$Rh_2(Opiv)_4$-Catalyzed Reactions of Diazo Compound Derived from Meldrum's Acid and Styrenes. Efficient Synthesis of Cyclopropanes

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The rhodium(II)-catalyzed reactions of diazo compound derived from Meldrum's acid with a variety of styrenes have been examined. These reactions provide a rapid route to the preparation of cyclopropanes with a variety of substituents on the benzene ring. The mechanistic pathway for the formation of these products has been also described in terms of a stepwise mechanism.

Key Words : $Rh_2(Opiv)_4$-catalyzed reactions, Diazo compound, Cyclopropanes

Introduction

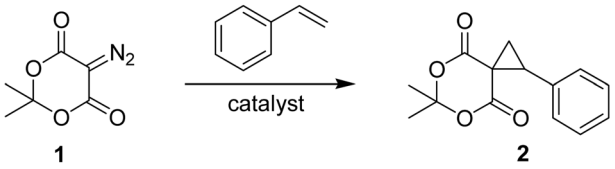
Cyclopropanes are widely found as a basic unit in a range of naturally occurring compounds.[1] They have also been used as versatile and important intermediates in the synthesis of more fuctionalized cycloalkanes, acyclic compounds, and natural products.[2] Numerous methods for the preparation of cyclopropanes have been reported by many groups.[2] Among these, most of these synthetic efforts have focused on the enantioselective molecules.[3] They are mostly classified as three types of reactions from olefins: halomethylmetal-mediated cyclopropanation reactions,[4] the transition metal-mediated decomposition of diazo compounds,[5] and nucleophilic addition followed by ring closure.[6]

We have recently been interested in the rhodium-catalyzed reactions of diazodicarbonyl compounds with several substrates.[7] In particular, we have used cyclic diazo compounds such as 2-diazo cyclohexane-1,3-dione, 3-diazo chroman-2,4-dione, and 2-diazo phenalene-1,3-dione with olefins.[8] For example, reaction of 2-diazo phenalene-1,3-dione with allylic halides gave [2,3]-rearranged products and dihydrofurans in good yields, whereas reactions with 1-hexene or ethyl vinyl ether afforded dihydrofurans in moderate yields (Scheme 1). In these cases, no cyclopropane adducts were isolated. While continuing our studies in the development of a new methodology using cyclic diazo compounds, we investigated the rhodium-catalyzed reactions of other diazo compound **1** derived from Meldrum's acid with a variety of styrenes. We report herein a new and efficient synthesis of cyclopropanes.

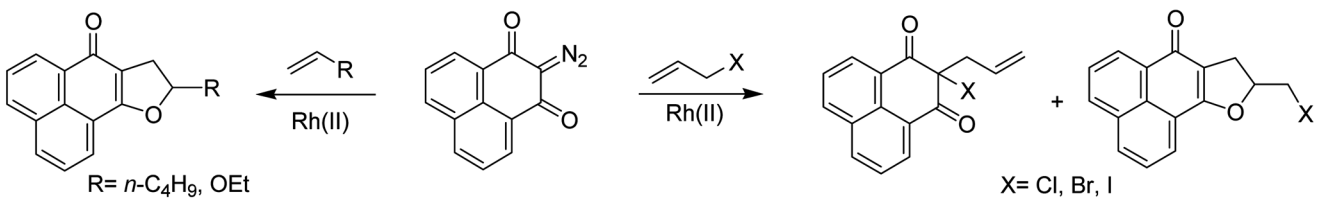
Results and Discussion

Diazo compound **1** was prepared by the diazotransfer reaction of the corresponding Meldrum's acid with mesyl azide in a 76% yield.[9] In order to check the reactivity of **1**, reaction with styrene was first examined using several metal catalysts in several solvents (Table 1). No products were seen with $Cu(OAc)_2$ (10 mol %) or $Pd(OAc)_2$ (10 mol %) at 70 °C for 10 h in fluorobenzene. As other catalysts, rhodium metals were used in fluorobenzene. The electron-poor rhodium trifluoroacetate (1 mol %) gave no product,

Table 1. Effect of metal catalysts and solvents in the reaction of **1** with styrene

