Synthesis of 2,4-Bis(aryloxy)-1,5-diarylpentane-1,5-diones by Base-Mediated Tandem Reaction

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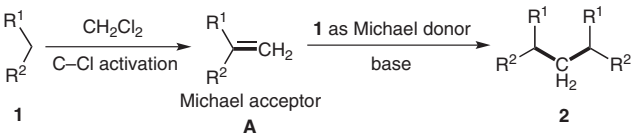
Abstract: A new, practical, base-mediated method has been developed for the synthesis of 2,4-bis(aryloxy)-1,5-diarylpentane-1,5-diones by a tandem α-methylenation–Michael reaction through activation of two C–Cl bonds. This method permits the use of dichloromethane instead of dibromomethane as a source of one carbon atom for the α-methylenation reaction. The products are useful in syntheses of polysubstituted pyridines and methylenebisbenzofurans.

Key words: tandem reactions, ketones, Michael additions

α-Methylene ketones are important units in numerous biologically active natural products, such as parthenolides, helenalin, and (+)-sclareolide.[1] They are also valuable as intermediates in organic synthesis.[1f,2–4] Consequently, the α-methylenation of ketones is an important transformation in organic synthesis.[1,2] Generally, α-methylene ketones are prepared by formation of the corresponding Mannich bases from ketone derivatives with subsequent deamination.[1f,2,3] However, in many cases it is not possible to perform both the Mannich reaction and the deamination in a single flask.[1f,2] Moreover, these transformations require excess amounts of both dibromomethane (10–25 equiv) and the secondary amine base (2–10 equiv), resulting in waste and pollution, and limiting their usefulness in organic synthesis. Although dichloromethane is less expensive and is usually employed as a medium for these reactions, no examples have been reported in which it replaces dibromomethane as a reactant. This is because the simultaneous activation of the two C–Cl bonds in dichloromethane is very difficult to achieve and the development of new approaches for the activation of C–Cl bonds presents a challenge.[5] After a serial of trials, we identified a novel base-mediated tandem method for the synthesis of 2,4-bis(aryloxy)-1,5-diarylpentane-1,5-diones through activation of the C–Cl bonds of dichloromethane. Intermediate **A** (Scheme 1) is generated by α-methylenation of ketone **1** by using dichloromethane as the methylene precursor. Intermediate **A** then undergoes Michael addition with a second molecule of ketone **1** to give the bis-1,5-diketone **2** (Scheme 1).[5] Bis-1,5-diketones[6] play an important role in the chemical and pharmaceutical industries because these compounds are important synthetic units for constructing complicated heterocyclic compounds such as bisbenzofurans[7] or dioxepines.[8]



Scheme 1 The base-mediated tandem method

We chose the reaction of 2-phenoxy-1-phenylethanone (**1a**) with dichloromethane as a model reaction to study the optimal conditions for the reaction, and our results are summarized in Table 1. To our delight, treatment of substrate **1a** with dichloromethane and cesium carbonate afforded the desired product **2a** in quantitative yield (Table 1, entry 1). Screening revealed that the amount of cesium carbonate affected the reaction. When 1.0 or 0.2 equivalents of cesium carbonate were used, the yield of **2a** fell to 48% and 18%, respectively (entries 2 and 3). The temperature also had a marked effect on the reaction. Whereas product **2a** was obtained in quantitative yield at 80 °C, the yield fell to 16% at 50 °C (entry 4), and no reaction occurred at room temperature (entry 5). We then examined a series of other bases (cesium hydroxide, potassium *tert*-butoxide, potassium carbonate, sodium ethoxide, potassium hydrogen carbonate, diethylamine, and triethylamine) (entries 6–12), all of which were less effective than cesium carbonate. It is noteworthy that unsatisfactory results were observed with the efficient Mannich bases diethylamine and triethylamine (entries 11 and 12).[2a] The optimal reaction conditions were also shown to be suitable when the reaction was scaled up to 2.0 mmol of substrate **1a** (entry 13).

Having identified the optimal conditions, we explored the scope of the tandem reaction (Table 2).[9] We treated a variety of 2-aryloxy-1-arylethanones **1b**–**n** with dichloromethane in the presence of cesium carbonate, and we obtained the corresponding products **2b**–**n** smoothly in moderate-to-excellent yields (entries 1–13). Initially, we

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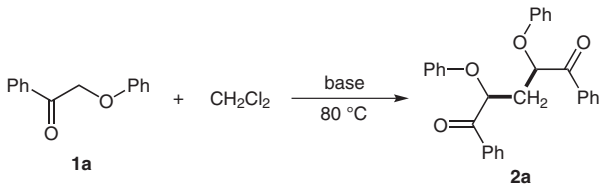
Table 1 Screening of Optimal Conditions for the Tandem Reaction

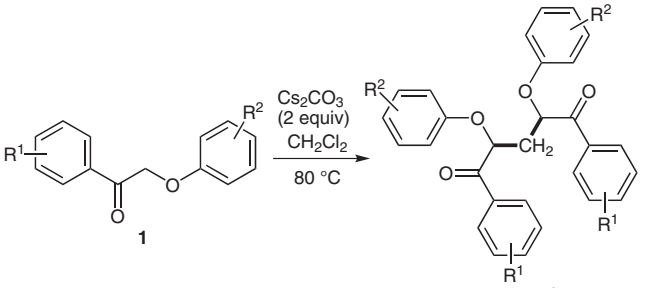


Entry[a]	Base (equiv)	Temp (°C)	Yield[b] (%)
1	Cs_2CO_3 (2)	80	quant
2	Cs_2CO_3 (1)	80	48
3	Cs_2CO_3 (0.2)	80	18
4	Cs_2CO_3 (2)	50	16
5	Cs_2CO_3 (2)	r.t.	0
6	CsOH (2)	80	40
7	*t*-BuOK (2)	80	23
8	K_2CO_3 (2)	80	10
9	NaOEt (2)	80	0
10	$KHCO_3$ (2)	80	0
11	Et_2NH (2)	80	5
12	Et_3N (2)	80	trace
13[c]	Cs_2CO_3 (2)	80	88

