Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2012, **10**, 3899

www.rsc.org/obc

PAPER

Cu(I)-catalyzed annulation for the synthesis of substituted naphthalenes using *o*-bromobenzaldehydes and β-ketoesters as substrates†

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Received 22nd November 2011, Accepted 9th March 2012
DOI: 10.1039/c2ob06963f

Cu(I)-catalyzed reaction of *o*-bromobenzaldehydes with β-ketoesters using Cs_2CO_3 as a base and 2-picolinic acid as an additive proceeds under mild conditions and gives access to substituted naphthalenes in a single step with yields ranging from 71 to 86%. The new annulation process relies on a domino Knoevenagel condensation/*C*-arylation/1,2-addition/carboxylic acid cleavage. The annulation can also be achieved with *o*-iodobenzaldehyde.

Introduction

Modern organic synthesis is unthinkable without Cu-catalyzed bond forming reactions as they are not restricted to the efficient construction of carbon–heteroatom bonds like C,N-, C,O- and C,S-bonds but also allow for the synthesis of C,C-bonds.[1] Among the most well known Cu(I)-catalyzed transformations are the reactions between (hetero)aryl halides and *N*-, *O*- and *S*-nucleophiles. In the past this type of reaction could only be achieved under harsh reaction conditions but meanwhile protocols have been improved considerably. This allows such reactions to be performed under comparable mild conditions. The scope of Cu(I)-catalyzed reactions can be extended substantially when bisfunctionalized (hetero)arenes are used as substrates in domino type processes.[2] This approach allows the synthesis of numerous heterocycles. Typical examples include the reactions of *o*-dihaloarenes,[3] *o*-haloanilines,[4] *o*-haloanilides[5] and *o*-halobenzamides[6] with suitable reaction partners. Recently, we have found that the reaction of *o*-bromobenzyl bromides with β-ketoesters can be used for the efficient preparation of 4*H*-chromenes.[7] We have proposed that this transformation proceeds as a *C*-benzylation/*O*-arylation process. In contrast to numerous examples known for the synthesis of heterocycles, Cu(I)-catalyzed processes have only rarely been exploited for the preparation of carbocycles.[8]

Highly substituted bicyclic and polycyclic aromatic compounds are common structural motifs of natural products and pharmaceuticals. In recent years such aromatic systems have attracted considerable attention for the construction of organic light emitting diodes, organic semiconductors and luminescent materials due to their unique photochemical and electrochemical properties.[9]

This is why there is continuing interest in the development of efficient methods for the construction of bicyclic and polycyclic aromatic compounds. Annulations are particular attractive because of the ease with which a great variety of aromatic systems can be synthesized. Among the best known annulations for the synthesis of aromatic rings are the 4 + 2 and the 2 + 2 + 2 annulations. The 4 + 2 annulations can be achieved by Diels-Alder reactions of *o*-quinodimethanes with acetylenic dienophiles[10] and of benzynes with dienes.[11] In addition, a number of transition metal based 4 + 2 annulations have been developed which include the Pd-catalyzed reaction between arene containing vinylic iodides and triflates with internal alkynes,[12] the Pd-catalyzed reaction of *o*-(2-alkenyl)aryl halides with 1,2-disubstituted alkynes,[13] the Rh-catalyzed reaction of an arylalkyne with an alkylalkyne,[14] the Au-catalyzed annulation of arylacetaldehydes with alkynes[15] or the reaction of *o*-dihaloarenes with zirconacyclopentadienes.[16] The 2 + 2 + 2 annulations have been performed by the Ir-catalyzed reaction of aroyl chlorides[17a] or benzoic acids[17b] with internal alkynes, the Ni-catalyzed reaction of *o*-diiodoarenes with alkynes,[18] the Pd-catalyzed reaction of *o*-diiodoarenes with alkynes,[19] the Pd-catalyzed cocyclization of benzynes with alkynes,[20] the Pd-catalyzed treatment of arenes with alkynes[21] and the Rh-catalyzed treatment of arenes with alkynes.[22]

Despite numerous approaches, the preparation of annulated aromatic systems bearing different substituents at specific positions employing easily available starting materials is far from being well established.

Recently, we have developed a new synthetic route towards substituted naphthalenes that relies on the Cu(I)-catalyzed reaction of an *o*-halobenzyl halide, preferably an *o*-bromobenzyl bromide, with two molecules of a β-ketoester (Scheme 1).[7] In this naphthalene synthesis three C,C-bonds are formed in one

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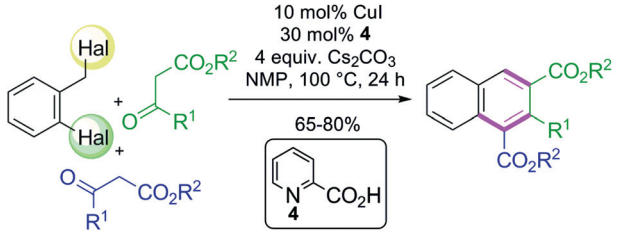
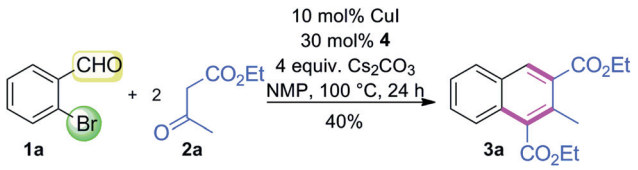
†Electronic supplementary information (ESI) available: ^1H and ^{13}C spectra of all compounds. See DOI: 10.1039/c2ob06963f



Scheme 1 Cu(I)-catalyzed synthesis of substituted naphthalenes by reaction of a 2-halobenzyl halide with two molecules of a β-ketoester.[7]



Scheme 2 Initial experiment for the Cu(I)-catalyzed reaction of *o*-bromobenzaldehyde (**1a**) with ethyl acetoacetate (**2a**).

synthetic operation. The approach is unique in the sense that three C-atoms of the newly formed aromatic ring stem from the *o*-halobenzyl halide, two from the first β-ketoester molecule and one C-atom from the second β-ketoester. So far the method has been restricted to *o*-halobenzyl halides as starting materials. Here we report that the new approach to annulated aromatic systems can be extended to *o*-halobenzaldehydes as substrates. *o*-Halobenzaldehydes are particular attractive starting materials as they can easily be obtained by numerous synthetic methods.[23]

