**Supporting Information for “Intermolecular Enol Ether-Alkyne Metathesis”
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General Information

Reactions were conducted under an argon atmosphere unless otherwise noted. Benzene was distilled from CaH_2 or drawn from a solvent purifier (alumina and Q5) immediately before use. Dichloromethane was distilled from CaH_2 or drawn from a solvent purifier (alumina) immediately before use. Ethyl vinyl ether and butyl vinyl ether were distilled from sodium. Vinyl acetate was distilled and stored over trace hydroquinone. Ruthenium carbenes **3-5** were purchased from Strem or 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). ^1H -NMR spectra were recorded at 400, or 500 MHz and ^{13}C -NMR spectra at either 75 or 125 MHz in the indicated solvent. ^1H -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 . Optical rotations were measured using the sodium D line in a thermostatted cell held at 25°C. Enantiomeric excesses were determined by HPLC using a Whelk-O1 column and isopropanol/hexane at the indicated ratio and rate, and UV-254 unless stated otherwise.

General Experimental for Cross Enyne Metathesis

E/Z Ethyl 4-benzoyloxy-3-methylene-1-pentenyl ether (**6B**)

Into an oven-dried Schlenk tube (50 mL capacity) equipped with magnetic stirbar and cold-finger condenser was added 10 mg of ruthenium [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)-(tricyclohexylphosphine)] **3** (0.012 mmol, 5 mol %), 41.1 mg 1-methylpropargyl benzoate (0.236 mmol, 1.0 eq), 203 μ L ethyl vinyl ether (153 mg, 2.12 mmol, 9.0 eq) and 2.0 mL freshly distilled benzene. The reaction vessel was then heated to reflux in an oil bath with stirring until all 1-methylpropargyl benzoate was consumed, cooled to room temperature, filtered through a plug of silica gel (elution with CH_2Cl_2) and concentrated *in vacuo* (rotatory evaporator) to yield a dark colored oil. The oil was then purified by flash chromatography (elution with 5% ethyl acetate/hexane) gave 58.1 mg of **6B** (99%) as a clear oil. GC retention time of 14.85 min, Analytical TLC (10% ethyl acetate/hexane) R_f 0.5. Proton NMR indicated a 0.59:1.0 (*Z:E*) ratio of isomers. ^1H -NMR (500 MHz, CDCl_3) δ 8.07-8.01 (m, 3.18 H), 7.53 (q, $J=7.5$ Hz, 1.59 H), 7.44-7.38 (m, 3.18 H), 6.73 (d, $J=13.0$ Hz, 1 H), 6.11 (d, $J=7.5$ Hz, 0.59 H), 5.76 (q, $J=6.5$ Hz, 0.59 H), 5.67 (q, $J=6.5$ Hz, 1 H), 5.50 (d, $J=13.0$ Hz, 1 H), 5.45 (s, 0.59 H), 5.25 (s, 0.59 H), 5.01 (s, 1 H), 4.94 (s, 1 H), 4.83 (d, $J=7.5$ Hz, 0.59 H), 3.88 (q, $J=7.0$ Hz, 1.18 H), 3.79 (q, $J=7.0$ Hz, 2 H), 1.51 (d, $J=6.5$ Hz, 3 H), 1.47 (d, $J=6.5$ Hz, 1.77 H), 1.3-1.25 (m, 4.77 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 165.7, 148.1, 147.4, 144.2, 143.2, 132.9, 132.7, 130.8, 130.5, 129.6, 129.5, 128.4, 128.3, 128.2, 112.1, 109.2, 104.7, 102.2, 73.4, 71.5, 69.0, 65.4, 20.4, 20.3, 15.3, 14.7. FT-IR (thin film, cm^{-1}) 2059, 1716, 1602. High resolution ESI molecular ion calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ 246.1256, found 269.1156 ($\text{M} + \text{Na}$), error 2.9 ppm.

