Supporting Information

Synthesis of 1,2-Aminoalcohols Through Enantioselective Aminoallylation of Ketones by Cu-Catalyzed Reductive Coupling

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General. 1H NMR spectra were recorded on Bruker 600 MHz spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as an internal standard (CDCl3: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, hept = heptet, br = broad, m = multiplet), and coupling constants (Hz). 13C NMR was recorded on a Bruker 600 MHz (151 MHz) instrument with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl3: 77.0 ppm). Chiral HPLC analyses were performed on a Shimadzu Prominence i-series LC-2030C using chiral Daicel columns purchased from Chiral Technologies, Inc. Liquid chromatography was performed using forced flow (flash chromatography) on silica gel purchased from Silicycle. Thin layer chromatography (TLC) was performed on glass-backed 250 μm silica gel F254 plates purchased from Silicycle. Visualization was achieved using UV light, a 10% solution of phosphomolybdic acid in EtOH, or potassium permanganate in water followed by heating. HRMS was collected using a Jeol AccuTOF-DART™ mass spectrometer using DART source ionization. All reactions were conducted in oven or flame dried glassware under an inert atmosphere of nitrogen or argon with magnetic stirring unless otherwise noted. Solvents were obtained from VWR as HPLC grade and transferred to septa sealed bottles, degased by Ar sparge, and analyzed by Karl-Fischer titration to ensure water content was ≤ 600 ppm. Me(MeO)2SiH was purchased from Alfa Aesar and used as received. Allenamides 11 and 23 were prepared in one step as described in the literature. 1 Ketones were purchased from Sigma Aldrich, TCI America, Alfa Aesar,
or Oakwood Chemicals and used as received. Ligands were obtained from the Strem Chemical Company. All other materials were purchased from VWR, Sigma Aldrich, Combi-Blocks, Alfa-Aesar, or Strem Chemical Company and used as received.

Table SI-1: Ligand Survey in the Cu-Catalyzed Reductive Coupling

![Diagram](image)

| Entry | Ligand             | % y   | dr 12a | er 12a | 12a:13a | b:l |
|-------|--------------------|-------|--------|--------|---------|-----|
| 1     | L1                 | 20    | 46:53  | >99:1  | >99:1   |     |
| 2     | L2                 | 55    | 51:42  | 87:13  | >99:1   |     |
| 3     | L3                 | 69    | 24:76  | >99:1  | 90:10   |     |
| 4     | (S,S,S)-Feringa    | 38    | 57:43  | >99:1  | 76:24   |     |
| 5     | (S,S)-Phenyl-BPE   | 64    | 20:80  | 89:11  | >99:1   |     |
| 6     | (S,S)-Ethyl-BPE    | 67    | 25:75  | 90:10  | 87:11   |     |
| 7     | (R,R)-QuinoxP*     | 63    | >99:1  | 81:19  | 93:7    |     |
| 8     | (R,R)-DuPhos       | 81    | >99:1  | 81:19  | 99:1    |     |
| 9     | (R,R,S,S)-DuanPhos | 82    | 18:82  | 84:16  | >99:1   |     |
| 10    | (R)-BINAP          | 82    | 18:82  | 83:17  | >99:1   |     |
| 11    | (R)-Tol-BINAP      | 57    | 77:23  | >99:1  | 81:19   |     |
| 12    | (R)-DM-BINAP       | 45    | 69:31  | >99:1  | >99:1   |     |
| 13    | (R)-SEGPHOS        | 51    | 30:70  | 86:14  | >99:1   |     |
| 14    | (R)-DTBM-SEGPHOS   | 26    | 68:32  | 82:18  | >99:1   |     |
| 15    | (R)-DM-SEGPHOS     | 50    | 69:31  | 86:14  | >99:1   |     |
| 16    | J-6                | 58    | 15:85  | 91:9   | >99:1   |     |
| 17    | J-7                | 70    | 18:82  | >99:1  | >99:1   |     |
| 18    | J-9                | 51    | 39:61  | 81:19  | >99:1   |     |
| 19    | J-11               | 60    | 28:72  | 78:22  | >99:1   |     |
| 20    | M-1                | 62    | 58:42  | >99:1  | >99:1   |     |
| 21    | M-2                | 68    | 37:63  | 87:13  | >99:1   |     |
| 22    | M-9                | 55    | 60:40  | >99:1  | >99:1   |     |
| 23    | W-1                | 13    | 70:30  | 86:14  | >99:1   |     |
| 24    | W-2                | 61    | 67:33  | 73:24  | >99:1   |     |
| 25    | W-3                | 64    | 57:43  | 90:10  | >99:1   |     |
| 26    | W-5                | 15    | 75:25  | 25:75  | >99:1   |     |
| 27    | W-6                | 59    | 60:40  | 84:16  | >99:1   |     |
| 28    | W-8                | 77    | 93:7   | 81:19  | >99:1   |     |
| 29    | W-9                | 52    | 62:38  | 55:45  | >99:1   |     |

*Reaction performed according to the general procedure employing 0.250 mmol of 8a, 0.375 mmol of 11, 0.50 mmol of Me(OMe)2SiH in 0.5 mL of toluene at rt for 24 h. *Yield of 12a determined by quantitative 1H NMR spectroscopy on the unpurified reaction mixture using dimethyl fumarate as the analytical standard. The ratio was determined by 1H NMR spectroscopic analysis on the unpurified reaction mixture. *Enantiomeric ratios were determined by chiral HPLC analysis. *b:l refers to the ratio of branched to linear isomers as defined by: (12a + 13a) : l-12a.
Table SI-2: Reducing Agent Survey in the Cu-Catalyzed Reductive Coupling

\[
\begin{array}{cccccc}
\text{Entry} & \text{Reductant} & \% \text{y} \, 12a^b & \text{dr} \, 12a^c & \text{er} \, 12a^d & 12a:13a^e & b:l^e \\
1 & \text{Me(MeO)\textsubscript{2}SiH} & 77 & >99:1 & 92:8 & 81:19 & >99:1 \\
2 & \text{PhSiH\textsubscript{3}} & 55 & >99:1 & 86:14 & >99:1 & 87:13 \\
3 & \text{PMHS} & 0 & - & - & - & - \\
4 & \text{Ph\textsubscript{2}SiH\textsubscript{2}} & 66 & >99:1 & 80:20 & 94:6 & 86:14 \\
5 & \text{(EtO)\textsubscript{3}SiH} & 28 & >99:1 & 84:16 & 77:23 & >99:1 \\
6 & \text{PhMe\textsubscript{2}SiH} & 0 & - & - & - & - \\
7 & \text{(pin)BH} & 16 & >99:1 & 70:30 & >99:1 & 63:37 \\
\end{array}
\]

\(^a\)Reaction performed according to the general procedure employing 0.250 mmol of \(8a\), 0.375 mmol of \(11\), 0.50 mmol of reductant in 0.5 mL of toluene at rt for 24 h. \(^b\)Yield of \(12a\) determined by quantitative \(^1\)H NMR spectroscopy on the unpurified reaction mixture using dimethyl fumarate as the analytical standard. \(^c\)The ratio was determined by \(^1\)H NMR spectroscopic analysis on the unpurified reaction mixture. \(^d\)Enantiomeric ratios were determined by chiral HPLC analysis. \(^e\)\(b:l\) refers to the ratio of branched to linear isomers as defined by: \((12a + 13a) : l-12a\).

Table SI-3: Solvent Survey in the Cu-Catalyzed Reductive Coupling

\[
\begin{array}{cccccc}
\text{Entry} & \text{Solvent} & \% \text{y} \, 12a^b & \text{dr} \, 12a^c & \text{er} \, 12a^d & 12a:13a^e & b:l^e \\
1 & \text{THF} & 60 & >99:1 & 89:11 & 79:21 & 96:4 \\
2 & \text{MTBE} & 45 & >99:1 & 90:10 & 64:36 & 90:10 \\
3 & \text{CH\textsubscript{2}Cl\textsubscript{2}} & 35 & >99:1 & 60:40 & >99:1 & 96:5 \\
4 & \text{Toluene} & 77 & >99:1 & 92:8 & 81:19 & >99:1 \\
5 & \text{PhCF\textsubscript{3}} & 62 & >99:1 & 96:4 & 71:29 & >99:1 \\
6 & \text{Fluorobenzene} & 50 & >99:1 & 91:8 & 70:30 & >99:1 \\
7 & \text{DMF} & 77 & >99:1 & 70:30 & >99:1 & 98:2 \\
8 & \text{1:1 DMF:Tol.} & 73 & >99:1 & 85:15 & 86:13 & >99:1 \\
9 & \text{3:7 DMF:Tol.} & 33 & >99:1 & 80:20 & 90:10 & >99:1 \\
10 & \text{3:7 DMF:PhCF\textsubscript{3}} & 63 & >99:1 & 90:10 & 89:14 & >99:1 \\
11 & \text{3:7 DMF:PhCF\textsubscript{3}} & 59 & >99:1 & 86:14 & 94:6 & >99:1 \\
12 & \text{3:7 DMF:PhCF\textsubscript{3}} & 68 & >99:1 & 84:16 & 98:2 & >99:1 \\
13 & \text{3:7 tetramethylurea:PhCF\textsubscript{3}} & 35 & >99:1 & 93:7 & 58:42 & >99:1 \\
14 & \text{3:7 N,N-diisopropylformamide:PhCF\textsubscript{3}} & 44 & >99:1 & 87:16 & 84:16 & >99:1 \\
15 & \text{3:7 N-formylpyrrolidine:PhCF\textsubscript{3}} & 0 & - & - & - & - \\
16 & \text{3:7 DMPU:PhCF\textsubscript{3}} & 74 & >99:1 & 86:14 & 88:11 & >99:1 \\
17 & \text{3:7 propylene carbonate:PhCF\textsubscript{3}} & 32 & >99:1 & 81:19 & >99:1 & >99:1 \\
\end{array}
\]

\(^a\)Reaction performed according to the general procedure employing 0.250 mmol of \(8a\), 0.375 mmol of \(11\), 0.50 mmol of \(\text{Me(MeO)\textsubscript{2}SiH}\) in 0.5 mL of solvent at rt for 24 h. \(^b\)Yield of \(12a\) determined by quantitative \(^1\)H NMR spectroscopy on the unpurified reaction mixture using dimethyl fumarate as the analytical standard. \(^c\)The ratio was determined by \(^1\)H NMR spectroscopic analysis on the unpurified reaction mixture. \(^d\)Enantiomeric ratios were determined by chiral HPLC analysis. \(^e\)\(b:l\) refers to the ratio of branched to linear isomers as defined by: \((12a + 13a) : l-12a\).
General procedure for the branched-selective Cu(W8) catalyzed reductive coupling by Method A.

To a 20 mL crimp-cap vial with stir-bar in an Ar-filled glove-box was charged 2.3 mg (0.0125 mmol) of Cu(OAc)$_2$ and 14.0 mg (0.0150 mmol) of Walphos-8. Toluene (0.5 mL) was then added, and the mixture was allowed to stir for 10 min. Allenamide 11 (47.0 mg, 0.375 mmol) followed by the ketone (0.250 mmol) was then charged, and the vial was sealed with a crimp-cap septum and removed from the glove-box. The reaction was then cooled in an ice bath, and dimethoxymethylsilane (62 µL, 0.5 mmol) was then charged by syringe (caution: dimethoxymethylsilane should be handled in a well-ventilated fume hood because it is known to cause blindness. Syringes were quenched with 2M NaOH, gas evolution!, prior to disposal) The reaction was then allowed to warm to rt and stirred for 24 h. The reaction was then quenched by the addition of 95 mg of NH$_4$F and 1.5 mL of MeOH followed by agitation at rt for 30 min – 1 h. To the mixture was then charged 5 mL of 5% NaHCO$_3$ followed by extraction with CH$_2$Cl$_2$ (2x4mL). The combined organics were dried with Na$_2$SO$_4$ and concentrated in vacuo. An aliquot of the crude mixture was analyzed by $^1$HNMR spectroscopy to determine the dr and b/l ratio. The crude residue was then purified by flash chromatography on silica gel to afford the desired product. Enantioselectivity was determined by chiral HPLC analysis relative to authentic racemate prepared by the same method using PCy$_3$ as ligand.

