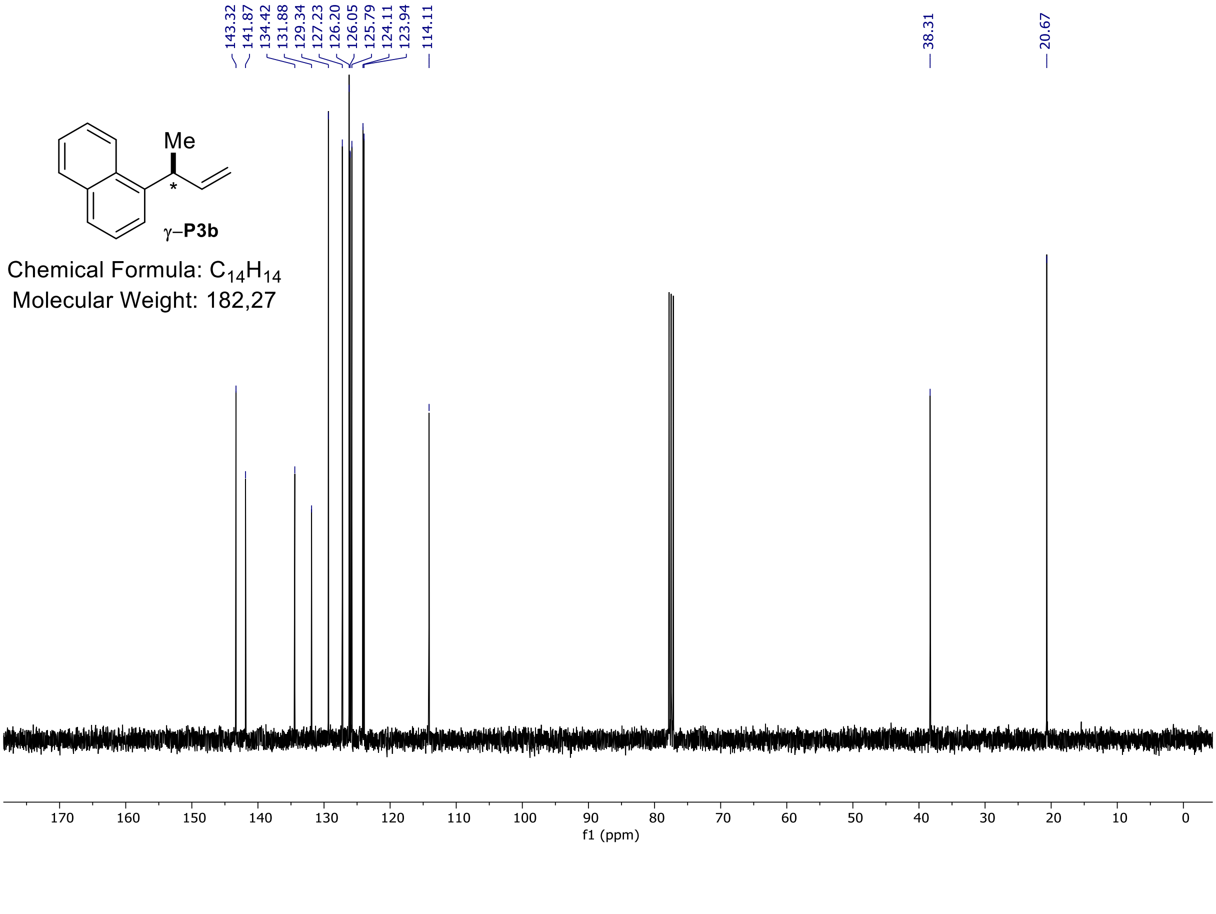
^{13}C NMR ($CDCl_3$, 101 MHz) of γ-P3a:



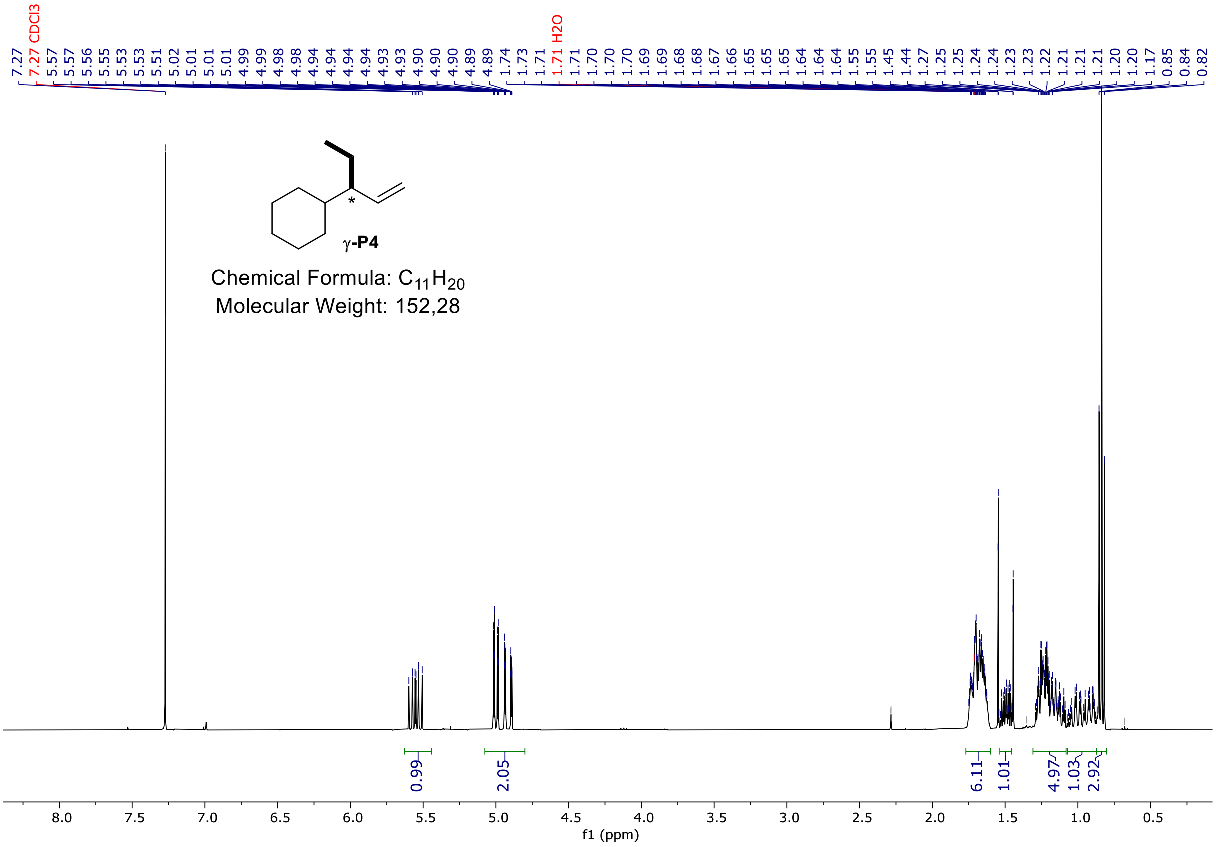
[1]H NMR ($CDCl_3$, 400 MHz) of γ-P3b:



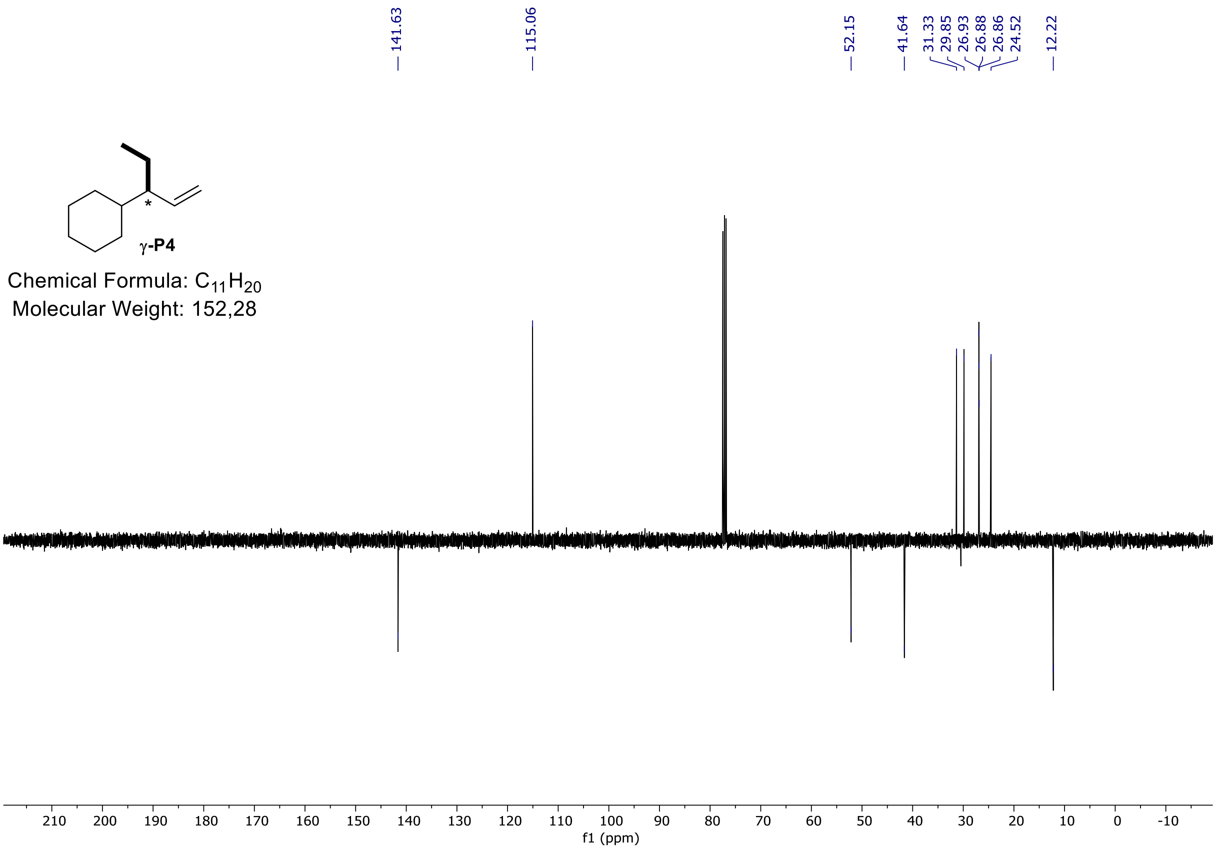
[13]C NMR ($CDCl_3$, 101 MHz) of γ-P3b:



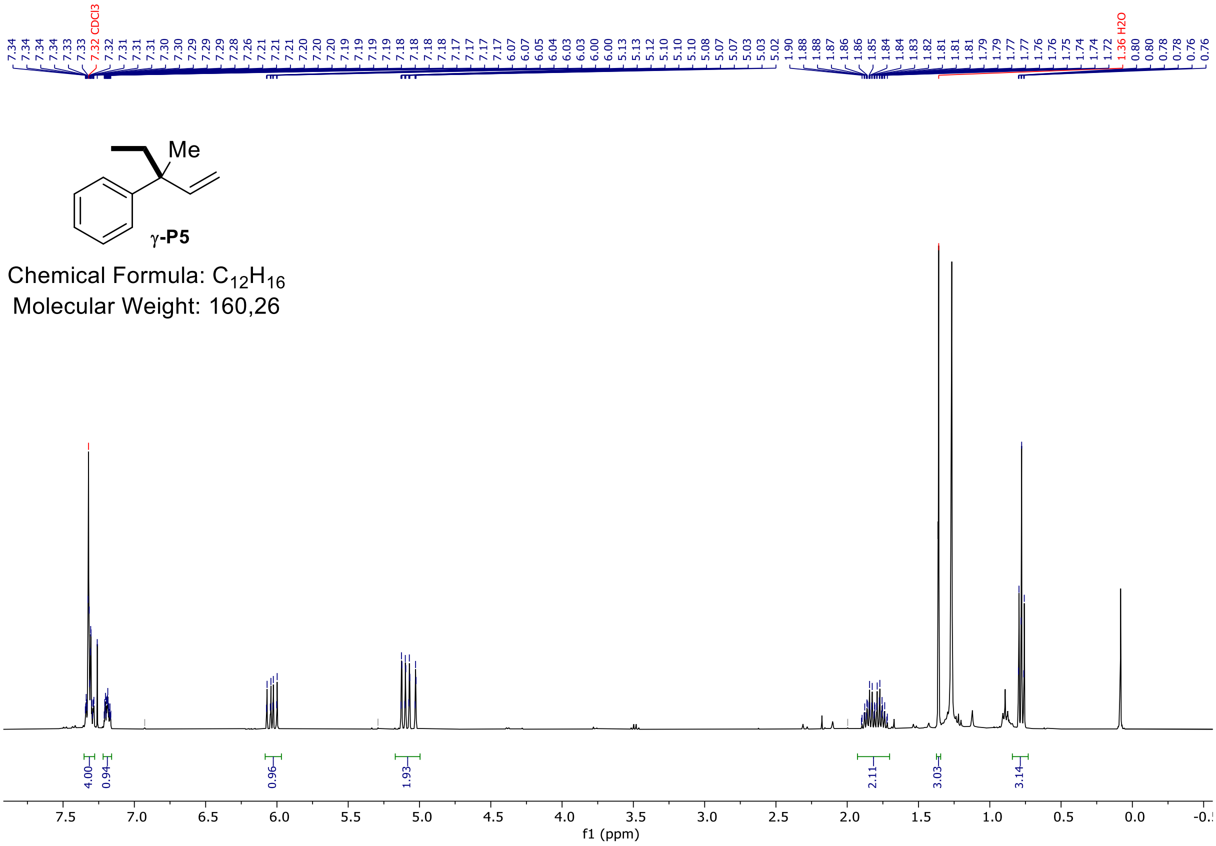
[1]H NMR ($CDCl_3$, 400 MHz) of γ-P4:



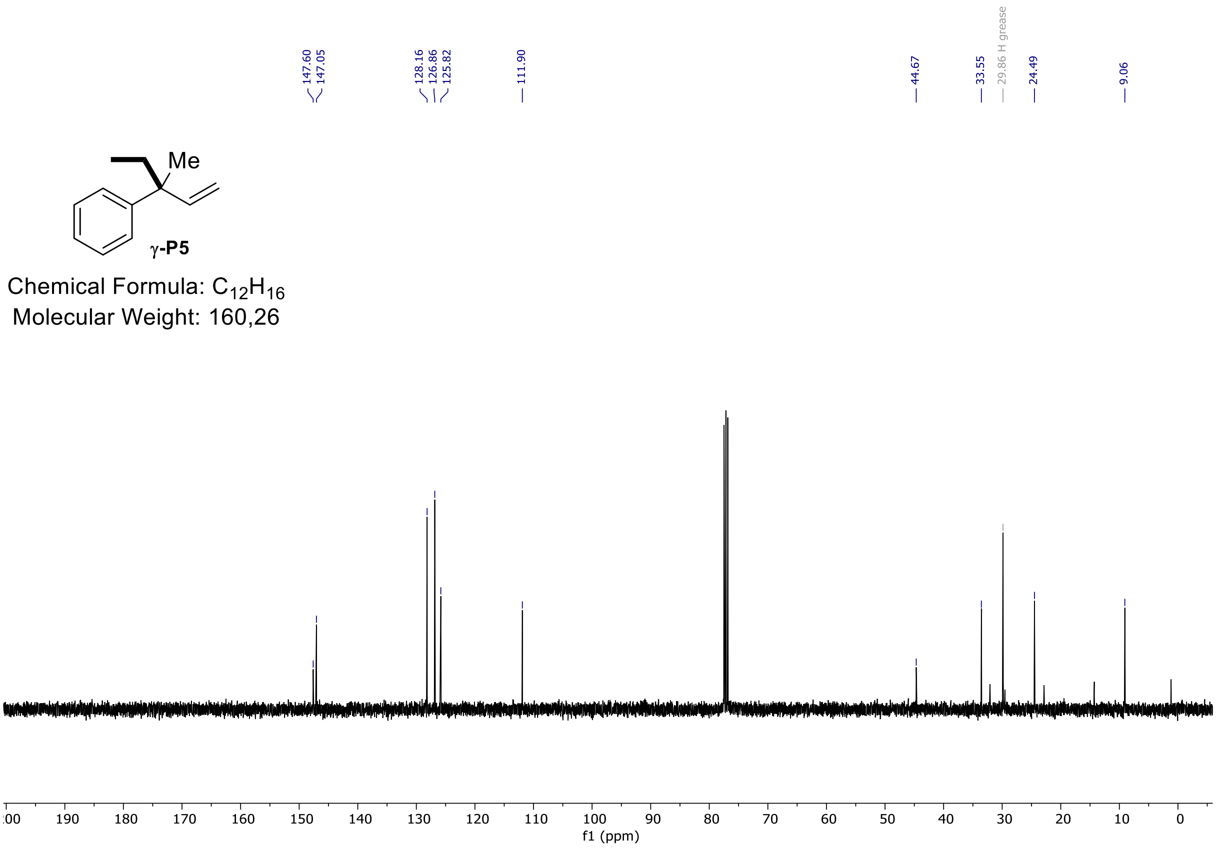
[13]C NMR ($CDCl_3$, 101 MHz) of γ-P4:



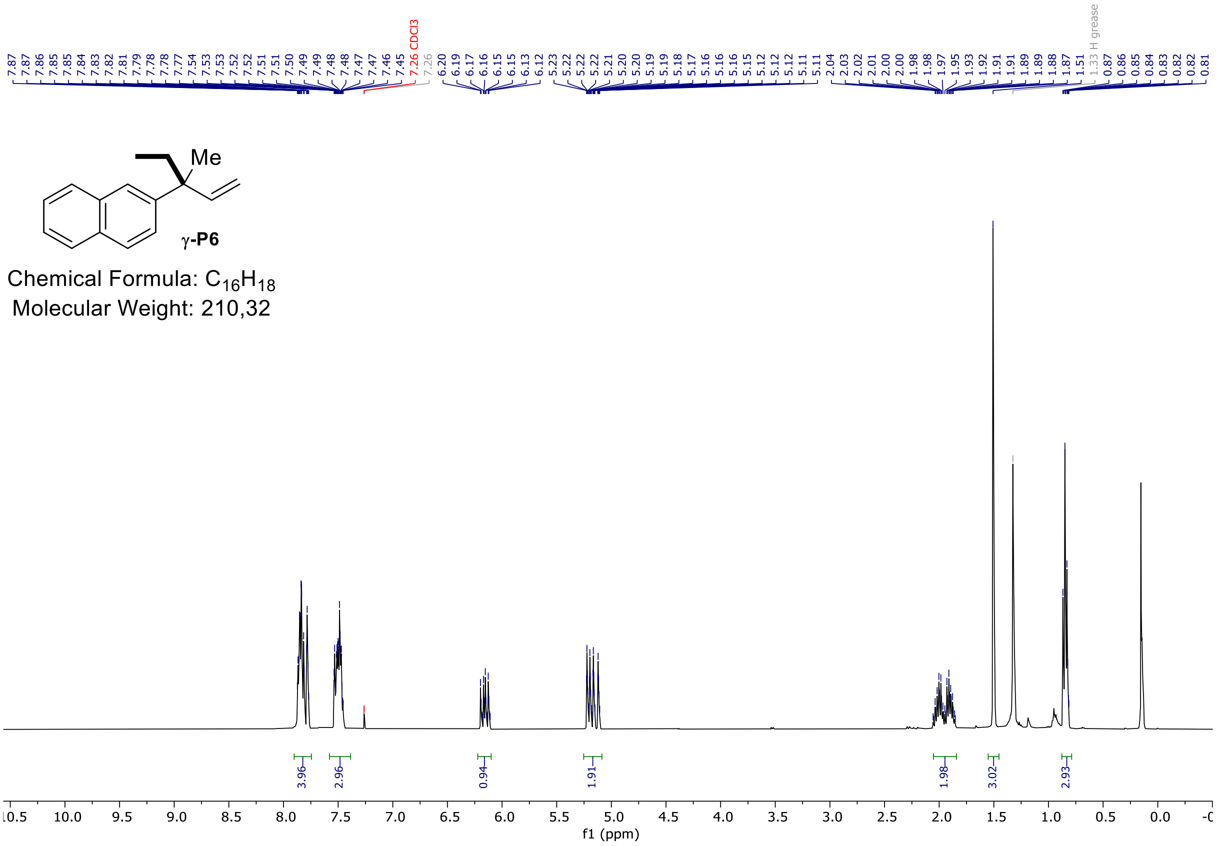
^{1}H NMR ($CDCl_3$, 400 MHz) of γ-P5:



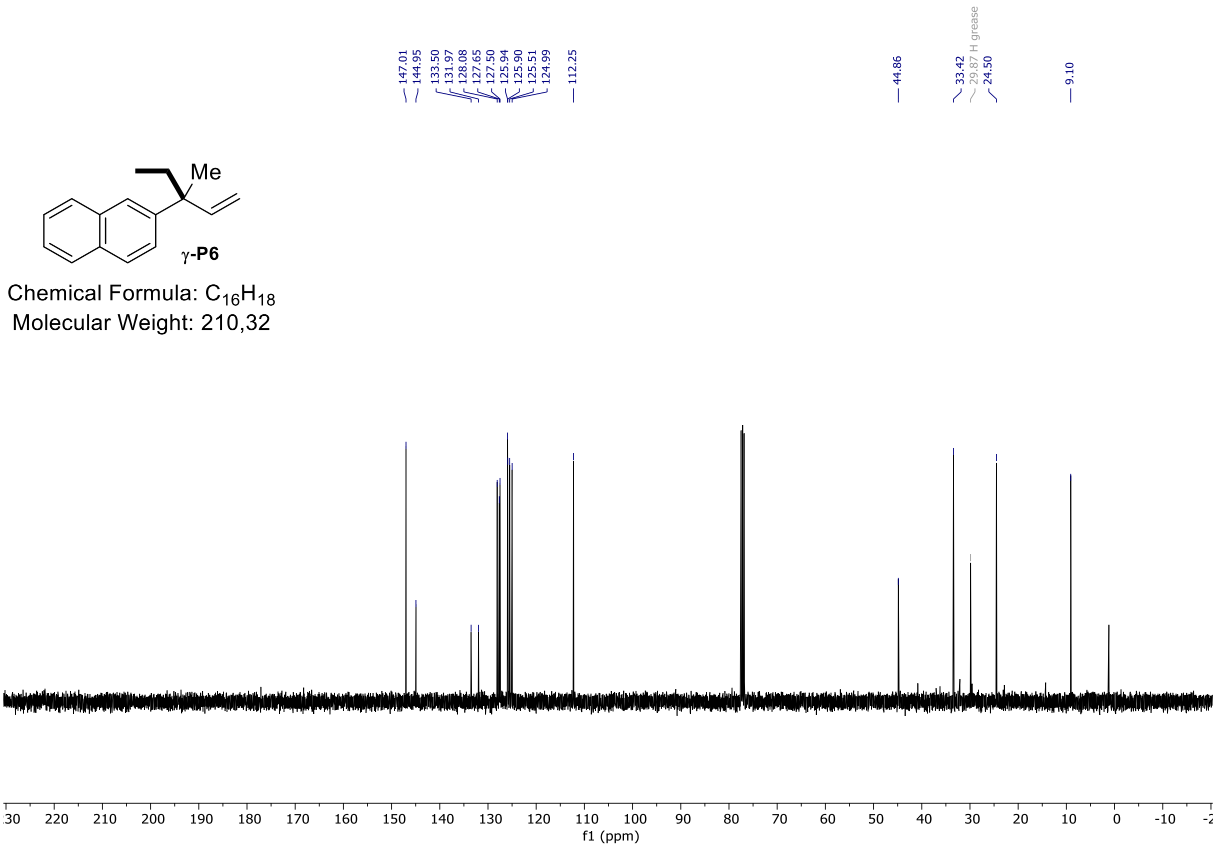
^{13}C NMR ($CDCl_3$, 101 MHz) of γ-P5:



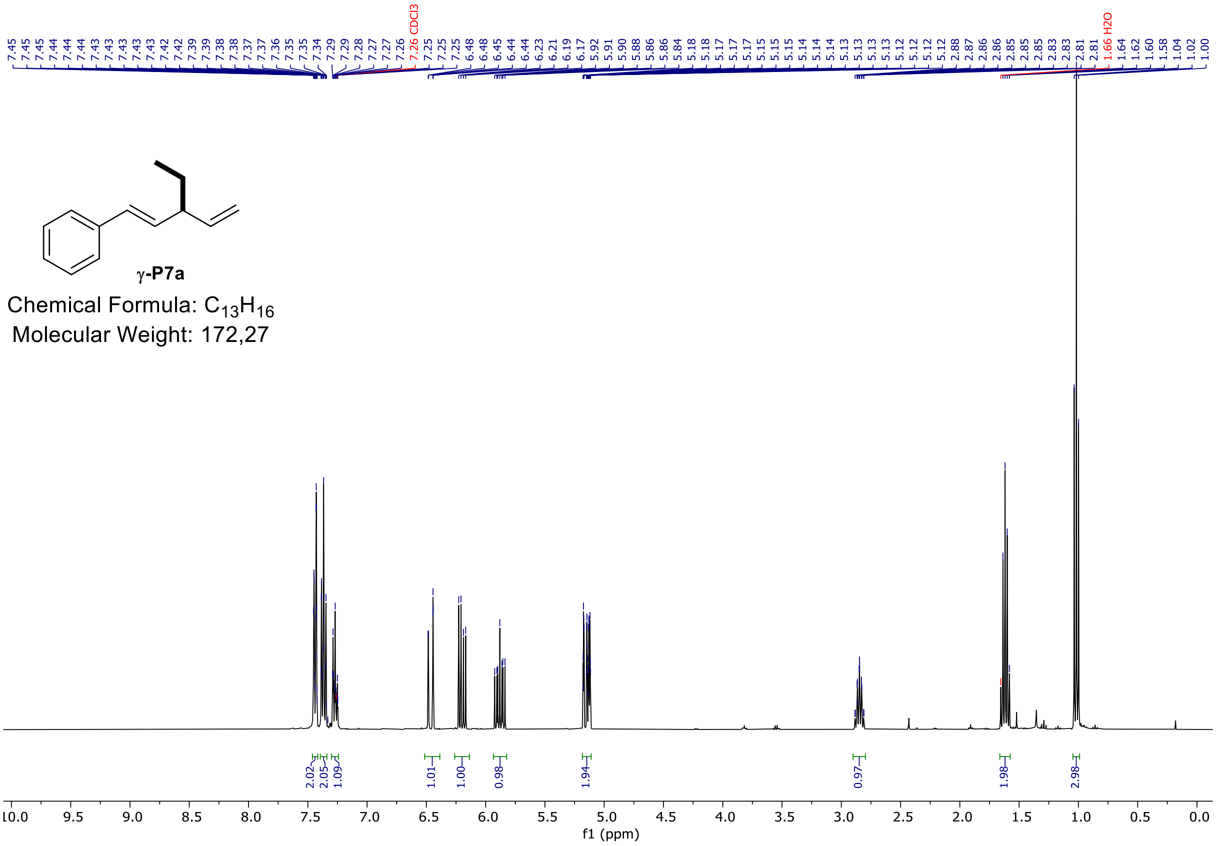
^{1}H NMR ($CDCl_3$, 400 MHz) of γ-P6:



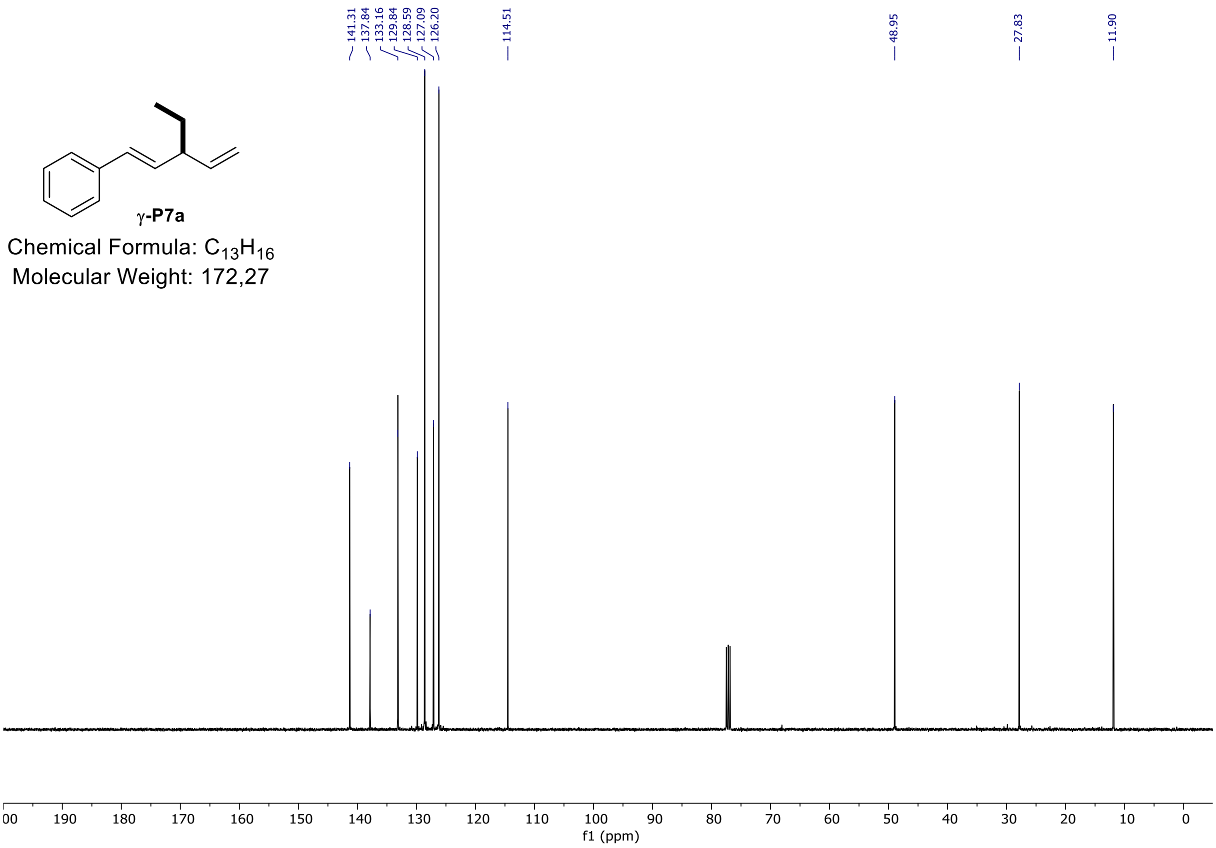
^{13}C NMR ($CDCl_3$, 101 MHz) of γ-P6:



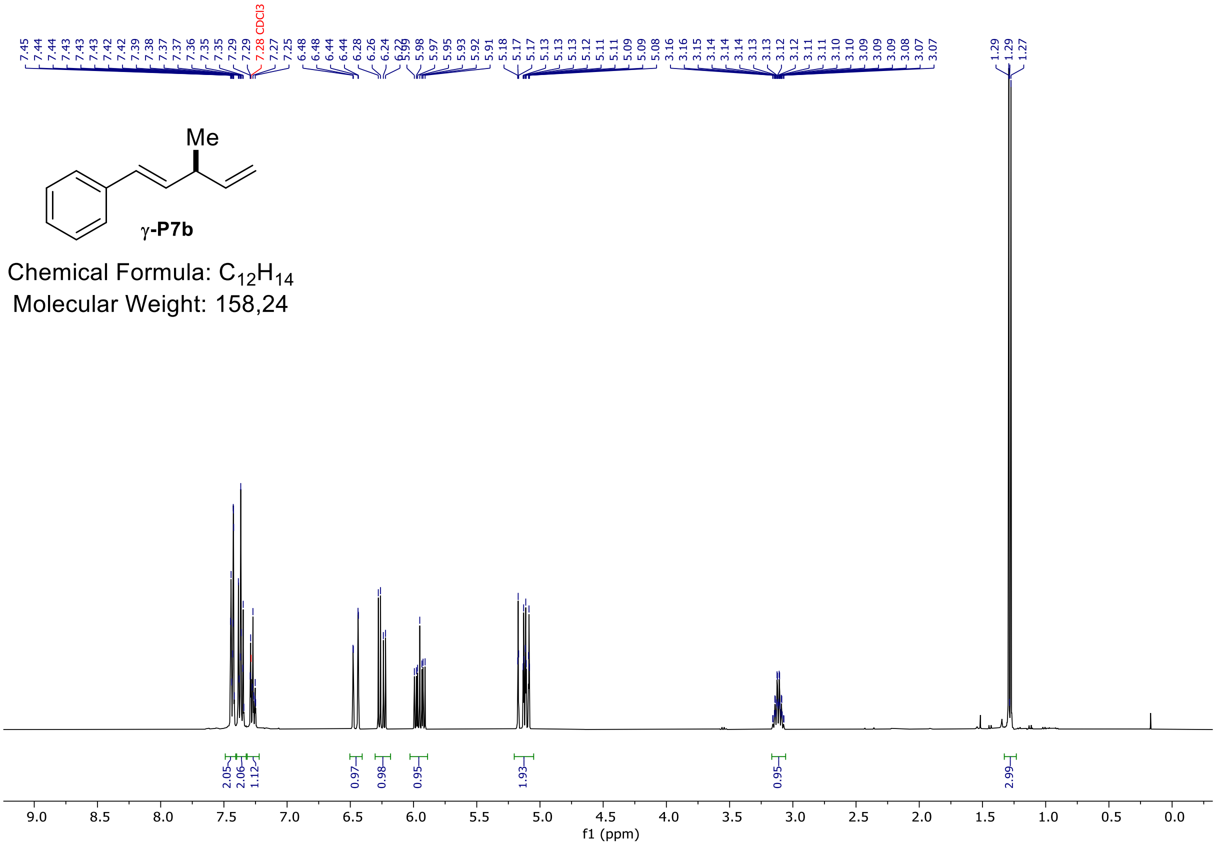
^{1}H NMR ($CDCl_3$, 400 MHz) of γ-P7a:



