Synthesis and Chemistry of Donor/Acceptor-Substituted Cyclopropenes

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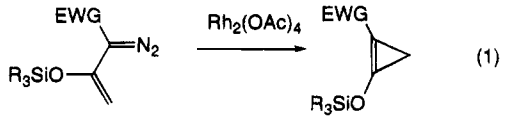
Rhodium(II) acetate, or trifluoroacetate-catalyzed decomposition of 1-diazo-2-(trialkylsiloxy)propenes with electron-withdrawing groups at the 1-position results in the formation of highly reactive cyclopropenes. These cyclopropenes contain both donor and acceptor substituents on the alkene and are very susceptible to ring opening and fragmentation reactions. Nevertheless, when appropriately functionalized with bulky substituents they can be of sufficient stability to be isolated and characterized.

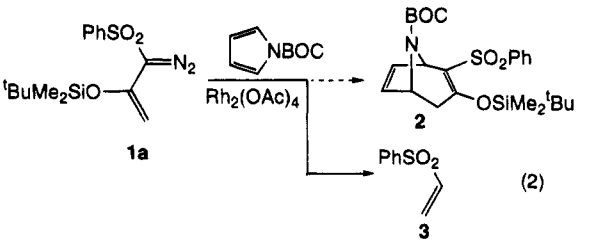
The diverse and unusual chemistry associated with the cyclopropene ring system is well documented.[1,2] The reactivity of the system is dominated by its inherent ring strain, and reactions involving cleavage of each of the bonds constituting the ring are known. Under thermal,[1-3] photochemical,[1-3] or metal-catalyzed[4] conditions, cyclopropenes undergo ring opening to vinylcarbene intermediates leading to a variety of different products. This paper will describe the chemistry of donor/acceptor-substituted cyclopropenes prepared by rhodium(II)-catalyzed decomposition of vinyldiazomethanes as illustrated in eq 1. Whereas donor/acceptor-substituted



(1)

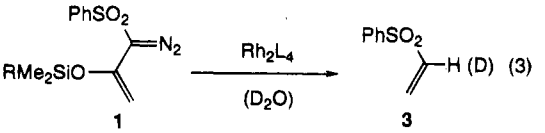
cyclopropanes have been extensively used in organic synthesis,[5] this is the first report on the chemistry of cyclopropenes with both donor and acceptor substituents on the double bond.

This project arose during studies to extend the new synthetic approach to tropanes based on the reaction of vinylcarbenoids with pyrroles.[6] The rhodium(II) acetate-catalyzed decomposition of siloxy-substituted vinyldiazomethane **1a** in the presence of *N*-BOC-pyrrole failed to produce any of the tropane system **2** that would be expected from a tandem cyclopropanation/Cope rearrangement.[7] Instead, the sole isolable compound from the reaction was the vinylsulfone **3** in very low yield. The intriguing transformation of **1a** to **3** involving loss of both the siloxy group and a carbon atom in addition to extrusion of nitrogen prompted us to investigate this process further.



(2)

In order to examine the conversion of the vinyldiazomethane **1a** to the vinylsulfone **3**, decomposition of **1a** was carried out in the absence of any trap for the vinylcarbenoid. Thus, rhodium(II) acetate-catalyzed decomposition of **1a** resulted in the formation of **3** in 10% yield.[8] Initial optimization of this reaction was achieved by the introduction of a more labile siloxy group. Hence, rhodium(II) acetate-catalyzed decomposition of the trimethylsilyl derivative **1b** produced **3** in 37% yield.[8] A further increase in the yield of **3** to 54%[8] was achieved by the use of rhodium(II) trifluoroacetate as catalyst for the decomposition of **1b**. Having developed an efficient method for the generation of the vinylsulfone **3** from the vinyldiazomethane **1b**, labeling studies were undertaken in order to gain insight into the likely mechanism of this transformation. Rhodium(II) trifluoroacetate-catalyzed decomposition of **1b** in the presence of small quantities of D_2O resulted in the formation of **3** (52% yield[8]) with 90% deuterium incorporation into the adjacent carbon to the sulfone.



(3)

a: R = ^{t}Bu; **b**: R = Me

Presumably, the formation of **3** would initially involve the rhodium(II)-catalyzed decomposition of **1** to give a vinylcarbenoid intermediate.[7] In order to probe the subsequent reaction pathway, decomposition of **1a** was repeated in the presence of a large excess (about 30-fold) of cyclopentadiene. This resulted in the formation in essentially quantitative yield of the tricyclic system **4**,

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(2) (a) Baird, M. S. *Top. Curr. Chem.* **1988**, *144*, 137. (b) Steinmetz, M. G.; Srinivasan, R.; Leigh, W. *J. Rev. Chem. Intermed.* **1984**, *5*, 57.

(3) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695.

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(5) (a) Salaun, J. R. Y. *Top. Curr. Chem.* **1988**, *144*, 1. (b) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73.

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(7) (a) Davies, H. M. L. *Tetrahedron* **1993**, *49*, 5203. (b) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem.* **1991**, *56*, 3817.

(8) The yields from the rhodium(II)-catalyzed reactions represent overall yields from the diazoketone precursors of the siloxy-substituted vinyldiazomethane.

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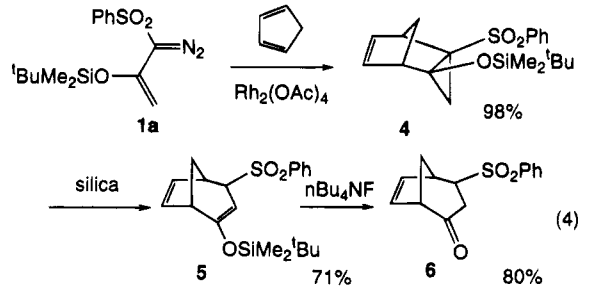
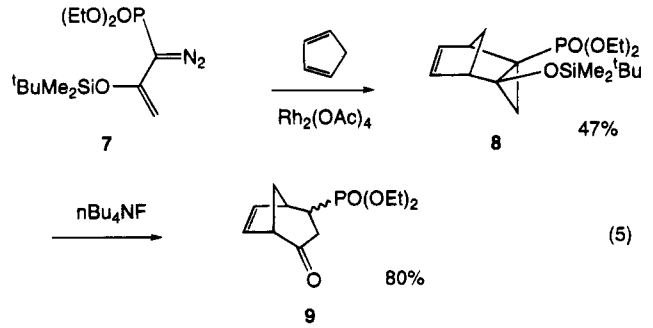
the Diels–Alder cycloadduct between a donor/acceptor cyclopropene and cyclopentadiene. The endo stereochemistry for **4** was based on the distinctive long range coupling between the two methylene groups that occurs for this particular isomer.[9,10] The adduct proved to be unstable upon chromatography and readily underwent rearrangement to the [3.2.1]bicyclooctadiene **5**. Hydrolysis of this silyl enol ether, either upon standing for prolonged periods or upon treatment with fluoride, produced the ketone **6**.

