SUPPORTING INFORMATION

Allylic Azide Rearrangement: Achieving Selectivity.

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General Information. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX- 400, AMX-500 or AMX-600 spectrometers in CDCl_3 with CHCl_3 (7.27 ppm for ^1H , 77ppm for ^{13}C) as a standard. Reagents and solvents were purchased from Aldrich, Acros or GFS and used without purification.

Typical experimental procedure for the Cu(I)-catalyzed triazole synthesis (products 2, 4, 6, 8, 10, 12):

Allylic azide (1 mmol) was mixed with phenylacetylene (1 mmol) in 1:1 mixture of $t\text{BuOH}:\text{H}_2\text{O}$ (2 ml) at room temperature (usually 23°C). To this mixture was added $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (0.05 mmol) and sodium ascorbate (0.10 mmol). The reaction was stirred overnight, then extracted with ethyl acetate, washed twice with dilute aqueous ammonium hydroxide and once with brine. The aqueous layer was back extracted once into ethyl acetate. The organic layers were combined, dried over MgSO_4 , and evaporated to dryness.

Typical experimental procedure A for the synthesis of azidoepoxides 13, 15, 17:

To an allylic azide (1 mmol) was added 0.3M aqueous solution of NaHCO_3 (7.5 ml) at room temperature. The inhomogeneous mixture was stirred vigorously and $m\text{-CPBA}$ (70%, 1.1 mmol) was added slowly as a solid. The reaction was stirred for 2-8 hours; progress was monitored by TLC. Upon completion the reaction was extracted three times into diethyl ether, washed twice with 10% aqueous NaOH , dried over MgSO_4 and evaporated.

Typical experimental procedure B for the synthesis of azidoepoxides 14, 16, 18:

Allylic azide (1 mmol) was dissolved in dry CH_2Cl_2 (3 ml). To the mixture was added dry $m\text{-CPBA}$ (1.3 mmol) portionwise as a solid. The reaction was stirred overnight; progress was monitored by TLC. Upon completion the mixture was diluted with more CH_2Cl_2 and washed twice with 10% aqueous NaOH , dried over MgSO_4 and evaporated.

Compound Characterization Data.

3-Methyl-but-2-enylazide (1a) and 1,1-Dimethyl-allylazide (1b): ^1H NMR (500MHz, CDCl_3): 5.93 (dd, $J = 17.6\text{Hz}$, $J = 10.6\text{Hz}$, 0.43H, **1b**); 5.41 (t, $J = 7.3\text{Hz}$, 1H, **1a**); 5.31 (d, $J = 17.6\text{Hz}$, 0.43H, **1b**); 5.24 (d, $J = 10.6\text{Hz}$, 0.43H, **1b**); 3.83 (d, $J = 7.3\text{Hz}$, 2H, **1a**); 1.88 (s, 3H, **1a**); 1.79 (s, 3H, **1a**); 1.42 (s, 2.58H, **1b**); ^{13}C NMR (500MHz, CDCl_3): 141.0; 139.5; 117.2; 113.7; 48.0; 32.5; 25.9; 25.9; 17.9.

1-(3-Methyl-but-2-enyl)-4-phenyl-1H-[1,2,3]triazole (2): ^1H NMR (500MHz, CDCl_3): 7.82 (d, $J = 7.0\text{Hz}$, 2H); 7.77 (s, 1H); 7.40 (dd, $J = 7.0\text{Hz}$, $J = 7.3\text{Hz}$, 2H); 7.31 (t, $J = 7.3$, 1H); 5.47 (t, $J = 7.3\text{Hz}$, 1H); 4.96 (d, $J = 7.3\text{Hz}$, 2H); 1.81 (s, 6H); ^{13}C NMR (500MHz, CDCl_3): 139.9; 130.8; 128.7; 127.9; 125.6; 119.1; 117.2; 48.0; 25.6; 18.0. EMS: $m/z = 214.2$ $[\text{M}+\text{H}]^+$, calcd 214.1 $[\text{M}+\text{H}]^+$.

