Cyclization of (2-Alkenylphenyl)carbonyl Compounds to Polycyclic Arenes Catalyzed by Copper(II) Trifluoromethanesulfonate or Trifluoromethanesulfuric Acid

by **Wei-Min Liu**, **Ya Lin Tnay**, **Kian Ping Gan**, **Zhen-Hong Liu**, **Wan Huei Tyan**, and **Koichi Narasaka***

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore (phone: +65-63168900; e-mail: narasaka@ntu.edu.sg)

Dedicated to Prof. *Dieter Seebach* on the occasion of his 75th birthday

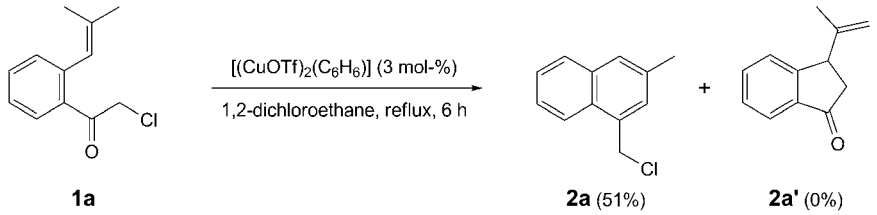
Various polycyclic arenes, such as naphthalenes, tetrahydroantharacenes, tetrahydrotetracenes, dihydropentacenes, and dihydropentaphenes are prepared from 2-alkenylphenyl ketones and aldehydes by the catalytic use of copper(II) trifluoromethanesulfonate ($Cu(OTf)_2$) or trifluoromethanesulfuric acid (TfOH).

Introduction. – Polycyclic aromatic hydrocarbons (polycyclic arenes) are widely employed as building blocks in the synthesis of biologically active compounds in the pharmaceutical industry [1]. In recent years, they have also attracted much attention as useful materials of organic electronic devices [2]. Therefore, many synthetic methods toward polycyclic arenes have been continuously explored [3]. Some extensively studied examples include the *Lewis* acid-catalyzed [4+2] benzannulation of 2-alkenylbenzaldehydes with alkynes [4] and the transition metal-catalyzed [2+2+2] cycloaddition of alkynes [5].

Recently, we reported the cyclization of *N*-alkenyl-*N*-benzoylsulfonamides to pyrrolidines *via N*-radical intermediates by using bis[copper(I)trifluoromethanesulfonate](benzene) complex, $[(CuOTf)_2(C_6H_6)]$, as a redox catalyst [6]. The efficient activity of $[(CuOTf)_2(C_6H_6)]$ prompted us to examine an α-keto radical formation from 2-chloro-1-[2-(2-methylprop-1-en-1-yl)phenyl]ethanone (**1a**) and the successive cyclization to 2,3-dihydro-3-(1-methylethenyl)-1*H*-inden-1-one (**2a′**). However, an unexpected naphthalene, *i.e.*, 1-(chloromethyl)-3-methylnaphthalene (**2a**), was obtained in 51% yield, in which a C–C bond was formed between the C=O C-atom and the Me group (*Scheme 1*).

Even though several transformations of similar 2-alkenylphenyl carbonyl compounds have been reported, including 6π-electrocyclization to 2*H*-pyrans [7], Rh-catalyzed cycloisomerization to indanones [8], and *Lewis* acid-catalyzed *Nazarov*-type cyclization to cyclopentenones [9], the above type of transformation from **1a** to **2a** has been not encountered. Hence, this Cu^I-catalyzed cyclization was studied in detailed. Here, we present a catalytic synthesis of various polycyclic arenes from (2-alkenylphenyl)carbonyl compounds **1**.

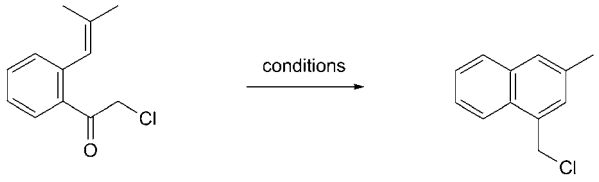
Scheme 1. *Formation of Naphthalene* **2a**



1a **2a** (51%) **2a'** (0%)

Results and Discussion. – As it was assumed that $[(CuOTf)_2(C_6H_6)]$ acts as a *Lewis* acid [10] in this naphthalene formation (*vide infra*), initial studies were aimed at screening the suitable *Lewis* acids as catalysts. As compiled in *Table 1*, $Cu(OTf)_2$ was found to be more effective than $[(CuOTf)_2(C_6H_6)]$ for the cyclization of **1a** to **2a**. Naphthalene **2a** was obtained in 70% yield after 1 h by using 5 mol-% of $Cu(OTf)_2$ in refluxing 1,2-dichloroethane ($ClCH_2CH_2Cl$; *Entry 2*). When other *Lewis* acids, such as $SnCl_4$ and $BF_3 \cdot OEt_2$ were used, the reactions resulted in complex mixtures, and **2a** was isolated in less than 10% yield (*Entries 3* and *4*). In addition, an alternative Cu^{II} catalyst, $Cu(OAc)_2$, could not promote this reaction (*Entry 5*).

