New Tandem Catalysis: Generating Multiple Contiguous Carbon-Carbon Bonds through a Ruthenium-Catalyzed Ring Closing Metathesis-Kharasch Addition

Benjamin A. Seigal, Cristina Fajardo[†], Marc L. Snapper*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

E-mail: marc.snapper@bc.edu

Supporting Information

General Information:	S1
Experimental Procedures:	S2
2,2,2-trichloro- <i>N</i> -(hepta-1,6-dien-3-yl)acetamide (3):	S2
(3 <i>aS</i> ,4 <i>S</i> ,6 <i>aS</i>)-3,3,4-trichloro-hexahydrocyclopenta[<i>b</i>]pyrrol-2(1 <i>H</i>)-one (4):	S3
(2 <i>H</i> -Indol-2-one, 3,3,4-trichlorooctahydro-, (3 <i>αα</i> ,4 <i>α</i> ,7 <i>αα</i>)- (9 <i>CI</i>) (6):	S3
2,2,2-trichloro- <i>N</i> -(nona-1,8-dien-3-yl)acetamide (7):	S4
(3 <i>aS</i> ,4 <i>S</i> ,8 <i>aS</i>)-3,3,4-trichloro-octahydrocyclohepta[<i>b</i>]pyrrol-2(1 <i>H</i>)-one (8):	S4
<i>N</i> -benzyl-2,2,2-trichloro- <i>N</i> -(octa-1,7-dien-3-yl)acetamide (9):	S5
2 <i>H</i> -Indol-2-one, 3,3,4-trichlorooctahydro-1-(phenylmethyl)-, (3 <i>αα</i> ,4 <i>α</i> ,7 <i>αα</i>)- (9 <i>CI</i>) (10):	S6
4-methyl- <i>N</i> -(octa-1,7-dien-3-yl)benzenesulfonamide (E):	S6
2,2,2-trichloro- <i>N</i> -(octa-1,7-dien-3-yl)- <i>N</i> -tosylacetamide (11):	S7
(3 <i>aS</i> ,4 <i>S</i> ,7 <i>aS</i>)-3,3,4-trichloro-1-tosyl-hexahydro-1 <i>H</i> -indol-2(3 <i>H</i>)-one (12):	S7
<i>N</i> -benzyl-2,2,2-tribromo- <i>N</i> -(octa-1,7-dien-3-yl)acetamide (13):	S8
(3 <i>aS</i> ,4 <i>S</i> ,7 <i>aS</i>)-1-benzyl-3,3,4-tribromo-hexahydro-1 <i>H</i> -indol-2(3 <i>H</i>)-one (14):	S9
3-(2-iodoethyl)octa-1,7-diene (G):	S9
9,9,9-trichloro-6-vinylnon-1-ene (15):	S10
1 <i>H</i> -Indene, 1,1,7-trichlorooctahydro-, (3 <i>αα</i> ,7 <i>αα</i> ,7 <i>αα</i>)- (9 <i>CI</i>) (16):	S11
(3 <i>R</i> ,3 <i>aS</i> ,7 <i>aS</i>)-3,4,4-trichloro-hexahydrofuro[2,3- <i>c</i>]pyridin-5(6 <i>H</i>)-one (18):	S11
2,2,2-trichloroethyl cyclohex-2-enylcarbamate (19):	S12
2,2-dichloroethyl cyclohex-2-enylcarbamate (20):	S12
2,2,2-trichloroethyl octa-1,7-dien-3-ylcarbamate (21):	S13
2,2,4-trichloro-4-phenylbutyl cyclohex-2-enylcarbamate (22):	S13
2,2,4-trichloro-4-phenyl-1-(2 <i>H</i> -pyrrol-1(5 <i>H</i>)-yl)butan-1-one (24):	S14
(3 <i>R</i> ,4 <i>S</i> ,7 <i>aR</i>)-3,4-dichloro-3-(2-chloro-2-phenylethyl)hexahydro-1 <i>H</i> -indol-2(3 <i>H</i>)-one (25):	S15
2-((3 <i>R</i> ,4 <i>S</i> ,7 <i>aR</i>)-3,4-dichloro-2-oxooctahydro-1 <i>H</i> -indol-3-yl)-1-phenylethyl nitrate (25a):	S15
2-((3 <i>R</i> ,4 <i>S</i> ,7 <i>aR</i>)-3,4-dichloro-2-oxooctahydro-1 <i>H</i> -indol-3-yl)-1-phenylethyl nitrate (25b):	S15
(3 <i>R</i> ,3 <i>aS</i> ,4 <i>S</i> ,6 <i>aS</i>)-3,4-dichloro-3-(2-chloro-2-phenylethyl)hexahydrocyclopenta[<i>b</i>]pyrrol-2(1 <i>H</i>)-one (26):	S16
2-((3 <i>R</i> ,3 <i>aS</i> ,4 <i>S</i> ,6 <i>aS</i>)-3,4-dichloro-2-oxooctahydrocyclopenta[<i>b</i>]pyrrol-3-yl)-1-phenylethyl nitrate (26a):	S16
2-((3 <i>R</i> ,3 <i>aS</i> ,4 <i>S</i> ,6 <i>aS</i>)-3,4-dichloro-2-oxooctahydrocyclopenta[<i>b</i>]pyrrol-3-yl)-1-phenylethyl nitrate (26b):	S16
NMR's	S18-S31

General Information: Starting materials and reagents were purchased from commercial suppliers and used without further purification except the following: tetrahydrofuran, benzene, diethyl ether, and dichloromethane were dried on alumina columns using a solvent dispensing system¹; pentane, hexanes, and ether used in chromatography were distilled prior to use. All reactions were conducted in oven (135 °C) or flame-dried glassware under an inert atm of dry nitrogen.

Infrared (**FTIR**) spectra were recorded on a Nicolet 210 FT-Infrared spectrophotometer or a Nicolet Avatar 360 spectrophotometer, ν_{max} cm⁻¹. Bands are

[†] Current Address: Universidad Autónoma de Madrid

¹ Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. *Organometallics* **1996**, *15*, 1518.

characterized as broad (br), strong (s), medium (m), and weak (w). Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on either a Varian Gemini-400 instrument (400 MHz), or a Varian Gemini-500 instrument (500 MHz). Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent reference as the internal standard (CHCl_3 : δ 7.26 ppm, C_6D_6 : δ 7.16 ppm, $\text{DMSO}-d_6$: δ 2.50 ppm). Data is reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, br = broad, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Unity-300 instrument (75 MHz), Varian Gemini-400 instrument, (100 MHz), or a Varian Gemini-500 instrument (125 MHz) with complete proton decoupling. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane with the solvent as the internal reference (CDCl_3 : δ 77.23 ppm, $\text{DMSO}-d_6$: δ 39.51 ppm). Elemental analyses (**Anal.**) were performed by Robertson Microlit Laboratories, Inc. Madison, NJ and are reported in percent abundance. High resolution mass spectral analyses (**HRMS**) were performed by Mass Spectrometry Facility, Boston College.

Experimental Procedures:

Trichloroacetonitrile (0.25 mL, 2.5 mmol) was added dropwise to a stirred solution of 2,6-heptadien-1-ol **A** (0.28 g, 2.5 mmol) and NaH, 60% dispersion in mineral oil (10 mg, 0.25 mmol) in dry ether (4 mL) at 0 °C. Once the addition was completed, the solution was allowed to stir for 30 min while warming to ambient temperature. Pentane (50 mL) and MeOH (1 drop) were added to quench the reaction and the resulting precipitate was filtered after the solution was allowed to stir for 5 min. The resulting solution was concentrated yielding the imideate as a yellow-brown oil.

