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Palladium catalyzed cyclocarbonylation of 3,3-diarylallyl acetates

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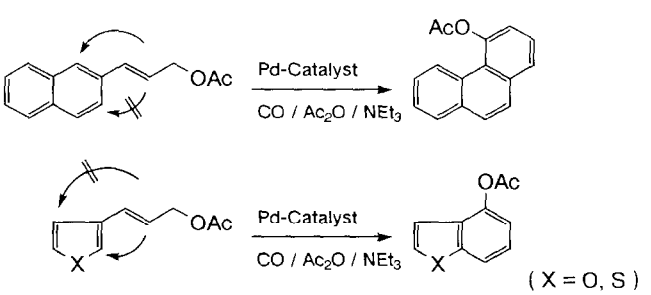
Abstract

Palladium-catalyzed cyclocarbonylation of 3,3-diarylallyl acetates afforded 4-aryl-substituted 1-naphthyl acetates where the cyclization occurred selectively on the more electron-rich ring.

Introduction

Transition metal catalyzed cyclocarbonylation is one of the most attractive tools for the synthesis of fused aromatic rings because it affords products having functional groups at specific positions. In the course of our study on the palladium complex catalyzed cyclocarbonylation of cinnamyl compounds [1], we noticed that the selectivity of our reaction was sometimes very similar to that of the benzannulation reaction of chromium-arylcarbene complexes with alkynes where alkenylketene complexes are assumed to be intermediates [2]. Thus, when 3-(2-naphthyl)-, 3-(3-furyl)-, and 3-(3-thienyl)allyl acetates were cyclocarbonylated by a palladium catalyst, 4-phenanthryl acetate, 7-acetoxybenzofuran, and 7-acetoxybenzothiophene, respectively, were obtained selectively (Scheme 1) in good yields, while when 2-naphthyl- and 3-furylcarbene-chromium complexes were allowed to react with



Scheme 1.

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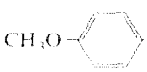
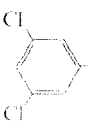
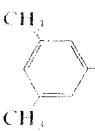
Table 1

Palladium catalyzed cyclocarbonylation of 3,3-diarylallyl acetates [a]

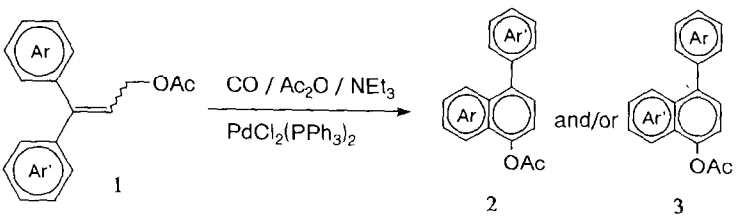
Entry	Substrate	Ar	Ar'	Reaction temp. (°C)	Isolated yield (%)	
					2	3
1	**1a**			160	72	
2	**1b**			160	84	
3	**1c**			160	56 [b]	33 [b]
4	**1d**			160	48 [b]	20 [b]
5				130	55 [b]	23 [b]
6				100	trace [b]	trace [b]
7	**1e**			160	41	0
8	**1f**			160	29	5
9	**1g**			160	39 [b]	39 [b]

[a] Reaction conditions: Substrate 5 mmol, $PdCl_2(PPh_3)_2$ 0.25 mmol, PPh_3 0.25 mmol, Ac_2O 10 mmol, NEt_3 11 mmol, benzene 5 mL, CO 55 kg/cm^2, at room temp., 160 °C, 6h. [b] Determined by GLC.

tolan, phenanthrene and benzofuran skeletons respectively were formed. These similarities between catalytic cyclocarbonylation and benzannulation suggest that the cyclization step of these reactions proceeds through a similar mechanism. On the other hand, Dötz reported that the benzannulation with tolan of some chromium diarylcarbene complexes having different aryl groups gave products formed by the cyclization at the more electron-deficient aryl groups [2b]. In order to obtain further information on the mechanism of the catalytic cyclocarbonylation, we have investigated the selectivity of the cyclocarbonylation of 3,3-diarylallyl acetates.

