Intramolecular Carbenoid Insertions: Reactions of α-Diazo Ketones Derived from Furanyl-, Thienyl-, (Benzofuranyl)-, and (Benzothienyl)acetic Acids with Rhodium(II) Acetate

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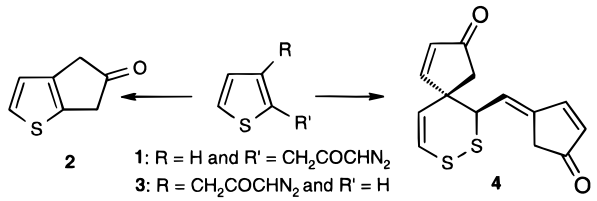
Received July 24, 1998

α-Diazo ketones tethered to furan, benzofuran, thiophene, and benzothiophene by a single methylene spacer have been shown to undergo atypical, rhodium(II) acetate catalyzed chemistry. For example, while treatment of 1-diazo-3-(3-furanyl)-2-propanone with $Rh_2(OAc)_4$ resulted in the expected 2-(4-oxo-2-cyclopentenylidene)acetaldehyde, isomeric 1-diazo-3-(2-furanyl)-2-propanone undergoes a vinylogous Wolff rearrangement and in the presence of water gives a mixture of 6a-methyl-2,3,3a,6a-tetrahydrofuro[*2,3-b*]furan-2-one and 2-(2-methyl-3-furyl)acetic acid. Rhodium acetate catalyzed decomposition of 1-diazo-3-(3-benzofuranyl)-2-propanone and 1-diazo-3-(2-benzofuranyl)-2-propanone are also shown to undergo vinylogous Wolff rearrangement despite the fact that this chemistry is not observed with homologous benzofuranyl systems. α-Diazo ketones derived from benzothienyl propionic acids undergo the expected cyclization with 1-diazo-4-(3-benzothienyl)-2-butanone and 1-diazo-4-(2-benzothienyl)-2-butanone giving rise to 1,2,3,4-tetrahydrodibenzo[*b,d*]thiophen-3-one and 1,2,3,4-tetrahydrodibenzo[*b,d*]thiophen-2-one, respectively. While decomposition of 1-diazo-3-(3-benzothienyl)-2-propanone resulted in the formation of 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one, the isomeric 1-diazo-3-(2-benzothienyl)-2-propanone gave a dimer which resulted from a [3 + 2] cycloaddition followed by a [1,3]-alkyl shift. Overall, the results from this study of intramolecular carbenoid insertion into five-membered heteroaromatic systems show that the resultant chemistry is dependent on the nature of the heteroatom, position of substitution, and the length of the aliphatic tether.

Introduction

A number of examples exist in the chemical literature describing the intramolecular insertion of metal-stabilized carbenoid species into five-membered heteroaromatic systems.[2] The outcome of these reactions is dependent not only on the nature of the heteroatom but also on the length of the aliphatic tether linking the diazo moiety with the aromatic fragment.[3] It has recently been demonstrated[4] that treatment of 1-diazo-3-(2-thienyl)-2-propanone (**1**) with catalytic rhodium(II) acetate yields 5,6-dihydro-4*H*-cyclopenta[*b*]thiophen-5-one (**2**) while, under the same conditions, the isomeric 1-diazo-3-(3-thienyl)-2-propanone (**3**) gives the spiro-disulfide (**4**). In light of the chemistry generally displayed by α-diazo ketones tethered to thienyl systems, these results are significant since the former compound (**1**) behaves like the other homologous members of the thienyl series while the latter diazo ketone (**3**) undergoes chemistry seen previously only in the furanyl series.[5] The unusual chemistry displayed by **3** can be attributed, in part, to the strain imparted by the short methylene tether to the intermediate cyclopropane generated. In the present study, we have expanded upon these initial results and prepared a series of heterocyclic systems linked to terminal α-diazo ketones by a single methylene tether in order to explore the scope and mechanistic details of these intramolecular carbenoid insertions. Results involving α-diazo ketones derived from benzothienyl propionic acids are also presented.

Scheme 1



Results and Discussion

Padwa has demonstrated[5] that the chemistry exhibited by α-diazo ketones containing benzofuranyl moieties is different to that shown by the analogous furanyl substrates. To examine the effect of a fused benzene on the reactions shown in Scheme 1, an investigation of α-diazo ketone systems containing benzothienyl fragments was undertaken. The α-diazo ketones were prepared from the

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(2) For general reviews of α-diazocarbonyl compounds, see: Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091. Doyle, M. P.; McKervey, M. A. *Chem. Commun.* **1997**, 983. Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides;* Wiley-Interscience: New York, 1998.

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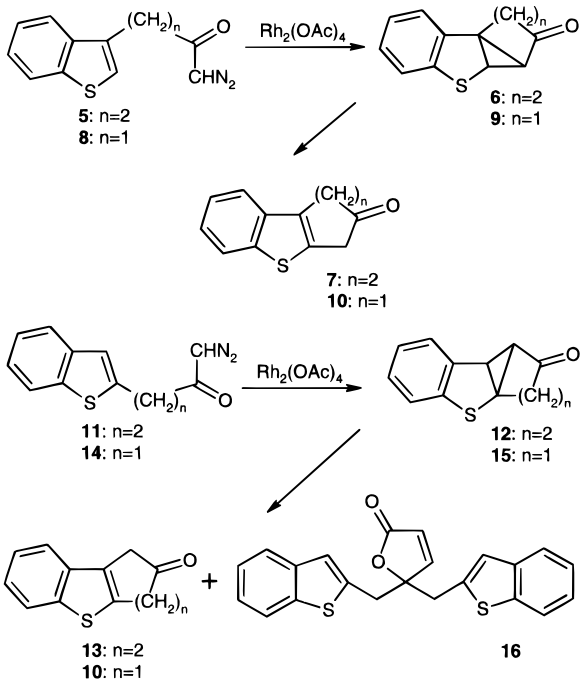
10.1021/jo9814593 CCC: $15.00 © 1998 American Chemical Society
Published on Web 12/10/1998