Table 1. *Optimization of Reaction Conditions for Synthesis of Naphthalene* **2a**[a])



1a **2a**

Entry	Solvent	Catalyst ([mol-%])	Temp. [°]	Time [h]	Yield [%][b])
1	$ClCH_2CH_2Cl$	$[(CuOTf)_2(C_6H_6)]$ (3)	82	6	51
2	$ClCH_2CH_2Cl$	$Cu(OTf)_2$ (5)	82	1	70
3	$ClCH_2CH_2Cl$	$BF_3 \cdot OEt_2$ (10)	82	1.5	10
4	$ClCH_2CH_2Cl$	$SnCl_4$ (10)	82	1.5	5
5	$ClCH_2CH_2Cl$	$Cu(OAc)_2$ (5)	82	21	[c])
6	$ClCH_2CH_2Cl$	TfOH (5)	82	0.25	52
7	$ClCH_2CH_2Cl$	TfOH (1)	82	1	57
8	Toluene	TfOH (1)	82	1	69
9	$ClCH_2CH_2Cl$	$Cu(OTf)_2$ (5)/4-Å mol. sieves	82	24	[c])

[a]) Reactions were carried out on a scale of 0.2 mmol of **1a** in various solvents (5 ml) under N_2. [b]) Actual yields of **2a**. [c]) Starting material was recovered.

Since it was taken into account that $Cu(OTf)_2$ may work not as a *Lewis* acid but as a source of trifluoromethanesulfonic acid (TfOH) as reported by *Markó* [11], and *Hintermann* and co-workers [12], the latter was employed as a catalyst. Although **2a** was obtained, the product yield was quite inconsistent: the use of an equimolar amount of TfOH gave a very messy mixture. With a catalytic amount of TfOH (5–10 mol-%),

sometimes no reaction was observed, and only a trace amount of naphthalene **2a** was obtained in some cases (*Entry 6*). Finally, TfOH was found to work as a catalyst, if a diluted $ClCH_2CH_2Cl$ solution of TfOH was prepared very freshly [12]. The reaction with such a fresh stock solution of TfOH (*ca.* 1 mol-%) provided **2a** in 57 and 69% yield in $ClCH_2CH_2Cl$ and toluene at 82°, respectively (*Entry 7* and *8*). To further demonstrate the role of TfOH as the active catalyst, the reaction of **1a** with $Cu(OTf)_2$ was conducted in the presence of molecular sieves (4 Å), aiming to trap any TfOH generated from $Cu(OTf)_2$. In fact, the cyclization did not occur, and the starting material **1a** was recovered (*Entry 9*). Hence, the cyclization was catalyzed by TfOH, and $Cu(OTf)_2$ was assumed to act as a source of a trace amount of TfOH.

Because the yield of cyclization varies between moderate to no reaction when using a stock solution of TfOH, we examined the ^{19}F-NMR (282 MHz) spectrum of TfOH in $CDCl_3$. As reported by *Hintermann* and co-workers [12], the initial main sharp signal at −75.87 ppm decreased gradually, and several other signals appeared by keeping the sample tube in an open air. This explains the inconsistency of the cyclization yields when a stock solution is used, and such a phenomenon leading toward erroneous results when using a stock solution of TfOH was also reported by *Hintermann* and co-workers.

Although TfOH was established as the real catalytic species in this cyclization reaction, the use of $Cu(OTf)_2$ was very reliable as the catalyst in the product yield as compared with TfOH in practice. Accordingly, the generality of this catalytic method for the formation of naphthalenes was first screened with 5 mol-% of $Cu(OTf)_2$ in refluxing $ClCH_2CH_2Cl$ (*Table 2*). Not only 2-(2,2-dimethylethenyl)phenyl ketones **1a**–**1e** but also aldehyde **1f** underwent cyclizations to naphthalenes **2a**–**2f** in good yields (60–70%; *Entries 1–6*). In the cyclization of dichloromethyl ketone **1b**, the cyclized product, 1-(dichloromethyl)-3-methylnaphthalene, was further hydrolyzed to 3-methylnaphthalene-1-carbaldehyde (**2b**), which was isolated in 77% yield.

Notably, the cyclization of α-keto ester **1g** also afforded the expected product **2g** in 69% yield (*Entry 7*), whereas, the reaction of β-keto ester **1h** did not give the expected product, ethyl (3-methylnaphthalen-1-yl)acetate (**2h**), but de(ethoxycarbonylated) product **2c** was obtained (*Entry 8*). 3-Bromothiophen-2-yl ketone **1i** was also cyclized to afford naphthalene **2i** in 81% yield (*Entry 9*), whereas thiophenyl ketone **1j** did not give any product by this $Cu(OTf)_2$-catalyzed reaction (*Entry 10*). In addition, 1-oxo-1-(pyridin-2-yl)acetate **1k** did not cyclize to **2k** (*Entry 11*). Presumably, in these cases, the stable complex formation might prevent the generation of TfOH from $Cu(OTf)_2$ (*Entries 10* and *11*).