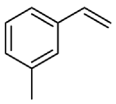
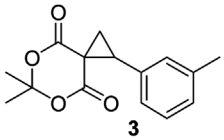
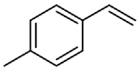
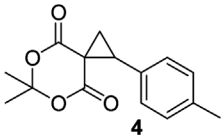
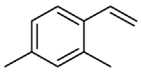
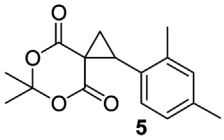
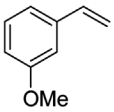
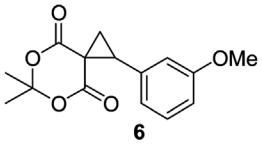
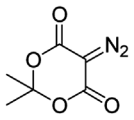
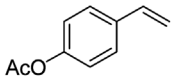
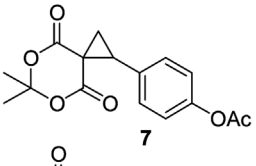
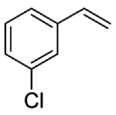
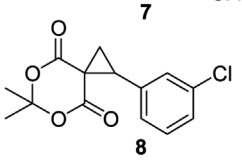
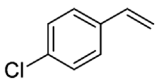
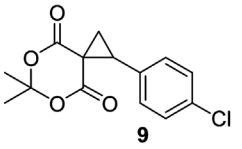
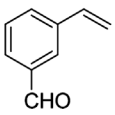
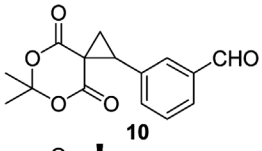
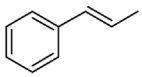
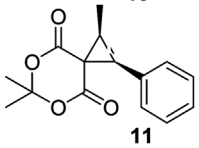
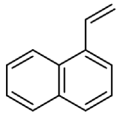
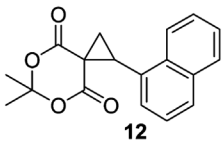
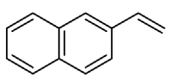
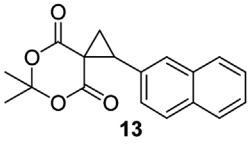


catalyst	condition	yield (%)
$Cu(OA)_2$ (10 mol%)	70 °C, 10 h, PhF	0
$Pd(OAc)_2$ (10 mol%)	70 °C, 10 h, PhF	0
$Rh_2(OCOCF_3)_4$ (1 mol%)	70 °C, 10 h, PhF	0
$Rh_2(OAc)_4$ (1 mol%)	70 °C, 10 h, PhF	10
$Rh_2(Opiv)_4$ (1 mol%)	70 °C, 3 h, PhF	94
$Rh_2(Opiv)_4$ (1 mol%)	70 °C, 4 h, PhCl	73
$Rh_2(Opiv)_4$ (1 mol%)	70 °C, 4 h, PhH	72
$Rh_2(Opiv)_4$ (1 mol%)	reflux, 4 h, CH_2Cl_2	85



Scheme 1

Table 2. Rhodium(II)-catalyzed reactions of **1** with a variety of styrenes

entry	diazo compound	styrene	time	product	yield (%)
1			3 h	 **3**	76
2			3 h	 **4**	94
3			3 h	 **5**	81
4			4 h	 **6**	64
5	 **1**		6 h	 **7**	37
6			4 h	 **8**	79
7			4 h	 **9**	80
8			6 h	 **10**	27
9			6 h	 **11**	42
10			4 h	 **12**	64
11			4 h	 **13**	66

whereas both rhodium acetate (1 mol %) and rhodium pivalate (1 mol %) afforded product **2** in 10 and 94% yields, respectively. Interestingly, we found that more electron-rich rhodium pivalate was much superior for this reaction. Other solvents included chlorobenzene (73%, 70 °C, 4 h) and benzene (72%, 70 °C, 4 h), and methylene chloride (85%,

reflux, 4 h). Compound **2** was easily separated by column chromatography and characterized by spectroscopic analysis. The ^{1}H NMR spectrum of **2** shows one methine proton at δ = 3.43 ppm as a triplet (J = 9.4 Hz) and two methylene peaks at 2.67 ppm as a double-doublet (J = 9.4, 4.8 Hz) and a 2.53 ppm as a double-doublet (J = 9.4, 4.8 Hz) associated with cyclopropane ring. The structure was further confirmed by the ^{13}C NMR spectrum, which shows the expected carbonyl peaks at 168.1 and 163.9 ppm due to two esters. Also, two ester carbonyl absorptions were found in the IR spectrum at 1765 and 1738 cm^{-1}.