Results and discussion

3,3-Diphenylallyl acetate (**1a**) was cyclocarbonylated in the presence of CO, Ac_2O, NEt_3, and a catalytic amount of $PdCl_2(PPh_3)_2$ to give 4-phenyl-1-naphthyl acetate (**2a**) in good yield (Table 1, Entry 1). The reaction was much slower than that of cinnamyl acetate, and a reaction time of 5–6 h was necessary to bring the reaction to completion even in the presence of 5% Pd catalyst [3].

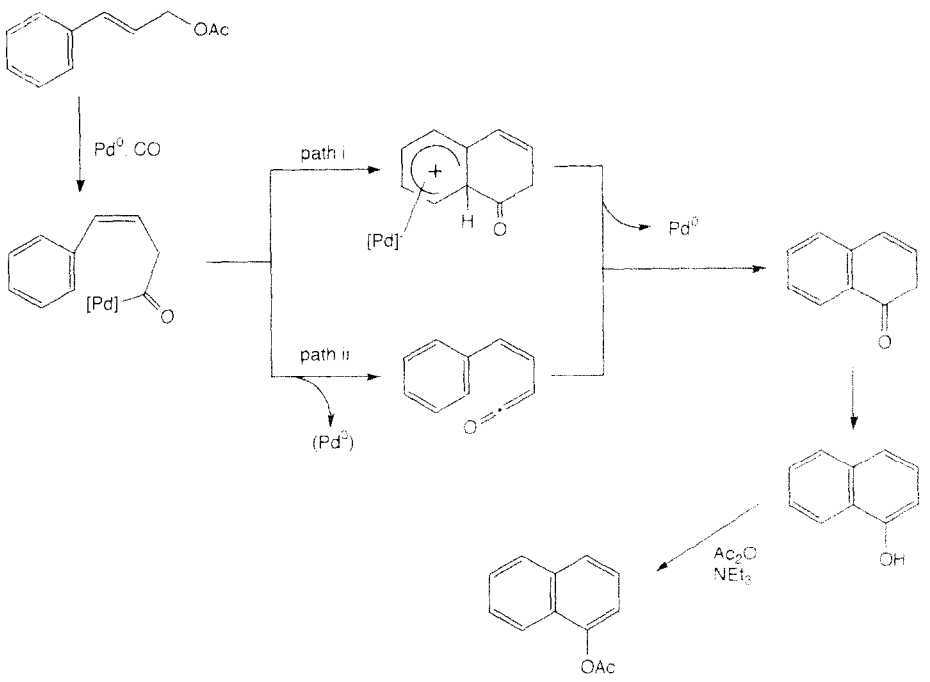


Scheme 2.

When an unsymmetrically disubstituted substrate was used, cyclization can *a priori* occur at two different positions (Scheme 2). In the case of 3-(2-furyl)-3-phenylallyl acetate (**1d**), annulation occurred both at the furan and the benzene ring to form 7-phenylbenzofuran and 4-(2-furyl)naphthalene skeletons, respectively (Entry 4), although benzofuran formation was somewhat favored. This selectivity was not affected when the reaction was carried out at a lower temperature (130 °C, Entry 5). Similar selectivity was also found in the cyclocarbonylation of 3-(4-methylphenyl)-3-(4-trifluoromethylphenyl)allyl acetate (**1c**), where the two aryl substituents have the same steric effect on the annulation (Entry 3).

Interestingly, the selectivity became stronger when allyl acetates substituted by a dichlorophenyl group (**1e** and **1f**) were employed (Entry 7, 8). Especially in the case of **1e**, the starting compound consisted of the pure *Z*-isomer, which has the acetoxymethyl moiety *cis* to the dichlorophenyl group around the C=C bond, but the only product obtained was **2e** formed from annulation on the tolyl group. Because the cyclocarbonylation of 3-(3,5-dimethylphenyl)-3-(4-methylphenyl)allyl acetate (**1g**) resulted in the formation of a 1 : 1 mixture of two isomeric products, **2g** and **3g** (Entry 9), the selectivities found for **1e** and **1f** are considered to arise not from the steric hindrance of the chloro groups but from their electronic effect. These results clearly show that cyclization occurs at the more electron-rich rings.

