# Supplementary Material

# Catalytic Intramolecular Addition of Metal Carbenes to Remote Furans

**Michael P. Doyle,* Brant J. Chapman, Wenhao Hu, and Chad S. Peterson**

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721 U.S.A.*
*mdoyle@u.arizona.edu*

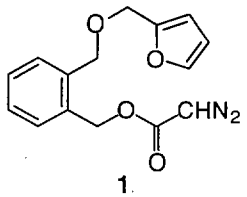
and

**M. Anthony McKervey* and Concepción F. Garcia**

*School of Chemistry, The Queen's University of Belfast, Belfast BT9 5AG, N. Ireland*
*tmckervey@quchem.com*

**2-(Furfuryloxymethyl)benzyl Alcohol**. 2-(2-*tert*-Butyldimethylsilyloxymethyl) benzyl alcohol (2.52 g, 10 mmol) was dissolved in 10 mL of $CH_2Cl_2$ and cooled to 0°C. To this solution was added freshly distilled $Et_3N$ (1.7 mL, 12 mmol) followed by dropwise addition of methanesulfonyl chloride (0.77 mL, 10 mmol) in $CH_2Cl_2$ (3 mL) over 20 min. After the addition was complete, stirring was continued at 0°C for an additional 90 min. The reaction mixture was then poured over ice and extracted with $CH_2Cl_2$ (3 x 50 mL). The $CH_2Cl_2$ solution was washed with brine, dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. In a separate flask, sodium hydride (0.4 g, 10 mmol, 60% in mineral oil) was washed with anhydrous hexanes (3 x 20 ml), then suspended in anhydrous THF (90 mL) and cooled to 0°C, whereupon furfuryl alcohol (0.90 g, 10 mmol) was added dropwise. After the addition was complete, the solution was allowed to warm to room temperature over 1 h, then cooled again to 0°C. The crude mesylate was dissolved in THF (10 mL) and added dropwise to the furfuryl alkoxide solution over 10 min. The solution was allowed to stir for 6 h, then the reaction was

quenched by the addition of 50 mL $H_2O$. The layers were separated, and the aqueous layer was extracted with ethyl acetate (3 x 75 mL). The combined organic layer was washed with brine, and the solvent was evaporated under reduced pressure. The crude mixture was then dissolved in THF (10 mL), and tetrabutylammonium fluoride (10 mL, 1 *M* in THF) was added rapidly. The solution was allowed to stir for 2 h, then the reaction was quenched by addition of 50 mL $H_2O$. The layers were separated, and the aqueous layer was extracted with ethyl acetate (3 x 75 mL). The combined organic layer was washed with brine, and the solvent was evaporated. Purification via column chromatography (7:3 hexanes:ethyl acetate) yielded 1.70 g (7.80 mmol, 78% yield) of the title compound as a colorless oil. $^1$H NMR ($CDCl_3$, 300 MHz) 7.43-7.25 (comp, 5H), 6.36-6.35 (m, 2H), 4.64 (s, 4H), 4.51 (s, 2H), 2.85 (br s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 150.9, 143.0, 140.5, 135.5, 130.0, 129.6, 128.9, 127.8, 110.3, 109.8, 70.9, 63.8, 63.5. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; found: C, 71.42; H, 6.51.

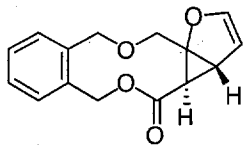



1

**2-(Furfuryloxymethyl)benzyl Diazoacetate (1).** A solution of 2-(furfuryloxymethyl)-benzyl alcohol (1.62 g, 7.43 mmol) in 7 mL of anhydrous THF was treated with triethylamine (0.2 mL) and diketene (0.69 mL, 8.9 mmol) at 0°C. The solution was allowed to stir at room temperature for 12 h, at which point $^1$H NMR analysis of the crude reaction mixture indicated complete conversion of the starting alcohol to the desired acetoacetate. The solution was then cooled to 0°C, triethylamine (1.24 mL, 8.92 mmol) and methanesulfonyl azide (1.08 g, 8.92 mmol) were added sequentially, after which the solution was allowed to warm to room temperature. Stirring was continued until $^1$H NMR analysis indicated that diazo transfer was complete. The solvent was removed under reduced pressure, then 50 mL of $H_2O$ and 50 mL of EtOAc were added. The layers were separated, and the aqueous layer was extracted with EtOAc (3