When one of the Me groups of the vinyl group was replaced with a Ph group, **1l**–**1n**, 3-phenylnaphthalenes **2l**–**2n** were obtained in 80–88% yields, regardless of the (*E*/*Z*)-configuration of the starting materials (*Entries 12–14*). From [(2-cyclohexanylidenemethyl)phenyl]carbonyl compounds, **1o**–**1r**, 1,2,3,4-tetrahydroanthracenes, **2o**–**2r**, were prepared in 60–97% yields (*Entries 15–18*). In contrast to the above cyclization, when aldehyde **1s** bearing cyclobutylidenemethyl group was treated with $Cu(OTf)_2$, a *Nazarov*'s cyclization product, indanone **3**, was obtained in 98% yield within 1 h (*Entry 19*) instead of the naphthalene formation (*vide infra*).

The cyclizations were also conducted by using TfOH as a catalyst. Although the desired products were obtained in good yields as shown in *Table 2* (yields in the parentheses), an extra care must be taken when handling TfOH due to its hygroscopic

Table 2. *Cyclization of 2-(β,β-Disubstituted-vinyl)phenyl Carbonyl Compounds* **1**[a])

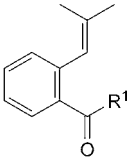
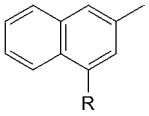
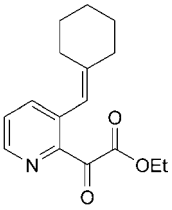
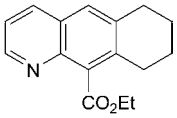
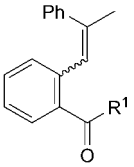
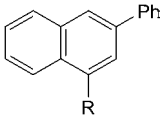
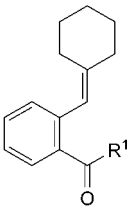
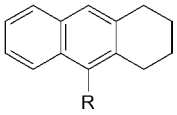
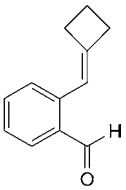
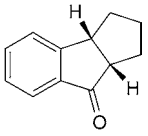
Entry	**1**	Time [h]	**2**	Yield [%][b])
				
1	**1a** $R^1 = CH_2Cl$	1	**2a** $R = CH_2Cl$	70 (52)
2	**1b** $R^1 = CHCl_2$	1	**2b** R = CHO	77
3	**1c** R^1 = Me	40	**2c** R = Me	65 (78)
4	**1d** R^1 = Ph	18	**2d** R = Ph	69 (78)
5	**1e** R^1 = Octyl	60	**2e** R = Octyl	67 (62)
6	**1f** R^1 = H	15	**2f** R = H	60 (64)
7	**1g** $R^1 = CO_2Et$	16	**2g** $R = CO_2Et$	69 (79)
8	**1h** $R^1 = CH_2CO_2Et$	50	**2h** $R = CH_2CO_2Et$[c])	70 (**2c**)[c])
9	**1i** R^1 = 3-Bromothiophen-2-yl	18	**2i** R = 3-Bromothiophen-2-yl	81
10	**1j** R^1 = Thiophen-2-yl	90	**2j** R = Thiophen-2-yl	0[d]) (71)
11	**1k**	18	**2k**	0[d]) (70)[e])
				
				
12	**1l** $R^1 = CH_2Cl$	2.5	**2l** $R = CH_2Cl$	83
13	**1m** R^1 = Me	2.5	**2m** R = Me	88
14	**1n** R^1 = Bn	2.5	**2n** R = Bn	80
				
15	**1o** R^1 = Me	21	**2o** R = Me	77 (70)
16	**1p** R^1 = Bn	17	**2p** R = Bn	63
17	**1q** R^1 = H	1.5	**2q** R = H	60 (52)

Table 2 (cont.)

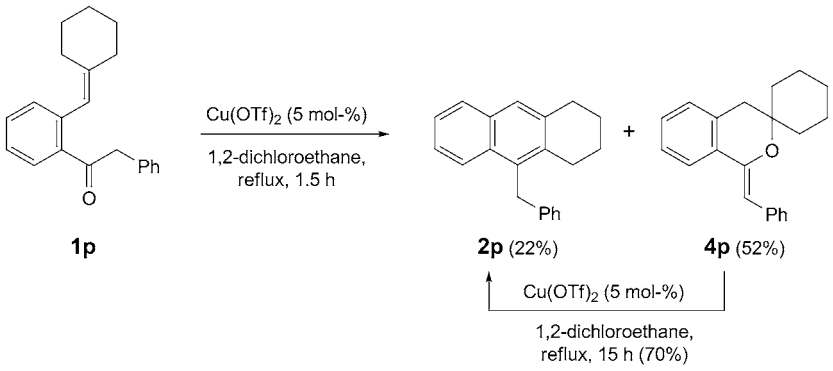
Entry	**1**	Time [h]	**2**	Yield [%][b])
18	**1r** $R^1 = CH_2CO_2Et$	8	**2r** R = Me	97
19	**1s** 	1	**3** 	98

[a]) Reactions were carried out on the scale of 0.3 mmol of **1** in $ClCH_2CH_2Cl$ (8 ml) under N_2. [b]) Actual yields of isolated **2** using $Cu(OTf)_2$, and TfOH in parentheses. [c]) Instead of **2h**, **2c** (R = Me) was obtained. [d]) The starting material was recovered. [e]) 110% of TfOH was used.