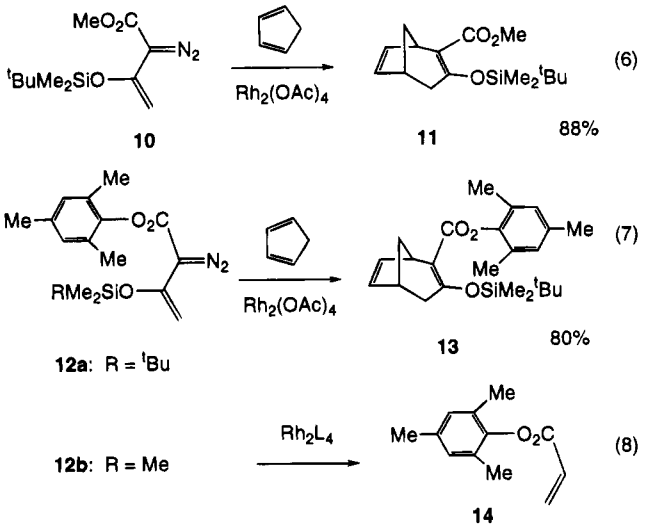


Similar chemistry was observed with the phosphonate derivative **7**. Rhodium(II) acetate-catalyzed decomposition of **7** in the presence of cyclopentadiene gave the cyclopropene cycloadduct **8** that was stable to chromatographic purification. Ring opening of **8** to the [3.2.1]-bicyclooct-6-en-4-one **9** was readily achieved by treatment of **8** with tetrabutylammonium fluoride.

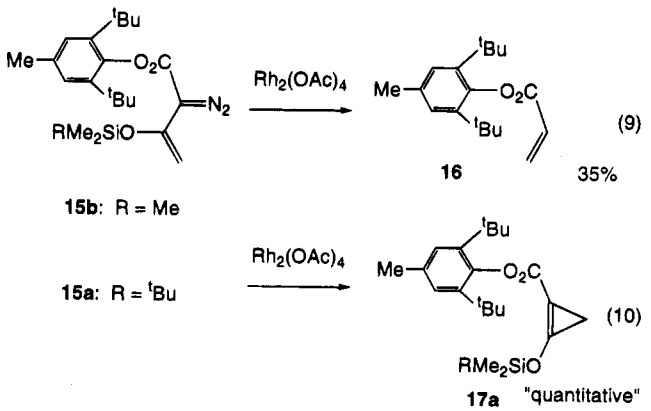


The tricyclic systems **4** and **8** are the apparent products of a cycloaddition reaction between cyclopentadiene and a cyclopropene. We have previously observed that cyclopropenes are not formed in metal-catalyzed decomposition of vinyldiazomethanes except when bulky functionality is present on the vinyl carbon adjacent to the carbenoid.[10] Furthermore, typical carbenoid reactivity in vinylcarbenoids is disrupted by having bulky ester groups adjacent to the carbenoid.[10,11] On the basis of these earlier observations, the study was expanded to a series of vinyldiazomethanes containing ester groups of varying size.

Rhodium(II) acetate-catalyzed decomposition of the methyl ester **10** in the presence of cyclopentadiene resulted in the formation of the [3.2.1]bicyclooctadiene **11** in 88% yield.[8] This compound is the expected product of a tandem cyclopropanation/Cope rearrangement. Increasing the size of the ester group to 2,4,6-trimethylphenyl as in **12a** still resulted in normal cyclopropanation chemistry. Rhodium(II) acetate-catalyzed decomposition of the *tert*-butyldimethylsilyl derivative **12a** in the presence of cyclopentadiene resulted in the formation of the corresponding [3.2.1]bicyclooctadiene **13** in 80% yield. However, decomposition of the trimethylsilyl derivative **12b** in the absence of cyclopentadiene gave a reaction similar to that observed for the sulfonyl system **1**. The acrylate **14** was formed and the yield varied markedly according to the catalyst used. With rhodium(II) acetate, the acrylate **14** was obtained in 5% yield,[8] while the yield of **14** increased to 30%[8] when rhodium(II) trifluoroacetate was used as catalyst.



Isolation of 2,4,6-trimethylphenyl acrylate **14** from the rhodium(II)-catalyzed decomposition of **12b** encouraged us to extend the study to the even bulkier ester 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT).[11,12] Rhodium(II) acetate-catalyzed decomposition of the trimethylsilyl derivative **15b** resulted in the formation of the acrylate **16** in 35% yield (eq 9),[8] but a dramatic change in the course of



the reaction was seen with the *tert*-butyldimethylsilyl derivative **15a** (eq 10). Neither the acrylate product **16** nor a cyclopentadiene cycloadduct was observed in the crude material from the rhodium(II) acetate-catalyzed decomposition of **15a** in the presence of cyclopentadiene. Instead, a product was formed that was unstable to chromatography. Clean conversion of **15a** to this product was achieved in essentially quantitative yield by carrying

(9) (a) Tori, K.; Ohtsurn, M *J. Chem. Soc., Chem. Commun.* **1966**, 866. (b) Kagi, R. I.; Johnson, B. L. *Aust. J. Chem.* **1975**, *28*, 2175.
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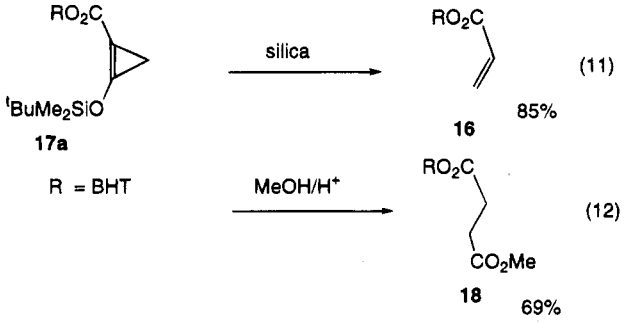
(11) Davies, H. M. L.; Hu, B. *Tetrahedron Lett.* **1991**, *33*, 453.
(12) For other examples of the use of BHT esters in carbenoid reactions see: (a) Doyle, M. P.; Bagheri, V.; Wandless, T. J.; Harn, N. K.; Brinker, D. A.; Eagle, C. T.; Loh, K. L. *J. Am. Chem. Soc.* **1990**, *112*, 1906. (b) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726.

