

A New Type of Carbonylation of Styrenes Catalyzed by Pd(OAc)₂ Combined with Molybdovanadophosphate

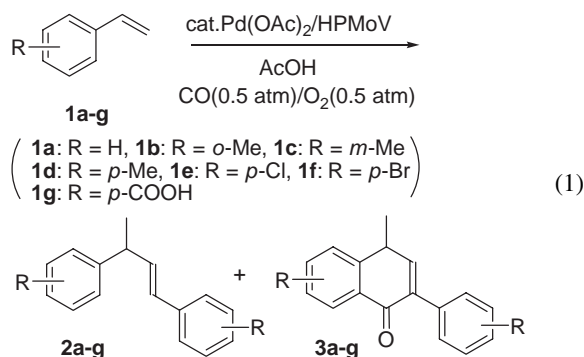
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A new type of carbonylation of styrenes was achieved under a 1:1 mixture of CO (0.5 atm) and O₂ (0.5 atm) in the presence of Pd(OAc)₂ combined with H₅PMo₁₀V₂O₄₀·*n*H₂O to give 4-methyl-2-phenylnaphthalen-1(4*H*)-one in 78% yield. Various substituted styrenes were also carbonylated to the corresponding substituted aryl-naphthalen-1(4*H*)-ones in moderate yields. The reaction was found to proceed in two stages involving the head-to-tail dimerization of styrenes, followed by carbonylation of the resulting dimers. Styrenes were efficiently dimerized under air (1 atm) in the absence of CO even at room temperature to produce head-to-tail dimers in good yields.

Palladium-catalyzed carbonylation of styrenes has been extensively investigated and reported to afford methyl cinnamate,¹ 2-phenylpropionate,² and dimethyl 2-phenylsuccinate.³ The same strategy has been extended to asymmetrical carboxylation and carbomethoxylation reactions.^{1,4} On the other hand, the dimerization of styrene leading to head-to-tail dimers is reported to be promoted by Pd complexes as well as several transition-metal complexes.⁵ We found that styrenes under a 1:1 mixture of CO and O₂ in the presence of Pd(OAc)₂ combined with H₅PMo₁₀V₂O₄₀·26H₂O (HPMoV) underwent selective dimerization–carbonylation to give the corresponding aryl-naphthalen-1(4*H*)-ones in fair to good yields. To our knowledge, this type of carbonylation of styrenes by a palladium catalyst has scarcely been studied, so far. In this paper, we report a new type of dimerization–carbonylation reaction of styrenes under a mixture of CO and O₂ catalyzed by Pd(OAc)₂ and HPMoV (Eq. 1).



In order to confirm the optimum reaction conditions of the present carbonylation, styrene (**1a**) was chosen as a model substrate and allowed to react under various reaction conditions. Table 1 shows the representative results for the carbonylation of **1a** under a mixture of CO and O₂ in the presence of catalytic amounts of Pd(OAc)₂ and H₅PMo₁₀V₂O₄₀·26H₂O (HPMoV).

The reaction of **1a** under a 1:1 mixture of CO (0.5 atm)/O₂

(0.5 atm) in the presence of Pd(OAc)₂ (0.1 mmol) and HPMoV (0.04 mmol) in acetic acid (5 mL) at 90 °C for 15 h (standard conditions) afforded *trans*-1,3-diphenyl-1-butene (**2a**) (7.5%) and 4-methyl-2-phenylnaphthalen-1(4*H*)-one (**3a**) (75%), which corresponds to a carbonylated product of dimer **2a** (Entry 1). It is interesting to note that the present reaction did not promote the carbonylation of the double bond of **1a** leading to cinnamic acid and 2-phenylpropionic acid which are usually obtained from carbonylation of **1a**.^{1–3} Although there have been numerous works on the carbonylation of **1a**, to our knowledge, the carbonylation of **1a** to **3a** has not yet been reported.