The oil was dissolved in xylenes (20 mL) and refluxed for 12 h. The reaction was then cooled to ambient temperature and the solvent was removed. The residue was purified by silica gel chromatography (1:9, ethyl acetate:hexanes) yielding trichloroacetamide **3** (300 mg, 1.5 mmol, 50% yield) as a colorless oil.

2,2,2-trichloro-N-(hepta-1,6-dien-3-yl)acetamide (3): ^1H NMR (CDCl_3 , 400 MHz): δ 6.62 (1H, br s), 5.80 (1H, ddt, J = 16.8, 10.0, 6.8 Hz), 5.80 (1H, ddd, J = 17.2, 10.4, 5.6 Hz), 5.25-5.18 (2H, m), 5.05 (1H, ddd, J = 17.2, 3.4, 1.6 Hz), 5.01 (1H, ddd, J = 10.4, 2.8, 1.2 Hz), 4.40 (1H, dddt, J = 14.8, 9.2, 6.0, 1.6 Hz), 2.14 (2H, dd, J = 14.4, 7.6 Hz), 1.81-1.66 (2H, m). ^{13}C NMR (CDCl_3 , 100 MHz): δ 161.1, 137.2, 136.4, 116.4, 116.0, 92.9, 53.4, 33.7, 30.1. **IR** (NaCl, thin film): 3414 (w), 3332 (m), 3074 (w), 2980 (w), 2854 (w), 1702 (s), 1639 (w), 1513 (s), 1444 (w), 1413 (w), 1300 (w), 1243 (w), 1047 (w), 916 (m), 853 (s), 821 (s), 733 (w), 676 (m) cm^{-1} . **Anal.**: Calcd for $\text{C}_9\text{H}_{12}\text{Cl}_3\text{NO}$: C, 42.13; H, 4.71; N, 5.46; Found: C, 42.17; H, 5.03; N, 5.37.

In a glove box, a solution of 2,2,2-trichloro-*N*-(hepta-1,6-dien-3-yl)acetamide **3** (51.0 mg, 0.200 mmol) in toluene (4 mL) was added to Grubbs' catalyst **1** (8.2 mg, 0.01 mmol) in a thick walled pressure tube and sealed with a Teflon screw cap. The tube was removed from the glove box and was allowed to stir at ambient temperature. After 2 h the reaction was placed in a 155 °C oil bath and allowed to stir for 135 min. The reaction was purified by silica gel chromatography (2:3, ethyl acetate:hexane) yielding Kharash product **4** (35 mg, 0.15 mmol, 77% yield) as a white solid.

(3aS,4S,6aS)-3,3,4-trichloro-hexahydrocyclopenta[*b*]pyrrol-2(1*H*)-one (4**):** ^1H NMR (CDCl_3 , 400 MHz): δ 6.53 (1H, br s), 4.62 (1H, dt, $J = 6.0, 3.6$ Hz), 4.43 (1H, t, $J = 3.6$ Hz), 3.66 (1H, dd, $J = 6.8, 3.2$ Hz), 2.35-2.20 (2H, m), 2.08-2.02 (1H, m), 1.90-1.85 (1H, m). ^{13}C NMR (CDCl_3 , 125 MHz): δ 169.1, 83.2, 66.1, 61.1, 56.1, 34.9, 30.9. **IR** (KBr pellet): 3257 (m), 2980 (w), 2955 (w), 1734 (s), 1696 (s), 1425 (m), 1356 (w), 1318 (w), 1274 (m), 1230 (w), 1098 (w), 972 (w), 909 (w), 872 (m), 840 (m), 796 (w), 739 (m) cm^{-1} . **M.P.:** 175-176 °C dec. **HRMS** ($m/z + \text{Na}$); Calcd: 249.9569; Found: 249.9564.

In a glove box, a solution of 2,2,2-trichloro-*N*-(octa-1,7-dien-3-yl)acetamide **5** (54.0 mg, 0.200 mmol) in toluene (4 mL) was added to Grubbs' catalyst **1** (8.2 mg, 0.01 mmol) in a thick walled pressure tube and sealed with a Teflon screw cap. The tube was removed from the glove box and was allowed to stir at ambient temperature. After 1 h the reaction was placed in a 155 °C oil bath and allowed to stir for 105 min. The reaction was purified by silica gel chromatography (2:3; ethyl acetate:hexane) yielding Kharash product **6** (38.5 mg, 0.17 mmol, 85% yield) as a white solid. All characterization data matched previously reported values.²

² Nagashima, H.; Wakamata, H.; Ozaki, N.; Ishii, T.; Watanabe, T.; Tajima, T.; Itoh, K. *J. Org. Chem.* **1992**, *57*, 1682-1689.

Trichloroacetonitrile (0.571 mL, 5.7 mmol) was added dropwise to a stirred solution of 2,8-nonadien-1-ol **B** (0.80 g, 5.7 mmol) and NaH (60% dispersion in mineral oil) (20.0 mg, 0.57 mmol) in dry ether (10 mL) at 0 °C. Once the addition was complete, the solution was allowed to stir 2 h while warming to ambient temperature. Pentane (30 mL) and MeOH (1 drop) were added to quench the reaction. After the reaction was allowed to stir for 5 min the resulting precipitate was filtered off, and the solvent was removed yielding the crude imidate as a yellow-brown oil.

The crude oil was dissolved in xylenes (40 mL) and refluxed for 12 h. The reaction was allowed to cool to ambient temperature and the solvent was removed under reduced pressure. The reaction was purified by silica gel chromatography (1:49, ethyl acetate:hexanes) yielding trichloroacetemide **7** (495 mg, 1.74 mmol, 30% yield) as a colorless oil.

2,2,2-trichloro-N-(nona-1,8-dien-3-yl)acetamide (7): ¹H NMR (CDCl₃, 400 MHz): δ 6.50 (1H, br s), 5.79 (1H, ddd, *J* = 17.2, 16.0, 5.2 Hz), 5.78 (1H, ddt, *J* = 17.2, 10.0, 6.8 Hz), 5.24 (1H, ddd, *J* = 17.2, 2.0, 0.8 Hz), 5.15 (1H, ddd, *J* = 10.4, 1.6, 0.8 Hz), 5.03 (1H, ddd, *J* = 17.2, 3.6, 1.6 Hz), 4.99 (1H, ddt, *J* = 10.0, 1.6, 0.8 Hz), 4.41 (1H, dtt, *J* = 13.6, 6.8, 1.6 Hz), 2.05 (2H, dd, *J* = 13.2, 6.8 Hz), 1.72-1.55 (2H, m), 1.47-1.34 (4H, m). ¹³C NMR (CDCl₃, 100 MHz): δ 161.1, 138.4, 136.7, 116.1, 114.8, 93.0, 53.8, 43.5, 33.7, 28.7, 25.2. IR (NaCl, thin film): 3433 (w), 3332 (m), 3069 (w), 2980 (w), 2930 (m), 2860 (w), 2357 (w), 2332 (w), 1696 (s), 1639 (w), 1513 (s), 1463 (w), 1438 (w), 1419 (w), 1237 (w), 985 (w), 922 (m), 827 (s), 733 (w), 683 (m) cm⁻¹. HRMS (*m/z* + Na); Calcd: 306.0195; Found: 306.0190.

In a glove box, a solution of 2,2,2-trichloro-N-(nona-1,8-dien-3-yl)acetamide **7** (15 mg, 0.052 mmol) in toluene (1 mL) was added to Grubbs' catalyst **1** (2 mg, 3.0 μmol) in a thick walled pressure tube and sealed with a Teflon screw cap. The reaction was removed from the glove box and allowed to stir in a 110 °C oil bath for 12 h. The temperature was increased to 155 °C and the reaction was allowed to stir for an additional hour. The reaction was purified by silica gel chromatography (1:1, ethyl acetate:hexane) yielding Kharasch product **8** (8.0 mg, 0.031 mmol, 60% yield) as a white solid. Recrystallation from hexanes:ethyl acetate provided X-ray quality crystals.

