Supporting Information for "Ethylene-Promoted Intermolecular Enyne Metathesis" by Anthony J. Giessert, Nicholas J. Brazis, and Steven T. Diver.

General Information

Reactions were conducted under argon atmosphere unless otherwise noted. Benzene was drawn from a solvent purifier (alumina and Q5) immediately before use. Dichloromethane was drawn from a solvent purifier (alumina) immediately before use. Ethyl vinyl ether, and *t*-butyl vinyl ether were distilled from sodium. Vinyl acetate, and vinyl benzoate were distilled. Ruthenium carbenes **3, 4** were purchased from Materia. Alkynes purchased from Aldrich Chemical Company were distilled before use. Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). ^{1}H-NMR spectra were recorded at 300, 400, or 500 MHz and ^{13}C-NMR spectra at either 75 or 125 MHz in the indicated solvent. ^{1}H-NMR spectra were referenced on the TMS signal for $CDCl_3$ solvent. The ^{13}C-NMR spectra were referenced at 77.0 ppm for $CDCl_3$.

Representative Experimental

Thiobenzoic acid (5-ethoxy-3-methylene-pent-4-enyl) ester (9)

To a Fisher-Porter Bottle was added 10 mg **3** (0.0118 mmol, 0.5 eq), 45.0 mg homopropargyl thiobenzoate **8** (0.236 mmol, 1 eq) dissolved in benzene (4 mL), and immediately followed by the addition of 203 µL of ethyl vinyl ether (153 mg, 2.12 mmol, 9 eq). The pressure vessel was then sealed and purged with ethylene (4 times at 5 psig, polymer grade) and sealed (5 psig ethylene). The reaction was stirred at room temperature for 20 h, depressurized, filtered through silica (1 inch plug elution with CH_2Cl_2) and concentrated *in vacuo* to yield a yellow-orange oil. The product was further purified by flash column chromatography (elution with hexane containing 1 % triethylamine) to yield 56.4 mg of **9** (91 %) as a clear oil. GC retention times of 16.47 and 16.65 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.28. Proton NMR indicated a 0.36:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.96-7.91 (m, 2.72 H), 7.56-7.51 (m, 1.36 H), 7.44-7.39 (m, 2.72 H), 6.79 (d, J = 13.0 Hz, 1 H), 5.97 (d, J = 7.0 H, 0.36 H), 5.56 (d, J= 13.0 Hz, 1 H), 5.12 (s, 0.36 H), 4.86 (s, 0.36 H), 4.84 (s, 1 H)), 4.81 (d, J = 7.0 Hz, 0.36 H), 4.75 (s, 1 H), 3.88-3.80 (m, 2.72 H), 3.22-3.16 (m, 2.72 H), 2.62 (t, J = 6.5 H, 0.72 H), 2.48 (t, J = 6.5 H, 2 H), 1.29 (t J =6.5 Hz, 4.08 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 192.2, 191.9, 148.2, 146.0, 142.1, 141.9, 137.3, 137.1, 133.3, 133.1, 128.6, 128.5, 127.2, 127.1, 114.1, 111.4, 107.6, 105.7, 68.9, 65.6, 36.5, 33.4, 28.6, 28.1, 15.3, 14.8; FT-IR (thin film, cm^{-1}) 3054, 1665, 1448, 1421, 1262, 1208, 1176; High resolution ESI molecular ion calcd for $C_{15}H_{18}O_2S$ 262.10275, found 285.0931 (M + Na), error 3.9 ppm.

Thiobenzoic acid (4-ethoxy-2-methylene-but-3-enyl) ester (2A)

Isolated yield: 58.6 mg (99 %). GC retention time of 15.97 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.43. Proton NMR indicated a 0.53:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 3.06 H), 7.55 (q, J = 7.5 Hz,