E/Z Ethyl 4-benzoyloxy-3-methylene-1-butenyl ether (**8A**)

As above, flash chromatography (elution with 3% ethyl ether/pentane) to yield 578 mg of **8A** (98%) as a clear oil. Analytical TLC (10 % ethyl acetate/hexane) R_f 0.34. Proton NMR indicated a 0.62:1.0 (*Z:E*) ratio of isomers. ^1H -NMR (500 MHz, CDCl_3) δ 8.09-8.05 (m, 3.24 H), 7.60-7.52 (m, 1.62 H), 7.45-7.40 (m, 3.24 H), 6.69 (d, $J=13.0$ Hz, 1 H), 6.04 (d, $J=7.0$ Hz, 0.62 H), 5.61 (d, $J=13.0$ Hz, 1 H), 5.30 (s, 0.62 H), 5.16 (s, 0.62 H), 5.06 (s, 1 H), 5.03 (s, 1.24H), 4.92 (s, 2 H), 4.91 (d obscured, $J=7.0$ Hz, 0.62 H), 4.78 (s, 1 H), 3.85-3.78 (m, 3.24 H), 1.28 (t, $J=7.0$ Hz, 3 H), 1.22 (t, $J=7.0$ Hz, 1.86 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 166.2, 166.1, 148.1, 146.7, 138.6, 138.4, 132.9, 132.7, 130.4, 130.0, 129.5, 129.4, 128.3, 128.2, 113.4, 112.7, 105.6, 103.7, 68.8, 67.2, 65.3, 65.0,

15.1, 14.6. FT-IR (thin film, cm^{-1}) 3152, 1725, 1373, 1276, 1209, 911, 746. High resolution ESI molecular ion calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3$ 232.1100, found 255.0998 ($\text{M} + \text{Na}$), error 2.3 ppm.

***E/Z* 4-Benzoyloxy-3-methylene-1-butenyl acetate (8B)**

As above, flash chromatography (elution with 10% ethyl acetate/hexane) to yield 56.2 mg of **8B** (97%) as a clear oil. GC retention times of 15.32 and 15.57 min (integral not determined because of overlapping peaks). Analytical TLC (10 % ethyl acetate/hexane) R_f 0.24. Proton NMR indicated a 0.56:1.0 (*Z:E*) ratio of isomers. ^1H -NMR (500 MHz, CDCl_3) δ 8.04 (t, $J=6.5$ Hz, 3.12 H), 7.60-7.51 (m, 2.56 H), 7.42 (t, $J=7.5$ Hz, 3.12 H), 7.09 (d, $J=7.0$ Hz, 0.56 H), 6.10 (d, $J=13.0$ Hz, 1.0 H), 5.40 (d, $J=7.0$ Hz, 0.56 H), 5.35 (s, 0.56 H), 5.33 (s, 0.56 H), 5.29 (s, 1.0 H), 5.21 (s, 1.0 H), 5.06 (s, 1.12 H), 4.95 (s, 2.0 H), 2.13 (s, 3.0 H), 2.06 (1.68 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 167.8, 167.2, 166.3, 166.1, 137.5, 137.2, 136.7, 133.8, 130.1, 130.0, 129.9, 129.6, 129.5, 128.4, 128.3, 118.7, 117.7, 114.7, 110.5, 66.5, 65.8, 64.5, 20.6, 15.2. FT-IR (thin film, cm^{-1}) 3152, 1760, 1721, 1373, 1270, 1216, 1102, 911, 746. High resolution ESI molecular ion calcd for $\text{C}_{14}\text{H}_{14}\text{O}_4$ 246.0892, found 269.0782 ($\text{M} + \text{Na}$), error 1.0 ppm.

***E/Z* Ethyl 4-benzyloxy-3-methylene-1-butenyl ether (8C)**

As above, then purified by preparative layer chromatography (elution with 10% ethyl acetate/hexane) to yield 42 mg of **8C** (82%) as a clear oil. GC retention time of 14.43 min. Analytical TLC (5% ethyl acetate/hexane) R_f 0.60. Proton NMR indicated a 0.65:1.0 (*Z:E*) ratio of isomers. ^1H -NMR (500 MHz, CDCl_3) δ 7.38-7.25 (m, 8.25 H), 6.77 (d, $J=13.0$ Hz, 1 H), 6.07 (d, $J=7.0$ Hz, 0.65 H), 5.58 (d, $J=13.0$ Hz, 1 H), 5.42 (s, 0.65 H), 5.21 (s, 0.65 H), 4.96 (s, 1 H), 4.94 (s, 1 H), 4.86 (d, $J=7.0$ Hz, 0.65 H), 4.53 (s, 1.3 H), 4.49 (s, 2 H), 4.16 (s, 1.3 H), 4.13 (s, 2 H), 3.88 (q, $J=7.0$, 1.3 H), 3.80 (q, $J=7.0$ Hz, 2H), 1.28 (t, $J=7.0$ Hz, 4.95 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 148.6, 147.0, 140.4, 138.3, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 127.4, 113.4, 112.7, 105.9, 103.7, 73.4, 71.9, 71.5, 71.4, 68.9, 65.4, 15.3, 14.8. FT-IR (thin film, cm^{-1}) 3054, 3986, 1422, 1265, 739, 705. High resolution EI molecular ion calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$ 218.1307, found 218.1311, error 1.7 ppm.