(3a*S*,4*S*,8a*S*)-3,3,4-trichloro-octahydrocyclohepta[*b*]pyrrol-2(1*H*)-one (8): ¹H NMR (CDCl₃, 400 MHz): δ 8.39 (1H, br s), 4.48 (1H, t, *J* = 10.4 Hz), 3.78 (1H, dd, *J* = 13.2, 8.0 Hz), 3.39 (1H, dd, *J* = 9.6, 8.8 Hz), 2.33, (1H, dd, *J* = 14.0, 5.2 Hz), 2.02 (1H, qd, *J* = 8.8, 1.2 Hz), 1.89 (2H, br dd, *J* = 15.6, 14.8 Hz), 1.77 (2H, dd, *J* = 9.6, 5.6 Hz), 1.50 (1H, qd, *J* = 10.4, 2.4 Hz), 1.31-1.22 (1H, m). ¹³C NMR (CDCl₃, 100 MHz): δ 168.8, 84.1, 60.4, 59.2, 57.4, 39.0, 32.0, 29.3, 27.7. IR (KBr pellet): 3200 (w), 3081 (w), 2930 (m), 2854 (w), 1727 (s), 1451 (w), 1381 (w), 1369 (w), 1344 (w), 1293 (w), 1243 (w), 1130 (w), 1029 (w), 996 (w), 853 (m), 796 (w), 739 (w), 702 (w), 639 (w) cm⁻¹. M.P.: 206-208 °C dec. HRMS (*m/z* + Na); Calcd: 277.9882; Found: 277.9877.

Trichloroacetyl chloride (0.150 mL, 0.76 mmol) was added dropwise to a stirred solution of *N*-benzylocta-1,7-dien-3-amine **C** (165 mg, 0.76 mmol) and triethyl amine (0.20 mL, 1.5 mmol) in diethyl ether (2.5 mL) at 0 °C. The reaction was allowed to stir for 36 h while warming to ambient temperature. The reaction was filtered and the solvent was removed under vacuum. The resulting oil was purified by silica gel chromatography (1:19, ethyl acetate:hexane) yielding product **9** (890 mg, 2.47 mmol, 82% yield) as a colorless oil.

***N*-benzyl-2,2,2-trichloro-*N*-(octa-1,7-dien-3-yl)acetamide (9):** ¹H NMR (CDCl₃, 400 MHz): δ 7.44-7.17 (5H, m), 6.08-3.39 (9H, m), 1.99-1.31 (6H, m). ¹³C NMR (CDCl₃, 125 MHz): δ 161.04, 161.02, 138.47, 138.41, 138.38, 138.35, 138.32, 138.27, 138.21, 138.17, 138.11, 138.08, 138.02, 138.00, 137.69, 137.65, 137.58, 135.85, 135.81, 135.79, 135.78, 135.76, 135.73, 135.70, 135.69, 135.62, 135.60, 135.56, 135.55, 135.49, 134.86, 134.79, 129.19, 128.94, 128.90, 128.86, 128.84, 128.63, 128.50, 128.45, 128.38, 128.15, 128.04, 128.02, 127.99, 127.94, 127.89, 127.87, 127.84, 127.82, 127.80, 127.77, 127.70, 127.52, 127.50, 127.43, 127.41, 127.37, 127.32, 127.21, 127.20, 127.13, 127.02, 126.88, 126.84, 126.75, 118.85, 118.72, 118.70, 118.66, 118.64, 118.62, 118.59, 118.57, 118.51, 118.49, 115.27, 115.15, 115.14, 115.11, 115.07, 115.05, 115.01, 114.97, 114.94, 94.02, 93.99, 93.86, 93.78, 93.72, 77.65, 77.62, 77.48, 77.37, 77.35, 77.23, 77.11, 76.98, 76.87, 76.77, 76.74, 76.66, 76.63, 76.55, 76.50, 65.67, 65.60, 65.57, 65.53, 61.44, 61.37, 61.32, 61.22, 54.44, 54.42, 54.37, 48.83, 48.80, 33.55, 33.47, 31.93, 31.86, 31.22, 31.19, 31.16, 31.12, 31.10, 31.06, 31.03, 26.12, 26.09, 26.07, 26.03, 26.00, 25.97, 25.96, 25.89, 25.82, 25.70, 25.68, 25.66. Note: the ¹H and ¹³C spectra show multiple rotomers, the compound decomposes upon heating to 60 °C in DMSO-*d*₆. IR (NaCl, thin film): 3074 (w), 3030 (w), 2986 (w), 2930 (m), 2854 (w), 1683 (s), 1633 (m), 1501

(w), 1457 (m), 1413 (m), 1331 (w), 1255 (w), 997 (m), 928 (m), 840 (m), 815 (m), 702 (w) cm^{-1} . **Anal.**: Calcd for $\text{C}_{17}\text{H}_{20}\text{Cl}_3\text{NO}$: C, 56.61; H, 5.59; N, 3.88; Found C, 56.32; H, 5.32; N, 3.67.

A solution of *N*-benzyl-2,2,2-trichloro-*N*-(octa-1,7-dien-3-yl)acetamide **9** (108 mg, 0.300 mmol) in toluene (3 mL) was added to in a Schlenk tube containing Grubbs' catalyst **1** (12 mg, 0.015 mmol) in a glove box. The reaction vessel was then fitted with a cold finger and a septum was placed over the sidearm. The tube was removed from the glove box, placed under positive nitrogen pressure and allowed to stir while refluxing. After 11 h the reaction was cooled to ambient temperature. Silica gel chromatography (1:3, diethyl ether:hexane) afforded the Kharash product **10** (87.0 mg, 0.261 mmol, 87% yield) as a slightly yellow oil.

2H-Indol-2-one, 3,3,4-trichlorooctahydro-1-(phenylmethyl)-, (3α,4α,7α)- (9Cl) (10): ^1H NMR (CDCl_3 , 400 MHz): δ 7.39-7.24 (5H, m), 4.98 (1H, d, $J = 15.2$ Hz), 4.76 (1H, dd, $J = 6.4, 4.0$ Hz), 4.21 (1H, d, $J = 14.8$ Hz), 3.74 (1H, ddd, $J = 11.2, 7.2, 6.0$ Hz), 3.26 (1H, dd, $J = 7.2, 2.4$ Hz), 2.41 (1H, ddt, $J = 14.8, 10.8, 4.0$ Hz), 1.99 (2H, m), 1.79-1.54 (3H, m). ^{13}C -NMR (CDCl_3 , 100 MHz): δ 165.6, 134.7, 128.9, 128.0, 82.6, 55.6, 55.1, 52.6, 48.8, 31.9, 26.1, 17.2. **IR** (NaCl, thin film): 3421 (br s), 2949 (w), 2860 (w), 1721 (s), 1646 (m), 1438 (w), 860 (w), 840 (w) cm^{-1} . **Anal.**: Calcd for $\text{C}_{15}\text{H}_{16}\text{Cl}_3\text{NO}$: C, 54.16; H, 4.85; N, 4.21; Found: C, 53.89; H, 4.74; N, 3.96.

A solution of toluenesulfonyl chloride (170 mg, 0.89 mmol) in CH_2Cl_2 (4.4 mL) was added to a stirred solution of 3-amino-1,7-octadiene **D** (93 mg, 0.74 mmol) and triethyl amine (0.125 mL, 0.89 mmol) in CH_2Cl_2 (3.4 mL). After the reaction was allowed to stir for 24 h, the mixture washed several times with water, dried over MgSO_4 , and concentrated. Silica gel chromatography (10:1, hexanes:ethyl acetate) yielded tosyl amine **E** (127 mg, 0.45 mg, 61% yield) as a colorless oil.