General procedure for the branched-selective Cu(W8) catalyzed reductive coupling by Method B.

To a 20 mL crimp-cap vial with stir-bar in an Ar-filled glove-box was charged 2.3 mg (0.0125 mmol) of Cu(OAc)$_2$ and 14.0 mg (0.0150 mmol) of Walphos-8. α,α,α-Trifluorotoluene (0.5 mL) was then added, and the mixture was allowed to stir for 10 min. Allenamide 11 (47.0 mg, 0.375 mmol) followed by the ketone (0.250 mmol) and tBuOH (48 µL, 0.500 mmol) was then charged. The vial was then sealed with a crimp-cap septum and removed from the glove-box. The reaction was then cooled in an ice bath, and dimethoxymethylsilane (62 µL, 0.5 mmol) was then charged by syringe (caution: dimethoxymethylsilane should be handled in a well-ventilated fume hood because it is known to cause blindness. Syringes were quenched with 2M NaOH, gas evolution!, prior to disposal) The mixture was then allowed to warm to rt and stirred for 24 h. The reaction was then quenched by the addition of 95 mg of NH$_4$F and 1.5 mL of MeOH followed by agitation at rt for 30 min – 1 h. To the mixture was then charged 5 mL of 5% NaHCO$_3$ followed by extraction with CH$_2$Cl$_2$ (2x4mL). The combined organics were dried with Na$_2$SO$_4$ and concentrated in vacuo. An aliquot of the crude mixture was analyzed by $^1$HNMR spectroscopy to determine the dr and b/l ratio. The crude residue was then purified by flash chromatography on silica gel to afford the desired product. Enantioselectivity was determined by chiral HPLC analysis relative to authentic racemate prepared by the same method using PCy$_3$ as ligand.
Analytical data for the reductive coupling products

3-((3S,4S)-4-hydroxy-4-phenylpent-1-en-3-yl)oxazolidin-2-one (12a): According to the Method A general procedure, a crude mixture of 80:20 12a:13b was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 46.3 mg (75%) of 12a in 91 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as an off-white solid as a single diastereomer as a 93:7 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically pure material could be obtained by slurrying the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 76% recovery with >99 er. Absolute and relative stereochemistry was determined by conversion to authentic material (see page S16). Rf = 0.12 (30% EtOAc/hexanes). 1HNMR (CDCl3, 600 MHz) δ: 7.47 (d, J = 7.90 Hz, 2H), 7.34 (t, J = 7.30 Hz, 2H), 7.23 – 7.28 (m, 1H), 6.29 (ddd, J = 16.40 Hz, J = 9.98 Hz, 8.50 Hz, 1H), 5.43 (d, J = 10.6 Hz, 1H), 5.36 (dt, J = 17.46 Hz, J = 1Hz, 1H), 4.29 (br s, 1H), 4.15 (d, J = 8.65 Hz, 1H), 4.02 (dt, J = 21.44 Hz, J = 8.81 Hz, J = 7.11 Hz, 2H), 3.53 (td, J = 15.61 Hz, J = 7.11 Hz, 1H), 3.23 (td, J = 17.62 Hz, J = 7.01 Hz, 1H), 1.53 (s, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.8, 145.8, 130.7, 128.1, 126.9, 124.5, 120.6, 67.0, 62.6, 45.0, 29.1 ppm. HRMS (DART) m/z calcd for C14H18NO3 [M + H]+: 248.1287; Found [M + H]+: 248.1264.

3-((3S,4S)-4-hydroxy-4-phenylhex-1-en-3-yl)oxazolidin-2-one (12b): According to the Method B general procedure, a crude mixture of >99:1 12b:13b was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 50.3 mg (77%) of 12b in 85 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as an off-white solid as a single diastereomer as a 96:4 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically pure material could be obtained by slurrying the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 81% recovery with >99 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.18 (30% EtOAc/hexanes). 1HNMR (CDCl3, 600 MHz) δ: 7.43 (d, J = 7.70 Hz, 2H), 7.34 (t, J = 7.08 Hz, 2H), 7.21-7.27 (m, 1H), 6.27 (ddd, J = 17.8 Hz, J = 10.3 Hz, J = 8.5 Hz, 1H), 5.41 (d, J = 10.3 Hz, 1H), 5.36 (d, J = 17.3 Hz, 1H), 4.27 (br s, 1H), 4.18 (d, J = 8.9 Hz, 1H), 3.98 (t, J = 8.6 Hz, 1H), 3.52 (q, 8.0 Hz, 1H), 3.25 (q, J = 8.0 Hz, 1.87 – 1.97 (m, 1H), 1.73 – 1.81 (m, 1H), 0.66 (t, J = 6.9 Hz, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.7, 143.2, 130.9, 130.7, 128.0, 126.7, 125.2, 120.5, 79.5, 66.8, 62.6, 45.0, 33.4, 7.3 ppm. HRMS (DART) m/z calcd for C15H19NO3 [M]+: 261.1365; Found [M]+: 261.1332.

(4S,5S)-5-ethyl-3-(2-hydroxyethyl)-5-phenyl-4-vinyloxazolidin-2-one (13b): According to the Method A general procedure, a crude mixture of 12:88 12b:13b was obtained and purified by silica gel chromatography (eluent: 0 – 30% EtOAc in CH2Cl2) to provide 45.8 mg (70%) of 13b as a thick glass as a single diastereomer as a 67:33 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.31 (30% EtOAc/CH2Cl2). 1HNMR (CDCl3, 600 MHz) δ: 7.33 – 7.41 (m, 4H), 7.31 (t, J = 6.6 Hz, 1H), 5.95 (dt, J = 17.1 Hz, 9.5 Hz, 1H, 5.53 (d, J = 10.3 Hz, 1H), 5.44 (d, J = 17.2 Hz, 1H), 4.21 (d, J = 9.5 Hz, 1H), 3.62 – 3.74 (m, 2H), 3.47 (dt, J = 14.8 Hz, 4.8 Hz, 1H), 3.17 (dt, 15.1 Hz, 5.2 Hz, 1H), 2.22 (br s, 1H), 2.07 (dq, J = 14.4 Hz, 6.1 Hz, 1H), 1.87 (dq, 15.4 Hz, 7.0 Hz, 1H), 0.76 (t, J = 7.2 Hz, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.2, 142.3, 132.3, 128.7, 127.8, 124.3, 123.2, 86.3, 71.5, 61.0, 45.1, 29.5, 7.6 ppm. HRMS (DART) m/z calcd for C15H19NO3 [M]+: 261.1365; Found [M]+: 261.1336.
3-((3S,4S)-4-hydroxy-4,6-diphenylhex-1-en-3-yl)oxazolidin-2-one (12c): According to the Method B general procedure, a crude mixture of >99:1 12c:13c was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 42.1 mg (55%) of 12c in 90 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as an off-white solid as a single diastereomer as a 97:3 mixture of (allene rearrangement products N-allyl and N-propenyl 4-phenyloxazolidin-2-one could not be removed by chromatography). Analytically and diastereomerically pure material could be obtained by slurrying the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 76% recovery with >99 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.21 (30% EtOAc/hexanes). 1HNMR (CDCl3, 600 MHz) δ: 7.48 (d, J = 7.9 Hz, 2H), 7.38 (t, J = 7.42 Hz, 1H), 7.27 (t, J = 6.7 Hz, 1H), 7.21 (t, J = 7.7 Hz, 2H), 7.12 (t, J = 7.7 Hz, 1H), 7.03 (d, J = 7.7 Hz, 2H), 6.29 (ddd, J = 17.4 Hz, J = 10.6 Hz, J = 9.1 Hz, 1H), 5.39 (d, J = 9.3 Hz, 1H), 5.31 (d, J = 17.2 Hz, 1H), 4.80 (br s, 1H), 4.05 (d, J = 9.3 Hz, 1H), 4.00 (q, J = 7.0 Hz, 1H), 3.94 (q, J = 8.8 Hz, 1H), 3.50 (q, J = 8.5 Hz, 1H), 3.16 (q, J = 6.8 Hz, 1H), 2.60 (td, J = 12.9 Hz, J = 4.9 Hz, 1H), 2.21 (td, J = 12.3 Hz, J = 5.0 Hz, 1H), 2.13 (td, J = 12.7 Hz, J = 3.6 Hz, 1H), 1.99 (td, J = 12.7 Hz, J = 4.3 Hz, 1H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.9, 143.5, 142.1, 130.6, 128.3, 128.2, 126.9, 125.1, 120.8, 79.4, 67.8, 62.8, 45.6, 42.7, 29.5 ppm. HRMS (DART) m/z calcd for C21H24NO3 [M + H]+: 338.1756; Found [M + H]+: 338.1735.

(4S,5S)-3-(2-hydroxyethyl)-5-phenethyl-5-phenyl-4-vinyloxazolidin-2-one (13c): According to the Method A general procedure, a crude mixture of 14:86 12c:13c was obtained and purified by silica gel chromatography (eluent: 0 – 30% EtOAc in CH2Cl2) to provide 66.7 mg (78%) of 13c as a thick glass as a single diastereomer as a 95:5 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.35 (30% EtOAc/CH2Cl2). 1HNMR (CDCl3, 600 MHz) δ: 7.40 – 7.46 (m, 4H), 7.33 – 7.39 (m, 1H), 7.23 (t, J = 7.8 Hz, 2H), 7.16 (t, J = 7.30 Hz, 1H), 7.06 (d, J = 7.30 Hz, 2H), 5.92 (dt, J = 16.6 Hz, 10.3 Hz, 1H), 5.50 (d, J = 10.2 Hz, 1H), 5.44 (d, J = 17.5 Hz, 1H), 4.23 (d, J = 9.7 Hz, 1H), 3.63 – 3.75 (m, 2H) 3.44 (ddd, J = 16.9 Hz, J = 7.2 Hz, 4.16 Hz, 1H), 3.18 (ddd, J = 17.2, J = 7.2 Hz, 3.8 Hz, 1H), 2.7 (td, J = 12.8 Hz, J = 5.1 Hz, 1H), 2.30 (dt, J = 12.6 Hz, 4.6 Hz, 1H), 2.08 – 2.22 (m, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.0, 142.3, 141.5, 132.2, 128.9, 128.5, 128.3, 128.0, 126.0, 126.1, 123.4, 85.6, 71.7, 60.9, 45.1, 39.0, 29.6 ppm. HRMS (DART) m/z calcd for C21H24NO3 [M + H]+: 338.1756; Found [M + H]+: 338.1735.

3-((3S,4S)-4-hydroxy-4-(4-(trifluoromethyl)phenyl)pent-1-en-3-yl)oxazolidin-2-one (12d): According to the Method B general procedure, the crude mixture of >99:1 12d:13d was obtained and purified by silica gel chromatography (eluent: 0 – 20% EtOAc in CH2Cl2) to provide 52.0 mg (66%) of 12d as a thick clear oil as a single diastereomer as a 88:12 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.49 (10% EtOAc/CH2Cl2). 1HNMR (CDCl3, 600 MHz) δ: 7.58 – 7.63 (m, 4H), 6.26 (ddd, J = 17.7 Hz, J = 9.9 Hz, J = 8.7 Hz, 1H), 5.46 (d, J = 10.2 Hz, 1H), 5.38 (d, J = 17.4 Hz, 1H), 4.64 (s, 1H), 4.17 (d, J = 8.6 Hz, 1H), 4.0 – 4.1 (m, 2H), 3.56 (q, J = 8.4 Hz, 1H), 3.28 (q, J = 7.5 Hz, 1H), 1.51 (s, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.9, 150.1, 130.1, 129.3, 129.0, 125 (q, JCF = 3.5), 125.0, 121.2, 121.8, 76.8, 66.9, 62.7, 40.1, 29.3 ppm. 19F NMR (565 MHz, CDCl3): – 62.4 ppm. HRMS (DART) m/z calcd for C18H24F3NO5Si [M]+: 419.1376; Found [M]+: 419.1376.
3-((3S,4S)-4-hydroxy-4-(4-chlorophenyl)pent-1-en-3-yl)oxazolidin-2-one (12e): According to the Method A general procedure, a crude mixture of 76:24 12e:13e was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 49.2 mg (70%) of 12e in 89 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a white solid as a single diastereomer as a 85:15 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically pure material could be obtained by slurring the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 65% recovery with 95:5 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.14 (30% EtOAc/hexanes).