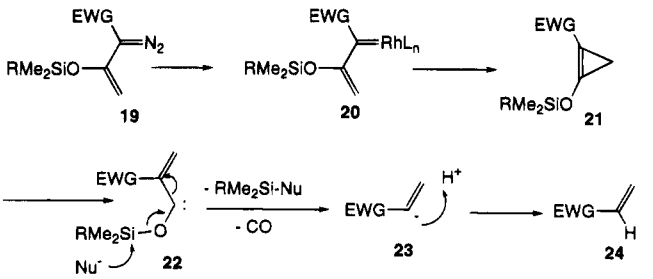
out the rhodium(II) acetate-catalyzed decomposition of **15** in the absence of any trap. The simple nature of the ^{1}H NMR spectrum of the product consisting of a signal for a methylene group (δ 2.08) in addition to the characteristic signals for the siloxy and BHT groups indicated that the product was the cyclopropene **17a**. Further support of this structural assignment was obtained from the infrared spectrum of **17a** which showed a strong absorption at 1852 cm^{-1}, distinctive for a 1,2-disubstituted cyclopropene.[13]

Further verification of the structure of **17a** was obtained through chemical transformations. On attempted flash chromatography, cyclopropene **17a** underwent rapid decomposition and the isolated product was the acrylate **16** in 85% yield.[8] Treatment of **17a** with acidic methanol resulted in the formation of the ring opened product **18** in 69% yield.[8]



A reasonable mechanism to explain this chemistry is shown in general terms in Scheme 1. Rhodium(II)-catalyzed decomposition of the vinyldiazomethane **19** would presumably generate the rhodium carbenoid intermediate **20**. We have previously shown[10] that the presence of bulky substituents adjacent to the carbenoid center is unfavorable to the participation of the carbenoid in intermolecular reactions. It would be reasonable to propose therefore that, when the electron-withdrawing group is bulky, **20** would undergo cyclization to the cyclopropene **21** in preference to an intermolecular cyclopropanation reaction with an alkene. The ring opening of cyclopropenes to vinylcarbenes is well documented,[1-3] and many examples are known of this process to be catalyzed by transition metal salts.[14,15] Ring opening of the cyclopropene **21** could lead to two possible vinylcarbenes, but the most favored would be **22** due to the stabilizing influence of the siloxy group. This step is not considered to be metal catalyzed by means of electrophilic attack on the strained double bond in **21** because such a process would be expected to lead to a different regiochemistry, regenerating the original vinylcarbenoid **20**.[14] Instead, the rhodium carboxylates may catalyze the ring opening of **21** by coordination to the electron-withdrawing group as this would be consistent with the obervation that higher yields of vinyl sulfone **2** and acrylate **14** were obtained when rhodium(II) trifluoroacetate was used as catalyst. The vinylcarbene **22** is set up to fragment to the carbanion **23** with concomitant loss of both the silyl group and carbon monoxide. This fragmentation hypothesis is supported by the deuterium incorporation experiments and the observation that the trimethylsilyl derivatives are much more prone to formation of the fragmentation products than are the *tert*-butyldimethylsilyl derivatives.

Scheme 1



In summary, rhodium(II)-catalyzed decomposition of sterically hindered vinyldiazomethanes results in the formation of donor/acceptor-substituted cyclopropenes. These compounds are particularly susceptible to ring opening and fragmentation reactions. Nevertheless, when appropriately functionalized with bulky substituents they can be of sufficient stability to be isolated and characterized.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded at 200 and 50.3 MHz, respectively. Mass spectral determinations were carried out at 70 eV. CH_2Cl_2 was freshly distilled from CaH_2. Pentane was dried over 4 Å molecular sieves. Column chromatography was carried out on silica gel 60 (230–400 mesh). (Phenylsulfonyl)propanone,[15] *p*-acetamidobenzenesulfonyl azide,[16] dirhodium tetrakis(trifluoroacetate),[17] (2,6-bis(1,1-dimethylethyl)-4-methylphenyl)-2-diazo-3-butenoate,[18] diethyl 1-diazo-2-oxopropylphosphonate,[19] and methyl 2-diazoacetoacetate[20] were prepared by literature procedures. Silylation of diazo ketones was achieved by a modified literature procedure.[21]

1-Diazo-1-(phenylsulfonyl)propanone. A solution of triethylamine (2.16 g, 21.3 mmol) in acetonitrile (20 mL) was added dropwise to a stirred solution of (phenylsulfonyl)-propanone (1.39 g, 7.02 mmol) and *p*-acetamidobenzenesulfonyl azide (1.88 g, 7.84 mmol) in acetonitrile (50 mL) under an argon atmosphere at 0 °C. The reaction was allowed to warm to room temperature and stirred overnight. Saturated ammonium chloride (100 mL) was then added, and the mixture was extracted with diethyl ether (5 × 50 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by column chromatography (75/25 diethyl ether–pentane) to yield a yellow solid (1.24 g, 79%): IR ($CHCl_3$) 3026, 2400, 2134, 2108, 1663, 1159 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.98–7.58 (m, 5 H), 2.28 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 185.4, 141.7, 134.0, 127.0, 27.0; MS *m*/*e* (relative intensity) 170 (34), 141 (20), 125 (6), 94 (46), 77 (100), 51 (44). Anal. Calcd for $C_9H_8N_2O_3S$: C, 48.21; H, 3.60; N, 12.5. Found: C, 48.41; H, 3.73; N, 12.31.

1-Diazo-1-(phenylsulfonyl)-2-((1,1-dimethylethyl)dimethylsiloxy)prop-2-ene (1a). *tert*-Butyldimethylsilyl trifluromethanesulfonate (1.55 mL, 6.75 mmol) was added to a stirred solution of 1-diazo-1-(phenylsulfonyl)propanone (1.15 g, 5.15 mmol) and triethylamine (1.08 mL, 7.84 mmol) in dry CH_2Cl_2 (15 mL) under an argon atmosphere at 0 °C. After the solution was stirred for 15 min at 0 °C, the solvent was

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(21) Ueda, Y.; Roberge, G.; Vinet, V. *Can. J. Chem.* **1984**, *62*, 2936.

removed under reduced pressure. The residue was diluted with hexanes (80 mL), and the resulting solution was washed with dilute $NaHCO_3$ (80 mL) and dilute NaCl (80 mL). The solution was dried ($MgSO_4$) and the solvent was removed under reduced pressure to yield **1a** as a crude orange oil in essentially quantitative yield. **1a** was used in subsequent steps without further purification: IR ($CHCl_3$) 3025, 2935, 2861, 2096, 1610, 1470, 1252 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90–7.48 (m, 5 H), 4.67 (d, 1 H, J = 2.9 Hz), 4.13 (d, 1 H, J = 2.9 Hz), 0.81 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 141.9, 139.5, 133.3, 129.0, 126.6, 90.8, 25.3, 17.9, −5.1 (C=N_2 signal not observed).