nature. Dryness of apparatus and solvents may affect the yields of cyclized products, and TfOH has to be added to mixture at 82° in the case of aldehydes. However, the merits of TfOH appeared in the cyclization of thiophen-2-yl and pyridin-2-yl derivatives, **1j** and **1k**, respectively, with which $Cu(OTf)_2$ might form stable chelate complexes. By the catalytic use of TfOH, 2-methyl-4-(thiophen-2-yl)naphthalene (**2j**) was obtained from thiophen-2-yl **1j**, in 71% yield, and pyridin-2-yl ketone **1k** successfully cyclized to **2k** with a slightly excess amounts of TfOH, in 70% yield (*Entries 10* and *11*).

As shown in *Entry 16* of *Table 2*, the $Cu(OTf)_2$-catalyzed reaction of benzyl ketone **1p** afforded the product in 63% yield after 17 h. If the reaction was stopped when **1p** was consumed (1.5 h), spiro-isochromane derivative **4p** was isolated along with the tetrahydronaphthalene **2p** in 52 and 22% yields, respectively (*Scheme 2*). Moreover, the treatment of **4p** under the same reaction conditions resulted in the formation of 1,2,3,4-tetrahydroantracene **2p** after 15 h in 70% yield. These results indicated that *O*-cyclization products (*cf.* **B** in *Scheme 4*) are presumably one of the intermediates in the formation of **2**, even though such an *O*-cyclization product was not isolated from the

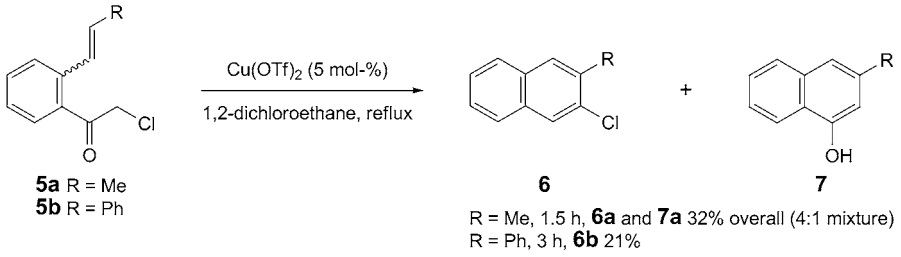
Scheme 2. *Isolation of Isochromane Intermediate* **4**



cyclization of other ketones. The conjugation with Ph group provides stabilization to allow isolation of the isochromane intermediate **4p**.

As shown in *Table 2*, the cyclization of the aryl carbonyl compounds having 2,2-disubstituted vinyl groups proceeded smoothly. However, when 2-(2-monosubstituted-vinyl)phenyl ketones **5** were treated with $Cu(OTf)_2$ under the same reaction conditions, a different type of cyclization was observed to give naphthalenes **6** and **7** (*Scheme 3*), where the cyclization occurred between 2-position of the vinyl group and α-C-atom to the C=O group. Thus, the 6π-electron cyclization of α-keto enoles occurred in the reaction of monosubstituted vinylphenyl ketones **5a** and **5b**.

Scheme 3. *Cyclization of 2-(2-Monosubstituted-vinyl)phenyl Ketones* **5**



5a R = Me
5b R = Ph

6 **7**

R = Me, 1.5 h, **6a** and **7a** 32% overall (4:1 mixture)
R = Ph, 3 h, **6b** 21%

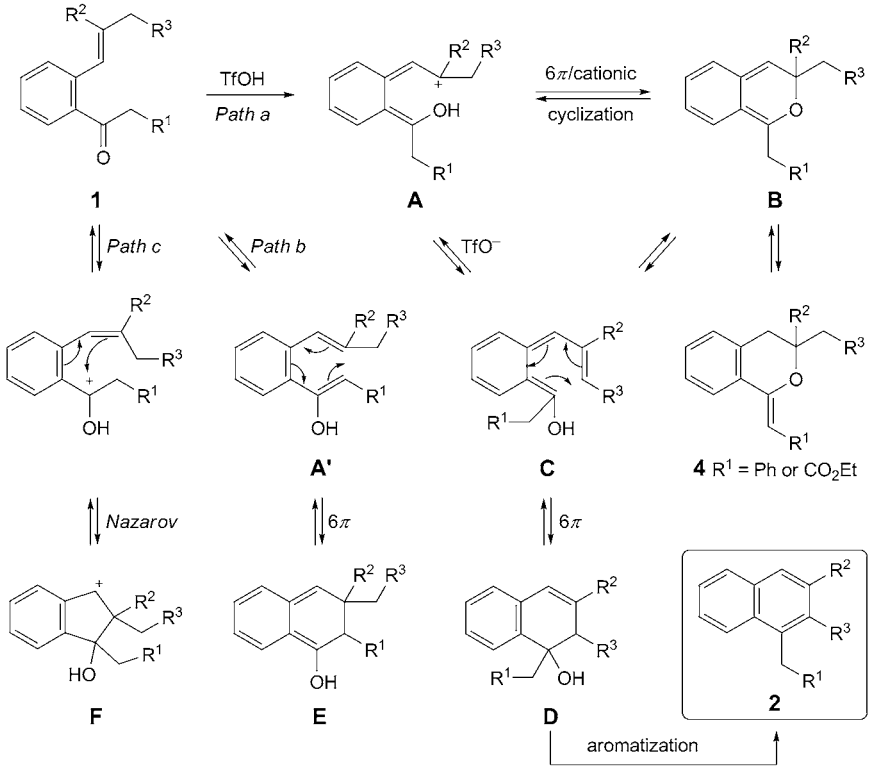
Based on these experimental evidences, a mechanism for the formation of naphthalene **2** is proposed as *Path a* in *Scheme 4*. Protonation of ketone **1** gives hexatriene **C** *via* a stable tertiary carbocation **A**. Hexatriene **C** then undergoes a 6π-electrocyclization [13] to result in dihydronaphthalene **D**, followed by the dehydration to provide naphthalene **2**. For the formation of isochromene **4**, a direct 6π-electrocyclization of **1** or a cationic cyclization [14] of **A** gives isochromene **B**. With the presence of a conjugated group such as Ph group at R^1, isochromene **B** undergoes isomerization to the more stable isochromane **4**. Subsequently, acid-promoted ring opening [15] of **B** occurs to give hexatriene **C**, which then undergoes another 6π-electrocyclization to give dihydronaphthalene **D**.