(E, Z)-4-Azido-2-methyl-but-2-en-1-ol (3a) and 2-azido-2-methyl-but-3-en-1-ol (3b): ^1H NMR (500MHz, CDCl_3): 5.84 (dd, $J = 13.9\text{Hz}$, $J = 10.6\text{Hz}$, 0.82H, **3b**); 5.62 (t, $J = 5.8\text{Hz}$, 1H, **3a trans**); 5.46 (t, $J = 6.6\text{Hz}$, 0.17H, **3a cis**); 5.36 (d, $J = 13.9\text{Hz}$, 0.82H, **3b**); 5.34 (d, $J = 8.8\text{Hz}$, 0.82H, **3b**); 4.18 (s, 0.34H, **3a cis**); 4.01 (s, 2H, **3a trans**); 3.84 (d, $J = 5.8\text{Hz}$, 2H **3a trans**, 0.34H **cis**); 3.50 (d, $J = 9.5\text{Hz}$, 0.82H, **3b**); 3.47 (d, $J = 9.5\text{Hz}$, 0.82H, **3b**); 1.76 (s, 0.51H, **3a cis**); 1.73 (s, 3H, **3a trans**); 1.40 (s, 2.46H, **3b**); ^{13}C NMR (500MHz, CDCl_3): 141.6; 136.97; 120.2; 117.2; 117.0; 115.6; 68.7; 67.4; 66.1; 61.2; 47.5; 29.2; 19.6; 18.7; 13.7.

(E, Z)-2-Methyl-4-(4-phenyl-[1,2,3]triazol-1-yl)-but-2-en-1-ol (4): ^1H NMR (500MHz, CDCl_3): 7.80 (m, 3.6H *cis-trans*); 7.41 (dd, $J = 7.0\text{Hz}$, $J = 7.3\text{Hz}$, 2.4H *cis-trans*); 7.33 (t, $J = 7.0$, 1.2H *cis-trans*); 5.77 (t, $J = 6.9\text{Hz}$, 1H *trans*); 5.57 (t, $J = 7.7\text{Hz}$, 0.10H *cis*); 5.08 (d, $J = 7.7\text{Hz}$, 0.2H *cis*); 5.05 (d, $J = 6.9\text{Hz}$, 2H *trans*); 4.32 (s, 0.2H *cis*); 4.12 (s, 2H *trans*); 1.88 (s, 0.6H *cis*); 1.82 (s, 3H *trans*); ^{13}C NMR (400MHz, CDCl_3): 147.7; 142.6; 142.2; 130.3; 128.7; 128.11; 125.5; 119.4; 119.3; 116.2; 66.8; 61.3; 47.6; 47.3; 21.6; 13.8. EMS: $m/z = 230.1$ $[\text{M}+\text{H}]^+$, calcd 230.1 $[\text{M}+\text{H}]^+$.

1,3-Dimethyl-but-2-enylazide (5a) and (E, Z)-1,1-dimethyl-but-2-enylazide (5b): ^1H NMR (500MHz, CDCl_3)(*trans*-**5b** only): 5.67 (dq, $J = 15.4\text{Hz}$, $J = 6.6\text{Hz}$, 0.53H, **5b**); 5.51 (d, $J = 15.4\text{Hz}$, 0.53H, **5b**); 5.14 (d, $J = 8.0\text{Hz}$, 1H, **5a**); 4.28 (dq, $J = 8.0\text{Hz}$, $J = 6.6\text{Hz}$, 1H, **5a**); 1.78 (s, 3H, **5a**); 1.75 (d, $J = 6.6\text{Hz}$, 1.59H, **5b**); 1.72 (s, 3H, **5a**); 1.32 (s, 3.18H, **5b**); 1.21 (d, $J = 6.6\text{Hz}$, 3H, **5a**); ^{13}C NMR (500MHz, CDCl_3): 130.8; 130.3; 124.2; 123.4; 62.3; 59.9; 25.6; 22.1; 18.2.