It was found that the yield of **3a** decreased with a decrease in the amount of HPMoV, whereas the amount of dimer **2a** increased (Entries 2 and 3). These results indicate that the quantity of the HPMoV catalyst is an important factor in promoting the carbonylation of the resulting dimer. When the quantity of the Pd(OAc)₂ catalyst was reduced to half and one-tenth, the yield of **3a** gradually decreased (Entries 4 and 5). Needless to say, no reaction took place in the absence of either HPMoV or Pd(OAc)₂ (Entries 6 and 7). To show the influence of the concentration of CO and O₂ on the present carbonylation, the reaction was carried out under varying CO and O₂ pressures. Under higher concentrations of either CO or O₂, the carbonylation of **1a** to **3a** was retarded, and the best result was obtained under a 1:1 mixture of CO and O₂ (Entries 8–11). The reaction of **1a** at 110 °C gave almost the same results as that of 90 °C, while the reaction at 70 °C resulted in a slight decrease in the yield of **3a** (Entries 12 and 13).

The carbonylation of several substituted styrenes was examined under several reaction conditions (Table 2). *o*-, *m*-, and *p*-Methyl styrenes, **1b**, **1c**, and **1d**, led to the corresponding methyl-substituted phenylnaphthalen-1(4*H*)-ones **3b**, **3c**, and **3d** in fair yields along with small amounts of dimers **2b** (3.6%), **2c** (3.4%), and **2d** (4.5%), respectively (Entries 2–4). Carbonylated products **3b** and **3d** were obtained as a single isomer from **1b** and **1d**, respectively, but a 92:8 regioisomeric mixture of **3c** and **3c'** was obtained from **1c**. However, car-

Table 1. Carbonylation of Styrene (**1a**) under CO and O₂ by Pd(OAc)₂ Combined with HPMoV^{a)}

Entry	Pd(OAc) ₂ /HPMoV (mmol)	CO/O ₂ (atm)	Temp /°C	Conv. /%	Yield/% ^{b)}	
					2a	3a
1	0.1/0.04	0.5/0.5	90	>99	7.5	75
2	0.1/0.02	0.5/0.5	90	>99	21	30
3	0.1/0.01	0.5/0.5	90	>99	42	10
4	0.05/0.04	0.5/0.5	90	>99	19	42
5	0.01/0.04	0.5/0.5	90	>99	1.6	37
6	0/0.04	0.5/0.5	90		no reaction	
7	0.1/0	0.5/0.5	90		no reaction	
8	0.1/0.04	0.3/0.7	90	>99	6.6	45
9	0.1/0.04	0.1/0.9	90	>99	11	32
10	0.1/0.04	0.7/0.3	90	>99	3.9	54
11	0.1/0.04	0.9/0.1	90	>99	32	9.5
12	0.1/0.04	0.5/0.5	110	>99	6.6	78(66)
13	0.1/0.04	0.5/0.5	70	>99	7.6	49

a) Styrene (**1a**) (2 mmol) was allowed to react in the presence of Pd(OAc)₂ and H₅PMoV₁₀V₂O₄₀·26H₂O (HPMoV) under CO and O₂ in AcOH (5 mL) at 70–110 °C for 15 h. b) GC yields. The number in parentheses shows isolated yield.

bonylated products were not obtained from *p*-chlorostyrene (**1e**), *p*-bromostyrene (**1f**), and *p*-vinylbenzoic acid (**1g**), because they easily polymerized under these conditions (Entries 5–7).

Since the present reaction was considered to proceed through the formation of dimer **2a**, the reaction of **1a** under the standard conditions (Entry 1 in Table 1) was followed by GC at suitable time intervals (Fig. 1).

The time-conversion curves for the reaction indicate that **2a** is quickly formed and then slowly carbonylated to **3a**. These results prompted us to carry out the carbonylation of styrene dimer **2a** under several conditions (Table 3).

The reaction of **2a** under standard conditions afforded **3a** in 53% yield at 99% conversion of **2a** (Entry 1). Under the present reaction conditions, a prolonged reaction resulted in the decomposition of **3a**. When the reaction time was shortened to 8 h, the yield of **3a** increased to 78% (Entry 2). Carbonylation at 65 °C for 15 h produced **3a** in 70% yield (Entry 3), but no carbonylation took place at room temperature (Entry 4). From the carbonylation under several varying CO and O₂ pressure, a 1:1 mixture of CO and O₂ was found to be best for the carbonylation of **2a** (Entries 5 and 6). The reaction with CO alone afforded **3a** in poor yield (Entry 7), probably because of the difficulty to regenerate of Pd^{II} from Pd⁰ in the absence of O₂. Removing either HPMoV or Pd(OAc)₂ from the catalytic system resulted in no or a trace amount of **3a** (Entries 8 and 9).