x 75 mL). The combined organic layer was washed with brine, and the solvent was evaporated under reduced pressure. The crude diazoacetoacetate was again dissolved in THF (10 mL), and $H_2O$ (10 mL) was added. To this rapidly stirring mixture was added $LiOH \cdot H_2O$ (0.89 g, 22 mmol). After 40 min, the layers were separated, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layer was washed with brine, and the solvent was evaporated. Purification by column chromatography (9:1 hexanes:ethyl acetate) yielded 1.79 g (6.26 mmol, 84% yield) of **1** as a yellow oil: $^1$H NMR (300 MHz, $CDCl_3$) δ 7.43-7.24 (comp, 5H), 6.35 (s, 2H), 5.29 (s, 2H), 4.78 (br s, 1H), 4.60 (s, 2H), 4.50 (s, 2H); $^{13}$C NMR (62.5 MHz, $CDCl_3$) δ 163.5, 151.5, 142.8, 136.2, 134.4, 129.3 129.3, 128.4, 128.1, 110.2, 109.5, 69.5, 64.0, 63.9, 46.2. Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93; N, 9.79; found: C, 62.81; H, 4.87; N, 9.73.

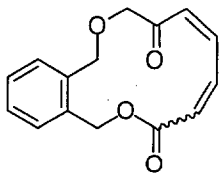
**Diazo Decomposition of 1 with Copper(I).** To a refluxing solution of $Cu(MeCN)_4PF_6$ (2.1 mg, 5.8 μmol) in $CH_2Cl_2$ (5 mL) was added **1** (0.145 g, 0.51 mmol) in $CH_2Cl_2$ (5.0 mL) over 5 h via syringe pump. The reaction solution was then allowed to cool to room temperature, and a small aliquot was removed for $^1$H NMR analysis. The relative ratio of products (prior to isomerization) was determined at this point. These analyses assured us that we were monitoring products formed under kinetic control. The catalyst was removed via filtration through a short plug of silica gel. Silica gel chromatography (8:2 hexanes:ethyl acetate) yielded a mixture of 3 compounds.




**2**

**5,6-Benzo-3,8,11-trioxa-1,10-*syn*-tricyclo[8.3.0.$^{1,10}$0$^{10,14}$]-*Z*-tetradeca-12-ene-2-one (2)** was isolated (0.043 g, 0.17 mmol, 33% yield) as a white solid (mp 118-120°C). $^1$H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.28 (comp, 4H), 6.33 (d, $J$ = 2.5 Hz, 1H), 5.39 (t, $J$ = 2.5 Hz, 1H), 5.36 (d, $J$ = 12.3 Hz, 1H), 5.12 (d, $J$ = 12.3 Hz, 1H), 4.88 (d, $J$ = 11.7 Hz,

1H), 4.33 (d, $J$ = 11.7 Hz, 1H), 4.21 (d, $J$ = 12.1 Hz, 1H), 3.76 (d, $J$ = 12.1 Hz, 1H), 2.97 (dd, $J$ = 3.6, 2.5 Hz, 1H), 1.17 (d, $J$ = 3.6 Hz, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.9, 146.6, 136.4, 135.7, 131.3, 131.1, 129.0, 128.8, 106.2, 73.0, 69.0, 66.9, 53.5, 35.0, 29.3. Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46; found: C, 69.64; H, 5.57.

