

Supporting Information

Further Studies of Cross Metathesis of α -Methylene Lactones

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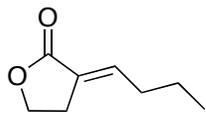
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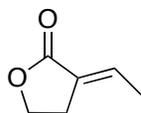
General Experimental. ^1H NMR spectra were recorded at 300 MHz and 400 MHz and chemical shifts are reported in units of parts per million (ppm). IR spectra were recorded on an FT-IR spectrometer. GC/MS spectra were obtained on a gas chromatograph equipped with a HP-1 methyl silicon column and detected on a low-resolution 5970 series mass selective detector. High resolution mass spectra were obtained on a JMS-AX505HA spectrometer. Column chromatography was performed using silica gel, 40 microns flash silica. Thin layer chromatography was performed on silica gel (Silica Gel 60 F₂₅₄) glass plates, and the compounds were visualized by UV, 5% phosphomolybdic acid in ethanol or 0.5% aqueous solution of KMnO_4 .

General cross-metathesis protocol. A solution of **1** (1 equiv) and olefin cross partner (1-1.5 equiv) in CH_2Cl_2 (0.3N-0.4N in lactone) was added 2,6 dichlorobenzoquinone (0.10 equiv), followed by the addition of **4** (0.05-0.10 equiv). The resultant solution, was heated at reflux under N_2 for 12-24 h. The reaction was monitored by ^1H NMR. Upon consumption of **1**, the solution was cooled and concentrated, and the brown residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc 80:20).



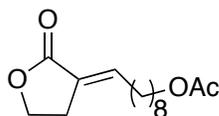
(E)- α -Butylidene- γ -butyrolactone (8a). Purification provided **8a**¹ as

a clear oil (55.0 mg, 79%): ¹H NMR (400 MHz, CDCl₃) δ 6.74 (tt, J = 7.5, 2.8 Hz, 1H), 4.38 (t, J = 7.5, 2H), 2.88 (m, 2H), 2.18 (m, 2H), 1.53 (sextet, J = 7.3 Hz, 2H), 0.96 (t, J = 7.4, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.5, 140.9, 125.5, 65.5, 32.3, 25.2, 21.6, 13.9.



(E)- α -Ethylidene- γ -butyrolactone (8b). Purification provided **8b**¹ as a

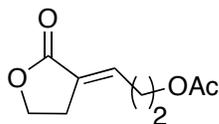
clear oil (45.9 mg, 80%): ¹H NMR (400 MHz, CDCl₃) δ 6.77 (tq, J = 7.1, 2.9 Hz, 1H), 4.36 (t, J = 7.5, 2H), 2.86 (m, 2H), 1.85 (dt, J = 7.1, 2.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.3, 135.8, 126.4, 65.5, 25.1, 15.8; **(Z)- α -Butylidene- γ -butyrolactone (8b).** Purification provided **8b**¹ as a clear oil (7.4 mg, 13%): ¹H NMR (400 MHz, CDCl₃) δ 6.34 (tq, J = 7.3, 2.3 Hz, 1H), 4.33 (t, J = 7.4, 2H), 2.93 (m, 2H), 2.20 (dt, J = 7.3, 2.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.4, 138.9, 124.5, 65.5, 29.3, 14.1;



Acetic acid 9-(2-oxodihydrofuran-3-ylidene)nonyl ester (8c).

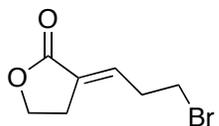
Purification provided **8c** as a clear oil (0.11 g, 78%): IR (KBr) 2929, 1757, 1739, 1679, 1243, 1031 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.66 (tt, J = 7.5, 2.8 Hz, 1H), 4.30 (t, J = 7.5, 2H), 3.97 (t, J = 6.7 Hz, 2H), 2.79 (tdt, J = 7.4, 2.6, 1.3 Hz, 2H), 2.12 (dt, J = 7.4, 7.4 Hz, 2H), 1.96 (s, 3H), 1.53 (m, 2H), 1.40 (m, 2H), 1.24 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 171.4, 171.2, 140.9, 125.3, 65.5, 64.6, 30.3, 29.3, 29.3, 29.2, 28.6, 28.2, 25.9,

25.1, 21.0; MS (EI) m/z 376 ($M^+ - CO_2$), 219, 205, 167 (100), 152, 115, 91; Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 66.87; H, 8.69.



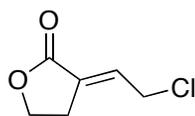
Acetic acid 3-(2-oxodihydrofuran-3-ylidene)propyl ester (8d).