1-(1,3-Dimethyl-but-2-enyl)-4-phenyl-1H-[1,2,3]triazole (6): ^1H NMR (500MHz, CDCl_3): 7.84 (d, $J = 7.0\text{Hz}$, 2H); 7.75 (s, 1H); 7.41 (dd, $J = 7.0\text{Hz}$, $J = 7.3\text{Hz}$, 2H); 7.32 (t, $J = 7.3\text{Hz}$, 1H); 5.47 (m, 2H); 1.80 (s, 3H); 1.75 (s, 3H); 1.68 (d, $J = 6.3\text{Hz}$, 3H); ^{13}C NMR (400MHz, CDCl_3): 138.2; 130.8; 128.7; 127.8; 125.5; 123.6; 117.4; 117.3; 54.7; 25.6; 22.1; 18.2. EMS: $m/z = 228.1$ $[\text{M}+\text{H}]^+$, calcd 228.1 $[\text{M}+\text{H}]^+$.

2-Azido-4-methyl-pent-3-en-1-ol (7a) and 4-azido-4-methyl-pent-2-en-1-ol (7b): ^1H NMR (500MHz, CDCl_3): 5.84 (dt, $J = 15.5\text{Hz}$, $J = 5.1\text{Hz}$, 0.22H, **7b**); 5.75 (d, $J = 15.5\text{Hz}$, 0.22H, **7b**); 5.15 (d, $J = 9.5\text{Hz}$, 1H, **7a**); 4.35 (m, 1H, **7a**); 4.21 (d, $J = 5.1\text{Hz}$, 0.44H, **7b**); 3.54 (m, 2H, **7a**); 1.83 (s, 3H, **7a**); 1.78 (s, 3H, **7a**); 1.36 (s, 1.32H, **7b**); ^{13}C NMR (500MHz, CDCl_3): 141.1; 134.6; 128.9; 118.5; 65.3; 63.1; 61.9; 29.9; 26.6; 26.0; 18.9.

4-Methyl-2-(4-phenyl-[1,2,3]triazol-1-yl)-pent-3-en-1-ol (8): ^1H NMR (400MHz, CDCl_3): 7.71 (s, 1H); 7.61 (d, $J = 7.0\text{Hz}$, 2H); 7.31 (m, 3H); 5.54 (d, $J = 9.1\text{Hz}$, 1H); 5.32 (m, 1H); 4.62 (br s, 1H); 4.07 (m, 2H); 1.79 (s, 3H); 1.71 (s, 3H); ^{13}C NMR (400MHz, CDCl_3): 146.9; 140.6; 130.4; 128.9; 128.2; 125.7; 119.8; 118.6; 65.2; 61.2; 25.7; 18.6. EMS: $m/z = 244.1$ $[\text{M}+\text{H}]^+$, calcd 244.1 $[\text{M}+\text{H}]^+$.

(E, Z)-But-2-enylazide (9a) and 1-methyl-allylazide (9b): ^1H NMR (500MHz, CDCl_3): 5.75 (m, 1.17H **9a cis-trans**, 0.57H **9b**); 5.54 (m, 1.17H, **9a cis-trans**); 5.26 (d, $J = 17.9\text{Hz}$, 0.57H, **9b**); 5.21 (d, $J = 10.3\text{Hz}$, 0.57H, **9b**); 3.99 (m, 0.17H, **9b**); 3.82 (d, $J = 7.3\text{Hz}$, 0.34H, **9a cis**); 3.68 (d, $J = 6.6\text{Hz}$, 2H, **9a trans**); 1.75 (d, $J = 6.2\text{Hz}$, 3H, **9a trans**); 1.70 (d, $J = 6.2\text{Hz}$, 0.51H, **9a cis**); 1.27 (d, $J = 6.6\text{Hz}$, 1.71H, **9b**); ^{13}C NMR (500MHz, CDCl_3): 136.8; 131.3; 123.9; 116.7; 116.6; 59.5; 52.6; 19.3; 17.4.