[a] Reaction conditions: **1a** (0.2 mmol), base, CH_2Cl_2 (1 mL), 16 h.
[b] Isolated yield.
[c] **1a** (2 mmol) and CH_2Cl_2 (2 mL)

examined the effects of substituents on the aryl ring of the 2-aryloxy moiety (entries 1–5). Several functional groups, including methyl, methoxy, chloro, and fluoro groups were well tolerated under the optimized conditions; for example, the chloro-substituted substrate **1d** reacted successfully with dichloromethane and cesium carbonate to give the desired product **2d** in 80% yield (entry 3). 1-(1-Naphthyl)-2-phenoxyethanone (**1f**) was also found to be a suitable substrate for the reaction under the optimized conditions (entry 5). We then examined a number of substrates **1g–l** bearing methyl, methoxy, or chloro substituents on the aryl ring of the 1-arylethanone moiety, and these were also found to be suitable substrates for the reaction with dichloromethane and cesium carbonate (entries 6–11). Moreover, good yields were achieved with the sterically hindered substrates **1h** and **1k** (entries 7 and 9). For example, the 2-methoxylated substrate **1k** reacted with dichloromethane and cesium carbonate smoothly to give the expected product **3k** in 90% yield (entry 10). Interestingly, 2-(4-methoxyphenoxy)-1-phenylprop-2-en-1-one (**3i**) was obtained as a byproduct in 7% yield from the reaction of substrate **1i** with dichloromethane (entry 8); this provides supporting evidence for the formation of intermediate **A** (Scheme 1). 2-(1-Naphthyloxy)-1-phenylethanone (**1m**) also reacted successful to give the corresponding product in 78% yield (entry 12). Furthermore, the heterocyclic substrate 2-phenoxy-1-(quinolin-8-yl)ethanone (**1n**) also reacted with dichloromethane and cesium carbonate to form the expected product **2n** in 50% yield (entry 13). With 1-methoxypropan-2-one (**14**), however, almost no reaction took place (entry 14).

Table 2 Cesium Carbonate Mediated Synthesis of 2,4-Bis(aryloxy)-1,5-diarylpentane-1,5-diones **2**



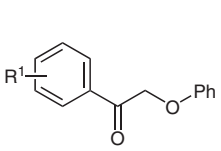
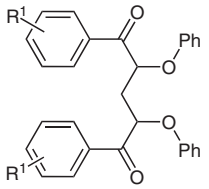
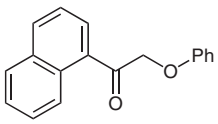
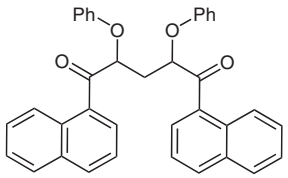
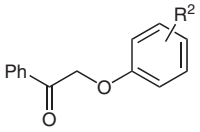
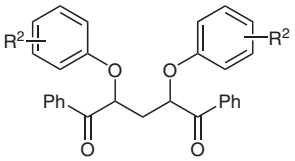
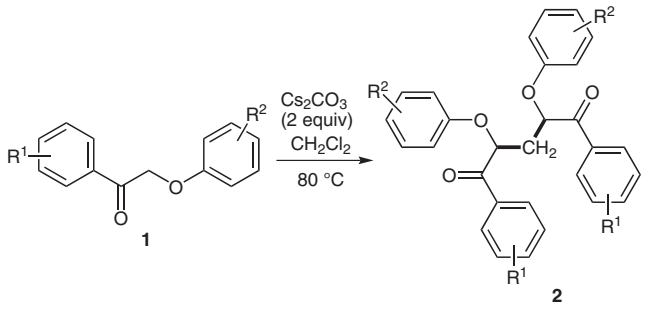
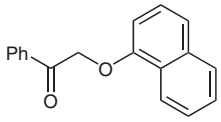
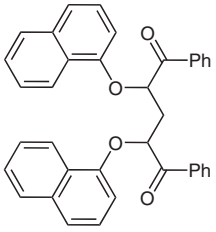
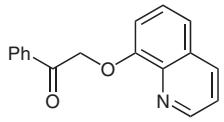
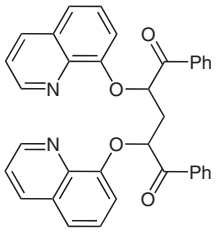
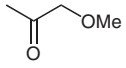
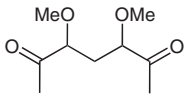
Entry[a]	Substrate	Product	Yield[b] (%)
1	 R[1] = 4-Me (**1b**)	 R[1] = 4-Me (**2b**)	91
2	R[1] = 4-MeO (**1c**)	R[1] = 4-MeO (**2c**)	83
3	R[1] = 4-Cl (**1d**)	R[1] = 4-Cl (**2d**)	80
4	R[1] = 4-F (**1e**)	R[1] = 4-F (**2e**)	76
5	 (**1f**)	 (**2f**)	quant
6	 R[2] = 4-Me (**1g**)	 R[2] = 4-Me (**2g**)	83
7	R[2] = 2-Me (**1h**)	R[2] = 2-Me (**2h**)	73
8	R[2] = 4-MeO (**1i**)	R[2] = 4-MeO (**2i**)	89[c]
9	R[2] = 3-MeO (**1j**)	R[2] = 3-MeO (**2j**)	91
10	R[2] = 2-MeO (**1k**)	R[2] = 2-MeO (**2k**)	90
11[d]	R[2] = 4-Cl (**1l**)	R[2] = 4-Cl (**2l**)	88

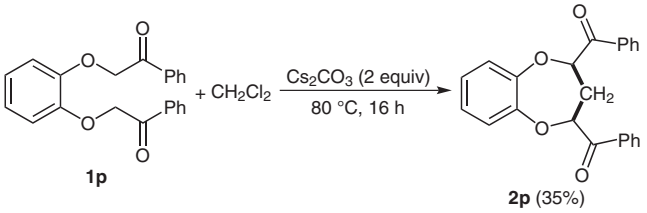
Table 2 Cesium Carbonate Mediated Synthesis of 2,4-Bis(aryloxy)-1,5-diarylpentane-1,5-diones **2** (continued)



Entry[a]	Substrate	Product	Yield[b] (%)
12	 (**1m**)	 (**2m**)	78
13[e]	 (**1n**)	 (**2n**)	50
14	 (**1o**)	 (**2o**)	trace

[a] Reaction conditions: **1** (0.2 mmol), Cs_2CO_3 (2.0 equiv), CH_2Cl_2 (1 mL), 80 °C, 16 h.
[b] Isolated yield.
[c] 2-(4-Methoxyphenoxy)-1-phenylprop-2-en-1-one (**3i**) was also obtained in 7% yield.
[d] 2 h.
[e] 48 h.

This new method can also be applied in a synthesis of dioxepines.[8] For example, 2,2′-[1,2-phenylenebis(oxy)]bis(1-phenylethanone) (**1p**) underwent a smooth tandem reaction with dichloromethane and cesium carbonate to afford the dioxepine **2p** in 35% yield after 16 hours (Scheme 2).