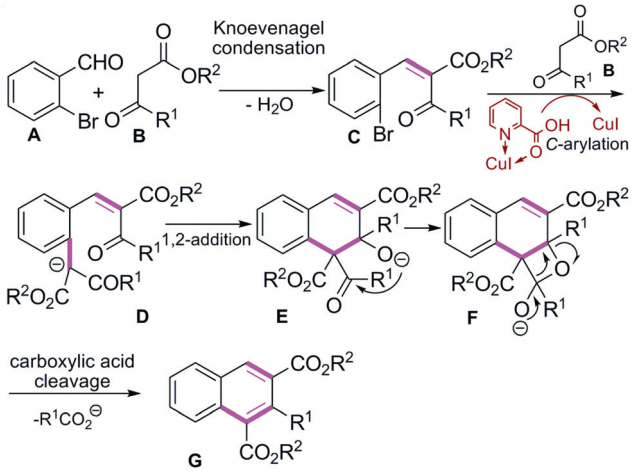
Results and discussion

We started with the reaction between *o*-bromobenzaldehyde (**1a**) with ethyl acetoacetate (**2a**) under the reaction conditions that had been proven successful for the reaction of *o*-bromobenzyl bromides with β-ketoesters.[7] Reaction of 1 equiv. **1a** with 3 equivs. of **2a** in the presence of 10 mol% CuI, 30 mol% 2-picolinic acid (**4**) and 4 equivs. Cs_2CO_3 at 100 °C for 24 h in *N*-methyl pyrrolidine delivered the expected naphthalene **3a** in 40% yield (Scheme 2).

This result clearly demonstrated that the annulation can also be achieved by using an *o*-bromobenzaldehyde as a substrate. However, it was obvious that the yield had to be improved substantially to make this an interesting synthetic method. Therefore, the reaction had to be optimized.

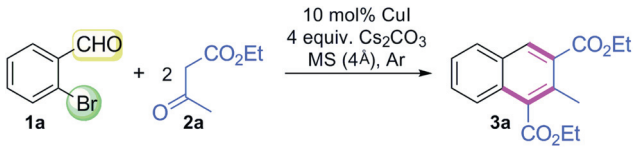
We propose that the annulation starts with a Knoevenagel condensation between the *o*-bromobenzaldehyde and the β-ketoester (**A** + **B** → **C**) (Scheme 3). This is followed by an intermolecular *C*-arylation of a second β-ketoester (**C** + **B** → **D**) and an intramolecular 1,2-addition (**D** → **E**). The final step of the sequence is the cleavage of the carboxylic acid (**E** → **F** → **G**).

During the first step of the reaction cascade, the Knoevenagel condensation, one equivalent of water is formed which might interfere with some of the following reaction steps of the sequence. Therefore, all further reactions were run in the presence of molecular sieves 4 Å to remove the water formed from the reaction mixture during the Knoevenagel condensation.



Scheme 3 Proposed mechanism for the reaction of *o*-bromobenzaldehyde **A** with β-ketoesters **B**.

Table 1 Optimization of the reaction between **1a** and **2a**[a,b]



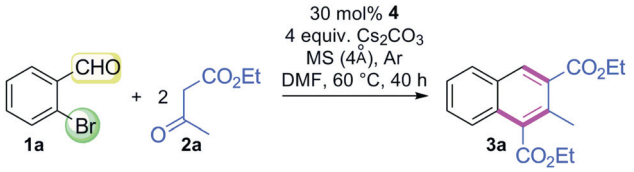
Entry	**4** (mol %)	*T* (°C)	*t* (h)	Solvent	**3a** Yield (%)
1	30	100	24	NMP	36
2	30	100	24	DMF	62
3	15	100	24	DMF	23
4	—	100	24	DMF	11
5	30	60	40	DMF	71
6	30	60	40	DMF	46[c]
7	30	60	40	DMF	45[d]

[a] Unless otherwise indicated, all reactions were performed using 0.5 mmol of **1a** and 1.5 mmol of **2a** in a sealed vial. [b] On the TLC traces of a side product with a higher R_f-value than **3a** was observed. [c] Reaction was performed using 1 mmol of **2a**. [d] Reaction was carried out under air.

However, with NMP as a solvent this measure did not pay off. But when NMP was replaced by DMF the yield of **3a** improved by 26% to 62% (Table 1, entry 1 and 2). Reduction of the amount of 2-picolinic acid (**4**) from 30 mol% to 15 mol% led to a substantial decrease of the yield to 23%, and when the reaction was performed in the absence of any 2-picolinic acid (**4**) only 11% of **3a** could be isolated (Table 1, entry 3 and 4). This clearly demonstrates that an additive like **4** which is believed to activate the CuI by complexation is necessary to guarantee high yields of the naphthalene. A further increase of the yield of **3a** to 71% could be achieved when the reaction was performed at 60 °C for 40 h (Table 1, entry 5). It was also found that the reaction needs to be performed with 3 equivs. **2a** and in the absence of oxygen (Table 1, entry 6 and 7).

Further experiments revealed that a reduction of the amount of CuI from 10 mol% to 5 mol% and 1 mol%, respectively, led to a decrease of the yield of **3a** from 71% to 39% and 21%, respectively (Table 1, entry 5 and Table 2, entry 1 and 2). Apart from

Table 2 The influence of different Cu-sources on the outcome of the reaction of **1a** with **2a**[a,b]



Entry	Cu-source (mol%)	**3a** Yield (%)
1	CuI; 5	39
2	CuI; 1	21
3	CuBr; 10	54
4	CuCl; 10	61
5	$CuOTf(MeCN)_4$; 10	29
6	$Cu(OAc)_2$; 10	23
7	Cu_2O; 10	35
8	—	—

[a] All reactions were performed using 0.5 mmol of **1a** and 1.5 mmol of **2a** in a sealed vial. [b] On the TLC traces of a side product with a higher R_f-value than **3a** was observed.

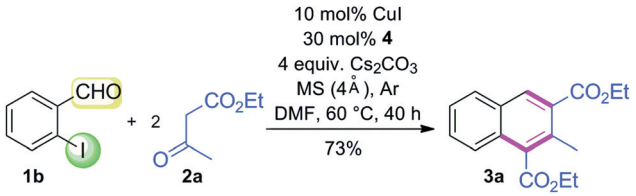
Table 3 The influence of different bases and solvents on the Cu(I)-catalyzed reaction of **1a** with **2a**[a,b]

Entry	Base (4 equiv.)	Solvent	**3a** Yield (%)
1	K_3PO_4	DMF	61
2	K_2CO_3	DMF	26
3	Cs_2CO_3	NMP	32
4	Cs_2CO_3	MeCN	51
5	Cs_2CO_3	THF	38
6	Cs_2CO_3	*iso*-PrOH	9

[a] All reactions were performed using 0.5 mmol of **1a** and 1.5 mmol of **2a** in a sealed vial. [b] On the TLC traces of a side product with a higher R_f-value than **3a** was observed.