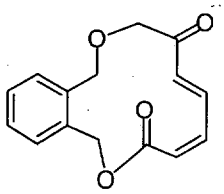


**4**

An inseparable mixture of ***E*-4** and ***Z*-4** with a **4*E*:4*Z*** ratio of 13:87 was isolated as an oil (0.052 g, 0.20 mmol, 40% yield). **9,10-Benzo-7,12-dioxacyclotrideca-2,3-*Z*-4,5-*E*-diene-1,6-dione (*E*-4)**: $^1$H NMR ($CDCl_3$, 400 MHz) δ 8.62 (dd, $J$ = 12.2 Hz, 15.4 Hz, 1H), 7.50-7.28 (comp, 4H), 6.86 (dd, $J$ = 12.2, 11.2 Hz, 1H), 6.14 (d, $J$ = 11.2 Hz, 1H), 6.02 (d, $J$ = 15.4 Hz, 1H), 5.30 (s, 2H), 4.58 (s, 2H), 4.26 (s, 2H). **9,10-Benzo-7,12-dioxacyclotrideca-2,3-*Z*-4,5-*Z*-diene-1,6-dione (*Z*-4)**: $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.50-7.28 (comp, 4H), 6.72 (dt, $J$ = 12.6, 2.6 Hz, 1H), 6.44 (dd, $J$ = 12.2, 12.6 Hz, 1H), 6.32 (ddd, $J$ = 12.2, 2.6, 2.1 Hz, 1H), 5.83 (dd, $J$ = 12.6, 2.1 Hz, 1H), 5.13 (s, 2H), 4.70 (s, 2H), 3.98 (s, 2H).

**Diazo Decomposition of 1 with Dirhodium(II) Carboxamidates**. To a refluxing solution of $Rh_2$(5*S*-MEPY)$_4$ (4.5 mg, 5.3 μmol) in $CH_2Cl_2$ (5 mL) was added **1** (0.145 g, 0.51 mmol) in $CH_2Cl_2$ (5 mL) over 5 h via syringe pump. The reaction was then allowed to cool to room temperature, and the solvent was removed in vacuo. The crude reaction mixture was then dissolved in $CDCl_3$. $^1$H NMR analysis showed alkenes ***E*-4** and ***Z*-4**, and a third minor compound tentatively identified by $^1$H NMR analysis as 5,6-benzo-9,12-oxo-3,7-dioxa-1,11-*syn*-tricyclo[8.1.1.$^{9,12}$0$^{1,11}$]-*Z*-dodeca-9-en-2-one (***syn*-3**), which converted over time or on silica stereospecifically to ***Z*-4**. The $^1$H NMR ($CDCl_3$, 300 MHz) spectrum of the reaction mixture revealed the following resonances attributable to ***syn*-3**: δ 5.23 (d, $J$ = 5.4 Hz, 1H), 4.93 (d, $J$ =

12.3 Hz, 1H), 4.74 (dd, $J$ = 5.1, 2.4 Hz, 1H), 2.80 (ddd, $J$ = 9.5, 5.4, 2.4 Hz, 1H), 1.60 (dd, $J$ = 9.5, 5.1 Hz, 1H). Silica gel chromatography (8:2 hexanes:ethyl acetate) of the reaction mixture yielded only ***Z*-4** and ***E*-4** as an inseparable mixture.



**5**

**9,10-Benzo,7,12-dioxacyclotrideca-2,3-*Z*-4,5-*E*-diene-1,6-dione (5).** Treatment of a crude mixture of ***Z*-4** and ***E*-4** in $CDCl_3$ (8 mg, 0.03 mmol) with catalytic iodine (0.1 mL, 0.02 M in $CDCl_3$, 7 mol %) at room temperature for 5 h resulted in the complete conversion of ***E*-4** to a third compound **5**, while ***Z*-4** remained unchanged for 2 days at room temperature. Treatment of a separate mixture of ***Z*-4** and ***E*-4** (0.212 g, 0.89 mmol) with stoichiometric iodine (1.8 mL, 0.5 M in $CH_2Cl_2$) resulted in complete conversion of both ***Z*-4** and ***E*-4** to **5** in 5 h. The brown solution was diluted by $CH_2Cl_2$ (25 mL) and washed sequentially with aqueous sodium thiosulfate (3 x 50 mL), water (50 mL), and brine (50 mL), and the solvent was evaporated to give 0.191 g (0.80 mmol, 90% yield) of a white solid (mp 150-152°C): $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.62 (dd, $J$ = 11.4, 16.7 Hz, 1H), 7.50-7.35 (comp, 4H), 6.75 (t, $J$ = 11.4 Hz, 1H), 6.05 (d, $J$ = 16.7 Hz, 1H), 6.04 (d, $J$ = 11.4 Hz, 1H), 5.42 (s, 2H), 4.74 (s, 2H), 4.34 (s, 2H); $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 198.1, 165.2, 143.8, 138.4, 136.1, 133.9, 132.8, 132.7, 131.3, 129.9, 129.4, 127.4, 75.7, 71.5, 64.9. MS (FAB), $m/z$ 517.1 (2M+H), 259.0 (MH). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46; found: C, 69.73; H, 5.52.