1.53 H), 7.65-7.41 (m, 3.06 H), 6.66 (d, J = 13.0 Hz, 1 H), 6.04 (d, J = 7.0 Hz, 0.53 H), 5.58 (d, J = 13.0 Hz, 1 H), 5.26 (s, 0.53 H), 5.18 (s, 0.53 H), 5.02 (s, 1 H), 4.96 (s, 1 H), 4.83 (d, J = 7.0 Hz, 0.53 H), 4.02 (s, 1.03 H), 3.90 (s, 2 H), 3.88-3.76 (m, 3.03 H) 1.32-1.25 (m, 4.59 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 176.5, 176.4, 148.6, 146.8, 139.0, 137.2, 136.8, 133.3, 133.0, 130.5, 128.5, 128.4, 127.2, 127.1, 115.7, 113.7, 106.3, 104.7, 68.9, 65.5, 34.9, 31.3, 15.2, 14.7; FT-IR (thin film, cm^{-1}) 3048, 2961, 2934, 2874, 1662, 1450, 1422, 1265, 917, 738; High resolution ESI molecular ion calcd for $C_{14}H_{16}O_2S$ 248.0866, found 248.0869, error 1.6 ppm.

Thiobenzoic acid S-(4-ethoxy-1-methyl-2-methylene-but-3-enyl) ester (2B)

Isolated yield: 45.1 mg (73 %). GC retention times of 15.98 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.23. Proton NMR indicated a 0.26:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.97-7.93 (m, 2.52 H), 7.62- 7.37 (m, 3.78 H), 6.72 (d, J = 13.0 Hz, 1 H), 6.14 (d, J = 7.0 Hz, 0.26 H), 5.59 (s, 0.26 H), 5.52 (d, J = 13.0 Hz, 1 H), 5.30 (s, 0.26 H), 5.02 (s, 2 H), 4.77 (d, J = 7.0 Hz, 0.26 H), 4.63-4.48 (m, 2.52 H), 3.91-3.77 (m, 2.52 H), 1.66 (d, J = 6.0 Hz, 3 H), 1.59 (d, J = 6.0 Hz, 0.78 H), 1.32-1.24 (m, 3.78 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 191.3, 190.8, 140.2, 139.8, 138.5, 138.1, 134.6, 134.1, 133.7, 133.5, 128.9, 128.8, 128.3, 127.9, 116.4, 114.2, 111.1, 109.7, 76.3, 75.9, 40.3, 39.6, 20.8, 20.3, 14.8, 13.9; FT-IR (thin film, cm^{-1}) 3065, 2993, 2940, 2861, 1683, 1448; High resolution ESI molecular ion calcd for $C_{15}H_{18}O_2S$ 262.1022, found 262.1034, error 4.4 ppm.

Acetic acid 3-benzoylsulfanylmethyl-buta-1,3-dienyl ester (10)

Isolated yield: 56.9 mg (92 %). GC retention times of 16.22 and 16.53 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.21. Proton NMR indicated a 1.0:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.95-7.92 (m, 4 H), 7.56-7.40 (m, 7 H), 7.07 (d, J = 7.0 Hz, 1 H), 6.06 (d, J = 13.0 Hz, 1 H), 5.33 (s, 1 H), 5.30 (d, J = 7.0

Hz, 1 H), 5.27 (s, 2 H), 5.13 (s, 1 H), 4.04 (s, 2 H), 3.89 (s, 2 H), 2.14 (s, 3 H), 2.12 (s, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 191.4, 191.1, 168.1, 167.6, 142.9, 142.0, 138.0, 137.8, 135.1, 133.9, 133.5, 133.1, 128.9, 128.4, 127.1, 126.9, 120.6, 118.9, 115.8, 111.570.1, 68.7, 43.2, 41.3; FT-IR (thin film, cm^{-1}) 3054, 2987, 1743, 1667, 1421; High resolution ESI molecular ion calcd for $C_{14}H_{14}O_3S$ 262.32516, found 285.0560 (M + Na), error 1.6 ppm.

