Supporting Information for:

Prevention of Undesirable Isomerization During Olefin Metathesis Reactions

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General Considerations. Manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry argon or in a nitrogen-filled Vacuum Atmospheres drybox (O_2 < 2.5 ppm). NMR spectra were recorded on a Varian Mercury 300 (299.817 MHz for ^1H). GC analysis were performed on Rtx-5 column (Restek, 5% diphenyl - 95% dimethyl polysiloxane) with HP 6890 GC.

Materials and Methods. CD_2Cl_2 was dried by distillation from CaH_2 and degassed by three freeze-pump-thaw cycles . The catalysts **1**, **2**, and **3** were obtained from Materia, Inc. and further purified by column chromatography using silica gel obtained from TSI.[1] 1,4-Benzoquinones, allyl ether

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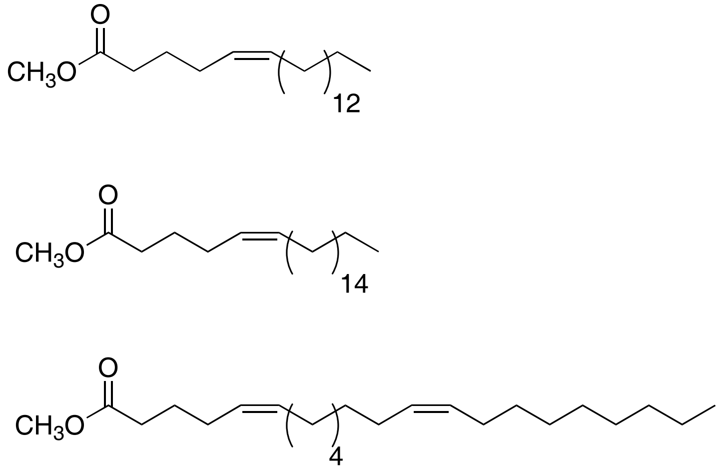
[1] We purified commercial ruthenium catalysts to eliminate the possibility that catalyst impurities caused the isomerization. However, purified catalysts behaved almost identical with unpurified commercial ones. For detailed catalyst purification procedure, see: Sutton, A. E.; Seigal, B. A.; Finnegan D. F.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 13390-13391.

and other additives were obtained from Aldrich and used as received. *N,N*-diallylaniline **19** was purchased from Pfaltz & Bauer and used as received. The complex **4**,[2] (*Z*)-5-*tert*-butyldimethylsilyloxy-2-pentenoate **5**,[3] (*Z*)-1,4-Bis(*tert*-butyldimethylsilyloxy)-2-butene **11**,[4] 11-eicosenyl acetate **16**[5] were prepared according to literature procedures. Meadowfoam oil methyl esters were produced by transesterification of Meadowfoam oil purchased from Natural Plant Products LLC, Oregon, USA.


MeC20:1 63%

MeC22:1 16%

MeC22:2 17%

Meadow Foam Oil Methyl Esters

General experimental procedure for Table 1, 2, and 3, and Scheme 2. Catalyst **2** (2 mol% or 5 mol%) and additive (0.1 ~ 1.0 equiv. of substrate) were dissolved in CD_2Cl_2 (0.7mL) in a 5mL vial in a nitrogen-filled Vacuum Atmospheres drybox. Substrate (0.16 mmol) was added to the solution, and the reaction mixture was transferred to an NMR tube fitted with a screw cap. The NMR tube was taken out

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[2] Hong, S. H.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 7414-7415.

[3] Herold, P.; Mohr, P.; Tamm, C. *Helv. Chim. Acta.* **1983**, *66*, 744-754.

[4] Jones, K.; Storey, J. M. D. *Tetrahedron* **1993**, *49*, 4901-4906.