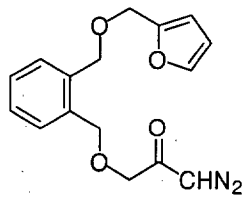
**2-(Hydroxymethyl)benzyl Bromide.** To a solution of 1,2-benzenedimethanol (1.0 g, 7.2 mmol) in $CH_2Cl_2$ (50 mL) was added phophorous tribromide (0.34 mL, 3.6 mmol) dropwise at 0°C and under $N_2$. The mixture was stirred for 3 h, and the dark solution was filtered through silica. The solvent was removed under reduced pressure to give a mixture of monobromide and dibromide. Column chromatography (85:15 hexanes:ethyl acetate) gave 2

compounds. 2-(Hydroxymethyl)benzyl bromide (mp 55-58°C) was isolated as the major product (0.75 g, 4.0 mmol, 56% yield): $^1$H NMR ($CDCl_3$, 300 MHz) δ 7.38-7.36 (comp, 4H), 4.77 (s, 2H), 4.58 (s, 2H), 2.38 (br s, 1H); MS, *m/z* 200 (M-1, 30), 182 (33), 121 (100), 103 (18), 91 (71), 77 (55), 65 (22), 51 (19), 39 (21). 1,2-Bis(bromomethyl)benzene was the minor product (0.46 g, 1.9 mmol, 27% yield). $^1$H NMR ($CDCl_3$, 300 MHz) δ 7.36-7.30 (comp, 4H), 4.70 (s, 4H); MS, *m/z* 264 (M,12), 183 (93), 104 (100), 91 (7), 77 (22), 63 (10), 51 (30), 39 (12).

**2-(Furfuryloxymethyl)benzyl Alcohol**. Sodium hydride (220 mg, 5.5 mmol, 60% in mineral oil) was washed with hexanes (3 x 5 mL) and suspended in THF (10 mL). A solution of furfuryl alcohol (490 mg, 5 mmol) in THF (5 mL) was added dropwise at 0°C under $N_2$. The white suspension was stirred at 0°C for 1 h. This suspension was cannulated to a solution of 2-(hydroxymethyl)benzyl bromide (1.1 g, 4.95 mmol) in THF (15 mL) at 0°C under $N_2$. The mixture was allowed to stir at room temperature overnight. Water was added, and extraction with $CH_2Cl_2$ gave a yellow oil. Purification by column chromatography (85:15 hexanes:ethyl acetate) gave 2-(furfuryloxymethyl)benzyl alcohol (0.80 g, 3.66 mmol, 74% yield): $^1$H NMR ($CDCl_3$, 300 MHz) δ 7.43-7.27 (comp, 5H), 6.36 (s, 2H), 4.64 (s, 2H), 4.51 (s, 2H), 2.97 (br t, 1H); MS, *m/z* 218 (M, 3), 200 (20), 171 (28), 149 (24), 135 (44), 132 (40), 128 (12), 119 (58), 104 (100), 97 (22), 91 (71), 81 (90), 77 (44), 65 (19), 53 (42), 39 (25).

**2-(2-Furfuryloxymethyl)benzyloxy Acetic Acid**. Sodium hydride (125 mg, 3.1 mmol, 60% dispersion in oil) was washed with hexane (3 x 5 mL), suspended in 5 mL of freshly distilled THF, and cooled to 0°C. To this suspension was added the 2-(furfuryloxymethyl)benzyl alcohol (388 mg, 2.06 mmol) in 10 mL of THF. The mixture was stirred and allowed to rise to room temperature. After 30 min the suspension was cooled, to 0°C and ethyl bromoacetate (0.3 mL, 2.3 mmol) was added via syringe. The reaction mixture was allowed to stir at room temperature for 18 h and the yellow suspension was then refluxed for 2 h. Water (10 mL) was added, and the majority of the THF was removed under reduced pressure. The residue was extracted with ethyl acetate (10 mL), washed with brine (25 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the resulting brown oil was