Purification provided **8d** as a clear oil (63.8 mg, 68%): IR (KBr) 1754, 1684, 1242, 1200, 1038 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.58 (tt, $J = 7.4, 2.9$ Hz, 1H), 4.28 (t, $J = 7.4$ Hz, 2H), 4.08 (t, $J = 6.5$ Hz, 2H), 2.81 (m, 2H), 2.44 (dt, $J = 7.0, 7.0$ Hz, 2H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.7, 135.3, 127.8, 65.3, 62.1, 29.4, 25.0, 20.7; MS (EI) m/z 141 ($M^+ - CH_3CO$), 124 (100), 112, 94, 83; Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.30; H, 6.82.



(E)- α -Bromopropylidene- γ -butyrolactone (8e). Purification provided

8e as a clear oil (41.0 mg, 43%): IR (KBr) 2921, 1744, 1680, 1223, 1168, 1027 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 6.71 (tt, $J = 7.4, 2.9$ Hz, 1H), 4.41 (t, $J = 7.4$ Hz, 2H), 3.49 (t, $J = 6.7$ Hz, 2H), 2.92 (m, 2H), 2.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 136.4, 128.3, 65.6, 33.4, 30.2, 25.4; MS (EI) m/z 146 ($M^+ - 2CO$), 125 (100), 97, 79; HRMS (FAB) calcd for $C_7H_{10}BrO_2$ ($M^+ + H$) m/z 204.9864. Found: 204.9868.



(E)- α -Chloroethylidene- γ -butyrolactone (8f). Purification

provided **8f** as a clear oil (18.0 mg, 44%): 1H NMR (300 MHz, $CDCl_3$) δ 6.82 (tt, $J = 7.6,$

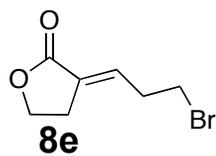
3.0 Hz, 1H), 4.44 (t, $J = 7.3$ Hz, 2H), 4.16 (d, $J = 7.7$ Hz, 2H), 3.01 (tdt, $J = 7.3, 3.0, 1.5$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.4, 133.3, 129.6, 65.6, 40.0, 25.1; MS (EI) m/z 146 (M^+), 111, 53 (100); Anal. Calcd for $\text{C}_6\text{H}_7\text{ClO}_2$: C, 49.17; H, 4.81. Found: C, 49.40; H, 4.98.

Lactone **2** was prepared from commercially available δ -hexanolactone.^{2,3}

¹Larson, G. L.; Betancourt de Perez, R. M. *J. Org. Chem.* **1985**, *50*, 5257-5260.

²Danishefsky, S.; Kitahara, T.; McKee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 6715-6717.

³Krawczyk, H.; Sliwinski, M. *Tetrahedron* **2003**, *59*, 9199-9211.



