Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

Catalytic synthesis of homoallyloxyalcohols and 1,2-bis(homoallyloxy)ethanes through ring-opening allylation of cyclic acetals with allylsilanes over solid acids

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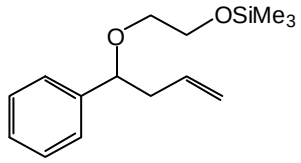
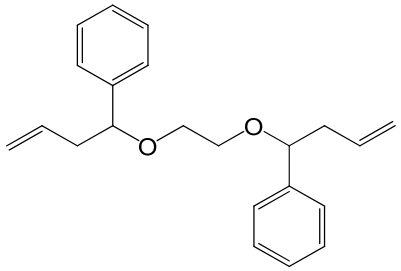
Product Characterization

trimethyl(2-(1-phenylbut-3-enyloxy)ethoxy)silane (3aa)



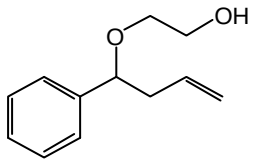
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 9H), 2.36-2.64 (m, 2H), 3.32-3.44 (m, 2H), 3.70 (t, *J* = 5.3 Hz, 2H), 4.31 (t, *J* = 6.5Hz, 1H), 4.98-5.06 (m, 2H), 5.70-5.84 (m, 1H), 7.23-7.43 (m, 5H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): -0.44, 42.6, 62.0, 70.0, 82.4, 116.7, 126.8, 127.5, 128.2, 134.9, 142.1; MS (EI) *m/z* (%): 45, 73(100), 82, 91, 117, 131, 179, 223(M^+-allyl). Elemental Analysis: Calcd for $C_{15}H_{24}O_2Si$: C, 68.13; H, 9.15. Found: C, 67.85; H, 9.33.

1,2-bis(1-phenylbut-3-enyloxy)ethane (4aa)



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35-2.63 (m, 4H), 3.36-3.51 (m, 4H), 4.32 (t, *J* = 8.8 Hz, 2H), 4.98-5.06 (m, 4H), 5.69-5.86 (m, 2H), 7.23-7.35 (m, 10H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): 42.6, 68.0, 82.1, 116.7, 126.8, 127.5, 128.2, 135.0, 142.0; MS (EI) *m/z* (%): 41, 51, 77, 91, 105, 120, 131(100), 151, 191, 281(M^+-allyl). Elemental Analysis: Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.41; H, 8.29.

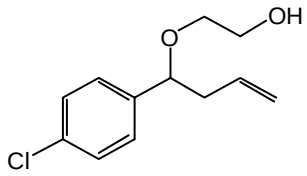
2-(1-phenylbut-3-enyloxy)ethanol (5aa)



^{1}H NMR (300 MHz, $CDCl_3$): δ 2.14 (br, 1H), 2.40-2.64 (m, 2H), 3.36-3.50 (m, 2H), 3.70 (t, *J* = 5.9Hz, 2H), 4.31 (t, *J* = 8.8 Hz, 1H), 5.03-5.10 (m, 2H), 5.72-5.86 (m, 1H), 7.26-7.37 (m, 5H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): 42.5, 61.9, 69.9, 82.2, 117.2, 126.6, 127.7, 128.4, 134.7, 141.7; MS (EI) *m/z* (%): 45, 51, 65, 77, 79, 91, 107(100),

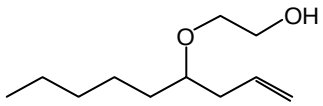
131, 151(M^+-allyl). Elemental Analysis: Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.51; H, 8.61.

2-(1-(4-chlorophenyl)but-3-enyloxy)ethanol (5ba)



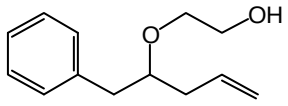
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (br, 1H), 2.26-2.54 (m, 2H), 3.26-3.38 (m, 2H), 3.61 (br, 2H), 4.21 (t, *J* = 6.6 Hz, 1H), 4.95-5.00 (m, 2H), 5.60-5.74 (m, 1H), 7.20 (dd, *J* = 26.7, 8.3 Hz, 4H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): 42.3, 61.8, 70.0, 81.5, 117.5, 127.9, 128.6, 133.3, 134.2, 140.1; MS (EI) *m/z* (%): 45(100), 51, 77, 113, 129, 141, 143, 185(M^+-allyl), 187. Elemental Analysis: Calcd for $C_{12}H_{15}ClO_2$: C, 63.58; H, 6.67. Found: C, 62.85; H, 6.69.