Although 6π-electrocyclization of the alternative enolate **A′** also gives dihydronaphthalene **E**, the successive aromatization of **E** to a naphthalene product may not proceed due to the geminal disubstituents R^2 and R^3CH_2 (*Path b*). Hence, the equilibrium favors the formation of naphthalene **2** *via Path a*, when 2-(2,2-disubstituted-vinyl)phenyl ketones **1** were used, while 2-(2-monosubstituted-vinyl)phenyl ketones **5** could give naphthalenes **6** and **7** *via Path b*.

According to preceding literatures [9], treatment of similar 2-alkenylbenzaldehydes with *Lewis* acids usually affords *Nazarov* products. However, *Nazarov* products were not obtained in the reactions of **1a**–**1s**, because the cationic intermediate **F** cannot rearrange into stable molecules (*Path c*). Only in the reaction of aldehyde **1s** having a cyclobutane moiety, *Nazarov* cyclization occurs exceptionally as the ring strain provided the driving force for the ring expansion rearrangement to give indanone **3**.

On the whole, due to the 2,2-disubstitution, all these possible cyclizations are under equilibrium, and the dehydration of the intermediate **D** may shift the equilibrium toward the formation of naphthalenes **2** as shown in *Scheme 4*.

Scheme 4. *A Proposed Mechanism from* **1** *to* **2**

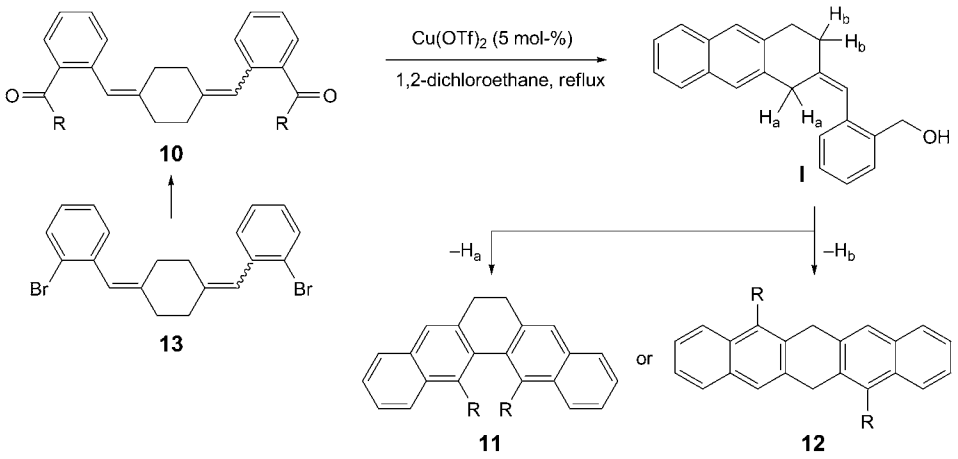


In view of applying this method to synthesize poly-fused arenes, the synthesis of tetra- and pentacyclic derivatives was examined. By employing naphthalene-2-carbaldehyde **8a** and ketone **8b**, tetrahydrotetracenes **9a** and **9b** were synthesized in 68 and 49% yield, respectively (*Scheme 5*). For the synthesis of pentacyclic derivatives, dialdehydes and diketones **10** were prepared as mixtures of *cis*/*trans* isomers and treated with the catalysts (*Table 3*). Although two reaction pathways were assumed to furnish pentaphene **11** and pentacene **12** derivatives, the double cyclization afforded 6,7-dihydropentaphenes **11a**–**11c** selectively in moderate yields from **10a**–**10c** (R = H or alkyl, 52–21%, *Entries 1–3*), whereas 6,13-dihydropentacene **12d** was obtained from **10d** in 19% yield. The X-ray crystal structures of **11c** and **12d** were shown in the *Figure*[1]).