Scheme 2 Synthesis of a dioxepine

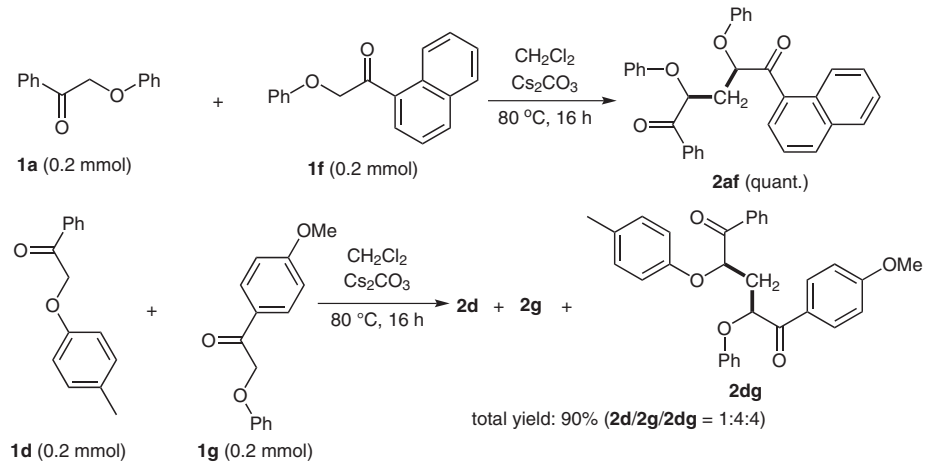
In an attempt to prepare nonsymmetric 2,4-bis(aryloxy)-1,5-diarylpentane-1,5-diones, we examined cross reactions between two different 2-phenoxy-1-arylethanones under the optimized conditions (Scheme 3). Interestingly, treatment of a 1:1 (molar) mixture of substrates **1a** and **1f** with dichloromethane and cesium carbonate gave the product **2af** exclusively in quantitative yield, whereas the corresponding reaction of substrates **1d** and **1g** (1:1 molar) with dichloromethane gave a 1:4:4 mixture or products **2d**, **2g**, and **2dg** in 90% total yield (Scheme 3).

Methylenebisbenzofurans are an important class of heteroaromatic ring systems that are present in a wide range of natural products.[7] We therefore decided to attempt to use products **2** in syntheses of these heteroaromatic ring systems (Scheme 4). To our delight, the methylenebisbenzofuran derivative **4a** was obtained by an iron(III) bromide-catalyzed Friedel–Crafts tandem cyclization of dione **2a**.

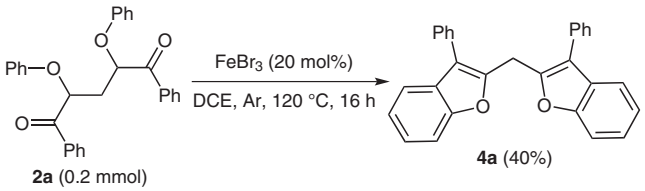
To confirm the mechanism of the tandem coupling reaction (Scheme 1), we carried out two control reactions (Scheme 5). Treatment of ketone **1a** with dichloromethane-d_2 and cesium carbonate gave the corresponding product **2a**-d_2 exclusively in good yield, confirming that dichloromethane acts as a one-carbon source in the reaction. Furthermore, the byproduct enone **3i** from the reaction of ketone **1i** was converted into product **2i** by Michael addition to substrate **1i** in the presence of cesium carbonate.

In summary, we have developed a new, simple, base-mediated method for the synthesis of 2,4-bis(aryloxy)-1,5-diarylpentane-1,5-diones through an α-methylenation–Michael tandem process with activation of two C–Cl bonds. The method permits the use of dichloromethane instead of dibromomethane as a new one-carbon source for the α-methylenation reaction. Importantly, the 2,4-bis(aryloxy)-1,5-diarylpentane-1,5-dione products are versatile intermediates for syntheses of polysubstituted pyridines or bisbenzofurans. Efforts are under way to apply the reaction and the products in organic synthesis.

NMR spectra were recorded on a Bruker Avance spectrometer operating at 500 MHz (^{1}H NMR) or 125 MHz (^{13}C NMR). Mass spectrometric analyses were performed on a GC/MS analyzer (Shimadzu GCMS-QP2010) and by using a Thermo MAT95XP-HRMS spectrometer in the EI mode. IR spectra were recorded on a Bruker vertex 70 FT-IR spectrophotometer. Melting points were recorded using a Hanon MP 100 apparatus and are uncorrected.



Scheme 3 Cross reactions of 2-phenoxy-1-arylethanones



Scheme 4 Synthesis of a methylenebisbenzofuran from dione **2a**

2,4-Bis(aryloxy)-1,5-diarylpentane-1,5-diones 2; General Procedure

A Schlenk tube was charged with the appropriate 2-(aryloxy)-1-arylethan-1-one **1** (0.2 mmol), Cs_2CO_3 (130.4 mg, 2 equiv), and CH_2Cl_2 (1.0 mL). The mixture was then stirred at 80 °C (oil bath temperature) under air for the indicated time until the starting material was consumed (TLC and GC/MS). When the reaction was complete, the mixture was cooled to r.t, diluted with Et_2O (10 mL), and washed with brine (3 × 3 mL). The aqueous phase was extracted with Et_2O (3 × 5 mL) and the organic phases were combined, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane–EtOAc).

2,4-Diphenoxy-1,5-diphenylpentane-1,5-dione (2a)

Colorless oil; yield: 43.6 mg [100%; two diastereomers (1.1:1)].

IR (KBr): 1693, 1587 cm^{-1}.

^1H NMR (500 MHz): δ = 8.13–8.09 (m, 4 H), 7.65–7.59 (m, 2 H), 7.54–7.47 (m, 4 H), 7.24–7.19 (m, 4 H), 6.97–6.92 (m, 2 H), 6.90–6.85 (m, 4 H), 6.00–5.83 (m, 2 H), 2.88–2.11 (m, 2 H).

^{13}C NMR (125 MHz): δ = 196.9, 196.6, 157.4, 156.9, 134.4, 134.1, 133.9, 129.6 (2 C), 129.0, 128.9, 128.8, 128.7, 122.0, 121.8, 115.5, 115.2, 76.2, 75.5, 36.8, 35.0.

LRMS (EI, 70 eV): *m/z* (%) = 436 [M^+] (1), 231 (100), 105 (51).

HRMS (EI): *m/z* [M^+] calcd for $C_{29}H_{24}O_4$: 436.1675; found: 436.1672.