(E,Z)-1-But-2-enyl-4-phenyl-1H-[1,2,3]triazole and 1-(1-methyl-allyl)-4-phenyl-1H-[1,2,3]-triazole: ^1H NMR (500MHz, CDCl_3): 7.85 (d, $J = 7.7\text{Hz}$, 2.36H **10a cis-trans**, 0.92H **10b**); 7.80 (s, 1.18H **10a cis-trans**, 0.46H **10b**); 7.43 (dd, $J = 7.7\text{Hz}$, $J = 7.3\text{Hz}$, 2.36H **10a cis-trans**, 0.92H **10b**); 7.34 (t, $J = 7.3\text{Hz}$, 1.18H **10a cis-trans**, 0.46H **10b**); 6.10 (ddd, $J = 16.7\text{Hz}$, $J = 10.6\text{Hz}$, $J = 5.9\text{Hz}$, 0.46H, **10b**); 5.88 (m, 1.17H, **10a cis-trans**); 5.73 (m, 1.17H, **10a cis-trans**); 5.33 (d, $J = 10.6\text{Hz}$, 0.46H, **10b**); 5.31 (m, 0.46H, **10b**); 5.29 (d, $J = 16.7\text{Hz}$, 0.46H, **10b**); 5.07 (d, $J = 6.9\text{Hz}$, 0.36H, **10a cis**); 4.96 (d, $J = 6.6\text{Hz}$, 2H, **10a trans**); 1.83 (d, $J = 6.9\text{Hz}$, 0.54H, **10a cis**); 1.78 (d, $J = 6.2\text{Hz}$, 3H, **10a trans**); 1.75 (d, $J = 6.9\text{Hz}$, 1.38H, **10b**); ^{13}C NMR (500MHz, CDCl_3): 147.6; 136.7; 132.3; 130.1; 130.6; 128.7; 127.9; 125.5; 124.0; 122.7; 119.3; 117.5; 58.6; 52.2; 46.6; 20.1; 17.6; 13.0. EMS: $m/z = 200.2$ $[\text{M}+\text{H}]^+$, calcd 200.1 $[\text{M}+\text{H}]^+$.

4-azido-but-2-en-1-ol (11a) and 2-azido-but-3-en-1-ol (11b): ^1H NMR (400MHz, CDCl_3): 5.93 (dt, $J = 16.7\text{Hz}$, $J = 5.3\text{Hz}$, 0.82H, **11a**); 5.82 (m, 0.82H, **11a**); 5.76 (dd, $J = 11.4\text{Hz}$, $J = 5.5\text{Hz}$, 1H, **11b**); 5.41 (d, $J = 11.4\text{Hz}$, 1H, **11b**); 5.38 (d, $J = 15.5\text{Hz}$, 1H, **11b**); 4.20 (d, $J = 5.3\text{Hz}$, 1.64H, **11a**); 4.07 (m, 1H, **11b**); 3.80 (d, $J = 6.2\text{Hz}$, 1.64H, **11a**); 3.66 (dd, $J = 11.4\text{Hz}$, $J = 4.4\text{Hz}$, 1H, **11b**); 3.55 (dd, $J = 11.4\text{Hz}$, $J = 7.3\text{Hz}$, 1H, **11b**); ^{13}C NMR (400MHz, CDCl_3): 134.2; 131.9; 124.1; 120.3; 66.3; 64.5; 62.5; 52.1.