4-methyl-N-(octa-1,7-dien-3-yl)benzenesulfonamide (E): ^1H NMR (CDCl_3 , 400 MHz): δ 7.73 (2H, d, $J = 8.0$ Hz), 7.27 (2H, d, $J = 8.4$ Hz), 5.69 (1H, ddt, $J = 16.8, 10.4, 6.4$ Hz), 5.34 (1H, ddd, $J = 16.8, 10.4, 6.4$ Hz), 5.08-4.90 (4H, m), 4.42 (1 H, d, $J = 8.0$ Hz), 3.76 (1H, dt, $J = 13.6, 6.8$ Hz), 2.41 (3H, s), 1.97 (2H, dd, $J = 14.0, 7.6$ Hz), 1.49-1.26 (4H, m). ^{13}C NMR (CDCl_3 ,

125 MHz): δ 143.0, 137.9, 135.6, 130.3, 129.4, 127.7, 115.8, 114.8, 56.2, 35.0, 33.2, 24.6, 21.6. **IR** (NaCl, thin film): 3276 (m), 3074 (w), 2980 (w), 2930 (m), 2860 (m), 1652 (w), 1595 (w), 1495 (w), 1438 (m), 1331 (s), 1161 (s), 1092 (s), 991 (m), 916 (m), 815 (m), 670 (s) cm^{-1} . **Anal.**: Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_2\text{S}$: C, 64.48; H, 7.58; N, 5.01; Found C, 64.30; H, 7.84; N, 4.62.

A solution of *N*-toluenesulfonyl-3-amino-1,7-octadiene **E** (28 mg, 0.10 mmol) in THF (0.35 mL) was added to a suspension of KH (23 mg, 0.57 mmol) in THF (0.10 mL). The reaction was allowed to stir for 45 min, at which time trichloroacetyl chloride (0.035 mL, 0.30 mmol) was added. The reaction was allowed to stir for 8 h, then diluted with ether and quenched with saturated NH_4Cl . The layers were separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were evaporated. Silica gel chromatography (8:1, hexane:ethyl acetate) yielded product **11** (32 mg, 0.075 mmol, 75% yield) as a white solid.

2,2,2-trichloro-*N*-(octa-1,7-dien-3-yl)-*N*-tosylacetamide (11**):** ^1H NMR (CDCl_3 , 400 MHz): δ 7.89 (2H, d, $J = 8.4$ Hz), 7.32 (2H, d, $J = 8.0$ Hz), 6.44 (1H, ddd, $J = 17.6, 9.6, 7.2$ Hz), 5.79 (1H, ddt, $J = 16.8, 10.0, 6.8$ Hz), 5.43 (1H, ddd, $J = 10.8, 2.0, 0.8$ Hz), 5.42 (1H, ddd, $J = 17.6, 2.0, 0.8$ Hz), 5.10 (1H, ddd, $J = 10.4, 7.2, 3.6$ Hz), 5.06-5.00 (2H, m), 4.98 (1H, ddt, $J = 10.4, 3.2, 1.2$ Hz), 2.59-2.49 (1H, m), 2.43 (3H, s), 2.17-2.09 (2H, m), 1.53 (1H, m), 1.37 (1H, qd, $J = 12.8, 7.2$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 159.0, 145.2, 138.0, 135.7, 135.1, 129.4, 129.3, 120.4, 115.3, 92.7, 65.1, 33.9, 33.6, 26.8, 22.0. **IR** (KBr pellet): 3081 (w), 2923 (w), 2879 (w), 1715 (s), 1639 (w), 1595 (w), 1375 (s), 1262 (m), 1167 (s), 1092 (m), 1067 (m), 953 (w), 916 (w), 815 (m), 752 (m), 683 (s) cm^{-1} . **M.P.**: 55-56 $^\circ\text{C}$. **Anal.**: Calcd for $\text{C}_{17}\text{H}_{20}\text{Cl}_3\text{NO}_3\text{S}$: C, 48.07; H, 4.75; N, 3.30; Found C, 48.28; H, 4.46; N, 3.24.

acetate:hexane) yielding the Kharash product **12** (32 mg, 0.081 mmol, 63% yield) as a white solid.

22.1, 17.4. IR (KBr pellet): 2930 (s), 2860 (m), 1759 (s), 1602 (w), 1357 (m), 1218 (m), 1180 (s), 1117 (m), 1092 (m), 985 (w), 853 (w), 815 (w), 670 (m) cm^{-1} . M.P.: 187-189 $^\circ\text{C}$. HRMS ($m/z + \text{Na}$); Calcd: 417.9814; Found: 417.9818.

Tribromoacetyl chloride (0.150 mL, 0.76 mmol) was added dropwise to a stirred solution of *N*-benzylocta-1,7-dien-3-amine **C** (165 mg, 0.76 mmol) and triethyl amine (0.20 mL, 1.5 mmol) in diethyl ether (3.8 mL) at 0 $^\circ\text{C}$. The reaction was allowed to stir for 12 h while warming to ambient temperature. The reaction was quenched with saturated NH_4Cl (8.0 mL), and extracted with ethyl acetate (3 x 5 mL). The organic layers were combined and washed with brine (10 mL) and dried over MgSO_4 . The solvent was removed and the resulting oil was purified by silica gel chromatography (1:19, ethyl acetate:hexanes) providing compound **13** (250 mg, 0.38 mmol, 50% yield) as a colorless oil.

A solution of *N*-benzyl-2,2-dibromo-*N*-(hepta-1,6-dien-3-yl)acetamide **13** (99.0 mg, 0.20 mmol) in toluene (2.0 mL) was added to a vial containing Grubbs' catalyst **1** (24.0 mg, 0.30 mmol) and sealed with a screw cap in a glove box. The vial was then removed from the glove box and the reaction was allowed to stir at ambient temperature for 14 h. The reaction mixture was purified by silica gel chromatography (20:79:1, ethyl acetate:hexanes:pyridine) yielding the Kharasch product **14** (50.5 mg, 0.106 mmol, 53% yield) as a colorless oil.

(3aS,4S,7aS)-1-benzyl-3,3,4-tribromo-hexahydro-1H-indol-2(3H)-one (14): ¹H NMR (CDCl₃, 400 MHz): δ 7.39-7.25 (5H, m), 4.92 (1H, d, *J* = 15.2 Hz), 4.89 (1H, d, *J* = 2.8 Hz), 4.19 (1H, d, *J* = 14.8), 3.74 (1H, ddd, *J* = 10.0, 7.6, 6.4 Hz), 3.57 (1H, dd, *J* = 7.6, 2.0 Hz), 2.61 (1H, ddt, *J* = 15.2, 10.8, 4.4 Hz), 2.01 (1H, dd, *J* = 15.2, 3.6 Hz), 1.94 (1H, dd, *J* = 8.8, 4.4 Hz), 1.76-1.60 (3H, m). ¹³C-NMR (CDCl₃, 125 MHz): δ 167.0, 135.3, 129.2, 129.0, 128.44, 128.37, 57.4, 54.0, 48.0, 46.2, 32.2, 25.6, 18.2. IR (NaCl, thin film): 2948 (w), 2860 (w), 2357 (w), 2332 (w), 1721 (s), 1620 (w), 1488 (w), 1457 (w), 1451 (w), 1419 (w), 1356 (w), 1262 (w), 1174 (w), 815 (w), 752 (w), 727 (w) cm⁻¹. HRMS (*m/z* + Na); Calcd: 485.8680; Found: 485.8684.