1-Diazo-1-(phenylsulfonyl)-2-(trimethylsiloxy)prop-2-ene (1b). Trimethylsilyl trifluoromethanesulfonate (0.66 mL, 3.30 mmol) was added to a stirred solution of triethylamine (0.60 mL, 4.20 mmol) and (phenylsulfonyl)propanone (0.67 g, 2.97 mmol) in dry CH_2Cl_2 (6 mL) under an argon atmosphere at 0 °C. After the solution was stirred for 15 min at 0 °C, the solvent was removed under reduced pressure and hexanes (15 mL) was added to the residue. The resulting oily residue was removed by gravity filtration through Whatman silicone-treated phase-separating paper. The organic layer was then concentrated *in vacuo*. The residue was redissolved in anhydrous hexanes (40 mL), and the organic layer was again removed *via* gravity filtration through Whatman silicone-treated phase-separating paper. Removal of the solvent *in vacuo* gave **1b** as a crude orange oil in essentially quantitative yield. **1b** was used in subsequent steps without further purification: IR (neat) 3066, 2961, 2091, 1725, 1614, 1448, 1256 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.91–7.49 (m, 5 H), 4.67 (d, 1 H, J = 2.8 Hz), 4.17 (d, 1 H, J = 2.8 Hz), 0.13 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 141.8, 139.6, 133.4, 129.0, 126.6, 90.8, −0.5 (C=N_2 signal not observed).

Phenyl Vinylsulfone (3). A solution of **1b** (0.116 g, 0.391 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a refluxing solution of $Rh_2(TFA)_4$ (0.0028 g, 0.00425 mmol) in dry CH_2Cl_2 (15 mL) under an argon atmosphere. The solution was heated at reflux for 2 h. After this time, the solvent was removed under reduced pressure. The residue was purified by column chromatography (50/50 diethyl ether–pentane) to yield **3** as a white solid (0.052 g, 54% for two steps from 1-diazo-1-(phenylsulfonyl)propanone), mp 64–66 °C (lit.[22] mp 66–67 °C): ^1H NMR ($CDCl_3$) δ 7.90–7.49 (m, 5 H), 6.65 (dd, 1 H, J = 16.5, 9.5 Hz), 6.44 (d, 1 H, J = 16.5 Hz), 6.03 (d, 1 H, J = 9.5 Hz); MS m/e (relative intensity) 168 (30) (M^+), 141 (4), 125 (100), 104 (4), 97 (9), 77 (66), 65 (13), 51 (32). Repeating the reaction in the presence of 4 equiv of D_2O resulted in the formation of **3** (52% for two steps from 1-diazo-1-(phenylsulfonyl)propanone) with 90% deuterium incorporation at the C-1 position: ^1H NMR ($CDCl_3$) δ 7.90–7.49 (m, 5 H), 6.43 (apparent t, 1 H, J = 2.5 Hz), 6.01 (br s, 1 H); MS m/e (relative intensity) 169 (1) (M^+), 141 (2), 125 (29), 105 (3), 97 (13), 77 (73), 65 (20), 51 (100).

2-(Phenylsulfonyl)-4-((1,1-dimethylethyl)dimethylsiloxy)tricyclo[3.2.1.0^{2,4}]oct-6-ene (4). A solution of **1a** (0.69 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a refluxing solution of freshly distilled cyclopentadiene (4.45 g, 67.3 mmol) and $Rh_2(OAc)_4$ (0.0091 g, 0.02 mmol) in CH_2Cl_2 (40 mL) under an argon atmosphere. After the reaction mixture was heated for a further 3 h, the solvent was removed under reduced pressure. The crude reaction mixture was triturated and filtered through Celite with pentane (200 mL total volume). The resulting solution was then concentrated, and the residue was purified by short path distillation (1.5 mmHg, 25–37 °C, 2 h) to yield **4** as a colorless gum (0.753 g, 98% for two steps from 1-diazo-1-(phenylsulfonyl)propanone): IR (neat) 3066, 2951, 2858, 2454, 2361, 1902, 1815, 1721, 1637, 1586 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.06–7.47 (m, 5 H), 6.16 (dd, 1 H, J = 5.5, 3.1 Hz), 5.96 (dd, 1 H, J = 5.7, 3.1 Hz), 3.22 (br s, 1 H), 2.65 (br s, 1 H), 2.57 (dd, 1 H, J = 6.3, 2.4 Hz), 1.79 (d, 1 H, J = 6.3 Hz), 1.58 (br d, 1 H, J = 8.3 Hz), 1.49 (br d, 1 H, J = 8.3 Hz), 0.97 (s, 9 H), 0.20 (s, 3 H), 0.15 (s, 3 H); ^{13}C NMR ($CDCl_3$) 139.6, 135.9, 134.5, 132.7, 128.2, 128.0, 72.2, 60.6, 51.6, 46.3, 45.8, 30.4, 25.2, 17.3, −4.5, −4.7; MS m/e (relative intensity) 376 (M^+) (10), 361 (1), 319 (2), 235 (63), 177 (7), 135 (28), 120 (37), 91 (77), 77 (100), 73 (68), 51 (34); HRMS calcd for $C_{20}H_{28}O_3SSi$: 376.1528. Found: 376.1516.