4-(4-Phenyl-[1,2,3]triazol-1-yl)-but-2-en-1-ol (12a) and 2-(4-Phenyl-[1,2,3]triazol-1-yl)-but-3-en-1-ol (12b): ^1H NMR (500MHz, CDCl_3): 7.79 (m, 3H **12a**, 3H **12b**); 7.40 (dd, $J = 8.0\text{Hz}$, $J = 7.3\text{Hz}$, 2H **12a**, 2H **12b**); 7.34 (m, 1H **12a**, 1H **12b**); 6.12 (ddd, $J = 16.7\text{Hz}$, $J = 10.6\text{Hz}$, $J = 5.9\text{Hz}$, 1H, **12b**); 5.95 (bs, 2H, **12a**); 5.42 (d, $J = 10.6\text{Hz}$, 1H, **12b**); 5.32 (d, $J = 17.2\text{Hz}$, 1H, **12b**); 5.15 (bs, 2H, **12b**); 4.99 (bs, 2H, **12a**); 4.24 (m, 2H **12a**, 1H **12b**); 4.13 (m, 1H, **12b**); ^{13}C NMR (400MHz, CDCl_3): 147.8; 147.2; 135.4; 132.4; 130.2; 130.1; 128.7; 128.7; 128.1; 128.14; 125.5; 125.5; 123.2; 120.2; 119.9; 119.5; 65.5; 64.1; 61.9; 51.7. EMS: $m/z = 216.1$ $[\text{M}+\text{H}]^+$, calcd 216.1 $[\text{M}+\text{H}]^+$.

C-(3,3-Dimethyl-oxiranyl)-methylazide (13a): ^1H NMR (400MHz, CDCl_3): 3.44 (m, 2H, **13a**); 2.98 (t, $J = 4.7\text{Hz}$, 1H, **13a**); 1.37 (s, 3H, **13a**); 1.33 (s, 3H, **13a**); ^{13}C NMR (400MHz, CDCl_3): 61.29; 58.51; 50.72; 24.73; 19.03;

(3-Aminomethyl-2-methyl-oxiranyl)-methanol (14a) and 2-Amino-2-oxiranyl-propan-1-ol (14b): ^1H NMR (400MHz, CDCl_3): 3.87 (m, 0.11H, **14b**); 3.72 (d, $J = 11.7\text{Hz}$, 1H, **14a**); 3.64 (d, $J = 11.7\text{Hz}$, 1H, **14a**); 3.46 (m, 2H, **14a**); 3.31 (dd, $J = 6.2\text{Hz}$, $J = 5.6\text{Hz}$, 1H, **14a**); 3.10 (dd, $J = 5.3\text{Hz}$, $J = 5.0\text{Hz}$, 0.11H, **14b**); 3.00 (d, $J = 4.7\text{Hz}$, 0.1, 1H, **14b**); 2.68 (m, 0.11H, **14b**); 1.42 (s, 0.33H, **14b**); 1.34 (s, 3H, **14a**); ^{13}C NMR (400MHz, CDCl_3): 64.5; 60.7; 57.0; 49.9; 14.2.

1-(3,3-Dimethyl-oxiranyl)-ethylazide (15a) and 1-methyl-1-(3-methyl-oxiranyl)-ethylazide (15b): ^1H NMR (600MHz, CDCl_3) (**15a** is a 50:50 mixture of diastereomers): 3.33 (m, 1H, **15a**); 3.06 (m, 0.11H, **15b**); 2.77 (d, $J = 8.3\text{Hz}$, 0.5H, **15a**); 2.70 (m, 0.11H, **15b**); 2.66 (d, $J = 8.7\text{Hz}$, 0.5H, **15a**); difficult attribution for CH_3 ; ^{13}C NMR (600MHz, CDCl_3): 66.4; 65.4; 57.9; 56.2; 24.6; 24.5; 19.0; 18.9; 17.4; 16.5.

