DOI: 10.1002/ejoc.201000497

ZnI_2-Catalyzed Benzannulation of *o*-Alkynylbenzaldehydes with Alkenes Leading to 1-Acyl-2-Substituted Naphthalenes

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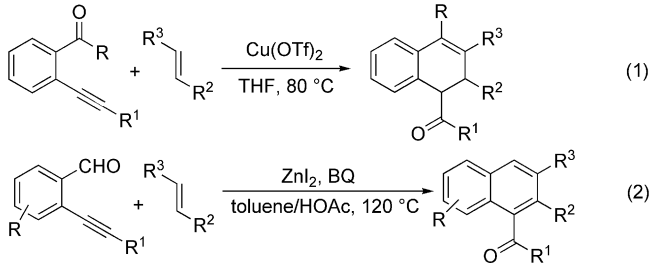
Keywords: Zinc / Annulation / Fused-ring systems / Alkenes

A new, practical route to 1-acyl-2-substituted naphthalenes has been developed by benzoquinone-promoted ZnI_2-catalyzed benzannulation of 2-alkynylbenzaldehydes with alkenes. This method allows three new bonds, two C=C bonds and one C=O bond, to be constructed in a single reaction.

Introduction

The naphthalene ring is a prominent structural motif found in a wide range of biologically active natural products, pharmaceuticals, and materials.[1] Techniques commonly used to prepare naphthalene or its derivatives include (i) introduction of substituents onto the preexisting naphthalene ring,[2] (ii) Diels–Alder reactions and [2+2+2] cyclotrimerization of alkynes, and (iii) [4+2] benzannulation of enynes.[2–7] However, these methods involve the use of relatively harsh reaction conditions, inaccessible substrates, and/or expensive catalysts. Alternatively, Lewis acid catalyzed benzannulation of alkynylbenzaldehydes with unsaturated compounds (alkynes or alkenes) has been recently employed as an efficient strategy to access naphthalene and its derivatives.[8–14] However, only a few papers have been reported, and the catalysts used are limited to Au or Cu Lewis acids.[8–13] For example, Asao and Yamamoto disclosed an efficient route to naphthalenes by gold-catalyzed [4+2] cycloaddition of *o*-alkynylbenzaldehydes with alkynes.[8] Subsequently, they described another $Cu(OTf)_2$-catalyzed [4+2] cycloaddition approach to 1,2-dihydronaphthalenes by using *o*-alkynyl(oxo)benzenes and alkenes as the reaction partners (Scheme 1, Equation 1).[9] Dyker and co-workers also provided similar results by using $AuCl_3$ catalysis.[10] Although Yao and co-workers reported a metal-free transformation for the synthesis of 2,3-dihydrophenanthren-4(1*H*)-one derivatives recently, an excess amount of Brønsted acids was required to promote the cationic cascade reactions of *o*-alkynylbenzaldehydes with alkenes.[14] With continuing interest in zinc chemistry,[15] we decide to explore the efficiency of zinc Lewis acids in the [4+2] cycloaddition transformation. Here, we report a new, practical, ZnI_2-catalyzed benzannulation protocol for the synthesis of 1-acyl-2-arylnaphthalenes (Scheme 1, Equation 2). It is noteworthy that the Zn-catalyzed protocol has different selectivity, particularly in the presence of 1,4-benzoquinone, from that reported for the Cu- or Au-catalyzed transformations.



Scheme 1. The [4+2] cycloaddition reactions.

Results and Discussion

We began our study with the reaction between 2-(2-phenylethynyl)benzaldehyde (**1a**) and 4-methylstyrene (**2a**) in toluene to explore the optimal reaction conditions. As shown in Table 1, a series of zinc halides were initially tested (Table 1, Entries 1–4). Whereas ZnF_2 gave a trace amount of target cycloaddition products **3** and **4** (Table 1, Entry 1), $ZnCl_2$ enhanced the yield to 57% with a 74:26 ratio of **3**/**4** (Table 1, Entry 2). To our delight, 82% total yield of products **3** and **4** was obtained in the presence of ZnI_2 (Table 1, Entry 4); however, a mixture of products **3** and **4** is unattractive in organic synthesis. After a series of trials, we found that Pd/C or 1,4-benzoquinone could improve the selectivity.[16] In the presence of ZnI_2 and Pd/C, the selectivity was shifted toward **3** (**3**/**4** = 84:16; Table 1, Entry 5). Although the yield had decreased to 55%, product **4** was ob-

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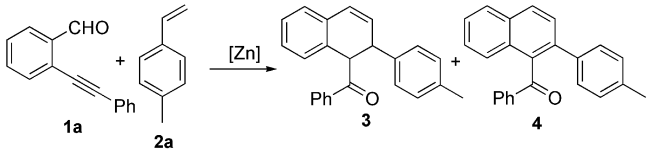
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201000497.

tained alone with the use of 1,4-benzoquinone as an additive (Table 1, Entry 6). The results demonstrated a solvent effect (Table 1, Entries 6–9). DMSO was found to be a unsuitable solvent (Table 1, Entry 7), and HOAc was superior to toluene (Table 1, Entry 8). It was pleasing to disclose that a mixed solvent, toluene/HOAc, afforded product **4** in 81% yield (Table 1, Entry 9). Among both the reaction temperature and the amount of ZnI_2 examined, it turned out that 30 mol-% of ZnI_2 at 120 °C gave the best results (Table 1, Entries 9–13). We also found that the amount of 1,4-benzoquinone had an effect on the reaction, and 1 equiv. of 1,4-benzoquinone lowered the yield to 63% (Table 1, Entry 14).