CuI, a number of other Cu compounds were tried as catalysts. It was found that the reaction of **1a** with **2a** using 10 mol% of CuBr or 10 mol% of CuCl as catalysts also resulted in the selective formation of **3a** in 54% and 61% yield, respectively (Table 2, entry 3 and 4). However, the yields were lower than with CuI and the same holds true for the use of $CuOTf(MeCN)_4$, Cu_2O and $Cu(OAc)_2$ as catalysts (Table 2, entry 5–7). It should be noted that in the absence of any Cu-source no formation of **3a** was observed (Table 2, entry 8).

Finally, the influence of different bases and solvents on the Cu (I)-catalyzed reaction of **1a** with **2a** was studied. It was found that the reaction using 4 equiv. of K_3PO_4 as a base selectively delivered the product **3a** in 61% yield (Table 3, entry 1). Even with K_2CO_3 as a base the reaction took place, but the yield of **3a** amounted to only 26% (Table 3, entry 2). Further experiments



Scheme 4 *o*-Iodobenzaldehyde (**1b**) as substrate for the synthesis of naphthalene **3a**.

revealed that the model reaction of **1a** with **2a** could also be performed in other solvents than DMF, but only at the cost of lower yields of **3a** (Table 3, entry 3–6).

The optimization of the model reaction of **1a** and **2a** with regard to the Cu-source, the base, the additive, the solvent and the reaction conditions clearly demonstrated that the highest yield of **3a** was obtained when 1 equiv. of **1a** and 3 equivs. of **2a** were reacted in the presence of 10 mol% CuI, 30 mol% 2-picolinic acid (**4**) and 4 equivs. Cs_2CO_3 in DMF at 60 °C for 40 h using molecular sieves (4 Å) as a drying agent.

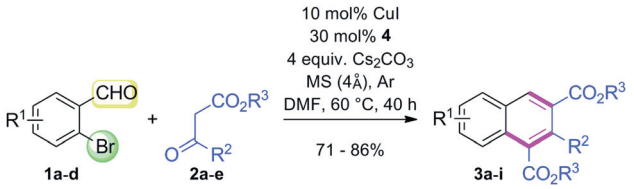
It was also studied whether the annulation can be performed using *o*-iodobenzaldehyde (**1b**) and *o*-chlorobenzaldehyde (**1c**) as the substrates. For this purpose, the reaction between *o*-iodobenzaldehyde (**1b**) and ethyl acetoacetate (**2a**) was performed under the reaction conditions that had proven successful for the reaction of **1a** with **2a**. It turned out that **3a** could be obtained with 73% yield (Scheme 4). Next, *o*-chlorobenzaldehyde (**1c**) was reacted with **2a** under a number of reaction conditions (see ESI†). However, in no case was the formation of **3a** observed. This is in agreement with the fact that, so far, the Cu-catalyzed reaction between chlorobenzene and β-ketoesters has not been achieved.

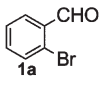
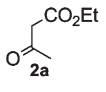
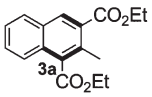
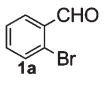
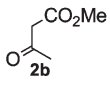
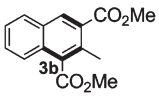
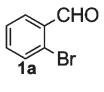
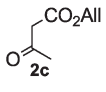
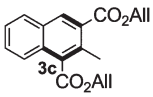
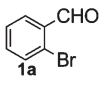
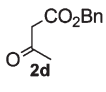
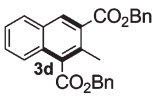
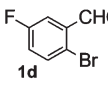
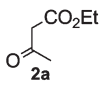
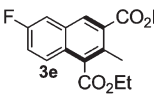
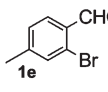
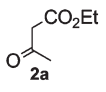
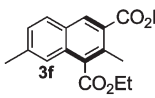
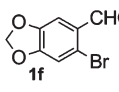
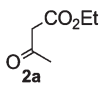
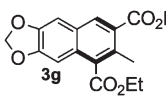
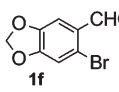
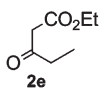
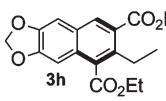
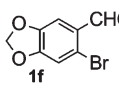
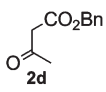
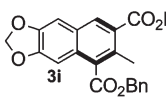
With the optimized reaction conditions the scope of the new three component reaction was investigated. It could be shown that numerous *o*-bromobenzaldehydes **1a,d–f** with different substitution patterns can be reacted with a number of β-ketoesters **2a–d** to produce the corresponding substituted naphthalenes **3a–i** with yields ranging from 71 to 86% (Table 4).

The new process using *o*-bromobenzaldehydes displays a number of advantages over the method using *o*-bromobenzyl bromides as substrates: (i) In contrast to benzyl bromides the corresponding benzaldehydes have no lachrymatory properties, (ii) the reaction temperatures are much lower and the yields of the naphthalenes are higher.

The assignment of each resonance in the ^{13}C NMR spectrum of **3a** as well as the connectivities of the individual ^{1}H spin systems has been carried out by gHSQC and gHMBC (Fig. 1). In the HMBC and ^{13}C NMR spectra for compound **3a** the proton 6-H is correlated with the quaternary carbon C-4a at δ = 130.69 ppm as well as with the tertiary carbon C-8 at δ = 124.28 ppm. The proton 8-H displayed $^{3}J_{CH}$-correlations with the quaternary carbons C-4a at δ = 130.69 ppm and the quaternary carbon C-1 at δ = 133.0 ppm. The proton 12-H is correlated with the quaternary carbon C-1 at δ = 133.0 ppm. The proton 4-H exhibited $^{3}J_{CH}$-correlations with the tertiary carbon C-5 at δ = 129.01 ppm and with the quaternary carbon C-9 at δ = 167.39 ppm. These observations and further analysis of the 1D- and the 2D NMR spectra established the structure of **3a**.

Table 4 The Cu(I)-catalyzed synthesis of naphthalenes **3a–i**[a,b]



Entry	1	2	Product	Yield (%)
1				71
2				73
3				75
4				78
5				73
6				86
7				80
8				81
9				80

[a] All reactions were performed using 0.5 mmol of **1** and 1.5 mmol of **2** in a sealed vial. [b] On the TLC traces of a side product with a higher R_f-value than **3** was observed.