2,4-Diphenoxy-1,5-diphenylpentane-1,5-dione-d_2 (2a-d_2)

Colorless oil; yield: 40.3 mg [92%; two diastereomers (1:1)].

^1H NMR (500 MHz): δ = 8.04–8.00 (m, 4 H), 7.56–7.50 (m, 2 H), 7.45–7.38 (m, 4 H), 7.17–7.11 (m, 4 H), 6.89–6.84 (m, 2 H), 6.82–6.78 (m, 4 H), 5.89 (s, 1 H), 5.75 (s, 1 H).

LRMS (EI, 70 eV): *m/z* (%) = 438 [M^+] (2), 231 (100).

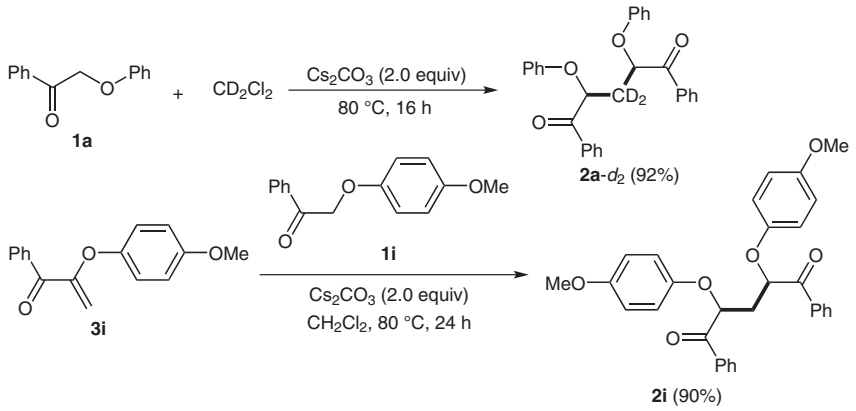
2,4-Diphenoxy-1,5-bis(4-tolyl)pentane-1,5-dione (2b)

Colorless oil; yield: 42.2 mg [91%; two diastereomers (1.3:1)].

IR (KBr): 1683, 1595 cm^{-1}.

^1H NMR (500 MHz): δ = 8.04–8.00 (m, 4 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.24–7.18 (m, 4 H), 6.95–6.91 (m, 2 H), 6.89–6.84 (m, 4 H), 5.97–5.79 (m, 2 H), 2.86–2.59 (m, 2 H), 2.43 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (125 MHz): δ = 196.5, 196.2, 157.4, 157.0, 145.2, 144.9, 131.9, 131.4, 129.8, 129.7, 129.6 (2 C), 129.5, 129.0, 128.9, 128.8, 121.8, 121.6, 115.5, 115.1, 76.1, 75.4, 60.4, 37.0, 35.1, 21.7, 21.0.



Scheme 5 Two control reactions

LRMS (EI, 70 eV): *m/z* (%) = 464 [M$^+$] (1), 371 (20), 345 (26), 251 (64), 223 (26), 158 (31), 119 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_4$: 464.1988; found: 464.1985.

1,5-Bis(4-methoxyphenyl)-2,4-diphenoxypentane-1,5-dione (2c)
Red oil; yield: 41.1 mg [83%; two diastereomers (1.2:1)].

IR (KBr): 1684, 1598 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.13–8.09 (m, 4 H), 7.25–7.18 (m, 4 H), 6.98 (d, *J* = 8.5 Hz, 2 H), 6.96–6.91 (m, 4 H), 6.87 (t, *J* = 7.5 Hz, 4 H), 5.93–5.74 (m, 2 H), 3.89 (s, 3 H), 3.86 (s, 3 H), 2.86–2.60 (m, 2 H).

^{13}C NMR (125 MHz): δ = 195.4, 195.1, 164.2, 164.1, 157.4, 157.0, 131.2, 131.1, 129.6, 127.4, 126.8, 121.8, 121.6, 115.4, 115.1, 114.2, 114.0, 76.1, 75.5, 55.6, 55.5, 37.2, 35.1.

LRMS (EI, 70 eV): *m/z* (%) = 496 [M$^+$] (2), 403 (12), 376 (7), 361 (26), 308 (6), 267 (27), 239 (14), 174 (33), 135 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_6$: 496.1886; found: 496.1883.

1,5-Bis(4-chlorophenyl)-2,4-diphenoxypentane-1,5-dione (2d)
Colorless oil; yield: 40.3 mg [80%; two diastereomers (1.1:1)].

IR (KBr): 1695, 1589, 1491 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.06–8.03 (m, 4 H), 7.49–7.44 (m, 4 H), 7.27–7.19 (m, 4 H), 6.99–6.94 (m, 2 H), 6.86–6.84 (m, 4 H), 5.86–5.73 (m, 2 H), 2.84–2.60 (m, 2 H).

^{13}C NMR (125 MHz): δ = 196.0, 195.7, 157.1, 156.7, 140.7, 140.5, 132.6, 132.2, 130.3, 130.2, 129.7, 129.4, 129.2, 122.2, 122.0, 115.4, 115.1, 76.5, 75.7, 36.5, 34.8.

LRMS (EI, 70 eV): *m/z* (%) = 504 [M$^+$] (1), 377 (23), 241 (15), 141 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{29}H_{22}{}^{35}Cl_2O_4$: 504.0895; found: 504.0894.

1,5-Bis(4-fluorophenyl)-2,4-diphenoxypentane-1,5-dione (2e)
Colorless oil; yield: 35.9 mg [76%; two diastereomers (1.1:1)].

IR (KBr): 1698, 1582, 1490 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.16–8.12 (m, 4 H), 7.26–7.12 (m, 8 H), 6.98–6.93 (m, 2 H), 6.87–6.85 (m, 4 H), 5.88–5.86 (m, 1 H), 5.77–5.75 (m, 1 H), 2.85–2.61 (m, 2 H).

^{13}C NMR (125 MHz): δ = 195.5, 195.2, 166.2 (d, J_{C-F} = 255.4 Hz, 1 C), 166.1 (d, J_{C-F} = 255.1 Hz, 1 C), 157.2, 156.7, 131.7 (d, J_{C-F} = 12.5 Hz, 1 C), 131.6 (d, J_{C-F} = 12.5 Hz, 1 C), 130.6 (d, J_{C-F} = 51.5 Hz, 1 C), 130.5 (d, J_{C-F} = 51.9 Hz, 1 C), 129.7, 122.1, 122.0, 116.3, 116.1, 116.0, 115.4, 115.1, 114.7, 76.4, 75.7, 36.6, 34.8.