A mixture of 2,7-octadienol **F** (12.6 g, 100 mmol), triethyl orthoacetate (55.0 mL, 300 mmol), and propionic acid (0.750 mL, 10.0 mmol) was allowed to reflux until ethanol (5.8 mL, 100 mmol) was collected in a Dean-Stark trap. The trap was then removed and the reaction was refluxed for an additional 48 h. The reaction was then cooled to ambient temperature, and diluted with 1 M HCl (30 mL) and allowed to stir for 20 min. The reaction was then diluted with saturated sodium bicarbonate until the pH was greater than 7.0. The layers were separated and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over MgSO₄. Filtration and removal of the solvent provided the crude ester (17.3 g, 88.2 mmol, 88% yield) as an oil.

Lithium aluminum hydride (1.81 g, 47.8 mmol) was added portion wise to a stirred solution of crude ester (4.68 g, 23.9 mmol) in dry ether (50 mL) at -78 °C. The mixture was allowed to warm to room temperature over 12 h. The reaction was quenched by dropwise addition of aqueous saturated sodium potassium tartrate (50 mL) and

allowed to stir for 3 h. The layers were separated and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were then washed with brine (100 mL), dried over MgSO₄ and concentrated to give alcohol **F** (3.64 g, 23.6 mmol, 99% yield).

Iodine (6.17 g, 24.3 mmol) was slowly added to a solution of triphenyl phosphine (5.25 g, 20.2 mmol), imidazole (1.51 g, 21.9 mmol), and alcohol **F** (2.50 g, 16.2 mmol) in dry acetonitrile (20 mL) and dry diethyl ether (30 mL) at 0 °C. Once the iodine addition was complete the solution was allowed to stir for 30 min at 0 °C. The reaction was washed with saturated sodium thiosulfate until the organic layer was colorless. The organic layer was then washed with brine (50 mL). The combined aqueous layers were extracted with Et₂O (50 mL). The combined organic layers were dried over MgSO₄ and concentrated. The residual oil was passed through a plug of silica gel with hexanes and concentrated yielding product **G** (2.80 g, 10.5 mmol, 65% yield).

3-(2-iodoethyl)octa-1,7-diene(G): ¹H NMR (CDCl₃, 400 MHz): δ 5.77 (1H, ddt, *J* = 17.2, 10.4, 6.8 Hz), 5.47-5.38 (1H, m), 5.07 (1H, dd, *J* = 11.2, 2.0 Hz), 5.04 (1H, s), 4.98 (1H, ddd, *J* = 17.2, 3.2, 2.0 Hz), 4.92 (1H, ddt, *J* = 10.4, 2.0, 1.2 Hz), 3.22 (1H, ddd, *J* = 9.6, 8.0, 5.2 Hz), 3.08-3.01 (1H, m), 2.11 (2H, dtd, *J* = 12.8, 8.8, 4.0 Hz), 2.06-1.97 (1H, m), 1.90 (1H, dddd, *J* = 16.4, 8.4, 8.4, 4.0 Hz), 1.71 (1H, dddd, *J* = 14.4, 9.6, 8.4, 3.6 Hz), 1.47-1.18 (4H, m). ¹³C NMR (CDCl₃, 100 MHz): δ 140.9, 138.7, 116.1, 114.6, 44.9, 38.7, 34.2, 33.9, 26.5, 5.5. IR (NaCl, thin film): 3087 (m), 2974 (m), 2930 (s), 2854 (m), 1828 (w), 1639 (m), 1425 (m), 1337 (w), 1237 (w), 1211 (w), 1174 (w), 997 (m), 916 (s), 601 (w) cm⁻¹. **Anal.**: Calcd for C₁₀H₁₇I: C, 45.47; H, 6.49; Found: C, 45.64; H, 6.56.

Chloroform (0.80 mL, 10 mmol) was added to a stirred solution of *n*-BuLi (5.8 mL 7.0 mmol, 1.2 M in hexane) in dry THF (10 mL) at -98 °C over 8 min. The solution was allowed to stir for 10 min at which time a solution of 3-(2-iodoethyl)octa-1,7-diene **G** (1.32 g, 5.00 mmol) in dry THF (2.5 mL) was added at a rate of 0.10 mL/min, followed by a solution of HMPA (1.30 mL, 7.5 mmol) in dry THF (2.5 mL) at the same rate. The reaction was allowed to stir at -98 °C for 30 min then was slowly allowed to warm to -75 °C. Once the temperature reached -75 °C the reaction was quenched with methanol (1.0 mL) and diluted with 1 M HCl (5 mL). The reaction was extracted with Et₂O (3 x 30 mL). The combined organic layers were washed with brine (75 mL), dried over MgSO₄, and concentrated. The residual black oil was passed through a plug of silica gel with pentanes. The concentrated eluent provided product **15** (900 mg, 3.5 mmol, 71% yield) as a colorless oil.

9,9,9-trichloro-6-vinylnon-1-ene (15): ¹H NMR (CDCl₃, 400 MHz): δ 5.80 (1H, ddt, *J* = 16.8, 10.0, 6.8 Hz), 5.40 (1H, ddd, *J* = 16.8, 8.8, 10.4 Hz), 5.06 (1H, dd, *J* = 10.4, 2.0 Hz), 5.02 (1H, ddd, *J* = 16.8, 2.0, 0.8 Hz), 4.99 (1H, dt, *J* = 17.2, 1.6 Hz), 4.95 (1H, ddt, *J* = 10.0, 2.0,

1.2 Hz), 2.71 (1H, ddd, $J = 10.8, 4.4, 2.0$ Hz), 2.58 (1H, ddd, $J = 14.8, 11.2, 4.4$ Hz), 2.08-2.00 (3H, m), 1.88 (1H, ddt, $J = 13.2, 12.0, 4.4$ Hz) 1.70 (1H, dddd, $J = 17.2, 10.0, 9.2, 4.4$ Hz) 1.47-1.30 (4H, m). ^{13}C NMR (CDCl_3 , 100 MHz): δ 141.8, 138.8, 115.8, 114.7, 100.5, 53.5, 43.5, 34.8, 34.0, 31.7, 26.7. **IR** (NaCl, thin film): 3074 (m), 2986 (m), 2930 (s), 2860 (m), 1639 (m), 1457, (w), 1419 (w), 1067 (w), 997 (m), 922 (s), 796 (m), 771 (s), 695 (s) cm^{-1} . **Anal.**: Calcd for $\text{C}_{11}\text{H}_{17}\text{Cl}_3$: C, 51.69; H, 6.70; Found: C, 51.65; H, 6.58.

A solution of 9,9,9-trichloro-6-vinylnon-1-ene **15** (51 mg, 0.20 mmol) in toluene (4 mL) was added to Grubbs' catalyst **1** (8 mg, 0.01 mmol) in a Schlenk tube in a glove box. The reaction vessel was then fitted with a cold finger and a septum was placed over the sidearm. The tube was removed from the glove box, placed under positive nitrogen pressure and the reaction was heated to reflux. After 7 h 20 min, the reaction was cooled to ambient temperature and the toluene mixture was loaded onto a silica gel column. Silica gel chromatography (100% pentanes) afforded the Kharasch product **16** (40. mg, 0.18 mmol, 89% yield) as a colorless oil. All characterization data matched literature values.³

A solution of *N*-(2-(allyloxy)but-3-enyl)-2,2,2-trichloroacetamide **17** (41 mg, 0.15 mmol) in toluene (15 mL) was added to Grubbs' catalyst **1** (6 mg, 7 μmol) in a thick walled pressure tube in a glove box. The reaction was sealed with a Teflon screw cap, removed from the glove box and allowed to stir at ambient temperature. After 90 min, the reaction was placed in a 155 $^{\circ}\text{C}$ oil bath and allowed to stir for 4.5 h. The reaction was purified by silica gel chromatography (1:1, ethyl acetate:hexane) yielding the Kharasch product **18** (26 mg, 0.16 mmol, 71% yield) as a white solid.