$\delta$ (d, J = 8.7 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 6.25 (ddd, J = 18.4 Hz, J = 17.4 Hz, J = 9.0 Hz 1H), 5.44 (d, J = 10.4 Hz, 1H), 5.36 (d, J = 17.3 Hz, 1H), 4.43 (s, 1H), 4.05 - 4.15 (m, 3H), 3.55 (dt, J = 7.6 Hz, J = 9.0 Hz, 1H), 5.4 (t, J = 8.4 Hz, 1H), 3.27 (dt, J = 7.9 Hz, J = 7.0 Hz, 1H), 1.50 (s, 3H) ppm. 13C NMR (151 MHz, CDCl 3): δ 158.9, 144.5, 132.8, 130.4, 128.4, 126.1, 121.1, 76.8, 67.0, 62.8, 45.2, 29.3 ppm. HRMS (DART) m/z calc'd for C14H17ClNO3 [M + H]+: 282.0897; Found [M + H]+: 282.0883.

3-((3S,4S)-4-hydroxy-4-(4-methoxyphenyl)pent-1-en-3-yl)oxazolidin-2-one (12f): According to the Method A general procedure, a crude mixture of 88:12 12f:13f was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 40.2 mg (58%) of 12f in 91 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a white solid as a single diastereomer as a 82:18 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically pure material could be obtained by slurring the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 62% recovery with >99:1 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.10 (30% EtOAc/hexanes).

$\delta$ (d, J = 7.7 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.26 (ddd, J = 17.5 Hz, J = 10.5, J = 8.9 Hz, 1H), 5.42 (d, J = 10.1 Hz, 1H), 5.35 (d, J = 17.1 Hz, 1H), 4.10 – 4.17 (m, 2H), 4.05 (t, J = 7.7 Hz, 1H), 3.52 (dt, J = 8.4 Hz, J = 8.4 Hz, 1H), 3.28 (dt, J = 8.2 Hz, J = 8.4 Hz, 1H), 1.50 (s, 3H) ppm. 13C NMR (151 MHz, CDCl 3): δ 158.9, 144.5, 132.8, 130.4, 128.4, 126.1, 121.1, 76.8, 67.0, 62.8, 45.2, 29.3 ppm. HRMS (DART) m/z calc'd for C15H20NO4 [M + H]+: 278.1392; Found [M + H]+: 278.1379.

3-((3S,4S)-4-(4-(dimethylamino)phenyl)-4-hydroxypent-1-en-3-yl)oxazolidin-2-one (12g): According to the Method A general procedure, a crude mixture of >99:1 12g:13g was obtained and purified by silica gel chromatography (eluent: 0 – 30% EtOAc in CH2Cl2) to provide 48.6 mg (67%) of 12g as thick glass as a single diastereomer as a 77:23 mixture of enantiomers and >99 mixture of 12g:13g. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.21 (10% EtOAc/CH2Cl2).

$\delta$ (d, J = 8.9 Hz, 2H), 6.72 (d, J = 7.7, 2H), 6.26 (ddd, J = 17.6 Hz, J = 10.5 Hz, J = 8.4 Hz, 1H), 5.41 (d, J = 10.4 Hz, 1H), 5.34 (d, J = 17.3 Hz, 1H), 4.17 (d, J = 8.4 Hz, 1H), 4.05 (t, J = 7.7 Hz, 1H), 3.51 (dt, J = 8.0 Hz, J = 8.4 Hz, 1H), 3.28 (dt, J = 8.2 Hz, J = 8.6 Hz, 1H), 2.95 (s, 6H), 1.51 (s, 3H) ppm. 13C NMR (151 MHz, CDCl 3): δ 158.7, 143.2, 130.9, 128.0, 126.7, 125.2, 120.5, 79.5, 66.8, 62.6, 45.0, 33.4, 7.3 ppm. HRMS (DART) m/z calc'd for C16H23N2O3 [M + H]+: 291.1709; Found [M + H]+: 291.1714.
3-((3S,4S)-4-hydroxy-4-(p-tolyl)pent-1-en-3-yl)oxazolidin-2-one (12h): According to the Method B general procedure, a crude mixture of >99:1 12h:13h was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 26.1 mg (40%) of 12h in 88 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a white solid as a single diastereomer as an 83:17 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically pure material could be obtained by slurring the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 77% recovery with 91:9 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.16 (30% EtOAc/hexanes). 

\[ \text{1HNMR (CDCl}_3\text{, 600 MHz)} \delta: 7.32 (d, J = 8.9 Hz, 2H), 6.72 (d, J = 7.7 Hz, 2H), 6.26 (dd, J = 17.6 Hz, J = 10.5 Hz, J = 8.4 Hz, 1H), 5.41 (d, J = 10.4 Hz, 1H), 5.34 (d, J = 17.3 Hz, 1H), 4.17 (d, J = 8.4 Hz, 1H), 4.05 (t, J = 7.7 Hz, 1H), 3.51 (dt, J = 8.0 Hz, J = 8.4 Hz, 1H), 3.28 (dt, J = 8.2 Hz, J = 8.6 Hz, 1H), 2.95 (s, 6H), 1.51 (s, 3H) ppm. \]

\[ \text{13C NMR (151 MHz, CDCl}_3\text{): } \delta 158.7, 142.7, 136.4, 130.8, 128.8, 124.4, 120.5, 76.8, 66.8, 62.6, 44.9, 29.2, 20.9 \text{ ppm} \]

\[ \text{HRMS (DART)} m/z \text{calcd for C}_{16}\text{H}_{23}\text{N}_{2}\text{O}_{3} \ [\text{M + H}]^+: 291.1709; \text{Found } [\text{M + H}]^+: 291.1714. \]

3-((3S,4S)-4-(benzo[d][1,3]dioxol-5-yl)-4-hydroxypent-1-en-3-yl)oxazolidin-2-one (12i): According to the Method A general procedure, a crude mixture of 88:12 12i:13i was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 54.6 mg (75%) of 12i in 87 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a white solid as a single diastereomer as an 80:20 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically and diastereomerically pure material could be obtained by slurring the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 75% recovery with 90:10 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.12 (30% EtOAc/hexanes). 

\[ \text{1HNMR (CDCl}_3\text{, 600 MHz)} \delta: 6.99 (s, 1H), 6.93 (dd, J = 8.18 Hz, J = 1.1 Hz, 1H), 6.78 (d, J = 8.30 Hz, 1H), 6.25 (ddd, J = 17.3 Hz, J = 10.8 Hz, J = 9.3 Hz, 1H), 5.96 (s, 2H), 5.42 (d, J = 10.3 Hz, 1H), 5.35 (d, J = 17.3 Hz, 1H), 4.21 (br, s, 1H), 4.05 - 4.14 (m, 3H), 3.6 (q, J = 8.4 Hz, 1H), 3.32 (q, J = 8.4 Hz, 3H), 1.49 (s, 3H) ppm. \]

\[ \text{13C NMR (151 MHz, CDCl}_3\text{): } \delta 158.9, 147.6, 146.4, 140.1, 130.4, 120.8, 117.8, 107.9, 105.6, 101.1, 76.9, 67.1, 62.7, 45.1, 29.5 \text{ ppm} \]

\[ \text{HRMS (DART)} m/z \text{calcd for C}_{15}\text{H}_{17}\text{NO}_{5} \ [\text{M + H}]^+: 291.1107; \text{Found } [\text{M + H}]^+: 291.1123. \]

3-((3S,4S)-4-hydroxy-4-(naphthalen-2-yl)pent-1-en-3-yl)oxazolidin-2-one (12j): According to the Method B procedure, a crude mixture of >99:1 12j:13j was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 37.1 mg (50%) of 12j in 88 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a white solid as a single diastereomer as a 85/15 mixture of enantiomers and >99:1 mixture of 12j:13j (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically and diastereomerically pure material could be obtained by slurring the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 80% recovery with 82:17 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.16 (30% EtOAc/hexanes). 

\[ \text{1HNMR (CDCl}_3\text{, 600 MHz)} \delta: 8.00 (s, 1H), 7.79 – 8.86 (m, 3H), 7.4 – 7.50 (m, 3H), 6.31 (ddd, J = 17.4 Hz, J = 10.4 Hz, J = 9.19 Hz, 1H), 5.43 (d, J = 10.2 Hz, 1H), 5.37 (d, J = 17.27 Hz, 1H), 4.59 (s, 1H), 4.26 (d, J = 8.5 Hz, 1H), 3.94 (q, J = 9.0 Hz, 1H), 3.89 (q, J = 8.4 Hz, 1H), 3.59 (q, J = 8.81 Hz, 1H), 3.22 (q, J = 8.81 Hz, 1H) 1.56 (s, 3H) ppm. \]

\[ \text{13C NMR (151 MHz, CDCl}_3\text{): } \delta 158.9, 143.3, 133.1, 132.3, 128.2, 127.8, 127.4, \]
3-((3S,4S)-4-hydroxy-4-(3-(trifluoromethyl)phenyl)pent-1-en-3-yl)oxazolidin-2-one (12k): According to the Method A general procedure, a crude mixture of 60:40 12k:13k was obtained and purified by silica gel chromatography (eluents: 0 – 20% EtOAc in CH$_2$Cl$_2$) to provide 33.9 mg (43%) of 12k as an oil as a single diastereomer as a 90:10 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. R$_f$ = 0.19 (10% EtOAc/ CH$_2$Cl$_2$).

$^1$HNMR (CDCl$_3$, 600 MHz) $\delta$: 7.74 (s, 1H), 7.69 (d, $J = 8.00$ Hz, 1H), 7.51 (d, $J = 8.24$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 6.25 (ddd, $J = 17.3$ Hz, $J = 10.8$ Hz, $J = 9.7$ Hz, 1H), 5.45 (d, $J = 9.9$ Hz, 1H), 5.38 (d, $J = 17.0$ Hz, 1H), 4.55 (br s, 1H), 4.18 (d, $J = 8.4$ Hz, 1H), 4.00 – 4.07 (m, 2H), 3.60 (q, $J = 8.4$ Hz, 1H), 3.28 (q, $J = 7.5$ Hz, 1H), 1.52 (s, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 158.8, 147.1, 130.3 (q, 2J$_{CF} = 33$ Hz), 129.4 (q, 1J$_{CF} = 274$ Hz), 128.8, 128.3, 123.7 (q, 3J$_{CF} = 4.2$ Hz), 123.7 (q, 3J$_{CF} = 4.6$ Hz), 121.3, 118.6, 66.7, 62.7, 61.7, 44.9, 29.1 ppm. $^{19}$F NMR (565 MHz, CDCl$_3$): – 62.5 ppm. HRMS (DART) m/z calcd for C$_{18}$H$_{20}$NO$_3$ [M + H]$^+$: 298.1443; Found [M + H]$^+$: 298.1435.

methyl 3-((2S,3S)-2-hydroxy-3-(2-oxooxazolidin-3-yl)pent-4-en-2-yl)benzoate (12l): According to the Method A general procedure, a crude mixture of 73:27 12l:13l was obtained and purified by silica gel chromatography (eluents: 0 – 20% EtOAc in CH$_2$Cl$_2$) to provide 35.9 mg (47%) of 12l as a thick glass as a single diastereomer as a 97:3 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. R$_f$ = 0.38 (10% EtOAc/ CH$_2$Cl$_2$).