Acetic acid 3-(1-benzoylsulfanyl-ethyl)-buta-1,3-dienyl ester (11)

Isolated yield: 56 mg (86 %). GC retention times of 16.2 and 16.48 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.20. Proton NMR indicated a 1.0:0.80 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.93-7.90 (m, 3.6 H), 7.55-7.51 (m, 2.6 H), 7.43-7.39 (m, 3.6 H), 7.12 (d, J = 7.0 Hz, 1 H), 6.00 (d, J = 13.0 Hz, 0.8 H), 5.46 (s, 0.8 H), 5.41 (s, 0.8 H), 5.26 (d, J = 7.0 Hz, 1 H), 5.22 (s, 1 H), 5.17 (s, 1 H), 4.70 (q, J = 7.0 Hz, 0.8 H), 4.52 (q, J = 7.0 Hz, 1 H), 2.12 (s, 3 H), 2.10 (s, 2.4 H), 1.58-1.52 (m, 5.4 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 191.5, 191.2, 167.7, 167.4, 143.2, 142.1, 137.0, 136.8, 134.5, 133.7, 133.6, 133.3, 128.6, 128.5, 127.3, 127.2, 117.7, 115.2, 115.0, 110.5, 42.9, 40.3, 31.5, 20.8, 20.5, 14.1; FT-IR (thin film, cm^{-1}) 2983, 2938, 2885, 1771, 1664, 1470, 1381, 1222; High resolution ESI molecular ion calcd for $C_{15}H_{16}O_3S$ 276.0820, found 299.0723 (M + Na), error 1.0 ppm.

Thiobenzoic acid *S*-[4-(*tert*-butyl-dimethyl-silanyloxy)-1-methyl-2-methylene-but-3-enyl] ester (12)

NMR yield of 99 % against mesitylene internal standard. Dienol ether **12** readily decomposed in air and on silica gel. Proton NMR indicated a 1.5:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ7.86-7.83 (m, 5 H), 7.50-7.42 (m, 2.5 H), 7.36-7.30 (m, 5 H), 6.62 (d, J = 12.0 Hz, 1 H), 6.24 (d, J = 7.0 Hz, 1.5 H), 5.59 (d, J = 12.0 Hz, 1 H), 5.54 (s, 1 H), 5.20 (s, 1 H), 4.90 (d, J = 7.0 Hz, 1.5 H), 4.91 (s, 1 H), 4.89 (s, 1 H), 4.74 (d, J = 7 Hz, 1.5 H), 4.50-4.43 (m, 2.5 H), 1.48

(d, J = 7.0 Hz, 3 H), 1.45 (d, J = 7.0 Hz, 4.5 H), 0.84 (s, 13.5 H), 0.78 (s, 9 H), 0.07 (s, 9 H), 0.02 (s, 6 H).

***tert*-Butyl-(5-ethoxy-3-methylene-pent-4-enyloxy)-dimethyl-silane (14)**

Isolated yield: 50.2 mg (83 %). GC retention times of 12.78 and 13.10 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f0.37. Proton NMR indicated a 0.36:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.59 (d, J = 13.0 Hz, 1 H), 4.93 (d, J = 7.0 Hz, 0.36 H), 5.16 (s, 0.36 H), 4.83 (s, 0.36 H), 4.79 (s, 1 H), 4.73 (d, J = 7.0 Hz, 0.36 H), 4.66 (s, 1 H), 3.88-3.65 (m, 5.44 H), 2.47 (t, J = 7.0 Hz, 0.72 H), 2.36 (t, J = 7.0 Hz, 2 H), 1.30-1.22 (m, 4.08 H), 0.82 (s, 12.24 H), 0.03 (s, 8.16 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 147.6 (CH), 145.9 (CH), 140.9, 140.6, 114.4 (CH_2), 111.6 (CH_2), 108.5 (CH), 106.5 (CH), 68.8 (CH_2), 65.4 (CH_2), 63.3 (CH_2), 62.8 (CH_2), 40.6 (CH_2), 36.6 (CH_2), 26.0 (CH_3), 25.9 (CH_3), 18.5, 18.4, 15.3 (CH_3), 14.9 (CH_3), -5.2 (CH_3), -5.4 (CH_3); FT-IR (thin film, cm^{-1}) 3054, 2986, 1421, 1275; High resolution ESI molecular ion calcd for $C_{14}H_{28}O_2Si$ 256.1859, found 279.1756 (M + Na), error 2.0 ppm.