Reactions of **1** with a variety of styrenes were carried out under optimized reaction conditions. A variety of styrenes were needed to investigate the influence of substituents on reactivity and the results are summarized in Table 2. Reactions of several styrenes that had an electron-donating group on the benzene ring were first attempted. Reaction of **1** with 3- and 4-methylstyrenes in the presence of 1 mol % of $Rh_2(Opiv)_4$ at 70 °C for 3 h gave cyclopropane **3** (76%) and **4** (94%), respectively (entries 1-2). With 2,4-dimethylstyrene, product **5** was also produced in an 81% yield (entry 3). Treatment with 3-methoxystyrene at 70 °C for 4 h afforded adduct **6** in a 64% yield (entry 4), whereas reaction with 4-acetoxystyrene at 70 °C for 6 h gave cyclopropane **7** in 37% yield (entry 5). On the other hand, reactions of several styrenes with an electron-withdrawing group on the benzene ring were also successful. When **1** was treated with 3 and 4-chlorostyrenes with 1 mol % of $Rh_2(Opiv)_4$ at 70 °C for 4 h, cyclopropanes **8** and **9** were produced in 79 and 80% yields, respectively (entries 6-7). However, reaction with 3-vinylbenzaldehyde at 70 °C for 6 h gave cyclopropane **10** (27%) in low yield (entry 8).

In order to extend the utility of these reactions, further reactions with other types of styrenes were next examined. Interestingly, reaction with *trans*-β-methylstyrene in the presence of 1 mol % of rhodium pivalate at 70 °C for 6 h gave product **11** in 42% yield (entry 9). The *cis*-stereochemistry was assigned as compared with coupling constant of a related compound obtained from the earlier reported data.[10] Further support was obtained from NOE interactions observed in the NOESY spectrum of **11**. The NOE correlations observed between H-1 and H-2 reflected the *cis* orientation. With 1-vinylnaphthalene and 2-vinylnaphthalene, products **12** and **13** were obtained in 64 and 66% yields, respectively (entries 10-11).

Although the exact mechanism of the reaction is still not clear, it is best described as shown in Scheme 2. The formation of **11** is exclusively *cis*-stereochemistry despite the use of *trans*-b-methylstyrene. This demonstrates a stepwise mechanism of the process. The diazo compound **1** first gives a carbenoid **14** (or carbene) by displacement of nitrogen by $Rh_2(Opiv)_4$.[11] The carbenoid **14** is trapped by the double bond of *trans*-b-methylstyrene to give intermediate **15**, which undergoes ring closure to give the cyclopropane product **11**.

In conclusion, the rhodium(II)-catalyzed reactions of the cyclic diazo compound **1** with a variety styrenes are described. These reactions provide a rapid method of making a variety of cyclopropanes.

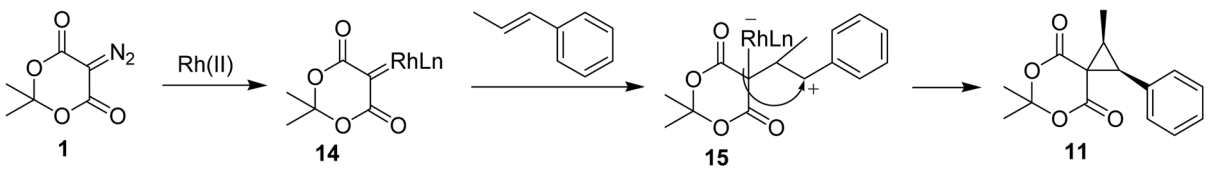
Experimental Section

All experiments were carried out under nitrogen atmosphere. Merck precoated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined with microcover glasses on a Fisher-Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer in $CDCl_3$ using 7.24 ppm as the solvent chemical shift. ^{13}C NMR spectra were recorded on a Bruker Model ARX (75 MHz) spectrometer in $CDCl_3$ using 77.0 ppm as the solvent chemical shift. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. High resolution mass spectra were obtained with a JEOL JMS-700 spectrometer at the Korea Basic Science Institute.