Table 1. Screening optimal conditions.[a]

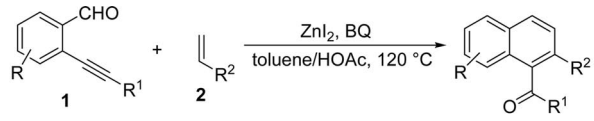


Entry	[Zn] (equiv.)	Solvent	Additive	*T* [°C]	Yield [%][b]
1	ZnF_2 (30)	toluene	–	80	trace
2	$ZnCl_2$ (30)	toluene	–	80	57 (74:26)
3	$ZnBr_2$ (30)	toluene	–	80	70 (55:45)
4	ZnI_2 (30)	toluene	–	80	82 (74:26)
5[c]	ZnI_2 (30)	toluene	–	80	80 (84:16)
6	ZnI_2 (30)	toluene	BQ	80	55 (0:100)
7	ZnI_2 (30)	DMSO	BQ	80	trace
8	ZnI_2 (30)	HOAc	BQ	80	69 (0:100)
9[d]	ZnI_2 (30)	toluene/HOAc	BQ	80	81 (0:100)
10[d]	ZnI_2 (30)	toluene/HOAc	BQ	60	64 (0:100)
11[d]	ZnI_2 (30)	toluene/HOAc	BQ	120	88 (0:100)
12[d]	ZnI_2 (20)	toluene/HOAc	BQ	120	72 (0:100)
13[d]	ZnI_2 (10)	toluene/HOAc	BQ	120	47 (0:100)
14[d,e]	ZnI_2 (30)	toluene/HOAc	BQ	120	63 (0:100)

[a] Reaction conditions: **1** (0.3 mmol), **2** (1.2 equiv.), [Zn], BQ (2.0 equiv.) in solvent (1.25 mL) for 24 h. [b] Isolated yield. The selectivity between products **3** and **4** is given in parenthesis. [c] Pd/C (10 mol-%) was added. [d] Toluene/HOAc = 4:1 (1.25 mL). [e] BQ (1 equiv.) was used.

The above results prompted us to explore both *o*-alkynylbenzaldehydes and alkenes in the tandem benzannulation–dehydrogenation reaction under the standard conditions (Table 2). Initially, a variety of alkenes **2b**–**j** were employed to react with 2-(phenylethynyl)benzaldehyde (**1a**) in the presence of ZnI_2 and 1,4-benzoquinone (Table 2, Entries 1–10). We found that aryl alkenes were more active than aliphatic alkenes, and substituents on the aryl moiety affected the reaction: electron-donating groups were found to be superior to electron-withdrawing groups (Table 2, Entries 1–9). Whereas 1-methoxy-4-vinylbenzene (**2e**), for instance, underwent the reaction with substrate **1a**, ZnI_2, and 1,4-benzoquinone smoothly in 78% yield (Table 2, Entry 4), substrate **2g** bearing a nitro group gave a lower yield of 38%. For aliphatic alkene **2j**, a low yield was observed under the same conditions (Table 2, Entry 9). Subsequently, the effect of substituents at the terminal end of the 2-ethynylbenzaldehydes was investigated (Table 2, Entries 10–13). The results showed that both electron-rich aryl and aliphatic groups disfavored the reaction (Table 2, Entries 10 and 13), whereas electron-deficient aryl groups were satisfactory for the reaction (Table 2, Entries 11 and 12). Sub-

Table 2. ZnI_2-catalyzed benzannulation reactions of *o*-alkynylbenzaldehydes (**1**) with alkenes (**2**) in the presence of 1,4-benzoquinone.[a]