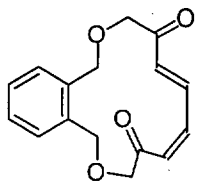
purified by column chromatography (3:17 ethyl acetate:hexanes) to give the ethyl ester of 2-(furfuryloxymethyl)benzyloxyacetic acid (0.30 g, 1.15 mmol, 56% yield): $^1$H NMR ($CDCl_3$, 300 MHz) 7.41 (comp, 4H), 7.33 (comp, 2H), 6.34 (comp, 2H), 4.68 (s, 2H), 4.64 (s, 2H), 4.49 (s, 2H), 4.22 (q, $J$ = 6.9 Hz, 2H), 4.07 (s, 2H), 1.28 (t, $J$ = 6.9 Hz, 3H). The ester was dissolved in 5 mL of ethanol, and 1 mL of NaOH aqueous solution (4 *M*) was added. The mixture was stirred at 80°C overnight. Water (5 mL) was added, and the ethanol removed under reduced pressure. The aqueous residue was extracted with ethyl acetate (5 ml), acidified with 1*N* HCl, then reextracted with ethyl acetate. The combined organic layer was washed with brine (20 mL), dried over anhydrous $MgSO_4$, and the solvent was removed to yield 2-(2-furfuryloxymethyl) benzyloxy acetic acid (0.27 g, 1.14 mmol, 99% yield): $^1$H NMR ($CDCl_3$, 300 MHz) δ 8.20 (br s, 1H), 7.42-7.29 (comp, 5H), 6.34 (br s, 2H), 4.67 (s, 2H), 4.63 (s, 2H), 4.49 (s, 2H), 4.11 (s, 2H). Anal. Calcd for $C_{15}H_{16}O_5$: C, 65.21; H, 5.79; found: C, 65.20; H, 5.83.




**6**

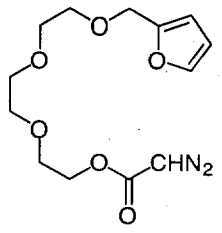
**3-[2-(Furfuryloxymethyl)benzyloxy]-1-diazo-2-propanone (6).** To a solution of 2-(2-furfuryloxymethyl)benzyloxy acetic acid (200 mg, 0.72 mmol), in dry THF (20 mL) at -10°C under Ar, was added triethylamine (0.16 mL, 0.8 mmol) and isobutylchloroformate (0.12 mL, 0.8 mmol). The mixture was stirred for 30 min, and ethereal diazomethane (5 mmol) was added dropwise over 30 min at -10°C. The mixture was then stirred overnight at room temperature. Diethyl ether (5 mL) was added and washed with water, saturated $NaHCO_3$ solution, and brine, and then dried over anhydrous $Na_2SO_4$. Evaporation of the solvent gave an oil which was purified by column chromatography (1:3 ethyl acetate:hexanes) to give 3-[2-(furfuryloxy-methyl)-benzyloxy]-1-diazo-2-propane **6** (0.17 g, 0.58 mmol, 80% yield) as a bright yellow oil:

$^1$H NMR ($CDCl_3$, 300 MHz) δ 7.43-7.30 (m, 5H), 6.35 (m, 2H), 5.76 (br s, 1H), 4.62 (s, 2H), 4.59 (s, 2H), 4.49 (s, 2H), 4.04 (m, 2H); IR (neat) 2110 ($C=N_2$), 1746 (C=O) $cm^{-1}$.