[5] Pederson, R. L.; Fellows, I. M.; Ung, T. A.; Ishihara, H.; Hajela, S. *Adv. Synth. Catal.* **2002**, *344*, 728-735.

of the drybox, and heated to 40 °C in an oil bath. The reaction was monitored by ^{1}H NMR. The conversion was measured by ^{1}H NMR using 20 mol% of anthracene as an internal standard.[6]

(*E*)-5-*tert*-butyldimethylsilyloxy-2-pentenoate (6).[3] ^{1}H NMR (CD_2Cl_2): δ6.96 (td, 1H, *J*=7.2, 15.6 Hz), 5.88 (td, 1H, *J*=1.5, 15.6 Hz), 3.74 (t, 2H, *J*=6.5 Hz), 3.70 (s, 3H), 2.41 (td, 2H, *J*=6.5, 7.2 Hz), 0.90 (s, 9H), 0.06 (s, 6H)

(*Z*) & (*E*) mixture of 5-*tert*-butyldimethylsilyloxy-4-pentenoate (*E/Z* ~ 1:1) (7).[7] ^{1}H NMR (CD_2Cl_2): δ6.30 (td, 1H, *J*=1.5, 12.3 Hz, *E*), 6.22 (dd, 1H, *J*=2.4, 6.0 Hz, *Z*), 4.95 (td, 1H, *J*=7.4, 12.0 Hz, *E*), 4.47 (dt, 1H, *J*=6.0, 7.0 Hz, *Z*), 2.40~2.15 (m, 8H, *E & Z*), 3.65 (s, 6H, *E & Z*), 0.94 (s, 9H, *Z*), 0.92 (s, 9H, *E*), 0.15 (s, 6H, *Z*), 0.13 (s, 6H, *E*)

2,5 Dihydrofuran (9). ^{1}H NMR (CD_2Cl_2): δ5.91 (t, 2H, *J*=0.9Hz), 4.60 (d, 4H, *J*=0.9Hz)

2,3-Dihydrofuran (10). ^{1}H NMR (CD_2Cl_2): δ6.32 (m, 1H), 4.95(m, 1H), 4.28 (t, 2H, *J*=9.6Hz), 2.59 (m, 2H)

(*E*)-1,4-Bis(*tert*-butyldimethylsilyloxy)-2-butene (12).[4] ^{1}H NMR (CD_2Cl_2): δ5.77 (t, 2H, *J*=3.0Hz), 4.18 (d, 4H, *J*=3.0Hz), 0.92 (s, 9H), 0.08 (s, 6H)

(*Z*) & (*E*) mixture of 1,4-Bis(*tert*-butyldimethylsilyloxy)-1-butene (*E/Z* ~ 1:1.4) (13).[8] ^{1}H NMR (CD_2Cl_2): δ6.29 (td, 1H, *J*=1.2, 12.1 Hz, *E*), 6.22 (td, 1H, *J*=1.5, 5.7 Hz, *Z*), 4.95 (td, 1H, *J*=7.2, 12.1 Hz,

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[6] Conversions measured by ^{1}H NMR were identical between with and without an internal standard.

[7] Ohba, T.; Ikeda, E.; Tsuchiya, N.; Nishimura, K.; Takei, H. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2629-2634.

[8] Kang, K. ; Weber, W. P. *Tetrahedron Lett.* **1985**, *26*, 5753-5754.

E), 4.49 (dt, 1H, *J*=5.7, 7.2 Hz, *Z*), 3.60 (t, 2H, *J*=6.9 Hz, *Z*), 3.57 (t, 2H, *J*=6.6 Hz, *E*), 2.30 (td, 2H, *J*=6.9, 7.2 Hz, *Z*), 2.09 (td, 2H, *J*=6.6, 7.2 Hz, *E*), 0.94 (s, 9H, *Z*), 0.91 (s, 9H, *E*), 0.15 (s, 6H, *E*), 0.07 (s, 6H, *Z*)

N-Phenyl-3-pyrroline (20).[9] ^{1}H NMR (CD_2Cl_2): δ7.24 (m, 2H), 6.67 (m, 1H), 6.54 (m, 2H), 5.99 (s, 2H), 4.12 (s, 4H)

N-Phenyl-2-pyrroline (21).[10] ^{1}H NMR (CD_2Cl_2): δ7.47, 7.30, and 6.56 (m, 5H aromatic), 7.13 (m, 1H), 6.35 (m, 1H), 3.30 (m, 2H), 2.02 (m, 2H)