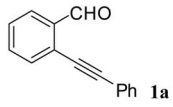
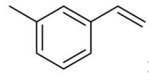
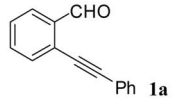
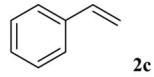
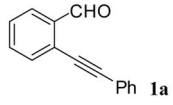
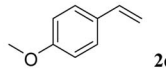
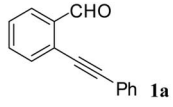
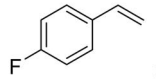
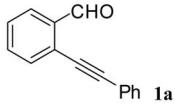
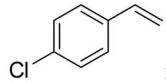
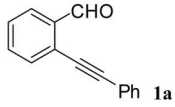
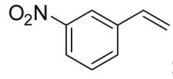
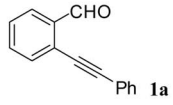
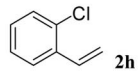
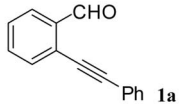
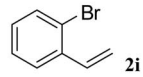
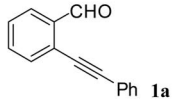
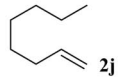
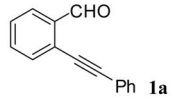
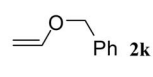
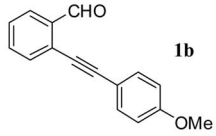
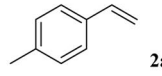
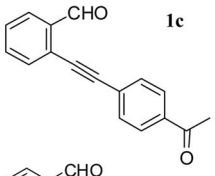
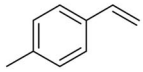
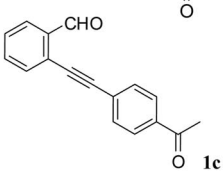
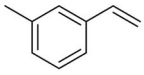
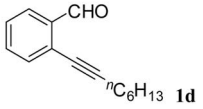
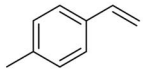
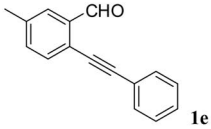
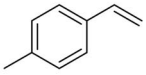
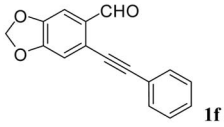
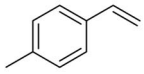
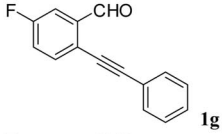
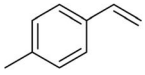
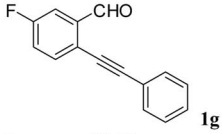
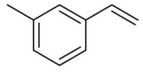
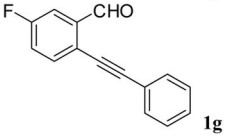
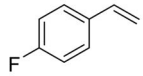
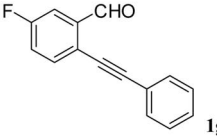
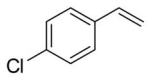
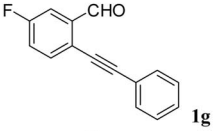
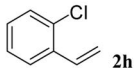
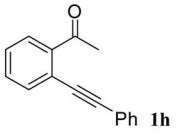
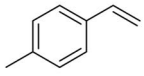
Entry	Substrate **1**	Alkene **2**	*t* [h]	Yield [%][b]
1			20	79 (**5**)
2			20	76 (**6**)
3			22	77 (**7**)
4			30	78 (**8**)
5			28	41 (**9**)
6			28	38 (**10**)
7			20	50 (**11**)
8			26	53 (**12**)
9			48	18 (**13**)
10			48	trace (**14**)
11			30	40 (**15**)

Table 2. *(Continued)*

Entry	Substrate **1**	Alkene **2**	*t* [h]	Yield [%][b]
12	 **1c**	 **2a**	17	76 (**16**)
13	 **1c**	 **2b**	22	61 (**17**)
14	 **1d**	 **2a**	70	30 (**18**)
15	 **1e**	 **2a**	20	45 (**19**)
16	 **1f**	 **2a**	24	55 (**20**)
17	 **1g**	 **2a**	20	80 (**21**)
18	 **1g**	 **2b**	23	73 (**22**)
19	 **1g**	 **2e**	19	61 (**23**)
20	 **1g**	 **2f**	18	65 (**24**)
21	 **1g**	 **2h**	32	45 (**25**)
22	 **1h**	 **2a**	24	trace (**26**)

[a] Reaction conditions: **1** (0.3 mmol), **2** (1.2 equiv.), ZnI_2 (30 mol-%), 1,4-benzoquinone (BQ, 2.0 equiv.) in toluene/HOAc (4:1, 1.25 mL) at 120 °C. [b] Isolated yield.

stituents on the aromatic ring of the benzaldehyde moiety were also examined (Table 2, Entries 14–20). Treatment of substrate **1e** or **1f**, having an electron-donating group, with 1-methyl-4-vinylbenzene, ZnI_2, and 1,4-benzoquinone afforded the corresponding product in 45 or 55% yield, respectively (Table 2, Entries 14 and 15), whereas weak electron-withdrawing substrate **1e** could react with alkene **2a** in good yield (Table 2, Entry 16). Moderate yields were still achieved from the reaction of substrate **1e** with other alkenes (Table 2, Entries 17–20). However, attempts to react substrate **1a** with 1,2-diphenylethene was not successful. It is noteworthy that the structure of **8** was unambiguously confirmed by X-ray single-crystal diffraction analysis (Figure 1).[17]

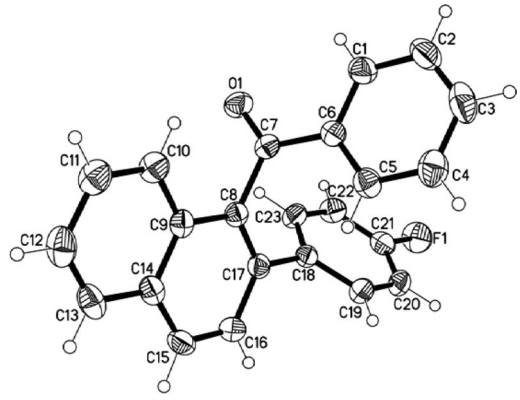
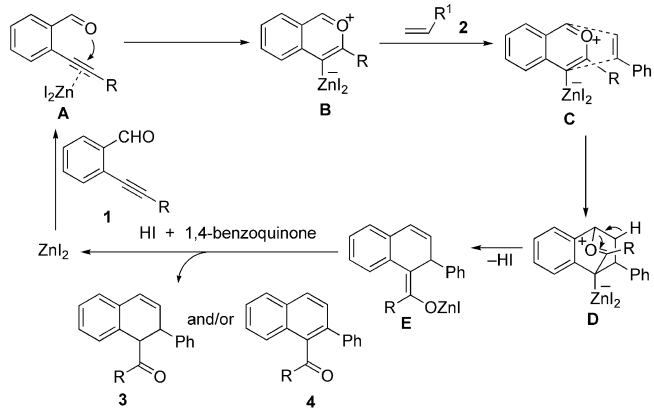


Figure 1. ORTEP diagram of the single-crystal X-ray structure of compound **8**.[17]