$^1$HNMR (CDCl$_3$, 600 MHz) $\delta$: 8.11 (s, 1H), 7.93 (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.44 (t, $J = 8.7$ Hz, 1H), 6.27 (ddd, $J = 17.5$ Hz, $J = 9.5$ Hz, $J = 9.0$ Hz, 1H), 5.45 (d, $J = 10.0$ Hz, 1H), 5.37 (d, $J = 17.6$ Hz, 1H), 4.63 (s, 1H), 4.15 (d, $J = 9.0$ Hz, 1H), 4.07 (q, $J = 8.2$ Hz, 1H), 4.01 (q, $J = 8.5$ Hz, 1H), 3.92 (s, 3H), 3.58 (q, $J = 8.5$ Hz, 1H), 3.27 (q, $J = 7.4$ Hz, 1H), 1.52 (s, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 167.1, 158.8, 146.5, 130.0, 129.9, 129.5, 128.4, 128.2, 125.5, 121.0, 76.8, 67.1, 62.7, 52.1, 45.3, 29.2 ppm. HRMS (DART) m/z calcd for C$_{16}$H$_{20}$NO$_5$ [M + H]$^+$: 306.1341; Found [M]$^+$: 306.1315.

3-((3S,4S)-4-(3-bromophenyl)-4-hydroxypent-1-en-3-yl)oxazolidin-2-one (12m): According to the Method A general procedure, a crude mixture of 74:26 12m:13m was obtained and purified by silica gel chromatography (eluents: 10 – 50% EtOAc in hexanes) to provide 67.0 mg (73%) of 12m in 89 wt% purity by quantitative $^1$H NMR spectroscopy using dimethylfumarate as analytical standard as a white solid as a single diastereomer as a 92:8 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically and diastereomerically pure material could be obtained by slurrying the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 80% recovery with 98:2 er. The stereochemistry was assigned by analogy to that of 12a. R$_f$ = 0.18 (30% EtOAc/hexanes).

$^1$HNMR (CDCl$_3$, 600 MHz) $\delta$: 7.64 (s, 1H), 7.40 (t, $J = 8.7$ Hz, 2H), 7.23 (t, $J = 7.6$ Hz, 1H), 6.26 (ddd, $J = 16.91$ Hz, $J = 9.8$ Hz, $J = 8.6$ Hz, 1H), 5.45 (d, $J = 10.6$ Hz, 1H), 5.37 (d, $J = 17.6$ Hz, 1H), 4.50 (br s, 1H), 4.05 – 4.15 (m, 3H), 3.57 (q, $J = 7.6$ Hz, 1H), 3.29 (q, $J = 7.55$ Hz, 1H) 1.50 (s, 3H) ppm. $^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 148.5, 130.3, 130.1, 129.9, 129.8, 127.8, 123.5, 122.5, 121.2, 76.8, 67.1, 62.8, 45.3, 29.2 ppm. HRMS (DART) m/z calcd for C$_{14}$H$_{17}$BrNO$_3$ [M + H]$^+$: 326.0392; Found [M + H]$^+$: 326.0380.
3-((3S,4S)-4-hydroxy-4-(3-methoxyphenyl)pent-1-en-3-yl)oxazolidin-2-one (12n): According to the Method A general procedure, a crude mixture of 70:30 12n:13n was obtained and purified by silica gel chromatography (eluent: 0 – 20% EtOAc in CH₂Cl₂) to provide 37.4 mg (54%) of 12n as a thick glass as a single diastereomer as a 96:4 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.41 (10% EtOAc/ CH₂Cl₂).

1H NMR (CDCl₃, 600 MHz): δ: 7.27 (t, J = 8.5 Hz, 1H), 7.09 (s, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.80 (dd, J = 8.3 Hz, J = 2.1 Hz, 1H), 6.29 (ddd, J = 18.0 Hz, J = 9.8 Hz, J = 9.0 Hz, 1H), 5.43 (d, J = 10.6 Hz, 1H), 5.36 (d, J = 17.3 Hz, 1H), 4.43 (s, 1H), 4.17 (d, J = 8.4 Hz, 1H), 4.00 – 4.07 (m, 2H), 3.82 (s, 3H), 3.56 (q, J = 9.9 Hz, 1H), 3.28 (q, J = 8.5 Hz, 1H), 1.51 (s, 3H) ppm. 13C NMR (151 MHz, CDCl₃): δ 159.5, 158.8, 147.7, 130.7, 129.1, 120.6, 120.2, 116.9, 112.2, 111.3, 110.5, 76.9, 66.8, 62.7, 61.8, 55.2, 45.1, 44.1, 29.2 ppm. HRMS (DART) m/z calcd for C₁₅H₂₀NO₄ [M + H]+: 278.1392; Found [M + H]+: 278.1379.

3-((3S,4S)-4-(3-(dimethylamino)phenyl)-4-hydroxypent-1-en-3-yl)oxazolidin-2-one (12o): According to the Method A general procedure, a crude mixture of 72:28 12o:13o was obtained and purified by silica gel chromatography (eluent: 0 – 30% EtOAc in CH₂Cl₂) to provide 39.9 mg (55%) of 12o as a thick yellow glass as a single diastereomer as a 92:8 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.19 (10% EtOAc/ CH₂Cl₂). 1HNMR (CDCl₃, 600 MHz): δ: 7.19 (t, J = 8.2 Hz, 1H), 6.90 (br s, 1H), 6.73 (d, J = 9.4 Hz, 1H), 6.61 (d, J = 8.3 Hz, 1H), 6.29 (ddd, J = 17.8 Hz, J = 9.1 Hz, J = 9.3 Hz, 1H), 5.40 (d, J = 9.93 Hz, 1H), 5.34 (d, J = 16.6 Hz, 1H), 4.33 (s, 1H), 4.16 (d, J = 8.8 Hz, 1H), 3.98 – 4.04 (m, 2H), 3.50 (q, J = 7.9 Hz, 1H), 3.24 (q, J = 8.3 Hz, 1H), 2.94 (s, 6H), 1.50 (s, 3H) ppm. 13C NMR (151 MHz, CDCl₃): δ 158.8, 150.5, 146.6, 131.0, 130.8, 128.7, 120.3, 112.7, 111.0, 109.1, 66.8, 62.7, 45.1, 40.7, 29.3 ppm. HRMS (DART) m/z calcd for C₁₆H₂₃N₂O₃ [M + H]+: 291.1709; Found [M + H]+: 291.1714.

3-((3S,4R)-4-(furan-2-yl)-4-hydroxypent-1-en-3-yl)oxazolidin-2-one (12p): According to the Method A general procedure, a crude mixture of >99:1 12p:13p was obtained and purified by silica gel chromatography (eluent: 0 – 50% EtOAc in hexanes) to provide 45.1 mg (76%) of 12p in 90 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a white solid as a single diastereomer as a 92:8 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.10 (30% EtOAc/hexanes).

Analytically and diastereomerically pure material could be obtained by slurrying the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 73% recovery with >99% er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.10 (30% EtOAc/hexanes). 1H NMR (CDCl₃, 600 MHz): δ: 7.35 (s, 1H), 6.3 (d, J = 2 Hz, 2H), 6.23 (ddd, J = 19.0, 17.2, 9.4, 1H), 5.42 (d, J = 10.2 Hz, 1H), 5.33 (d, J = 17.1 Hz, 1H), 4.63 (br, s, 1H), 4.21 (dd, J = 17.1 Hz, J = 8.9 Hz, 1H), 4.10 - 4.18 (m, 2H), 3.55 (dt, J = 8.4 Hz, J = 8.4, 1H), 3.34 (dt, J = 7.9 Hz, J = 8.9 Hz, 1H), 1.53 (s, 3H) ppm. 13C NMR (151 MHz, CDCl₃): δ 159.1, 158.3, 141.5, 130.1, 121.2, 110.6, 105.8, 74.5, 66.1, 62.9, 45.1, 25.9 ppm. HRMS (DART) m/z calcd for C₁₂H₁₆NO₄ [M + H]+: 238.1079; Found [M + H]+: 238.1079.
3-((3S,4R)-4-hydroxy-4-(5-methylthiophen-2-yl)pent-1-en-3-yl)oxazolidin-2-one (12q): According to the Method A general procedure, a crude mixture of >99:1 12q:13q was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 59.5 mg (89%) of 12q in 91 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a yellow solid as a single diastereomer as a 90:10 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically and diastereomerically pure material could be obtained by slurrying the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 70 recovery with 75:25 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.20 (30% EtOAc/hexanes). 1HNMR (CDCl3, 600 MHz) δ: 6.76 (d, J = 3.3 Hz, 1H), 6.60 (d, J = 3.3 Hz, 1H), 6.22 (dd, J = 17.3 Hz, J = 10.0 Hz, J = 8.6 Hz, 1H), 5.41 (d, J = 10.3 Hz, 1H), 5.35 (d, J = 17.1 Hz, 1H), 4.40 (br s, 1H), 4.14 – 4.22 (m, 1H), 3.40 (br, s, 1H), 3.30 (q, J = 8.8 Hz, 1H), 2.84 (t, J = 7.0 Hz, 2H), 2.14 (dt, J = 13.2 Hz, J = 5.3 Hz, 1H), 1.77 – 1.83 (m, 1H), 1.55 (s, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 159.3, 140.0, 136.6, 131.1, 129.0, 122.7, 121.1, 76.1, 67.5, 62.8, 44.9, 29.7, 15.2 ppm. HRMS (DART) m/z calcd for C13H18NO3S [M + H]+: 268.1007; Found [M + H]+: 268.0996.

3-((3S,4R)-4-hydroxy-4-(1-tosyl-1H-pyrrol-2-yl)pent-1-en-3-yl)oxazolidin-2-one (12r): According to the Method A general procedure, a crude mixture of >99:1 12r:13r was obtained and purified by silica gel chromatography (eluent: 20 – 70% EtOAc in hexanes) to provide 78.1 mg (80%) of 12r as a thick glass as a single diastereomer as a 76:24 mixture of enantiomers. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.07 (30% EtOAc/hexanes). 1HNMR (CDCl3, 600 MHz) δ: 7.70 (d, J = 8.6 Hz, 2H), 7.9 (d, J = 8.6 Hz, 2H), 7.13 (t, J = 2.0 Hz, 1H), 7.10 – 7.12 (m, 1H), 6.22 – 6.25 (m, 1H), 6.15 (ddd, J = 17.2 Hz, J = 10.3 Hz, J = 8.8 Hz, 1H), 5.39 (dd, J = 10.1 Hz, J = 0.7, 1H), 5.30 (dd, J = 17.0 Hz, J = 0.8 Hz, 1H), 3.97 (dd, J = 9.2 Hz, J = 1.1 Hz, 1H), 3.92 – 3.96 (m, 1H), 3.87 (br s, 1H), 3.49 (dt, J = 6.6 Hz, J = 8.9 Hz, 1H), 3.26 (t, J = 7.7 Hz, J = 8.4 Hz, 1H), 2.40 (s, 3H), 1.44 (s, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.7, 144.8, 135.9, 135.3, 130.3, 129.9, 126.6, 121.3, 120.9, 116.9, 111.6, 74.2, 66.1, 62.4, 44.3, 28.3, 21.5 ppm. HRMS (DART) m/z calcd for C19H23N2O5S [M + H]+: 391.1328; Found [M + H]+: 391.1352.