(3R,3aS,7aS)-3,4,4-trichloro-hexahydrofuro[2,3-*c*]pyridin-5(6*H*)-one (18): ^1H NMR (CDCl_3 , 400 MHz): δ 7.13 (1H, br s), 4.55 (1H, dt, $J = 8.0, 4.0$ Hz), 4.32 (1H, dd, $J = 10.4, 6.8$ Hz), 4.19 (1H, dt, $J = 7.6, 6.4$ Hz), 3.86 (1H, ddd, $J = 14.0, 4.0, 2.0$ Hz), 3.71 (1H, dd, $J = 9.2, 8.0$ Hz), 3.61 (1H, dd, $J = 8.4, 6.0$ Hz), 3.52 (1H, ddd, $J = 15.0, 5.2, 3.2$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ 163.9, 81.8, 75.0, 73.9, 62.9, 57.1, 44.1. **IR** (KBr

³ Lee, G. M.; Weinreb, S. M. *J. Org. Chem.* **1990**, 55, 1281-1285.

pellet): 3244 (br m), 3125 (w), 2961 (w), 2930 (w), 2886 (w), 1702 (s), 1469 (w), 1356 (w), 1262 (w), 1237 (w), 1111 (w), 1086 (m), 1060 (m), 1041 (m), 966 (m), 796 (m), 765 (m), 658 (w) cm^{-1} . **M.P.:** 122-125 °C. **HRMS** (m/z + Na); Calcd: 265.9518; Found: 265.9518.

Grubbs catalyst **1** (40.0 mg, 0.05 mmol) was added to a stirred solution of 2,2,2-trichloroethyl octa-1,7-dien-3-ylcarbamate **21** (350 mg, 1.16 mmol) in toluene (20 mL) at 60 °C. After 2 h, the solvent was removed and the reaction was purified by silica gel chromatography (8:92, ethyl acetate:hexane) yielding the product **19** (275 mg, 1.01 mmol, 87% yield) as a white solid.

2,2,2-trichloroethyl cyclohex-2-enylcarbamate (19): ^1H NMR (CDCl_3 , 400 MHz): δ 5.87 (1H, dtd, J = 10.0, 4.0, 1.6 Hz), 5.62 (1H, ddd, J = 10.0, 5.6, 2.4 Hz), 4.98 (1H, br s), 4.72 (2H, d, J = 1.2 Hz), 4.23 (1H, br s), 2.02-1.90 (3H, m), 1.69-1.54 (3H, m). ^{13}C NMR (CDCl_3 , 100 MHz): δ 153.8, 131.4, 127.4, 95.9, 74.7, 47.0, 29.8, 25.1, 19.9. **IR** (KBr pellet): 3339 (s), 2942 (m), 1740 (s), 1709 (s), 1532 (s), 1318 (w), 1243 (s), 1130 (m), 1086 (m), 1054 (m), 1041 (m), 972 (w), 834 (m), 809 (m), 727 (m) cm^{-1} . **M.P.:** 65-67 °C. **HRMS** (m/z + Na); Calcd: 293.9831; Found: 293.9833.

In a glove box, Grubbs' catalyst **1** (6 mg, 7 μmol) was added to a solution of 2,2,2-trichloroethyl cyclohex-2-enylcarbamate **19** (40. mg, 0.15 mmol) in toluene (3 mL) in a thick walled glass pressure vessel. This vessel was sealed with a Teflon screw cap and removed from the glove box. The reaction was allowed to stir at 155 °C for 4 h. The reaction was purified by silica gel chromatography (8:92, ethyl acetate:hexane) yielding the dichloride **20** (29 mg, 0.12 mmol, 83% yield) as a white solid.

2,2-dichloroethyl cyclohex-2-enylcarbamate (20): ^1H NMR (DMSO-d_6 , 500 MHz): δ 6.30 (1H, t, J = 5.0 Hz), 6.42 (1H, t, J = 5.5 Hz), 5.79 (1H, ddd, J = 9.5, 6.0, 3.5 Hz), 5.70 (1H, d, J = 10.0 Hz), 4.42 (2H, t, J = 5.0 Hz), 4.04-4.02 (1H, m), 1.97-1.96 (2H, m), 1.83-1.79 (1H, m), 1.77-1.71 (1H, m), 1.57-1.46 (2H, m). ^{13}C

NMR (DMSO- d_6 , 125 MHz): δ 155.2, 129.9, 129.2, 71.2, 68.8, 47.4, 29.7, 25.0, 20.4. **IR** (KBr pellet): 3326 (s), 3037 (w), 2936 (m), 2860 (w), 1690 (s), 1532 (m), 1438 (w), 1344 (w), 1312 (w), 1255 (m), 1136 (w), 1067 (m), 1041 (w), 777 (m), 727 (w) cm^{-1} . **M.P.**: 68-70 °C. **Anal.**: Calcd for $\text{C}_9\text{H}_{13}\text{Cl}_2\text{NO}_2$: C, 45.40; H, 5.50; N, 5.88; Found: C, 45.11; H, 5.54; N, 5.60.

TrocCl (1.00 mL, 7.2 mmol) was added dropwise to a stirred solution of octa-1,7-dien-3-amine **D** (738 mg, 6.0 mmol), and triethyl amine (1.68 mL, 12 mmol) in CH_2Cl_2 (50 mL) at 0 °C. The reaction was allowed to warm to ambient temperature over 4 h. The solvent was removed and the reaction was purified by silica gel chromatography (8:92, ethyl acetate:hexane) yielding product **21** (1.4 g, 4.6 mmol, 77% yield) as a colorless oil.

2,2,2-trichloroethyl octa-1,7-dien-3-ylcarbamate (21): ^1H NMR (CDCl_3 , 400 MHz): δ 5.77 (1H, ddt, $J = 16.8, 10.4, 6.4$ Hz), 5.79-5.72 (1H, m), 5.19 (1H, dt, $J = 17.2, 1.2$ Hz), 5.13 (1H, dt, $J = 10.4, 1.2$ Hz), 5.00 (1H, dq, $J = 17.2, 1.6$ Hz), 4.96 (1H, ddt, $J = 10.4, 2.0, 1.2$ Hz), 4.92 (1H, br s), 4.72 (2H, s), 4.18 (1H, dt, $J = 13.2, 7.2$ Hz), 2.07 (2H, dd, $J = 13.2, 6.4$ Hz), 1.64-1.42 (4H, m). ^1H NMR (C_6D_6 , 400 MHz): δ 5.64 (1H, ddt, $J = 16.8, 10.4, 6.8$ Hz), 5.42 (1H, ddd, $J = 16.8, 10.4, 6.0$ Hz), 4.99 (1H, dt, $J = 17.2, 1.2$ Hz), 4.97 (1H, dq, $J = 17.2, 1.6$ Hz), 4.94 (1H, ddt, $J = 10.4, 2.4, 1.2$ Hz), 4.89 (1H, dt, $J = 10.4, 1.2$ Hz), 4.60 (2H, dd, $J = 12.0, 10.0$ Hz), 4.55 (1H, br d, $J = 8.4$ Hz), 4.12 (1H, br s), 1.84 (2H, br s), 1.22-1.06 (4H, m). ^{13}C NMR (CDCl_3 , 100 MHz): δ 154.3, 138.8, 115.4, 115.1, 97.0, 95.2, 75.0, 54.1, 34.9, 34.2, 25.8. **IR** (NaCl, thin film): 3332 (w), 2986 (w), 2936 (m), 1727 (s), 1532 (m), 1482 (m), 1432 (m), 1381 (w), 1281 (s), 1237 (w), 1167 (s), 1117 (m), 1067 (w), 928 (w), 827 (w), 802 (w), 720 (m) cm^{-1} . **HRMS** ($m/z + \text{Na}$): Calcd: 322.0144; Found: 322.0142.