A plausible mechanism as outlined in Scheme 2 was proposed for the present reaction on the basis of the present results and the reported mechanism.[8–14] The coordination of the triple bond of substrate **1** to ZnI_2 enhances the electrophilicity of the alkyne, leading to intermediate **A**, and then nucleophilic attack of the carbonyl oxygen atom to the electron-deficient alkyne in intermediate **A** gives intermediate **B**. The Diels–Alder reaction of intermediate **B** with styrene **2** affords intermediate **D** through intermediate **C**. As a result of the instability of intermediate **D**, the cleavage of the carbon–oxygen bond takes place, followed by elimination of a proton to produce zinc-enolate **E** and HI. Intermediate **E** can proceed through two steps together with the regeneration of the active Zn catalyst: (1) protonation to



Scheme 2. A possible mechanism.

give **3** and (2) dehydrogenation to yield **4**. 1,4-benzoquinone is required for the dehydrogenation of intermediate **E**, leading to target product **4**.[16]

Conclusions

In summary, we have developed the first example of the Zn-catalyzed benzannulation of *o*-alkynylbenzaldehydes with alkenes for the synthesis of 1-acyl-2-substituted naphthalenes. In the presence of ZnI_2 and 1,4-benzoquinone, a variety of *o*-alkynylbenzaldehydes successfully underwent the reaction with alkenes to selectively prepare 1-acyl-2-substituted arylnaphthalenes in moderate to good yields. The present tandem benzannulation–dehydrogenation reaction represents a practical route to the naphthalene skeleton. On the basis of the results, several features should be noted: (1) The selectivity is different from that reported for Cu- or Au-catalyzed transformations. (2) Two C=C bonds and one C=O bond were formed in a single reaction. (3) 1,4-Benzoquinone can shift the selectivity to improve the reaction.

Experimental Section

General Remarks: NMR spectroscopy was performed with a Bruker-300 spectrometer operating at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR). TMS (tetramethylsilane) was used an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed by GC–MS analysis (SHIMADZU GC–MS-QP2010 plus).

Typical Experimental Procedure for the Zn-Catalyzed Benzannulation Reaction: To a Schlenk tube was added **1** (0.3 mmol), alkene **2** (1.2 equiv.), ZnI_2 (30 mol-%), 1,4-benzoquinone (2 equiv.), and toluene/HOAc (4:1, 1.25 mL). Then, the tube was charged with argon, and the mixture was stirred at 120 °C (oil bath temperature) for the indicated time until complete consumption of the starting material as monitored by TLC and GC–MS analysis. After the reaction was finished, the reaction mixture was cooled to room temperature, diluted with diethyl ether, and washed with brine. The aqueous phase was re-extracted with EtOAc. The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product.

Phenyl(2-*p*-tolyl-1,2-dihydronaphthalen-1-yl)methanone (3):[18] Following the general procedure, the title compound was obtained in 67% yield (65 mg). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.7 Hz, 2 H, Ar-H), 7.57–7.51 (m, 1 H, Ar-H), 7.42 (m, 2 H, Ar-H), 7.25–7.15 (m, 3 H, Ar-H), 7.13–7.04 (m, 4 H, Ar-H), 6.84 (d, J = 7.5 Hz, 1 H, Ar-H), 6.22 (dd, J = 9.9, 1.8 Hz, 1 H, =C-H), 5.97 (d, J = 6.6 Hz, 1 H, CH=C-H), 4.98 (d, J = 7.5 Hz, 1 H, CHC-H), 4.13 (t, J = 4.8 Hz, 1 H, =CH-C-H), 2.24 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.0, 139.9, 137.1, 136.6, 133.7, 133.0, 131.8, 130.4, 129.6, 129.4, 128.9, 128.7 (2 C), 128.6, 128.3, 128.1, 127.7 (2 C), 127.6, 127.2, 126.6, 53.4, 43.5, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 2918, 1667, 1237 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 324 (11) [M]$^+$, 219 (100), 204 (42), 105 (38), 77 (29).

Phenyl(2-*p*-tolylnaphthalen-1-yl)methanone (4):[9] Following the general procedure, the title compound was obtained in 88% yield (85 mg). Yellow solid, m.p. 152.8–155.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.5 Hz, 1 H, Ar-H), 7.94 (d, J = 7.8 Hz, 1 H, Ar-H), 7.74–7.65 (m, 3 H, Ar-H), 7.59–7.37 (m, 4 H, Ar-H), 7.29–7.22 (m, 4 H, Ar-H), 7.05 (d, J = 7.8 Hz, 2 H, Ar-H), 2.26 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.8, 137.9, 137.4, 137.3, 137.2, 135.5, 133.2, 132.3, 130.7, 129.6, 129.4, 129.3, 129.0, 128.3, 128.2, 127.8, 127.1, 126.2, 125.5, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 2917, 1734, 1664, 1529 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 322 (41) [M]$^+$, 245 (39), 219 (100), 202 (30), 105 (84).