When pure *cis*-**10a** and *trans*-**10a** were isolated, and treated with $Cu(OTf)_2$ separately under the same reaction conditions, only 6,7-dihydropentaphene **11a** was obtained from both stereoisomers. Hence, the dual cyclization proceeds in a stepwise manner, giving intermediate **I**. Then, the competitive deprotonation between H_a and H_b

[1]) CCDC-893291 (**11c**) and -893292 (**12d**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table 3. *Synthesis of 6,7-Dihydropentaphenes* **10**[a])



Entry	**10**	Time [h]	Product	Yield [%][b])
1	**10a** R = H	4	**11a** R = H	52
2	**10b** R = Me	8	**11b** R = Me	40
3	**10c** R = Octyl	12	**11c** R = Octyl	21
4	**10d** R = CO_2Et	24	**12d** R = CO_2Et	19

[a]) Reactions were carried out on the scale of 0.3 mmol of **9** in $ClCH_2CH_2Cl$ (8 ml) under N_2. [b]) Actual yields of isolated **11** or **12**.

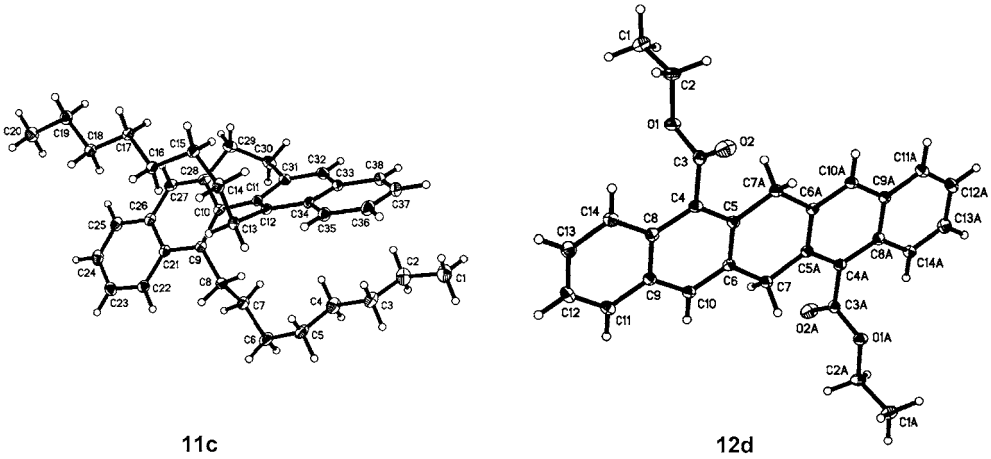
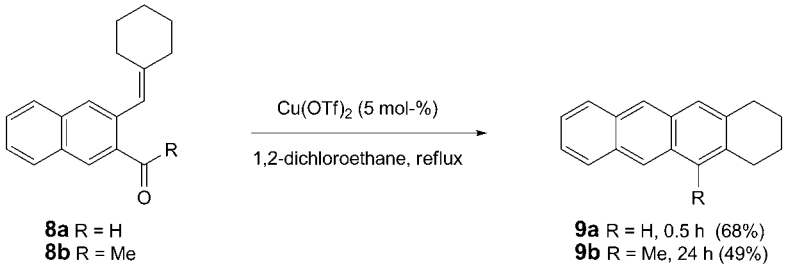


Figure. *X-Ray crystral structures of* **11c** *and* **12d**

controls the formation of non-linear product **11** or linear product **12**. Although the enolization by the deprotonation of H_b is preferable to lead to the formation of dihydropentaphenes **10a**–**10c**, the EtOCO group sterically prevents the cyclization to dihydropentaphene **11d**, to afford an alternative product, dihydropentacene **12d**.

Scheme 5. *Synthesis of Tetrahydrotetracenes* **9**



8a R = H
8b R = Me

9a R = H, 0.5 h (68%)
9b R = Me, 24 h (49%)

Conclusions. – A method for the preparation of various naphthalene derivatives **2** from (2-alkenylphenyl)carbonyl compounds **1** has been disclosed by the catalytic use of $Cu(OTf)_2$ or TfOH. This method is also applicable to the synthesis of various polycyclic arenes, such as tetrahydroanthracenes, tetrahydrotetracenes, dihydropentaphenes, and dihydropentacenes.

Experimental Part

General. All org. solvents used in this study were dried over appropriate drying agents and distilled prior to use. TLC: *Merck 60 F_{254}* pre-coated silica gel plates (SiO_2; 0.2 mm thickness); visualized using UV radiation (254 nm). Flash column chromatography (FC): *Merck* SiO_2 *60* with dist. solvents. M.p.: *Buchi B-54* melting point apparatus; uncorrected. IR Spectra: *Shimazu IR Prestige-21* FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker Avance 500*, *400*, and *300* spectrometers at 500, 400 or 300 MHz and 125, 100 or 75 MHz in $CDCl_3$, resp.; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-ESI-MS: *Finnigan MAT 95 XP* mass spectrometer (*Thermo Electron Corporation*); in *m*/*z*.