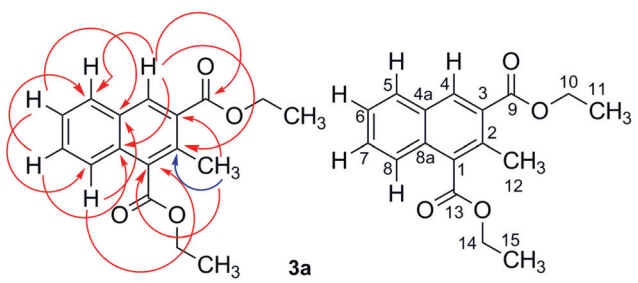


Fig. 1 Important HMBC correlations (H → C) of **3a** (blue arrow: ^2J; red arrows: ^3J).

Conclusions

In conclusion, a simple to execute and efficient one pot synthesis of substituted naphthalenes from easily accessible starting materials has been developed. The Cu(I)-catalyzed reaction of one molecule of an *o*-bromobenzaldehyde with two molecules of a β-ketoester is regarded as a Domino Knoevenagel condensation/*C*-arylation/1,2-addition/carboxylic acid cleavage process which delivers the products selectively and with high yields under mild reaction conditions. *o*-Iodobenzaldehyde can also be used as a substrate for this type of annulation.

Experimental

General remarks

All starting materials were purchased from commercial suppliers (Sigma-Aldrich Chemical Co., Acros Organics, Alfa-Aesar). The *o*-bromobenzaldehydes were used without further purification. All β-ketoesters were freshly distilled over $MgSO_4$ prior to use. All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring. Solvents used in extraction and purification were distilled prior to use. TLC was performed on Alugram SIL G/UV_{254} (Macherey and Nagel). Compounds were visualized with UV light (λ = 254 nm) and/or by immersion in ethanolic vanillin solution followed by heating. Products were purified by flash chromatography on silica gel 60 M, 230–400 mesh (Macherey & Nagel). Melting points were determined on a Büchi melting point apparatus B-545 with open capillary tubes and are not corrected. IR spectra were measured on a Perkin-Elmer Spectrum One FT-IR-spectrometer. UV/VIS spectra were recorded with a Varian Cary 50. ^{1}H (^{13}C) NMR spectra were recorded at 300 (75) MHz on a Varian ^{Unity}Inova spectrometer using $CDCl_3$ as solvent. The ^{1}H and ^{13}C chemical shifts were referenced to residual solvent signals at $\delta_{H/C}$ 7.26/77.00 ($CDCl_3$) relative to TMS as internal standards. HSQC-, HMBC- and COSY-spectra were recorded on a Varian ^{Unity}Inova at 300 MHz. Coupling constants *J* [Hz] were directly taken from the spectra and are not averaged.

General procedure for the Cu(I)-catalyzed synthesis of naphthalenes 3a–i

An oven dried 10 mL vial was charged successively with 9.5 mg (0.05 mmol) CuI (99.999%), 18.6 mg (0.15 mmol) 2-picolinic acid (99%) (**4**), 652 mg (2.0 mmol) Cs_2CO_3 (99.9%), 0.5 mmol of an *o*-bromobenzaldehyde **1** and 160 mg molecular sieves (4 Å). The vial was sealed, evacuated and backfilled with argon (six times). Then, 1.5 mmol freshly distilled β-ketoester **2** and 3 mL of freshly distilled DMF were added using a syringe. The reaction mixture was heated in an oil bath at 60 °C for 40 h and the reaction was monitored by TLC (PE–EtOAc = 5 : 1). After cooling to room temperature the reaction mixture was partitioned between 50 mL ethyl acetate and 20 mL brine. The aqueous phase was extracted with ethyl acetate (2 × 40 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue thus obtained was purified by flash column chromatography over silica gel (PE–EtOAc = 20 : 1).

Spectral data for naphthalenes 3a–i

Diethyl-2-methylnaphthalene-1,3-dicarboxylate (3a). (a) According to the general procedure, 92.5 mg (0.5 mmol) *o*-bromobenzaldehyde (**1a**) and 195 mg (1.5 mmol) ethyl acetoacetate (**2a**) were reacted to afford 102 mg (71%) diethyl-2-methylnaphthalene-1,3-dicarboxylate (**3a**) after column chromatography as a colourless oil. (b) According to the general procedure 116.0 mg (0.5 mmol) *o*-iodobenzaldehyde (**1b**) and 195 mg (1.5 mmol) ethyl acetoacetate (**2a**) were reacted to afford 104 mg (73%) diethyl-2-methylnaphthalene-1,3-dicarboxylate (**3a**) after column chromatography as a colourless oil. R_f = 0.43 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 3100 (w; CH_2, CH_3), 1708 (s; C═O), 1379 (m; alkane C–H), 1297 (m; ester C–O), 1226 (s; ester C–O), 1046 (s), 1012 (m), 960 (m), 895 (m; arom. C–H), 850 (m; arom. C–H), 784 (s), 752 (s; alkane C–H), 735 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (log ε) = 233 (4.69), 282 (3.66), 335 nm (2.58); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (t, ^3J (10-H, 11-H) = 6.9 Hz, 3H; 11-H_3), 1.46 (t, ^3J (14-H, 15-H) = 6.9 Hz, 3H; 15-H_3), 2.67 (s, 3H; 12-H_3), 4.42 (q, ^3J (10-H, 11-H) = 7.1 Hz, 2H; 10-H_2), 4.55 (q, ^3J (14-H, 15-H) = 7.2 Hz, 2H; 14-H_2), 7.50 (ddd, ^3J (6-H, 7-H) = 6.8 Hz, ^3J (5-H, 6-H) = 7.9 Hz, ^4J (6-H, 8-H) = 1.2 Hz, 1H; 6-H), 7.60 (ddd, ^3J (6-H, 7-H) = 6.9 Hz, ^3J (7-H, 8-H) = 6.9 Hz, ^4J (5-H, 7-H) = 1.4 Hz, 1H; 7-H), 7.72 (d, ^3J (7-H, 8-H) = 6.9 Hz, 1H; 8-H), 7.89 (br d, ^3J (5-H, 6-H) = 8.3 Hz, 1H; 5-H), 8.45 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.33 (C-11 and C-15), 18.43 (C-12), 61.2 (C-10), 61.6 (C-14), 124.28 (C-8), 126.28 (C-6), 129.0 (C-3), 129.01 (C-5), 129.04 (C-7), 130.69 (C-4a), 131.10 (C-8a), 132.05 (C-2), 132.63 (C-4), 133.0 (C-1), 167.39 (C-9), 169.59 ppm (C-13); MS (EI, 70 eV): *m*/*z* (%) = 287 (14) $[M + 1]^+$, 286 (100) $[M^+]$, 257 (14) $[C_{16}H_{17}O_3]^+$, 241 $[C_{16}H_{17}O_2]^+$, 229 (32) $[C_{15}H_{17}O_2]^+$, 212 (63) $[C_{15}H_{16}O]^+$, 184 (24) $[C_{14}H_{16}]^+$, 139 (22) $[C_{11}H_7]^+$, 115 $[C_9H_5]^+$; HRMS (EI, M^+) calculated for $C_{17}H_{18}O_4$: 286.1205; found: 286.1177.