***E/Z* Ethyl 4-(4-butyldiphenylsiloxy)-3-methylene-1-butenyl ether (8D)**

As above, then purified by preparative layer chromatography (elution with 5% ethyl acetate/hexane) to yield 84 mg of **8D** (97%) as a clear oil. Analytical TLC (5% ethyl acetate/hexane) R_f 0.38. Proton NMR indicated a 0.47:1.0 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.71-7.64 (m, 5.88 H), 7.44-7.30 (m, 8.82 H), 6.54 (d, $J=13.0$ Hz, 1 H), 5.93 (d, $J=7.0$ Hz, 0.47 H), 5.54 (d, $J=13.0$ Hz, 1 H), 5.42 (s, 0.47 H), 5.29 (s, 0.47 H), 5.09 (s, 1 H), 4.90 (s, 1 H), 4.81 (d, $J=7.0$ Hz, 0.47 H), 4.39 (s, 0.94 H), 4.27 (s, 2 H), 3.78-3.71 (m, 2.94 H), 1.25 (t, $J=7.0$ Hz, 3 H), 1.13 (t, $J=7.0$ Hz, 1.41 H), 1.08 (s, 4.23 H), 1.06 (s, 9 H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 147.3, 146.1, 142.9, 142.5, 135.5, 129.7, 127.7, 127.6, 110.1, 109.6, 105.9, 104.1, 68.6, 66.2, 65.3, 64.3, 26.9, 26.8, 19.4, 19.3, 15.1, 14.8. FT-IR (thin film, cm^{-1}) 2934, 2896, 2858, 1667, 1471, 112, 909, 737. High resolution ESI molecular ion calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{Si}$ 366.2015, found 389.1923 ($\text{M} + \text{Na}$), error 2.6 ppm.

***E/Z* Ethyl 5-phenyl-4-acetoxy-3-methylene-1-pentenyl ether (10A)**

As above, purification by flash chromatography (elution with 5% ethyl acetate/hexane) to yield 54 mg of **10A** (88%) as a clear oil. GC retention times of 15.08 and 15.13 min (integral not determined because of overlapping peaks). Analytical TLC (5% ethyl acetate/hexane) R_f 0.27. Proton NMR indicated a 0.52:1.0 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.28-7.16 (m, 7.6 H), 6.72 (d, $J=13.0$ Hz, 1 H), 6.10 (d, $J=7.0$ Hz, 0.52 H), 5.69 (q, $J=4.5$ Hz, 0.52 H), 5.49 (q, $J=4.5$ Hz, 1 H), 5.45 (d, $J=13.0$ Hz, 1 H), 5.35 (s, 0.52 H), 5.05 (s, 0.52 H), 4.90 (s, 1 H), 4.82 (d, $J=7.0$ Hz, 0.52 H), 4.79 (s, 1 H), 3.95-3.89 (m, 1.04 H), 3.80 (q, $J=7.0$ Hz, 2 H), 3.07-2.93 (m, 3.04 H), 2.87-2.82 (m, 0.52 H), 1.99 (s, 3 H), 1.95 (s, 1.56 H), 1.31-1.27 (m, 4.56 H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 170.0, 169.5, 148.2, 147.2, 142.4, 141.9, 137.9, 137.4, 129.4, 129.3, 128.2, 128.0, 126.5, 126.2, 112.8, 110.3, 104.5, 102.5, 76.7, 75.5, 69.1, 65.4, 40.8, 40.5, 21.2, 21.1, 15.3, 14.7. FT-IR (thin film, cm^{-1}) 3054, 2985, 1732, 1265, 1240, 720. High resolution EI molecular ion calcd for $\text{C}_{16}\text{H}_{20}\text{O}_3$ 260.1407, found 260.1397, error 3.8 ppm.