2-(Phenylsulfonyl)-4-((1,1-dimethylethyl)dimethylsiloxy)bicyclo[3.2.1]octa-2,6-diene (5). Attempted purification of **4** (0.73 g, 1.9 mmol) by column chromatography (10/90 diethyl ether–pentane) resulted in the formation of **5** (0.52 g, 71%) and **6** (0.10 g, 20%). **5**: IR (neat) 2954, 2932, 2886, 2859, 1636, 1472, 1464, 1448, 1341, 1306 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88–7.48 (m, 5 H), 6.34 (dd, 1 H, J = 5.3, 3.1 Hz), 5.82 (dd, 1 H, J = 5.3, 3.2 Hz), 4.19 (br s, 1 H), 3.41 (apparent d, 1 H, J = 3.4 Hz), 3.12 (br s, 1 H), 2.58 (br s, 1 H), 1.77 (d, 1 H, J = 10.2 Hz), 1.66 (apparent dt, 1 H, J = 10.2, 4.6 Hz), 0.87 (s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.5, 141.0, 137.7, 133.5, 130.9, 129.0, 128.9, 90.1, 63.5, 45.5, 37.8, 36.8, 25.6, 18.0, −4.3; MS m/e (relative intensity) 376 (M^+) (9), 319 (5), 235 (15), 177 (10), 135 (32), 91 (28), 77 (35), 73 (100), 51 (14); HRMS calcd for $C_{20}H_{28}O_3SSi$ 376.1528, found 376.1535. Anal. Calcd for $C_{20}H_{28}O_3Si$: C, 63.80; H, 7.50. Found: C, 63.86; H, 7.48.

2-(Phenylsulfonyl)-4-*oxo*-bicyclo[3.2.1]oct-6-ene (6). Tetrabutylammonium fluoride (1.1 mL, 1.1 mmol, 1 M solution in tetrahydrofuran) was added to a stirred solution of **5** (0.18 g, 0.37 mmol) in dry tetrahydrofuran (5 mL) at room temperature. The solution was then allowed to stir for 30 min. The reaction mixture was poured into water (15 mL) and extracted with CH_2Cl_2 (3 × 40 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography (50/50 diethyl ether–pentane) to yield **6** as a clear oil (0.078 g, 80%): IR (neat) 3074, 3046, 3025, 3016, 2951, 1716, 1480, 1448, 1309 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.89–7.52 (m, 5 H), 6.21 (dd, 1 H, J = 5.3, 3.1 Hz), 6.01 (dd, 1 H, J = 5.3, 3.2 Hz), 3.37 (dd, 1 H, J = 5.2, 3.0 Hz), 3.26 (dd, 1 H, J = 9.0, 5.1 Hz), 3.15 (broad t, 1 H, J = 4.2, 3.3 Hz), 2.81 (dd, 1 H, J = 18.5, 5.0 Hz), 2.64 (d, 1 H, J = 12.2 Hz), 2.53 (dd, 1 H, J = 18.6, 9.0 Hz), 1.55 (dt, 1 H, J = 12.1, 4.2 Hz); ^{13}C NMR ($CDCl_3$) δ 201.2, 137.6, 137.2, 134.0, 133.8, 129.4, 128.6, 59.2, 54.5, 37.5, 34.7, 34.0; MS m/e (relative intensity) 262 (M^+) (8), 120 (100), 93 (92), 91 (92), 77 (87), 65 (20), 51 (13); HRMS calcd for $C_{14}H_{14}O_3S$ 262.0664, found 262.0672.

Diethyl 3-Diazo-2-(((1,1-dimethylethyl)dimethylsilyl)oxy)propene-3-phosphonate (7). *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.76 mL, 3.6 mmol) was added to a stirred solution of diethyl 1-diazo-2-oxopropylphosphonate (0.224 g, 1 mmol) and triethylamine (0.409 g, 4 mmol) in dry CH_2Cl_2 (10 mL) at 0–5 °C under an argon atmosphere, and the mixture was stirred at 0–5 °C for 4 h. The solvent was then removed, and the residue was extracted with pentane (3 × 30 mL). The combined extracts were washed with dilute aqueous sodium bicarbonate solution and saturated NaCl, dried (Na_2SO_4), and concentrated *in vacuo* to give **7** as an orange liquid (0.68 g, 74%) which was used immediately: IR (neat) 2950, 2930, 2860, 2090, 1300, 1260, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.27 (d, 1 H, J = 2.6 Hz), 4.15 (m, 4 H), 4.11 (d, 1 H, J = 2.6 Hz), 1.34 (t, 6 H, J = 7.0 Hz), 0.90 and 0.83 (2 × s, 9 H), 0.19 and −0.02 (2 × s, 6 H).

Diethyl 4-(((1,1-Dimethylethyl)dimethylsilyl)oxy)tricyclo[3.2.1.0^{2,4}]oct-6-ene-2-phosphonate (8). A solution of **7** (0.300 g, 0.9 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise to a solution of cyclopentadiene (2.07 g, 31 mmol) and $Rh_2(OAc)_4$ (0.0054 g, 0.012 mmol) in dry CH_2Cl_2 (10 mL) and the mixture heated at reflux under an argon atmosphere. On completion of the addition, the solution was heated for a further 2 h at reflux. The solvent was then removed *in vacuo*, and flash chromatography (30/70 ethyl acetate–hexanes) of the residue yielded **8** as a colorless oil (0.155 g, 47%): IR ($CDCl_3$) 2983, 2957, 2931, 2858, 1473, 1392, 1320, 1284, 1240, 1204, 1027 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.10 (dd, 1 H, J = 5.2, 3.3 Hz), 5.79 (dd, 1 H, J = 5.3, 3.3 Hz), 4.08 (m, 4 H), 3.10 (m, 1 H), 2.65 (br s, 1 H), 2.36 (dd, 1 H, J = 7.3, 1.6 Hz), 1.90 (ddd, 1 H, J = 16.6, 5.6, 2.6 Hz), 1.74 (dd, 1 H, J = 7.5, 1.6 Hz), 1.42 (t, 1 H, J = 5.8 Hz), 1.26 (td, 6 H, J = 7.0 and 1.8 Hz), 0.85 (s, 9 H), 0.07 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 135.0, 134.1 (d), 72.0 (d), 61.6, 61.3, 60.8 (d), 51.4, 46.2, 31.4,

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25.5, 17.6, −4.1 and −4.2; MS *m/e* 372 (M^+) (9), 315 (10), 287 (4), 235 (58), 215 (6), 177 (78), 137 (10), 121 (21), 103 (22), 75 (25), 73 (100); HRMS calcd for $C_{18}H_{33}O_4PSi$ 372.1886, found 372.1888.