We have already proposed a reaction mechanism for cyclocarbonylation, which involves intramolecular cyclization of intermediary acylpalladium complexes such as (Z-ArCH=CHCH$_2$CO)Pd(OAc)(PPh$_3$)$_n$ or (Z-ArCH$_2$CH=CHCO)Pd(OAc)(PPh$_3$)$_n$ ($n = 1$, 2), to afford cyclic ketones (Scheme 3). The subsequent isomerization to naphthol and acetylation produce the final product. Two mechanisms are possible for the cyclization step. One involves the intramolecular electrophilic attack of the acyl group coordinated to palladium on the aromatic ring (path i). In the other mechanism, the cyclization proceeds via an alkenylketene intermediate formed by the β-elimination of the butenoyl-palladium complex (path ii). Involvement of alkenylketene intermediates has also been proposed for the benzannulation reaction (*vide supra*), where the intermediates are formed by the coupling of CO and alkenylcarbene ligands [2a]. The selectivity of the cyclocarbonylation demonstrated here is consistent with an electrophilic reaction on an aromatic ring. However, it is opposite to the selectivities reported for benzannulation (*vide supra*) [2]. On account of the difference in selectivity between both reactions, the mechanism including electrophilic attack of the acyl group (path i) seems to be much more favored, although involvement of the alkenylketene intermediates (path ii) cannot be completely ruled out because of the large difference in reaction temperatures, that is, 160 °C for the palladium catalyzed cyclocarbonylation and 50–70 °C for the benzannulation of arylcarbene complexes.



Scheme 3. Mechanism of palladium catalyzed cyclocarbonylation. [Pd] = $Pd(OAc)(PPh_3)_n$, $n = 1, 2$.

In conclusion, cyclocarbonylation has been shown to be effective for the synthesis of biaryl systems and its cyclization step has been proved to be an electrophilic reaction. Further studies of the reaction mechanism and application to the synthesis of natural products are currently under way.

Experimental

^1H and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions. $SiMe_4$ served as an internal standard. GLC analyses were performed with a flame ionization detector and a 25 m capillary column with He carrier. High resolution mass spectra were recorded with an electron impact mode (HREIMS). IR spectra were recorded as KBr disks unless otherwise noted.

$PdCl_2(PPh_3)_2$ was prepared by a published method [4]. Ac_2O, NEt_3, and all solvents were dried, and then distilled under nitrogen. The general procedure for the preparation of substrates was as described for **1b**. The substrates **1c**, **d**, **f**, and **g** were obtained as *E*/*Z* mixtures and employed in the catalytic reaction without separation. The *E*/*Z* configurations of **1c**–**f** were determined by ^1H–^1H 2D-NOESY NMR. That of **1g** was not determined.

*3,3-Diphenylallyl acetate (**1a**)*

Colorless oil after purification by silica gel column chromatography (EtOAc/hexane, 1 : 19). Obtained in 73% yield from benzophenone. ^1H NMR [5] δ 2.03 (s, 3H, $COCH_3$), 4.63 (d, $J = 7.0$ Hz, 2H, CH_2), 6.18 (t, $J = 7.0$ Hz, 1H, vinyl), 7.15–7.34 (m, 10H, Ar). ^{13}C NMR δ 20.8, 62.5, 122.3, 127.5, 127.6, 127.7, 128.1,

128.2, 129.5, 138.6, 141.4, 146.2, 170.5. HREIMS: Calc. for $C_{17}H_{16}O_2$: 252.1150. Found: 252.1174. IR (neat) 1744 cm^{-1} (C=O).