Phenyl(2-*m*-tolylnaphthalen-1-yl)methanone (5): Following the general procedure, the title compound was obtained in 79% yield (76 mg). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.5 Hz, 1 H, Ar-H), 7.94 (d, J = 8.6 Hz, 1 H, Ar-H), 7.75 (d, J = 8.5 Hz, 1 H, Ar-H), 7.65–7.60 (m, 2 H, Ar-H), 7.58 (d, J = 8.5 Hz, 1 H, Ar-H), 7.56–7.40 (m, 3 H, Ar-H), 7.27–7.10 (m, 5 H, Ar-H), 6.98 (d, J = 7.5 Hz, 1 H, Ar-H), 2.25 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.7, 140.1, 138.1, 137.7, 137.6, 135.6, 133.1, 132.4, 130.7, 130.3, 129.5, 129.4, 128.3 (2 C), 128.2, 128.1, 127.6, 127.2, 126.6, 126.2, 125.6, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 1667, 1255 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 322 (100) [M]$^+$, 307 (35), 256 (14), 245 (96), 201 (27). HRMS (EI) for $C_{24}H_{18}O$ [M]$^+$ calcd. 322.1352; found 322.1355.

Phenyl(2-phenylnaphthalen-1-yl)methanone (6):[18] Following the general procedure, the title compound was obtained in 76% yield (70 mg). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.5 Hz, 1 H, Ar-H), 7.94 (d, J = 9.2 Hz, 1 H, Ar-H), 7.74 (d, J = 8.2 Hz, 1 H, Ar-H), 7.64–7.41 (m, 5 H, Ar-H), 7.38–7.34 (m, 3 H, Ar-H), 7.25–7.16 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.7, 140.2, 137.9, 137.5, 135.7, 133.3, 132.5, 130.7, 129.6, 129.5, 128.8, 128.3, 128.2, 128.0, 127.6, 127.5, 127.3, 126.4, 125.6 ppm. IR (KBr): $\tilde{\nu}$ = 2937, 1727, 1580 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 308 (99) [M]$^+$, 231 (100), 202 (52), 105 (29), 77 (35).

[2-(4-Methoxyphenyl)naphthalen-1-yl](phenyl)methanone (7):[18] Following the general procedure, the title compound was obtained in 77% yield (78 mg). Yellow solid, m.p. 186.4–189.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.5 Hz, 1 H, Ar-H), 7.92 (d, J = 8.0 Hz, 1 H, Ar-H), 7.70 (d, J = 8.2 Hz, 1 H, Ar-H), 7.62 (d, J = 8.4 Hz, 2 H, Ar-H), 7.56–7.37 (m, 4 H, Ar-H), 7.29–7.21 (m, 4 H, Ar-H), 6.75 (d, J = 8.7 Hz, 2 H, Ar-H), 3.72 (s, 3 H, -OCH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.9, 158.9, 137.9, 137.0, 133.2, 132.6, 132.2, 130.6 (2 C), 129.6, 129.4, 128.3 (2 C), 128.1, 127.7, 127.1, 126.1, 125.4, 113.7, 55.2 ppm. IR (KBr): $\tilde{\nu}$ = 3309, 1663, 1517, 1237 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 338 (100) [M]$^+$, 261 (79), 189 (19), 105 (29).

[2-(4-Fluorophenyl)naphthalen-1-yl](phenyl)methanone (8):[18] Following the general procedure, the title compound was obtained in 78% yield (76 mg). Yellow solid, m.p. 180.1–182.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, J = 8.5 Hz, 1 H, Ar-H), 7.94 (d, J = 7.8 Hz, 1 H, Ar-H), 7.71 (d, J = 8.5 Hz, 1 H, Ar-H), 7.60 (dd, J = 7.8, 1.0 Hz, 2 H, Ar-H), 7.53–7.41 (m, 4 H, Ar-H), 7.33–7.22 (m, 4 H, Ar-H), 6.91 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.6, 162.2 (d, $^1J_{C,F}$ = 243.4 Hz), 137.8, 136.3, 136.22, 136.18, 135.8, 133.4, 132.4, 131.2, 131.1, 130.6, 129.5 (2 C), 128.4, 128.2, 127.4, 127.3, 126.4, 125.5, 115.2 (d, $^2J_{C,F}$ = 21.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 1666, 1504, 1235 cm^{-1}. LRMS (EI, 70 eV): *m*/*z* (%) = 326 (93) [M]$^+$, 249 (100), 220 (41), 105 (40).

[2-(4-Chlorophenyl)naphthalen-1-yl](phenyl)methanone (9): Following the general procedure, the title compound was obtained in 41% yield (42 mg). Yellow solid, m.p. 168.4–170.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.4 Hz, 1 H, Ar-H), 7.94 (d, J = 7.8 Hz, 1 H, Ar-H), 7.70 (d, J = 8.2 Hz, 1 H, Ar-H), 7.61 (d, J = 7.2 Hz, 2 H, Ar-H), 7.55–7.40 (m, 4 H, Ar-H), 7.29–7.18 (m,

6 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4, 138.6, 137.7, 136.0, 135.8, 133.6, 133.5, 132.5, 130.7, 130.6, 129.6 (2 C), 128.4 (2 C), 128.2, 127.4, 127.3, 126.5, 125.6 ppm. IR (KBr): $\tilde{\nu}$ = 2917, 1667, 1236 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) =344 (31) $[M + 2]^+$, 342 (100) $[M]^+$, 265 (79), 202 (50), 105 (56), 77 (48). HRMS (EI) for $C_{23}H_{15}ClO$ $[M]^+$ calcd. 342.0806; found 342.0808.