Diethyl 4-Oxobicyclo[3.2.1]oct-6-ene-2-phosphonate (9). Tetrabutylammonium fluoride (1 M solution in THF, 0.9 mL, 0.9 mmol) was added dropwise to a stirred solution of **8** (0.122 g, 0.3 mmol) in THF (5 mL) at room temperature. The mixture was stirred for a further 30 min at room temperature and then poured onto ice−water (15 mL). The aqueous mixture was extracted with CH_2Cl_2 (3 × 40 mL). The combined extracts were dried (Na_2SO_4), evaporated, and subjected to flash chromatography (ethyl acetate−hexanes) to yield **9** (0.068 g, 80%) as a 2:1 mixture of exo/endo stereoisomers: IR ($CDCl_3$) 2984, 1712, 1237, 1055, 1028 cm^{-1}; ^1H NMR ($CDCl_3$) (major isomer) δ 6.30 (dd, 1 H, *J* = 5.6, 2.8 Hz), 6.04 (dd, 1 H, *J* = 5.6, 3.0 Hz), 4.10 (m, 4 H), 3.16 (m, 1 H), 3.04 (m, 1 H), 2.92 - 2.10 (m, 4 H), 1.92 (d, 1 H, *J* = 10.6 Hz) and 1.31 (t, 1 H, *J* = 7.0 Hz); MS *m/e* 258 (M^+) (38), 230 (7), 192 (51), 165 (100), 137 (59), 120 (22), 109 (40), 91 (60), 77 (30), 65 (37), 39 (21). Anal. Calcd for $C_{12}H_{19}O_4P$: 0.25 H_2O: C, 54.85; H, 7.48. Found: C, 54.90; H, 7.68.

Methyl 2-Diazo-3-(((1,1-dimethylethyl)dimethylsilyl)-oxy)-3-butenoate (10).[18] *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.56 mL, 2.4 mmol) was added to a stirred solution of methyl 2-diazoacetoacetate (0.288 g, 2 mmol) and triethylamine (0.310 g, 3 mmol) in dry CH_2Cl_2 (5 mL) at 0−5 °C under an argon atmosphere, and the mixture was stirred at 0−5 °C for 30 min. The solution was then diluted with petroleum ether (20 mL), washed with dilute aqueous sodium bicarbonate solution and saturated brine, dried (Na_2SO_4), and concentrated *in vacuo* to give **10**[18] as an orange liquid in quantitative yield: IR (neat) 2956, 2859, 2104, 1718, 1685, 1616, 1473, 1437 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.02 (d, 1 H, *J* = 2.0 Hz), 4.27 (d, 1 H, *J* = 2.0 Hz), 3.82 (s, 3H), 0.94 (s, 9H), 0.25 (s, 6H).

Methyl 3-(((1,1-Dimethylethyl)dimethylsilyl)oxy)bicyclo[3.2.1]octa-2,6-diene-2-carboxylate (11). A solution of **10** (0.376 g, 1.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 45 min to a solution of cyclopentadiene (3.19 g, 48 mmol) and $Rh_2(OAc)_4$ (0.0105 g, 0.02 mmol) in CH_2Cl_2 (20 mL) heated at reflux under an argon atmosphere, and the mixture was then heated for a further 2 h at reflux. The solvent was then removed *in vacuo*, and the residue was purified by flash chromatography (5/95 diethyl ether−pentane) to yield **11** as a colorless oil (0.367 g, 85%): IR ($CDCl_3$) 2952, 2860, 1679, 1605, 1438, 1375, 1254, 1200, 1071 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23 (dd, 1 H, *J* = 5.5, 2.8 Hz), 5.67 (dd, 1 H, *J* = 5.5, 2.8 Hz), 3.64 (s, 3 H), 3.37 (m, 1 H), 2.75 (m, 1 H), 2.36 (dd, 1 H, *J* = 18.1, 5.2 Hz), 1.85 (d, 1 H, *J* = 18.1 Hz), 1.80 (dd, 1 H, *J* = 10.1, 6.1 Hz), 1.50 (d, 1 H, *J* = 10.1 Hz), 0.87 (s, 9 H), 0.10 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.0, 157.6, 139.7, 130.2, 115.7, 50.8, 40.6, 38.8, 38.2, 35.2, 25.7, 18.3, −3.7; MS *m/e* 294 (M^+) (0.32), 279 (21), 263 (24), 238 (100), 205 (10), 177 (9), 131 (20), 120 (12), 103 (23), 89 (66), 75 (78), 59 (71); HRMS calcd for $C_{16}H_{26}O_3Si$ 294.1651, found 294.1652.

2,4,6-Trimethylphenyl 2-Diazo-3-butenoate. Diketene (16.81 g, 199 mmol) in acetone (40 mL) was added dropwise over 1 h to a stirred solution of the phenol (6.80 g, 50 mmol), sodium acetate (0.43 g, 5.2 mmol), and tosyl azide (13.82 g, 70 mmol) in dry CH_3CN (100 mL) at reflux under an argon atmosphere.[12a] The reaction mixture was cooled and stirred at room temperature for 12 h at which point it was quenched with water. The mixture was extracted with diethyl ether, and the extract was washed with 15% aqueous potassium hydroxide, dried ($MgSO_4$), and then concentrated *in vacuo*. The residue was purified by column chromatography (10/90−20/80 diethyl ether−pentane) to yield the title compound (10.59 g, 86%) as a yellow solid, mp 54−55 °C: IR ($CHCl_3$) 3018, 2144, 1728, 1655, 1370, 1326, 1241 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (s, 2 H), 2.52 (s, 3 H), 2.28 (s, 3 H), 2.15 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 189.8, 159.3, 144.8, 135.9, 129.7, 129.3, 28.2, 20.6, 16.2. Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.39; H, 5.73; N, 11.38. Found: C, 63.29; H, 5.76; N, 11.29.

2,4,6-Trimethylphenyl 3-((1,1-Dimethylethyl)dimethylsiloxy)-2-diazo-3-butenoate (12a). *tert*-Butyldimethylsilyl trifluoromethanesulfonate (1.22 mL, 5.31 mmol) was added slowly to a stirred solution of 2,4,6-trimethylphenyl 2-diazo-3-butenoate (1.0 g, 4.08 mmol) and triethylamine (0.85 mL, 6.10 mmol) in CH_2Cl_2 (10 mL) at 0 °C under an argon atmosphere. The mixture was stirred overnight and then diluted with hexanes (80 mL). The solution was stirred for 30 min further. The organic layer was successively washed with dilute $NaHCO_3$ solution (80 mL) and dilute NaCl solution (80 mL), dried ($MgSO_4$), and then concentrated *in vacuo* to yield **12a** as a crude orange solid in essentially quantitaive yield which was used in subsequent steps without further purification: IR ($CHCl_3$) 3018, 2107, 1718, 1353, 1239 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.87 (s, 2 H), 5.07 (d, *J* = 2.2 Hz, 1 H), 4.30 (d, *J* = 2.2 Hz, 1 H), 2.27 (s, 3 H), 2.15 (s 6 H), 0.95 (s, 9 H), 0.29 (s, 6 H); ^{13}C NMR ($CDCl_3$) 162.0, 145.3, 140.4, 135.5, 130.1, 129.2, 90.7, 66.2, 25.7, 25.6, 20.7, 18.1, 16.3, −4.8.