Dimethyl-2-methylnaphthalene-1,3-dicarboxylate (3b). According to the general procedure, 92.5 mg (0.5 mmol) *o*-bromobenzaldehyde (**1a**) and 174 mg (1.5 mmol) methyl acetoacetate (**2b**) were reacted to afford 94 mg (73%) dimethyl-2-methylnaphthalene-1,3-dicarboxylate (**3b**) after column chromatography as a colourless oil. R_f = 0.49 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 3100 (w; CH_3), 1712 (s; C═O), 1381 (m; alkane C–H), 1297 (m; ester C–O), 1240 (s; ester C–O), 1046 (s), 965 (m), 878 (m; arom. C–H), 855 (m; arom. C–H), 763 (s), 751 (s; alkane C–H), 735 cm^{-1} (w); UV/Vis (CH_3CN): λ_{max} (log ε) = 234 (4.47), 282 nm (3.47); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 (s, 3H; 11-H_3), 3.96 (s, 3H; 10-H_3), 4.06 (s, 3H; 13-H_3), 7.54 (ddd, ^3J (6-H, 7-H) = 6.9 Hz, ^3J (5-H, 6-H) = 8.0 Hz, ^4J (6-H, 8-H) = 1.2 Hz, 1H; 6-H), 7.64 (ddd, ^3J (6-H, 7-H) = 7.0 Hz, ^3J (7-H, 8-H) = 7.1 Hz, ^4J (5-H, 7-H) = 1.4 Hz, 1H; 7-H), 7.73 (d, ^3J (7-H, 8-H) = 6.9 Hz, 1H; 8-H), 7.89 (br d, ^3J (5-H, 6-H) = 8.3 Hz, 1H; 5-H), 8.48 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.57 (C-11), 52.23 (C-10), 52.48 (C-13), 124.34 (C-8), 126.37 (C-6), 128.47 (C-3), 129.08 (C-5), 129.17 (C-7), 130.66 (C-4a), 131.20 (C-8a), 132.37 (C-2), 132.84 (C-4), 133.01 (C-1), 167.70 (C-9), 170.04 ppm (C-12); MS (EI, 70 eV): *m*/*z* (%) = 259 (14) $[M + 1]^+$, 258 (100) $[M^+]$, 257 (14) $[M - 1]^+$, 243 (14) $[M - CH_3]^+$, 227 (78) $[M - CO]^+$, 211 (10), 198 (72), 169 (15), 139 (28) $[C_{11}H_7]^+$, 128 (10), 98 (10); HRMS (EI, M^+) calculated for $C_{15}H_{14}O_4$: 258.0892; found: 258.0900.

Diallyl-2-methylnaphthalene-1,3-dicarboxylate (3c). According to the general procedure, 92.5 mg (0.5 mmol) *o*-bromobenzaldehyde (**1a**) and 213 mg (1.5 mmol) allyl acetoacetate (**2c**) were reacted to afford 117 mg (75%) diallyl-2-methylnaphthalene-1,3-dicarboxylate (**3c**) after column chromatography as a colourless oil. R_f = 0.40 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 2943 (w; CH_2, CH_3), 1716 (s; C═O), 1467 (m), 1438 (m), 1392 (w; alkane C–H), 1297 (m; ester C–O), 1228 (s; ester C–O), 1213 (s; ester C–O), 1046 (m), 1067 (m), 1045 (m), 991 (s), 938 (s; arom. C–H), 919 (s; arom. C–H) (s), 783 (s), 749 (s; alkane C–H) (s), 730 cm^{-1} (m); UV/Vis (CH_3CN): λ_{max} (log ε) = 235 (4.75), 282 (3.72), 334 nm (2.62); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.67 (s, 3H; 13-H_3), 4.87 (ddd, ^2J (10-H, 10-H) = 1.6 Hz, ^3J (10-H, 11-H) = 5.7 Hz, ^4J (10-H, 12-H) = 1.3 Hz, 2H; 10-H_2), 4.98 (ddd, ^2J (15-H, 15-H) = 1.6 Hz, ^3J (15-H, 16-H) = 6.0 Hz, ^4J (15-H, 17-H) = 1.2 Hz, 2H; 15-H_2), 5.33 (ddt, ^2J (12a-H, 12b-H) = 1.4 Hz, $^3J_{cis}$ (11-H, 12b-H) = 10.4 Hz, ^4J (10-H, 12b-H) = 1.4 Hz, 1H; 12b-H), 5.35 (ddt, ^2J (17a-H, 17b-H) = 1.4 Hz, $^3J_{cis}$ (16-H, 17b-H) = 10.7 Hz, ^4J (15-H, 17b-H) = 1.2 Hz, 1H; 17b-H), 5.45 (ddt, ^2J (12a-H, 12b-H) = 1.4 Hz, $^3J_{trans}$ (11-H, 12a-H) = 17.4 Hz, ^4J (10-H, 12a-H) = 1.4 Hz, 1H; 12a-H), 5.47 (ddt, ^2J (17a-H, 17b-H) = 1.4 Hz, $^3J_{trans}$ (16-H, 17a-H) = 17.2 Hz, ^4J (15-H, 17a-H) = 1.4 Hz, 1H; 17a-H), 6.06 (m, 1H; 11-H), 6.11 (m, 1H; 16-H), 7.51 (ddd, ^3J (6-H, 7-H) = 6.9 Hz, ^3J (5-H, 6-H) = 7.7 Hz, ^4J (6-H, 8-H) = 1.3 Hz, 1H; 6-H), 7.60 (ddd, ^3J (6-H, 7-H) = 6.9 Hz, ^3J (7-H, 8-H) = 8.4 Hz, ^4J (5-H, 7-H) = 1.5 Hz, 1H; 7-H), 7.73 (br d, ^3J (7-H, 8-H) = 8.1 Hz, 1H; 8-H), 7.90 (br d, ^3J (5-H, 6-H) = 8.1 Hz, 1H; 5-H), 8.50 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.55 (C-13), 65.85 (C-10), 66.21 (C-15), 118.67 (C-12), 119.65 (C-17), 124.31 (C-8), 126.36 (C-6), 128.51 (C-3), 129.1 (C-5), 129.18 (C-7), 130.67 (C-4a), 131.22 (C-8a), 131.56 (C-16), 132.08 (C-11), 132.35 (C-2), 132.73 (C-1), 132.98 (C-4), 166.88 (C-9), 169.21 ppm (C-14); MS (EI, 70 eV): *m*/*z* (%) = 311 (7) $[M + 1]^+$, 310 (36) $[M^+]$, 269 (52) $[C_{16}H_{13}O_4]^+$, 253 (64) $[C_{16}H_{13}O_3]^+$, 227 (84) $[C_{14}H_{11}O_3]^+$, 211 (72) $[C_{14}H_{11}O_2]^+$, 181 (64) $[C_{13}H_9O]^+$, 139 (100) $[C_{11}H_7]^+$, 115 (24) $[C_9H_7]^+$; HRMS (EI, M^+) calculated for $C_{19}H_{18}O_4$: 310.1206; found: 310.1197.