**7**

**$Rh_2(pfb)_4$-Catalyzed Decomposition of Diazoketone 6.** Diazoketone **6** (150 mg, 0.51 mmol) was dissolved in 10 mL of freshly distilled $CH_2Cl_2$ and added to $Rh_2(pfb)_4$ (26 mg, 0.024 mmol, 1.5% mol) in 10 mL of $CH_2Cl_2$ via syringe pump over 10 h at room temperature. The reaction solution was passed through a plug of silica gel, and the crude product was purified by column chromatography (1:3 ethyl acetate:hexanes) to give 10,11-benzo-8,13-dioxacyclotrideca-2*Z*,4*E*-dien-1,6-dione **7** (53 mg, 0.24 mmol, 46% yield). $^1$H NMR ($CDCl_3$, 500 MHz) δ 8.12 (dd, *J* = 9.5, 9.6 Hz, 1H), 7.38-7.37 (comp, 4H), 6.59 (t, *J* = 7.2 Hz, 1H), 6.06 (dd, *J* = 9.5, 6.9 Hz, 2H), 4.68 (s, 2H), 4.58 (s, 2H), 4.24 (s, 2H), 4.16 (s, 2H); HECTOR and COSY experiments performed; $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 199.0, 198.2, 141.9, 137.7, 135.6, 135.3, 134.0, 131.7, 131.4, 128.9, 128.6, 76.6, 75.5, 73.8, 72.0; MS, *m/z* 277 (M+5, 18), 272 (M, 2), 242 (6), 183 (10), 155 (10), 149 (20), 135 (16), 119 (48), 104 (100), 91 (50), 81 (50), 77 (36), 65 (74), 53 (22), 39 (28).




**8**

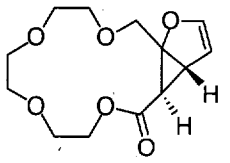
**8-(Furfuryloxy)-3,6-dioxaoctyl Diazoacetate (8).** Furfuryl alcohol (4.32 mL, 50 mmol) was dissolved in 30 mL of $CH_2Cl_2$ and cooled to -10°C. To this solution was added $Et_3N$

(6.96 mL, 50 mmol) and methanesulfonyl chloride (3.89 mL, 50 mmol) simultaneously during 30 min. The reaction mixture was allowed to stir at –10°C for 1 h. The $CH_2Cl_2$ solution was washed with 50 mL of cold 3% $NaHCO_3$, cold water and 30 mL of cold brine, then dried over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. In a separate flask, triethylene glycol (7.0 mL, 52 mmol) was dissolved in THF (100 mL) and potassium *tert*-butoxide (6.0 g, 53 mmol) in THF (100 mL) was added dropwise during 30 min at 23°C. The solution was stirred for an additional 1 h. The crude mesylate was dissolved in THF (60 mL) and added to the alkoxide solution over 10 min. The solution was allowed to stir for 24 h at 23°C. Celite (20 g) was added to the stirred solution and the mixture filtered under vacuum.. After filtration, the THF solution was concentrated under reduced pressure, and the residue was purified by column chromatography (2:1 hexanes:ethyl acetate) to give 8-(furfuryloxy)-3,6-dioxaoctan-1-ol as a yellow oil (4.04 g, 18 mmol, 36% yield): $^1$H NMR ($CDCl_3$, 250 MHz) δ 7.40 (s, 1H), 6.33 (s, 2H), 4.50 (s, 2H), 3.7-3.5 (comp, 12H), 1.01 (s, 1H); $^{13}$C NMR ($CDCl_3$, 62.5 MHz) δ 151.6, 142.7, 110.2, 109.3, 72.4, 70.5, 70.4, 70.3, 69.1, 64.9, 61.6; MS (FAB+) *m/z* 231 (M+1).

A solution of 8-(furfuryloxy)-3,6-dioxaoctan-1-ol (2.3 g, 10.0 mmol) in 10 mL of THF was treated with triethylamine (0.28 mL, 2.0 mmol) and diketene (0.89 mL, 11.5 mmol) at 0°C. The solution was allowed to come to room temperature and stirred for 4 h. The solution was cooled to 0°C, triethylamine (1.39 mL, 10 mmol) was added, followed by $MsN_3$ (1.3 g, 11.0 mmol), and the solution was allowed to warm to room temperature. Stirring was continued for 15 h whereupon the solvent was removed under reduced pressure, 50 mL of $H_2O$ and 100 mL of EtOAc were added, the layers were separated, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layer was washed with brine, and the solvent was evaporated under reduced pressure. The crude diazoacetoacetate was dissolved in acetonitrile (10 mL), and LiOH (0.67 g, 28 mmol) in $H_2O$ (10 mL) was added at 0°C. The reaction mixture was allowed to warm to room temperature for 1 h. The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layer was washed with brine, and the solvent was evaporated under reduced pressure. Purification by column chromatography (3:1