*3,3-Di(4-methylphenyl)allyl acetate (**1b**)*

A mixture of 4,4′-dimethylbenzophenone (50 mmol), ethyl bromoacetate (55 mmol), zinc (coarse powder, 55 mmol), $(MeO)_3B$ (20 mL), and THF (20 mL) was stirred for 16 h at room temperature. The mixture was then hydrolyzed with glycerin (20 mL) and aqueous NH_3 (28%, 20 mL), and was extracted with ether. The extract was washed (H_2O) and dried ($MgSO_4$), and the solvent was evaporated to give a β-hydroxy ester (9.3 g, 63%) as yellow blocks: IR (KBr) 1711 cm^{-1} (C=O), 3500 cm^{-1} (OH). A benzene solution (100 mL) of the ester (9.3 g) and *p*-toluenesulfonic acid (0.3 g) was boiled under reflux for 5 h to effect dehydration. The mixture was washed (10% $NaHCO_3$, H_2O) and evaporation of the solvent gave a crude unsaturated ester as a yellow oil (9.0 g): IR (neat) 1726 cm^{-1} (C=O), 1610 cm^{-1} (C=C). The crude ester (9.0 g) was stirred with diisobutylaluminium hydride (75 mmol) in toluene (100 mL) for 16 h at room temperature. The mixture was then treated with 1 *N* aq. HCl (100 mL) and was extracted with ether. Evaporation of the solvent and recyrstallization from hexane gave allylic alcohol as colorless blocks (5.64 g). The alcohol (10 mmol) was stirred with Ac_2O (12 mmol), NEt_3 (15 mmol), DMAP (20 mg), and ether (20 mL) for 36 h at room temperature. The mixture was then diluted with ether, and was washed (diluted aq. HCl, 10% aq. $NaHCO_3$, and water), and dried ($MgSO_4$). Evaporation of the solvent gave a white powder (2.6 g, 93%). Recrystallization from hexane gave pure **1b** as colorless blocks. M.p. 85–87 °C. ^1H NMR δ 2.06 (s, 3H, $COCH_3$), 2.32 (s, 3H, Ar–CH_3), 2.37 (s, 3H, Ar–CH_3), 4.63 (d, J = 7.0 Hz, 2H, CH_2), 6.11 (t, J = 7.0 Hz, 1H, vinyl), 7.04–7.21 (m, 8H, Ar). ^{13}C NMR δ 21.0, 21.1, 21.2, 62.8, 121.1, 127.6, 128.8, 128.9, 129.6, 135.8, 137.4, 137.6, 138.9, 146.2, 170.8. HREIMS: Calc. for $C_{19}H_{20}O_2$: 280.1463. Found: 280.1472. IR 1744 cm^{-1} (C=O).

*3-(4-Methylphenyl)-3-(4-trifluoromethylphenyl)allyl acetate (**1c**, E/Z = 36 : 64)*

Pale yellow solid after purification by silica gel column chromatography (EtOAc/hexane, 1 : 14). Obtained in 69% yield from 4-methylphenyl 4-trifluoromethylphenyl ketone. *E*-isomer; ^1H NMR δ 2.07 (s, 3H, $COCH_3$), 2.38 (s, 3H, Ar–CH_3), 4.67 (d, J = 6.9 Hz, 2H, CH_2), 6.20 (t, J = 6.9 Hz, 1H, vinyl), 7.05 (d, J = 7.9 Hz, 2H, Ar), 7.20 (d, J = 7.9 Hz, 2H, Ar), 7.36 (d, J = 7.9 Hz, 2H, Ar), 7.52 (d, J = 7.9 Hz, 2H, Ar). *Z*-isomer; ^1H NMR δ 2.06 (s, 3H, $COCH_3$), 2.33 (s, 3H, Ar–CH_3), 4.59 (d, J = 7.1 Hz, 2H, CH_2), 6.23 (t, J = 7.1 Hz, 1H, vinyl), 7.11 (s, 4H, Ar), 7.31 (d, J = 7.9 Hz, 2H, Ar), 7.64 (d, J = 7.9 Hz, 2H, Ar).

*3-(2-Furyl)-3-phenylallyl acetate (**1d**, E/Z = 91 : 9)*

Colorless oil after purification by silica gel column chromatography (EtOAc/hexane, 1 : 9). Obtained in 49% yield from 2-furyl phenyl ketone. *E*-isomer; ^1H NMR δ 2.03 (s, 3H, $COCH_3$), 4.58 (d, J = 7.3 Hz, 2H, CH_2), 5.91 (d, J = 3.4 Hz, 1H, furyl), 6.31 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 6.37 (t, J = 7.3 Hz, 1H, vinyl), 7.24–7.28 and 7.33–7.48 (m, 6H, Ph and furyl). *Z*-isomer; ^1H NMR δ 2.09 (s, 3H, $COCH_3$), 5.10 (d, J = 6.1 Hz, 2H, CH_2), 5.78 (t, J = 6.1 Hz, 1H, vinyl), 6.24 (d, J = 3.4 Hz, 1H, furyl), 6.41 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 7.24–7.28 and 7.33–7.48 (m, 6H, Ph and furyl).