Typical Procedure With Cu(OTf)$_2$. $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) was added to a soln. of *2-chloro-1-[2-(2-methylprop-1-en-1-yl)phenyl]ethanone* (**1a**; 62 mg, 0.3 mmol) in $ClCH_2CH_2Cl$ (8 ml) at r.t. The mixture was then heated at reflux at 82°. The reaction was only stopped when the starting material was totally consumed according to TLC analysis. The mixture is then concentrated under reduced pressure, and the crude mixture was purified by FC (AcOEt/hexane 1:50) to give *1-(chloromethyl)-3-methylnaphthalene* (**2a**) in 70% yield as a pale yellow solid.

Typical Procedure With TfOH. TfOH (1.3 µl, 0.015 mmol) was added to a soln. of **1a** (62 mg, 0.3 mmol) in $ClCH_2CH_2Cl$ (8 ml) at 82°. The reaction was only stopped when the starting material was totally consumed according to TLC analysis. The mixture was then concentrated under reduced pressure, and the crude mixture was purified by FC (AcOEt/hexane 1:50) to give **2a** in 52% yield as a pale yellow solid.

Data of **2a**. Yield: 70%. Pale yellow solid. M.p. 41°. R_f (AcOEt/hexane 1:50) 0.40. IR (NaCl, $CHCl_3$): 2974, 2854, 1595, 1448, 844. ^1H-NMR (500 MHz): 8.10 (*d*, *J* = 8.0, 1 H); 7.81 (*d*, *J* = 8.0, 1 H); 7.63 (*s*, 1 H); 7.49–7.56 (*m*, 2 H); 7.39 (*s*, 1 H); 5.03 (*s*, 2 H); 2.51 (*s*, 3 H). ^{13}C-NMR (125 MHz): 134.9; 134.3; 132.8; 130.0; 129.4; 128.7; 128.2; 126.2; 125.9; 123.5; 44.6; 21.5. HR-ESI-MS: 191.0629 ($[M+H]^+$, $C_{12}H_{12}{}^{35}Cl^+$; calc. 191.0628).

3-Methylnaphthalene-1-carbaldehyde (**2b**). Yield: 77%. Yellow oil. R_f (AcOEt/hexane 1:50) 0.26. IR (NaCl, neat): 2974, 2252, 1689, 1384, 906, 732. ^1H-NMR (400 MHz): 10.37 (*s*, 1 H); 9.19 (*d*, *J* = 8.4, 1 H); 7.84–7.88 (*m*, 3 H); 7.58–7.64 (*m*, 2 H); 2.61 (*s*, 3 H). ^{13}C-NMR (100 MHz): 193.5; 138.8; 134.6; 134.3; 134.2; 131.3; 128.9; 128.1; 127.8; 126.9; 124.6; 21.2. HR-ESI-MS: 171.0804 ($[M+H]^+$, $C_{12}H_{11}O^+$; calc. 171.0810).

1,3-Dimethylnaphthalene (**2c**). Yield: 65%. Yellow oil. R_f (AcOEt/hexane 1:20) 0.75. IR (NaCl, neat): 2939, 1600, 1508, 1440, 1409, 1026, 860, 744. ^1H-NMR (400 MHz): 7.97 (*dd*, *J* = 3.2, 5.6, 1 H); 7.79 (*dd*, *J* = 3.2, 5.6, 1 H); 7.47–7.51 (*m*, 3 H); 7.21 (*s*, 1 H); 2.70 (*s*, 3 H); 2.51 (*s*, 3 H). ^{13}C-NMR (100 MHz):

135.1; 134.1; 133.9; 130.9; 129.0; 127.9; 125.7; 125.3; 124.9; 124.0; 21.7; 19.3. HR-ESI-MS: 157.1015 ($[M+H]^+$, $C_{12}H_{13}^+$; calc. 157.1017).

3-Methyl-1-phenylnaphthalene (**2d**). Yield: 69%. Pale yellow oil. R_f (AcOEt/hexane 1:20) 0.66. IR (NaCl, neat): 3053, 3028, 2916, 1597, 1492. ^{1}H-NMR (300 MHz): 7.83–7.90 (*m*, 2 H); 7.66 (*s*, 1 H); 7.36–7.53 (*m*, 7 H); 7.31 (*s*, 1 H); 2.57 (*s*, 3 H). ^{13}C-NMR (75 MHz): 140.8; 140.1; 134.9; 134.1; 130.0; 129.8; 129.2; 128.2; 127.6; 127.2; 126.6; 125.8; 125.1; 21.6. HR-ESI-MS: 219.1174 ($[M+H]^+$, $C_{17}H_{15}^+$; calc. 219.1174).