LRMS (EI, 70 eV): *m/z* (%) = 472 [M$^+$] (1), 215 (12), 125 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{29}H_{22}F_2O_4$: 472.1486; found: 472.1483.

1,5-Di-1-naphthyl-2,4-diphenoxypentane-1,5-dione (2f)
White solid; yield: 53.6 mg [quant; two diastereomers (1.2:1)]; mp 127.6–131.3 °C.

IR (KBr): 1692, 1593 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.74 (s, 1 H), 8.69 (s, 1 H), 8.13–8.12 (m, 2 H), 8.01 (d, *J* = 8.0 Hz, 1 H), 7.94–7.87 (m, 5 H), 7.66–7.58 (m, 3 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.23 (t, *J* = 8.0 Hz, 4 H), 6.98–6.90 (m, 6 H), 6.18–6.02 (m, 2 H), 3.05–2.77 (m, 2 H).

^{13}C NMR (125 MHz): δ = 196.8, 196.6, 157.5, 157.0, 140.0, 135.9, 132.5 (2 C), 131.7, 131.2, 130.8, 130.7, 129.9, 129.8, 129.7 (2 C), 129.1, 129.0, 128.8, 127.9, 127.8, 127.1, 126.9, 124.1, 124.0, 122.0, 121.8, 115.5, 115.2, 76.5, 75.8, 37.2, 35.8.

LRMS (EI, 70 eV): *m/z* (%) = 536 [M$^+$] (3), 443 (25), 416 (5), 381 (41), 287 (71), 194 (64), 155 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{37}H_{28}O_4$: 536.1988; found: 536.1986.

2,4-Bis(4-methylphenoxy)-1,5-diphenylpentane-1,5-dione (2g)
Colorless oil; yield: 38.5 mg [83%; two diastereomers (1.1:1)].

IR (KBr): 1691, 1593 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.13–8.08 (m, 4 H), 7.63–7.58 (m, 2 H), 7.52–7.45 (m, 4 H), 7.03–6.99 (m, 4 H), 6.80–6.75 (m, 4 H), 5.96–5.77 (m, 2 H), 2.86–2.57 (m, 2 H), 2.25 (s, 3 H), 2.23 (s, 3 H).

^{13}C NMR (125 MHz): δ = 197.2, 196.8, 155.4, 154.9, 134.5, 134.0 (2 C), 133.8, 131.3, 131.0, 129.0, 128.8, 128.7, 115.5, 115.1, 76.5, 75.8, 36.8, 34.9, 20.4.

LRMS (EI, 70 eV): *m/z* (%) = 464 [M$^+$] (1), 371 (21), 251 (63), 119 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_4$: 464.1988; found: 464.1985.

2,4-Bis(2-methylphenoxy)-1,5-diphenylpentane-1,5-dione (2h)
Colorless oil; yield: 33.9 mg [73%; two diastereomers (1:1)].

Diastereomer 1
IR (KBr): 1695, 1585, 1495 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.14 (d, *J* = 7.5 Hz, 4 H), 7.63 (t, *J* = 7.5 Hz, 2 H), 7.52 (t, *J* = 7.5 Hz, 4 H), 7.16 (d, *J* = 7.0 Hz, 2 H), 6.98–6.95 (m, 2 H), 6.84 (t, *J* = 7.5 Hz, 2 H), 6.52 (d, *J* = 8.0 Hz, 2 H), 6.06–6.03 (m, 2 H), 2.69 (t, *J* = 6.5 Hz, 2 H), 2.45 (s, 6 H).

^{13}C NMR (125 MHz): δ = 196.8, 155.3, 134.1, 133.9, 131.2, 129.0, 128.6, 126.8, 126.8, 121.4, 111.6, 75.8, 37.0, 16.6.

LRMS (EI, 70 eV): *m/z* (%) = 464 [M$^+$] (1), 251 (62), 119 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_4$: 464.1988; found: 464.1987.

Diastereomer 2
Colorless oil

IR (KBr): 1695, 1585 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.09 (d, *J* = 7.5 Hz, 4 H), 7.59 (t, *J* = 7.5 Hz, 2 H), 7.47 (t, *J* = 7.5 Hz, 4 H), 7.13 (d, *J* = 7.0 Hz, 2 H), 7.07 (d, *J* = 7.5 Hz, 2 H), 6.86 (t, *J* = 7.5 Hz, 2 H), 6.79 (d, *J* = 8.5 Hz, 2 H), 5.89 (t, *J* = 6.0 Hz, 2 H), 2.97–2.69 (m, 2 H), 2.21 (s, 6 H).

^{13}C NMR (125 MHz): δ = 196.7, 155.1, 134.5, 133.8, 131.2, 128.8 (2 C), 127.0, 126.8, 121.3, 111.4, 75.4, 34.4, 16.5.

LRMS (EI, 70 eV): *m/z* (%) = 464 [M$^+$] (1), 251 (60), 119 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_4$: 464.1988; found: 464.1985.

2,4-Bis(4-methoxyphenoxy)-1,5-diphenylpentane-1,5-dione (2i)
Red oil; yield: 44.1 mg [89%; two diastereomers (1.1:1)].

IR (KBr): 1683, 1495 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.10–8.07 (m, 4 H), 7.63–7.58 (m, 2 H), 7.51–7.45 (m, 4 H), 6.87–6.73 (m, 8 H), 5.92–5.72 (m, 2 H), 2.80 (s, 3 H), 2.68 (s, 3 H), 2.84–2.53 (m, 2 H).

^{13}C NMR (125 MHz): δ = 197.4, 197.0, 154.7, 154.5, 151.7, 151.1, 134.5, 134.0, 133.8, 129.0, 128.8 (2 C), 128.7, 117.0, 116.5, 114.7, 77.3, 76.6, 55.6 (2 C), 36.9, 35.2.

LRMS (EI, 70 eV): *m/z* (%) = 496 [M$^+$] (3), 373 (35), 267 (14), 237 (100), 123 (90).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_6$: 496.1886; found: 496.1883.

2,4-Bis(3-methoxyphenoxy)-1,5-diphenylpentane-1,5-dione (2j)
Red oil; yield: 45.1 mg [91%; two diastereomers (1.3:1)].

IR (KBr): 1683, 1595 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.10 (t, *J* = 7.0 Hz, 4 H), 7.64–7.58 (m, 2 H), 7.53–7.46 (m, 4 H), 7.14–7.07 (m, 2 H), 6.52–6.49 (m, 3 H), 6.49–6.43 (m, 3 H), 5.97–5.80 (m, 2 H), 3.73 (s, 3 H), 3.70 (s, 3 H), 2.70–2.59 (m, 2 H).