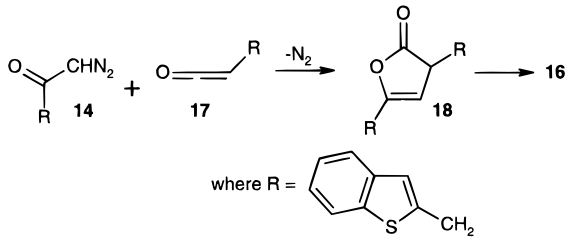
Scheme 2



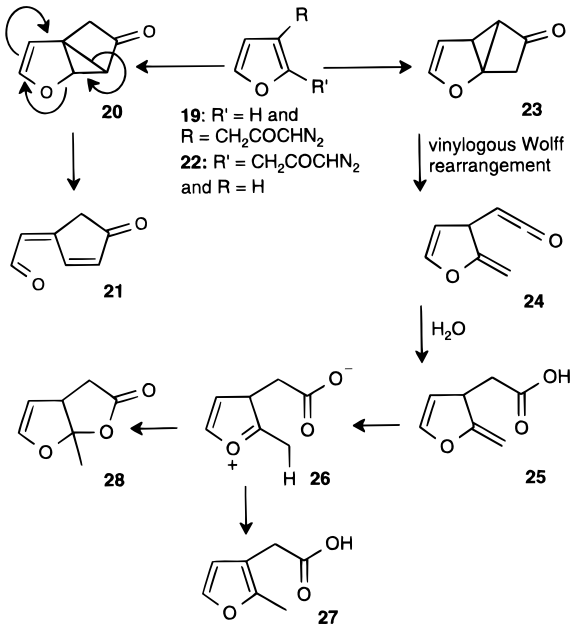
corresponding carboxylic acids by conversion to their acid chlorides followed by reaction with ethereal diazomethane. Despite differences in tether length and substitution pattern, the reactions carried out by compounds **5**, **8**, **11**, and **14** (Scheme 2) are remarkably consistent and typical of the reactions seen in the analogous thienyl series. For example, decomposition of 1-diazo-4-(3-benzothienyl)-2-butanone (**5**) in the presence of rhodium acetate allowed for the generation of a keto carbenoid species which added across the thienyl π-bond to produce the cyclopropane **6**. Treatment of **6** (which has been isolated and characterized) with a drop of TFA allowed for an acid-catalyzed ring opening to yield 1,2,3,4-tetrahydrodibenzo[*b,d*]thiophen-3-one (**7**) in 91% yield. Similarly, treatment of 1-diazo-3-(3-benzothienyl)-2-propanone (**8**) with $Rh_2(OAc)_4$ produced 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (**10**) (77% yield) without isolation of the intermediate cyclopropane **9**. Unlike the intermediate cyclopropane generated in the conversion of **3** → **4**, the [4 + 2]-cycloreversion of **9** is avoided since a similar unraveling would lead to the disruption of aromaticity.

Substitution of the tethered diazo ketone at the 2-position of the benzothiophene had little effect on the chemistry with 1-diazo-4-(2-benzothienyl)-2-butanone (**11**) cyclizing to an isolable cyclopropane **12**, which unraveled over time to give 1,2,3,4-tetrahydrodibenzo[*b,d*]thiophen-2-one (**13**) exclusively. Shortening the linking tether to a single methylene spacer to give 1-diazo-3-(2-benzothienyl)-2-propanone (**14**), however, allowed for the production not only of the expected 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (**10**) (in 21% yield) but also of a dimer **16**. The structure of spiro compound **16** has been secured by NMR and MS and, as illustrated in Scheme 3, is the result of a [3 + 2] cycloaddition involving the α-diazo ketone **14** and the ketene **17** generated by a Wolff rearrangement of **14**.[6] The initial lactone formed (**18**)

Scheme 3



Scheme 4



then undergoes a [1,3]-alkyl shift to the more thermodynamically favored α,β-unsaturated lactone (**16**). It is not clear why **14** is the only member of this benzothienyl series which participates in this type of chemistry.

Given the successful conversion of **3** → **4**, the decomposition chemistry of the analogous 1-diazo-3-(3-furanyl)-2-propanone (**19**) was next examined. As with homologous members of this series, treatment of **19** (Scheme 4) with $Rh_2(OAc)_4$ allows for the addition of the keto carbenoid generated to the furanyl π-bond to give cyclopropane **20**. [4 + 2]-cycloreversion of this intermediate then affords the keto−aldehyde (**21**) in quantitative yield (as determined by ^{1}H NMR spectroscopy). Attempts to purify the 2-(4-oxo-2-cyclopentenylidene)acetaldehyde (**21**) by column chromatography on silica gel resulted in decomposition.