(5-Ethoxy-3-methylene-pent-4-enyloxymethyl)-benzene (16)

Isolated yield: 230 mg (84 %). GC retention times of 14.42 and 14.55 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f0.34. Proton NMR indicated a 0.38:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40-7.25 (m, 6.9 H), 6.58 (d, J = 13.0 Hz, 1 H), 5.95 (d, J = 7.0 Hz, 0.38 H), 5.57 (d, J = 13.0 Hz, 1 H), 5.28 (s, 0.38 H), 4.91 (s, 0.38 H), 4.84 (s, 1 H), 4.69 (d, J = 7.0 Hz, 0.38 H), 4.72 (s, 1 H), 4.53 (s, 2.76 H), 3.82-3.74 (m, 2.76 H), 3.65-3.58 (m, 2.76 H), 2.71-2.46 (m, 2.76 H), 1.29-1.23 (m, 4.14 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 144.2, 143.7, 142.6, 141.7, 132.8, 132.6, 130.5, 129.8, 129.6, 128.8, 128.3, 128.2, 111.4, 109.3, 108.1, 102.7, 73.5, 71.4, 70.0, 68.1, 38.7, 36.0, 28.9, 28.0, 20.5, 20.1; FT-IR (thin film,

cm^{-1}) 2938, 2834, 1719, 1479, 1293, 1076, 1028; High resolution ESI molecular ion calcd for $C_{15}H_{20}O_2$ 232.1463, found 255.1356 (M + Na), error 1.9 ppm.

1-Ethoxy-3-(2-methoxymethoxy-ethyl)-buta-1,3-diene (18)

Isolated yield: 40.0 mg (91 %). GC retention times of 11.56 and 11.76 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.24. Proton NMR *E* isomer. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.57 (d, J = 13.0 Hz, 1 H), 5.53 (d, J = 13.0 Hz, 1 H), 4.82 (s, 1 H), 4.70 (s, 1 H), 4.58 (s, 2 H), 3.76 (t, J = 7.0 Hz, 2 H), 3.61 (q, J = 6.0 Hz, 2 H), 3.33 (s, 3 H), 2.42 (t, J = 7.0 Hz, 2 H), 1.24 (t, J = 6.0 H, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 147.5, 145.9, 140.6, 139.5, 114.1, 113.9, 111.3, 109.2, 108.2, 106.1, 96.4, 96.3, 67.2, 66.5, 65.7, 65.4, 33.1, 31.5, 14.8, 14.1; FT-IR (thin film, cm^{-1}) 2926, 2898, 2880, 1675, 1410, 1275, 1149; High resolution ESI molecular ion calcd for $C_{10}H_{18}O_3$ 186.1256, found 209.1143 (M + Na), error 2.4 ppm.

[3-(2-Benzyloxy-ethyl)-buta-1,3-dienyloxy]-tert-butyl-dimethyl-silane (19)

Isolated yield: 53.7 mg (72 %). GC retention time of 16.09 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.42. Proton NMR indicated a 1.53:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.40-7.23 (M, 12.65 H), 6.58 (d, J = 13.0 Hz, 1 H), 6.13 (d, J = 7.0 Hz, 1.53 H), 5.71 (d, J = 13.0 Hz, 1 H), 5.14 (s, 1.53 H), 5.03 (d, J = 7.0 Hz, 1.53 H), 4.84 (s, 1.53 H), 4.80 (s, 1 H), 4.69 (s, 1 H), 4.51-4.49 (m, 5.06 H), 3.63-3.56 (m, 5.06 H), 2.66-2.43 (m, 5.06 H), 0.91-0.88 (m, 22.77 H), 0.13-0.11 (m, 15.18 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 141.9, 140.8, 139.6, 138.8, 130.0, 129.6, 128.4, 128.3, 127.7, 127.6, 127.5 127.4, 115.3, 114.2, 111.6, 109.7, 73.0, 72.9, 72.8, 70.2, 69.4, 69.1 25.6, 25.5, 18.3, 18.1, -5.2, -5.5; FT-IR (thin film, cm^{-1}) 3029, 2962, 2928, 2854, 1479; High resolution ESI molecular ion calcd for $C_{19}H_{30}O_2Si$ 318.2015, found 341.1903 (M + Na), error 1.4 ppm.