2-(non-1-en-4-yloxy)ethanol (5ea)



^{1}H NMR (300 MHz, $CDCl_3$): 0.89 (t, *J* = 6.6 Hz, 3H), 1.21-1.52 (m, 8H), 2.27 (br, 3H), 3.36 (quint, *J* = 5.9 Hz, 1H), 3.53-3.60 (m, 2H), 3.70 (br, 2H), 5.05-5.12 (m, 2H), 5.76-5.90 (m, 1H)**;** ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): 14.0, 22.6, 25.0, 31.9, 33.8, 38.3, 62.0, 69.9, 79.4, 117.0, 135.0**;** MS (EI) *m/z* (%): 45, 55(100), 73, 83, 101, 145(M^+-allyl). Elemental Analysis: Calcd for $C_{11}H_{22}O_2$; C, 70.92; H, 11.90; Found: C, 68.54; H, 12.34.

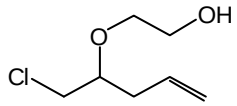
2-(1-phenylpent-4-en-2-yloxy)ethanol (5fa)



^{1}H NMR (400 MHz, $CDCl_3$): 1.91 (br, 1H), 2.34 (t, *J* = 6.5Hz, 2H), 2.83 (d, *J* = 6.4Hz, 2H), 3.44 (m, 1H), 3.54-3.65 (m, 4H), 5.13-5.18 (m, 2H), 5.85-5.96 (m, 1H), 7.24-7.35 (m, 5H) ; ^{13}C {^{1}H} NMR (100.61 MHz. $CDCl_3$): 38.6, 40.8, 61.9, 70.7, 80.9, 117.6,

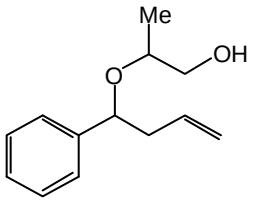
126.4, 128.4, 129.4, 134.7, 138.9; MS (EI) *m/z* (%): 45(100), 73, 91, 121, 165(M^+-allyl). Elemental Analysis: Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found : 75.02 ; H, 8.83.

2-(1-chloropent-4-en-2-yloxy)ethanol (5ga)



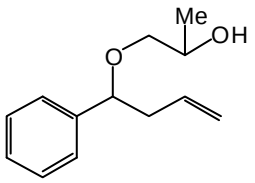
^{1}H NMR (400 MHz, $CDCl_3$): 2.23 (br, 1H), 2.41 (t, *J* = 6.2Hz, 2H), 3.53-3.64 (m, 3H), 3.67-3.76 (m, 4H), 5.12-5.21 (m, 2H), 5.77-5.87 (m, 1H); ^{13}C {^{1}H} NMR (100.61 MHz. $CDCl_3$): 36.7, 45.8, 61.9, 71.2, 79.2, 118.4, 133.4; MS (EI) *m/z* (%): 45(100), 67, 73, 123(M^+-allyl), 125. Elemental Analysis: Calcd for $C_7H_{13}ClO_2$: C, 51.07; H, 7.96; Found: C, 52.99 ; H, 8.02.

2-(1-phenylbut-3-enyloxy)propan-1-ol (5ha) [mixture of 1 :1 diastereoisomers]



^{1}H NMR (400 MHz, $CDCl_3$): 0.99 (d, *J* = 6.3Hz, 3H: **diastereoisomer A**), 1.15 (d, *J* = 6.0Hz, 3H : **diastereoisomer B**), 2.40-2.65 (m, 3H), 3.42-3.67 (m, 3H), 4.45 (m, 1H), 5.02-5.19 (m, 2H), 5.75-5.93 (m, 1H), 7.27-7.40 (m, 5H); ^{13}C {^{1}H} NMR (100.61 MHz. $CDCl_3$): 15.6(**diastereoisomer B**), 17.6(**diastereoisomer A**), 42.8, 43.1, 65.8, 66.7, 72.8, 75.1, 79.2, 81.0, 117.0, 117.7, 126.5, 126.8, 127.6, 127.8, 128.3, 128.5, 134.9, 135.3, 142.2, 143.1; MS (EI) *m/z* (%): 31, 79, 91, 107(100), 131, 165(M^+-allyl). Elemental Analysis (mixture of **5ha** and **5ha'**): Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 74.85; H, 9.22.