*(Z)-3-(3,5-Dichlorophenyl)-3-(4-methylphenyl)allyl acetate (**1e**)*

Obtained in 39% yield from 3,5-dichlorophenyl 4-methylphenyl ketone. Purified by silica gel column chromatography (ether/hexane, 1 : 9). Colorless blocks from hexane. M.p. 64–65 °C. ^{1}H NMR δ 2.08 (s, 3H, $COCH_3$), 2.34 (s, 3H, Ar–CH_3), 4.58 (d, J = 7.0Hz, 2H, CH_2), 6.18 (t, J = 7.0 Hz, 1H, vinyl), 7.09 (d, J = 1.8 Hz, 2H, Ar), 7.10–7.11 (m, 4H, Ar), 7.35 (d, J = 1.8 Hz, 2H, Ar). ^{13}C NMR δ 20.9, 21.1, 62.1, 122.9, 127.4, 128.0, 128.0, 129.2, 135.0, 137.3, 138.4, 141.8, 143.9, 170.8. HREIMS: Calc. for $C_{18}H_{16}O_2Cl_2$: 334.0528. Found: 334.0495. IR 1744 cm^{-1} (C=O).

*3-(3,5-Dichlorophenyl)-3-(4-methoxyphenyl)allyl acetate (**1f**, E/Z = 36 : 64)*

Colorless oil after purification by silica gel column chromatography (EtOAc/hexane, 1 : 7). Obtained in 78% yield from 3,5-dichlorophenyl 4-methoxyphenyl ketone. *Z*-isomer ^{1}H NMR δ 2.08 (S, 3H, $COCH_3$), 3.81 (s, 3H, OCH_3), 4.56 (d, J = 7.0 Hz, 2H, CH_2), 6.14 (t, J = 7.0 Hz, 1H vinyl), 6.84 (d, J = 9.2 Hz, 2H, Ar), 7.09 (d, J = 1.9 Hz, 2H, Ar), 7.14 (d, J = 9.2 Hz, 2H, Ar), 7.38 (t, J = 1.9 Hz, 1H, Ar). *E*-isomer ^{1}H NMR δ 2.05 (s, 3H, $COCH_3$), 3.85 (s, 3H, OCH_3), 4.65 (d, J = 7.0 Hz, 2H, CH_2), 6.11 (t, J = 7.0 Hz, 1H, vinyl), 6.93 (d, J = 8.9 Hz, 2H, Ar), 7.07 (d, J = 8.9 Hz, 2H, Ar), 7.13 (d, J = 1.8 Hz, 2H, Ar), 7.26 (t, J = 1.8 Hz, 1H, Ar).

*3-(3,5-Dimethylphenyl)-3-(4-methylphenyl)allyl acetate (**1g**, E/Z or Z/E = 53 : 47)*

Colorless oil after purification by silica gel column chromatography (EtOAc/hexane, 1 : 24). Obtained in 65% yield from 3,5-dimethylphenyl 4-methylphenyl ketone. ^{1}H NMR δ 2.05 (s, 6H, $COCH_3$), 2.25 (s, 6H, *m*-CH_3), 2.29 (s, 6H, *m*-CH_3), 2.32 (s, 3H, *p'*-CH_3), 2.37 (s, 3H, *p'*-CH_3), 4.62 (d, J = 7.0 Hz, 2H, CH_2), 4.63 (d, J = 7.0 Hz, 2H, CH_2), 6.100 (t, J = 7.0 Hz, 1H, vinyl), 6.104 (t, J = 7.0 Hz, 1H, vinyl), 6.78 (s, 2H, *o*-H), 6.87 (s, 2H, *o*-H), 6.90 (s, 1H, *p*-H), 6.95 (s, 1H, *p*-H), 7.06 (d, J = 7.9 Hz, 2H, Ar), 7.07 (d, J = 7.9 Hz, 2H, Ar), 7.15 (d, J = 7.9 Hz, 2H, Ar), 7.17 (d, J = 7.9 Hz, 2H, Ar).