While the isomeric 1-diazo-3-(2-furanyl)-2-propanone (**22**) has previously been studied by Padwa,[5] the compound was shown to carry out only an intermolecular Buchner reaction with the solvent benzene. Given our experience and that of Durst[7] working with comparable diazo compounds, we decided to revisit this system and examine its intramolecular carbenoid insertion chemistry. Initial experiments with α-diazo ketone **22** and rhodium(II) acetate in dry dichloromethane under an argon atmosphere at room temperature gave the mixture of products reported by Padwa. When water was introduced, however, the reaction proceeded smoothly so as

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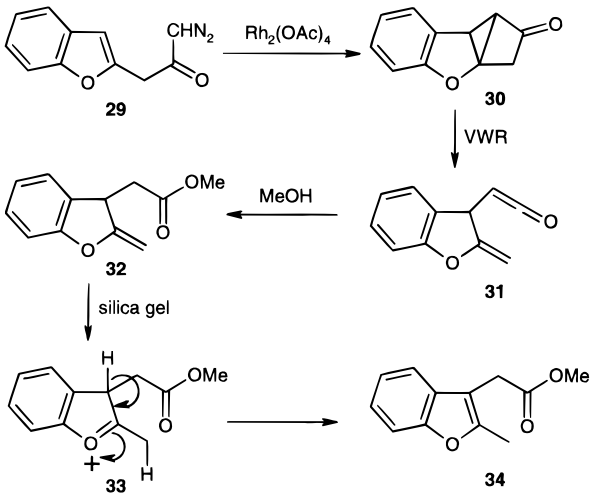
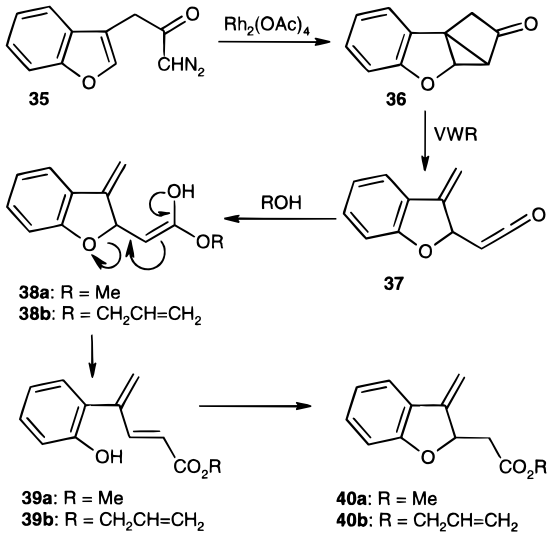
(7) Babu, S. D.; Hrytsak, M. D.; Durst, T. *Can. J. Chem.* **1989**, *67*, 1071.

Scheme 5



Scheme 6



to allow for the production of only two products: (2-methyl-3-furanyl)acetic acid (**27**)[8] and the bicyclic lactone **28**. It would appear that the intermediate cyclopropane produced (**23**) does not unravel by the usual [4 + 2]-cycloreversion but, rather, opens via a vinylogous Wolff rearrangement (VWR). Although such rearrangement on a furanyl system has not been previously observed, Smith has demonstrated the operation of VWR mechanism in the reactions of a number of β,γ-unsaturated-α-diazo ketones.[9] Rearrangement of **23** via the VWR gave the vinyl ketene intermediate **24** which in the presence of water was trapped to yield acid **25**. Protonation of the exocyclic double bond gives the oxonium ion **26** which can either lose a proton to rearomatize to **27** in 60% yield or cyclize to **28** in 15% yield.

A study of the closely related α-diazo ketones containing benzofuranyl fragments was also undertaken. Exploratory experiments involving the treatment of 1-diazo-3-(2-benzofuranyl)-2-propanone (**29**) (Scheme 5) with rhodium acetate in dichloromethane resulted in a complex mixture and an inability to isolate any carbenoid insertion product. This led us to believe that, unlike the other homologous members of the benzofuranyl series,[5] **29** behaved very much like 1-diazo-3-(2-furanyl)-2-propanone (**22**) in that the intermediate cyclopropane participated in a vinylogous Wolff rearrangement. This was confirmed when the rhodium acetate decomposition of **29** was repeated in the presence of methanol. The reaction was monitored *via* ^{1}H NMR and clearly showed the formation of one major product which we assigned as **32**. Clearly the VWR is the lower energy pathway given that [4 + 2]-cycloreversion of **30** would not only lead to disruption of aromaticity in the benzene moiety but would also produce a highly strained cyclobutenone system. When a preparative scale reaction was carried out and the product purified by silica gel chromatography, ^{1}H NMR revealed that the product **32** had isomerized to methyl (2-methyl-3-benzofuranyl)acetate (**34**) presumably *via* protonation of the exocyclic double bond to yield oxonium ion **33** followed by rearomatization.

Reactions involving the treatment of 1-diazo-3-(3-benzofuranyl)-2-propanone (**35**, Scheme 6) with rhodium acetate quickly revealed that the vinylogous Wolff rearrangement was again at work. Catalytic decomposition of **35** takes place to give cyclopropane **36** which undergoes a VWR to **37**. The trapping of the intermediate ketene by methanol, however, lead ultimately to the isolation of the polyunsaturated phenolic ester **39a** whose structure has been confirmed by MS, ^{1}H and ^{13}C NMR, and 2D-COSY. Rather than tautomerize to **40a** as would be expected, enol **38a** collapses to give the ring-opened product **39a**. The additional conjugation possessed by **39a** explains, in part, the preference for its formation over **40a**. While the production of **40a** could also be the result of a retro-Michael addition of **39a**, this is unlikely since there was no evidence of **40a** detected in the reaction mixture. Further evidence for the mechanism shown in Scheme 6 was provided when the reaction of **35** was repeated in the presence of allyl alcohol to yield only compound **39b** and no **40b**. We are currently studying **39b** to determine whether the compound can be induced to carry out an intramolecular Diels−Alder reaction. It should also be noted that a sample of **40b** (prepared by refluxing a sample of the unsaturated ester **39b** in toluene for 24 h) was stable and did not undergo a retro-Michael addition at room temperature.

The results from our study show that resultant chemistry of the intramolecular carbenoid insertion into furanyl- and thienyl-based systems is dependent on the nature of the heteroatom, position of substitution, the length of the aliphatic tether, and the substitution on the aromatic moiety. Clearly the high degree of strain imparted to intermediate cyclopropanes by single methylene tethers allows for some rather atypical chemistry and facile access to a number of novel ring systems.