2-Azido-2-(3,3-dimethyl-oxiranyl)-ethanol (16a) and [3-(1-Azido-1-methyl-ethyl)-oxiranyl]-methanol (16b): ^1H NMR (400MHz, CDCl_3) (**16a** is a 60:40 mixture of diastereomers): 3.96 (m, 0.12H, **16b**); 3.89 (dd, $J = 11.6\text{Hz}$, $J = 3.5\text{Hz}$, 1H, **16a**); 3.89 (dd, $J = 11.6\text{Hz}$, $J = 6.4\text{Hz}$, 1H, **16a**); 3.69 (dd, $J = 11.4\text{Hz}$, $J = 4.7\text{Hz}$ 0.66H, **16a**); 3.65 (dd, $J = 11.4\text{Hz}$, $J = 6.4\text{Hz}$ 0.66H, **16a**); 3.45 (m, 0.66H, **16a**); 3.38 (m, 1H, **16a**); 3.23 (m, 0.06H, **16b**); 3.05 (d, $J = 2.3\text{Hz}$, 0.06H, **16b**); 2.91 (d, $J = 8.8\text{Hz}$, 0.66H, **16a**); 2.86 (d, $J = 9.1\text{Hz}$, 1H, **16a**); 1.41 (s, 3H, **16a**); 1.40 (s, 3H, **16a**); 1.37 (s, 1.98H, **16a**); 1.35 (s, 1.98H, **16a**); 1.34 (s, 0.18H, **16b**); 1.32 (s, 0.18H, **16b**); ^{13}C NMR (500MHz, CDCl_3): 63.7; 63.4; 63.3; 62.4; 62.1; 61.1; 58.9; 58.0; 24.5; 24.4; 19.2; 19.0.

C-(3-Methyl-oxiranyl)-methylazide (17a) and 1-Oxiranyl-ethylazide (17b): ^1H NMR (400MHz, CDCl_3) (**17a** is a 86:14 mixture of diastereomers): 3.48 (dd, $J = 13.3\text{Hz}$, $J = 3.5\text{Hz}$, 1H, **17a**); 3.40 (m, 0.16H, **17a**); 3.31 (dd, $J = 13.3\text{Hz}$, $J = 4.8\text{Hz}$, 1H, **17a**); 3.15 (m, 0.16H, **17a**); 2.98 (m, 1H, **17a**); 2.92 (m, 1H, **17a**); 2.82 (m, 0.12H, **17b**); 2.75 (m, 0.12H, **17b**); 2.68 (m, 0.12H, **17b**); 1.35 (d, $J = 5.3\text{Hz}$, 3H, **17a**); ^{13}C NMR (400MHz, CDCl_3): 57.1; 52.9; 51.9; 17.1;

(3-Azidomethyl-oxiranyl)-methanol (18a) and 2-azido-2-oxiranyl-ethanol (18b): ^1H NMR (400MHz, CDCl_3): 3.91 (dd, $J = 12.9\text{Hz}$, $J = 2.0\text{Hz}$, 1H, **18a**); 3.80 (m, 0.98H, **18b**); 3.63 (dd, $J = 12.9\text{Hz}$, $J = 4.1\text{Hz}$, 1H, **18a**); 3.57 (dd, $J = 13.6\text{Hz}$, $J = 3.2\text{Hz}$, 1H, **18a**); 3.47 (m, 0.49H, **18b**); 3.38 (m, 0.49H, **18b**); 3.31 (dd, $J = 13.6\text{Hz}$, $J = 5.6\text{Hz}$, 1H, **18a**); 3.23 (m, 1H, **18a**); 3.13 (m, 1H, **18a**); 3.11 (m, 0.49H, **18b**); 3.02 (m, 0.49H, **18b**); 2.82 (m, 0.49H, **18b**); 2.72 (m, 0.49H, **18b**); ^{13}C NMR (400MHz, CDCl_3): 69.1; 64.8; 63.8; 62.7; 62.6; 60.9; 56.5; 53.7; 51.5; 50.9; 45.2; 44.7; 44.4.