2,4,6-Trimethylphenyl 3-(Trimethylsiloxy)-2-diazo-3-butenoate (12b). Trimethylsilyl trifluoromethanesulfonate (0.94 mL, 5.18 mmol) was added to a stirred solution of 2,4,6-trimethylphenyl 2-diazo-3-butenoate (1.00 g, 4.09 mmol) and triethylamine (0.85 mL, 6.10 mmol) in dry CH_2Cl_2 (10 mL) at 0 °C under an argon atmosphere, and the mixture was stirred at room temperature for 30 min. Anhydrous hexanes (40 mL) was then added, and the mixture was stirred for 15 min. The organic layer was removed *via* gravity filtration through Whatman silicone-treated phase-separating paper and concentrated *in vacuo*. The residue was redissolved in anhydrous hexanes (40 mL), and the organic layer was again removed *via* gravity filtration through Whatman silicone-treated phase-separating paper and concentrated *in vacuo* to give **12b** as a crude orange oil in essentially quantitative yield. **12b** was used in subsequent steps without further purification: IR (neat) 2959, 2922, 2096, 1724, 1608, 1485, 1347, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.87 (s, 2 H), 5.05 (d, 1 H, *J* = 2.1 Hz), 4.32 (d, 1 H, *J* = 2.1 Hz), 2.26 (s, 3 H), 2.15 (s, 6 H), 0.29 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 161.4, 145.1, 140.0, 135.0, 129.7, 128.9, 90.9, 65.6, 20.3, 15.9, −0.6.

2,4,6-Trimethylphenyl 3-((1,1-Dimethylethyl)dimethylsiloxy)bicyclo[3.2.1]octa-2,6-diene-2-carboxylate (13). A solution of **12a** (0.51 g, 1.4 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a refluxing solution of freshly distilled cyclopentadiene (3.20 g, 48 mmol) and $Rh_2(OAc)_4$ (0.0074 g, 0.02 mmol) in CH_2Cl_2 (25 mL) under an argon atmosphere. On completion of the addition, the solution was heated for a further 8 h at reflux. The mixture was then cooled and concentrated *in vacuo*. The residue was purified by column chromatography (10/90 diethyl ether−pentane) to yield **13** as a white solid (0.45 g, 80% for two steps from 2,4,6-trimethylphenyl 2-diazo-3-butenoate), mp 50.5−53 °C: IR ($CHCl_3$) 3027, 2955, 2932, 2860, 1721, 1599, 1376, 1365, 1253, 1244, 1213 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.85 (s, 2 H), 6.39 (dd, 1 H, *J* = 5.5, 2.7 Hz), 5.79 (dd, 1 H, *J* = 5.5, 2.8 Hz), 3.65 (dd, 1 H, *J* = 4.4, 2.9 Hz), 2.86 (m, 1 H), 2.51 (dd, 1 H, *J* = 18.2, 5.0 Hz), 2.25 (s, 3 H), 2.11 (s, 6 H), 2.08−1.92 (m, 2 H), 1.67 (δ, 1 H, *J* = 10.0 Hz), 0.90 (s, 9 H), 0.17 (s, 3 H), 0.06 (s, 3 H); ^{13}C ($CDCl_3$) δ 163.2, 160.0, 146.2, 139.9, 134.5, 130.3, 129.9, 129.0, 114.7, 40.6, 39.0, 38.2, 35.7, 25.8, 20.8, 18.4, 16.4, −3.5; MS *m/e* (relative intensity) 398 (M^+) (10), 383 (2), 341 (9), 263 (100), 235 (2), 183 (8), 136 (7), 119 (5), 91 (6), 73 (63); HRMS calcd for $C_{24}H_{34}O_3Si$ 398.2277, found 398.2271. Anal. Calcd for $C_{24}H_{34}O_3Si$: C, 72.32; H, 8.60. Found: C, 72.29; H, 8.65.

2,4,6-Trimethylphenyl Propenoate (14). A solution of **12b** (0.11 g, 0.33 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a refluxing solution of $Rh_2(TFA)_4$ (0.0022 g, 0.0033 mmol) in CH_2Cl_2 (30 mL) under an argon atmosphere, and the mixture was heated for a further 9 h. The mixture was then concentrated *in vacuo*, and the residue was purified by column chromatography (5/95 diethyl ether−pentane) to yield **14** as a colorless oil (0.019 g, 30% for two steps from 2,4,6-trimethylphenyl 2-diazo-3-butenoate): IR ($CHCl_3$) 3006, 2927, 2873, 1736, 1484, 1405, 1381, 1260, 1237, 1208 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88 (s, 2 H), 6.71 (d, *J* = 17.3 Hz, 1 H), 6.35 (dd, *J* = 17.3 Hz, *J* = 10.4 Hz, 1 H), 6.05 (d, *J* = 10.4 Hz, 1 H), 2.27 (s, 3 H), 2.10 (s, 6 H); ^{13}C ($CDCl_3$) δ 164.0, 135.4, 132.4, 129.7, 129.6, 129.1, 127.6, 20.8, 16.2; MS *m/e* (relative intensity) 190

(M^+) (10), 136 (38), 121 (8), 91 (9), 58 (53), 55 (100); HRMS calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0991.

2,6-Bis(1,1-dimethylethyl)-4-methylphenyl 3-((1,1-Dimethylethyl)dimethylsiloxy)-2-diazo-3-butenoate (15a). *tert*-Butyldimethylsiloxy trifluoromethanesulfonate (0.56 mL, 2.44 mmol) was added slowly to a stirred solution of 2,6-bis-(1,1-dimethylethyl)-4-methylphenyl 2-diazo-3-butenoate[12a] (0.60 g, 1.8 mmol) and triethylamine (0.38 mL, 2.23 mmol) in CH_2Cl_2 (4 mL) at 0 °C under an argon atmosphere. The mixture was stirred overnight and then diluted with hexanes (80 mL). The solution was stirred for 30 min. The organic layer was successively washed with dilute $NaHCO_3$ solution (40 mL) and dilute NaCl solution (40 mL), dried ($MgSO_4$), and then concentrated *in vacuo* to yield **15a** as a yellow solid, in essentially quantitative yield. The product so obtained was used in subsequent steps without further purification: IR ($CHCl_3$) 3035, 2965, 2104, 1721, 1610, 1471, 1194 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (s, 2 H), 5.07 (d, J = 2.1 Hz, 1 H), 4.30 (d, J = 2.1 Hz, 1 H), 2.30 (s, 3 H), 1.30 (s, 18 H), 0.95 (s, 9 H), 0.25 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 164.0, 144.8, 142.4, 140.0, 134.8, 130.3, 127.0, 91.6, 66.6, 35.2, 31.6, 25.7, 21.5, 18.2, −4.8.