3-((S)-1-(S)-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)allyl)oxazolidin-2-one (12s): According to the Method A general procedure, a crude mixture of >99:1 12s:13s and 1:2 b:l was obtained and purified by silica gel chromatography (eluent: 10 – 50% EtOAc in hexanes) to provide 29.1 mg (28%) of 12s in 88 wt% purity by quantitative 1H NMR spectroscopy using dimethylfumarate as analytical standard as a yellow solid as a single diastereomer as a 76:24 mixture of enantiomers (allene rearrangement products N-allyl and N-propenyl oxazolidin-2-one could not be removed by chromatography). Analytically and diastereomerically pure material could be obtained by slurrying the material in 10 vol. of hot 30% EtOAc in hexanes followed by cooling to rt in 66% recovery with 70:30 er. The stereochemistry was assigned by analogy to that of 12a. Rf = 0.11 (30% EtOAc/hexanes). 1HNMR (CDCl3, 600 MHz) δ: 7.48 – 7.52 (m, 1H), 7.15 – 7.23 (m, 2H), 7.07 – 7.10 (m, 1H), 6.17 (ddd, J = 17.6 Hz, J = 10.5 Hz, J = 8.8 Hz, 1H), 5.35 (d, J = 10.0 Hz, 1H), 5.28 (d, J = 17.6 Hz, 1H), 4.34 (d, J = 8.5 Hz, 1H), 4.28 (dt, J = 8.8 Hz, J = 8.2 Hz, 1H), 4.22 (dt, J = 6.2 Hz, 9.1 Hz, 1H), 3.75 (dt, J = 6.4 Hz, J = 8.8 Hz, 1H), 3.40 (br s, 1H), 3.30 (q, J = 8.8 Hz, 1H), 2.84 (t, J = 7.0 Hz, 2H), 2.14 (dt, J = 13.2 Hz, J = 5.3 Hz, 1H), 1.85 – 1.92 (m, 2H), 1.77 – 1.83 (m, 1H), 1.55 (s, 3H) ppm. CDCl3: δ 159.3, 140.0, 136.6, 131.1, 129.0,
127.6, 126.2, 125.8, 120.9, 75.4, 64.6, 62.7, 44.6, 44.6, 34.5, 28.6, 19.0. HRMS (DART) m/z calcd for C₁₆H₂₀NO₃ [M + H]^+: 274.1444; Found [M + H]^+: 274.1444.

(S)-3-(4-hydroxy-4-methylpent-1-en-3-y1)oxazolidin-2-one (12t): According to the general procedure, the product was purified by silica gel chromatography (eluent: 0 – 40% EtOAc in CH₂Cl₂) to provide 23.6 mg (51%) of 12t as a white solid as a single diasteromer. The stereochemistry was assigned by analogy to that of 12a. Rᵢ = 0.24 (40% EtOAc/CH₂Cl₂). ¹H NMR (CDCl₃, 600 MHz) δ: 6.07 (ddd, J = 17 Hz, J = 10 Hz, J = 8.8 Hz, 1H), 5.38 (d, J = 10 Hz, 1H), 5.32 (d, J = 17 Hz, 1H), 4.35 (t, J = 8.5 Hz, 2H), 3.94 (d, J = 8.8 Hz, 1H), 3.82 (dd, J = 16 Hz, J = 8.5 Hz, 1H), 3.62 (dd, J = 16 Hz, J = 8.5 Hz, 1H), 2.51 (s, 1H), 1.31 (s, 3H), 1.24 (s, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 159.1, 131.1, 121.0, 72.9, 65.6, 62.6, 43.7, 27.8, 27.5. HRMS (DART) m/z calcd for C₉H₁₆NO₃ [M + H]^+: 186.1130; Found [M + H]^+: 186.1131.

(Z)-3-(4-hydroxy-4,4-diphenylbut-1-en-1-yl)oxazolidin-2-one (l-12u): According to the general procedure, the product was purified by silica gel chromatography (eluent: 0 – 10% EtOAc in CH₂Cl₂) to provide 24.2 mg (33%) of l-12u as a white solid. Rᵢ = 0.27 (10% EtOAc/CH₂Cl₂). ¹H NMR (CDCl₃, 600 MHz) δ: 7.35 (d, J = 8.0 Hz, 4H), 7.21 (t, J = 8.0 Hz, 4H), 7.12 (t, J = 8.0 Hz, 2H), 6.11 (d, J = 9.4 Hz, 1H), 4.77 (q, J = 9.1 Hz, 1H), 4.26 (t, J = 8.3 Hz, 2H), 3.79 (t, J = 7.8 Hz, 2H), 3.26 (s, 1H), 3.07 (d, J = 7.8 Hz, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ 156.8, 146.4, 128.2, 126.9, 125.8, 125.8, 112.1, 77.1, 62.2, 45.9, 39.2. HRMS (DART) m/z calcd for C₁₉H₂₀NO₃ [M + H]^+: 310.1443; Found [M + H]^+: 310.1435.
Reaction Performed on 1.0 mmol scale:

To a 20 mL crimp-cap vial with stir-bar in an Ar-filled glove-box was charged 9.2 mg (0.05 mmol) of Cu(OAc)₂ and 56.0 mg (0.06 mmol) of Walphos-8. α,α,α-Trifluorotoluene (2.0 mL) was then added, and the mixture was allowed to stir for 10 min. Allenamide 11 (188.0 mg, 1.5 mmol) followed by ketone 8b (1.0 mmol) and tBuOH (0.192 mL, 2.00 mmol) was then charged. The vial was then sealed with a crimp-cap septum and removed from the glove-box. The reaction was then cooled in an ice bath, and dimethoxymethylsilane (0.248 μL, 2.0 mmol) was then charged by syringe (caution: dimethoxymethylsilane should be handled in a well-ventilated fume hood because it is known to cause blindness. Syringes were quenched with 2M NaOH, gas evolution!, prior to disposal) The mixture was then allowed to warm to rt and stirred for 24 h. The reaction was then quenched by the addition of 380 mg of NH₄F and 6.0 mL of MeOH followed by agitation at rt for 30 min – 1 h. The crude mixture was then transferred to a separatory funnel to which 20 mL of 5% NaHCO₃ was then charged and agitated. The mixture was then extracted with CH₂Cl₂ (2x10mL). The combined organics were dried with Na₂SO₄ and concentrated in vacuo. An aliquot of the crude mixture was analyzed by ¹H NMR spectroscopy to determine the dr (>99) and b/l (>99) ratio. The crude residue was then purified by flash chromatography on silica gel (gradient, 0 – 20% EtOAc in CH₂Cl₂). The first spot to elute was isolated as a (W8)Cu complex that was then de-complexed for recovery of W8 (see below). The product spot (Rf = 0.31, 10% EtOAc in CH₂Cl₂) was then collected and concentrated in vacuo to afford 188 mg (72%) of 12b. Enantioselectivity was determined by chiral HPLC analysis to be 96:4.

Recovery of W8: The (W8)Cu complex obtained from the above reaction was further purified by flash chromatography on silica gel (gradient, 0 – 15% EtOAc in hexanes) to afford 71.0 mg of an orange solid. This material was then dissolved in 3.0 mL of 2:1 pentane:MTBE and then 1 mL of 50% NH₄OH solution was added. The mixture was then agitated vigorously for 5 minutes upon which the lower blue aqueous layer was removed. The organic layer was then washed twice with 1 mL of 50% NH₄OH, dried with Na₂SO₄ and concentrated in vacuo to yield 45.1 mg (81% recovery) of W8 as an orange solid. Use of this recovered ligand in the Cu-catalyzed reductive coupling with propiophenone provided identical results to that obtained with the commercially obtained W8.

Large Scale recrystallization of 12a:

To a 20 mL crimp-cap vial with a stir-bar was charged 357.0 mg of 12a of 91 wt% with 90/10 er. To the vial was then added 2.0 mL of 30% EtOAc/Hexanes solution and heated to 40 °C while stirring vigorously. After 30 min of stirring, the mixture was allowed to cool to rt and stir for and additional 30 min and then filtered to yield 237 mg (73%) of analytically pure 12a with >99:1 er.
**Oxazolidinone Removal:**

To a solution of 210 mg (0.850 mmol) of **12a** in 2.0 mL of THF at 0 °C was charged 34 mg (0.850 mmol) of NaH. The reaction was then allowed to warm to room temperature and stirred for 1 h. The reaction was then quenched by the addition of 5 mL of 1M HCl and extracted with CH2Cl2 (3 X 10 mL). The combined organics were dried with Na2SO4 and concentrated in vacuo. The crude residue was purified by flash chromatography (silica gel, gradient, 20 – 50% EtOAc/hexanes) to afford 209.1 mg (99%) of **13a** as a thick waxy oil. Rf = 0.18 (10% EtOAc/CH2Cl2). 1H NMR (CDCl3, 600 MHz) δ: 7.35 – 7.41 (m, 4H), 7.32 (t, J = 6.7 Hz, 1H), 5.91 (dt, J = 16.6 Hz, J = 10.1 Hz, 1H), 5.53 (d, J = 10.2 Hz, 1H), 5.43 (d, J = 16.2 Hz, 1H), 5.22 (d, J = 9.5 Hz, 1H), 3.67 – 3.75 (m, 2H), 3.45 (dd, J = 14.8 Hz, J = 6.3 Hz, J = 4.2 Hz, 1H), 3.19 (dd, J = 14.6 Hz, J = 6.9 Hz, J = 3.7 Hz, 1H), 1.63 (s, 3H) ppm. 13C NMR (151 MHz, CDCl3): δ 158.0, 144.1, 132.3, 128.7, 127.9, 123.8, 123.1, 83.4, 70.8, 60.8, 45.0, 23.9 ppm. HRMS (DART) m/z calcd for C14H18NO3 [M + H]+: 248.1287; Found [M + H]+: 248.1287.

To a solution of 209.1 mg (0.846 mmol) of **13a** in 4.2 mL of CH2Cl2 at 0 °C was charged 141 μL (1.02 mmol) of triethylamine followed by 177 mg (0.931 mmol) of TsCl. The mixture was stirred for 30 min at 0 °C, allowed to warm to rt and stirred for 8 h. To the mixture was charged 2 mL of 10% NH4Cl followed by extraction with CH2Cl2 (3x2mL). The combined organics were dried with anhydrous Na2SO4, and volatile material was removed in vacuo. The crude residue was then dissolved in 8.0 mL of glyme and charged with 360 mg (2.54 mmol) of NaI and 383 μL (2.54 mmol) of DBU and refluxed for 8 h. The mixture was diluted with 30 mL of 1:1 mixture of Et2O and H2O and stirred for 10 min upon which organics were extracted with Et2O (2x10 mL). The combined organic layers were washed with brine, dried with anhydrous Na2SO4, filtered, and volatiles removed in vacuo. The crude residue was then dissolved in 5.0 mL of THF in a 20 mL scintillation vial. To the solution was added 1.7 mL (8.46 mmol) of 5.0 M aqueous H2SO4. The vial was purged with argon, sealed, and immersed in an oil bath at 50 °C. After 2.5 h, the reaction was cooled to rt and 10 mL of saturated aqueous NaHCO3 was charged. The mixture was extracted with CH2Cl2 (3x5mL), dried with anhydrous Na2SO4, and concentrated in vacuo. The crude residue was purified by flash chromatography (silica gel, gradient, hexanes to 60% EtOAc/hexanes) to afford 134.2 mg (78%) of **20** as a White solid. Rf = 0.19 (40% EtOAc/hexanes). Spectral data was identical to that made previously.2
Absolute and relative stereochemistry determination:

\[ \text{20} \xrightarrow{\text{KOTBu, THF}} \text{EtO}_2\text{C} \xrightarrow{\text{NaBH}_4} \text{HO} \]

Diastereo- and enantiopure 20 prepared by our previous work\(^2\) was converted to 13a by the given two-step procedure\(^3\) and then compared to 13a prepared using the current Cu(OAc)\(_2\)/W\(_8\) catalysts system followed by carbonate rearrangement. The major diastereomer and enantiomer formed from the Cu(OAc)\(_2\)/W\(_8\) catalysts system was the same as that of authentic 13a prepared by the given procedure by comparison of the authentic material by \(^1\)HNMR spectroscopy and chiral HPLC analysis.