General Procedure for the Synthesis of Cyclopropanes. To a solution of diazo compound **1** (1.0 mmol) and styrene (2 mmol) in fluorobenzene (2 mL) was added rhodium pivalate (0.01 mmol) at room temperature. The reaction mixture was stirred at 70 °C for 3-6 h. The solvent was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel to give the product.

6,6-Dimethyl-1-phenyl-5,7-dioxaspiro[2.5]octane-4,8-dione (2). Reaction of **1** (170 mg, 1.0 mmol) and styrene (208 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **2** (231 mg, 94%) as a solid: mp 130-131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (5H, s), 3.43 (1H, t, J = 9.4 Hz), 2.67 (1H, dd, J = 9.4, 4.8 Hz), 2.53 (1H, dd, J = 9.4, 4.8 Hz), 1.71 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 163.9, 131.6, 129.9, 129.6, 129.1, 128.8, 105.3, 44.9, 33.5, 28.3, 28.1, 23.3; IR (KBr) 3011, 1765, 1738, 1501, 1460, 1435, 1387, 1348, 1290, 1225, 1204, 1177, 1036, 963, 876, 831, 719 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{14}O_4$: 246.0892. Found: 246.0891.

6,6-Dimethyl-1-*m*-tolyl-5,7-dioxaspiro[2.5]octane-4,8-dione (3). Reaction of **1** (170 mg, 1.0 mmol) and 3-



Scheme 2

methylstyrene (236 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **3** (198 mg, 76%) as a solid: mp 87-89 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (1H, d, J = 7.3 Hz), 7.11 (1H, s), 7.11-7.09 (2H, m), 3.39 (1H, t, J = 9.5 Hz), 2.65 (1H, dd, J = 9.5, 4.7 Hz), 2.51 (1H, dd, J = 9.5, 4.7 Hz), 2.33 (3H, s), 1.71 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 163.9, 138.5, 131.4, 130.5, 130.0, 128.7, 127.1, 105.3, 45.1, 35.5, 28.3, 28.1, 23.3, 21.8; IR (KBr) 2993, 2920, 1762, 1735, 1440, 1383, 1346, 1209, 1055, 968, 829, 790 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{16}O_4$: 260.1049. Found: 260.1047.

6,6-Dimethyl-1-*p*-tolyl-5,7-dioxaspiro[2.5]octane-4,8-dione (4). Reaction of **1** (170 mg, 1.0 mmol) and 4-methylstyrene (236 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **4** (244 mg, 94%) as a solid: mp 137-138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (2H, d, J = 8.2 Hz), 7.12 (2H, d, J = 8.2 Hz), 3.40 (1H, t, J = 9.4 Hz), 2.65 (1H, dd, J = 9.4, 4.8 Hz), 2.51 (1H, dd, J = 9.4, 4.8 Hz), 2.31 (3H, s), 1.71 (3H, s), 1.70 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 164.0, 139.1, 129.8, 129.5, 128.4, 105.3, 45.3, 33.7, 28.3, 28.1, 23.3, 21.6; IR (KBr) 3002, 2925, 1765, 1737, 1614, 1350, 1298, 1200, 1187, 1049, 1022, 964, 822 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{16}O_4$: 260.1049. Found: 260.1049.

1-(2,4-Dimethylphenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]-octane-4,8-dione (5). Reaction of **1** (170 mg, 1.0 mmol) and 2,4-dimethylstyrene (264 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **5** (222 mg, 81%) as a solid: mp 100-101 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (1H, d, J = 7.6 Hz), 6.99 (1H, d, J = 7.6 Hz), 6.98 (1H, s), 3.53 (1H, t, J = 9.4 Hz), 2.58 (1H, dd, J = 9.4, 4.8 Hz), 2.47 (1H, dd, J = 9.4, 4.8 Hz), 2.28 (3H, s), 2.25 (3H, s), 1.75 (3H, s), 1.72 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 164.5, 138.7, 138.1, 131.5, 129.1, 127.7, 126.9, 105.3, 43.5, 32.0, 28.5, 28.0, 25.9, 21.5, 20.1; IR (KBr) 3000, 2924, 1763, 1738, 1393, 1325, 1296, 1223, 1202, 1186, 1046, 968, 880, 822 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{18}O_4$: 274.1205. Found: 274.1202.