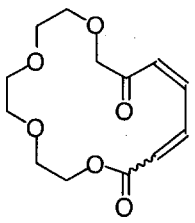
hexanes:ethyl acetate) yielded 8-(furfuryloxy)-3,6-dioxa-1-octyl diazoacetate **8** as a yellow oil (1.8 g, 6.0 mmol, 60% yield): $^1$H NMR ($CDCl_3$, 250 MHz) δ 7.40 (s, 1H), 6.33 (s, 2H), 4.82 (s, 1H), 4.50 (s, 2H), 4.31 (t, $J$ = 4.5 Hz, 2H), 3.70 (t, $J$ = 4.8 Hz, 2H), 3.65 (s, 8H); $^{13}$C NMR ($CDCl_3$, 62.5 MHz) δ 166.5, 151.4, 142.4, 109.9, 109.1, 70.3, 68.9, 64.7, 63.6, 45.9; MS (FAB+) *m/z*: 299 (M+1).

**Diazo Decomposition of 8**: To a refluxing solution of $Rh_2(OAc)_4$ (2.2 mg, 0.005 mmol) in $CH_2Cl_2$ (5 mL) was added **8** (149 mg, 0.500 mmol) in $CH_2Cl_2$ (5 mL) over 5 h via syringe pump. The reaction was then allowed to cool to room temperature, and the solvent was evaporated under reduced pressure. The relative ratio of the products was determined by $^1$H NMR analysis. Silica gel chromatography (hexanes:ethyl acetate = 2:1) yielded three compounds. Identical procedures were used with $Rh_2(oct)_4$, $Rh_2(pfb)_4$ and $Cu(MeCN)_4PF_6$.



**10**

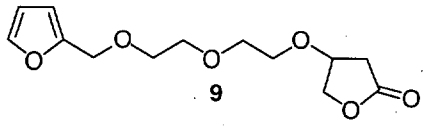
**3,6,9,12,15-Pentoxa-1,18-*syn*-tricyclo[12.3.0$^{1,14}$0$^{14,18}$]octadeca-16*Z*-ene-2-one (10)**: $^1$H NMR ($CDCl_3$, 250 MHz) δ 6.41 (d, $J$ = 2.6 Hz, 1H), 5.45 (t, $J$ = 2.6 Hz, 1H), 4.66 (ddd, $J$ = 10.0, 5.3, 1.5 Hz, 1H), 4.10 (d, $J$ = 11.7 Hz, 1H), 4.05 (d, $J$ = 11.7 Hz, 1H), 4.0-3.4 (comp, 11H), 2.97 (dd, $J$ = 2.6, 3.6 Hz), 1.24 (d, $J$ = 3.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 62.5 MHz) δ 171.9, 146.7, 106.1, 76.8, 70.5, 70.4, 70.2, 69.5, 68.9, 68.1, 63.6, 34.2, 27.0.



**11**

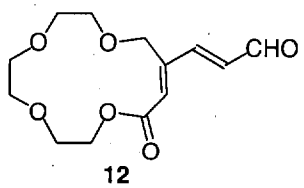
**8,11,14,17-Tetroxa-cycloheptadecan-2*Z*,4*Z*-diene-1,6-dione (*Z*-11)**: $^1$H NMR ($CDCl_3$, 250 MHz) δ 7.73 (ddd, *J* = 11.6, 10.5, 1.3 Hz, 1H), 7.42 (ddd, *J* = 11.9, 10.5, 1.3 Hz) , 1H, 6.96 (dt, *J* = 11.9, 1.3 Hz, 1H), 5.98 (dt, *J* = 11.6, 1.3 Hz, 1H), 4.37-4.30 (comp, 2H), 4.05 (s, 2H), 3.80-3.55 (comp, 10 H).

**8,11,14,17-Tetroxa-cycloheptadecan-2*E*,4*Z*-diene-1,6-dione (*E*-11)**: $^1$H NMR ($CDCl_3$, 250 MHz) δ 7.69 (dd, J = 12.2, 15.0 Hz, 1H), 6.68 (t, *J* = 12.2 Hz, 1H), 6.12 (d, *J* = 12.2 Hz, 1H), 6.11 (d, *J* = 15.0 Hz, 1H), 4.68 (s, 2H), 4.40-4.34 (comp, 2H), 3.86-3.80 (comp, 2H), 3.75-3.60 (comp, 8H).