On the basis of these results, each step of carbonylation of styrenes, i.e., dimerization and carbonylation was examined in one-pot. The dimerization was carried out in the presence of Pd(OAc)₂ (0.1 mmol) and HPMoV (0.04 mmol) in acetic acid (5 mL) under air (1 atm) at 25–50 °C for 2–6 h, and then, the mixture was reacted under CO (0.5 atm) and O₂ (0.5 atm) at 70–90 °C for 15 h (Table 4).

Styrene **1a** and *o*-, *m*-, and *p*-methyl styrenes **1b**, **1c**, and **1d** smoothly dimerized by Pd(OAc)₂ combined with HPMoV under air even at room temperature to afford the corresponding styrene dimers, **2a**, **2b**, **2c**, and **2d**, in 96, 77, 74, and 67% yields, respectively (Entries 1–4). Substrates, **1e**–**1g** also dimerized to give dimers **2e**–**2g** in 88, 80, and 57% yields,

respectively (Entries 5–7). After completion of the dimerization, the air in the reaction system was replaced with a mixture of CO (0.5 atm) and O₂ (0.5 atm) and allowed to react under prescribed conditions. In the same manner as **2a**, all of the dimers, except for *p*-bromostyrene dimer **2f** and *p*-vinylbenzoic acid dimer **2g**, were carbonylated to give the corresponding products **3b**–**3e** in 45–78% yields (Entries 1–5). However, no carbonylation products were obtained from **2f** and **2g**, because of the formation of a complex mixture of polymerized products (Entries 6 and 7).

It is thought that the reaction proceeds through alkene coordination of the dimer **2** to Pd^{II}, followed by orthopalladation in the aryl group of **2**. Subsequent CO insertion and reductive elimination affords **3** and a Pd⁰ species, which is reoxidized with O₂ to Pd^{II} by the action of HPMoV.

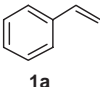
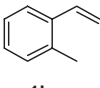
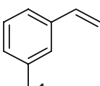
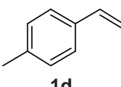
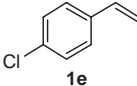
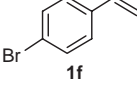
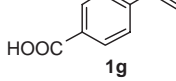
In conclusion, we found that the reaction of styrene derivatives under CO and O₂ in the presence of Pd(OAc)₂ and HPMoV afforded styrene dimers and their carbonylated products, phenylnaphthalen-1(4*H*)-ones, as the major products. The present reaction is thought to be a new type of the carbonylation of styrenes. In addition, it was found that styrenes efficiently dimerized in the Pd(OAc)₂/HPMoV catalytic system under air at room temperature to afford head-to-tail styrene dimers in high yields.

Experimental

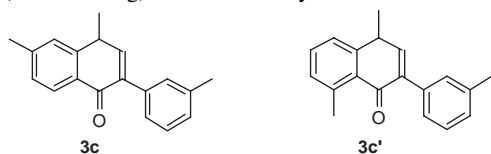
All solvents and reagents were purchased from commercial sources and used without further treatment. GC analysis was performed on a GC, equipped with a flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). Mass spectra were determined at ionization energy of 70 eV on a GCMS. ¹H and ¹³C NMR were measured at 400 and 100 MHz, respectively, in CDCl₃ with Me₄Si as an internal standard.

Typical Procedure for the Carbonylation of Styrene (1a). A solution of Pd(OAc)₂ (22 mg, 0.1 mmol), HPMoV (88 mg, 0.04 mmol), and styrene (**1a**) (208 mg, 2 mmol) in acetic acid (5 mL) was placed in a flask (30 mL). The flask was filled with a mixture of CO (0.5 atm) and O₂ (0.5 atm), and the reaction mixture was allowed to react while stirring at 90 °C for 15 h. The reaction was

Table 2. One-Step Carbonylation of Substituted Styrenes by Pd(OAc)₂ Combined with HPMoV^{a)}