[2-(3-Nitrophenyl)naphthalen-1-yl](phenyl)methanone (10): Following the general procedure, the title compound was obtained in 38% yield (40 mg). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.20 (s, 1 H, Ar-H), 8.08–8.01 (m, 2 H, Ar-H), 7.97 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.73–7.67 (m, 2 H, Ar-H), 7.62–7.37 (m, 7 H, Ar-H), 7.29–7.23 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.0, 148.0, 141.8, 137.7, 136.4, 135.5, 134.7, 133.8, 132.8, 130.5, 130.0, 129.5, 129.2, 128.6, 128.3, 127.6, 127.0, 126.8, 125.7, 124.1, 122.3 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 1668, 1529, 1350 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 353 (100) $[M]^+$, 276 (63), 105 (100), 77 (59). HRMS (EI) for $C_{23}H_{15}NO_3$ $[M]^+$ calcd. 353.1046; found 353.1050.

[2-(2-Chlorophenyl)naphthalen-1-yl](phenyl)methanone (11): Following the general procedure, the title compound was obtained in 50% yield (51 mg). Yellow solid, m.p. 154.6–157.2 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.94 (m, 2 H, Ar-H), 7.74 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.65 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.57–7.38 (m, 5 H, Ar-H), 7.38–7.23 (m, 3 H, Ar-H), 7.20–7.07 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.0, 137.9, 137.8, 136.7, 134.7, 133.3, 132.9, 132.7, 132.5, 130.7, 130.0, 129.5, 129.4, 129.1, 128.6, 128.2, 128.0, 127.2, 126.7, 126.2, 125.7 ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2922, 1667, 1236 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 344 (4) $[M + 2]^+$, 342 (11) $[M]^+$, 307 (100) $[M - Cl]^+$, 202 (15), 153 (13), 77 (16). HRMS (EI) for $C_{23}H_{15}ClO$ $[M]^+$ calcd. 342.0806; found 342.0808.

[2-(2-Bromophenyl)naphthalen-1-yl](phenyl)methanone (12): Following the general procedure, the title compound was obtained in 53% yield (61 mg). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.94 (m, 2 H, Ar-H), 7.73 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.67 (d, *J* = 5.2 Hz, 2 H, Ar-H), 7.57–7.39 (m, 5 H, Ar-H), 7.38–7.14 (m, 4 H, Ar-H), 7.04–6.99 (m, 1 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.0, 139.7, 137.8, 136.6, 136.1, 133.3, 132.8, 132.6, 130.7, 129.5, 129.2, 129.0, 128.8, 128.5, 128.2, 127.7, 127.2, 126.8, 126.7, 125.7, 123.2 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 1668, 1236 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 388 (98) $[M + 2]^+$, 386 (100) $[M]^+$, 230 (11), 202 (10), 153 (15). HRMS (EI) for $C_{23}H_{15}BrO$ $[M]^+$ calcd. 386.0301; found 386.0303.

(4-Methoxyphenyl)(2-*p*-tolylnaphthalen-1-yl)methanone (15): Following the general procedure, the title compound was obtained in 40% yield (42 mg). Yellow solid, m.p. 173.9–176.8 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.92 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.71–7.63 (m, 3 H, Ar-H), 7.58–7.42 (m, 3 H, Ar-H), 7.29 (d, *J* = 8.1 Hz, 2 H, Ar-H), 7.06 (d, *J* = 7.9 Hz, 2 H, Ar-H), 6.74 (d, *J* = 9.0 Hz, 2 H, Ar-H), 3.77 (s, 3 H, -OCH_3), 2.27 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.2, 163.6, 137.4, 137.0, 135.8, 132.3, 132.1, 131.2, 130.7, 129.2 (2 C), 129.1, 129.0, 128.1, 127.8, 127.0, 126.1, 125.6, 113.6, 55.4, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 2920, 1595, 1245 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 352 (97) $[M]^+$, 245 (32), 202 (27), 135 (100), 77 (31). HRMS (EI) for $C_{25}H_{20}O_2$ $[M]^+$ calcd. 352.1458; found 352.1460.

1-[4-(2-*p*-Tolyl-1-naphthoyl)phenyl]ethanone (16): Following the general procedure, the title compound was obtained in 76% yield (83 mg). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.8 Hz, 1 H, Ar-H), 7.94 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.79 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.71–7.67 (m, 3 H, Ar-H), 7.58–7.45 (m, 3 H, Ar-H), 7.23 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.03 (d, *J* = 7.8 Hz, 2 H, Ar-H), 2.53 (s, 3 H, -$COCH_3$), 2.24 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.2, 197.6, 141.0, 140.0, 137.7, 137.4, 137.0, 132.3, 130.5, 129.9, 129.6, 129.4, 129.1, 128.3, 128.2, 127.7, 127.4, 126.3, 125.1, 122.4, 26.8, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 2921, 1670, 1231 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 364 (96) $[M]^+$, 349 (24), 245 (100), 202 (41), 167 (20). HRMS (EI) for $C_{26}H_{20}O_2$ $[M]^+$ calcd. 364.1458; found 364.1459.

1-[4-(2-*m*-Tolyl-1-naphthoyl)phenyl]ethanone (17): Following the general procedure, the title compound was obtained in 61% yield (67 mg). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.96 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.79 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.74–7.65 (m, 3 H, Ar-H), 7.59–7.44 (m, 3 H, Ar-H), 7.18–7.06 (m, 3 H, Ar-H), 6.98–6.96 (m, 1 H, Ar-H), 2.54 (s, 3 H, -$COCH_3$), 2.24 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 197.5, 141.2, 139.9, 137.9, 134.9, 132.4, 130.5, 130.3, 129.9, 129.5, 128.4, 128.3, 128.2, 128.1 (2 C), 127.5, 127.4, 126.6, 126.4, 125.2, 122.3, 26.8, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 1686, 1233 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 364 (100) $[M]^+$, 349 (46), 245 (98), 202 (44). HRMS (EI) for $C_{26}H_{20}O_2$ $[M]^+$ calcd. 364.1458; found 364.1459.