***E/Z* Ethyl 5-phenyl-4-(*t*-butyldimethylsiloxy)-3-methylene-1-pentenyl ether (10B)**

As above, reaction went to 99% conversion (GC). Purification by flash chromatography (elution with 5% ethyl acetate/hexane) to yield 88.2 mg of **10B** (38%) as a clear oil. GC retention time of 15.83 min. Analytical TLC (5% ethyl acetate/hexane) R_f 0.42. Proton NMR indicated a 0.78:1.0 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.19-7.08 (m, 8.90 H), 6.80 (d, $J=13.0$ Hz, 1 H), 6.02 (d, $J=7.5$ Hz, 0.78 H), 5.42 (d, $J=13.0$ Hz, 1 H), 5.28 (s, 0.78 H), 5.09 (s, 0.78 H), 4.83 (d, $J=7.5$ Hz, 0.78 H), 4.75 (s, 1 H), 4.72 (s, 1 H), 4.40 (s, 0.78 H), 4.22 (s, 1 H), 3.89-3.81 (m, 1.56 H), 3.79-3.72 (m, 2 H), 2.85-2.78 (m, 1.78 H), 2.73-2.68 (m, 1 H), 2.56-2.50 (m, 0.78 H), 1.27-1.22 (m, 5.34 H), 0.72 (d, $J=10.0$ Hz, 16.02 H), -0.22 (s, 3 H), -0.27 (s, 2.34 H), -0.37 (s, 3 H), -0.44 (s, 2.34 H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 148.3, 146.8, 130.3, 130.1, 128.2, 128.0, 126.3, 126.0, 112.2, 109.3, 105.0, 103.3, 94.6, 77.4, 77.1, 68.9, 65.3, 45.2, 44.9, 25.9, 25.8, 18.2, 15.5, 14.9, -4.9, -5.0, -5.5. FT-IR (thin film, cm^{-1}) 3053, 2983, 2956, 2929, 2853, 1651, 1417, 1265, 1091, 909, 443. High resolution ESI molecular ion calcd for $\text{C}_{20}\text{H}_{32}\text{O}_2\text{Si}$ 332.2172 found 355.2070 ($\text{M} + \text{Na}$), error 1.7 ppm.

***E/Z* *N,N*-(4-Butoxy-2-methylene-3-butenyl)(butyl)tosylamine (12)**

As above, purification by flash chromatography (elution with 5% ethyl acetate/hexane) to yield 45 mg of **12** (92%) as a clear oil. GC retention times of 21.75 and 21.99 min., (integral not determined because of overlapping peaks). Analytical TLC (10% ethyl acetate/hexane) R_f 0.30. Proton NMR indicated a 1.0:1.7 (*Z:E*) ratio of isomers, *Z* isomer was recovered from a thermal Diels-Alder reaction and characterized. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.70 (d, $J=8.4$ Hz, 2 H), 7.31 (d, $J=8.4$ Hz, 2 H), 6.95 (d, $J=13.0$ Hz, 1 H), 5.52 (d, $J=13.0$ Hz, 1 H), 4.90 (s, 1 H), 4.75 (s, 1 H), 3.80-3.73 (m, 4 H), 3.03 (t, $J=7.5$ Hz, 2 H), 2.43 (s, 3 H), 1.70-1.59 (m, 2 H), 1.48-1.34 (m, 4 H), 1.27-1.16 (m, 2 H), 0.95 (t, $J=7.5$ Hz, 3 H), 0.83 (t, $J=7.5$ Hz, 3 H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 149.8, 143.1, 138.9, 129.6, 127.3, 113.2, 105.5, 70.3, 51.8, 47.7, 31.4, 30.2, 21.5, 20.1, 19.0, 13.8, 13.7. FT-IR (thin film, cm^{-1}) 2962, 2935, 2874, 1162, 1088, 911; High resolution ESI molecular ion calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_3\text{S}$ 365.2025, found 388.1917 ($\text{M} + \text{Na}$), error 0.0 ppm.

***E/Z* Ethyl 4-phenyl-4-acetoxy-3-methylene-1-butenyl ether (**14**)**

As above, flash chromatography (elution with 5% ethyl acetate/hexane) to yield 55.6 mg of **14** (96%) as a clear oil (99% conversion by GC). GC retention time of 15.83 min. Analytical TLC (5% ethyl acetate/hexane) R_f 0.17. Proton NMR indicated a 0.63:1.0 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.40-7.20 (m, 8.15 H), 6.54 (d, $J=13.0$ Hz, 1 H), 6.46 (s, 0.63 H), 6.40 (s, 1.0 H), 6.04 (d, $J=7.0$ Hz, 0.63 H), 5.66 (s, 0.63 H), 5.41 (d, $J=13.0$ Hz, 1 h), 5.29 (s, 0.63 H), 5.09 (s, 1 h), 5.04 (s, 1 H), 4.65 (d, $J=7.0$ Hz, 0.63 H), 3.90-3.80 (m, 1.26 H), 3.70 (q, $J=7.0$ Hz, 2 H), 2.11 (s, 4.89 H), 1.24 (t, $J=7.0$ Hz, 1.89 H), 1.21 (t, $J=7.0$ Hz, 3 H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 169.9, 169.8, 148.8, 147.8, 141.9, 140.9, 139.0, 138.4, 128.4, 128.2, 128.1, 127.8, 127.4, 127.3, 114.1, 110.9, 104.6, 102.1, 77.5, 75.7, 69.0, 65.3, 21.3, 21.2, 15.2, 14.6. FT-IR (thin film, cm^{-1}) 3054, 2986, 1742, 1422, 1273, 896. High resolution ESI molecular ion calcd for $\text{C}_{15}\text{H}_{18}\text{O}_3$ 246.1256 found 269.1111 ($\text{M} + \text{Na}$), error 5.9 ppm.