**Alkylation:** To a solution of 20 (20.0 mg, 0.0984 mmol) in 0.25 mL of THF at 0 °C was charged 0.11 mL of a 1.0 M (0.11 mmol) solution of KO'Bu in THF. The mixture was then allowed to stir for 10 min before the addition of 12 μL (11 mg, 0.11 mmol) of ethyl bromoacetate. The mixture was warmed to rt and allowed to stir for 3 h. To the reaction was added 2 mL of 10% aqueous NH\(_4\)Cl, and the mixture was extracted with CH\(_2\)Cl\(_2\) (3x2mL). The combined organics were dried with anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo to afford SI-1. This material was used directly in the next step without further purification.

**Reduction:** To a solution of SI-1 in 0.25 mL of 7:1 THF:EtOH was charged 11.2 mg (0.295 mmol) of NaBH\(_4\), and the resultant mixture was allowed to stir at rt for 3 h. The reaction was then cooled to 0 °C, and 2 mL of 10% aqueous NH\(_4\)Cl was carefully added (gas evolution!). The mixture was then warmed to rt and extracted with EtOAc (3x2mL). The combined organics were dried with anhydrous Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo to afford 17.1 mg (70%, 2 steps) of 13a as a colorless oil. \(^1\)HNMR spectroscopy matched that of the material prepared using the current Cu(OAc)\(_2\)/W\(_8\) catalysts system followed by carbonate rearrangement (Scheme 3). Chiral HPLC analysis of this material relative to the material prepared from the Cu(OAc)\(_2\)/W\(_8\) catalysts system followed by carbonate rearrangement is given below:

**Chiral HPLC analysis** (Chiralpak AD-3 x 250 mm, heptane/ethanol = 85/15, flow rate = 1.2 mL/min, \( \lambda = 254 \text{ nm} \) \( t_R = 5.2 \text{ min (major)}, 5.7 \text{ min (minor)} \)): **Racemic 13a:**
Authentic 13a:  

![Graph of Authentic 13a](image)

Authentic 13a + racemic spike:

![Graph of Authentic 13a + racemic spike](image)

13a from Cu(OAc)$_2$/W8 reaction followed by carbonate rearrangement using NaH:

![Graph of 13a from Cu(OAc)$_2$/W8 reaction followed by carbonate rearrangement using NaH](image)

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 5.225     | 92.704| 7757   | M    | 0.000 |
| 2    | 5.725     | 7.296 | 685    | M    | 0.000 |
| Total|           | 100.00| 8492   |      | 0.000 |
Chiral HPLC analysis of the reductive coupling products:

\[
\text{Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, } \lambda = 190 \text{ nm) } t_R = 18.9 \text{ min (minor), 23.6 min (major):}
\]

Racemic 12a:

12a from the Cu(OAc)$_2$/W8 reaction:
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 213$ nm) $t_R = 12.1$ min (major), 13.9 min (minor):

Racemic 12b:

![Graph of Racemic 12b]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 12.388    | 55.520| 79455  | M    | 0.000 |
| 2    | 14.103    | 44.480| 56283  | M    | 0.000 |
| Total| 100.000   | 135727|        |      | 0.000 |

12b from the Cu(OAc)$_2$/W8 reaction:

![Graph of 12b from Cu(OAc)$_2$/W8 reaction]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 12.126    | 95.743| 263538 | M    | 0.000 |
| 2    | 13.915    | 4.257 | 16458  | M    | 0.000 |
| Total| 100.000   | 270396|        |      | 0.000 |
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 205 nm) tR = 7.3 min (minor), 8.0 min (major):

Racemic 13b:

![Graph of racemic 13b]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 7.330     | 47.091| 180354 | M    | 47.091|
| 2    | 7.952     | 52.099| 210977 | M    | 52.099|
| Total|           | 100.000| 391331 | M    | 100.000|

13b from the Cu(OAc)$_2$/W8 reaction:

![Graph of 13b from Cu(OAc)$_2$/W8 reaction]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 7.312     | 32.865| 134820 | M    | 32.865|
| 2    | 8.010     | 67.135| 232609 | M    | 67.135|
| Total|           | 100.000| 367590 | M    | 100.000|
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, \( \lambda = 206 \text{ nm} \)) \( t_R = 11.8 \text{ min (minor), 12.8 min (major)} \):

Racemic 12c:

![Graph of racemic 12c](image)

| Peak | Ret. Time | Area%  | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 12.042    | 49.514 | 101377 | M    | 0.000 |
| 2    | 12.582    | 59.035 | 90034  | M    | 0.000 |
| Total|           | 100.000| 191411 |      | 0.000 |

12c from the Cu(OAc)$_2$/W8 reaction:

![Graph of Cu(OAc)$_2$/W8 reaction](image)

| Peak | Ret. Time | Area%  | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 11.781    | 3.306  | 3431   | M    | 0.000 |
| 2    | 12.036    | 96.694 | 62430  | M    | 0.000 |
| Total|           | 100.000| 65861  |      | 0.000 |
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, \( \lambda = 206 \) nm) \( t_R = 12.1 \) min (minor), 13.1 min (major):

**Racemic 13c:**

![Graph showing HPLC analysis](Image)

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 12.042    | 49.314| 101377 | M    | 0.000 |
| 2    | 12.582    | 50.086| 90034  | M    | 0.000 |
| Total|           | 100.00| 191411 |      | 0.000 |

**13c from the Cu(OAc)$_2$/W8 reaction:**

![Graph showing HPLC analysis](Image)

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 12.086    | 5.145 | 51976  | M    | 0.000 |
| 2    | 13.111    | 94.855| 694801 | M    | 0.000 |
| Total|           | 100.00| 790777 |      | 0.000 |
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, \( \lambda = 190 \text{ nm} \)) \( t_R = 8.7 \text{ min (major)}, 10.3 \text{ min (minor)} \):

**Racemic 12d:**

![Racemic 12d chromatogram](image1)

| Peak | Ret. Time | Area\% | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 8.707     | 48.368 | 20117  | M    | 48.368|
| 2    | 10.364    | 51.632 | 19433  | M    | 51.632|
| Total|           | 100.000| 39550  |      | 100.000|

**12d from the Cu(OAc)$_2$/W8 reaction:**

![12d from Cu(OAc)$_2$/W8 chromatogram](image2)

| Peak | Ret. Time | Area\% | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 8.651     | 87.737 | 454671 | M    | 0.000 |
| 2    | 10.315    | 12.263 | 56670  | M    | 0.000 |
| Total|           | 100.000| 522541 |      | 0.000 |
Chiral HPLC analysis (Chiracel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 209 nm) tR = 11.3 min (major), 12.6 min (minor):

Racemic 12e:

![Chiral HPLC graph for racemic 12e]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 11.155    | 50.396| 213615 | M    | 0.000 |
| 2    | 12.457    | 45.604| 155616 | M    | 0.000 |
| Total|           | 100.00| 469453 |      | 0.000 |

12e from the Cu(OAc)₂/W8 reaction:

![Chiral HPLC graph for 12e from Cu(OAc)₂/W8 reaction]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 11.314    | 96.267| 280384 | M    | 96.267|
| 2    | 12.633    | 13.733| 51135  | M    | 13.733|
| Total|           | 100.00| 333222 |      | 100.00|
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 190$ nm) $t_R = 11.1$ min (major), 11.7 min (minor):

**Racemic 12f:**

12f from the Cu(OAc)$_2$/W8 reaction:
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) t<sub>R</sub> = 9.0 min (minor), 9.6 min (major):

**Racemic 12g:**

![Chiral HPLC graph for racemic 12g]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 9.982     | 51.740| 185680 | M    | 51.740|
| 2    | 9.634     | 48.260| 145818 | M    | 48.260|
| Total|           | 100.00| 331699 |      | 100.00|

**12g from the Cu(OAc)<sub>2</sub>/W8 reaction:**

![Chiral HPLC graph for 12g from Cu(OAc)<sub>2</sub>/W8 reaction]

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 9.982     | 23.067| 202239 | M    | 23.067|
| 2    | 9.562     | 76.933| 708796 | M    | 76.933|
| Total|           | 100.00| 991036 |      | 100.00|
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 258 nm) tR = 14.3 min (minor), 18.1 min (major):

Racemic 12h:

12h from the Cu(OAc)$_2$/W8 reaction:
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 190 nm) tR = 26.9 min (minor), 29.8 min (major):

Racemic 12i:

12i from the Cu(OAc)$_2$/W8 reaction:
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) tᵣ = 18.4 min (minor), 20.5 min (major):

**Racemic 12j:**

![Graph of Racemic 12j](image1)

| Peak | Ret. Time | Area % | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 18.304    | 51.871 | 49620  | M    | 0.000 |
| 2    | 20.402    | 48.129 | 37307  | M    | 0.000 |
| Total|           | 100.000| 87327  |      | 0.000 |

**12j from the Cu(OAc)₂/W8 reaction:**

![Graph of Cu(OAc)₂/W8 reaction](image2)

| Peak | Ret. Time | Area % | Height | Mark |
|------|-----------|--------|--------|------|
| 1    | 18.426    | 14.644 | 10430  | M    |
| 2    | 20.510    | 85.356 | 49691  | M    |
| Total|           | 100.000| 60121  |      |
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 10.0 min (minor), 11.4 min (major):

Racemic 12k:

![Graph of racemic 12k](image)

| Peak | Ret. Time | Area % | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 10.140    | 50.030 | 8151   | M    | 0.000 |
| 2    | 11.549    | 49.970 | 7961   | M    | 0.000 |
| Total|           | 100.000| 16112  |      | 0.000 |

12k from the Cu(OAc)₂/W8 reaction:

![Graph of Cu(OAc)₂/W8 reaction](image)

| Peak | Ret. Time | Area % | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 10.024    | 10.401 | 863    | M    | 0.000 |
| 2    | 11.412    | 89.599 | 5144   | M    | 0.000 |
| Total|           | 100.000| 7612   |      | 0.000 |
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, \( \lambda = 254 \text{ nm} \)) \( t_R = 11.9 \text{ min (minor), 15.1 min (major):} \)

**Racemic 12l:**

12l from the Cu(OAc)\(_2\)/W8 reaction:
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 220$ nm) $t_R = 10.1$ min (major), 10.7 min (minor):

**Racemic 12m:**

![Graph of Chiral HPLC analysis for racemic 12m](image)

| Peak | Ret. Time | Area % | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 9.966     | 52.848 | 9083 M |      | 0.000 |
| 2    | 10.543    | 47.152 | 9389 M |      | 0.000 |
| Total|           | 100.000| 18472 |      | 0.000 |

**12m from the Cu(OAc)$_2$/W8 reaction (Method B):**

![Graph of Chiral HPLC analysis for 12m from Cu(OAc)$_2$/W8](image)

| Peak | Ret. Time | Area % | Height | Mark | Conc. |
|------|-----------|--------|--------|------|-------|
| 1    | 10.062    | 95.273 | 872763 M |      | 95.273 |
| 2    | 10.741    | 4.727  | 61775 M |      | 4.727 |
| Total|           | 100.000| 934538 |      | 100.000 |
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 285 nm) tR = 24.0 min (minor), 32.6 min (major):

Racemic 12n:

![Chiral HPLC Chromatogram for Racemic 12n](image)

| Peak | Ret. Time | Area% | Height | Mark | Conc.  |
|------|-----------|-------|--------|------|--------|
| 1    | 23.956    | 52.108| 21285  | M    | 52.108 |
| 2    | 31.954    | 47.892| 14863  | M    | 47.892 |
| Total|           | 100.000| 36152 |      | 100.000|