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6.68

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3.46

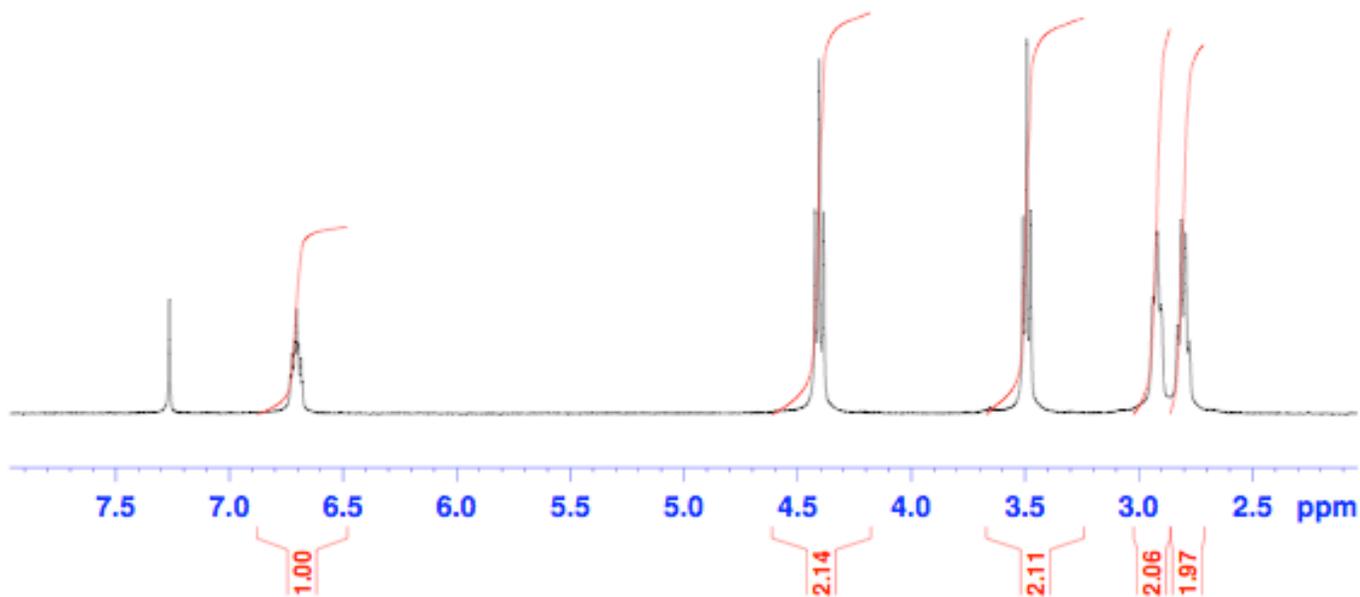
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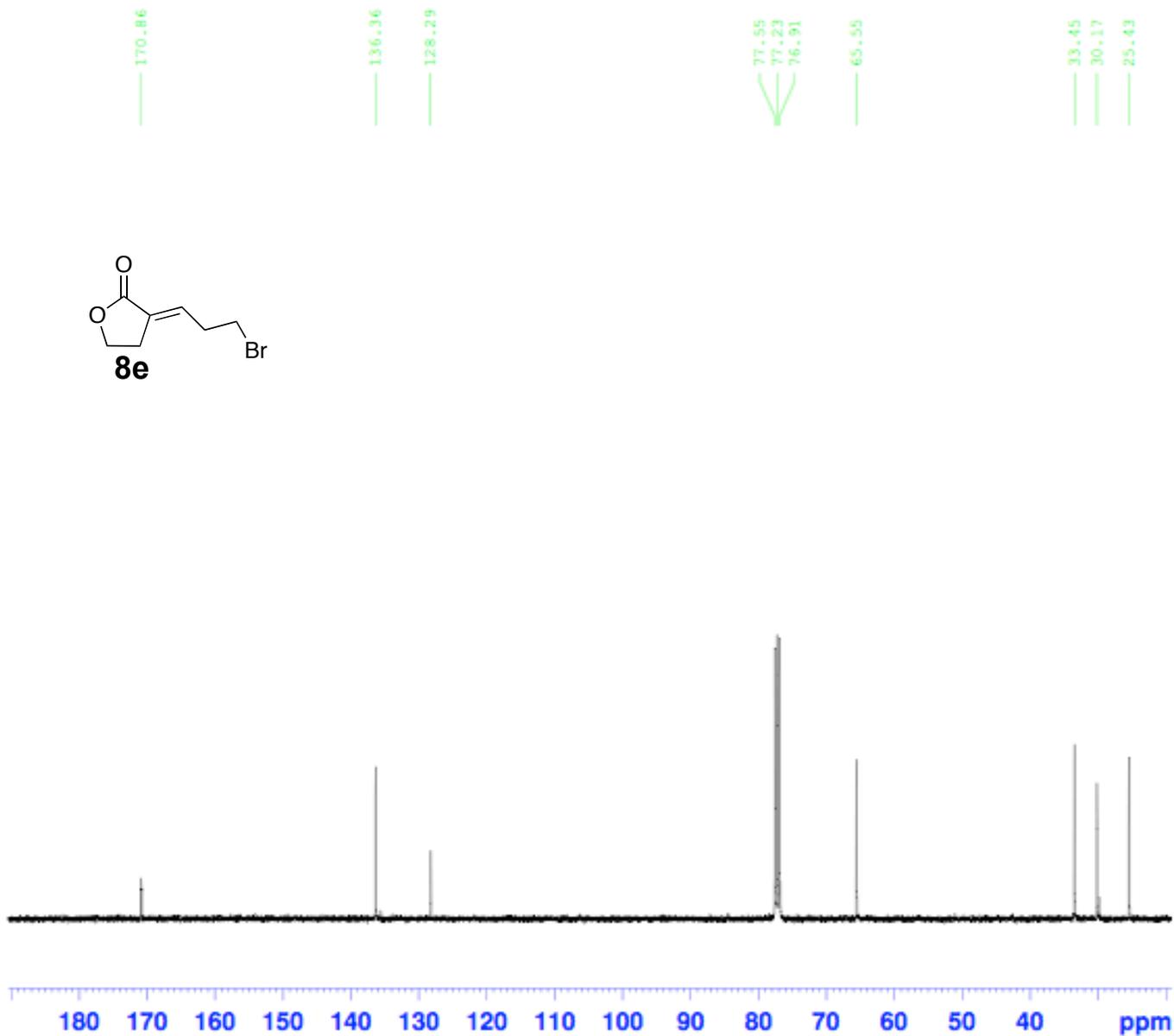
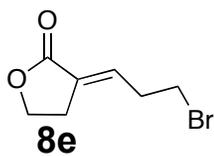
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