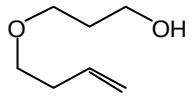
1-(1-phenylbut-3-enyloxy)propan-2-ol (5ha') [mixture of 1 :1 diastereoisomers]



^{1}H NMR (400 MHz, $CDCl_3$): 1.11 (d, *J* = 6.5Hz, 3H : **diastereoisomer A**), 1.13 (d, *J* =

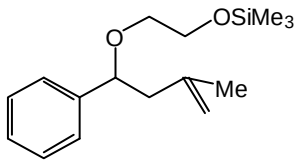
6.4Hz, 3H, : **diastereoisomer B**), 2.40-2.65 (m, 3H), 3.07-3.38 (m, 2H), 3.91-4.04 (m, 1H), 4.30-4.36 (m, 1H), 5.02-5.19 (m, 2H), 5.75-5.93 (m, 1H), 7.27-7.40 (m, 5H) ; ^{13}C {^{1}H} NMR (100.61 MHz. $CDCl_3$): 18.5 (**diastereoisomer A**), 18.8 (**diastereoisomer B**), 42.6, 42.6, 66.3, 66.8, 74.1, 74.8, 82.1, 82.7, 117.21, 117.25, 126.6, 127.7, 128.5, 134.8, 141.7, 141.8.

3-(but-3-enyloxy)propan-1-ol (5ia) [CAS (1154407-97-2)]



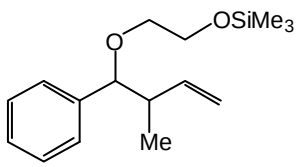
^{1}H NMR (400 MHz, $CDCl_3$): 1.81 (quint, J = 5.7Hz, 2H), 2.32 (q, J = 6.6Hz, 2H), 2.76 (br, 1H), 3.48 (t, J = 6.7Hz, 2H), 3.60 (t, J = 5.8Hz, 2H), 3.73 (t, J = 5.7Hz, 2H), 5.02-5.11 (m, 2H), 5.74-5.84 (m, 1H); ^{13}C {^{1}H} NMR (100.61 MHz. $CDCl_3$): 31.9, 34.2, 61.8, 70.1, 70.4, 116.6, 135.1 ; MS (EI) *m/z* (%): 31(100), 41, 45, 59, 89(M^+-allyl).

trimethyl(2-(3-methyl-1-phenylbut-3-enyloxy)ethoxy)silane



^{1}H NMR (300 MHz, $CDCl_3$): 0.10 (s, 9H), 1.72 (s, 3H), 2.30 (dd, J = 14.3, 5.6 Hz, 1H), 2.57 (dd, J = 14.1, 7.9 Hz, 1H), 3.34-3.41 (m, 2H), 3.66-3.71 (m, 2H), 4.43 (dd, J = 7.8, 5.6 Hz, 1H), 4.71 (d, J = 18.3 Hz, 2H), 7.25-7.35 (m, 5H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): -0.49, 22.9, 46.5, 62.0, 69.9, 81.5, 112.6, 126.7, 127.4, 128.2, 142.4(2C); MS (EI) *m/z* (%): 45, 73(100), 82, 117, 145, 179, 223(M^+-methallyl). Elemental Analysis: Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 68.52; H, 9.46.

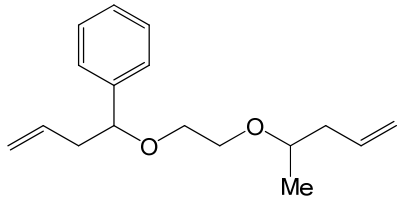
trimethyl(2-(2-methyl-1-phenylbut-3-enyloxy)ethoxy)silane
[mixture of 1:1 diastereoisomers]



^{1}H NMR (400 MHz, $CDCl_3$): 0.02 (s, 9H), 0.03 (s, 9H: diastereoisomer), 0.78 (d, J =