^{13}C NMR (125 MHz): δ = 196.8, 196.5, 160.8, 158.6, 158.1, 134.4, 134.1, 133.9, 130.1 (2 C), 129.0, 128.9, 128.8, 128.7, 107.7, 107.5, 107.4, 107.0, 102.2, 101.8, 76.2, 75.5, 55.2 (2 C), 36.6, 34.9.

LRMS (EI, 70 eV): *m/z* (%) = 496 [M$^+$] (2), 376 (9), 267 (27), 135 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_6$: 496.1886; found: 496.1884.

2,4-Bis(2-methoxyphenoxy)-1,5-diphenylpentane-1,5-dione (2k)
Red oil; yield: 44.6 mg [90%; two diastereomers (1.3:1)].

IR (KBr): 1688, 1575 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.23 (d, *J* = 7.5 Hz, 3 H), 8.15 (d, *J* = 7.0 Hz, 1 H), 7.62–7.55 (m, 2 H), 7.52–7.44 (m, 4 H), 7.05–6.90 (m, 3 H), 6.86–6.81 (m, 4 H), 6.78–6.74 (m, 1 H), 6.18 (t, *J* = 3.5 Hz, 1 H), 5.94 (d, *J* = 6.5 Hz, 1 H), 3.62 (s, 3 H), 3.59 (s, 3 H), 2.93–2.56 (m, 2 H).

^{13}C NMR (125 MHz): δ = 197.0, 196.8, 150.3, 150.2, 147.3, 146.5, 134.8, 133.9, 133.8, 133.5, 129.0, 128.9, 128.8, 128.7, 128.6, 128.0, 122.9, 122.8, 120.9, 120.7, 117.8, 117.1, 112.3, 112.0, 78.8, 76.8, 55.5, 55.4, 38.0, 34.4.

LRMS (EI, 70 eV): *m/z* (%) = 496 [M$^+$] (1), 403 (10), 361 (24), 135 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{31}H_{28}O_6$: 496.1886; found: 496.1885.

2,4-Bis(4-chlorophenoxy)-1,5-diphenylpentane-1,5-dione (2l)
Colorless oil; yield: 44.3 mg [88%; two diastereomers (1.3:1)].

IR (KBr): 1691, 1593 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.08–8.05 (m, 4 H), 7.66–7.61 (m, 2 H), 7.54–7.48 (m, 4 H), 7.20–7.15 (m, 4 H), 6.83–6.80 (m, 2 H), 6.80–6.74 (m, 4 H), 5.91–5.77 (m, 2 H), 2.88–2.60 (m, 2 H).

^{13}C NMR (125 MHz): δ = 196.4, 196.0, 155.9, 155.4, 1343, 134.1, 133.7, 129.6, 129.5, 129.1, 129.0, 128.7, 128.6, 127.1, 126.8, 116.8, 116.5, 76.5, 75.8, 36.6, 35.3.

LRMS (EI, 70 eV): *m/z* (%) = 504 [M$^+$] (1), 399 (4), 377 (29), 271 (32), 241 (16), 144 (34), 105 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{29}H_{22}{}^{35}Cl_2O_4$: 504.0895; found: 504.0893.

2,4-Bis(1-naphthyloxy)-1,5-diphenylpentane-1,5-dione (2m)
White solid, yield: 41.8 mg [78%; two diastereomers (1.3:1)]; mp 111.4–112.1 °C.

IR (KBr): 1693, 1573 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.50 (d, *J* =8.5 Hz, 1 H), 8.24 (d, *J* =8.5 Hz, 1 H), 8.20 (d, *J* =7.5 Hz, 2 H), 8.12 (d, *J* =8.0 Hz, 2 H), 7.80–7.77 (m, 2 H), 7.63 (t, *J* =7.5 Hz, 1 H), 7.56–7.24 (m, 11 H), 7.09 (d, *J* =8.0 Hz, 1 H), 6.82 (d, *J* =7.5 Hz, 1 H), 6.57 (t, *J* =7.5 Hz, 1 H), 6.32 (d, *J* =6.5 Hz, 1 H), 6.11 (d, *J* =6.0 Hz, 2 H), 3.14–2.92 (m, 2 H).

^{13}C NMR (125 MHz): δ = 196.6 (2 C), 152.8, 152.6, 134.7 (2 C), 134.3, 134.2, 134.1, 134.0, 129.1, 128.9, 128.8, 128.7, 127.7, 127.5, 126.6, 125.6, 125.5 (3 C), 122.0, 121.8, 121.5 (3 C), 106.1, 105.7, 76.5, 76.0, 36.9, 34.9.

LRMS (EI, 70 eV): *m/z* (%) = 536 [M$^+$] (4), 393 (23), 287 (8), 257 (100), 105 (96).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{37}H_{28}O_4$: 536.1988; found: 536.1986.

1,5-Diphenyl-2,4-bis(quinolin-8-yloxy)pentane-1,5-dione (2n)
Red oil; yield: 26.9 mg (50%).

IR (KBr): 1691, 1597, 1569 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.45–8.40 (m, 6 H), 7.99 (d, *J* =8.0 Hz, 2 H), 7.62 (t, *J* =7.0 Hz, 2 H), 7.57–7.54 (m, 4 H), 7.32 (d, *J* =8.0 Hz, 2 H), 7.24–7.20 (m, 4 H), 7.08 (d, *J* =8.5 Hz, 2 H), 6.87 (d, *J* =7.0 Hz, 2 H), 2.93–2.91 (m, 2 H).

^{13}C NMR (125 MHz): δ = 197.1, 153.9, 148.8, 140.9, 135.6, 134.3, 133.7, 129.5, 129.0, 126.3, 121.4, 121.3, 114.6, 79.7, 38.1.

LRMS (EI, 70 eV): *m/z* (%) = 538 [M$^+$] (1), 394 (41), 376 (3), 288 (65), 275 (5), 170 (95), 105 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{35}H_{26}N_2O_4$: 538.1893; found: 538.1889.

3,4-Dihydro-2*H*-1,5-benzodioxepine-2,4-diylbis(phenylmethanone) (2p)
Colorless oil; yield: 12.5 mg (35%).

IR (KBr): 1698, 1585 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.00 (d, *J* = 7.0 Hz, 4 H), 7.62 (t, *J* = 7.5 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 4 H), 6.99 (s, 4 H), 5.84 (t, *J* = 7.5 Hz, 2 H), 2.81–2.78 (m, 2 H).