Ethenolysis of Meadowfoam oil methyl ester 14.[11] Meadowfoam oil methyl ester **14** was degassed with anhydrous argon for 10 minutes. 10 g (31.3 mmol) of **14** was added to two Fisher-Porter bottles. To one bottle was added 1,4-benzoquinone (20 mg, 0.19 mmol) followed by ruthenium catalyst **1** (77 mg, 0.094 mmol) at room temperature. To the other bottle was added only catalyst **1** (77 mg), as the control reaction. Both bottles were pressurized with ethylene (130 psi), and stirred for 66.5 hrs at 40 ^{o}C. The reaction mixture was collected during the reaction, and then quenched with an excess amount of 1 M THMP solution (trishydroxymethyl phosphine in IPA), stirred at ~ 50 ^{o}C for 1h and then analyzed by GC and GC-MS. GC and GC/MS results: t_R 1.67 min (Methyl 5-hexenoate **15**, M^+=128), t_R 1.73 and 1.77 min (isomerized products of **15**, M^+=128), t_R 2.04 min (cyclooctene[12], M^+=110), t_R 2.09 min (1-Decene, M^+=140), t_R 8.88 min (1-Hexadecene, M^+=224), t_R 16.39 min (Methyl 5-Eicosenoate, M^+=324), t_R 18.34 min (Methyl 5,13-Docosadienoate, M^+=350), t_R 18.65 min (Methyl 5-Docosenoate, M^+=352).

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[9] Martinez, V.; Blais, J.-C.; Bravic, G.; Astruc, D. *Organometallics* **2004**, *23*, 861-874.

[10] Seto, Y.; Guengerich, F. P. *J. Biol. Chem.* **1993**, *268*, 9986-9997.

[11] Acetic acid was not as effective as 1,4-benzoquinone in ethenolysis.

Figure S1. GC Traces of Ethnolysis of Meadowfoam Oil Methyl Ester 14 Without 1,4-Benzoquinone (Control)

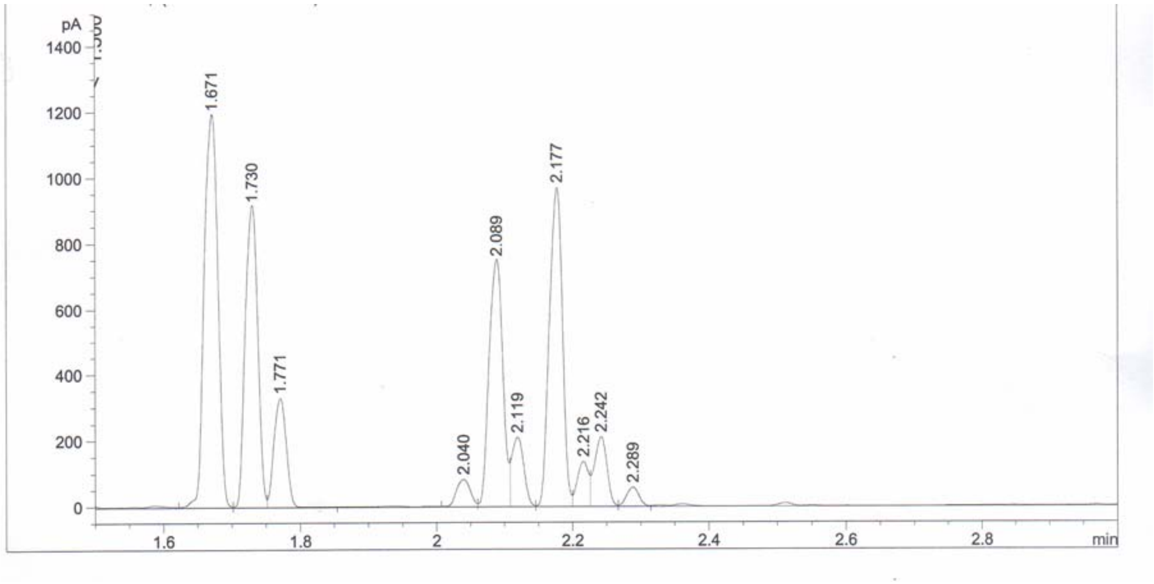
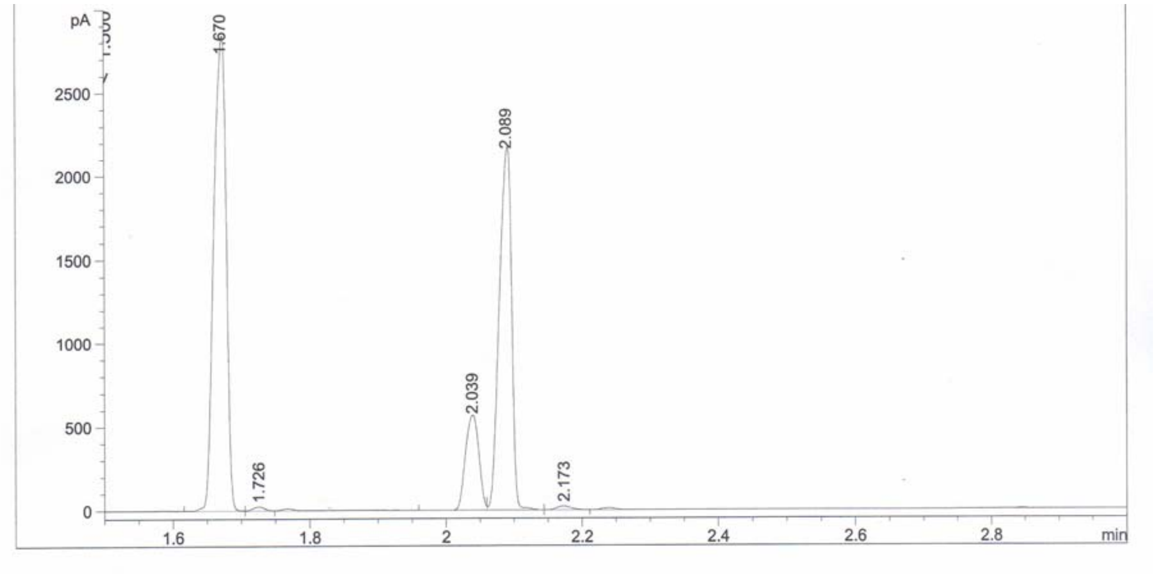