***E/Z* 1-Butoxy-3-phenyl-1,3-butadiene (**16A**)**

As above, plug filtration (elution with 1 % ethyl acetate/hexane) to yield 90.6 mg of **16A** (90%) as a clear oil (99% conversion by GC). GC retention time of 13.24 and 13.36 min. Analytical TLC (10% ethyl acetate/hexane) R_f 0.17. Proton NMR indicated a 0.63:1.0 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.43-7.20 (m, 8.15 H), 6.44 (d, $J=13.0$ Hz, 1 H), 6.26 (s, 0.63 H), 5.80 (s, 0.63 H), 5.79 (d, $J=13.0$ Hz, 1 H), 5.45 (s, 0.63 H), 5.07 (s, 1 h), 5.01 (d, $J=7.0$ Hz, 0.63 H), 4.88 (s, 1 h), 3.88 (t, $J=6.5$ Hz, 1.26 H), 3.35 (t, $J=6.5$ Hz, 2 H), 1.67-1.60 (m, 3.26 H), 1.41-1.36 (m, 3.26 H), 0.97-0.91 (m, 4.89 H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 150.9, 148.4, 145.7, 143.1, 142.3, 140.9, 128.0, 127.9, 126.9, 126.5, 125.8, 125.4, 114.9, 111.3, 107.8, 104.0, 73.3, 69.7, 31.8, 31.3, 19.1, 19.0, 13.7, 13.6. FT-IR (thin film, cm^{-1}) 3057, 2960, 2930, 2871, 1769, 1747, 1444. High resolution EI molecular ion calcd for $\text{C}_{14}\text{H}_{18}\text{O}$ 202.1352 found 202.1355, error 1.3 ppm.

***E/Z*1-Acetoxy-3-phenyl-1,3-butadiene (16B)**

As above, column chromatography (elution with 3 % ethyl acetate/hexane) to yield 150.2 mg (80 %) **16B** as a yellow oil. GC retention time of 12.43 and 12.68 min. Analytical TLC (10 % ethyl acetate/hexane) R_f 0.3. Proton NMR indicated a 1:1 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.38-7.15 (m, 12 H), 6.30 (d, $J=13.0$ Hz, 1 H), 5.59 (d, $J=7.0$ Hz, 1 H), 5.56 (s, 1 H), 5.52 (s, 1 H), 5.26 (s, 1 H), 5.14 (s, 1 H), 2.13 (s, 3 H), 1.95 (s, 3 H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 167.7, 167.6, 144.1, 141.6, 141.3, 139.6, 138.8, 135.1, 128.3, 128.0, 127.8, 127.7, 127.4, 126.7, 117.9, 117.0, 116.3, 112.0, 20.7, 20.4. FT-IR (thin film, cm^{-1}) 3090, 3052, 3020, 1756, 1653, 1380, 1218, 909. High resolution ESI molecular ion calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2$ 188.0783 found 211.0728 ($\text{M} + \text{Na}$), error 0.9 ppm.