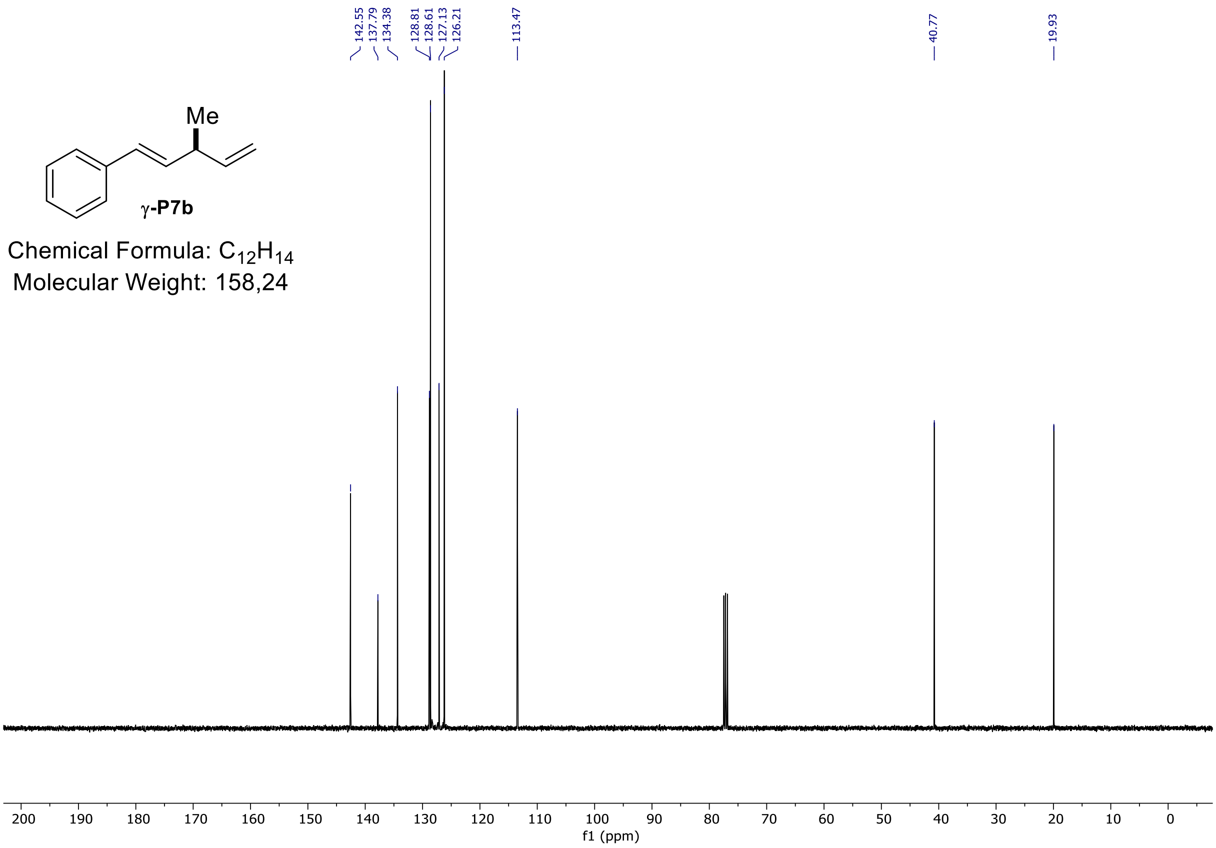
^{13}C NMR ($CDCl_3$, 101 MHz) of γ-P7a:



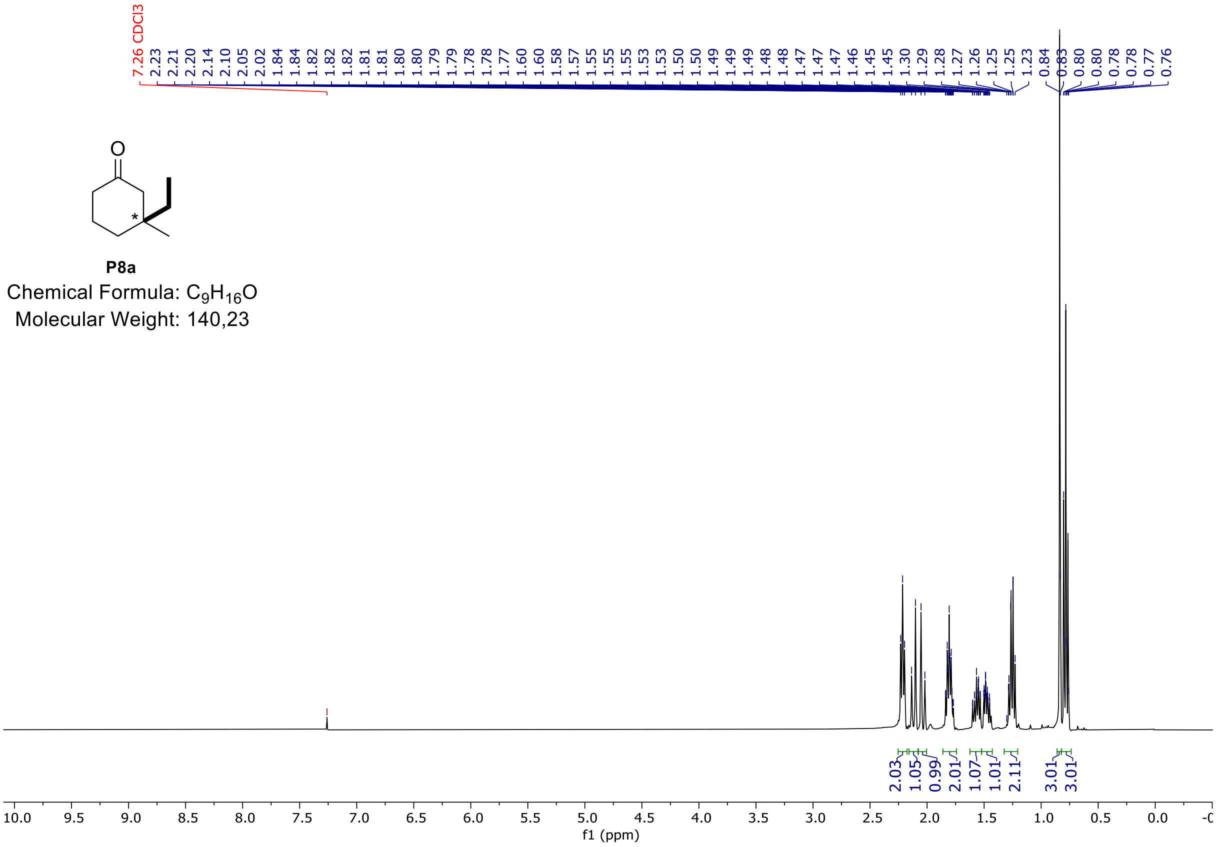
^{1}H NMR ($CDCl_3$, 400 MHz) of γ-P7b:



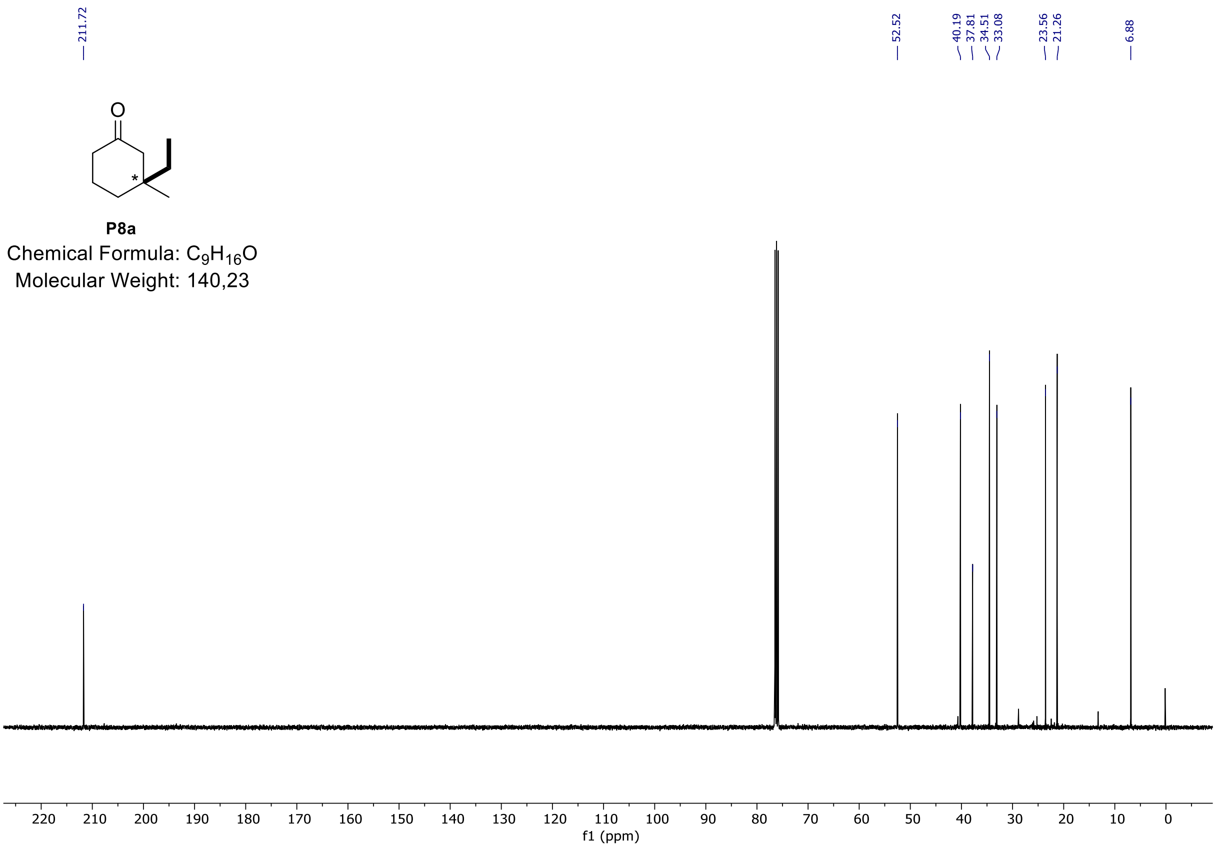
^{13}C NMR ($CDCl_3$, 101 MHz) of γ-P7b:



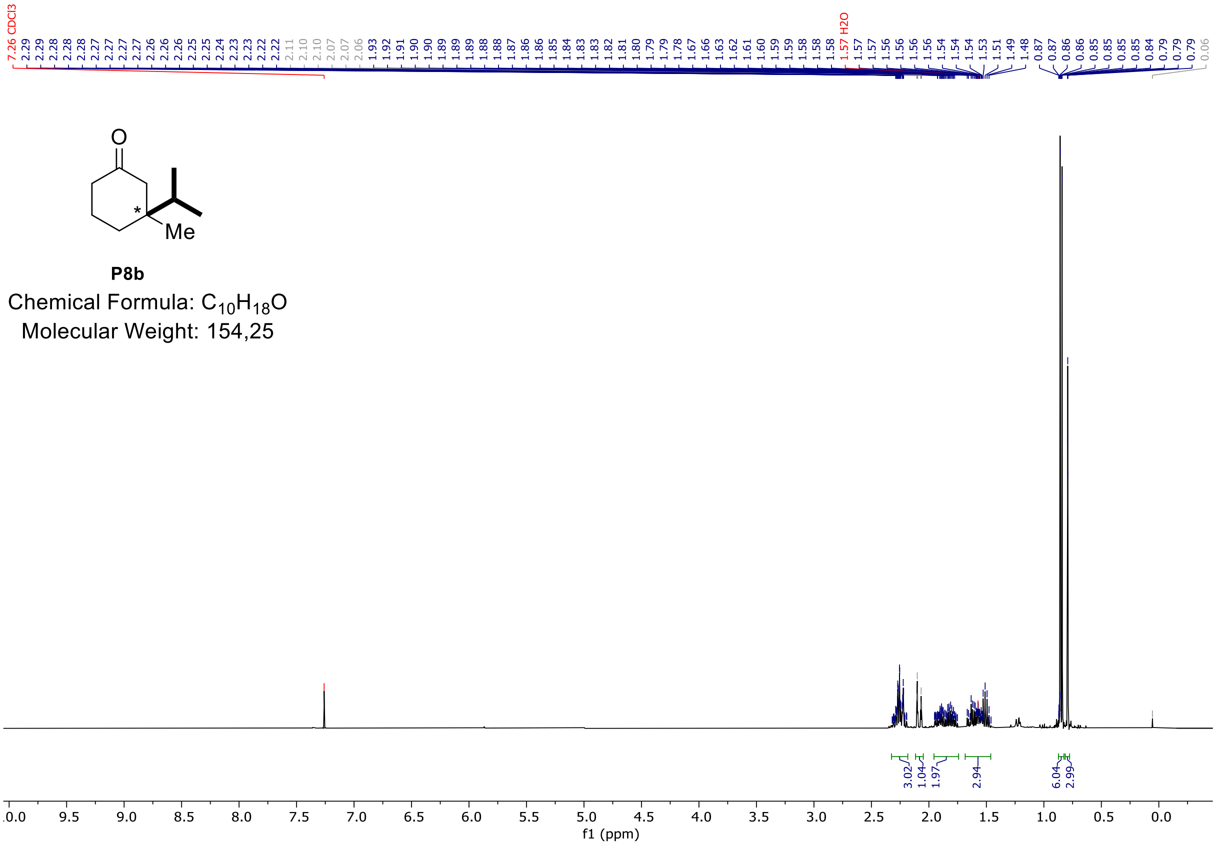
[1]H NMR ($CDCl_3$, 400 MHz) of P8a:



[13]C NMR ($CDCl_3$, 101 MHz) of P8a:

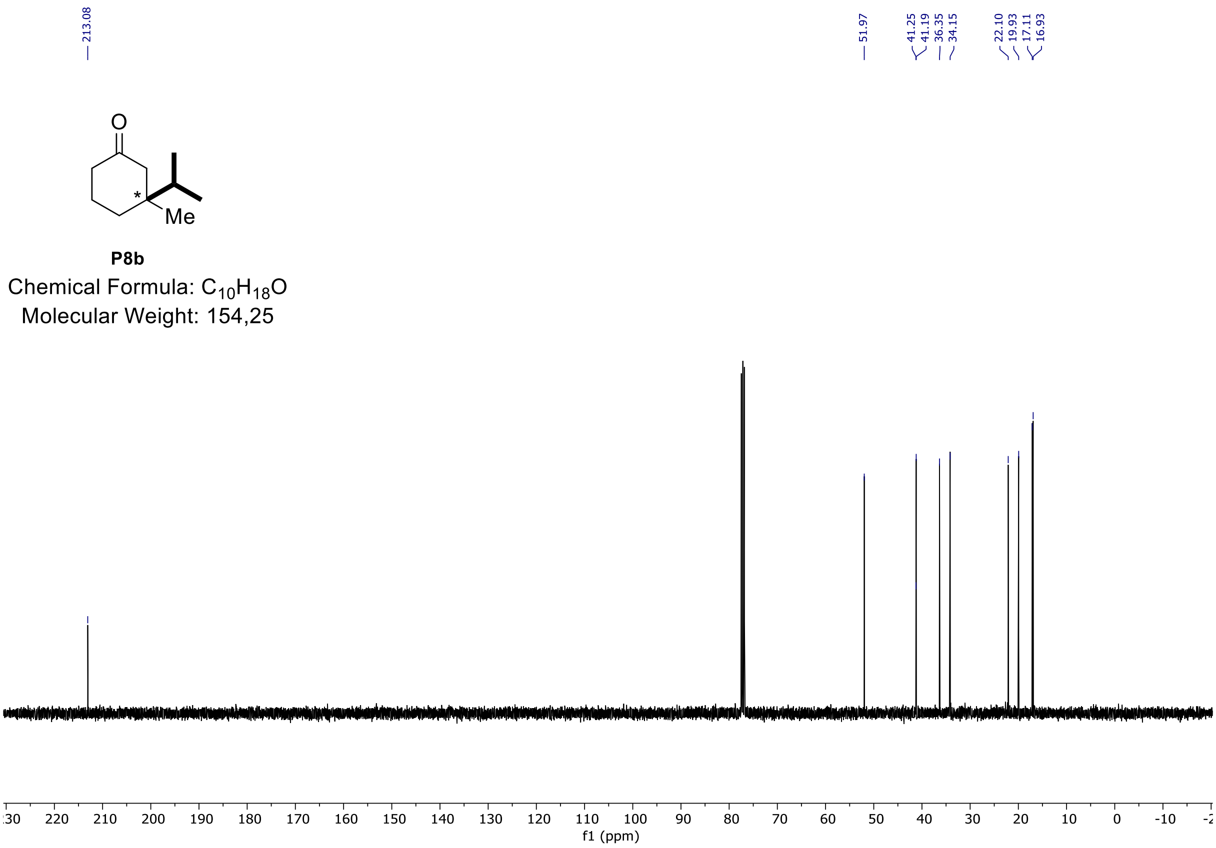


^{1}H NMR ($CDCl_3$, 400 MHz) of P8b:



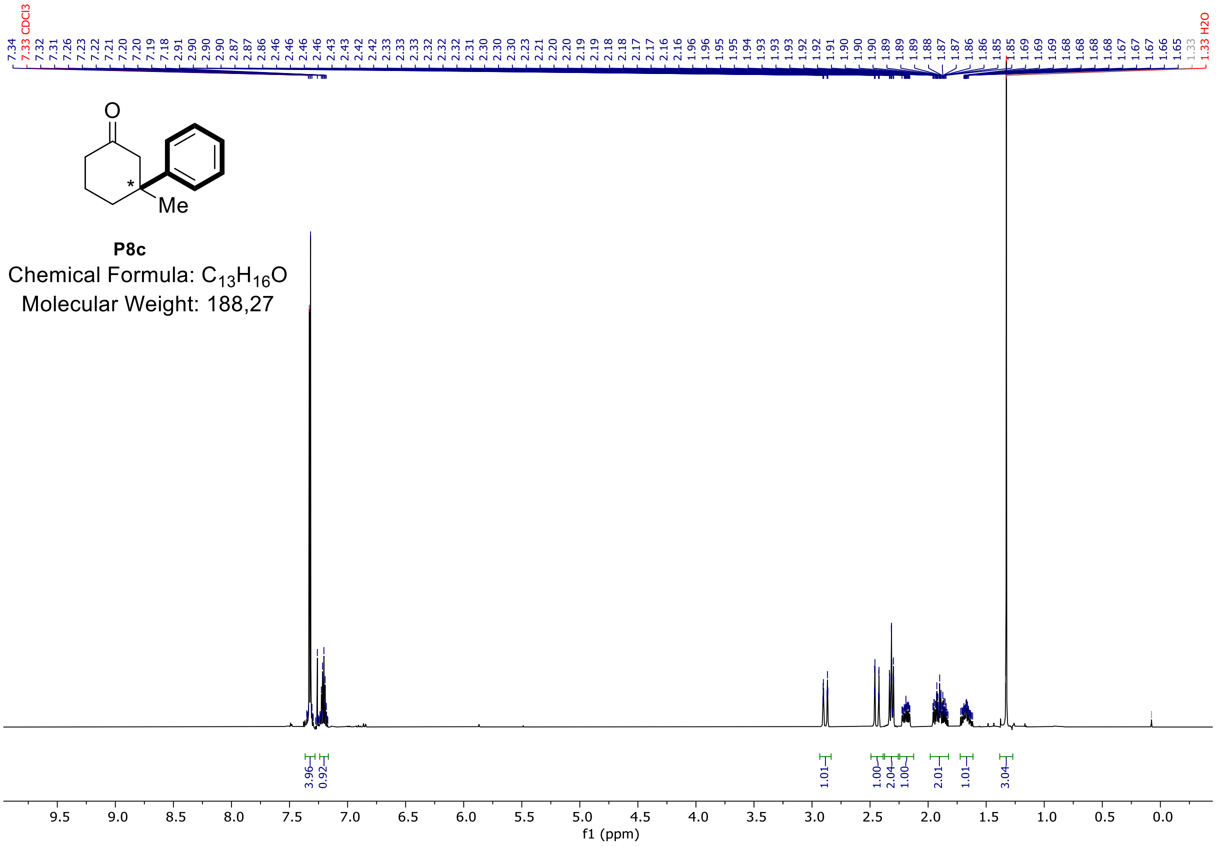
P8b
Chemical Formula: $C_{10}H_{18}O$
Molecular Weight: 154,25

^{13}C NMR ($CDCl_3$, 101 MHz) of P8b:

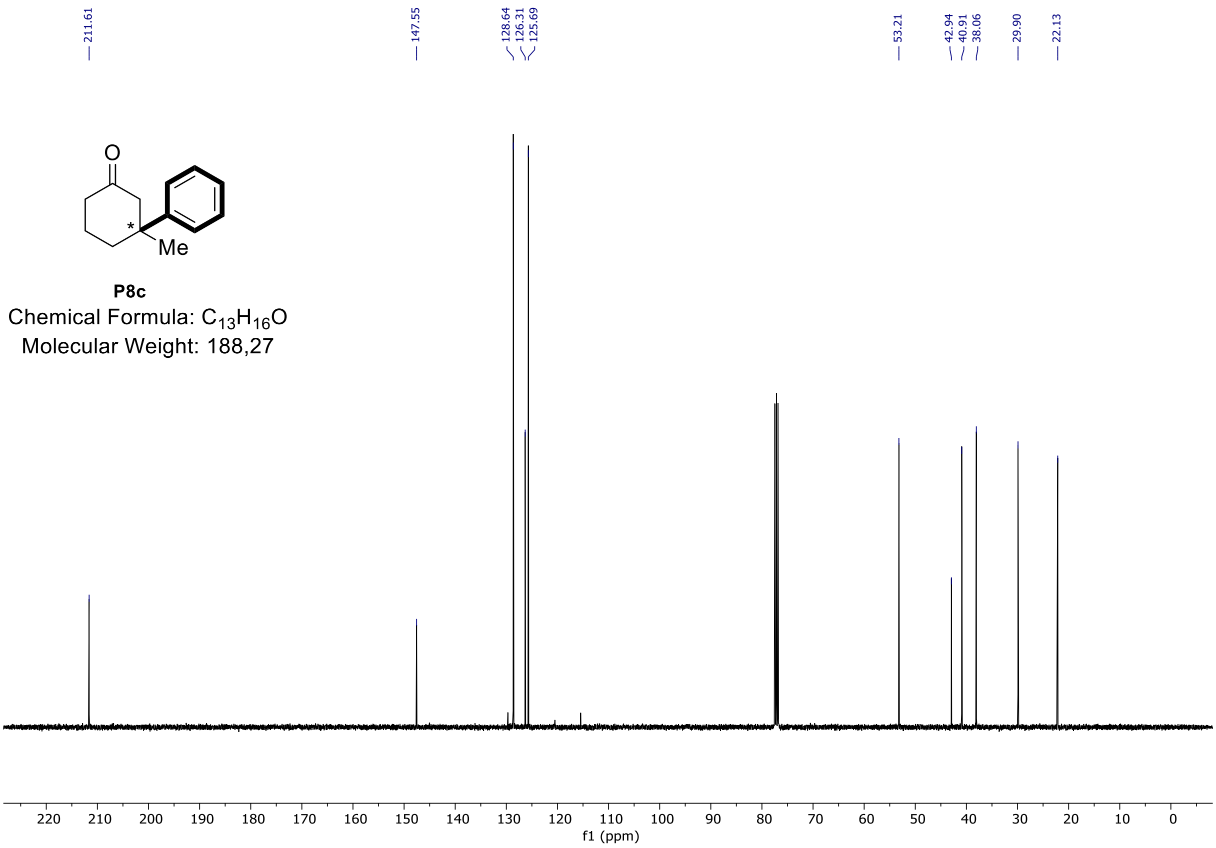


P8b
Chemical Formula: $C_{10}H_{18}O$
Molecular Weight: 154,25

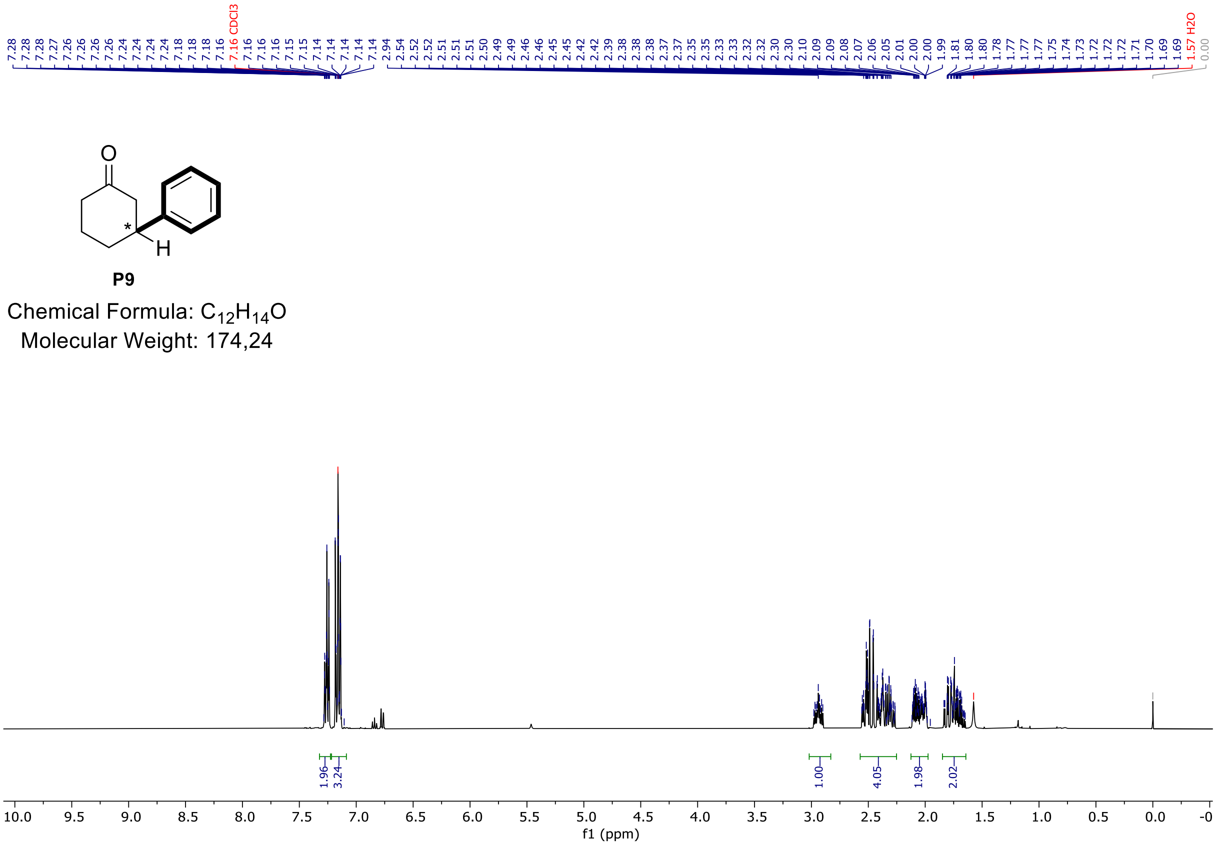
^{1}H NMR (CDCl$_3$, 400 MHz) of P8c:



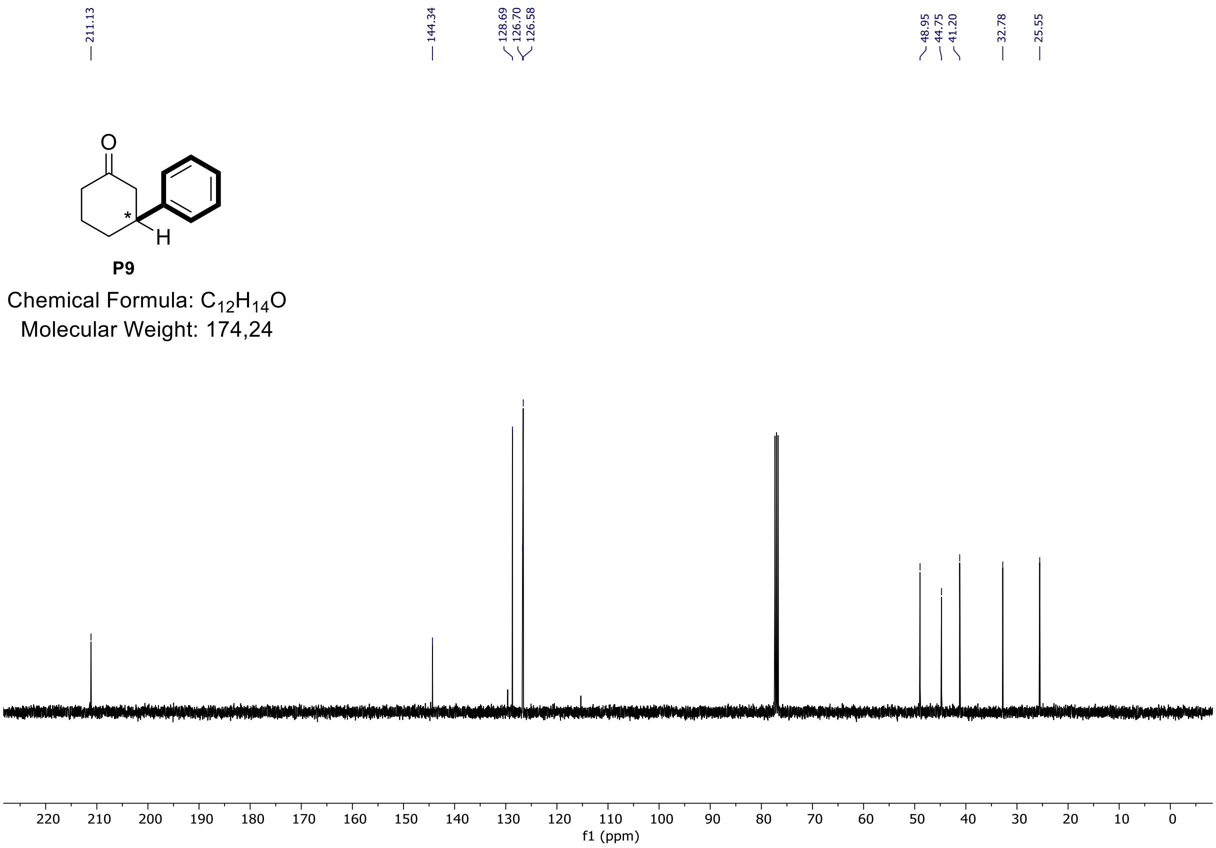
^{13}C NMR (CDCl$_3$, 101 MHz) of P8c:



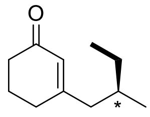
^{1}H NMR ($CDCl_3$, 400 MHz) of P9:



^{13}C NMR ($CDCl_3$, 101 MHz) of P9:



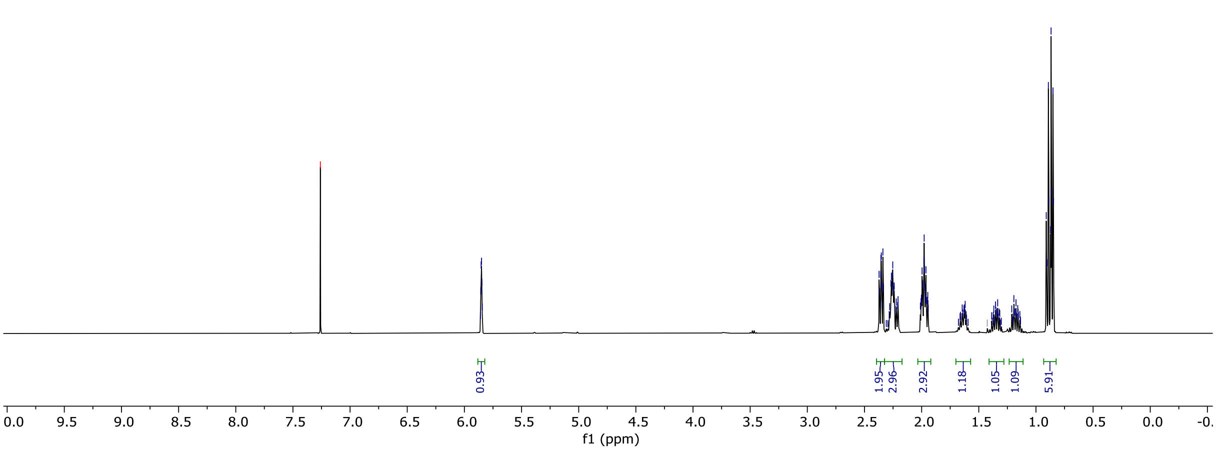
^{1}H NMR ($CDCl_3$, 400 MHz) of *1,6*-P10a:



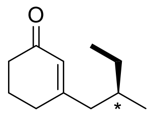
***1,6*-P10a**

Chemical Formula: $C_{11}H_{18}O$

Molecular Weight: 166,26



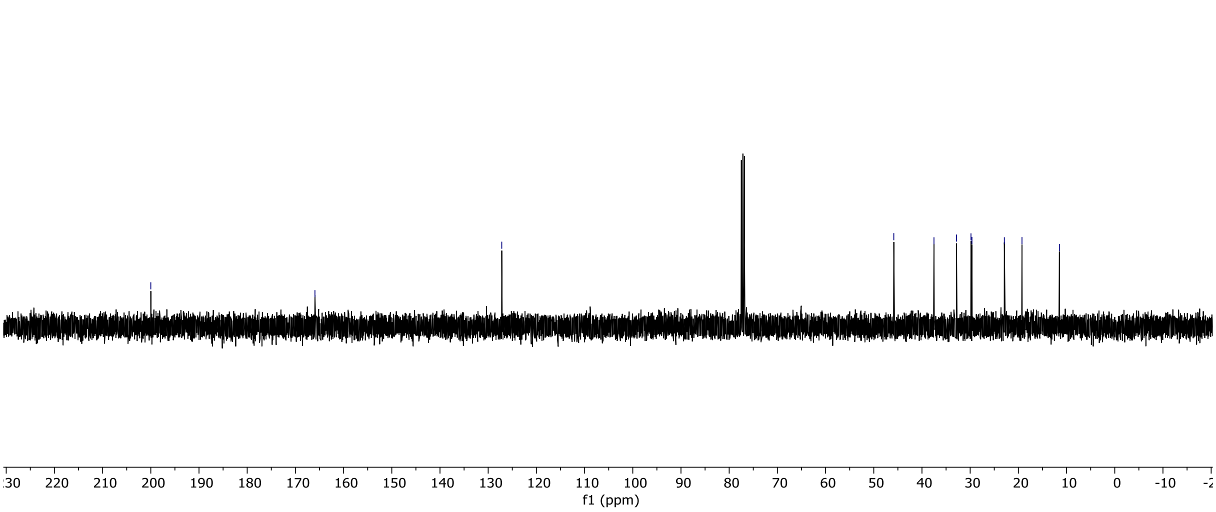
^{13}C NMR ($CDCl_3$, 101 MHz) of *1,6*-P10a:



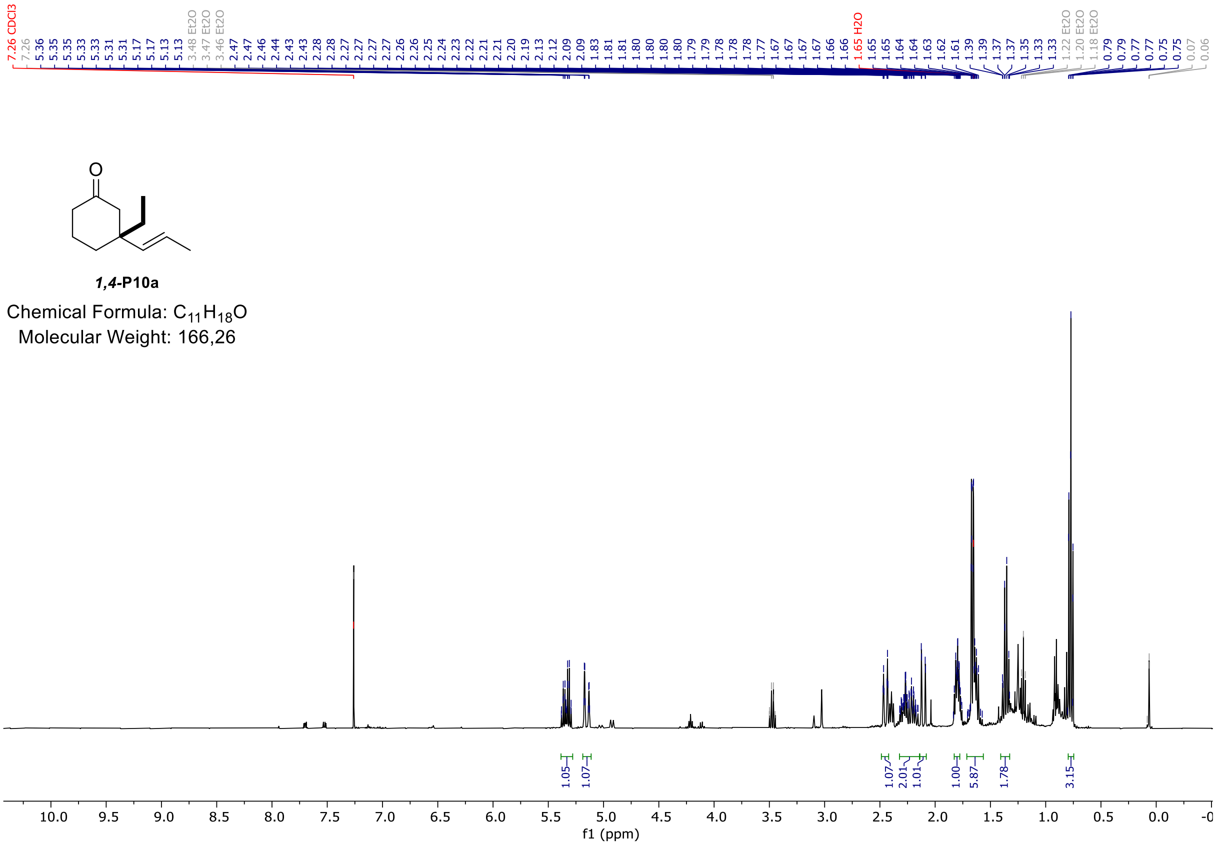
***1,6*-P10a**

Chemical Formula: $C_{11}H_{18}O$

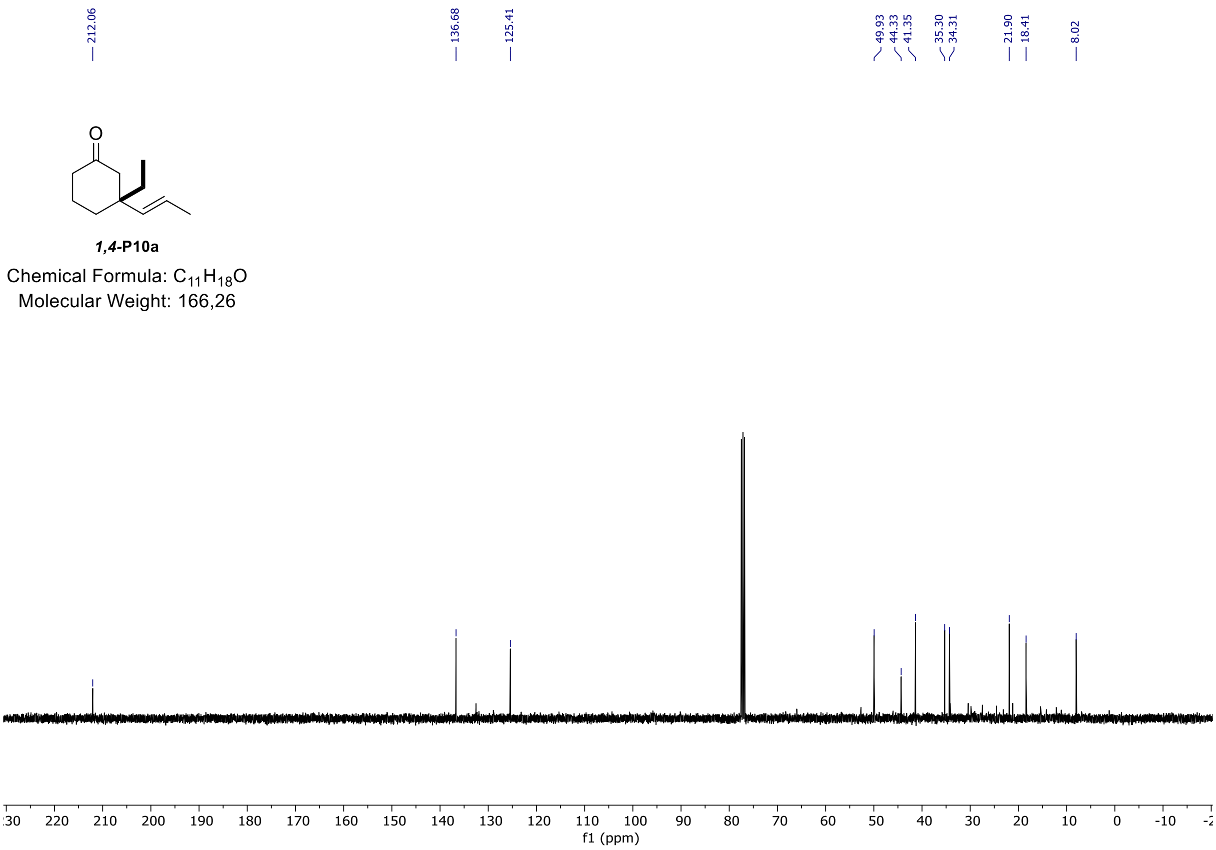
Molecular Weight: 166,26



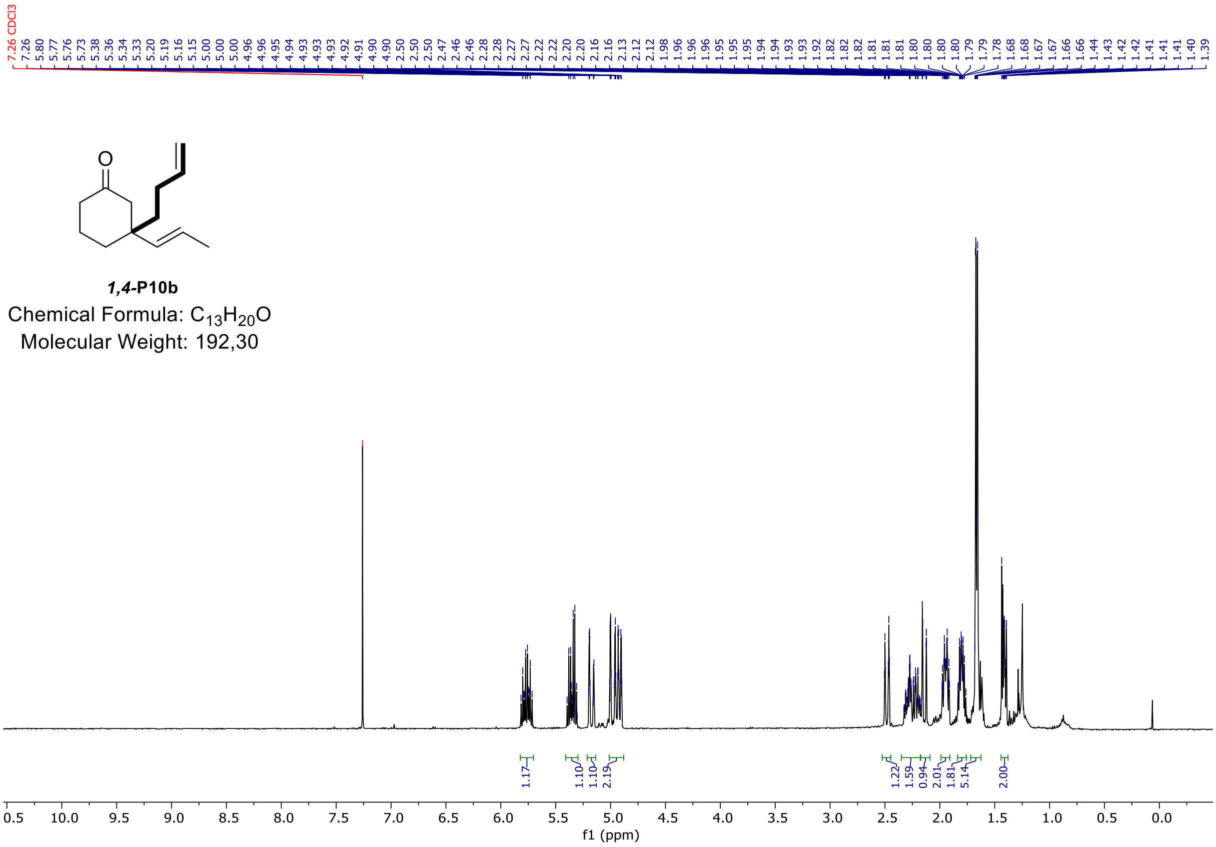
^{1}H NMR ($CDCl_3$, 400 MHz) of *1,4*-P10a:



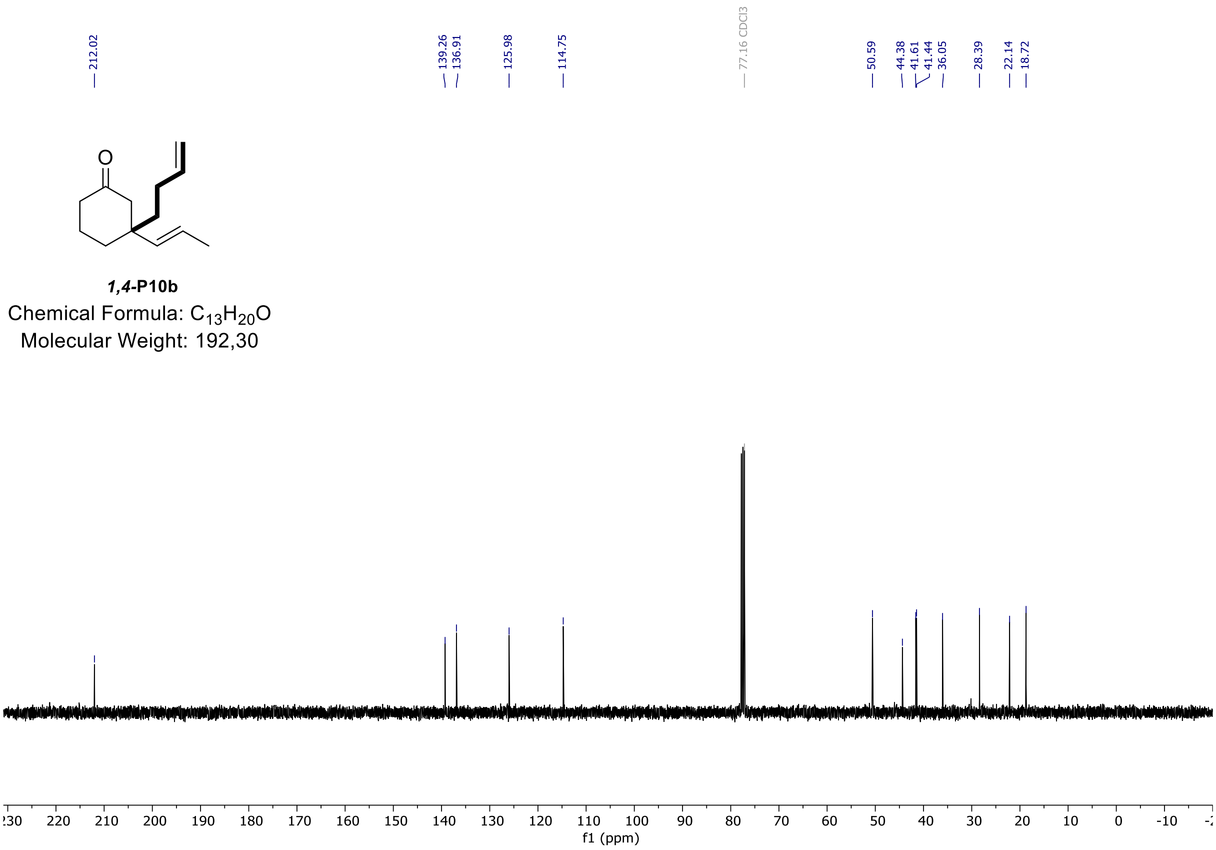
^{13}C NMR ($CDCl_3$, 101 MHz) of *1,4*-P10a:



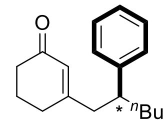
^{1}H NMR ($CDCl_3$, 400 MHz) of *1,4*-P10b:



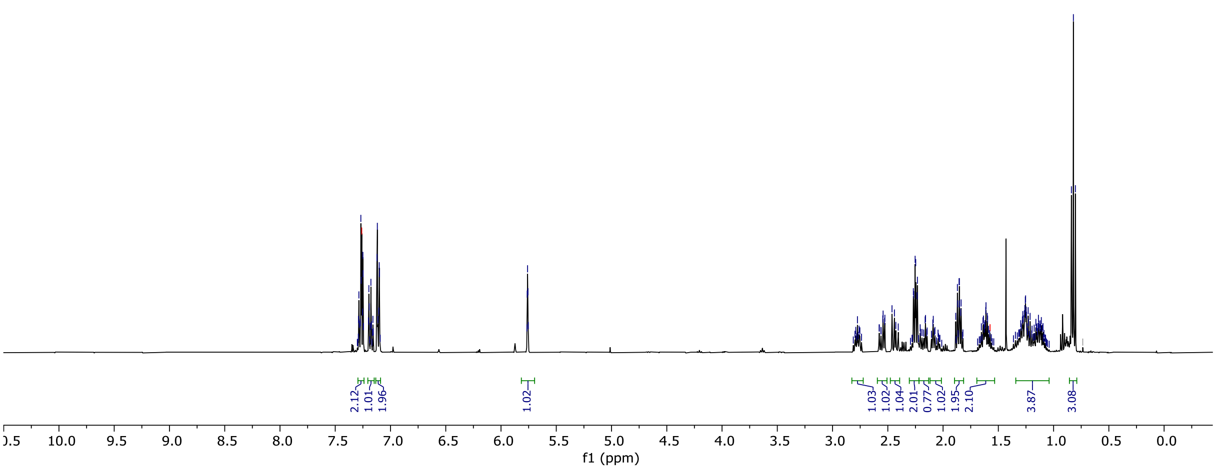
^{13}C NMR ($CDCl_3$, 101 MHz) of *1,4*-P10b:



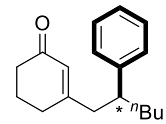
^{1}H NMR ($CDCl_3$, 400 MHz) of *1,6*-P11a:



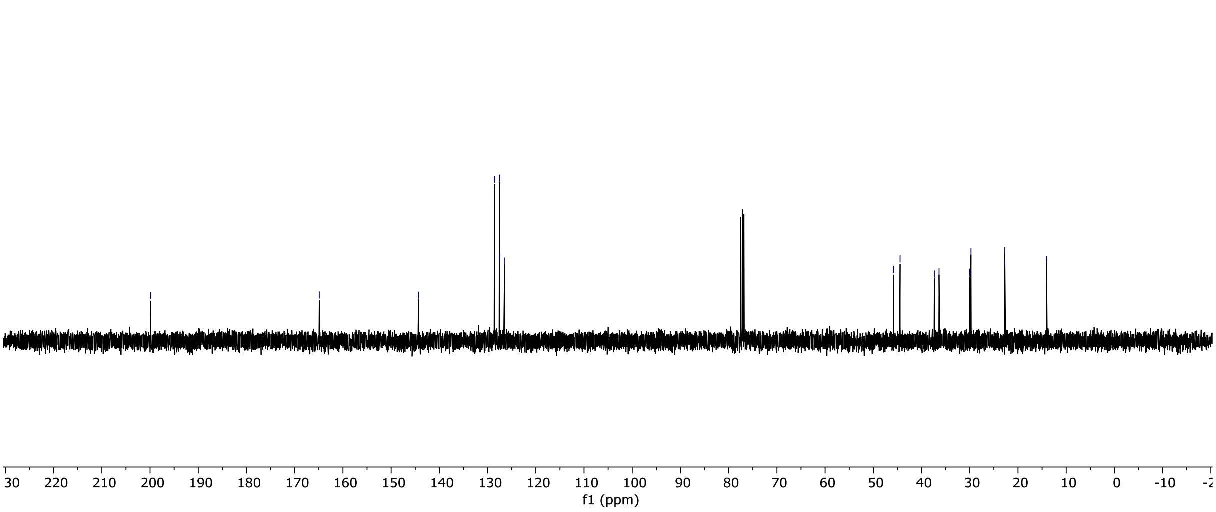
***1,6*-P11a**
Chemical Formula: $C_{18}H_{24}O$
Molecular Weight: 256,39



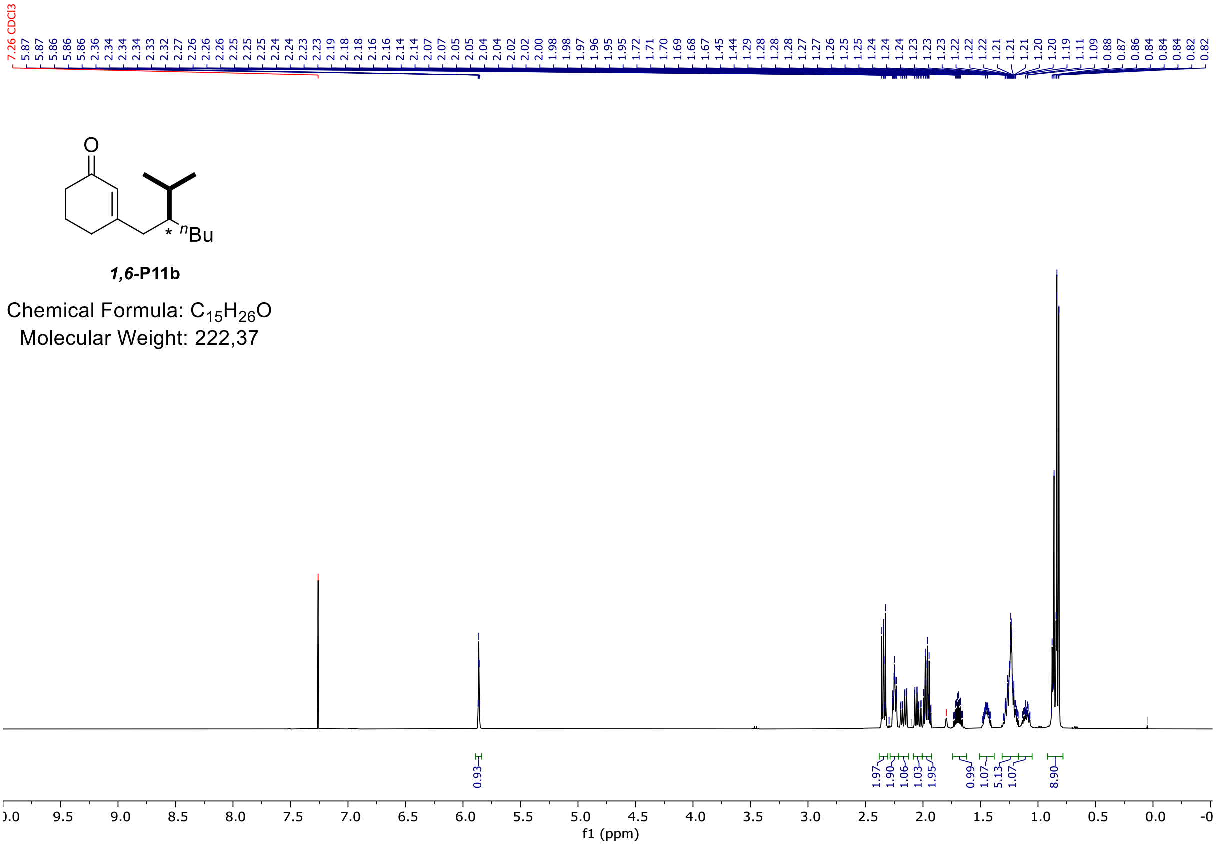
^{13}C NMR ($CDCl_3$, 101 MHz) of *1,6*-P11a:



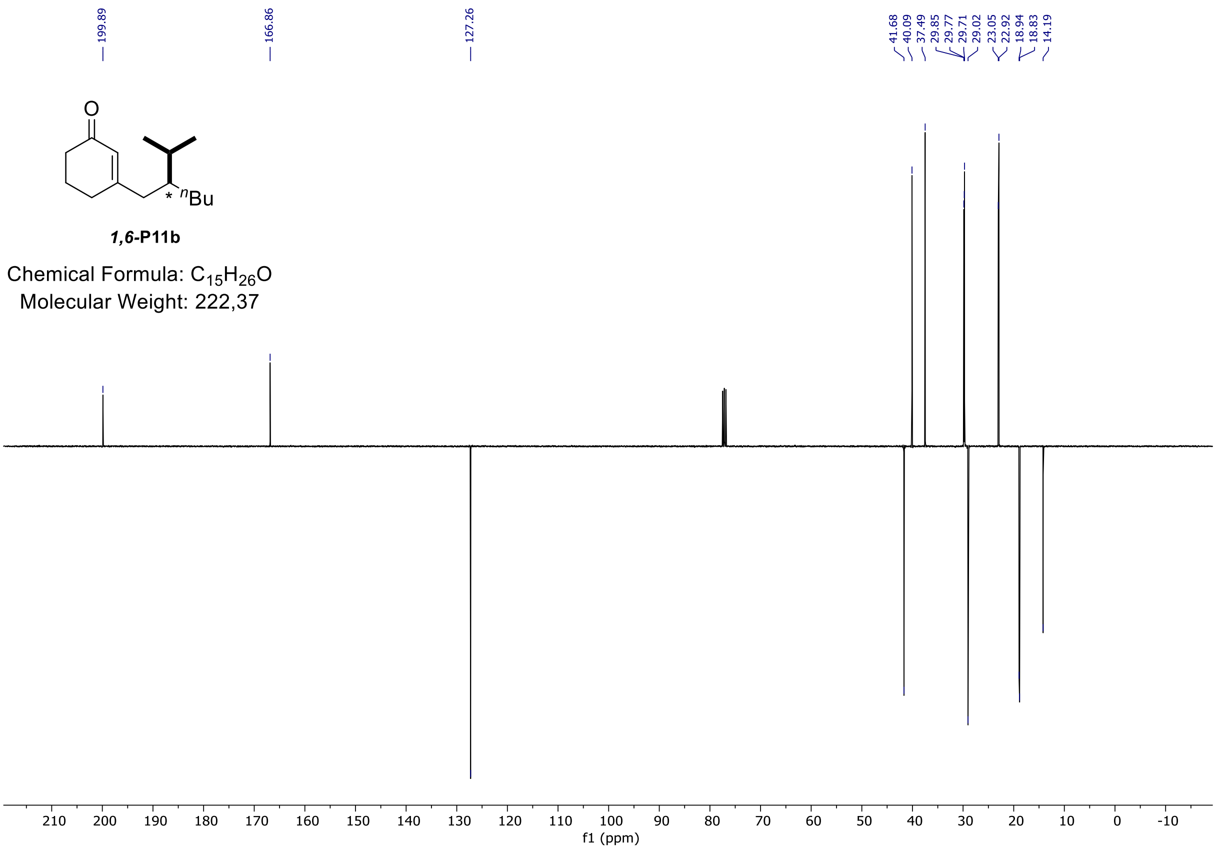
***1,6*-P11a**
Chemical Formula: $C_{18}H_{24}O$
Molecular Weight: 256,39



^{1}H NMR ($CDCl_3$, 400 MHz) of *1,6*-P11b:



^{13}C NMR ($CDCl_3$, 101 MHz) of *1,6*-P11b:



1.8. X-Ray crystallography:

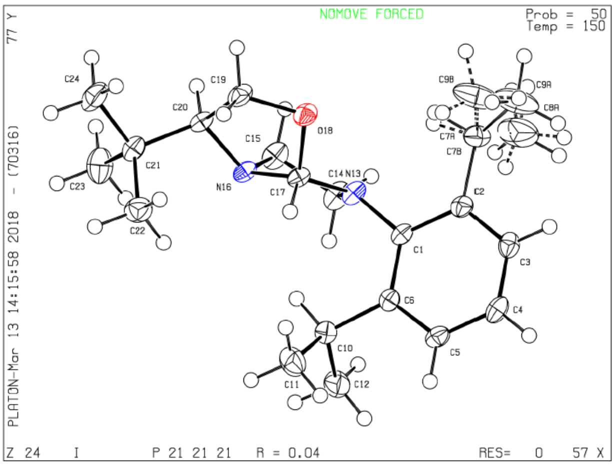
Data were collected on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector using MoKα radiation (0.71073 Å) at T = 150 K.

All the structures were solved by dual-space algorithm using the *SHELXT* program[1], and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[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).

[1] Sheldrick, G. M. SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. Found. Adv*. **71**, 3–8 (2015).
[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 A Wavelength=0.71073

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 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C21 H34 N2 O	C21 H34 N2 O
Sum formula	C21 H34 N2 O	C21 H34 N2 O
Mr	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	

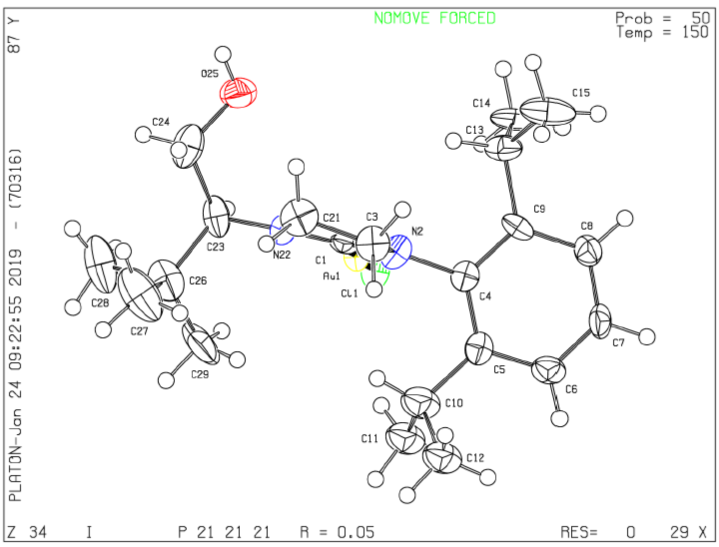
Correction method= # Reported T Limits: Tmin=0.838 Tmax=0.989
AbsCorr = MULTI-SCAN

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 A Wavelength=0.71073

Cell:	a=9.7764(12)	b=14.6129(18)	c=16.587(2)
	alpha=90	beta=90	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
F000	1112.0	1112.0
F000’	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	

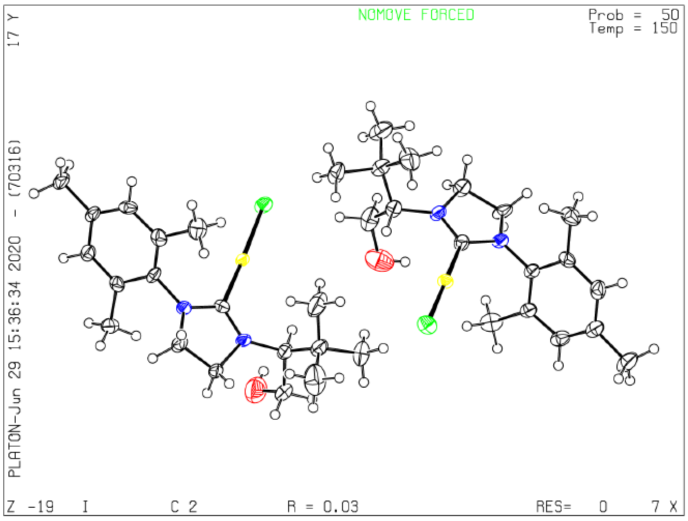
Correction method= # Reported T Limits: Tmin=0.530 Tmax=0.827
AbsCorr = MULTI-SCAN

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: C-C = 0.0140 A 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
Dx,g cm-3	1.758	1.758
Z	8	8
Mu (mm-1)	7.618	7.617
F000	2032.0	2032.0
F000'	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(max)= 27.527

R(reflections)= 0.0290(8163) wR2(reflections)= 0.0619(8916)

S = 1.024 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*)

E= -1005.88698357 A.U.

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
H	1.425792	-2.345002	0.676593
C	3.424514	-3.009760	1.106748
H	3.098931	-4.033591	1.354070
H	4.421613	-3.089032	0.642499
H	3.541083	-2.454287	2.051259
C	2.234320	-3.116629	-1.138943
H	1.425967	-2.682578	-1.745249
H	3.161854	-3.114070	-1.736238
H	1.972129	-4.167508	-0.930853
C	1.110452	2.647176	0.046070
H	0.176199	2.207503	0.423166
C	0.771015	3.360070	-1.275804

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
H	-4.997071	-0.102289	1.785326
H	-5.619077	1.266763	0.833053
C	-5.239257	-0.903219	-0.846443
H	-6.163860	-0.343880	-1.062564
H	-5.499625	-1.718612	-0.150553
H	-4.905369	-1.360602	-1.791897

TS1-(*S*,*S*)

E= -1005.85251466 A.U.

C	1.799039	0.135689	0.159487
C	2.551926	-1.037085	-0.089103
C	3.809225	-0.884304	-0.690960
H	4.411900	-1.768072	-0.908074
C	4.302113	0.376213	-1.026348
H	5.283745	0.468796	-1.498393
C	3.547440	1.517468	-0.763045
H	3.945111	2.498640	-1.032771
C	2.282924	1.423777	-0.163636
C	2.019913	-2.430946	0.240826
H	1.224004	-2.312023	0.992464
C	3.094136	-3.335768	0.868745
H	2.635828	-4.272914	1.222510
H	3.873612	-3.616098	0.142061
H	3.591681	-2.853726	1.726033
C	1.372905	-3.099655	-0.990600
H	0.448507	-2.587803	-1.310564
H	2.081249	-3.129240	-1.835404
H	1.101424	-4.140645	-0.747410
C	1.463713	2.687491	0.083388
H	0.574132	2.402689	0.665121

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	4.594207	1.138878
H	3.114424	4.112408	0.375603
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
H	-3.179173	1.971289	1.070803
H	-4.599041	1.084831	1.689780
H	-4.788196	2.272011	0.379147
C	-5.258149	-0.248017	-0.616216
H	-5.970292	0.532715	-0.928446
H	-5.693910	-0.767433	0.254114
H	-5.180040	-0.974513	-1.437954

Carbene C

E= -1005.86847669 A.U.