12n from the Cu(OAc)2/W8 reaction:

![Chiral HPLC Chromatogram for 12n from Cu(OAc)2/W8](image)

| Peak | Ret. Time | Area% | Height | Mark | Conc.  |
|------|-----------|-------|--------|------|--------|
| 1    | 24.045    | 4.292 | 283    | M    | 4.292  |
| 2    | 32.647    | 95.708| 3525   | M    | 95.708 |
| Total|           | 100.000| 3613  |      | 100.000|
Chiral HPLC analysis (Chiralpak AD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 190 nm) t_R = 13.4 min (major), 14.7 min (minor):

Racemic 12o:

![Chiral HPLC trace and table for racemic 12o](image)

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 13.259    | 50.931| 508325 | M    | 50.531|
| 2    | 14.469    | 49.069| 498699 | M    | 49.069|
| Total|           | 100.000| 1005023|      | 100.000|

12o from the Cu(OAc)₂/W8 reaction:

![Chiral HPLC trace and table for 12o from Cu(OAc)₂/W8 reaction](image)

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 13.428    | 51.997| 309834 | M    | 51.957|
| 2    | 14.672    | 8.003 | 31327  | M    | 8.003 |
| Total|           | 100.000| 340561 |      | 100.000|
Chiral HPLC analysis (Chiralcel OD-3 x 190 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 190 nm) \( t_R = 13.6 \text{ min} \) (major), 16.4 min (minor):

**Racemic 12p:**

![Chiral HPLC Racemic 12p](chart1.png)

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 13.633    | 49.549| 299112 | M    | 0.000 |
| 2    | 16.347    | 50.451| 269835 | M    | 0.000 |
| Total| 100.000   | 566047|        |      | 0.000 |

**12p from the Cu(OAc)$_2$/W8 reaction:**

![Chiral HPLC Cu(OAc)$_2$/W8 Reaction](chart2.png)

| Peak | Ret. Time | Area% | Height | Mark | Conc. |
|------|-----------|-------|--------|------|-------|
| 1    | 13.605    | 92.354| 236268 | M    | 0.000 |
| 2    | 16.426    | 7.646 | 231693 | M    | 0.000 |
| Total| 100.000   | 259458|        |      | 0.000 |
Chiral HPLC analysis (Chiralpak AD-3 x 254 mm, heptane/isopropanol = 95/5, flow rate = 1.0 mL/min, $\lambda = 254$ nm) $t_R = 20.3$ min (minor), 22.1 min (major):

Racemic 12q:

12q from the Cu(OAc)$_2$/W8 reaction:
Chiral HPLC analysis (Chiralpak AD-3 x 220 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 17.7 min (minor), 19.2 min (major):

Racemic 12r:

12r from the Cu(OAc)₂/W8 reaction:
Chiral HPLC analysis (Chiralpak AD-3 x 210 mm, heptane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 210 nm) \( t_R = 26.6 \text{ min (major), 29.3 min (minor)} \):

**Racemic 12s:**

![Graph of Racemic 12s]

| Peak | Ret. Time | Area% | Height | Mark | Conc.  |
|------|-----------|-------|--------|------|-------|
| 1    | 26.333    | 53.325| 171652 | M    | 0.000 |
| 2    | 28.964    | 46.674| 150227 | M    | 0.000 |
| Total| 100.000   | 329919|        |      | 0.000 |

**12s from the Cu(OAc)$_2$/W8 reaction:**

![Graph of 12s from Cu(OAc)$_2$/W8 reaction]

| Peak | Ret. Time | Area% | Height | Mark | Conc.  |
|------|-----------|-------|--------|------|-------|
| 1    | 26.538    | 71.600| 185354 | M    | 0.000 |
| 2    | 29.276    | 28.400| 75477  | M    | 0.000 |
| Total| 100.000   | 260830|        |      | 0.000 |
Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 205$ nm) $t_R = 10.4$ min (minor), 11.1 min (major):

**Racemic 12t:**

![Graph 1](image1)

| Peak | Ret. Time | Area % | Height | Mark | Conc.  |
|------|-----------|--------|--------|------|-------|
| 1    | 10.273    | 48.961 | 117280 | M    | 48.961|
| 2    | 11.042    | 51.039 | 119555 | M    | 51.039|
| Total|           | 100.000| 226239 |      | 100.000|

**12t from the Cu(OAc)$_2$/W8 reaction:**

![Graph 2](image2)

| Peak | Ret. Time | Area % | Height | Mark | Conc.  |
|------|-----------|--------|--------|------|-------|
| 1    | 10.362    | 22.665 | 20738  | M    | 0.000 |
| 2    | 11.000    | 77.345 | 33662  | M    | 0.000 |
| Total|           | 100.000| 112694 |      | 0.000 |
Mechanistic Experiments (Scheme 3):

Figure SI-1. Proposed catalytic cycle

Hydrometalation of 11 by a W8CuH catalyst affords SI-2\(^8\) that adds to ketone 8 through a closed chair-like transition state\(^{2,6,9,10}\) providing branched intermediate SI-3. The addition step (SI-2 + 8 → SI-3) is likely stereodetermining, however, the enantiopurity of product 12 derived from this intermediate will be affected if this addition step were reversible. For instance, the subsequent silylation or migration steps of SI-3 for catalytic turnover affording products 12 or 13, respectively may enhance or erode the initial stereoselectivity set in the addition step since turnover of the initially formed diastereomeric mixture of SI-3 will proceed at different rates through diastereomeric transition states. Under this scenario, the addition step could be highly stereoselective providing SI-3 in high d.r., but if the minor diastereomer undergoes migration to SI-5 faster than the major one, overall poor enantioselectivity of 13 would be obtained, as was observed. This effect is exacerbated when using more sterically demanding ketones (e.g. propiophenone: \(R^1 = Et\)) whereby the migration rate would increase due to the enhanced Thorpe-Ingold effect while the silylation rate may decrease due to the increased steric demand. This can account for the increased amounts of 13 obtained when utilizing propiophenone.

Attempted retroallylation of 12a:

A crimp-cap vial with magnetic stir-bar was charged with 1.7 mg (0.0091 mmol) of CuI, 1.0 mg (0.0091 mmol) of KO\(\text{Bu}\), 2.6 mg (0.0091 mmol) of PCy\(_3\), and 0.20 mL of THF in the glove-box, and the resultant mixture
was allowed to stir for 30 min. Next, 12a (15.0 mg, 0.0607 mmol) was charged and the vial was sealed, removed from the glove-box, and allowed to stir at rt for 24 h. To the mixture was then added 0.2 mL of 50% aqueous NH₄OH and 1.0 mL of water followed by extraction with CH₂Cl₂ (2x1mL). The combined organics were dried with anhydrous Na₂SO₄ and concentrated in vacuo. The crude mixture was then analyzed by quantitative ¹H NMR spectroscopy using dimethyl fumarate as analytical standard.

**Synthesis of b-17:**

The Cu-catalyzed reductive coupling of N-allenyl pyrrolidinone and acetophenone (8a) was performed according to the Method A general procedure. The products were purified by silica gel chromatography (eluent: 0 – 30% EtOAc in CH₂Cl₂) to provide 35.5 mg (58%) of b-17 as a white solid as a single diastereomer and 22.0 mg (36%) of l-17 as a thick oil. The enantiopurity of b-17 was determined by chiral HPLC analysis relative to authentic racemic material prepared using PCy₃ as ligand in the reductive coupling reaction. The stereochemistry of b-17 was assigned by analogy to that of 12a.

**1-((3S,4S)-4-hydroxy-4-phenylpent-1-en-3-yl)pyrrolidin-2-one (b-17):**

$R_f = 0.40$ (30% EtOAc/CH₂Cl₂). ¹H NMR (CDCl₃, 600 MHz) $\delta$: 7.46 (d, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 8.2$ Hz, 2H), 7.22 (t, $J = 7.4$ Hz, 1H), 6.37 (dd, $J = 18.1$ Hz, $J = 9.6$ Hz, 8.50 Hz, 1H), 6.33 (s, 1H), 5.36 (d, $J = 9.6$ Hz, 1H), 5.24 (d, $J = 17.4$ Hz, 1H), 3.92 (d, $J = 8.4$ Hz, 1H), 3.32 (dt, $J = 10.8$ Hz, 6.9 Hz, 1H), 2.88 (dt, $J = 12.4$ Hz, 5.5 Hz, 1H), 2.17 (dd, $J = 17.6$ Hz, $J = 10.0$ Hz, $J = 7.8$ Hz, 1H), 2.02 (dd, $J = 17.3$ Hz, $J = 10.0$ Hz, $J = 6.5$ Hz, 1H), 1.72 – 1.82 (m, 1H), 1.53 – 1.61 (m, 1H), 1.50 (s, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃): $\delta$ 176.4, 146.7, 131.3, 127.9, 126.6, 124.6, 119.4, 76.75, 70.3, 50.6, 31.6, 28.5, 18.9 ppm. HRMS (DART) m/z calcd for C₁₅H₂₀NO₂ [M + H]⁺: 246.1494; Found [M + H]⁺: 246.1485.

**Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, $\lambda = 190$ nm) $t_R = 14.9$ min (minor), 16.0 min (major):**
Racemic $b$-17:

A crimp-cap vial with magnetic stir-bar was charged with 2.3 mg (0.012 mmol) of CuI, 1.4 mg (0.012 mmol) of KO$_2$Bu, 0.012 mmol of ligand (W8 or PCy$_3$), and 0.50 mL of THF in the glove-box, and the resultant mixture was allowed to stir for 30 min. Next, $b$-17 (30.0 mg, 0.122 mmol) was charged and the vial was sealed, removed from the glove-box, and allowed to stir at rt for 24 h. To the mixture was then added 0.5 mL of 50% aqueous NH$_4$OH and 1.0 mL of water followed by extraction with EtOAc (3x2mL). The combined organics were dried with anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude mixture was then analyzed by quantitative $^1$H NMR spectroscopy using dimethyl fumarate as analytical standard to determine the amounts of $b$-17, $l$-17, 8a, 18, and 19. The identity of N-allyl pyrrolidine-2-one (18)$^4$ and (Z)-N-propenyl pyrrolidine-2-one (19)$^3$ were confirmed in relation to authentic material. The enantiopurity of recovered $b$-17 (silica gel chromatography) was determined by chiral HPLC analysis.