***E/Z*Butyl 3-methylene-1-nonenyl ether (18A)**

As above, flash chromatography (elution with hexane) to yield 91 mg of **18A** (86%) as a clear oil (99% conversion by GC). GC retention time of 12.62 and 12.91 min. Analytical TLC (10% ethyl acetate/hexane) R_f 0.64. Proton NMR indicated a 1.5:1.0 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 6.58 (d, $J=13.0$ Hz, 1 H), 5.96 (d, $J=7.0$ Hz, 1.5 H), 5.56 (d, $J=13.0$ Hz, 1H), 5.13 (s, 1.5 H), 4.82 (s, 1.5 H), 4.76 (s, 1 H), 4.72 (d, $J=7.0$ Hz, 1.5 H), 4.67 (s, 1 H), 3.81 (t, $J=6.5$ Hz, 3.0 H), 3.74 (t, $J=6.5$ Hz, 2 H), 2.2 (t, $J=8.0$ Hz, 3.0 H), 2.13 (t, $J=8.0$ Hz, 2 H), 1.68-1.60 (m, 5 H), 1.51-1.28 (m, 25 H), 0.96-0.86 (m, 15 H). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ 147.6, 146.2, 144.4, 144.3, 112.0, 109.8, 108.1, 106.1, 73.1, 69.4, 37.3, 32.9, 31.9, 31.8, 31.7, 31.4, 29.3, 29.2, 29.1, 28.3, 22.7, 22.6, 19.1, 19.0, 14.1, 14.0, 13.8, 13.8. FT-IR (thin film, cm^{-1}) 3052, 2956, 2930, 2855, 1747, 1465. High resolution EI molecular ion calcd for $\text{C}_{14}\text{H}_{26}\text{O}$ 210.1978 found 210.1982, error 1.7 ppm.

***E/Z*1-Acetoxy-3-hexyl-1,3-butadiene (18B)**

As above, flash chromatography (elution with hexane) to yield 68 mg of **18B** (70%) as a clear oil (99% conversion by GC). GC retention time of 11.96 and 12.17 min. Analytical TLC (10% ethyl acetate/hexane) R_f 0.1. Proton NMR indicated a 1.0:1.0 (*Z:E*) ratio of isomers. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ 7.09 (d, $J=13.0$ Hz, 1 H), 7.00 (d, $J=7.0$ Hz, 1 H), 6.05 (d, $J=13.0$ Hz, 1 H), 5.24 (d, $J=7.0$ Hz, 1 H), 5.11 (s, 1 H), 4.97 (s, 1 H), 4.94 (s, 1 H), 4.91 (s, 1 H), 2.28 (t, $J=7.0$

Hz, 2 H), 2.20-2.13 (m, 8 H), 1.50-1.38 (m, 4 H), 1.30-1.24 (m, 12 H), 0.89-0.84 (m, 6 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 168.1, 167.5, 143.2, 142.9, 135.8, 132.8, 117.6, 116.5, 115.0, 113.2, 36.9, 36.4, 32.3, 31.8, 31.7, 31.6, 29.2, 28.9, 27.9, 22.6, 20.8, 20.7, 14.1, 14.0. FT-IR (thin film, cm^{-1}) 2956, 2930, 2860, 1747, 1710, 1385. High resolution EI molecular ion calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2$ 196.1458 found 196.1463, error 2.8 ppm.

3-Acetoxymethyl-4-butoxy-2-methylene-3-butenyl acetate (20)

As above, flash chromatography (elution with hexane) to yield 56.1 mg of **20** (98%) as a clear oil (99% conversion by GC). GC retention time of 14.67 min. Analytical TLC (10% ethyl acetate/hexane) R_f 0.64. Proton NMR indicated a 0.43:1.0 (*Z:E*) ratio of isomers. ^1H -NMR (500 MHz, CDCl_3) δ 6.49 (s, 1 H), 6.38 (s, 0.43 H), 5.26 (s, 0.43 H), 5.21 (s, 0.43 H), 5.11 (s, 1 H), 5.09 (s, 1 H), 4.88 (s, 1 H), 4.86 (s, 1 H), 4.72 (s, 0.43 H), 4.62 (s, 0.43 H), 3.89 (t, $J=6.5$ Hz, 2 H), 3.85 (t, $J=6.5$ Hz, 0.86 H), 2.14-2.04 (m, 4.29 H), 1.65-1.60 (m, 2.86 H), 1.43-1.38 (m, 2.86 H), 0.95-0.92 (m, 4.29 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 171.3, 171.1, 170.7, 170.6, 150.6, 149.4, 138.7, 138.3, 113.6, 112.4, 111.3, 108.7, 73.8, 73.4, 66.4, 65.6, 65.2, 58.1, 31.8, 31.6, 21.2, 21.1, 21.0, 20.9, 18.9, 18.8, 13.7, 13.6. FT-IR (thin film, cm^{-1}) 2962, 2935, 2871, 1744, 1678, 1375. High resolution ESI molecular ion calcd for $\text{C}_{14}\text{H}_{22}\text{O}_5$ 270.1467 found 293.1359 ($\text{M} + \text{Na}$), error 2.0 ppm.