C	1.846372	0.150953	0.156387
C	2.716518	-0.951740	-0.017862
C	4.006514	-0.703305	-0.507342
H	4.696618	-1.535462	-0.659761
C	4.423594	0.592352	-0.811922
H	5.433323	0.764659	-1.193960
C	3.553359	1.665733	-0.634978
H	3.888494	2.674681	-0.886909
C	2.252382	1.470042	-0.147289
C	2.250809	-2.380195	0.253459
H	1.413910	-2.321650	0.966357
C	3.331742	-3.263085	0.896268
H	2.902842	-4.235166	1.188206
H	4.160904	-3.474927	0.202001
H	3.759598	-2.795269	1.797334
C	1.698173	-3.027661	-1.031763
H	0.846416	-2.459790	-1.434813
H	2.475709	-3.074853	-1.811943
H	1.357231	-4.057100	-0.831539
C	1.303611	2.657547	-0.012497

H	0.413200	2.310991	0.531893
C	0.820744	3.128542	-1.396878
H	1.661579	3.495252	-2.008702
H	0.093081	3.950930	-1.297288
H	0.336368	2.306169	-1.944704
C	1.910631	3.816211	0.795915
H	2.251774	3.482663	1.789099
H	1.164119	4.613693	0.943127
H	2.773987	4.270353	0.282974
N	0.525735	-0.083095	0.664483
C	0.232200	-0.027342	2.116083
H	0.371060	0.999931	2.496673
H	0.907068	-0.686840	2.683331
C	-1.235767	-0.477897	2.157445
H	-1.349396	-1.504515	2.550741
H	-1.869265	0.185106	2.764294
N	-1.612973	-0.440449	0.726458
C	-0.563141	-0.285483	-0.100567
H	-1.370802	-1.029873	-1.693870
O	-2.169301	-1.533529	-1.992752
C	-2.799876	-1.949847	-0.814803
H	-2.255291	-2.793390	-0.335136
H	-3.796501	-2.338560	-1.078113
C	-2.948706	-0.857289	0.269533
H	-3.411481	-1.367064	1.134267
C	-3.899623	0.345026	-0.069291
C	-3.402360	1.185266	-1.260961
H	-3.338905	0.583100	-2.176353
H	-2.401050	1.599355	-1.068034
H	-4.090052	2.030093	-1.433756
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
C	-5.303498	-0.206040	-0.389993
H	-6.019607	0.623821	-0.501992
H	-5.679541	-0.860236	0.415470
H	-5.317684	-0.778111	-1.329547

TS2

E= -2080.06204983 A.U.

C	-2.148073	1.085665	0.395359
C	-2.755397	1.633526	-0.766107
C	-4.083347	1.279798	-1.047011
H	-4.571175	1.686503	-1.935770
C	-4.799161	0.430832	-0.204483
H	-5.834708	0.171173	-0.440450
C	-4.196363	-0.075258	0.944326
H	-4.767998	-0.729846	1.605721
C	-2.867633	0.238433	1.271497
C	-2.050485	2.643827	-1.672157
H	-0.977152	2.623968	-1.441236
C	-2.554654	4.073384	-1.390472
H	-2.007060	4.807510	-2.004058
H	-3.627220	4.170013	-1.626492
H	-2.425559	4.352003	-0.332826
C	-2.179212	2.313738	-3.168247
H	-1.836618	1.291480	-3.386585
H	-3.217208	2.406644	-3.526609
H	-1.562283	3.005388	-3.763233

C	-2.262832	-0.304304	2.561321
H	-1.175127	-0.157701	2.513165
C	-2.483143	-1.815943	2.732172
H	-3.544305	-2.067506	2.896359
H	-1.911411	-2.180578	3.598606
H	-2.123886	-2.370077	1.852113
C	-2.798491	0.464849	3.785010
H	-2.618938	1.548738	3.701730
H	-2.308102	0.110477	4.706202
H	-3.885493	0.320866	3.905678
N	-0.794475	1.461023	0.704535
C	-0.493814	2.583755	1.617063
H	-0.503921	2.235333	2.663543
H	-1.233489	3.390447	1.514311
C	0.910888	2.981426	1.163222
H	0.906927	3.856766	0.485938
H	1.568901	3.210449	2.007786
N	1.352872	1.783361	0.407659
C	0.304248	0.993776	0.080292
O	1.331258	1.298543	-2.422389
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
C	3.985624	2.359241	1.730882
H	3.234223	2.001425	2.44981
H	3.840440	3.440501	1.568508
H	4.971786	2.229179	2.204330
C	5.127477	2.025068	-0.453948
H	6.066253	1.919877	0.112486
H	5.032329	3.085210	-0.744385
H	5.238523	1.430001	-1.372663
Au	0.596848	-1.635185	0.003495
S	0.310083	-2.625385	-2.162208
Cl	1.128044	-1.656026	2.332909
C	-0.554377	-1.457792	-3.265093
C	-0.982147	-3.898199	-1.953334
H	-0.748018	-1.951717	-4.228462
H	-1.492979	-1.115791	-2.807673
H	0.123322	-0.604489	-3.407889
H	-1.194805	-4.357405	-2.929787
H	-0.576708	-4.653235	-1.267245
H	-1.894082	-3.461834	-1.523937
H	0.608557	0.999205	-1.826722

AuCl-**1a**

E= -1602.01926817 A.U.

Au	0.296075	1.342075	-0.617538
Cl	0.208630	3.516703	-1.435812
C	0.376301	-0.540815	0.096954
N	-0.700133	-1.255720	0.475762
C	-0.329265	-2.567821	1.027378
H	-0.955927	-3.365178	0.601724
H	-0.470762	-2.572202	2.122872

C	-2.064151	-0.800069	0.478797
C	-2.564503	-0.116849	1.611479
C	-3.909788	0.277882	1.596259
H	-4.321573	0.815048	2.453961
C	-4.728431	0.006882	0.501534
H	-5.773235	0.327968	0.508540
C	-4.214039	-0.664993	-0.605962
H	-4.862253	-0.860290	-1.463371
C	-2.877071	-1.085073	-0.642914
C	-1.695511	0.216196	2.820909
H	-0.684976	-0.171646	2.624766
C	-1.557040	1.737154	3.014512
H	-2.527245	2.203719	3.250307
H	-1.161485	2.219822	2.107676
H	-0.870755	1.957854	3.848407
C	-2.209439	-0.468123	4.100762
H	-3.210297	-0.102145	4.381663
H	-1.533670	-0.263022	4.947071
H	-2.280485	-1.561147	3.978585
C	-2.336969	-1.786105	-1.886315
H	-1.313032	-2.121296	-1.664371
C	-2.236549	-0.807961	-3.071832
H	-1.605186	0.058406	-2.821252
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

H	1.776805	-3.071854	1.430411
H	1.277185	-3.311968	-0.270497
N	1.487087	-1.284267	0.280893
C	2.821625	-0.880085	-0.183093
H	2.643359	0.043102	-0.754613
C	3.361157	-1.908072	-1.186258
H	4.274294	-1.495837	-1.646868
H	3.650167	-2.848172	-0.674961
O	2.358507	-2.144998	-2.156064
H	2.738340	-2.661762	-2.877323
C	3.818254	-0.497481	0.968489
C	4.153957	-1.675214	1.905325
H	3.277743	-1.999242	2.487515
H	4.921802	-1.365623	2.632282
H	4.553161	-2.548656	1.365621
C	5.125593	0.027869	0.336253
H	5.770053	0.464250	1.115480
H	4.924199	0.816691	-0.406749
H	5.707473	-0.767251	-0.155657
C	3.199235	0.637336	1.806693
H	3.900719	0.951501	2.596157
H	2.266624	0.318120	2.294901
H	2.963719	1.517528	1.188696

AuCl·SMe₂

E= -1074.18126143 A.U.

Au	-0.409676	-0.000026	-0.077411
S	1.908626	0.000037	-0.483047
Cl	-2.682994	0.000084	0.262282
C	2.591874	-1.403833	0.465268
C	2.592000	1.403840	0.465245
H	3.687301	-1.391643	0.372701
H	2.286916	-1.350053	1.518701
H	2.192564	-2.319555	0.009816
H	3.687453	1.391220	0.373079
H	2.193198	2.319622	0.009475
H	2.286641	1.350395	1.518581

SMe₂

E= -478.080470814 A.U.

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

L1aH

E= -1006.35203589 A.U.

C	0.507484	-0.030590	-0.344450
N	-0.543574	-0.012579	0.449191
C	-0.094150	-0.087889	1.856794
H	-0.639844	-0.880685	2.386597
H	-0.303570	0.870121	2.358855
C	-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
C	-4.586100	0.323377	-0.695026
H	-5.635560	0.408406	-0.986699
C	-4.005586	-0.936163	-0.554165
H	-4.609355	-1.827228	-0.738723
C	-2.661651	-1.078583	-0.181433
C	-1.690483	2.681499	0.140267
H	-0.680228	2.402255	0.480962
C	-1.517965	3.477314	-1.167217
H	-2.488617	3.817403	-1.560894
H	-1.037778	2.872937	-1.953426
H	-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
C	-2.056203	-2.473280	-0.040414
H	-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
C	-2.763708	-3.292377	1.054940
H	-3.817399	-3.485875	0.799649

H	-2.749737	-2.773679	2.026834
H	-2.271076	-4.269132	1.183014
C	1.418592	-0.375943	1.716583
H	2.034146	0.279974	2.342353
H	1.659351	-1.424541	1.944275
N	1.670084	-0.136554	0.272293
C	2.933314	-0.443124	-0.437020
H	2.641206	-0.507311	-1.497303
C	3.386923	-1.854997	-0.040261
H	4.192465	-2.164884	-0.725383
H	3.806397	-1.861495	0.984243
O	2.255663	-2.697139	-0.146474
H	2.531530	-3.618111	-0.050108
C	4.013061	0.684182	-0.344791
C	4.468922	0.976185	1.098591
H	3.673727	1.442012	1.700725
H	5.307571	1.688908	1.082953
H	4.822128	0.074892	1.623236
C	5.236311	0.250707	-1.181366
H	5.940184	1.091447	-1.273506
H	4.948517	-0.050932	-2.201936
H	5.787563	-0.581964	-0.718782
C	3.427577	1.970689	-0.957877
H	4.172932	2.779837	-0.931058
H	2.542858	2.323316	-0.404605
H	3.139755	1.822825	-2.011946
H	0.415557	0.034175	-1.430653

TS1-(*R*,*S*)

E= -1005.84221194 A.U.

C	1.888789	-0.017519	0.065929
C	2.718435	-1.140810	-0.157229
C	4.080670	-0.916756	-0.405069
H	4.743817	-1.767757	-0.579576
C	4.598263	0.375837	-0.446855
H	5.662512	0.532203	-0.642098
C	3.757195	1.471667	-0.256959
H	4.173035	2.479402	-0.313260
C	2.387941	1.307282	-0.000237
C	2.176871	-2.568421	-0.171138
H	1.094345	-2.519260	0.014734
C	2.798928	-3.433001	0.939920
H	2.353310	-4.441224	0.944002
H	3.885528	-3.551753	0.798709
H	2.643016	-2.987903	1.935696
C	2.353733	-3.223579	-1.553106
H	1.878512	-2.621443	-2.342781
H	3.417995	-3.340418	-1.814405
H	1.896140	-4.226359	-1.566370
C	1.490069	2.525824	0.209922
H	0.454094	2.236712	-0.021124
C	1.808946	3.679036	-0.754316
H	2.785427	4.150235	-0.551130
H	1.039398	4.460772	-0.659052
H	1.801097	3.336700	-1.800223
C	1.548330	3.006271	1.672569
H	1.262837	2.211220	2.380017
H	0.862668	3.855028	1.828310

H	2.564796	3.337841	1.944918
N	0.503403	-0.224870	0.386142
C	0.027159	-0.624058	1.722929
H	0.455743	0.017954	2.505908
H	0.315300	-1.667316	1.942004
C	-1.496910	-0.465037	1.577968
H	-2.051490	-1.269978	2.078773
H	-1.839251	0.501306	1.986134
N	-1.682839	-0.483950	0.112008
C	-0.514854	-0.180718	-0.484086
H	-0.674932	0.589793	-1.374415
C	-2.648518	1.573649	-0.823535
H	-3.473285	1.903307	-1.496258
H	-2.836285	2.087718	0.154297
C	-2.865321	0.026425	-0.614640
H	-2.753305	-0.408207	-1.621786
C	-4.248409	-0.473720	-0.106416
C	-4.704864	0.160908	1.225253
H	-4.708111	1.260003	1.171685
H	-4.078655	-0.133376	2.079501
H	-5.732917	-0.161744	1.457889
C	-4.219398	-2.009623	0.032686
H	-5.213760	-2.390529	0.317960
H	-3.502880	-2.346860	0.796591
H	-3.936902	-2.487745	-0.919279
C	-5.300752	-0.118481	-1.181574
H	-6.278173	-0.549651	-0.911505
H	-5.018418	-0.520206	-2.168217
H	-5.433831	0.968157	-1.286613
O	-1.414893	1.836756	-1.338524

2a-(*R*,*S*)

E= -1005.88006165 A.U.

C	-1.851186	0.076101	0.109304
C	-2.387160	1.370464	-0.117287
C	-3.749604	1.486322	-0.430222
H	-4.179342	2.475100	-0.611633
C	-4.567436	0.360917	-0.517439
H	-5.626856	0.472321	-0.764092
C	-4.032076	-0.906407	-0.293302
H	-4.680349	-1.783066	-0.370012
C	-2.676294	-1.074467	0.023682
C	-1.527385	2.630946	-0.041690
H	-0.500380	2.324357	0.202585
C	-1.997359	3.579452	1.076162
H	-1.324801	4.449516	1.155660
H	-3.013255	3.962294	0.884469
H	-2.013578	3.072768	2.054042
C	-1.467246	3.362977	-1.394982
H	-1.109056	2.697857	-2.196477
H	-2.457431	3.741766	-1.697112
H	-0.784065	4.226404	-1.339290
C	-2.110560	-2.474055	0.240349
H	-1.087926	-2.344105	0.621630
C	-1.988301	-3.234998	-1.092226
H	-2.969758	-3.356923	-1.581007
H	-1.569228	-4.241374	-0.924456
H	-1.316221	-2.703060	-1.781305
C	-2.909760	-3.279053	1.278287
H	-2.995768	-2.736558	2.233568
H	-2.414322	-4.243097	1.479777

H	-3.931644	-3.505858	0.931526
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	4.552389	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

Alcoholate

E= -1005.84132451 A.U.

C	-1.863174	0.064995	0.060392
C	-2.251899	1.396420	-0.225974
C	-3.509225	1.595566	-0.815228
H	-3.834746	2.611077	-1.052420
C	-4.350653	0.522761	-1.103907
H	-5.326029	0.703131	-1.563081
C	-3.950522	-0.779911	-0.809794
H	-4.617924	-1.612325	-1.044908
C	-2.703663	-1.038024	-0.223460
C	-1.364414	2.599804	0.082730
H	-0.422550	2.234323	0.517044
C	-2.014577	3.529889	1.123661
H	-1.328265	4.351490	1.383271
H	-2.944516	3.981264	0.741232
H	-2.265469	2.990618	2.051293
C	-0.984398	3.372511	-1.193080
H	-0.483021	2.719862	-1.924012
H	-1.868880	3.813543	-1.681436
H	-0.290343	4.192007	-0.949733
C	-2.284738	-2.475881	0.068299
H	-1.303884	-2.439641	0.565702
C	-2.098694	-3.283120	-1.229425
H	-3.045839	-3.380304	-1.784613
H	-1.738092	-4.299876	-1.004481
H	-1.367714	-2.804585	-1.899783
C	-3.260539	-3.178867	1.028387
H	-3.377510	-2.618215	1.969465
H	-2.896859	-4.189013	1.276775

H	-4.262136	-3.289874	0.582435	C	3.012036	0.018328	0.528863
N	-0.588866	-0.178794	0.674071	H	3.569067	-0.097203	1.471840
C	-0.364245	-0.185295	2.129603	C	3.727302	-0.868823	-0.536199
H	-0.983832	-0.952905	2.616623	C	3.373278	-0.456894	-1.979406
H	-0.632854	0.794710	2.559970	H	3.618553	0.604190	-2.131649
C	1.150282	-0.480650	2.234732	H	2.310365	-0.626624	-2.224322
H	1.677133	0.228911	2.887013	H	3.956816	-1.060449	-2.693774
H	1.355604	-1.502829	2.593557	C	3.398729	-2.356896	-0.314331
N	1.634724	-0.339921	0.848339	H	2.335228	-2.585084	-0.496469
C	0.603297	-0.161474	0.040947	H	3.640519	-2.673536	0.714738
H	0.685073	-0.092046	-1.040309	H	3.991344	-2.985146	-0.999754
O	4.049774	2.131085	-0.239547	C	5.241509	-0.645494	-0.331716
C	2.957130	1.597483	0.159117	H	5.817702	-1.172563	-1.110180
H	2.070462	1.572194	-0.596961	H	5.568425	-1.032451	0.648921
H	2.447050	2.047695	1.087365	H	5.450997	0.433421	-0.375118

- **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 occuring 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.