Experimental Section

Starting materials were purchased from Aldrich Chemical Co. and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz or 500 MHz with chloroform-*d* as the solvent and internal reference unless otherwise noted. Ions for low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were generated using electron impact (EI). Silica gel used for column chromatography (5.0% of 100 mesh up; 47.6% of 100−200 mesh and 47.4% of 200 mesh down) was purchased from Aldrich Chemical Co. Silica gel 60 F_{254} (E. Merck Co.) plates of 0.2 mm thickness were

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used for analytical thin-layer chromatography (TLC). Visualization was achieved using a UV lamp at 254 nm or via treatment of the TLC with either a molybdic acid spray (20 g of molybdic acid and 15 g of ceric sulfate dissolved in 1 L of 10% sulfuric acid), a vanillin spray (5 g of vanillin dissolved in 200 mL of 95% ethanol followed by addition of 5 mL of sulfuric acid slowly), or a potassium permanganate dip (12.5 g of potassium permanganate and 62.5 g of sodium carbonate added to 1.25 L of water) followed by gentle heating.

General Procedure for the Preparation of the Diazo Ketones. The precursor carboxylic acid (4 mmol) was dissolved in dry dichloromethane (50 mL) and stirred in an ice bath under argon atmosphere. Oxalyl chloride (0.40 mL, 4.5 mmol) was added to the reaction mixture followed by a catalytic amount of DMF (2 drops). The reaction mixture was stirred for 30 min and then removed from the ice bath and stirred at room temperature for 2 h. The reaction mixture was then evaporated under reduced pressure to give an oily residue. Traces of oxalyl chloride were removed by redissolving the oil in dry benzene (25 mL) and evaporating the solvent under reduced pressure. The crude acid chloride was redissolved in 25 mL of dichloromethane and the solution then added over 10 min to 50 mL of an ice-cold solution of dry ethereal diazomethane (approximately 20 mmol) and stirred under an argon atmosphere for 2 h. The reaction mixture was evaporated under reduced pressure to give crude diazo ketone which was purified by column chromatography on silica gel.

General Procedure for the Rhodium Acetate Catalyzed Decomposition of the Diazo Ketones. To a stirred solution of rhodium acetate (~1 mg) in dichloromethane (100 mL) under argon atmosphere, was added a solution of the diazo ketone (generally 0.5 mmol) in dichloromethane (1 mL) over 10 h using a syringe pump. The reaction mixture was stirred for an additional 5 h after the addition is complete at which time the solvent was evaporated under a reduced pressure and the residue purified by column chromatography using silica gel.

Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-4-(3-benzothienyl)-2-butanone (5). 1-Diazo-4-(3-benzothienyl)-2-butanone (**5**) was prepared from 3-(3-benzothienyl)propionic acid[10] using the general procedure given above. The reaction mixture was purified by silica gel column chromatography using dichloromethane as the eluent. The yield of **5** (pale yellow oil) was 70%: TLC, R_f = 0.26 (dichloromethane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.76 (2H, t, J = 7 Hz, CH_2), 3.20 (2H, t, J = 7 Hz, CH_2), 5.21 (1H, s, CHN_2), 7.13 (1H, s, SCH), 7.38 (2H, m, Ar H), 7.77 (1H, d, J = 7 Hz, Ar H) 7.86 (1H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.00, 40.44, 55.10, 121.88, 122.28, 123.36, 124.45, 124.77, 135.38, 139.00, 140.88, 194.14; MS [EI+] *m/z* (RI%) 202 $[M - N_2]^+$ (25), 174 $[M - CO - N_2]^+$ (80), 161 $[M - COCHN_2]^+$ (55).

Rhodium acetate decomposition of **5** was carried out using the general procedure outlined above. The reaction mixture was purified by silica gel column chromatography using dichloromethane as the eluent and yielded 1,2,3a,3b-tetrahydro-3*H*-benzo[*b*]cyclopenta[1,3]cyclopropa[1,2-*d*]thiophen-3-one (**6**) (oil) in 91% yield: TLC, R_f = 0.32 (dichloromethane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.50 (1H, d, J = 1 Hz, CH), 2.25 (1H, m, J = 11, 10, 8 Hz), 2.38 (1H, m, J = 11, 10, 8 Hz), 2.49 (1H, m, J = 13, 8, 8 Hz), 2.87 (1H, m, J = 13, 10, 10 Hz), 3.56 (1H, d, J = 1 Hz, CH), 7.14−7.27 (3H, m, Ar H), 7.37 (1H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.17, 34.69, 37.15, 37.90, 50.23, 122.86, 124.46, 124.94, 128.70, 138.10, 142.10, 211.88; MS [EI+] *m/z* (RI%) 202 $[M]^+$ (50), 200 (100), 174 $[M - CO]^+$ (37), 160 (70); HRMS for $C_{12}H_{10}OS$ calculated *m/e* 202.0452, observed *m/e* 202.0448.

To a solution containing **6** (20 mg, 0.1 mmol) in dichloromethane (10 mL) is added 1 drop of trifluoroacetic acid. The reaction mixture is stirred at room temperature for 10 min at which time the solvent was evaporated under a reduced pressure and the residue chromatographed on silica gel using dichloromethane as the eluent. 1,2,3,4-Tetrahydrodibenzo-[*b*,*d*]thiophen-3-one (**7**) (oil) was isolated in a yield of 97%: TLC, R_f = 0.71 (dichloromethane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.81 (2H, t, J = 7 Hz, CH_2), 3.16 (2H, t, J = 7 Hz, CH_2), 3.75 (2H, s, CH_2), 7.35 (2H, m, Ar H), 7.60 (1H, d, J = 7 Hz, Ar H), 7.78 (1H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.86 (CH_2), 38.67 (CH_2), 40.37 (CH_2), 121.32, 122.96, 124.81, 129.29, 132.83, 138.43, 139.60, 210.77 (CO); MS [EI+] *m/z* (RI%) 202 $[M]^+$ (67), 173 (16), 160 (100) $[M - CH_2CO]^+$; HRMS for $C_{12}H_{10}OS$ calculated *m/e* 202.0452, observed *m/e* 202.0450.

Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(3-benzothienyl)-2-propanone (8). 1-Diazo-3-(3-benzothienyl)-2-propanone (**8**) was prepared from 2-(3-benzothienyl)acetic acid[11] using the general procedure given above. The reaction mixture was purified by silica gel column chromatography using hexanes−dichloromethane (1:2) as the eluent. The yield was of **8** (oil) was 77%: TLC, R_f = 0.61 (1:1 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.82 (s, 2H, CH_2), 5.11 (s, 1H, CHN_2), 7.27 (s, 1H, Ar H), 7.33−7.39 (m, 2H, Ar H), 7.72 (dd, 1H, J = 7, 2 Hz, Ar H), 7.85 (dd, 1H, J = 7, 2 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.93, 54.59, 121.68, 122.82, 124.33, 124.56, 124.90, 128.96, 138.28, 140.21, 191.78; MS [EI+], *m/z* (RI%) 216 $[M]^+$ (13), 187 (28), 160 $[M - CO - N_2]^+$ (40), 147 $[M - COCHN_2]^+$ (100), 115 (52); HRMS for $C_{11}H_8N_2OS$ calculated *m/e* 216.0357, observed *m/e* 216.0364.

Rhodium acetate decomposition of **8** was carried out using the general procedure outlined above. Silica gel column chromatography using hexanes−dichloromethane (1:2) as the eluent yielded 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (**10**) as an oil in 73% yield: TLC, R_f = 0.20 (1:1 dichloromethane−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.53 (2H, s, CH_2), 3.64 (2H, s, CH_2), 7.30−7.41 (2H, m, Ar H), 7.60 (1H, d, J = 7 Hz, Ar−H), 7.85 (1H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.78, 42.44, 121.84, 123.25, 124.45, 124.72, 134.75, 135.19, 136.89, 141.95, 213.16; MS [EI+] *m/z* (RI%) 188 $[M]^+$ (38), 160 $[M - CO]^+$ (100), 115 (29); HRMS for $C_{10}H_8O_2S$ calculated *m/e* 188.0296, observed *m/e* 188.0292.

Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-4-(2-benzothienyl)-2-butanone (11). 1-Diazo-4-(2-benzothienyl)-2-butanone (**11**) was prepared from 3-(2-benzothienyl)propionic acid[12] using the general procedure described above. The reaction mixture was purified by silica gel column chromatography using ethyl acetate−hexanes (1:4) as the eluent. The yield of **11** (oil) was 65%: TLC, R_f = 0.19 (1:4 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.79 (2H, br t, CH_2), 3.27 (2H, t, J = 7 Hz, CH_2), 5.26 (1H, br s, CHN_2), 7.05 (1H, s, SCCH), 7.30 (2H, m, Ar H), 7.68 (1H, d, J = 7 Hz, Ar H), 7.77 (1H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.93, 41.77, 54.99, 120.44, 121.44, 122.52, 124.31, 124.51, 139.43, 140.02, 144.25, 193.02; MS [EI+] *m/z* (RI%) 230 $[M]^+$ (11), 202 $[M - N_2]^+$ (13), 161 $[M - COCHN_2]^+$ (28), 147 (80); HRMS for $C_{12}H_{10}N_2OS$ calculated *m/e* 230.0514, *m/e* observed 230.0516.

Rhodium acetate decomposition of **11** was carried out using the general procedure outlined above. The reaction mixture was purified by silica gel column chromatography using ethyl acetate−hexane (1:4) as the eluent and yielded 1,2,3a,3b-tetrahydro-3*H*-benzo[*b*]cyclopenta[2,3]cyclopropa[1,2-*d*]thiophen-3-one (**12**) (oil) in 70% yield and 1,2,3,4-tetrahydrodibenzo[*b*-,*d*]thiophen-2-one (**13**) (oil) in 15% yield. Note that the intermediate cyclopropane **12** isomerized to **13** over time on standing. Alternatively, treatment of a solution of **12** in dichloromethane with a drop of TFA allowed for quantitative conversion to **13**. Data for **12**: TLC, R_f = 0.30 (1:4 ethyl acetate−hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.45 (1H, br s, CH), 2.16−2.39 (3H, m, 3 of CH_2CH_2), 2.56 (1H, m, 1 of CH_2CH_2), 3.34 (1H, d, J = 1 Hz, CH), 7.07−7.22 (3H, m, Ar H), 7.38 (1H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.41, 34.69, 37.00, 40.45, 48.81, 122.83, 125.18, 126.16, 128.28, 138.04, 141.89, 211.38; MS [EI+] *m/z* (RI%) 202 $[M]^+$

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(37), 174 [M − CO]$^+$ (100), 160 [M − $COCH_2$]$^+$ (51), 146 (41); HRMS for $C_{12}H_{10}OS$ *m/e* calculated 202.0452, observed *m/e* 202.0448. Data for **13**: TLC, R_f = 0.41 (1:4 ethyl acetate−hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.87 (2H, t, J = 7 Hz, CH_2), 3.30 (2H, t, J = 7 Hz, CH_2), 3.67 (2H, s CH_2), 7.39 (2H, m, Ar H), 7.54 (1H, d, J = 7 Hz, Ar H), 7.82 (1H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.10, 39.07, 39.54, 120.80, 122.97, 124.83, 124.91, 127.30, 135.52, 138.96, 140.07, 210.04; MS [EI+] *m/z* (RI%) 202 [M]$^+$ (64); 173 (19); 160 [M − CH_2=C=O]$^+$ (100); 147 (11); HRMS for $C_{12}H_{10}OS$ calculated *m/e* 202.0452, observed *m/e* 202.0449.

Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(2-benzothienyl)-2-propanone (14). 1-Diazo-3-(2-benzothienyl)-2-propanone (**14**) was prepared from 2-(2-benzothienyl)acetic acid[13] using the general procedure described above. The reaction mixture was purified by column chromatography using silica gel with hexanes−dichloromethane (1:2) as eluent. The yield was of **14** (oil) was 76%: TLC, R_f = 0.64 (1:1 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.85 (2H, s, CH_2), 5.31 (1H, s, CHN_2), 7.14 (1H, s, Ar H), 7.26−7.35 (2H, m, Ar H), 7.70 (1H, d, J = 6.8 Hz, Ar H), 7.77 (1H, d, J = 7.1 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.44, 54.97, 122.15, 123.23, 123.87, 124.27, 124.43, 136.69, 139.74, 140.05, 190.71; MS[EI+], *m/z* (RI%) 216 [M]$^+$ (13), 188 [M − N_2]$^+$ (69), 160 [M − CO−N_2]$^+$ (100), 147 [M − $COCHN_2$]$^+$ (90), 115 (57); HRMS for $C_{11}H_8N_2OS$ calculated *m/e* 216.0357, observed *m/e* 216.0368.

Diazo ketone **14** (140 mg, 0.66 mmol) in dichloromethane (1 mL) was added to a solution of rhodium(II) acetate (1 mg) in dichloromethane (50 mL) via a syringe pump over 12 h. The solvent was evaporated under reduced pressure and the products separated by silica gel column chromatography using dichloromethane−hexanes (1:1) as the eluent. The reaction yielded 2,3-dihydro-1*H*-benzo[*b*]cyclopenta[*d*]thiophen-2-one (**10**) (26 mg, 0.14 mmol, 21% yield) and the dimeric product **16** (71.0 mg, 0.19 mmol, 58% based on starting material) which was recrystallized from ethyl acetate. Data for **16**: TLC, R_f = 0.71 (1:1 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.44 and 3.49 (2H each, each d, J = 15 Hz, 2 × CH_2), 5.88 (1H, d, J = 6 Hz, CH), 7.10 (2H, s, 2 × SCCH), 7.27−7.32 (4H, m, Ar−H), 7.39 (1H, d, J = 6 Hz, CH), 7.68 (2H, d, J = 7 Hz, Ar H), 7.75 (2H, d, J = 7 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.62, 89.45, 122.54, 123.43, 123.69, 124.72, 124.82, 125.22, 136.84, 140.00, 140.38, 157.26, 168.05; MS[EI+] *m/z* (RI%) 376 [M]$^+$ (18), 147 (100); HRMS for $C_{22}H_{16}O_2S_2$ calculated *m/e* 376.0592, observed *m/e* 376.0570.

Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(3-furanyl)-2-propanone (19). 1-Diazo-3-(3-furanyl)-2-propanone (**19**) was prepared from 2-(3-furanyl)acetic acid[14] using the general procedure described above. The reaction mixture was purified by column chromatography using silica gel with hexanes−dichloromethane (1:2) as eluent yielding a yellow oil. The yield was 75%: TLC, R_f = 0.26 (1:2 hexanes−dichloromethane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.42 (2H, s, CH_2), 5.22 (1H, s, CHN_2), 6.31 (1H, d, J = 3 Hz, Ar H), 7.34 (1H, d, J = 3 Hz, Ar H), 7.38 (1H, s, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.12, 54.49, 111.25, 117.85, 140.60, 143.43, 192.34; MS[EI+] *m/z* (RI%) 150 [M]$^+$ (4), 136 [M − N_2]$^+$ (80), 94 [M − C(O)N_2]$^+$ (100), 81 [M − $COCHN_2$]$^+$ (99); HRMS for $C_7H_6N_2O_2$ calculated *m/e* 150.0429, observed *m/e* 150.0430.

Rhodium acetate decomposition of **19** was carried out using the general procedure outlined above to yield 2-(4-oxo-2-cyclopentenylidene)acetaldehyde (**21**) in quantitative yield (as evidenced by NMR). Attempts to purify **21** using silica gel resulted in decomposition. Data for the product: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.14 (2H, s, CH_2), 6.14 (1H, d, J = 7.0 Hz, CH), 6.70 (1H, d, J = 6 Hz, CH), 8.55 (1H, d, J = 6 Hz, CH), 10.14 (1H, d, J = 7 Hz, CH); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 39.66, 124.49, 141.47, 151.68, 154.74, 188.51, 202.15; MS[EI+] *m/z* (RI%) 122 [M]$^+$ (100), 94 [M − CO]$^+$ (37), 66 (37); HRMS for $C_7H_6O_2$ *m/e* calculated 122.0368, observed *m/e* 122.0372.

Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(2-furanyl)-2-propanone (22). 1-Diazo-3-(2-furanyl)-2-propanone (**22**) was prepared from 2-(2-furanyl)acetic acid[14] using the general procedure described above. The reaction mixture was purified by column chromatography using silica gel using ethyl acetate−hexanes (1:4) as the eluent yielding **22** as a yellow oil. The yield was 82%: TLC, R_f = 0.36 (1:2 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.63 (2H, s, CH_2), 5.19 (1H, s, CHN_2), 6.20 (1H, d, J = 3 Hz, Ar H), 6.33 (1H, dd, J = 2, 3 Hz, Ar H), 7.36 (1H, d, J = 2 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.31, 54.55, 108.56, 110.74, 142.35, 148.27, 190.24; MS [EI+] *m/z* (RI%) 150 [M]$^+$ (30), 136 [M − N_2]$^+$ (72), 94 (100), 81 [M + 1 − $COCHN_2$]$^+$ (80); HRMS for $C_7H_6N_2O_2$ calculated *m/e* 150.0429, observed *m/e* 150.0446.