(7-Ethoxy-2-methyl-1,3-dioxo-2,3,3',4,7,7'-hexahydro-1H-isoindol-5-yl)methyl benzoate (21)

To a pressure tube was added 113.8 mg **8A** (0.49 mmol, 1 eq), 489.9 mg *N*-methyl maleimide (4.41 mmol, 9 eq), 2.7 mg hydroquinone (0.025 mmol, 0.05 eq) and 5 mL toluene. The reaction vessel was sealed and heated to 180 °C for 66 h, cooled to room temperature, concentrated *in vacuo* (rotary evaporator) and purified by flash chromatography (elution with 10 % ethyl acetate/hexane to 50 % ethyl acetate/hexane) to yield 94.6 mg of **21** (84 %, based on *E*-isomer of **8A**) as an oil. Analytical TLC (50 % ethyl acetate/hexane) R_f 0.6. ^1H -NMR (500 MHz, CDCl_3) δ 8.06 (d, $J=8.5$ Hz, 2 H), 7.59 (t, $J=8.0$ Hz, 1 H), 7.46 (t, $J=8.0$ Hz, 2 H), 6.15 (d, $J=4.5$ Hz, 1 H), 4.81 (s, 2 H), 4.36 (d, $J=4.5$ Hz, 1 H), 3.47 (q, $J=7.0$ Hz, 2 H), 3.10 (br s, 2 H), 2.98 (s, 3 H), 2.70, d, $J=14.5$ Hz, 1 H), 2.54-2.50 (m, 1 H), 1.09 (t, $J=7.0$ Hz, 3 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 179.6, 179.5, 166.0, 138.1, 133.2, 129.7, 129.6, 128.4, 125.2, 70.4, 66.5, 64.5, 44.9, 37.3, 24.6, 23.5, 15.2.

FT-IR (thin film, cm^{-1}) 1700, 1471, 1384, 1270, 1107, 909, 726. High resolution ESI molecular ion calcd for $\text{C}_{19}\text{H}_{21}\text{O}_5\text{N}$ 343.1420, found 366.1316 ($\text{M} + \text{Na}$), error 1.2 ppm.

2-Acetoxy-4-hexyl-1-methyl-3-cyclohexenecarbaldehyde (**22**)

Into an oven-dried 50 mL schlenk flask equipped with a magnetic stirbar and rubber septum was added 110 mg crushed 4Å MS (Aldrich) followed by sequential addition of 0.5 mL 0.02 M solution of *R*(+) BINOL in CH_2Cl_2 (10 μmol , 10 mol %) and 33 μL of 0.3 M $(i\text{-PrO})_2\text{TiCl}_2$ in toluene (9.9 μmol). The deep red solution was stirred for 1.5 h at rt, then 8.8 μL methacrolein (distilled, 0.106 mmol, 1 eq.) was added by microliter syringe followed by 0.5 mL of a 0.85 M solution of diene **18B** (83.5 mg, 0.426 mmol, 4 eq) in toluene. The solution was stirred at room temperature for 21 h, diluted with Et_2O (20 mL) and washed with NaHCO_3 , filtered through celite, separated and dried (MgSO_4) to give a crude yellow oil that was purified by flash chromatography on silica gel (3 cm $\times$ 20 cm column) eluted with 10 % ethyl acetate-hexanes to give 19.7 mg (70 %) cycloadduct **22** (R_f 0.14) as a 3.5 : 1.0 mixture of diastereomers (determined by ^1H NMR). $[\alpha]_D^{25} = +60.96$. The enantiomeric excess was determined by hplc (*R,R* Whelk-O1, 1 % IPA-hexanes, flow rate = 0.5 mL/min, UV-220 nm) which showed the major diastereomer at 15.06 and 15.77 min in a 4.34 : 1.00 ratio (62.5 % ee). Spectroscopic data for the major diastereomer: ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 9.67 (s, 1H) 5.51 (br d, $J=3.0$ Hz, 1H) 5.27 (br d, $J=3.0$ Hz, 1H) 2.08-1.96 (m, 8H), 1.66-1.63 (m, 1H) 1.41-1.25 (m, 9H) 1.06 (s, 3H) 0.88 (t, $J=7.0$ Hz, 3H). ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 204.4, 170.7, 144.7, 117.6, 72.71, 47.60, 37.07, 31.61, 28.90, 27.34, 25.82, 25.17, 24.98, 22.55, 17.63, 14.04. FT-IR (thin film, cm^{-1}) 2929, 1733, 1371, 1235, 1017. HR-MS (EI^+) calcd for $\text{C}_{16}\text{H}_{26}\text{O}_3$ 266.1876, found 266.1887 (M^+), error 4 ppm.