Palladium catalyzed cyclocarbonylation of 3,3-diarylallyl acetates

The following procedure is representative. A mixture of **1a** (5 mmol), $PdCl_2(PPh_3)_2$ (0.25 mmol), Ac_2O (10 mmol), NEt_3 (11 mmol), and benzene (4 mL) in a stainless steel autoclave was pressurized with CO (55 kg/cm^2 at room temperature) and was heated at 160 °C for 6 h with stirring. Then the autoclave was cooled and CO was discharged. The mixture was diluted with ether, washed (dilute aq. HCl, saturated aq. $NaHCO_3$, and water), and dried ($MgSO_4$). Solvent was evaporated and crude product was purified by silica gel column chromatography (EtOAc/hexane, 1 : 19) and recrystallization (hexane) to give 4-phenyl-1-naphthyl acetate (**2a**) as pale orange blocks. M.p. 69–70 °C. ^{1}H NMR δ 2.41 (s, 3H, $COCH_3$), 7.29 (d, J = 7.6 Hz, 1H, Ar), 7.37 (d, J = 7.6 Hz, 1H, Ar), 7.39–7.52 (m, 6H, Ar), 7.80 (d, J = 8.4 Hz, 1H, Ar), 7.97 (d, J = 8.4 Hz, 1H, Ar). ^{13}C NMR δ 21.0, 117.6, 121.3, 126.3, 126.4, 126.48, 126.50, 126.9, 127.4, 128.3, 130.1, 132.8, 138.5, 140.2, 146.1, 169.5 HREIMS: Calc. for $C_{18}H_{14}O_2$: 262.0994. Found: 262.1024. IR 1759 cm^{-1} (C=O).

*7-Methyl-4-(4-methylphenyl)-1-naphthyl acetate (**2b**)*

Pale orange blocks after purification by silica gel column chromatography ($ClCH_2CH_2Cl$/hexane, 3 : 7) and recrystallization from hexane. M.p. 107–109 °C.

^{1}H NMR δ 2.44 (s, 3H, Ar–CH_3), 2.49 (s, 3H, $COCH_3$), 2.51 (s, 3H, Ar–CH_3), 7.23 (d, J = 7.6 Hz, 1H, Ar), 7.27 (d, J = 8.5 Hz, 1H, Ar), 7.28 (d, J = 8.0 Hz, 2H, Ar), 7.31 (d, J = 7.6 Hz, 1H, Ar), 7.36 (d, J = 8.0 Hz, 2H, Ar), 7.65 (s, 1H, Ar), 7.81 (d, J = 8.5 Hz, 1H, Ar). ^{13}C NMR δ 21.0, 21.2, 21.8, 117.7, 120.1, 125.4, 126.5, 127.1, 128.7, 128.9, 130.0, 131.2, 136.1, 136.9, 137.4, 138.3, 145.4, 169.7. HREIMS: Calc. for $C_{20}H_{18}O_2$: 290.1307. Found: 290.1290. IR 1755 cm^{-1} (C=O).

*7-Methyl-4-(4-trifluoromethylphenyl)-1-naphthyl acetate (**2c**)*

Separated from **3c** by silica gel column chromatography (EtOAc/benzene/hexane, 2 : 5 : 30). Colorless needles from hexane. M.p. 96–97°C. ^{1}H NMR δ 2.50 (s, 3H, $COCH_3$), 2.52 (s, 3H, Ar–CH_3), 7.26 (d, J = 7.6 Hz, 1H, Ar), 7.30 (d, J = 8.5 Hz, 1H, Ar), 7.31 (d, J = 7.6 Hz, 1H, Ar), 7.57 (d, J = 7.9 Hz, 2H, Ar), 7.69 (s, 1H, Ar), 7.69 (d, J = 8.5 Hz, 1H, Ar), 7.73 (d, J = 7.9 Hz, 2H, Ar). HREIMS: Calc. for $C_{20}H_{15}O_2F_3$: 344.1024. Found: 344.1021. IR 1756 cm^{-1} (C=O).