Rhodium(II) acetate (approximately 1 mg) is added to a stirred solution containing 1-diazo-3-(2-furanyl)-2-propanone (**22**) (100 mg, 0.67 mmol) in dichloromethane (100 mL) and water (0.5 mL). The reaction was stirred for 1 h at which time the solvent is evaporated under reduced pressure. Silica gel column chromatography using ethyl acetate−hexanes (1:1) as eluent yielded 2-(2-methyl-3-furanyl)acetic acid (**27**, amorphous solid) in 60% (56.3 mg, 0.40 mmol) and 6a-methyl-2,3,3a,6a-tetrahydrofuro[2,3-*b*]furan-2-one (**28**, oil) in 15% (14.2 mg, 0.10 mmol). Data for **27**: TLC, R_f = 0.28 (ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.22 (3H, s, CH_3), 3.38 (2H, s, CH_2), 6.28 (1H, d, *C*H=CHO), 7.24 (1H, d, CH=*C*HO); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.82, 31.05, 111.02, 111.92, 140.30, 149.24, 176.85 (C=O); MS [EI+], *m/z* (RI%) 140 [M]$^+$ (55), 95 (100); HRMS for $C_7H_8O_3$ calculated *m/e* 140.0473, observed *m/e* 140.0479. Data for **28**: TLC, R_f = 0.24 (dichloromethane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.74 (3H, s, CH_3), 2.58 (1H, dd, J = 2, 18 Hz, one of CH_2), 2.86 (1H, dd, J = 9, 18 Hz, one of CH_2), 3.40 (1H, m, CH), 4.99 (1H, m, Ar H), 6.33 (1H, m, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.55, 34.79, 46.52, 104.67, 116.43, 144.99, 173.87; MS [EI+] *m/z* (RI%) 140 [M]$^+$ (100), 98 [M−CH_2C=O]$^+$ (90), 97 (66), 81 (69); HRMS for $C_7H_8O_3$ calculated *m/e* 140.0473, observed *m/e* 140.0475.

Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(2-benzofuranyl)-2-propanone (29). 1-Diazo-3-(2-benzofuranyl)-2-propanone (**29**) was prepared from 2-(2-benzofuranyl)acetic acid[13,15] using the general procedure described above. The reaction mixture was purified by column chromatography using silica with dichloromethane−hexanes (1:1) as eluent. The yield of **29** (oil) was 66%: TLC, R_f = 0.28 (dichloromethane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77 (2H, s, CH_2), 5.31 (1H, s, CHN_2), 6.60 (1H, s, Ar−H), 7.15−7.28 (2H, m, Ar−H), 7.43 (1H, d, J = 8 Hz, Ar−H), 7.52 (1H, d, J = 8 Hz, Ar−H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 40.76, 55.04, 105.62, 111.06, 120.79, 122.92, 124.18, 128.40, 151.18, 155.01, 184.55; MS [EI+], *m/z* (RI%) 200 [M]$^+$ (34), 172 [M − N_2]$^+$ (82), 144 [M − CO−N_2]$^+$ (62), 131 [M − $COCHN_2$]$^+$ (100), 115 (56); HRMS for $C_{11}H_8N_2O_2$ calculated *m/e* 200.0586, observed *m/e* 200.0574.

Rhodium(II) acetate (approximately 1 mg) was added to a stirred solution of 1-diazo-3-(2-benzofuranyl)-2-propanone (**29**) (100 mg, 0.5 mmol) in dichloromethane (50 mL) and methanol (0.1 mL). The reaction solution was stirred at room temperature for 2 h at which time the solvent was evaporated under reduced pressure. The residue was purified by column chromatography using silica gel and dichloromethane−hexanes (1:2) as eluent to yield methyl 2-(2-methylbenzo[*b*]furan-3-yl)acetate (**34**, oil) as the only isolable product. The yield was 58% (42 mg, 0.29 mmol): TLC, R_f = 0.20 (dichloromethane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.42 (3H, s, CCH_3), 3.60 (2H, s, CH_2), 3.67 (3H, s, OCH_3), 7.13−7.26 (2H, m, Ar H), 7.32−7.4 (1H, m, Ar H), 7.41−7.47 (1H, m, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.37, 30.03, 52.41, 108.11, 111.02, 119.22, 122.81, 123.79, 129.55, 152.55, 154.88, 171.65; MS [EI+] *m/z* (RI%) 204 [M]$^+$ (52), 145 [M − COOMe]$^+$ (100); HRMS for $C_{12}H_{12}O_3$ calculated *m/e* 204.0786, observed *m/e* 204.0789.

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Synthesis and Rhodium(II) Acetate Catalyzed Decomposition of 1-Diazo-3-(3-benzofuranyl)-2-propanone (35). 1-Diazo-3-(3-benzofuranyl)-2-propanone (**35**) was prepared from 2-(3-benzofuranyl)acetic acid[16] using the general procedure described above. The reaction mixture was purified by column chromatography with ethyl acetate−hexanes (1:4) as eluent. The yield of **35** (oil) was 74% (400 mg, 2.0 mmol): TLC, R_f = 0.48 (1:1 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.65 (2H, s, CH_2), 5.23 (1H, s, CHN_2), 7.21−7.32 (2H, m, Ar H), 7.46−7.54 (2H, m, Ar H), 7.56 (1H, s, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 35.68, 54.57, 111.55, 113.62, 119.55, 122.81, 124.67, 127.32, 142.95, 155.24, 191.54; MS [EI+] *m*/*z* (RI%) 200 $[M]^+$ (7), 172 $[M - N_2]^+$ (100), 144 (31), 131 $[M - COCHN_2]^+$ (69), 115 (50); HRMS for $C_{11}H_8O_2N_2$ calculated *m*/*e* 200.0588, observed *m*/*e* 200.0575.