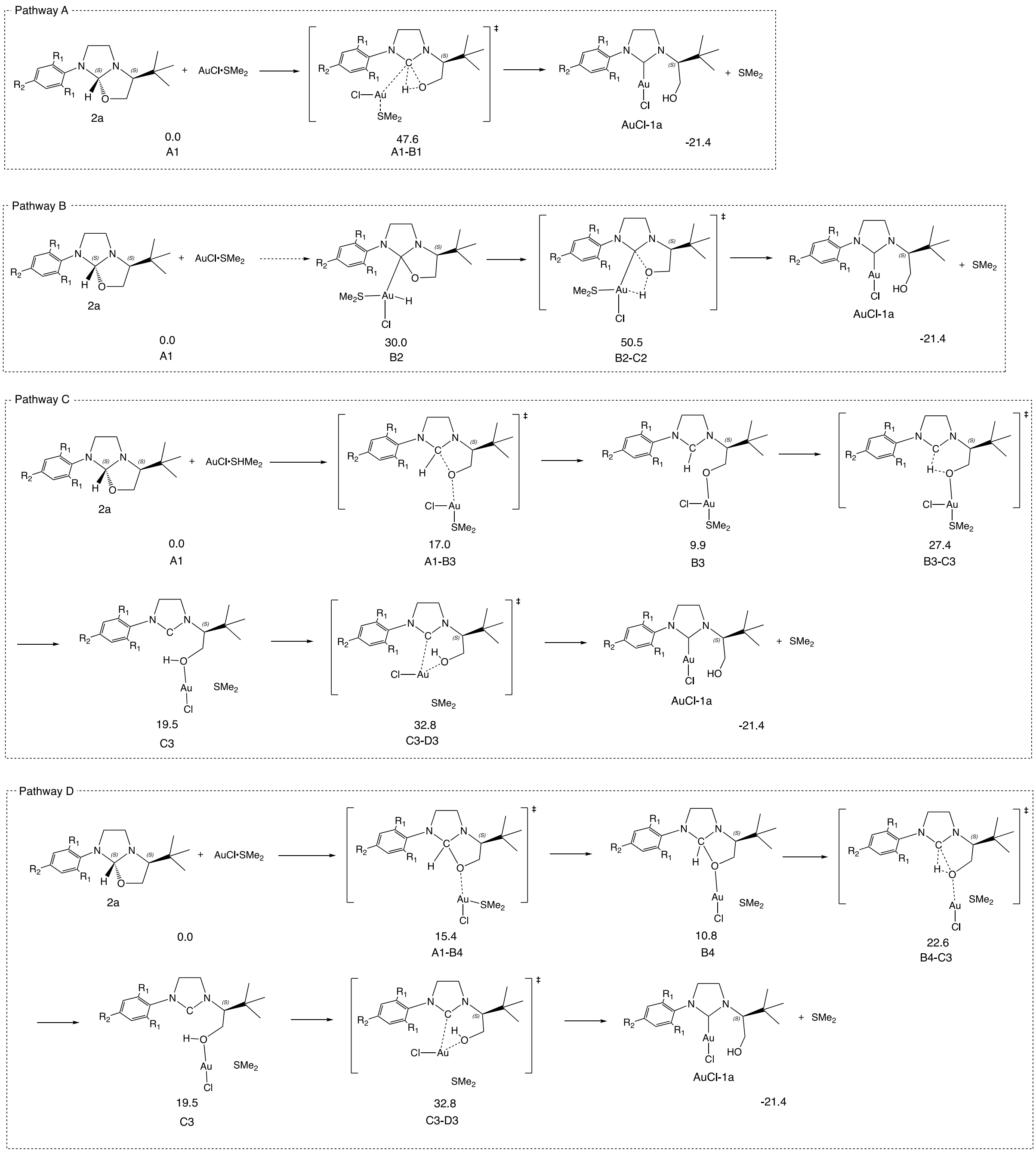

Pathway A
2a
+ AuCl•SMe2
0.0
A1
47.6
A1-B1
AuCl-1a
+ SMe2
-21.4
Pathway B
30.0
B2
50.5
B2-C2
Pathway C
+ AuCl•SHMe2
17.0
A1-B3
9.9
B3
27.4
B3-C3
19.5
C3
32.8
C3-D3
Pathway D
15.4
A1-B4
10.8
B4
22.6
B4-C3

Figure S1

A1-B1

E= -2080.00535731 A.U.

C	2.416705	0.602107	0.114712
C	2.938732	0.426444	1.419059
C	4.043676	-0.425421	1.570910
H	4.459234	-0.586808	2.568252
C	4.623857	-1.060948	0.476357
H	5.482526	-1.722199	0.619349
C	4.118049	-0.844844	-0.804447
H	4.591309	-1.336757	-1.656742
C	3.013993	-0.008575	-1.018677
C	2.377998	1.147303	2.641725
H	1.485783	1.708286	2.337456
C	3.401045	2.151030	3.206467
H	2.961970	2.712059	4.047457
H	4.307659	1.646813	3.580365
H	3.719813	2.879614	2.443258
C	1.906433	0.165063	3.727394
H	1.141034	-0.519361	3.333310
H	2.737319	-0.435415	4.134035
H	1.450700	0.718190	4.563668
C	2.546797	0.260914	-2.448207
H	1.569529	0.763806	-2.391180
C	2.342972	-1.020332	-3.273652
H	3.291521	-1.556659	-3.437727
H	1.938994	-0.765453	-4.266756
H	1.634375	-1.709531	-2.791953
C	3.524018	1.213807	-3.167529
H	3.673620	2.155161	-2.614768
H	3.150503	1.465202	-4.173647
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
H	-2.549680	3.076080	-2.344601
H	-3.167120	4.393518	-1.308736
H	-4.298288	3.336615	-2.184178
C	-4.546727	2.801256	0.493350
H	-5.497682	2.815009	-0.062713
H	-4.389375	3.811542	0.907450
H	-4.669315	2.105317	1.337297

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	1.243818
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 A.U.

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
H	-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	2.273725	-2.657266
H	-4.022358	2.740254	-2.592300
H	-2.762684	3.959907	-2.308240
C	-2.010936	-1.949788	1.605909
H	-1.012581	-1.490894	1.667827
C	-1.839240	-3.366027	1.031571
H	-2.797844	-3.906719	0.981335
H	-1.171593	-3.961054	1.676328
H	-1.402951	-3.349105	0.021783
C	-2.583435	-2.011794	3.036627
H	-2.691213	-1.009638	3.480786
H	-1.928867	-2.607266	3.695020
H	-3.580274	-2.482644	3.043954
N	-1.179723	0.752076	0.803301
C	-1.023222	1.471061	2.063124
H	-1.528829	0.943949	2.887011
H	-1.441463	2.498345	2.020738
C	0.500999	1.487840	2.219839
H	0.863658	2.371327	2.759757
H	0.850017	0.594052	2.765605
N	1.012851	1.468548	0.846423
C	-0.008555	0.877823	-0.004347
H	-0.583111	-0.770269	-1.772589
O	-0.138366	1.749152	-1.113142
C	1.048105	2.510285	-1.219946
H	0.811377	3.445969	-1.743853
H	1.808907	1.960086	-1.804033
C	1.489721	2.719907	0.236336
H	0.914068	3.578374	0.645189
C	2.997290	3.063631	0.439139

C	3.915259	1.909158	0.007293
H	3.803046	1.660507	-1.059536
H	3.696368	1.008055	0.596818
H	4.970745	2.179257	0.172538
C	3.276694	3.378412	1.921680
H	3.142226	2.491734	2.559627
H	2.618266	4.178952	2.298666
H	4.317052	3.718473	2.049972
C	3.311468	4.323445	-0.394019
H	4.345025	4.657443	-0.210688
H	2.641492	5.159185	-0.130657
H	3.214672	4.139747	-1.475806
Au	0.601400	-1.035429	-0.790625
S	2.520511	-1.548708	0.917499
Cl	1.154271	-3.189161	-1.891164
C	3.922934	-1.963666	-0.174854
C	2.095052	-3.227704	1.488687
H	4.721614	-2.417778	0.428802
H	3.569640	-2.643777	-0.963351
H	4.283014	-1.026018	-0.617308
H	2.950809	-3.648240	2.035910
H	1.236150	-3.133170	2.166120
H	1.825378	-3.843306	0.618314

B2-C2

E= -2080.00477573 A.U.

C	2.161032	-0.880370	0.287178
C	2.809204	-0.992956	-0.969334
C	4.038623	-0.338604	-1.146945
H	4.540314	-0.401129	-2.115233
C	4.640188	0.370220	-0.111898
H	5.598235	0.871625	-0.272747
C	4.028233	0.415610	1.139640
H	4.525978	0.941370	1.957709
C	2.792755	-0.205602	1.370022
C	2.267649	-1.856974	-2.104107
H	1.260985	-2.190227	-1.828505
C	3.134663	-3.119936	-2.277451
H	2.709691	-3.773870	-3.056759
H	4.166190	-2.869591	-2.576792
H	3.193091	-3.701794	-1.343397
C	2.139925	-1.091055	-3.431498
H	1.539710	-0.175734	-3.314788
H	3.122018	-0.798362	-3.838530
H	1.647379	-1.723305	-4.187799
C	2.224330	-0.205948	2.789351
H	1.183463	-0.554473	2.729539
C	2.193533	1.183148	3.446453
H	3.204456	1.598906	3.583789
H	1.730270	1.119701	4.444481
H	1.604212	1.898563	2.857443
C	3.008038	-1.186345	3.687533
H	3.059144	-2.198332	3.257162
H	2.541123	-1.262396	4.683429
H	4.045769	-0.842944	3.830188
N	0.880639	-1.495776	0.506306
C	0.730835	-2.772146	1.217056
H	1.521899	-2.904077	1.965237
H	0.773575	-3.623973	0.512842
C	-0.661307	-2.602391	1.825336

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
H	-2.073734	3.878934	-0.117899
H	-2.894113	3.017569	1.231167
H	0.692179	4.784667	1.378081
H	1.713735	3.391972	0.886623
H	0.574518	4.107587	-0.302970

A1-B3

E= -2080.06298648 A.U.

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

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
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
Au	1.865254	-0.424246	-0.320320
S	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
H	3.447741	-3.855044	1.676588
H	2.011129	-2.739557	1.856848
H	2.180424	-3.793801	0.401224
H	5.026850	-1.723519	2.247817
H	4.912297	-0.170063	1.350264
H	3.522873	-0.696501	2.378906

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E= -2080.07363201 A.U.

C	-2.910785	-0.615742	-0.204486
C	-2.723827	-1.820764	-0.917061
C	-3.384725	-2.963982	-0.446612
H	-3.254867	-3.912849	-0.972261
C	-4.190707	-2.914153	0.688918
H	-4.694053	-3.818319	1.041197
C	-4.343392	-1.717359	1.386119
H	-4.959056	-1.696594	2.288132
C	-3.710105	-0.542401	0.958268
C	-1.799252	-1.921865	-2.125956

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				

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C	-2.796790	-1.284940	0.023986
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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
H	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
H	-1.315735	2.882304	1.683589
H	-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

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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
H	0.982490	-2.568011	0.913091
H	2.041478	-3.944043	1.292782
H	1.085195	-3.178011	2.582261
C	4.166630	1.261162	-1.778403
H	3.648374	1.947283	-1.092334
C	3.313497	1.183157	-3.058100
H	3.771949	0.512731	-3.803284
H	3.212070	2.179111	-3.519657
H	2.304330	0.801618	-2.840234
C	5.551857	1.866144	-2.063967
H	6.162371	1.932670	-1.149195
H	5.449089	2.881967	-2.478892
H	6.117422	1.270208	-2.798145
N	2.774008	0.641256	0.724248
C	3.361834	1.556262	1.731335
H	4.144232	2.179986	1.266279
H	3.827899	0.987329	2.549650
C	2.139667	2.378476	2.180187
H	1.795825	2.104153	3.193400
H	2.328065	3.460868	2.170034
N	1.121958	1.987296	1.181550
C	1.507293	0.947908	0.423937
H	0.111505	0.428326	-0.128570
O	-0.957513	0.476244	-0.068232
C	-1.219327	1.255878	1.101689
H	-1.079010	0.634729	2.005562
H	-2.270493	1.573544	1.071916
C	-0.269743	2.469295	1.206703
H	-0.432282	2.869313	2.223378
C	-0.549966	3.663519	0.227230

C	-0.464612	3.250484	-1.253620
H	-1.229735	2.507416	-1.515319
H	0.517746	2.817529	-1.498605
H	-0.607837	4.135786	-1.894613
C	0.477899	4.782935	0.489151
H	1.500544	4.468195	0.229277
H	0.470103	5.109343	1.542964
H	0.242206	5.663691	-0.128688
C	-1.956416	4.221437	0.524491
H	-2.143579	5.116237	-0.089922
H	-2.058082	4.520664	1.581642
H	-2.753790	3.497587	0.299780
Au	-1.963625	-1.361988	-0.376406
S	-5.189378	1.413751	0.237556
Cl	-3.046632	-3.349455	-0.738485
C	-5.635577	-0.125388	1.106787
C	-5.208575	0.815779	-1.484053
H	-6.646558	-0.456238	0.822679
H	-4.910224	-0.925932	0.896207
H	-5.626500	0.098145	2.183394
H	-6.216107	0.476922	-1.770795
H	-4.923815	1.663891	-2.123162
H	-4.485869	-0.002139	-1.626937

C3-D3

E= -2080.03028049 A.U.

C	2.269384	-1.131036	0.462849
C	1.945406	-2.418009	0.959659
C	2.601654	-3.524159	0.402876
H	2.362284	-4.526159	0.765120
C	3.538515	-3.372625	-0.616708
H	4.028505	-4.250614	-1.045244
C	3.847250	-2.100092	-1.090215
H	4.584286	-1.991298	-1.889257
C	3.235516	-0.955484	-0.558327
C	0.924723	-2.642436	2.073324
H	0.401138	-1.688385	2.238908
C	1.614975	-3.048136	3.391123
H	0.877023	-3.141885	4.204793
H	2.119258	-4.022641	3.286201
H	2.380357	-2.321108	3.707673
C	-0.149078	-3.676157	1.690458
H	-0.638572	-3.421290	0.739160
H	0.276945	-4.688401	1.596262
H	-0.922119	-3.723074	2.475197
C	3.634930	0.413592	-1.103436
H	3.127927	1.179026	-0.499136
C	3.159917	0.600710	-2.555688
H	3.646046	-0.120921	-3.232260
H	3.403187	1.613380	-2.917727
H	2.072342	0.455604	-2.640552
C	5.147325	0.670160	-0.973833
H	5.489635	0.554420	0.066999
H	5.392452	1.693722	-1.301447
H	5.736701	-0.022384	-1.595953
N	1.629588	0.019636	1.042651
C	2.063535	0.542412	2.359710
H	3.095305	0.931319	2.279542
H	2.053055	-0.238840	3.129506
C	1.041892	1.651868	2.607081

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
H	-2.162618	3.396129	-0.216964
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
H	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
H	-3.513180	-2.325665	0.856293
H	-3.541224	-1.924526	2.605677
H	-6.118742	-0.594755	-0.183524
H	-5.243646	0.893846	-0.655606
H	-4.526078	-0.707224	-1.022954

A1-B4

E= -2080.06341895 A.U.

C	0.755469	2.292883	-0.330594
C	-0.416880	2.880891	-0.873812
C	-0.977915	3.986227	-0.217027
H	-1.880513	4.449725	-0.621936
C	-0.406281	4.503638	0.943995
H	-0.862460	5.361839	1.444720
C	0.757821	3.933585	1.456581
H	1.210470	4.360005	2.355398
C	1.370265	2.838281	0.828414
C	-1.047681	2.374781	-2.167704
H	-0.557736	1.420534	-2.408905
C	-0.775854	3.352991	-3.327780
H	-1.170366	2.949266	-4.274555
H	-1.262496	4.326986	-3.152089
H	0.301006	3.543390	-3.462162
C	-2.552601	2.095265	-2.031726
H	-2.759237	1.375452	-1.224411
H	-3.129513	3.013120	-1.830980
H	-2.944738	1.658424	-2.963752
C	2.687997	2.308357	1.394899
H	3.019437	1.469406	0.767224
C	2.532892	1.773169	2.830357

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
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
C	-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

B4

E= -2080.06848479 A.U.

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

H	-1.261268	1.257563	-2.285271
C	-1.950044	3.152591	-3.038116
H	-2.216387	2.754100	-4.030863
H	-2.672889	3.948264	-2.791913
H	-0.958436	3.625584	-3.116261
C	-3.369049	1.380347	-1.926681
H	-3.420769	0.583988	-1.169795
H	-4.162520	2.114310	-1.710455
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B4-C3

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