1-(3-Methoxyphenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]-octane-4,8-dione (6). Reaction of **1** (170 mg, 1.0 mmol) and 3-methoxystyrene (268 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **6** (177 mg, 64%) as a solid: mp 84-85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (1H, d, J = 7.7 Hz), 6.90 (1H, d, J = 7.7 Hz), 6.84-6.82 (2H, m), 3.78 (3H, s), 3.39 (1H, t, J = 9.4 Hz), 2.64 (1H, dd, J = 9.4, 4.7 Hz), 2.51 (1H, dd, J = 9.4, 4.7 Hz), 1.71 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 163.9, 159.9 133.1, 129.8, 122.4, 115.5, 114.5, 105.3, 55.7, 44.9, 33.5, 28.3, 28.1, 23.4; IR (KBr) 2993, 1763, 1736, 1605, 1460, 1383, 1335, 1304, 1256, 1209, 1042, 970, 872, 831, 797 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{16}O_5$: 276.0998. Found: 276.0999.

1-(4-Acetoxyphenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]-octane-4,8-dione (7). Reaction of **1** (170 mg, 1.0 mmol) and 4-acetoxystyrene (324 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **7** (112 mg, 37%) as a solid: mp 174-175 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (2H, d, J = 8.6 Hz), 7.07 (2H, d, J = 8.6 Hz), 3.40 (1H, t, J = 9.4 Hz), 2.63 (1H, dd, J = 9.4, 4.7 Hz), 2.53 (1H, dd, J = 9.4, 4.7 Hz), 2.27 (3H, s), 1.72 (3H, s), 1.70 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 168.0, 163.9, 151.3, 131.0, 129.0, 122.0, 105.4, 44.2, 33.5, 28.4, 28.0, 23.6, 21.6; IR (KBr) 3097, 3003, 2951, 1759, 1736, 1607, 1516, 1443, 1393, 1383, 1370, 1339, 1300, 1221, 1196, 1171, 1055, 1020, 972, 910, 855, 833 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{16}O_6$: 304.0947. Found: 304.0945.

1-(3-Chlorophenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]-octane-4,8-dione (8). Reaction of **1** (170 mg, 1.0 mmol) and 3-chlorostyrene (277 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **8** (222 mg, 79%) as a solid: mp 156-157 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.18 (4H, m), 3.39 (1H, t, J = 9.4 Hz), 2.61 (1H, dd, J = 9.4, 4.7 Hz), 2.51 (1H, dd, J = 9.4, 4.7 Hz), 1.73 (3H, s), 1.72 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 163.9, 134.8, 133.7, 130.1, 130.0, 129.3, 128.1, 105.5, 43.5, 33.1, 28.5, 28.1, 23.6; IR (KBr) 3102, 2990, 1765, 1736, 1397, 1385, 1335, 1296, 1219, 1179, 1051, 1020, 970, 880, 785 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{13}ClO_4$: 280.0502. Found: 280.0503.

1-(4-Chlorophenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]-octane-4,8-dione (9). Reaction of **1** (170 mg, 1.0 mmol) and 4-chlorostyrene (277 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **9** (225 mg, 80%) as a solid: mp 157-158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (2H, d, J = 8.7 Hz), 7.25 (2H, d, J = 8.7 Hz), 3.39 (1H, t, J = 9.4 Hz), 2.61 (1H, dd, J = 9.4, 4.7 Hz), 2.53 (1H, dd, J = 9.4, 4.7 Hz), 1.72 (3H, s), 1.70 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 163.9, 135.1, 131.2, 130.1, 129.1, 105.5, 43.9, 33.3, 28.4, 28.0, 23.5; IR (KBr) 3110, 3002, 1765, 1736, 1501, 1399, 1385, 1329, 1302, 1217, 1179, 1088, 1047, 1017, 966, 880, 829, 789, 729 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_{13}ClO_4$: 280.0502. Found: 280.0499.