Figure S2. GC Traces of Ethnolysis of Meadowfoam Oil Methyl Ester 14 With 1,4-Benzoquinone



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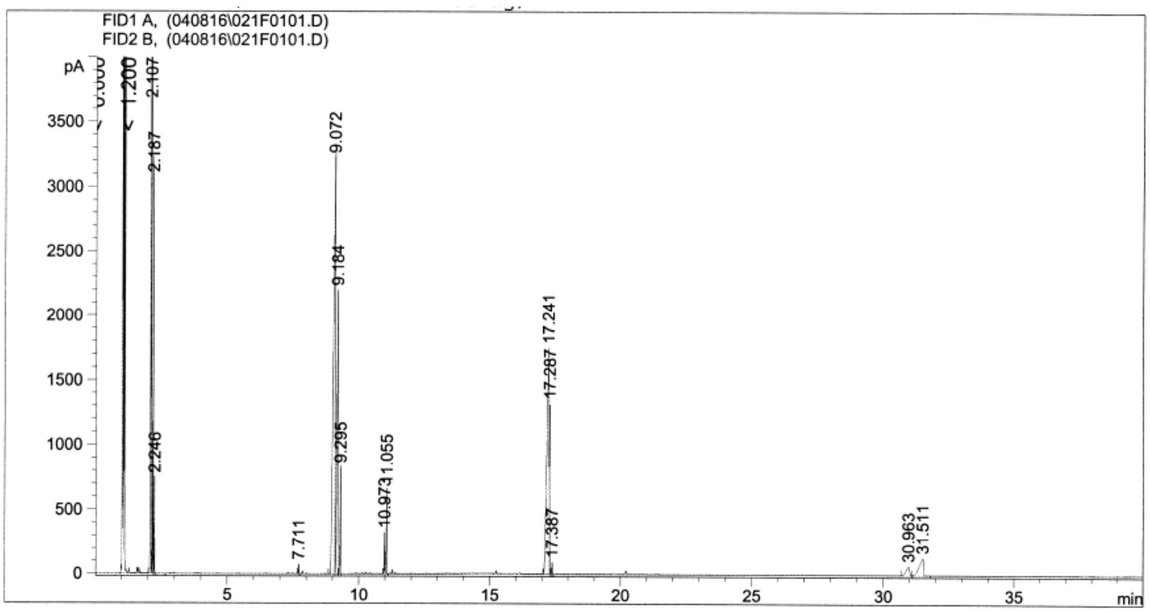
[12] Cyclooctene is formed from intramolecular ring-closing metathesis of **MeC22:2**.