6-Carbomethoxy-5,6-dihydro-2-butoxy-4-phenyl-2H-pyran (*cis*-**23**)

Into an oven-dried 50 mL schlenk flask equipped with magnetic stirbar and rubber septum was added 271 mg **16A** (1.34 mmol) dissolved in 1 mL CH_2Cl_2 . The flask was cooled to -40 $^\circ\text{C}$ in an acetonitrile/dry ice bath, and then a solution of 29.5 mg methyl glyoxylate (0.335 mmol) in 1 mL CH_2Cl_2 was added via syringe. The vessel was warmed to ambient temperature and stirred for 12 h under an argon atmosphere. The solution was then concentrated *in vacuo* (rotary evaporator) and the resultant oil was purified via flash chromatography on silica gel (gradient elution with 2.5 % ethyl acetate-hexanes to 10 % ethyl acetate-

hexanes) to give 81.1 mg (83%) dihydropyran **23** as a 1.0 : 0.52 mixture of *cis:trans* diastereomers (determined by ^1H NMR). R_f 0.29 (10 % ethyl acetate-hexanes). ^1H -NMR (500 MHz, CDCl_3) δ 7.43 (t, $J=7$ Hz, 3.04 H), 7.36-7.30 (m, 4.56 H), 6.11 (s, 0.52 H), 6.04 (s, 1.00 H), 5.31 (s, 1.52 H), 4.70 (dd, $J=6.5$, 4.5 Hz, 0.52 H), 4.52 (dd, $J=12$, 2 Hz, 1.0 H), 3.97-3.94 (m, 1 H), 3.92-3.86 (m, 0.52 H), 3.84 (s, 1.52 H), 3.79 (s, 3.04 H), 3.61-3.54 (m, 1.52 H), 2.87 (dd, $J=17$, 7.5 Hz, 1 H), 2.70 (m, 2.04 H), 1.64-1.59 (m, 3.04 H), 1.45-1.35 (m, 3.04 H), 0.93 (t, $J=7.5$ Hz, 4.56 H). ^{13}C -NMR (125 MHz, CDCl_3) δ 171.7, 171.2, 138.8, 138.7, 137.6, 137.5, 128.5, 128.4, 128.2, 128.1, 125.3, 125.2, 121.9, 120.8, 97.2, 95.4, 70.0, 68.4, 68.3, 66.3, 52.3, 52.2, 31.8, 31.7, 29.5, 28.4, 19.3, 19.2, 13.9, 13.8; FT-IR (thin film, cm^{-1}) 2956, 2871, 1741, 1136, 1050. High resolution EI molecular ion calcd for $\text{C}_{17}\text{H}_{22}\text{O}_4$ 290.1518 found 290.1521, error 0.9 ppm.

6-Carbomethoxy-5,6-dihydro-2-butoxy-4-phenyl-2H-pyran (*trans*-**23**)

Into an oven-dried 50 mL schlenk flask equipped with magnetic stirbar and rubber septum was added 81.1 mg **23** (1.0:0.52 *cis:trans*, 0.279 mmol) dissolved in 2 mL CH_2Cl_2 . The flask was then cooled to 0 °C (ice bath), and 3.8 mg ZnCl_2 was added. The flask was swirled to ensure all of the ZnCl_2 was in solution, and the reaction was stirred at 0 °C for 3 h under an argon atmosphere. The solution was quenched with saturated NaHCO_3 and then extracted twice with ether. The combined ether layers were washed with brine, dried (MgSO_4), filtered and concentrated *in vacuo* (rotary evaporator). The obtained oil was purified via flash chromatography on silica gel (eluted with 10 % ethyl acetate-hexanes) to give 70.7 mg (87 %) of *trans*-**23**. R_f 0.29 10 % (ethyl acetate-hexanes). ^1H -NMR (300 MHz, CDCl_3) δ 7.43 (t, $J=7$ Hz, 2 H), 7.36-7.30 (m, 3 H), 6.11 (s, 1 H), 5.31 (s, 1 H), 4.63 (m, 1 H), 3.94-3.78 (m, 4 H), 3.64-3.52 (m, 1H), 2.71 (m, 2 H), 1.64-1.56 (m, 2 H), 1.48-1.34 (m, 2 H), 0.94 (t, $J=7.2$ Hz, 3 H). ^{13}C -NMR (75 MHz, CDCl_3) δ 171.7, 138.8, 137.6, 128.5, 128.2, 125.3, 120.9, 95.4, 68.3, 66.4, 52.3, 31.8, 29.6, 19.3, 13.8. FT-IR (thin film, cm^{-1}) 2956, 2872, 1741, 1135, 1040.