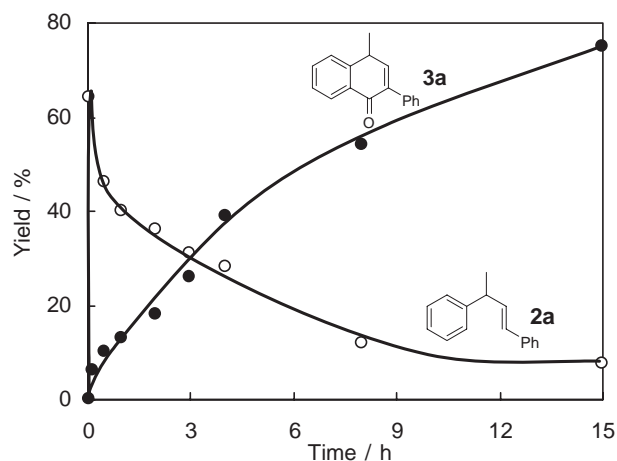
Entry	Substrate	Temp/°C	Time/h	Product	Yield/% ^{b)}
1		110	15	3a	78 (66)
2 ^{c)}		60	15	3b	48 (40)
3 ^{d),e)}		70	13	3c	68 (66)
4 ^{f)}		70	15	3d	57 (52)
5		80	15	3e	1
6		80	15	3f	n.d. ^{g)}
7		80	15	3g	n.d. ^{g)}

a) Styrenes **1a–1g** (2 mmol) were allowed to react in the presence of Pd(OAc)₂ (0.1 mmol) and HPMoV (0.04 mmol) under CO (0.5 atm)/O₂ (0.5 atm) in AcOH (5 mL). b) GC yields. The numbers in parentheses show isolated yields. c) Pd(OAc)₂ (0.2 mmol) was used. d) Pd(OAc)₂ (0.15 mmol) was used. e) A 92:8 mixture of **3c** and **3c'** was obtained. f) EtCO₂H (5 mL) was used. g) Not detected by GC.



quenched with acetone, and the solution was filtered. GC measurement of the liquid indicated that *trans*-1,3-diphenyl-1-butene (**2a**) (7.5%) and 4-methyl-2-phenylnaphthalen-1(4H)-one (**3a**) (75%) are formed as the major products. The conversions and yields of products were estimated from the peak areas based on the internal standard technique. The products were isolated by column chromatography (230–400 mesh silica gel, hexane:ethyl acetate = 10:1) and were characterized by ¹H, ¹³C NMR, GC-MS, and IR. Compounds **2a**,^{5b} **2b**,⁶ **2c**,⁷ **2d**,⁸ **2e**,^{5d} **2f**,^{5b} and **2g**^{5b} have been reported previously.

4-Methyl-2-phenyl-1(4H)-naphthalenone (3a): ¹H NMR (400 MHz, CDCl₃) δ 1.37 (d, *J* = 6.8 Hz, 3H), 4.35–4.40 (m, 1H), 7.34–7.44 (m, 4H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.58–7.65 (m, 4H), 7.87 (d, *J* = 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 18.8 (CH₃), 36.7 (CH), 124.2 (CH), 125.0 (CH), 127.7 (CH), 128.7 (CH), 129.3 (CH), 130.8 (CH), 133.8 (CH), 134.7 (CH), 134.8 (C), 136.7 (C), 140.7 (C), 155.9 (C), 194.1 (C); IR (neat, cm⁻¹) 570, 736, 765, 1631, 1697, 2968 cm⁻¹; GC-MS (EI, 70 eV) *m/z* 77, 91, 116, 128, 191, 219, 234 [M]⁺; HRMS (EI, 70 eV) *m/z*

Fig. 1. Time-conversion curves for carbonylation of styrene (**1a**) by Pd(OAc)₂/HPMoV under the same conditions as Entry 1 in Table 1.Table 3. Carbonylation of Styrene Dimer **2a** by Pd(OAc)₂ Combined with HPMoV^{a)}

Entry	CO/O ₂ (atm)	Temp/°C	Time/h	Conv./%	3a / % ^{b)}
1	0.5/0.5	90	15	99	53
2	0.5/0.5	90	8	92	78
3	0.5/0.5	65	15	88	70
4	0.5/0.5	25	15	no reaction	
5	0.3/0.7	65	15	87	64
6	0.7/0.3	65	15	91	77
7	1.0/0	65	15	28	1.8
8 ^{c)}	0.5/0.5	65	15	4	<1
9 ^{d)}	0.5/0.5	65	15	49	n.d. ^{e)}