$b$-17 from the Cu(OAc)$_2$/W8 reaction:

Retroallylation experiments employing $b$-17:

A crimp-cap vial with magnetic stir-bar was charged with 2.3 mg (0.012 mmol) of CuI, 1.4 mg (0.012 mmol) of KO$_2$Bu, 0.012 mmol of ligand (W8 or PCy$_3$), and 0.50 mL of THF in the glove-box, and the resultant mixture was allowed to stir for 30 min. Next, $b$-17 (30.0 mg, 0.122 mmol) was charged and the vial was sealed, removed from the glove-box, and allowed to stir at rt for 24 h. To the mixture was then added 0.5 mL of 50% aqueous NH$_4$OH and 1.0 mL of water followed by extraction with EtOAc (3x2mL). The combined organics were dried with anhydrous Na$_2$SO$_4$ and concentrated in vacuo. The crude mixture was then analyzed by quantitative $^1$H NMR spectroscopy using dimethyl fumarate as analytical standard to determine the amounts of $b$-17, $l$-17, 8a, 18, and 19. The identity of N-allyl pyrrolidine-2-one (18)$^4$ and (Z)-N-propenyl pyrrolidine-2-one (19)$^3$ were confirmed in relation to authentic material. The enantiopurity of recovered $b$-17 (silica gel chromatography) was determined by chiral HPLC analysis.
Reaction using W8 as ligand:

44% $b$-$17$ (70:30 er); 3% $l$-$17$; 28% acetophenone ($8a$); 23% $N$-allyl pyrrolidine-2-one ($18$); and 19% ($Z$)-$N$-propenyl pyrrolidine-2-one ($19$)

$^1$H NMR (CDCl$_3$, 600 MHz) of the unpurified reaction mixture:

Re-isolated $b$-$17$ from the CuI/W8/KO$_2$Bu reaction:

Chiral HPLC analysis (Chiralcel OD-3 x 250 mm, heptane/isopropanol = 90/10, flow rate = 1.0 mL/min, $\lambda$ = 190 nm)
Reaction using PC\textsubscript{3} as ligand:

0\% \textit{b}-17; 43\% \textit{l}-17; 32\% acetophenone (8a); 19\% \(N\)-allyl pyrrolidine-2-one (18); and 15\% (Z)-\(N\)-propenyl pyrrolidine-2-one (19)

\(^1\)H NMR (CDCl\textsubscript{3}, 600 MHz) of the unpurified reaction mixture:

A proposed mechanism is outlined in Figure SI-2. Alcohol exchange leads to SI-8 that upon retroallylation to release acetophenone (8a) affords \(N\)-allyl Cu-complex \textit{l}-SI-9 that can equilibrate to \textit{b}-SI-9. Reaction of \textit{b}-SI-9 with acetophenone leads to formation of linear isomer \textit{l}-17 whereas reaction of \textit{l}-SI-9 with acetophenone regenerates \textit{b}-17 rationalizing the change in er for recovered \textit{b}-17 observed in this experiment. Protonolysis of \textit{l}-SI-9 and \textit{b}-SI-9 is proposed to occur through chair-like transition states SI-TS1 and SI-TS2, respectively. The exclusive formation of the Z-stereoisomer of 19 in these experiments strongly suggests this type of protonolysis pathway that is similar to that for the addition of related analogues of \textit{b}-SI-9 to ketone electrophiles providing Z-enamides.\(^6,7\) However, direct protonolysis of \textit{l}-SI-9 and \textit{b}-SI-9 cannot be ruled out.
Figure SI-2. Proposed Retroallylation Mechanism.

Analysis of product 12a enantiopurity throughout the progress of the reaction:

Three reactions were setup at the same time according to the Method A general procedure utilizing 9.7 μL (10 mg, 0.083 mmol) of acetophenone. Each reaction was quenched and worked up at different time points and 12a was isolated and the enantiopurity determined (Table SI-4). The enantiopurity did not vary over time.

Table SI-4: Enantiopurity of 12a vs Time.

| Entry | Reaction time (h) | %12a<sup>a</sup> | 12a:13a<sup>b</sup> | Er of 12a<sup>c</sup> |
|-------|------------------|-----------------|-------------------|-------------------|
| 1     | 6                | 17              | 67:33             | 93:7              |
| 2     | 12               | 30              | 68:32             | 93:7              |
| 3     | 19               | 53              | 70:30             | 93:7              |

<sup>a</sup>Yield of 12a determined by quantitative <sup>1</sup>H NMR spectroscopy on the unpurified reaction mixture using dimethyl fumarate as the analytical standard. <sup>b</sup>The ratio was determined by <sup>1</sup>H NMR spectroscopic analysis on the unpurified reaction mixture. <sup>c</sup>Enantiomeric ratios were determined by chiral HPLC analysis on purified material (flash chromatography).
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NMR Data:

**1H NMR (CDCl₃), 600 MHz**

![1H NMR spectrum of compound 12a]

**13C NMR (CDCl₃), 151 MHz**

![13C NMR spectrum of compound 12a]
$^{1}H$ NMR (CDCl$_3$), 600 MHz

$^{13}C$ NMR (CDCl$_3$), 151 MHz
$^1$H NMR (CDCl$_3$), 600 MHz

$^{13}$C NMR (CDCl$_3$), 151 MHz

Current Data Parameters

OBSNR: 8K2-027
EXPFO: 6
FRODO: 1

F2 - Acquisition Parameters
Date: 20210531
Time: 15:25 h
INSTROM: agilent
PRESID: 2148659_0003
FULPROG: zg30
TD: 65536
SOLVENT: CDCl$_3$
NS: 16
DS: 2
SNR: 12019, 230 Hz
FOURS: 0, 206798 Hz
AQ: 2.7566976 sec
MU: 1, 191.
DM: 41.600 ussec
GR: 6.80 usec
TE: 99.3 Hz
DI: 1.0000000 sec
TD2: 1
DF1: 600.008750 MHz
NUC1: 1H
DF2: 15.50 ussec
PLM1: 13.23000035 W

F2 - Processing parameters
SI: 65536
SF: 600.0050161 MHz
NUME: EM
ZEB: 0
LE: 0.30 Hz
GB: 0
PC: 1.00

Current Data Parameters

OBSNR: 8K2-027
EXPFO: 6
FRODO: 1

F2 - Acquisition Parameters
Date: 20210531
Time: 15:25 h
INSTROM: agilent
PRESID: 2148659_0003
FULPROG: zg30
TD: 65536
SOLVENT: CDCl$_3$
NS: 16
DS: 2
SNR: 12019, 230 Hz
FOURS: 0, 206798 Hz
AQ: 2.7566976 sec
MU: 1, 191.
DM: 41.600 ussec
GR: 6.80 usec
TE: 99.3 Hz
DI: 1.0000000 sec
TD2: 1
DF1: 600.008750 MHz
NUC1: 1H
DF2: 15.50 ussec
PLM1: 13.23000035 W

F2 - Processing parameters
SI: 65536
SF: 600.0050161 MHz
NUME: EM
ZEB: 0
LE: 0.30 Hz
GB: 0
PC: 1.00
$^1$H NMR (CDCl$_3$), 600 MHz

$^{13}$C NMR (CDCl$_3$), 151 MHz
1H NMR (CDCl₃), 600 MHz

13C NMR (CDCl₃), 151 MHz
$^1$H NMR (CDCl$_3$), 600 MHz

$^{13}$C NMR (CDCl$_3$), 151 MHz

Current Data Parameters
NAME: RKE2-113
EXPNO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date_ 20210415
Time 16:51 h
INSTRUM spect
PROCED E146858_0003
POLPROG 2pg30
TO 6536
SOLVENT CDCl$_3$
NS 20
DS 2
SNR 32015.230 Hz
FOURNES 0.366798 Hz
AQ 2.7362976 sec
MG 14.94 sec
DM 41.600 usec
DB 6.50 usec
TE 296.6 K
TD 2.0000000 sec
TDO 1
SFOIL 600.000000 MHz
NUC1 1H
P1 15.50 usec
PW1 13.233000035 W

F2 - Processing parameters
SI 6536
SF 600.0000000 MHz
KOW 2M
SSB 0
LS 0.30 Hz
GB 0
PC 1.00
$^{19}$F NMR (CDCl$_3$) 565 MHz

$^1$H NMR (CDCl$_3$), 600 MHz
$^{13}$C NMR (CDCl$_3$), 151 MHz

$^1$H NMR (CDCl$_3$), 600 MHz
$^{13}$C NMR (CDCl$_3$), 151 MHz

$^{1}H$ NMR (CDCl$_3$), 600 MHz
$^{13}$C NMR (CDCl$_3$), 151 MHz

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

$^1$H NMR (CDCl$_3$), 600 MHz

![$^1$H NMR spectrum](image)
$^{13}$C NMR (CDCl$_3$), 151 MHz

$^1$H NMR (CDCl$_3$), 600 MHz
$^{13}$C NMR (CDCl$_3$), 151 MHz

$^1$H NMR (CDCl$_3$), 600 MHz
$^{13}$C NMR (CDCl$_3$), 151 MHz

$^1$H NMR (CDCl$_3$), 600 MHz

Current Data Parameters
NAME: rkk2-153_2
EMPRO: 1
PROCND: 1
F2 - Acquisition Parameters
Date: 20210416
Time: 9:38 h
INSTRUM: spect
PROCND: 2146858_0002 1
FIDPROG: 3545
SOVLEN: CDCl$_3$
OFF
SNR: 30231,883 Hz
FIDRES: 1.123759 mm
AQ: 0.949996 usec
BG: 199.73
DM: 13.800 usec
tE: 298.1 K
D1: 2.00000000 sec
T2: 0.50000000 sec
RFQ: 150.884444 Hz
NCH: 15
F1: 17,72 usec
PLFW: 77,6568786 W
RFQ2: 600.00740000 Hz
NCH2: 3500
CDSPPG: 1
CDS: 10.00 usec
FLW2: 13,23200055 W
FLW3: 0.847699 W
RFQ1: 0.2084000 W
F2 - Processing parameters
SI: 32768
SF: 150.8773773 Hz
WOM: EM
CS: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
13C NMR (CDCl3), 151 MHz

19F NMR (CDCl3) 565 MHz
$^{1}H$ NMR (CDCl$_3$), 600 MHz

$^{13}C$ NMR (CDCl$_3$), 151 MHz
**1H NMR (CDCl₃), 600 MHz**

![1H NMR spectrum](image)

**13C NMR (CDCl₃), 151 MHz**

![13C NMR spectrum](image)
S64

1H NMR (CDCl₃), 600 MHz

13C NMR (CDCl₃), 151 MHz
$^{13}$C NMR (CDCl$_3$), 151 MHz

$^1$H NMR (CDCl$_3$), 600 MHz
1H NMR (CDCl₃), 600 MHz

13C NMR (CDCl₃), 151 MHz
$^1$H NMR (CDCl$_3$), 600 MHz

$^{13}$C NMR (CDCl$_3$), 151 MHz
$^1$H NMR (CDCl₃), 600 MHz

12t

$^{13}$C NMR (CDCl₃), 151 MHz

12t

Current Data Parameters
NAME  jdsz-074
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Data_ 20201003
Time 12:26 h
INSTROM spect
PROCNR 1595801_0104
PULPROG ze30
TD 65536
SOLVENT CDCl₃
NS 16
JW 2
DMR 12019.25 Hz
FDRES 0.364794 Hz
AQ 2.7262976 sec
BG 194.75 Hz
DW 41600 usec
GE 6.20 usec
TE 296.1 K
D1 2.0000000000 sec
d0 599.956047 MHz
NN1 18
P1 9.79 usec
PLW1 11.99499589 W

F2 - Processing parameters
SI 61056
SP 595.015015 MHz
NOW EM
SUB 0.30 Hz
TR 1.00
$^1$H NMR (CDCl₃), 600 MHz

$^{13}$C NMR (CDCl₃), 151 MHz
$^{1}H$ NMR (CD$_{3}$Cl), 600 MHz

$^{13}C$ NMR (CD$_{3}$Cl), 151 MHz
$^{1}H$ NMR (CDCl$_3$), 600 MHz

$^{13}C$ NMR (CDCl$_3$), 151 MHz

Current Data Parameters
NAME: REMK2-M009
EXPNM: 1
PROCNO: 1

F2 - Acquisition Parameters
Date: 20200906
Time: 13:10 h
INSTRUM: spect
PROCNO: 2148568_0003 (1)
PULFREQ: 2530
TD: 65536
SOLVENT: CDCl$_3$
NS: 20
DS: 2
SWH: 12019.230 Hz
FIDRES: 0.369798 Hz
AQ: 2.7952395 sec
NQ: 199,73
NW: 41600 usec
DE: 6.50 usec
TE: 29.0 K
DI: 1.0000000000 sec
TD: 1
SFQ: 600.0007050 MHz
NQCI: 1H
F1: 15.00 usec
PLM1: 13.232000035 W

F2 - Processing parameters
SI: 65536
SF: 600.000517 MHz
WOW: HM
SSB: 0
LB: 0.30 Hz
UB: 0
PC: 1.00
$^1$H NMR (CDCl$_3$), 600 MHz

$^{13}$C NMR (CDCl$_3$), 151 MHz
$^1$H NMR (CDCl$_3$), 600 MHz

$^{13}$C NMR (CDCl$_3$), 151 MHz