Benzoic acid 4-benzoyloxy-1-methyl-2-methylene-but-3-enyl ester (21)

Isolated yield: 269 mg (89 %). GC retention times of 19.30 and 20.23 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.24. Proton NMR indicated 1.0:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.16-8.07 (m, 8 H), 7.90 (d, J = 13.0 Hz, 1 H), 7.65-7.43 (m, 13 H), 6.26 (d, J = 13.0 Hz, 1 H), 5.97 (q, J = 6.0 Hz, 1 H), 5.81 (q, J = 6.0 Hz, 1 H), 5.59 (s, 1 H), 5.58 (s, 1 H), 5.50 (d, J = 7.0 Hz, 1 H), 5.32 (s, 1 H), 5.23 (s, 1 H), 1.62 (d, J = 6.0 Hz, 3 H), 1.57 (d, J = 6.0 Hz, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 165.6, 165.0, 163.5, 163.3, 142.9, 142.3, 137.1, 135.0, 133.8, 133.6, 133.0, 132.9, 130.5, 130.1, 130.0, 129.9, 129.7, 129.6, 128.7, 128.5, 128.4, 128.3, 116.2, 114.5, 114.3, 109.6, 72.7, 71.4, 20.5, 20.4 ; FT-IR (thin film, cm^{-1}) 1735, 1720, 1459, 1281, 1110; High resolution ESI molecular ion calcd for $C_{20}H_{18}O_4$ 322.12051, found 345.1097, error 0.4 ppm.

Benzoic acid 4-(tert-butyl-dimethyl-silanyloxy)-1-methyl-2-methylene-but-3-enyl ester (22)

Isolated yield: 76.2 mg (91 %). GC retention times of 16.22 and 16.31 min. (integral not determined because of overlapping peaks), Analytical TLC (10% ethyl acetate/hexane) R_f 0.26. Proton NMR indicated a 1.59:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.06-8.02 (m, 5.18 H), 7.52-7.36 (m, 7.77 H), 6.73 (d, J = 13.0 Hz, 1 H), 6.28 (d, J =7.0 Hz, 1.59 H), 5.83 (q, J = 7.0 Hz, 1.59 H), 5.71-5.63 (m, 2 H), 5.41 (s, 1.59 H), 5.23 (s, 1.59 H), 5.01 (s, 1 H), 4.93-4.90 (m, 2.59 H), 1.52-1.45 (m, 7.77 H), 0.93 (s, 9 H), 0.87 (s, 14.31 H), 0.16 (s, 9.54 H), 0.11 (s, 6 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 165.9, 165.8, 144.3, 143.8, 142.9, 141.3, 133.1, 132.9, 131.1, 129.9, 129.8, 128.6, 128.5, 128.4, 111.9, 111.8, 110.2, 106.3, 73.5, 71.7, 25.8, 25.5, 21.0, 20.5, 18.5, 18.3, -5.04, -5.16; FT-IR (thin film, cm^{-1}) 3065, 3032, 2960, 1717, 1496, 1454, 1073; High resolution ESI molecular ion calcd for $C_{19}H_{28}O_3Si$ 332.18077, found 355.1690 (M + Na), error 2.8 ppm.

Benzoic acid 4-tert-butoxy-1-methyl-2-methylene-but-3-enyl ester (23)