^{13}C NMR (125 MHz): δ = 195.4, 149.0, 134.6, 133.9, 129.0, 128.8, 123.9, 121.3, 79.1, 33.9.

LRMS (EI, 70 eV): *m/z* (%) = 358 [M$^+$] (6), 253 (65), 144 (28), 121 (54), 105 (100).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{23}H_{18}O_4$: 358.1205; found: 358.1202.

1-(1-Naphthyl)-2,4-diphenoxy-5-phenylpentane-1,5-dione (2af)
White solid; yield: 48.6 mg [quant, two diastereomers (1:1)]; mp 106.4–108.1 °C.

IR (KBr): 1695, 1589, 1487 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.74–8.70 (m, 1 H), 8.15–8.09 (m, 3 H), 8.02–7.87 (m, 3 H), 7.66–7.46 (m, 5 H), 7.25–7.20 (m, 4 H), 6.98–6.85 (m, 6 H), 6.18–5.83 (m, 2 H), 3.04–2.62 (m, 2 H).

^{13}C NMR (125 MHz): δ = 196.9 (2 C), 196.8, 196.6, 171.1, 157.4 (3 C), 157.0, 156.9, 136.0, 135.9, 134.4 (2 C), 134.1, 133.9, 132.5, 132.4, 131.7 (2 C), 131.2, 130.8, 130.7 (2 C), 129.9, 129.8, 129.7 (2 C), 129.6, 129.1, 129.0 (2 C), 128.9, 128.8, 128.7 (2 C), 127.8 (2 C), 127.1, 126.9, 124.1 (2 C), 124.0, 123.9, 122.0, 121.8, 115.5, 115.2 (2 C), 76.4, 76.3, 76.2, 75.8, 75.6 (2 C), 75.5, 37.2, 37.0, 36.8, 35.3, 35.0.

LRMS (EI, 70 eV): *m/z* (%) = 486 [M$^+$] (1), 393 (41), 331 (23), 287 (14), 237 (100), 105 (69).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{33}H_{26}O_4$: 486.1831; found: 486.1834.

1-(4-Methoxyphenyl)-4-(4-methylphenoxy)-2-phenoxy-5-phenylpentane-1,5-dione (2dg)
Red oil; yield: 38.4 mg [40%, two diastereomers (1.2:1)].

IR (KBr): 1693, 1579 cm^{-1}.

^{1}H NMR (500 MHz): δ = 8.12–8.08 (m, 4 H), 7.63–7.57 (m, 1 H), 7.52–7.45 (m, 2 H), 7.23–7.19 (m, 2 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 7.00–6.97 (m, 2 H), 6.94 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 5.94–5.75 (m, 2 H), 3.89 (s, 3 H), 2.86–2.55 (m, 2 H), 2.25 (s, 3 H).

^{13}C NMR (125 MHz): δ = 197.2, 196.9, 195.4, 195.1, 164.2, 164.1, 157.5, 157.0, 155.4, 154.9, 134.5, 134.0 (2 C), 133.8, 131.3, 131.2, 131.1, 131.0, 130.0, 129.6 (2 C), 129.0, 128.8, 128.7, 127.4, 126.9,

121.8, 121.6, 115.5 (2 C), 115.1, 114.2, 114.1, 76.6, 76.0, 75.9, 75.5, 55.6, 55.5, 37.0, 35.1, 22.6, 20.4.

LRMS (EI, 70 eV): *m/z* (%) = 480 [M^+] (1), 345 (23), 251 (7), 135 (100).

HRMS (EI): *m/z* [M^+] calcd for $C_{31}H_{28}O_5$: 480.1937; found: 480.1940.

2-(4-Methoxyphenoxy)-1-phenylprop-2-en-1-one (3i)
Colorless oil; yield: 3.6 mg (7%).

IR (KBr): 1698, 1558 cm^{-1}.

^1H NMR (500 MHz): δ = 7.92 (d, *J* = 7.5 Hz, 2 H), 7.56 (d, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.03 (d, *J* = 8.5 Hz, 2 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 5.27 (s, 1 H), 4.94 (s, 1 H), 3.79 (s, 3 H).

^{13}C NMR (125 MHz): δ = 191.0, 158.3, 156.5, 148.3, 136.6, 132.8, 129.6, 128.3, 121.1, 114.9, 102.8, 55.6.

LRMS (EI, 70 eV): *m/z* (%) = 254 [M^+] (12), 119 (6), 135 (100).

HRMS (EI): *m/z* [M^+] calcd for $C_{16}H_{14}O_3$: 254.0943; found: 254.0940.

2,2′-Methylenebis(3-phenyl-1-benzofuran)(4a)
Colorless oil; yield: 32.1 mg (40%).

^1H NMR (500 MHz): δ = 7.59–7.55 (m, 6 H), 7.48–7.41 (m, 6 H), 7.38–7.36 (m, 2 H), 7.29–7.23 (m, 4 H), 4.43 (s, 2 H).

^{13}C NMR (125 MHz): δ = 154.4, 149.3, 132.0, 129.2, 128.8, 128.5, 127.4, 124.2, 122.8, 119.8, 118.8, 111.3, 25.2.

LRMS (EI, 70 eV): *m/z* (%) = 401 (28), 400 [M^+] (100), 323 (34), 305 (16), 218 (27).

HRMS (EI): *m/z* [M^+] calcd for $C_{29}H_{20}O_2$: 400.1463; found: 400.1459.

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Supporting Information

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

Reference

(1) (a) Kleinman, E. F. In *Comprehensive Organic Synthesis*; Vol. 2; Trost, B. M.; Fleming, I., Eds.; Pergamon: Oxford, **1991**, 893. (b) Shono, T.; Nishiguchi, I.; Komamura, T.; Sasaki, M. *J. Am. Chem. Soc.* **1979**, *101*, 984. (c) Huet, F.; Pellet, M.; Conia, J. M. *Tetrahedron Lett.* **1977**, 3505. (d) Holy, N. L.; Wang, Y. F. *J. Am. Chem. Soc.* **1977**, 99, 944. (e) Ksander, G. M.; McMurry, J. E.; Johnson, M. *J. Org. Chem.* **1977**, *42*, 1180. (f) Danishefsky, S.; Kitahara, T.; McKee, R.; Schuda, P. F. *J. Am. Chem. Soc.* **1976**, *98*, 6715. (g) Grieco, P. A. *Synthesis* **1975**, 67. (h) Tramontini, M. *Synthesis* **1973**, 703. (i) Lee, K.-H.; Huang, E.-S.; Piantadosi, C.; Pagano, J. S.; Geissmann, T. A. *Cancer Res.* **1971**, *31*, 1649. (j) Kupchan, S. M.; Eakin, M. A.; Thomas, A. M. *J. Med. Chem.* **1971**, *14*, 1147.