1-(2-*p*-Tolylnaphthalen-1-yl)heptan-1-one (18): Following the general procedure, the title compound was obtained in 30% yield (30 mg). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.90–7.76 (m, 3 H, Ar-H), 7.65 (m, 2 H, Ar-H), 7.57–7.51 (m, 1 H, Ar-H), 7.43–7.34 (m, 2 H, Ar-H), 7.19 (d, *J* = 8.1 Hz, 1 H, Ar-H), 2.96 (t, *J* = 7.3 Hz, 2 H, -$COCH_2$), 2.48 (s, 3 H, -CH_3), 1.78 (m, 2 H, -CH_2), 1.81–1.43 (m, 6 H, -$CH_2CH_2CH_2$), 0.96 (t, *J* = 7.1 Hz, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 210.4, 137.5, 132.5, 130.8, 129.4 (2 C), 129.3, 129.2, 128.2, 127.9, 127.7, 127.3, 127.1, 126.6, 124.8, 31.4, 28.5, 23.6 (2 C), 22.4, 21.0, 14.0 ppm. IR (KBr): $\tilde{\nu}$ = 2925, 1698, 812 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 330 (2) $[M]^+$, 328 (24), 300 (48), 243 (49), 229 (100), 207 (23). HRMS (EI) for $C_{24}H_{26}O$ $[M]^+$ calcd. 330.1978; found 330.1981.

(6-Methyl-2-*p*-tolylnaphthalen-1-yl)(phenyl)methanone (19): Following the general procedure, the title compound was obtained in 45% yield (45 mg). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.83 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.65–7.62 (m, 2 H, Ar-H), 7.50–7.47 (m, 2 H, Ar-H), 7.41–7.35 (m, 2 H, Ar-H), 7.28–7.21 (m, 4 H, Ar-H), 7.02 (d, *J* = 7.8 Hz, 2 H, Ar-H), 2.41 (s, 3 H, -CH_3), 2.24 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.1, 138.0, 137.4, 137.0, 134.9, 133.1, 130.9, 130.6, 129.6, 129.3, 129.1, 128.9, 128.6, 128.5, 128.2, 127.9, 127.2, 126.8, 124.4, 21.9, 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 2920, 1667, 1238, 822 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 336 (100) $[M]^+$, 321 (72), 259 (91), 149 (85), 105 (67). HRMS (EI) for $C_{25}H_{20}O$ $[M]^+$ calcd. 336.1509; found 336.1510.

Phenyl[6-*p*-tolylnaphtho(2,3-*d*)(1,3)dioxol-5-yl]methanone (20): Following the general procedure, the title compound was obtained in 55% yield (60 mg). Yellow solid, m.p. 197.5–200.4 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 6.9 Hz, 1 H, Ar-H), 7.63–7.59 (m, 2 H, Ar-H), 7.41–7.35 (m, 2 H, Ar-H), 7.25–7.20 (m, 5 H, Ar-H), 7.01–6.98 (m, 3 H, Ar-H), 5.99 (s, 2 H, -OCH_2O-), 2.23 (s, 3 H. -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.9, 148.6, 147.7, 137.8, 137.4, 136.8, 136.1, 134.8, 133.2, 129.6 (2 C), 129.2, 128.9, 128.3, 128.2, 127.5, 126.6, 104.0, 101.9, 101.3, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 2918, 1663, 1465, 1248 cm^{-1}. LRMS (EI, 70 eV): *m/z* (%) = 366 (100) $[M]^+$, 289 (89), 231 (18), 105 (24), 77 (34). HRMS (EI) for $C_{25}H_{18}O_3$ $[M]^+$ calcd. 366.1250; found 366.1252.

(6-Fluoro-2-*p*-tolylnaphthalen-1-yl)(phenyl)methanone (21): Following the general procedure, the title compound was obtained in 80% yield (82 mg). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.5 Hz, 1 H, Ar-H), 7.71–7.68 (m, 1 H, Ar-H), 7.64–7.51

(m, 4 H, Ar-H), 7.43–7.38 (m, 1 H, Ar-H), 7.31–7.18 (m, 5 H, Ar-H), 7.03 (d, J = 8.4 Hz, 2 H, Ar-H), 2.24 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.4, 160.6 (d, $^1J_{C,F}$ = 246.2 Hz), 137.7, 137.3, 137.0, 133.4, 133.3, 129.6, 129.3, 129.0, 128.9, 128.7, 128.7, 128.3, 128.1, 128.0, 127.7, 117.4 ($^2J_{C,F}$ = 25.1 Hz), 111.3, ($^2J_{C,F}$ = 20.3 Hz), 21.1 ppm. IR (KBr): $\tilde{\nu}$ = 2921, 1666, 1241 cm^{-1}. LRMS (EI, 70 eV): m/z (%) = 340 (100) [M]$^+$, 263 (88), 220 (37), 105 (52), 77 (44). HRMS (EI) for $C_{24}H_{17}FO$ [M]$^+$ calcd. 340.1258; found 340.1262.