2,6-Bis(1,1-dimethylethyl)-4-methylphenyl 3-(Trimethylsiloxy)-2-diazo-3-butenoate (15b). Trimethylsilyl trifluoromethanesulfonate (0.21 mL, 1.2 mmol) was added to a stirred solution of 2,6-bis(1,1-dimethylethyl)-4-methylphenyl 2-diazo-3-butenoate (0.30 mL, 0.91 mmol) and triethylamine (0.38 mL, 1.4 mmol) in CH_2Cl_2 (4 mL) at 0 °C under an argon atmosphere, and the mixture was stirred for a further 30 min. Anhydrous hexanes (15 mL) was then added, and the mixture was stirred for 15 min. The organic layer was removed via gravity filtration through Whatman silicone-treated phase-separating paper and concentrated *in vacuo*. The residue was redissolved in anhydrous hexanes (30 mL), and the top organic layer was again decanted through Whatman silicone treated-phase-separating paper and then concentrated *in vacuo* to give **15b** as an orange oil in essentially quantitative yield. **15b** was used in subsequent steps without further pufication: IR (neat) 3055, 2959, 2874, 2093, 1714, 1612, 1395, 1354, 1255, 1219 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.13 (s, 2 H), 5.07 (d, J = 2.1 Hz, 1 H), 4.30 (d, J = 2.1 Hz, 1 H), 2.30 (s, 3 H), 1.30 (s, 18 H), 0.30 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 163.8, 144.7, 142.3, 139.8, 134.6, 126.96, 91.7, 66.4, 35.1, 31.4, 31.3, 21.3, −0.34.

2,6-Bis(1,1-dimethylethyl)-4-methylphenyl Propenoate (16). A solution of **15b** (0.103 g, 0.26 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a refluxing solution of $Rh_2(TFA)_4$ (0.0018 g, 0.027 mmol) in CH_2Cl_2 (30 mL) under an argon atmosphere, and the mixture was heated for a further 2 h. The mixture was then concentrated *in vacuo*, and the residue was purified column chromatography (1/99 diethyl ether–pentane) to yield **16** as a white solid (0.026 g, 35% for two steps from 2,6-bis(1,1-dimethylethyl)-4-methylphenyl 2-diazo-3-butenoate, mp 57–58 °C: IR ($CHCl_3$) 3690, 3007, 2967, 1738, 1599, 1405 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10 (s, 2 H), 6.60 (d, J = 16.5 Hz, 1 H), 6.38 (dd, J = 16.5 Hz, J = 9.5 Hz, 1 H), 6.05 (d, J = 9.5 Hz, 1 H), 2.30 (s, 3 H), 1.33 (s, 18 H); ^{13}C NMR ($CDCl_3$) 166.4, 145.5, 142.0, 134.6, 132.6, 129.3, 127.0, 35.3, 31.5, 21.5; MS m/e (relative intensity) 274 (M^+) (10), 220 (42), 205 (27), 119 (5), 91 (8), 57 (29), 55 (100). Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.78; H, 9.56. Found: C, 78.67; H, 9.61.

2,6-Bis(1,1-dimethylethyl)-4-methylphenyl) 1-((1,1-Dimethylethyl)dimethylsiloxy)cycloprop-1-ene-2-carboxylate (17a). A solution of **15a** (0.20 g, 0.45 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a refluxing solution of the $Rh_2(OAc)_4$ (0.011 g, 0.0025 mmol) in CH_2Cl_2 (50 mL) under an argon atmosphere, and the mixture was heated for a further 2 h. The mixture was then concentrated *in vacuo*. Pentane (50 mL) was added to the residue, and the solution was filtered through Celite. Removal of the solvent gave **17a** in essentially quantitative yield as a pale yellow oil: IR (neat) 3074, 2959, 2863, 2123, 2099, 1852, 1717, 1620, 1598, 1472 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10 (s, 2 H), 2.30 (s, 3 H), 2.08 (s, 2 H), 1.33 (s, 18 H), 0.98 (s, 9 H), 0.35 (s, 6 H). This compound was insufficiently stable for elemental analysis.

2,6-Bis(1,1-dimethylethyl)-4-methyl-phenyl Methyl Ethane-1,2-dicarboxylate (18). **16** (0.30 g, 0.72 mmol) was added to a solution of concentrated HCl (1.0 mL, 12 mmol) in anhydrous methanol (50 mL), and the mixture was stirred for 12 h. Saturated aqueous sodium bicarbonate (50 mL) was then added, and the resulting mixture was extracted with CH_2Cl_2 (4 × 25 mL). The organic layer was dried ($MgSO_4$) and then concentrated *in vacuo*. The residue was purified by column chromatography (5/95 diethyl ether–pentane) to yield **18** as a white solid (0.165 g, 69% for three steps from [2,6-bis(1,1-dimethylethyl)-4-methylphenyl 2-diazo-3-butenoate], mp 32–33 °C: IR 3043, 2949, 2875, 1726, 1598, 1419, 1365, 1270, 1247; ^1H NMR ($CDCl_3$) δ 7.12 (s, 2 H), 3.71 (s, 3 H), 3.00 (t, J = 7.3 Hz, 2 H), 2.74 (t, J = 7.3 Hz, 2 H), 2.32 (s, 3 H), 1.33 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 172.4, 145.6, 141.9, 134.6, 127.0, 51.8, 35.2, 31.4, 30.7, 28.6, 21.5; MS m/e (relative intensity) 334 (2), 303 (9), 220 (58), 205 (83), 115 (100), 87 (17), 57 (42), 55 (45); HRMS calcd for $C_{20}H_{30}O_4$ 334.2144, found, 334.2144. Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.81; H, 9.05. Found: C, 71.68; H, 9.01.

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Supporting Information Available: Copies of ^1H NMR spectra of **4**, **6**, **8**, **11**, **14**, and **17a** (6 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.

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