**9**

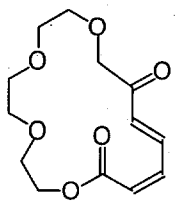
**Diazo Decomposition of 8 with $Rh_2$(5*S*-MEPY)$_4$.** To a refluxing solution of $Rh_2$(5*S*-MEPY)$_4$ (2.3 mg, 1.0 mol %) in $CH_2Cl_2$ (2.5 mL) was added **8** (74.5 mg, 0.25 mmol) in $CH_2Cl_2$ (2.5 mL) over 2.5 h via syringe pump. The reaction was then allowed to cool to room temperature. A small aliquot was removed and analyzed by $^1$H NMR. Column chromatography (1:1 hexanes:ethyl acetate) yielded 4-(6-furfuryloxy-1,4-dioxa)hexyldihydro-2(3*H*)-furanone **9** (48 mg, 0.18 mmol, 71%). $^1$H NMR (250 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 1.0, 1.5 Hz, 1H), 6.40-6.30 (comp, 2H), 4.50 (s, 2H), 4.37 (s, 2H), 3.64 (s, 4H), 3.63 (s, 5H), 2.70-2.60 (comp, 2H); $^{13}$C NMR (62.5 MHz, $CDCl_3$) δ 175.6, 151.6, 142.7, 110.2, 109.3, 75.0, 73.2, 70.6, 70.6, 69.2, 68.6, 65.0, 35.0; IR (soln., $CH_2Cl_2$) 1782 cm$^{-1}$ (C=O).




**12**

**3-(2-Formyl-1*E*-ethenyl)-5,8,11,14-tetroxacyclotetradeca-2*Z*-ene-1-one (12)**: Treatment of **10** (90.3 mg, 0.33 mmol) in $CDCl_3$ (0.5 mL) with catalytic iodine (0.8 mg,

3.3 μmol) at room temperature for 4 h resulted in over 95% conversion to **12**: $^1$H NMR ($CDCl_3$, 250 MHz) δ 9.65 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 16.0 Hz, 1H), 6.60 (dd, *J* = 7.7, 16.0 Hz), 6.25 (s, 1H), 4.91 (s, 2H), 4.44-4.38 (comp, 2H), 3.80-3.74 (comp, 2H), 3.70-3.56 (comp, 8H); $^{13}$C NMR ($CDCl_3$, 62.5 MHz) δ 193.6, 165.4, 151.3, 145.8, 133.4, 128.1, 71.5, 69.8, 69.5, 69.4, 68.3, 66.1, 63.5; HRMS (FAB): 271.1194 for $C_{13}H_{19}O_6$ (M+1); calcd 271.1182.



**13**

**8,11,14,17-Tetroxa-cycloheptadecan-2*Z*,4*E*-diene-1,6-dione (13)**: Treatment of ***Z*-11** (11.3 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL) with catalytic iodine (0.1 mg, 0.0004 mmol) at room temperature for 20 min resulted in the complete conversion to **13**, or treatment of ***E*-11** (42.5 mg, 0.16 mmol) in $CDCl_3$ (0.5 mL) with catalytic iodine (0.4 mg, 0.0016 mmol) at room temperature for 2 h resulted in the complete conversion to the same compound **13**. $^1$H NMR ($CDCl_3$, 250 MHz) δ 8.05 (dd, *J* = 11.5, 16.5 Hz, 1H), 6.66 (t, *J* = 11.5 Hz, 1H), 6.21 (d, *J* = 16.5 Hz), 5.97 (d, *J* = 11.5 Hz, 1H), 4.91 (s, 2H), 4.50-4.42 (comp, 2H), 3.84-3.53 (comp, 10H); $^{13}$C NMR ($CDCl_3$, 62.5 MHz) δ 202.3, 165.4, 140.0, 137.5, 135.3, 125.7, 73.9, 73.3, 70.9, 70.1, 69.7, 69.5, 64.3; HRMS (FAB): 271.1188 for $C_{13}H_{19}O_6$ (M+1); calcd 271.1182.