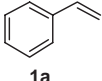
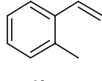
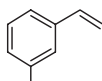
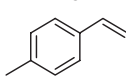
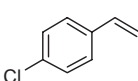
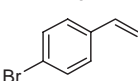
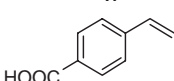
a) **2a** (1 mmol) was allowed to react in the presence of Pd(OAc)₂ (0.1 mmol) and HPMoV (0.04 mmol) under CO and O₂ in AcOH (5 mL). b) GC yields. c) The reaction was carried out in the presence of Pd(OAc)₂ (0.5 mmol) without HPMoV. d) The reaction was carried out in the presence of HPMoV (0.04 mmol) without Pd(OAc)₂. e) Not detected by GC.

calcd for C₁₇H₁₄O [M]⁺ 234.1045, found 234.1048.

4,5-Dimethyl-2-*o*-tolyl-1(4H)-naphthalenone (3b): ¹H NMR (400 MHz, CDCl₃) δ 1.21 (d, *J* = 7.1 Hz, 3H), 2.43 (s, 3H), 2.45 (s, 3H), 4.36–4.41 (m, 1H), 7.25–7.59 (m, 6H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 1.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.7 (CH₃), 18.2 (CH₃), 20.1 (CH₃), 35.7 (CH), 121.9 (CH), 126.0 (CH), 127.8 (CH), 128.4 (CH), 129.0 (CH), 130.5 (CH), 131.7 (CH), 134.3 (CH), 135.0 (C), 136.2 (C), 137.1 (C), 138.4 (C), 142.3 (C), 154.0 (C), 194.2 (C); IR (neat, cm⁻¹) 720, 752, 767, 1045, 1275, 1620, 1687, 2966, 3000 cm⁻¹; GC-MS (EI, 70 eV) *m/z* 77, 91, 116, 141, 229, 247, 262 [M]⁺; HRMS (EI, 70 eV) *m/z* calcd for C₁₉H₁₈O [M]⁺ 262.1358, found 262.1346.

4,6-Dimethyl-2-*m*-tolyl-1(4H)-naphthalenone (3c): ¹H NMR (400 MHz, CDCl₃) δ 1.21 (d, *J* = 6.7 Hz, 3H), 2.23 (s, 3H), 2.28 (s, 3H), 4.11–4.16 (m, 1H), 6.99–7.28 (m, 6H), 7.45 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 18.6 (CH₃), 19.1 (CH₃), 21.4 (CH₃), 36.3 (CH), 122.2 (CH), 127.7 (CH), 128.6 (CH), 129.4 (CH), 130.0 (CH), 131.6 (CH), 133.2 (CH), 134.0 (C), 134.2 (CH), 134.9 (C), 138.3 (C), 139.2 (C), 141.0 (C),

Table 4. Dimerization and Carbonylation of Substituted Styrenes by Pd(OAc)₂ Combined with HPMoV^{a)}

Entry	Substrate	Dimerization			Carbonylation		
		Temp/°C	Time/h	Yield/% ^{b)}	Temp/°C	Time/h	Yield/% ^{b)}
1	 1a	rt	2	2a (96)	80	15	3a (78)
2	 1b	50	3	2b (77)	90	15	3b (54)
3 ^{c)}	 1c	rt	6	2c (74)	70	15	3c (68)
4	 1d	rt	5	2d (67)	90	15	3d (56)
5	 1e	rt	2	2e (88)	90	15	3e (45)
6	 1f	rt	2	2f (80)	90	15	3f (n.d. ^{d)}
7 ^{e)}	 1g	rt	4	2g (57)	90	15	3g (n.d. ^{d)}

a) Styrenes **1a–1g** (2 mmol) were allowed to react in the presence of Pd(OAc)₂ (0.1 mmol) and HPMoV (0.04 mmol) under air (1 atm) in AcOH (5 mL) at 20–50 °C for 2–6 h, and then at 70–90 °C for 15 h after replacing air by CO (0.5 atm)/O₂ (0.5 atm). b) GC yields. c) A 92:8 mixture of **3c** and **3c'**. d) Not detected by GC. e) AcOH (2 mL) was used.