(6-Fluoro-2-*m*-tolylnaphthalen-1-yl)(phenyl)methanone (22): Following the general procedure, the title compound was obtained in 73% yield (75 mg). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.6 Hz, 1 H, Ar-H), 7.76–7.73 (m, 1 H, Ar-H), 7.63–7.54 (m, 4 H, Ar-H), 7.41–7.38 (m, 1 H, Ar-H), 7.28–7.22 (m, 3 H, Ar-H), 7.16–7.00 (m, 4 H, Ar-H), 2.25 (s, 3 H, -CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.3, 160.6 (d, $^1J_{C,F}$ = 245.9 Hz), 139.8, 137.8, 137.0, 135.7, 133.5, 133.3, 130.2, 129.5 (2 C), 128.8, 128.7, 128.3 (2 C), 128.2, 128.1, 127.7, 126.5, 117.4 (d, $^2J_{C,F}$ = 25.1 Hz), 111.3 (d, $^2J_{C,F}$ = 20.3 Hz), 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1663, 1240 cm^{-1}. LRMS (EI, 70 eV): m/z (%) = 340 (100) [M]$^+$, 325 (52), 263 (75), 220 (32), 105 (47). HRMS (EI) for $C_{24}H_{17}FO$ [M]$^+$ calcd. 340.1258; found 340.1262.

[6-Fluoro-2-(4-fluorophenyl)naphthalen-1-yl](phenyl)methanone (23): Following the general procedure, the title compound was obtained in 61% yield (63 mg). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.5 Hz, 1 H, Ar-H), 7.76–7.71 (m, 1 H, Ar-H), 7.61–7.54 (m, 4 H, Ar-H), 7.45–7.40 (m, 1 H, Ar-H), 7.32–7.21 (m, 5 H, Ar-H), 6.95–6.89 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.2, 162.2 (d, $^1J_{C,F}$ = 246.1 Hz), 160.7 (d, $^1J_{C,F}$ = 246.5 Hz), 137.6, 135.9, 133.6, 131.1, 131.0, 129.5, 128.9, 128.8, 128.6, 128.4, 128.2, 128.1, 127.6, 117.6 (d, $^2J_{C,F}$ = 21.4 Hz), 115.4 (d, $^2J_{C,F}$ = 25.2 Hz), 111.3 (d, $^2J_{C,F}$ = 20.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3060, 1663, 1507, 1224 cm^{-1}. LRMS (EI, 70 eV): m/z (%) = 344 (97) [M]$^+$, 267 (100), 238 (47), 105 (80), 77 (59). HRMS (EI) for $C_{23}H_{14}F_2O$ [M]$^+$ calcd. 344.1007; found 344.1011.

[2-(4-Chlorophenyl)-6-fluoronaphthalen-1-yl](phenyl)methanone (24): Following the general procedure, the title compound was obtained in 65% yield (70 mg). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.5 Hz, 1 H, Ar-H), 7.74–7.69 (m, 1 H, Ar-H), 7.61–7.53 (m, 4 H, Ar-H), 7.47–7.41 (m, 1 H, Ar-H), 7.30–7.18 (m, 7 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 199.1, 160.8 (d, $^1J_{C,F}$ = 246.8 Hz), 138.3, 137.5, 133.73, 133.67, 133.5, 130.7, 129.5, 128.94, 128.87, 128.50, 128.48, 128.42, 128.25, 128.13, 127.6, 117.7 (d, $^2J_{C,F}$ = 25.1 Hz), 111.3 (d, $^2J_{C,F}$ = 20.5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3060, 1664, 1497, 1240 cm^{-1}. LRMS (EI, 70 eV): m/z (%) = 360 (100) [M]$^+$, 283 (69), 220 (46), 105 (98). HRMS (EI) for $C_{23}H_{14}ClFO$ [M]$^+$ calcd. 360.0712; found 360.0713.

[2-(2-Chlorophenyl)-6-fluoronaphthalen-1-yl](phenyl)methanone (25): Following the general procedure, the title compound was obtained in 45% yield (49 mg). Yellow solid, m.p. 133.7–137.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.5 Hz, 1 H, Ar-H), 7.78–7.73 (m, 1 H, Ar-H), 7.72–7.54 (m, 4 H, Ar-H), 7.47–7.39 (m, 1 H, Ar-H), 7.28–7.21 (m, 5 H, Ar-H), 7.14–7.08 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.6, 160.9 (d, $^1J_{C,F}$ = 246.4 Hz), 137.7, 136.9, 134.1, 133.9, 133.8, 133.5, 132.5, 129.5, 129.4, 129.2, 128.7, 128.3, 128.2, 128.0, 127.9, 127.6, 126.3, 117.4 (d, $^2J_{C,F}$ = 25.1 Hz), 111.4 (d, $^2J_{C,F}$ = 24.5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3062, 1664, 1238 cm^{-1}. LRMS (EI, 70 eV): m/z (%) = 360 (1) [M]$^+$, 325 (100), 220 (13), 105 (20), 77 (21). HRMS (EI) for $C_{23}H_{14}ClFO$ [M]$^+$ calcd. 360.0712; found 360.0713.

Supporting Information (see footnote on the first page of this article): NMR spectra (^{1}H and ^{13}C) of compounds **3**–**12** and **15**–**25**.

Acknowledgments

The authors thank the National Natural Science Foundation of China (No. 20872112) and the Zhejiang Provincial Natural Science Foundation of China (No. Y407116) for financial support.

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Received: April 12, 2010
Published Online: June 18, 2010