Dibenzyl-2-methylnaphthalene-1,3-dicarboxylate (3d). According to the general procedure, 92.5 mg (0.5 mmol) *o*-bromobenzaldehyde (**1a**) and 288 mg (1.5 mmol) benzyl acetoacetate (**2d**) were reacted to afford 160 mg (78%) dibenzyl-2-methylnaphthalene-1,3-dicarboxylate (**3d**) after column chromatography as a colourless oil. R_f = 0.41 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 3031 (w; CH_2, CH_3), 2955 (w; CH_2, CH_3), 1712 (s; C═O), 1497 (m), 1455 (m), 1358 (m; alkane C–H), 1296 (m; ester C–O), 1196 (s; ester C–O), 1139 (s; ester C–O), 1062 (m), 1042 (m), 1027 (m), 973 (m; arom. C–H), 909 (m; arom. C–H), 789 (m), 747 (s; alkane C–H), 696 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (log ε) = 235 nm (4.32); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.63 (s, 3H; 17-H_3), 5.40 (s, 2H; 10-H_2), 5.52 (s, 2H; 19-H_2), 7.47 (overlapped, 1H; 6-H), 7.50–7.53 (overlapped, 10H; 12-H, 12′-H, 13-H, 13′-H, 14-H, 14′-H, 15-H, 15′-H, 16-H and 16′-H), 7.54 (ddd, ^3J (6-H, 7-H) = 6.9 Hz, ^3J (7-H, 8-H) = 8.5 Hz, ^4J (5-H, 7-H) = 1.6 Hz, 1H; 7-H), 7.64 (br d, ^3J (7-H, 8-H) = 8.4 Hz,

1H; 8-H), 7.87 (br d, ^3J (5-H, 6-H) = 8.4 Hz, 1H; 5-H), 8.49 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.56 (C-17), 66.97 (C-10), 67.41 (C-19), 124.26 (C-8), 126.32 (C-6), 128.33 (C-12 and C-16), [128.35, 128.40, 128.42, 128.56, 128.66 (overlapped, C-3, C-13, C-13′, C-14, C-14′, C-15, C-15′)], 128.71 (C-12′ and C-16′), 129.09 (C-5), 129.16 (C-7), 130.62 (C-4a), 131.23 (C-8a), 132.39 (C-1), 132.69 (C-2), 133.04 (C-4), 135.29 (C-11′), 135.85 (C-11), 167.01 (C-9), 169.34 ppm (C-18); MS (EI, 70 eV): *m*/*z* (%) = 411 (6) $[M + 1]^+$, 410 (22) $[M^+]$, 319 (78) $[M - C_7H_7]^+$, 310 (57) $[C_{20}H_{13}O_3]^+$, 283 (13) $[C_{20}H_{11}O_2]^+$, 229 (6), 139 (8) $[C_{11}H_7]^+$, 91 (100) $[C_7H_7]^+$; HRMS (EI, M^+) calculated for $C_{27}H_{22}O_4$: 410.1519; found: 410.1541.

Diethyl-6-fluoro-2-methylnaphthalene-1,3-dicarboxylate (3e). According to the general procedure, 101 mg (0.5 mmol) 2-bromo-5-fluorobenzaldehyde (**1d**) and 195 mg (1.5 mmol) ethyl acetoacetate (**2a**) were reacted to afford 112 mg (73%) diethyl-6-fluoro-2-methylnaphthalene-1,3-dicarboxylate (**3e**) after column chromatography as a colourless oil. R_f = 0.45 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 2979 (w; CH_2, CH_3), 1728 (s; C═O), 1713 (s; C═O), 1507 (m), 1479 (m), 1452 (s), 1383 (m; alkane C–H), 1326 (m; alkane C–H), 1282 (m; ester C–O), 1207 (s; ester C–O), 1153 (m), 1129 (m), 1071 (m), 1045 (s), 1013 (m), 914 (m; arom. C–H), 854 (m; arom. C–H), 828 (m), 779 (w; alkane C–H), 769 cm^{-1} (w; alkane C–H); UV/Vis (CH_3CN): λ_{max} (log ε) = 238 (4.68), 231 (4.68), 277 (3.78), 328 nm (3.05); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (t, ^3J (10-H, 11-H) = 7.2 Hz, 3H; 11-H_3), 1.46 (t, ^3J (14-H, 15-H) = 7.2 Hz, 3H; 15-H_3), 2.64 (s, 3H; 12-H_3), 4.43 (q, ^3J (10-H, 11-H) = 7.4 Hz, 2H; 10-H_2), 4.55 (q, ^3J (14-H, 15-H) = 7.4 Hz, 2H; 14-H_2), 7.36 (ddd, ^3J (7-H, 8-H) = 9.3 Hz, ^3J (6-F, 7-H) = 8.3 Hz, ^4J (5-H, 7-H) = 2.5 Hz, 1H; 7-H), 7.51 (dd, ^3J (5-H, 6-F) = 9.1 Hz, ^4J (5-H, 7-H) = 2.6 Hz, 1H; 5-H), 7.73 (dd, ^3J (7-H, 8-H) = 9.4 Hz, ^4J (6-F, 8-H) = 5.5 Hz, 1H; 8-H), 8.36 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3 (C-11 and C-15), 18.28 (C-12), 61.35 (C-10), 61.74 (C-14), 112.0 (d, ^2J (C-5, 6-F) = 19.8 Hz, C-5), 119.3 (d, ^2J (C-7, 6-F) = 25.2 Hz, C-7), 126.96 (d, ^3J (C-8, 6-F) = 8.9 Hz, C-8), 128.1 (d, ^4J (C-8a, 6-F) = 1.0 Hz, C-8a), 130.26 (C-3), 131.37 (C-2), 131.51 (C-4a), 131.60 (C-4), 133.1 (br s, C-1), 160.55 (d, *J* (C-6, 6-F) = 247.9 Hz, C-6), 167.17 (C-9), 169.27 ppm (C-13); MS (EI, 70 eV): *m*/*z* (%) = 305 (14) $[M + 1]^+$, 304 (92) $[M^+]$, 276 (12) $[M - CO]^+$, 259 (71), 248 (48), 230 (100), 202 (42), 157 (25), 146 (12), 133 (5); HRMS (EI, M^+) calculated for $C_{17}H_{17}FO_4$: 304.1111; found: 304.1109.