1-(3-Formylphenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]-octane-4,8-dione (10). Reaction of **1** (170 mg, 1.0 mmol) and 3-vinylbenzaldehyde (264 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **10** (96 mg, 35%) as a solid: mp 149-150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.0 (1H, s), 7.84-7.81 (2H, m), 7.61-7.49 (2H, m), 3.51 (1H, t, J = 9.4 Hz), 2.69 (1H, dd, J = 9.4, 4.7 Hz), 2.57 (1H, dd, J = 9.4, 4.7 Hz), 1.73 (3H, s), 1.71 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2, 167.8, 164.0, 136.8, 135.6, 133.1, 130.8, 130.5, 129.6, 105.6, 43.4, 33.0, 28.6, 28.0, 23.8; IR (KBr) 3098, 2992, 2795, 2712, 1763, 1734, 1698, 1586, 1454, 1399, 1385, 1333, 1296, 1208, 1161, 1051, 1020, 972, 889, 831, 802 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{14}O_4$: 274.0841. Found: 274.0844.

1,6,6-(Trimethyl-2-phenyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (11). Reaction of **1** (170 mg, 1.0 mmol) and *trans*-β-methystyrene (236 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **11** (109 mg, 42%) as a solid: mp 87-88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.25 (5H, m), 3.56 (1H, d, J = 9.9 Hz), 3.16-3.06 (1H, m), 1.71 (3H, s), 1.69 (3H, s), 1.62 (3H, d, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 165.1, 132.9, 129.7, 128.7, 128.6, 104.9, 50.4, 37.0, 36.6, 28.3, 28.1, 12.7; IR (KBr) 3065, 2938, 1761, 1734, 1464, 1397, 1385, 1306, 1225, 1140, 1032, 989, 930, 822, 762 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{16}O_4$: 260.1049. Found: 260.1046.

6,6-Dimethyl-1-naphthalen-1-yl-5,7-dioxaspiro[2.5]-octane-4,8-dione (12). Reaction of **1** (170 mg, 1.0 mmol) and 1-vinylnaphthalene (308 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **12** (190 mg, 64%) as a solid: mp 118-119 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (1H, d, J = 8.1 Hz), 7.88-7.80 (2H, m), 7.54-7.44 (4H, m) 4.11 (1H, t, J = 9.5 Hz), 2.80 (1H, dd, J = 9.5, 4.7 Hz), 2.62 (1H, dd, J = 9.5, 4.7 Hz), 1.71 (3H, s), 1.64 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 164.1, 134.0, 133.0, 129.7, 129.6, 128.5, 127.7, 127.1, 126.4, 125.6, 123.1, 105.5, 41.9, 32.2, 28.4, 28.2, 26.0; IR (KBr) 3065, 2938, 1761, 1734, 1464, 1397, 1385, 1306, 1225, 1140, 1032, 989, 930, 822, 762 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{16}O_4$: 296.1049. Found: 296.1053.

6,6-Dimethyl-1-naphthalen-2-yl-5,7-dioxaspiro[2.5]-octane-4,8-dione (13). Reaction of **1** (170 mg, 1.0 mmol) and 2-vinylnaphthalene (308 mg, 2.0 mmol) under $Rh_2(Opiv)_4$ (6 mg) afforded **13** (196 mg, 66%) as a solid: mp 141-142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.78 (4H, m, 5.53-7.45 (2H, m), 7.40 (1H, d, J = 8.7 Hz), 3.59 (1H, t, J = 9.5 Hz), 2.81 (1H, dd, J = 9.5, 4.7 Hz), 2.61 (1H, dd, J = 9.5, 4.7 Hz), 1.72 (3H, s), 1.71 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 164.0, 133.6, 133.3, 129.5, 129.0, 128.5, 128.1, 127.1, 126.9, 105.4, 45.3, 33.7, 28.4, 28.1, 23.6; IR (KBr) 2998, 1767, 1742, 1339, 1300, 1213, 1150, 1049, 1017, 965, 828, 745 cm^{-1}; HRMS m/z (M^+) calcd for $C_{18}H_{16}O_4$: 296.1049. Found: 296.1048.

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