Isolated yield: 115 mg (89 %). GC retention times of 15.10 and 15.18 min. (integral not determined because of overlapping peaks). Analytical TLC (10% ethyl acetate/hexane) R_f 0.47. Proton NMR indicated a 0.8:1.0 (*Z:E*) ratio of isomers. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.12-8.05 (m, 3.6 H), 7.64-7.37 (m, 1.8 H), 7.45-7.43 (m, 3.6 H), 6.82 (d, J = 13.0 Hz, 1 H), 6.36 (d, J = 7.0 Hz, 0.8 H), 5.86 (q, J = 7.0 H, 0.8 H), 5.75 (q, J = 7.0 Hz, 1 H), 5.68 (d, J = 13.0 Hz, 1 H), 5.46 (s, 0.8 H), 5.24 (s, 0.8 H), 5.04 (s, 1 H), 4.95 (s, 1 H), 4.89 (d, J =7.0 Hz, 0.8 H), 1.55-1.48 (m, 5.4 H), 1.33 (s, 7.2 H), 1.27 (s, 9 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 177.6, 177.3, 144.7, 144.3, 143.2, 142.3, 133.4, 133.2, 131.4, 131.2, 130.3, 130.1, 128.9, 128.8, 111.9, 109.9, 108.6, 103.2, 74.0, 71.9, 31.1, 28.6, 24.2, 23.8, 21.0, 20.2; FT-IR (thin film, cm^{-1}) 2991, 1726, 1656, 1461, 1266; High resolution ESI molecular ion calcd for $C_{17}H_{22}O_3$ 274.1569, found 297.1459 (M + Na), error 3.4 ppm.

5-(2-Benzyloxy-ethyl)-3-ethoxy-3,6-dihydro-[1,2]dioxine (24)

To a 40 mL pyrex test tube equipped with magnetic stirbar was added 59 mg of **16** (0.254 mmol, 1 eq), CH_2Cl_2 (19 mL) and methanol (1 mL). To the resulting solution was added 1 crystal rose Bengal, the tube was then cooled to -10°C (ethanol/ice). Oxygen was then perfused through the solution and then photolyzed with a 450 W UV immersion lamp (Ace glass cat. number 7825-34) for 4 hours, the volume of CH_2Cl_2/methanol was reestablished at 1 h intervals. Conversion was monitored by tlc, and the resulting solution was concentrated *in vacuo* (rotary evaporator) then purified by flash column chromatography (elution with 10 % ethyl acetate/hexane) to yield 60 mg (66 %) of **24** as a slightly yellow oil. Analytical TLC (25 % ethyl acetate/hexane) R_f 0.45. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37-7.25 (m, 5 H), 5.683 (s, 1 H), 5.7 (s, 1 H), 4.73 (d, J = 27.5 Hz, 1 H), 4.94 (s, 2 H), 4.24 (d, J = 27.5 Hz, 1 H), 3.94-3.91 (m, 1 H), 3.64-3.53 (m, 3 H), 2.37 (t, J = 7.0 Hz, 2 H), 1.28 (t, J = 7.5 Hz, 3 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 138.7, 137.9, 130.6, 128.4, 127.6, 117.7, 97.2, 73.0, 71.8, 68.2, 63.9, 33.0,

15.1; FT-IR (thin film, cm^{-1}) 3020, 2970, 2861, 2849, 1456; High resolution ESI molecular ion calcd for $C_{15}H_{20}O_4$ 264.1362, found 287.1256 (M + Na), error 0.9 ppm.

3-(2-Benzyloxy-ethyl)-furan (25)

To a 50 mL round bottom flask equipped with magnetic stirbar was added 100 mg (.378 mmol, 1 eq.) of **24** in CH_2Cl_2 (2 mL), 98.9 mg (1.51 mmol, 4 eq) zinc dust, and 45 mg (0.75 mmol, 2 eq) acetic acid in CH_2Cl_2 (1.5 mL) at room temperature. The reaction mixture was stirred for two hours then plug filtered through celite, concentrated *in vacuo* (rotary evaporator), and purified by flash chromatography (elution with CH_2Cl_2) to yield 62 mg (82 %) of **25**. Analytical TLC (25 % ethyl acetate/hexane) R_f 0.63. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.37-7.33 (m, 5 H), 7.30-7.28 (m, 2 H), 6.32 (s, 1 H), 4.59 (s, 2 H), 3.65 (t, J = 7.0 Hz, 2 H), 2.75 (t, J = 7.0 Hz, 2 H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.6, 139.5, 138.3, 128.4, 127.6, 127.5, 121.8, 111.2, 72.9, 70.1, 25.5; FT-IR (thin film, cm^{-1}) 3159, 3053, 2938, 2876, 1461, 1381; High resolution ESI molecular ion calcd for $C_{13}H_{14}O_2$ 202.0994, found 225.0884 (M + Na), error 1.0 ppm.