Table S1. Ethnolysis of Meadowfoam Oil Methyl Ester (reported as percent GC Area)

Time (hr)	Reaction	Methyl 5-Eicosenoate	1-Decene	Methyl 5-hexenoate **15**	**%Isomerized 15**
0	Benzoquinone	63	0	0	0
	Control	63	0	0	0
1	Benzoquinone	31	7	10	0
	Control	39	6	8	0
3	Benzoquinone	30	8	11	0
	Control	33	7	9	1
21.3	Benzoquinone	28	7	11	1
	Control	31	7	9	3
66.5	Benzoquinone	29	7	10	1
	Control	31	4	5	49

Ethenolysis of 11-Eicosenyl Acetate 16. 11-Eicosenyl acetate **16** was degassed with anhydrous Argon for 10 minutes. 8 g (23.7 mmol) of **16** was added to two Fisher-Porter bottles. To one bottle was added 1,4-benzoquinone (15 mg, 0.14 mmol) followed by ruthenium catalyst **1** (59 mg, 0.071 mmol) at room temperature. To the other bottle was added only catalyst **1** (59 mg), as the control reaction. Both bottles were pressurized with ethylene (130 psi) and stirred for 41.5 hrs at 40 ^oC or room temperature. During the reaction, samples were collected and analyzed. The reactions were quenched with an excess amount of 1 M THMP solution (trishydroxymethyl phosphine in IPA) at ~ 50 ^oC for 1h, then analyzed by GC and GC-MS. GC and GC/MS results: t_R 2.10 min (1-Decene **17**, M^+=140), t_R 2.19 and 2.25 min (isomerized products of **17**, M^+=140), t_R 9.05 min (11-Dodecenyl acetate **18**, M^+=226), t_R 9.18 and 9.30 min (isomerized products of **18**, M^+=226), t_R 10.96 and t_R 11.03 min (9-Octadecene, M^+=252), t_R 17.27 min (11-Eicosenyl acetate, M^+=338), t_R 30.36 and t_R 31.33 min (11-Docosenyl 1,22-Diacetate, M^+=424).

Figure S3. GC Traces of Ethnolysis of 11-Eicosenyl Acetate 16 Without 1,4-Benzoquinone (Control)



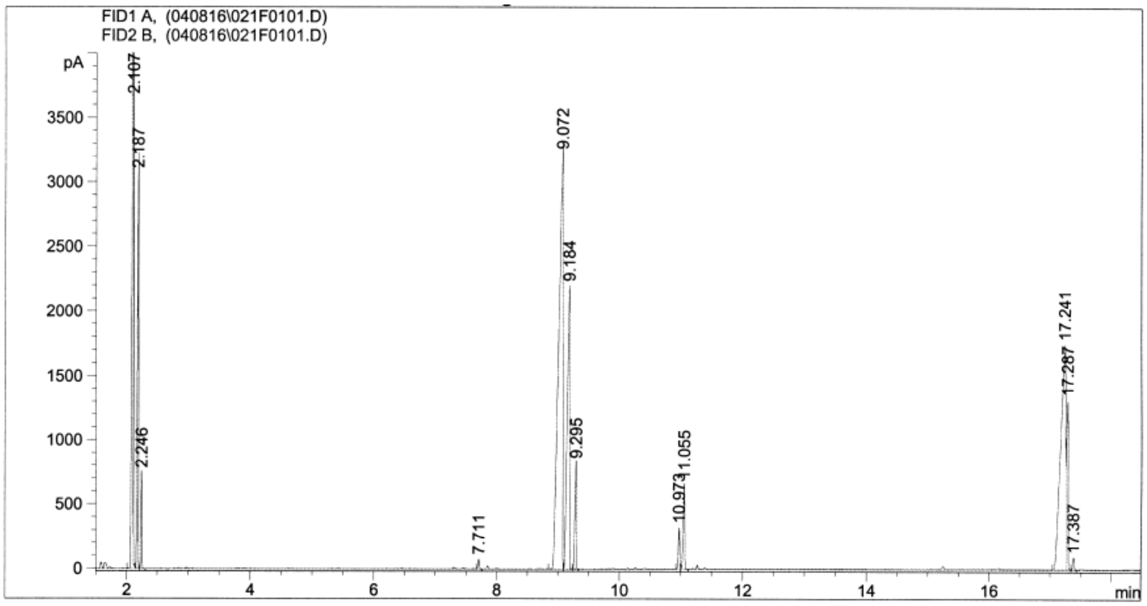


Figure S4. GC Traces of Ethnolysis of 11-Eicosenyl Acetate 16 With 1,4-Benzoquinone