(2) (a) Andrisano, R.; Angeloni, A. S.; De Maria, P.; Tramontini, M. *J. Chem. Soc. C* **1967**, 2307. (b) Farberov, M. I.; Mironov, G. S. *Dokl. Akad. Nauk SSSR* **1963**, *148*, 1095; *Chem. Abstr.* **1963**, *59*, 5062. (c) Ahond, A.; Cave, A.; Kan-Fan, C.; Potier, P. *Bull. Soc. Chim. Fr.* **1970**, 2707. (d) Holy, N. L.; Wang, Y. F. *J. Am. Chem. Soc.* **1977**, *99*, 944. (e) Horák, V.; Michl, J.; Zuman, P. *Tetrahedron Lett.* **1961**, 744. (f) Angeloni, A. S.; Angiolini, L.; De Maria, P.; Fini, A. *J. Chem. Soc. C* **1968**, 2295. (g) Johnson, W. S.; Szmuszkovicz, J.; Rogier, E. R.; Hadler, H. I.; Wynberg, H. *J. Am. Chem. Soc.* **1956**, *78*, 6285.

(3) (a) Hon, Y.-S.; Hsu, T.-R.; Chen, C.-Y.; Lin, Y.-H.; Chang, F.-J.; Hsieh, C.-H.; Szua, P.-H. *Tetrahedron* **2003**, *59*, 1509. (b) Chang, F.-J.; Lu, L.; Lin, W.-C. *Tetrahedron* **1998**, *54*, 5233. (c) Hon, Y.-S.; Lin, W.-C. *Tetrahedron Lett.* **1995**, *36*, 7693. (d) Hon, Y.-S.; Chang, F.-J.; Lu, L. *J. Chem. Soc., Chem. Commun.* **1994**, 2041.

(4) For selected papers on other methods, see: (a) Riofski, M. V.; John, J. P.; Zheng, M. M.; Kirshner, J.; Colby, D. A. *J. Org. Chem.* **2011**, *76*, 3676. (b) Jin, Y.-H.; Fang, F.; Zhang, X.; Liu, Q.-Z.; Wang, H.-B.; Tian, S.-K. *J. Org. Chem.* **2011**, *76*, 4163. (c) Erkkilä, A.; Pihko, P. M. *J. Org. Chem.* **2006**, *71*, 2538.

(5) For transition-metal-catalyzed activation of the both C–Cl bonds in CH_2Cl_2, see: (a) Aguilar, D.; Contel, M.; Urriolabeitia, E. P. *Chem.–Eur. J.* **2010**, *16*, 9287. (b) Xiang, X.; Shen, Q.-S.; Wang, J.-L.; Zhu, Z.-Y.; Huang, W.; Zhou, X.-G. *Organometallics* **2008**, *27*, 1959. (c) Tsai, C.-C.; Hsieh, I.-L.; Cheng, T.-T.; Tsai, P. K.; Lin, K.-W.; Yan, T.-H. *Org. Lett.* **2006**, *8*, 2261. (d) Yan, T.-H. TsaiChien, C.-T.; Cho, C.-C.; Huang, P.-C. *Org. Lett.* **2004**, *6*, 4961. (e) Hunt, C. Jr; Fronczek, F. R.; Billodeaux, D. R.; Stanley, G. G. *Inorg. Chem.* **2001**, *40*, 5192. (f) Brunet, J.-J.; Couillens, X.; Daran, J. C.; Diallo, O.; Lepetit, C.; Neibecker, D. *Eur. J. Inorg. Chem.* **1998**, 349. (g) Suisse, P.; Pellegrini, S.; Castanet, Y.; Mortreux, A.; Lecoulier, S. *J. Chem. Soc., Chem. Commun.* **1995**, 847. (h) Rondon, D.; Delbeau, J.; He, X.-D.; Sabo-Etienne, S.; Chaudret, B. *J. Chem. Soc., Dalton Trans.* **1994**, 1895. (i) Suzuki, H.; Kakigano, T.; Igarashi, M.; Tanaka, M.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 283. (j) Marder, T. B.; Fultz, W. C.; Calabrese, J. C.; Harlow, R. L.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1987**, 1543. (k) Jandik, P.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 73.

(6) (a) Li, H.-J.; He, Z.-H.; Guo, X.-W. Li W.-J.; Zhao, X.-H.; Li, Z.-P. *Org. Lett.* **2009**, *11*, 4176. (b) Lecomte, V.; Bolm, C. *Adv. Synth. Catal.* **2005**, *347*, 1666. (c) Karvembu, R.; Natarajan, K. *Polyhedron* **2002**, *21*, 219. (d) Maruyama, K.; Kubo, K.; Toda, Y.; Kawase, K.; Mashino, T.; Nishinaga, A. *Tetrahedron Lett.* **1995**, *36*, 5609. (e) Wilson, B. D. *J. Org. Chem.* **1962**, *28*, 314. (f) Martin, D. F.; Shamma, M.; Fernelius, W. C. *J. Am. Chem. Soc.* **1958**, *80*, 5851.

(7) (a) Chilin, A.; Conconi, M. T.; Marzaro, G.; Guiotto, A.; Urbani, L.; Tonus, F.; Parnigotto, P. *J. Med. Chem.* **2010**, *53*, 1862. (b) Icli, M.; Pamuk, M.; Algi, F.; Onal, A. M.; Cihaner, A. *Chem. Mater.* **2010**, *22*, 4034. (c) Grenier, C. R. G.; George, S. J.; Joncheray, T. J.; Meijer, E. W.; Reynolds, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 10694.

(8) (a) Zhou, L.; Shi, Y.; Xiao, Q.; Liu, Y.-Z.; Ye, F.; Zhang, Y.; Wang, J. B. *Org. Lett.* **2011**, *13*, 968. (b) Auzias, M.; Häussinger, D.; Neuburger, M.; Wegner, H. A. *Org. Lett.* **2011**, *13*, 474. (c) Maimone, T. J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2010**, *132*, 9990. (d) Guo, X.-W.; Yu, R.; Li, H.-J.; Li, Z.-P. *J. Am. Chem. Soc.* **2009**, *131*, 17387.

(9) The configuration of products **2** was unambiguously assigned by means of an X-ray single-crystal diffraction analysis of product **2k**. See the Supporting Information for detailed data.