156.7 (C), 195.0 (C); IR (neat, cm⁻¹) 693, 787, 1113, 1324, 1609, 1628, 1696, 2925, 2965 cm⁻¹; GC-MS (EI) *m/z* 77, 91, 116, 141, 247, 262 [M]⁺; HRMS (EI, 70 eV) *m/z* calcd for C₁₉H₁₈O [M]⁺ 262.1358, found 262.1356.

4,8-Dimethyl-2-*m*-tolyl-1(4H)-naphthalenone (3c'): ¹H NMR (400 MHz, CDCl₃) δ 1.38 (d, *J* = 6.8 Hz, 3H), 2.40 (s, 3H), 2.74 (s, 3H), 4.32–4.37 (m, 1H), 7.13–7.48 (m, 7H), 7.56 (d, *J* = 1.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 18.6 (CH₃), 19.1 (CH₃), 21.4 (CH₃), 36.3 (CH), 122.2 (CH), 127.6 (CH), 128.3 (CH), 128.5 (CH), 129.4 (CH), 129.9 (CH), 131.6 (CH), 133.1 (CH), 134.0 (C), 134.9 (C), 138.3 (C), 139.2 (C), 141.0 (C), 156.6 (C), 195.0 (C); IR (neat, cm⁻¹) 702, 785, 1226, 1262, 1478, 1594, 1627, 1693, 2924, 2963 cm⁻¹; GC-MS (EI) *m/z* 77, 91, 116, 141, 247, 262 [M]⁺. HRMS (EI) *m/z* calcd for C₁₉H₁₈O [M]⁺ 262.1358, found 262.1359.

4,8-Dimethyl-2-*p*-tolyl-1(4H)-naphthalenone (3d): ¹H NMR (400 MHz, CDCl₃) δ 1.39 (d, *J* = 6.9 Hz, 3H), 2.40 (s, 3H), 2.44 (s, 3H), 4.32–4.40 (m, 1H), 7.24–7.56 (m, 6H), 7.62 (d, *J* = 1.6 Hz, 1H), 7.70 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 18.9 (CH₃), 21.1 (CH₃), 21.5 (CH₃), 36.4 (CH), 124.1 (CH), 124.7 (CH), 129.5 (CH), 131.0 (CH), 132.0 (C), 133.7 (CH), 136.0 (CH), 137.0 (C), 137.6 (C), 139.7 (C), 140.0 (C), 153.4 (C), 194.3 (C); IR (neat, cm⁻¹) 753, 1160, 1281, 1608, 1626, 1693, 2968 cm⁻¹; GC-MS (EI) *m/z* 77, 91, 116, 141, 247, 262 [M]⁺; HRMS (EI) *m/z* calcd for C₁₉H₁₈O [M]⁺ 262.1358, found 262.1361.

7-Chloro-2-(4-chlorophenyl)-4-methyl-1(4H)-naphthalene (3e): ¹H NMR (400 MHz, CDCl₃) δ 1.38 (d, *J* = 7.3 Hz, 3H),

4.33–4.38 (m, 1H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.48–7.61 (m, 5H), 7.84 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 18.7 (CH₃), 36.3 (CH), 124.1 (CH), 126.3 (CH), 129.1 (CH), 132.0 (CH), 132.9 (C), 133.2 (C), 134.2 (C), 134.9 (CH), 135.7 (CH), 138.2 (C), 140.8 (C), 153.7 (C), 192.6 (C); IR (neat, cm⁻¹) 593, 723, 825, 1093, 1254, 1491, 1589, 1622, 1693 cm⁻¹; GC-MS (EI) *m/z* 77, 91, 116, 141, 247, 262, 302 [M]⁺; HRMS (EI) *m/z* calcd for C₁₇H₁₂OCl₂ [M]⁺ 302.0265, found 302.0273. Anal. Found: C, 67.23; H, 3.98%. Calcd for C₁₇H₁₂Cl₂O: C, 67.35; H, 3.99%.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas “Advanced Molecular Transformations of Carbon Resources” from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and the “High-Tech Research Center” Project for Private Universities: matching fund subsidy from the Ministry of Education, Culture, Sports, Science and Technology, Japan, 2005–2009.

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