*4-(4-Methylphenyl)-7-trifluoromethyl-1-naphthyl acetate (**3c**)*

Colorless needles from hexane. M.p. 120–122°C. ^{1}H NMR δ 2.45 (s, 3H, Ar–CH_3), 2.51 (s, 3H, $COCH_3$), 7.31 (d, J = 8.4 Hz, 2H, Ar), 7.33 (d, J = 8.4 Hz, 2H, Ar), 7.39 (d, J = 7.9 Hz, 1H, Ar), 7.52 (d, J = 7.9 Hz, 1H, Ar), 7.60 (d, J = 9.1 Hz, 1H, Ar), 8.03 (d, J = 9.1 Hz, 1H, Ar), 8.24 (s, 1H, Ar). HREIMS: Calc. for $C_{20}H_{15}O_2F_3$: 344.1024. Found: 344.1011. IR 1757 cm^{-1} (C=O).

*4-Acetoxy-7-phenylbenzofuran (**2d**)*

Separated from **3d** by silica gel column chromatography (ether/hexane, 1 : 6). Pale brown blocks from benzene–hexane. M.p. 52–54°C. ^{1}H NMR δ 2.41 (s, 3H, $COCH_3$), 6.74 (d, J = 2.3 Hz, 1H, furyl), 7.09 (d, J = 7.09 Hz, 1H, Ar), 7.39 (t, J = 8.0 Hz, 1H, Ar), 7.44 (d, J = 7.9 Hz, 1H, Ar), 7.49 (t, J = 8.0 Hz, 2H, Ar), 7.66 (d, J = 2.3 Hz, 1H, furyl), 7.81 (d, J = 8.0 Hz, 2H, Ar). ^{13}C NMR δ 21.0, 104.0, 115.8, 121.6, 123.8, 124.1, 127.7, 128.58, 128.61, 135.9, 143.0, 145.1, 153.2, 169.0. HREIMS: Calc. for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0763. IR 1756 cm^{-1} (C=O).

*4-(2-Furyl)-1-naphthyl acetate (**3d**)*

Pale brown blocks from benzene–hexane. M.p. 86–89°C. ^{1}H NMR δ 2.48 (s, 3H, $COCH_3$), 6.58 (dd, J = 1.8, 3.4 Hz, 1H, furyl), 6.69 (dd, J = 0.6, 3.4 Hz, 1H, furyl), 7.29 (d, J = 7.9 Hz, Ar), 7.53–7.58 (m, 2H, Ar), 7.62 (dd, J = 0.6, 1.8 Hz, 1H, furyl), 7.70 (d, J = 7.9 Hz, 1H, Ar), 7.92–7.94 (m, 1H, Ar), 8.39–8.41 (m, 1H, Ar). ^{13}C NMR δ 21.0, 109.4, 111.4, 117.7, 121.5, 125.9, 126.0, 126.5, 127.00, 127.04, 127.1, 131.7, 142.5, 146.6, 152.9, 169.3. HREIMS: Calc. for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0779. IR 1755 cm^{-1} (C=O).

*4-(3,5-Dichlorophenyl)-7-methyl-1-naphthyl acetate (**2e**)*

Purified by silica gel column chromatography (ether/hexane, 1 : 7). Colorless needles from hexane. M.p. 159–161°C. ^{1}H NMR δ 2.51 (s, 3H, $COCH_3$), 2.54 (s, 3H, Ar–CH_3), 7.25 (d, J = 7.5 Hz, 1H, Ar), 7.30 (d, J = 7.5 Hz, 1H, Ar), 7.33 (d, J = 8.6 Hz, 1H, Ar), 7.36 (d, J = 2.1 Hz, 2H, Ar), 7.43 (t, J = 2.1 Hz, 1H, Ar), 7.68 (s, 1H, Ar), 7.70 (d, J = 8.6 Hz, 1H, Ar). ^{13}C NMR δ 21.1, 21.9, 117.7, 120.5, 125.62, 125.64, 127.2, 127.5, 128.5, 129.4, 130.6, 134.8, 135.4, 136.6, 143.4, 146.4, 169.5. HREIMS: Calc. for $C_{18}H_{14}O_2Cl_2$: 344.0371. Found: 344.0325. IR 1748 cm^{-1} (C=O).