Rhodium(II) acetate (approximately 1 mg) was added to a stirred solution of 1-diazo-3-(3-benzofuranyl)-2-propanone (**35**) (100 mg, 0.5 mmol) in dichloromethane (50 mL) and methanol (0.1 mL). The reaction solution was stirred at room temperature for 2 h at which time the solvent was evaporated under reduced pressure. The residue was purified by column chromatography using silica gel with dichloromethane as eluent. The yield was 71% (72 mg, 0.35 mmol) of the phenolic diene (**39a**, oil): TLC, R_f = 0.17 (1:2 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.74 (3H, s, OCH_3), 5.33 (1H, s, OH), 5.61 and 5.89 (each 1H, d, J = 1.5 Hz, $=CH_2$), 5.67 (1H, d, J = 16 Hz, CH=C*H*CO_2Me), 6.92−7.30 (4H, m, Ar H), 7.53 (1H, d, J = 16 Hz, C*H*=CHCO_2Me); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 52.14, 116.31, 120.97, 122.27, 124.76, 127.85, 130.13, 130.50, 142.72, 145.69, 152.95, 167.79; MS [EI+] *m*/*z* (RI%) 204 $[M]^+$ (73), 189 $[M - CH_3]^+$ (11), 172 $[M - CH_3OH]^+$ (45), 145 $[M - CO_2CH_3]^+$ (100), 115 (50); HRMS for $C_{12}H_{12}O_3$: calculated *m*/*e* 204.0786, observed *m*/*e* 204.0788.

The catalytic decomposition of **35** was repeated, as described above, in the presence of allyl alcohol. The product allyl-(2Z)-4-(2-hydroxyphenyl)-2,4-pentadienoate (**39b**) (oil) was purified by column chromatography using silica gel and dichloromethane as eluent: TLC, R_f = 0.28 (ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.62 (2H, m, CH_2), 5.08 (1H, s, OH), 5.22 (1H, dd, J = 10 and 2 Hz, CH=CH*H*), 5.30 (1H, dd, J = 2 and 17 Hz, CH=C*H*H), 5.60 (1H, d, J = 2 Hz, C=CH*H*), 5.67 (1H, d, J = 16 Hz, CH=C*H*CO_2), 5.89 (1H, br, C=C*H*H), 5.85−5.96 (1H, m, C*H*=CHH), 6.90−6.94 (2H, m, Ar H), 7.04 (1H, m, Ar H), 7.23−7.25 (1H, m, Ar H), 7.55 (1H, d, J = 16 Hz, C*H*=CHCO_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 65.32, 115.88, 118.53, 120.64, 122.16, 124.21, 127.64, 129.78, 130.05, 132.03, 142.15, 145.27, 152.42, 166.39; MS [EI+] *m*/*z* (RI%) 230 $[M]^+$ (100), 189 $[M - C_3H_5]^+$ (79), 145 $[M - CO_2 - C_3H_5]^+$ (71), 115 (63); HRMS for $C_{14}H_{14}O_3$ calculated *m*/*e* 230.0943, observed *m*/*e* 230.0958.

Synthesis of Allyl 2-(3-Methylene-2,3-dihydrobenzo[*b*]furan-2-yl)acetate (40b) *via* the Intramolecular Michael Addition of Allyl (2Z)-4-(2-hydroxyphenyl)-2,4-pentadienoate (39b). A solution of **39b** (50 mg, 220 mmol) in 5 mL of toluene was refluxed for 2 days at which time the solvent was evaporated under a reduced pressure. The residue was purified by column chromatography using ethyl acetate−hexanes (1:3) as the eluent. The conversion to **40b** (oil) was 18% (9.1 mg, 0.04 mmol) with the remainder being recovered starting material (**39b**): TLC, R_f = 0.61 (1:5 ethyl acetate−hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.81 (2H, m, CH_2COO), 4.69 (2H, dd, J = 2 and 6 Hz, O*C*H_2CH=CH_2), 4.97 (1H, m, CH=CH*H*), 5.24−5.45 (2H, m, alkenic protons), 5.59 (1H, m, C*H*CH_2COO), 5.90 (1H, m, CH_2C*H*=CH_2), 6.83−6.92 (2H, m, Ar H), 7.20 (1H, t, J = 8 Hz, Ar H), 7.37 (1H, d, J = 8 Hz, Ar H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.80, 65.93, 81.83, 101.18, 109.32, 111.22, 118.89, 121.30, 121.45, 131.17, 132.42, 147.23, 159.50, 170.29; MS [EI+] *m*/*z* (RI%) 230 $[M]^+$ (67), 145 $[M - CO_2 - C_3H_5]^+$ (100); HRMS for $C_{14}O_{14}O_3$ calculated *m*/*e* 230.09429, observed *m*/*e* 230.09358.

Acknowledgment. The authors wish to thank Brock University and the Natural Sciences and Engineering Research Council of Canada for their financial support, Mr. Tim Jones for mass spectral analysis, and Dr. John Valliant (McMaster University) for the NMR spectroscopy of **16**.

Supporting Information Available: Supporting Information Available: ^{1}H NMR spectra of compounds **5**−**8**, **10**−**14**, **16**, **19**, **21**, **22**, **27**−**29**, **34**, **35**, **39a**,**b**, and **40b** (21 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9814593

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