Diethyl-7-methyl-2-methylnaphthalene-1,3-dicarboxylate (3f). According to the general procedure, 99.5 mg (0.5 mmol) 2-bromo-4-methylbenzaldehyde (**1e**) and 195 mg (1.5 mmol) ethyl acetoacetate (**2a**) were reacted to afford 128 mg (86%) diethyl-7-methyl-2-methylnaphthalene-1,3-dicarboxylate (**3f**) after column chromatography as a colourless oil. R_f = 0.44 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 2900 (w; CH_2, CH_3), 2150 (m), 1705 (s; C═O), 1650 (w), 1440 (m; alkane C–H), 1300 (m; ester C–O), 1235 (s; ester C–O), 1200 (s), 1196 (s), 1180 (s), 1170 (m), 1040 (m), 1031 (s), 813 (m; arom. C–H), 780 cm^{-1} (s; alkane C–H); UV/Vis (CH_3CN): λ_{max} (log ε) = 242 (4.52), 273 nm (4.47); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (t, ^3J (10-H, 11-H) = 7.0 Hz, 3H; 11-H_3), 1.46 (t, ^3J (14-H, 15-H) = 6.9 Hz, 3H; 15-H_3), 2.52 (s, 3H; 16-H_3), 2.65 (s, 3H; 12-H_3), 4.43 (q, ^3J (10-H, 11-H) = 7.1 Hz, 2H; 10-H_2), 4.57 (q, ^3J (14-H, 15-H) = 7.2 Hz, 2H; 14-H_2), 7.33 (dd, ^3J (5-H, 6-H) = 7.9 Hz, ^4J (6-H, 8-H) = 1.3 Hz, 1H; 6-H), 7.46 (s, 1H; 8-H), 7.75 (d, ^3J (5-H, 6-H) = 7.9 Hz, 1H; 5-H), 8.42 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.33 (C-11 and C-15), 18.48 (C-12), 22.2 (C-16), 61.1 (C-10), 61.5 (C-14), 123.28 (C-7), 127.9 (C-8), 128.6 (C-5), 128.9 (C-6), 129.0 (C-3), 131.34 (C-4a), 132.1 (C-8a), 132.4 (C-2), 132.5 (C-4), 139.3 (C-1), 167.46 (C-9), 169.8 ppm (C-13); MS (EI, 70 eV): *m*/*z* (%) = 301 (18) $[M + 1]^+$, 300 (98) $[M^+]$, 286 (4) $[C_{17}H_{18}O_4]^+$, 271 (11) $[C_{16}H_{15}O_4]^+$, 255 (95) $[C_{17}H_{19}O_2]^+$, 253 (42) $[C_{16}H_{13}O_3]^+$, 226 (100) $[C_{15}H_{17}O_2]^+$, 198 (42), 153 (16), 115 (7) $[C_9H_5]^+$; HRMS (EI, M^+) calculated for $C_{18}H_{20}O_4$: 300.1362; found: 300.1383.

Diethyl-2-methyl-6,7-methylenedioxy-naphthalene-1,3-dicarboxylate (3g). According to the general procedure, 114 mg (0.5 mmol) 2-bromo-4,5-methylenedioxybenzaldehyde (**1f**) and 195 mg (1.5 mmol) ethyl acetoacetate (**2a**) were reacted to afford 133 mg (80%) diethyl-2-methyl-6,7-methylenedioxy-naphthalene-1,3-dicarboxylate (**3g**) after column chromatography as a colourless oil. R_f = 0.42 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 2963 (w; CH_2, CH_3), 2906 (w; CH_2, CH_3), 1704 (s; C═O), 1490 (m), 1458 (m), 1366 (w; alkane C–H), 1243 (s; ester C–O), 1204 (s; ester C–O), 1076 (m), 1035 (s), 943 (m; arom. C–H), 925 (m; arom. C–H), 803 (s; alkane C–H), 696 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (log ε) = 290 (3.82), 331 nm (3.07); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (t, ^3J (10-H, 11-H) = 7.1 Hz, 3H; 11-H_3), 1.44 (t, ^3J (14-H, 15-H) = 7.0 Hz, 3H; 15-H_3), 2.61 (s, 3H; 12-H_3), 4.39 (q, ^3J (10-H, 11-H) = 7.1 Hz, 2H; 10-H_2), 4.52 (q, ^3J (14-H, 15-H) = 7.1 Hz, 2H; 14-H_2), 6.07 (s, 2H; 16-H_2), 7.01 (s, 1H; 8-H), 7.14 (s, 1H; 5-H), 8.27 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.33 (C-11 and C-15), 18.32 (C-12), 61.03 (C-10), 61.59 (C-14), 100.9 (C-8), 101.58 (C-16), 104.68 (C-5), 127.19 (C-3), 127.91 (C-4a), 128.89 (C-8a), 130.99 (C-2), 131.47 (C-4), 132.39 (C-1), 147.81 (C-6), 150.29 (C-7), 167.44 (C-9), 169.77 ppm (C-13); MS (EI, 70 eV): *m*/*z* (%) = 331 (16) $[M + 1]^+$, 330 (88) $[M^+]$, 301 (7) $[M - Et]^+$, 285 (62) $[C_{16}H_{13}O_5]^+$, 273 (82) $[C_{15}H_{13}O_5]^+$, 256 (100) $[C_{15}H_{12}O_4]^+$, 228 (44) $[C_{14}H_{12}O_3]^+$, 199 (20) $[C_{13}H_{11}O_2]^+$, 184 (30) $[C_{12}H_8O_2]^+$, 171 (11), 143 (10), 126 (22), 115 (24) $[C_9H_7]^+$, 77 (10) $[C_6H_5]^+$; HRMS (EI, M^+) calculated for $C_{18}H_{18}O_6$: 330.1103; found: 330.1092.