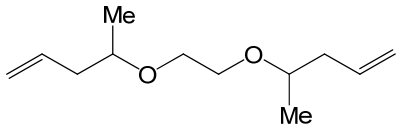
6.6 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H: diastereoisomer), 2.40-2.48 (m, 1H), 3.22-3.37 (m, 2H), 3.59-3.64 (m, 2H), 4.00 (d, *J* = 2.8 Hz, 1H), 4.02 (d, *J* = 3.1 Hz, 1H: diastereoisomer), 4.78-4.84 (m, 2H), 4.87-4.94 (m, 2H: diastereoisomer), 5.56-5.66 (m, 1H), 5.79-5.91 (m, 1H: diastereoisomer), 7.14-7.24 (m, 5H); ^{13}C {^{1}H} NMR (100.61 MHz. $CDCl_3$): 15.6, 16.1(dr), 44.1, 44.5(dr), 62.0, 70.2, 70.3(dr), 86.4, 86.7(dr), 114.2, 114.3(dr), 127.3, 127.4(dr), 127.6, 127.9, 140.7, 140.8, 140.9(dr), 141.2(dr); MS (EI) *m/z* (%): 45, 73(100), 82, 91, 117, 145, 179, 223 (M^+-$CH_3CHCH{=}CH_2$). (dr = diastereoisomers). Elemental Analysis: Calcd for $C_{16}H_{26}O_2Si$: C, 69.01; H, 9.41. Found: C, 70.37; H, 9.24.

(1-(2-(pent-4-en-2-yloxy)ethoxy)but-3-enyl)benzene (4ca) [mixture of 1 :1 diastereoisomers]



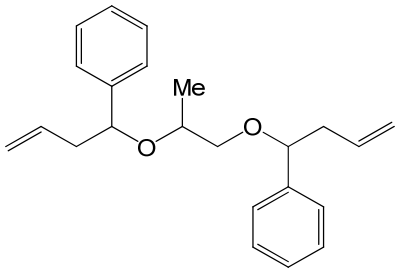
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (d, *J* = 6.2 Hz, 3H: **diastereoisomer A**), 1.14 (d, *J* = 6.2 Hz, 3H: **diastereoisomer B**), 2.12-2.21 (m, 1H), 2.27-2.45 (m, 2H), 2.54-2.64 (m, 1H), 3.38-3.63 (m, 5H), 4.33 (t, *J* = 6.5 Hz, 1H), 4.98-5.10 (m, 4H), 5.72-5.98 (m, 2H), 7.22-7.36 (m, 5H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): 19.3(dr), 19.5(dr), 40.8(dr), 40.9(dr), 42.6, 67.7, 68.3(dr), 68.4(dr), 75.3, 82.3, 116.6(dr), 116.7(dr), 117.0, 126.8, 127.5, 128.3, 134.9, 135.1(dr), 135.2(dr), 142.1; MS (EI) *m/z* (%): 41, 69(100), 91, 105, 107, 131, 151, 219(M^+-allyl). (dr = diastereoisomers) Elemental Analysis: Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 77.19; H, 9.40.

1,2-bis(pent-4-en-2-yloxy)ethane



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (d, J = 6.0 Hz, 6H), 2.12-2.38 (m, 4H), 3.46-3.64 (m, 6H), 5.00-5.10 (m, 4H), 5.75-5.89 (m, 2H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): 19.4, 40.8, 68.0, 75.5, 116.7, 135.1; MS (EI) *m/z* (%): 41(100), 69, 89, 97, 113, 157(M^+-allyl). Elemental Analysis: Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 80.71; H, 11.75.

1,2-bis(1-phenylbut-3-enyloxy)-1-methylethane [mixture of 1:0.7 diastereoisomers]



^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (d, *J* = 6.5 Hz, 3H: **diastereoisomer A**), 1.02 (d, *J* = 6.5 Hz, 3H: **diastereoisomer B**), 2.31-2.62 (m, 4H), 3.18-3.42 (m, 2H), 3.52 (quint, *J* = 5.8 Hz, 1H), 4.28 (t, *J* = 6.6 Hz, 1H), 4.50-4.59 (m, 1H), 4.96-5.08 (m, 4H), 5.69-5.87 (m, 2H), 7.22-7.38 (m, 10H); ^{13}C {^{1}H} NMR (75.45 MHz. $CDCl_3$): 18.5, 18.6, 42.7, 42.8, 42.9, 42.9, 72.1, 72.2, 72.7, 73.1, 80.6, 80.8, 82.5, 116.5, 116.8, 126.70, 126.74, 126.9, 127.4, 127.5, 128.1, 128.3, 135.0, 135.1, 135.2, 142.0, 142.1, 143.0; MS (EI) *m/z* (%): 41, 77, 91, 105, 116, 131(100), 165, 205. 295(M^+-allyl). Elemental Analysis: Calcd for $C_{23}H_{28}O_2$: C, 82.10; H, 8.39. Found: C, 80.72; H, 8.60.