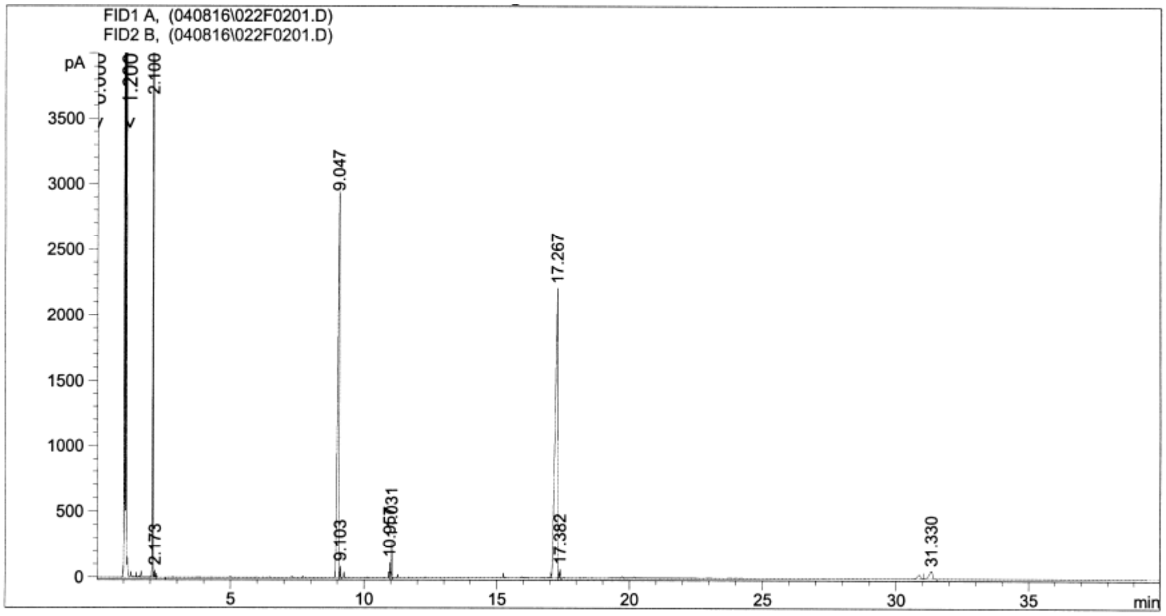


Table S2. Ethenolysis of 11-Eicosenyl Acetate 16 (reported as percent GC Area)

Time (min)	Reaction	11-Eicosenyl acetate	1-Decene **17**	11-Dodecenyl acetate, **18**	9-Octadecene	11-Docosenyl 1,22-Diacetate	**%Isomerized 17, %Isomerized 18**
0	Benzoquinone	98	0	0	0	0	0, 0
	Control	98	0	0	0	0	0, 0
100	Benzoquinone	42	23	32	1	2	0, 0
	Control	27	28	39	2	3	1, 1
1110	Benzoquinone	41	22	32	2	2	0, 1
	Control	23	22	32	3	4	22, 23
2490	Benzoquinone	41	22	32	2	2	1, 2
	Control	23	20	28	3	4	30, 32

Effect of benzoquinone structure on prevention of olefin isomerization. Catalyst **2** (69 mg, 5 mol%) and additive (10 mol%) were dissolved in CD_2Cl_2 (4 mL) in a 50mL schlenk tube in a nitrogen-filled Vacuum Atmospheres drybox. The flask was removed from the drybox. Diallyl ether **8** (0.2 ml, 1.6 mmol) was added to the solution, and the reaction mixture was heated to 40 ^{o}C in an oil bath. After 24 hrs, conversions were determined by ^{1}H NMR.