*4-(3,5-Dichlorophenyl)-7-methoxy-1-naphthyl acetate (**2f**)*

Separated from **3f** by silica gel column chromatography (ether/hexane, 1 : 4). Pale yellow needles from hexane. M.p. 163–165 °C. ^{1}H NMR δ 2.49 (s, 3H, $COCH_3$), 3.92 (s, 3H, OCH_3), 7.14–7.17 (m, 2H, Ar), 7.20 (d, J = 7.8 Hz, 1H, Ar), 7.25 (d, J = 7.8 Hz, 1H, Ar), 7.34 (d, J = 1.8 Hz, 2H, Ar), 7.41 (t, J = 1.8 Hz, 1H, Ar), 7.70 (d, J = 8.9 Hz, 1H, Ar). ^{13}C NMR δ 21.1, 55.3, 100.0, 118.2, 119.5, 124.2, 127.46, 127.49, 127.8, 128.3, 128.5, 134.8, 135.4, 143.3, 145.8, 158.2, 169.3. HREIMS: Calc. for $C_{19}H_{14}O_3Cl_2$: 360.0320. Found: 360.0298. IR 1753 cm^{-1} (C=O).

*6,8-Dichloro-4-(4-methoxyphenyl)-1-naphthyl acetate (**3f**)*

Pale yellow needles from hexane. M.p. 131–135 °C. ^{1}H NMR δ 2.44 (s, 3H, $COCH_3$), 3.89 (s, 3H, OCH_3), 7.03 (d, J = 8.4 Hz, 2H, Ar), 7.21 (d, J = 7.8 Hz, 1H, Ar), 7.31 (d, J = 8.4 Hz 2H, Ar), 7.43 (d, J = 7.8 Hz, 1H, Ar), 7.55 (d, J = 2.1 Hz, 1H, Ar), 7.79 (d, J = 2.1 Hz, 1H, Ar). ^{13}C NMR δ 21.7, 55.4, 114.1, 121.3, 125.3, 128.6, 129.4, 129.9, 130.6, 131.1, 131.3, 131.8, 135.7, 138.7, 145.1, 159.4, 170.2. HREIMS: Calc. for $C_{19}H_{14}O_3Cl_2$: 360.0320. Found: 360.0313. IR 1750 cm^{-1} (C=O).

*4-(3,5-Dimethylphenyl)-7-methyl-1-naphthyl acetate (**2g**)*

Purification of a reaction mixture by silica gel column chromatography (ether/hexane, 1 : 19) gave a colorless oil which was a mixture with **3g**. ^{1}H NMR δ 2.39 (s, 6H, *m*-CH_3), 2.49 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 7.06–7.08 (m, 3H, Ar), 7.21–7.33 (m, 3H, Ar), 7.65 (s, 1H, Ar), 7.81 (d, J = 8.5 Hz, 1H, Ar).

*6,8-Dimethyl-4-(4-methylphenyl)-1-naphthyl acetate (**3g**)*

Recrystallization of a mixture with **2g** from hexane gave pure **3g** as colorless blocks. M.p. 118–120 °C. ^{1}H NMR δ 2.34 (s, 3H, Ar–CH_3), 2.42 (s, 3H, $COCH_3$), 2.45 (s, 3H, Ar–CH_3), 2.78 (s, 3H, Ar–CH_3), 7.07 (d, J = 7.9 Hz, 1H, Ar), 7.11 (br s, 1H, Ar), 7.27–7.34 (m, 5H, Ar), 7.49 (br s, 1H, Ar). ^{13}C NMR δ 21.2, 21.5, 21.7, 23.8, 118.5, 124.2, 124.8, 126.5, 128.9, 130.0, 131.8, 132.3, 134.7, 135.4, 136.8, 138.2, 138.6, 146.8, 170.1. HREIMS: Calc. for $C_{21}H_{20}O_2$: 304.1464. Found: 304.1469. IR 1754 cm^{-1} (C=O).

References and notes

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3 Cinnamyl acetate was cyclocarbonylated to 1-naphthyl acetate under similar conditions as indicated for Table 1 in 81% yield (reaction time 1.5 h; see ref. 1(b)). Judging from the CO absorption, this reaction was completed within 0.5 h.

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