In a glove box, a mixture of Grubbs' catalyst **1** (8.2 mg, 0.01 mmol) and diene **21** (60 mg, 0.20 mmol) were diluted with toluene (4 mL) in a Schlenk flask. The flask was fitted with a cold finger and the side arm was sealed with a septum. The flask was

removed from the glove box, and placed under positive nitrogen pressure. The reaction was stirred at 110 °C for 30 min, at which time styrene (0.11 mL, 1.0 mmol) was added and the reaction was allowed to stir for an additional 4 h at 110 °C. The reaction was purified by silica gel chromatography (10:89:1, ether:hexane:pyridine) yielding the Kharash product **22** (47.4 mg, 0.13 mmol, 63% yield) as a colorless oil.

22

2,2,4-trichloro-4-phenylbutyl cyclohex-2-enylcarbamate (22): ^1H NMR (CDCl_3 , 400 MHz): δ 7.44-7.30 (5H, m), 5.86 (1H, ddd, $J = 12.0, 6.0, 4.0$ Hz), 5.61 (1H, dd, $J = 10.0, 3.2$ Hz), 5.27 (1H, t, $J = 6.0$ Hz), 4.83 (1H, br d, $J = 7.6$ Hz), 4.45 (1H, dd, $J = 12.0, 3.2$ Hz), 4.35 (1H, dd, $J = 12.0, 6.8$ Hz), 4.19 (1H, br s), 3.17 (1H, dd, $J = 15.2, 6.4$ Hz), 3.06 (1H, dd, $J = 15.2, 6.4$ Hz), 2.01 (2H, ddd, $J = 6.0, 4.0, 2.0$ Hz), 1.95-1.88 (1H, m), 1.68-1.52 (3H, m). ^{13}C NMR (CDCl_3 , 100 MHz): δ 154.1, 141.0, 131.3, 129.0, 128.9, 127.4, 127.3, 87.4, 71.2, 58.6, 53.4, 45.9, 29.9, 25.1, 19.9. IR (NaCl, thin film): 3420 (w), 3332 (m), 3068 (w), 3030 (w), 2936 (m), 2860 (m), 1715 (s), 1513 (s), 1415 (m), 1425 (m), 1318 (m), 1230 (s), 1155 (m), 1130 (m), 1079 (m), 972 (m), 771 (m), 727 (m), 689 (s) cm^{-1} . HRMS ($m/z + \text{Na}$); Calcd: 398.0457; Found: 398.0455.

23 **24**

In a glove box, a mixture of Grubbs' catalyst **1** (8.2 mg, 0.01 mmol) and *N,N*-diallyl-2,2,2-trichloroacetamide **23** (48.0 mg, 0.20 mmol) was diluted with toluene (4 mL) in a Schlenk flask. The flask was fitted with a cold finger and the side arm was sealed with a septum. The flask was removed from the glove box, and placed under positive nitrogen pressure. The reaction was allowed to stir at ambient temperature for 90 min, at which time styrene (0.11 mL, 1.0 mmol) was added and the reaction was heated to reflux for 4 h. The reaction was purified by silica gel chromatography (10:89:1, ether:hexane:pyridine) yielded the Kharash product **24** (46 mg, 0.145 mmol, 73% yield) as a colorless oil.

24

2,2,4-trichloro-4-phenyl-1-(2H-pyrrol-1(5H)-yl)butan-1-one (24): ^1H NMR (CDCl_3 , 400 MHz): δ 7.48-7.27 (5H, m), 5.85 (2H, dt, $J = 4.4, 4.0$ Hz), 5.37 (1H, t, $J = 5.6$ Hz), 4.77 (2H, td, $J = 3.6, 1.6$ Hz), 4.31-4.30 (2H, m), 3.48 (1H, dd, $J = 11.4, 5.6$ Hz), 3.41 (1H, dd, $J = 11.4, 5.6$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz): δ 162.8, 142.2, 128.9, 128.6, 127.5, 125.8, 124.7, 82.3, 58.9, 56.5, 54.7. IR (NaCl, thin film): 3068 (w), 3024 (w), 2936 (w), 2867 (w), 2363 (w), 2351 (w), 1797 (w), 1658 (s), 1627 (m), 1427 (w), 1419 (m), 1356 (w), 1186 (w), 991 (w), 966 (w), 702 (m), 670 (m), 651 (m) cm^{-1} . HRMS ($m/z + \text{Na}$); Calcd: 340.0039; Found: 340.0040.

In a glove box, a solution of 2,2,2-trichloro-*N*-(octa-1,7-dien-3-yl)acetamide **5** (54.0 mg, 0.20 mmol) in xylenes (4 mL) was added to Grubbs' catalyst **1** (8.2 mg, 0.01 mmol) in a flask and fitted with a reflux condenser. The flask was removed from the glove box and was allowed to reflux for 105 min, at which time styrene (114 μ L, 1.0 mmol) was added and the reaction was allowed to reflux for an additional 4 h. The reaction was purified by silica gel chromatography (3:7; ethyl acetate:hexane) yielding the desired Kharasch product **25** as a 1:1 mixture of diastereomers (54 mg, 0.15 mmol, 78%) as an oil that solidifies upon standing. If instead, the reaction is purified by chromatography on 10% AgNO₃/SiO₂ (wt/wt) column (1:4; ethyl acetate:hexane) the nitrated Kharasch products **25a** and **25b** are isolated separately in a 1:1 ratio in 62% overall yield.

(3R,4S,7aR)-3,4-dichloro-3-(2-chloro-2-phenylethyl)hexahydro-1H-indol-2-one (25): ¹H-NMR (CDCl₃, 300 MHz): δ 7.44-7.28 (10H, m), 5.22 (1H, dd, J = 8.1, 4.8 Hz), 4.97 (1H, dd, J = 7.2, 5.1 Hz), 4.76 (1H, dd, J = 7.8, 3.9 Hz), 4.51 (1H, dd, J = 6.3, 3.9), 3.89-3.77 (2H, m), 3.44 (1H, dd, J = 7.5, 2.4 Hz), 3.12 (1H, dd, J = 7.5, 2.7 Hz), 3.04-2.82 (4H, m), 2.38-2.27 (2H, m), 1.99-1.89 (4H, m), 1.78-1.62 (4H, m). ¹³C-NMR (CDCl₃, 125 MHz): δ 172.6, 172.1, 141.2, 141.1, 128.9, 128.8, 128.7, 128.6, 126.80, 128.77, 68.7, 68.5, 59.0, 58.9, 57.5, 57.0, 50.0, 49.8, 49.0, 48.7, 48.5, 48.2, 32.1, 32.0, 29.6, 29.5, 17.82, 17.76. **IR:** (thin film, NaCl): 3238 (br w), 3109 (w), 3064 (w), 3031 (w), 2947 (w), 2868 (w), 1715 (s), 1455 (w), 1434 (w), 1225 (w) cm⁻¹. **M.P.:** 103-105 °C.