Diethyl-2-ethyl-6,7-methylenedioxy-naphthalene-1,3-dicarboxylate (3h). According to the general procedure, 114 mg (0.5 mmol) 2-bromo-4,5-methylenedioxybenzaldehyde (**1f**) and 216 mg (1.5 mmol) ethyl propionylacetate (**2e**) were reacted to afford 139 mg (81%) diethyl-2-ethyl-6,7-methylenedioxy-naphthalene-1,3-dicarboxylate (**3h**) after column chromatography as a colourless oil. R_f = 0.43 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 2979 (w; CH_2, CH_3), 2904 (w; CH_2, CH_3), 1713 (s; C═O), 1497 (m), 1503 (m), 1479 (s), 1462 (s), 1368 (m; alkane C–H), 1242 (s; ester C–O), 1196 (s; ester C–O), 1070 (m), 1035 (s), 932 (m; arom. C–H), 861 (m; arom. C–H), 808 (m), 766 cm^{-1} (w; alkane C–H); UV/Vis (CH_3CN): λ_{max} (log ε) = 248 (4.29), 291 nm (3.73); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.26 (t, ^3J (12-H, 13-H) = 7.5 Hz, 3H; 13-H_3), 1.43 (t, ^3J (10-H, 11-H) = 7.2 Hz, 3H; 11-H_3), 1.45 (t, ^3J (15-H, 16-H) = 7.1 Hz, 3H; 16-H_3), 3.04 (t, ^3J (12-H, 13-H) = 7.5 Hz, 2H; 12-H_2), 4.39

(q, ^3J (10-H, 11-H) = 7.1 Hz, 2H; 10-H_2), 4.53 (q, ^3J (15-H, 16-H) = 7.1 Hz, 2H; 15-H_2), 6.07 (s, 2H; 17-H_2), 6.99 (s, 1H; 8-H), 7.14 (s, 1H; 5-H), 8.26 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.29 (C-11 and C-16), 16.10 (C-13), 25.06 (C-12), 61.06 (C-10), 61.55 (C-15), 100.92 (C-8), 101.55 (C-17), 104.62 (C-5), 126.65 (C-3), 127.98 (C-4a), 128.92 (C-8a), 131.84 (C-2), 131.94 (C-4), 136.90 (C-1), 147.85 (C-6), 150.21 (C-7), 167.42 (C-9), 169.72 ppm (C-14); MS (EI, 70 eV): *m*/*z* (%) = 345 (18) $[M + 1]^+$, 344 (100) $[M^+]$, 315 (32) $[M - Et]^+$, 299 (38) $[C_{17}H_{15}O_5]^+$, 287 (42), 270 (44), 213 (12), 175 (44), 135 (26), 115 (24) $[C_9H_7]^+$; HRMS (EI, M^+) calculated for $C_{19}H_{20}O_6$: 344.1259; found: 344.1286.

Dibenzyl-2-methyl-6,7-methylenedioxy-naphthalene-1,3-dicarboxylate (3i). According to the general procedure, 114 mg (0.5 mmol) 2-bromo-4,5-methylenedioxybenzaldehyde (**1f**) and 288 mg (1.5 mmol) benzyl acetoacetate (**2d**) were reacted to afford 183 mg (80%) dibenzyl-2-methyl-6,7-methylenedioxy-naphthalene-1,3-dicarboxylate (**3i**) after column chromatography as a pale yellow solid. M.p. = 151–152 °C; R_f = 0.40 (PE–EtOAc = 5 : 1); IR (ATR): $\tilde{\nu}$ = 1710 (s; C═O), 1497 (m), 1463 (m), 1316 (m; alkane C–H), 1270 (m; ester C–O), 1247 (s; ester C–O), 1203 (s; ester C–O), 1073 (m), 1032 (s), 938 (m; arom. C–H), 914 (m; arom. C–H), 849 (m), 753 (s; alkane C–H), 701 cm^{-1} (s); UV/Vis (CH_3CN): λ_{max} (log ε) = 250 (4.54), 293 nm (3.70); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.57 (s, 3H; 17-H_3), 5.37 (s, 2H; 10-H_2), 5.48 (s, 2H; 19-H_2), 6.05 (s, 2H; 20-H_2), 6.91 (s, 1H; 8-H), 7.11 (s, 1H; 5-H), 7.32–7.50 (overlapped, 10H; 12-H, 12′-H, 13-H, 13′-H, 14-H, 14′-H, 15-H, 15′-H, 16-H and 16′-H), 8.30 (s, 1H; 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.45 (C-17), 66.82 (C-10), 67.43 (C-19), 100.84 (C-8), 101.59 (C-20), 104.69 (C-5), 126.58 (C-3), 127.85 (C-4a), 128.30 (C-12 and C-16), [128.30, 128.59, 128.68, 128.69 (overlapped, C-13, C-13′, C-14, C-14′, C-15, C-15′, C-16 and C-16′)], 128.74 (C-12′ and C-16′), 129.09 (C-8a), 131.33 (C-2), 131.84 (C-4), 132.03 (C-1), 135.24 (C-11), 135.97 (C-11′), 147.85 (C-6), 150.41 (C-7), 167.05 (C-9), 169.53 ppm (C-18); MS (EI, 70 eV): *m*/*z* (%) = 455 (3) $[M + 1]^+$, 454 (10) $[M^+]$, 363 (93) $[M - C_7H_7]^+$, 345 (5) $[C_{21}H_{13}O_5]^+$, 327 (2) $[C_{20}H_{13}O_4]^+$, 273 (3), 213 (2), 184 (3), 126 (3), 91 (70) $[C_7H_7]^+$; HRMS (EI, M^+) calculated for $C_{28}H_{22}O_6$: 454.1428; found: 454.1433.

Acknowledgements

We thank Dr. J. Conrad for NMR spectra and Dr. A. Baskakova for mass spectra.

Notes and references

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