2-((3R,4S,7aR)-3,4-dichloro-2-oxooctahydro-1H-indol-3-yl)-1-phenylethyl nitrate (25a): ¹H-NMR: (CDCl₃, 500 MHz): δ 7.40-7.35 (5H, m), 6.06 (1H, dd, J = 8.5, 2.5 Hz), 4.52 (1H, q, J = 4.0 Hz), 3.91 (1H, q, J = 7.5 Hz), 3.00 (1H, dd, J = 7.0 Hz), 2.77 (1H, dd, J = 16.0, 9.0 Hz), 2.65 (1H, dd, J = 16.0, 2.5 Hz), 2.32 (1H, ddd, J = 14.5, 10.0, 4.5 Hz), 1.96-1.90 (2H, m), 1.79-1.61 (2H, m). ¹³C- (CDCl₃, 125 MHz): δ 172.4, 138.1, 129.4, 129.3, 126.2, 81.5, 68.0, 56.5, 50.8, 50.0, 43.7, 32.2, 28.9, 17.6. **IR:** (thin film, NaCl): 3215 (br w), 3106 (w), 3067 (w), 2948 (w), 2899 (w), 2870 (w), 1716 (s), 1636 (s), 1456 (w), 1456 (w), 1317 (w), 1292 (w), 1273 (s), 1228 (w), 855 (m) cm⁻¹. **HRMS** (m/z + H); Calcd: 373.0722; Found 373.0733. **M.P.:** 120-122 °C.

2-((3R,4S,7aR)-3,4-dichloro-2-oxooctahydro-1H-indol-3-yl)-1-phenylethyl nitrate (25b): $^1\text{H-NMR}$: (CDCl_3 , 500 MHz): δ 7.40-7.35 (5H, m), 6.95 (1H, br s), 6.35 (1H, dd, $J = 8.0, 4.5$ Hz), 4.57 (1H, d, $J = 2.5$ Hz), 3.84 (1H, ddd, $J = 16.5, 11.5, 6.5$ Hz), 3.06 (1H, dd, $J = 7.5, 2.0$ Hz), 2.58 (1H, d, $J = 7.5$ Hz), 2.57 (1H, d, $J = 4.0$ Hz), 2.32 (1H, ddt, $J = 15.0, 11.0, 4.5$ Hz), 2.04-1.95 (2H, m), 1.81-1.61 (3H, m). $^{13}\text{C-NMR}$: (CDCl_3 , 125 MHz): δ 172.7, 138.1, 129.5, 129.3, 126.3, 81.6, 66.9, 56.7, 50.5, 49.7, 44.7, 32.0, 29.8, 17.3. **IR**: (thin film, NaCl): 3403 (br s), 3268 (br m), 3122 (w), 2947 (w), 1715 (s), 1634 (s), 1316 (w), 1295 (w), 1272 (s), 856 (m), 844 (w), 769 (w) cm^{-1} . **M.P.**: 152-153 $^\circ\text{C}$.

In a glove box, a solution of 2,2,2-trichloro-*N*-(hepta-1,6-dien-3-yl)acetamide **3** (39.0 mg, 0.15 mmol) in xylenes (3 mL) was added to Grubbs' catalyst **1** (6.0 mg, 0.007 mmol) in a flask and fitted with a reflux condenser. The flask was removed from the glove box and was allowed to reflux for 135 mins, at which time styrene (0.086 mL, 0.76 mmol) was added and the reaction was allowed to reflux for an additional 4 h. The reaction was purified by silica gel chromatography (3:7; ethyl acetate:hexane) yielding the desired Kharasch product **26** (25 mg, 0.079 mmol, 52%) as a viscous oil. If instead, the reaction is purified by chromatography on 10% $\text{AgNO}_3/\text{SiO}_2$ (wt/wt) column (1:4; ethyl acetate:hexane) the nitrated Kharasch products **26a** and **26b** are isolated separately in a 1:1 ratio in 48% yield. The structural assignment for **25b** was confirmed through single crystal X-ray crystallography.

(3R,3aS,4S,6aS)-3,4-dichloro-3-(2-chloro-2-phenylethyl)hexahydro-cyclopenta[b]pyrrol-2(1H)-one (26): $^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ 7.45-7.30 (10H, m), 5.36 (1H, dd, $J = 10.0, 3.2$ Hz), 5.25 (1H, dd, $J = 8.4, 5.6$ Hz), 4.81 (1H, d, $J = 3.2$ Hz), 4.43 (1H, d, $J = 2.0$ Hz), 4.31 (1H, t, $J = 6.8$ Hz), 4.16 (1H, t, $J = 6.8$ Hz), 3.82 (1H, d, $J = 7.6$ Hz), 3.03 (1H, dd, $J = 14.8, 5.6$ Hz), 2.91 (1H, d, $J = 7.2$ Hz), 2.81 (1H, dd, $J = 15.2, 3.6$ Hz), 2.73 (1H, dd, $J = 14.8, 8.0$ Hz), 2.58 (1H, dd, $J = 15.2, 10.0$ Hz), 2.36-2.26 (2H, m), 2.20-1.99 (3H, m), 1.91-1.68 (3H, m). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 174.3, 173.5, 141.3, 140.7, 129.4, 129.3, 129.1, 129.0, 128.9, 127.4, 127.3, 127.1, 70.7, 70.6, 63.9, 63.1, 59.4, 58.9, 57.64, 57.57, 56.8, 56.6, 50.5, 49.3, 35.1, 34.7, 31.4, 31.3. **IR** (thin film, NaCl): 3395 (br s), 3272 (br s), 3066 (m), 3032 (w), 2972 (w), 2945 (w), 1725 (s), 1493 (w), 1455 (m), 1434 (m), 1378 (w), 1325 (m), 1296 (m), 1273 (m), 1234 (w), 996 (w), 848 (w), 768 (m) cm^{-1} .

2-((3*R*,3*aS*,4*S*,6*aS*)-3,4-dichloro-2-oxooctahydrocyclopenta[*b*]-pyrrol-3-yl)-1-phenylethyl nitrate (26a): $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 7.41-7.37 (5H, m), 6.60 (1H, br s), 6.28 (1H, dd, $J = 8.0, 3.5$ Hz), 4.66 (1H, dt, $J = 4.0, 3.5$ Hz), 4.27 (1H, t, $J = 6.5$ Hz), 3.01 (1H, dd, $J = 7.5, 2.0$ Hz), 2.77 (1H, dd, $J = 15.0, 8.0$ Hz), 2.46 (1H, dd, $J = 7.3, 3.5$ Hz), 2.25 (2H, td, $J = 5.0, 2.0$ Hz), 2.02-1.97 (1H, m), 1.82-1.76 (1H, m). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 172.5, 137.8, 129.6, 129.4, 126.6, 81.4, 69.3, 62.6, 60.3, 56.2, 47.2, 34.9, 31.6. **IR** (thin film, NaCl): 3192 (br w), 3091 (br w), 3067 (br w), 1699 (s), 1639 (s), 1278 (m), 856 (m) cm^{-1} . **HRMS** ($m/z + \text{H}$); Calcd: 359.0565; Found 359.0572. **M.P.:** 132-134 $^{\circ}\text{C}$.

2-((3*R*,3*aS*,4*S*,6*aS*)-3,4-dichloro-2-oxooctahydrocyclopenta[*b*]-pyrrol-3-yl)-1-phenylethyl nitrate (26b): $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.39-7.36 (5H, m), 6.77 (1H, br s), 6.34 (1H, dd, $J = 10.2, 3.0$ Hz), 4.69 (1H, td, $J = 5.1, 2.4$ Hz), 4.31 (1H, t, $J = 5.7$ Hz), 3.58 (1H, dd, $J = 7.8, 2.1$ Hz), 2.58 (1H, dd, $J = 15.9, 3.0$ Hz), 2.44 (1H, dd, $J = 15.6, 10.2$ Hz), 2.38-2.25 (2H, m), 2.07-1.98 (1H, m), 1.84-1.73 (1H, m). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 173.3, 137.7, 129.5, 129.3, 126.3, 82.0, 69.2, 62.6, 58.3, 56.3, 45.4, 35.3, 31.6. **IR** (thin film, NaCl): 3404 (br s), 1714 (s), 1637 (s), 1274 (m), 849 (m) cm^{-1} . **HRMS** ($m/z + \text{H}$); Calcd: 359.0565; Found 359.0568. **M.P.:** 152-153 $^{\circ}\text{C}$