3-Methyl-1-octylnaphthalene (**2e**). Yield: 67%. Yellow oil. R_f (AcOEt/hexane 1:20) 0.83. IR (NaCl, neat): 2924, 2852, 1602, 1465. ^{1}H-NMR (400 MHz): 7.95–7.97 (*m*, 1 H); 7.72–7.75 (*m*, 1 H); 7.45 (*s*, 1 H); 7.39–7.42 (*m*, 2 H); 7.15 (*s*, 1 H); 3.00 (*t*, $J=8.0$, 2 H); 2.46 (*s*, 3 H); 1.72–1.70 (*m*, 2 H); 127–142 (*m*, 10 H); 0.88 (*t*, $J=6.4$, 3 H). ^{13}C-NMR (100 MHz): 138.8; 134.9; 134.2; 130.1; 128.1; 128.0; 125.4; 125.3; 124.7; 123.7; 33.1; 31.9; 30.9; 29.9; 29.5; 29.3; 22.7; 21.7; 14.1. HR-ESI-MS: 255.2118 ($[M+H]^+$, $C_{19}H_{27}^+$; calc. 255.2113).

2-Methylnaphthalene (**2f**). Yield: 60%. White solid. M.p. 35°. R_f (AcOEt/hexane 1:20) 0.76. IR (NaCl, $CHCl_3$): 3016, 2854, 1595, 1448, 813. ^{1}H-NMR (400 MHz): 7.77–7.84 (*m*, 3 H); 7.65 (*s*, 1 H); 7.42–7.50 (*m*, 2 H); 7.35 (*d*, $J=8.4$, 1 H); 2.55 (*s*, 3 H). ^{13}C-NMR (100 MHz): 135.4; 133.6; 131.7; 128.1; 127.7; 127.6; 127.2; 126.8; 125.8; 124.9; 21.7. HR-ESI-MS: 143.0861 ($[M+H]^+$, $C_{11}H_{11}^+$; calc. 143.0861).

Ethyl 3-Methylnaphthalene-1-carboxylate (**2g**). Yield: 69%. Yellow oil. R_f (AcOEt/hexane 1:10) 0.66. IR (NaCl, neat): 2974, 2252, 1707, 1246, 1193, 906, 732.^{1}H-NMR (400 MHz): 8.82 (*d*, $J=8.8$, 1 H); 8.01 (*d*, $J=1.2$, 1 H); 7.77–7.79 (*m*, 2 H); 7.46–7.52 (*m*, 2 H); 4.46 (*q*, $J=7.2$, 2 H); 2.52 (*s*, 3 H); 1.46 (*t*, $J=7.2$, 3 H). ^{13}C-NMR (100 MHz): 167.7; 134.1; 134.0; 132.1; 129.6; 127.8; 127.3; 126.7; 126.2; 125.6; 61.0; 21.3; 14.4. HR-ESI-MS: 215.1073 ($[M+H]^+$, $C_{14}H_{15}O_2^+$; calc. 215.1072).

3-Bromo-2-(3-methylnaphthalen-1-yl)thiophene (**2i**). Yield: 81%. Yellow solid. M.p. 83°. R_f (AcOEt/hexane 1:20) 0.70. IR (NaCl, $CHCl_3$): 3016, 2902, 2399, 1602, 1500, 1440, 1340, 862, 669. ^{1}H-NMR (400 MHz): 7.84 (*d*, $J=8.0$, 1 H); 7.72–7.74 (*m*, 2 H); 7.40–7.52 (*m*, 4 H); 7.17 (*d*, $J=5.6$, 1 H); 2.57 (*s*, 3 H). ^{13}C-NMR (100 MHz): 136.7; 134.7; 133.9; 131.6; 130.5; 130.4; 130.1; 128.5; 127.7; 126.2; 126.0; 125.9; 125.7; 110.9; 21.6. HR-ESI-MS: 302.9848 ($[M+H]^+$, $C_{15}H_{12}{}^{79}BrS^+$; calc. 302.9843).

2-(3-Methylnaphthalen-1-yl)thiophene (**2j**). Only obtained by the procedure using TfOH. Yield: 71%. Orange oil. R_f (AcOEt/hexane 1:3) 0.84. IR (NaCl, neat): 3049, 2918, 2854, 1625, 1598, 1504. ^{1}H-NMR (300 MHz): 8.19 (*d*, $J=8.0$, 1 H); 7.84 (*d*, $J=9.0$, 1 H); 7.65 (*s*, 1 H); 7.42–7.49 (*m*, 4 H); 7.26–7.27 (*m*, 1 H); 7.20 (*dd*, $J=3.3$, 5.1, 1 H); 2.55 (*s*, 3 H). ^{13}C-NMR (100 MHz): 141.9; 134.8; 134.2; 132.3; 130.5; 130.2; 127.7; 127.4; 127.3; 127.2; 126.1; 125.58; 125.56; 125.5; 21.5. HR-ESI-MS: 247.0556 ($[M+Na]^+$, $C_{15}H_{12}NaS^+$; calc. 247.0557).

Ethyl 6,7,8,9-Tetrahydrobenzo[g]quinoline-10-carboxylate (**2k**). Only obtained by the procedure using TfOH, and required basic workup with aq. Na_2CO_3 soln. and extraction with CH_2Cl_2 before purification. Yield: 70%. White solid. M.p. 98°. R_f (AcOEt/hexane 1:3) 0.41. IR (NaCl, $CHCl_3$): 3018, 2939, 1720, 1276, 1029, 669. ^{1}H-NMR (300 MHz): 8.83 (*dd*, $J=1.6$, 4.2, 1 H); 7.99 (*dd*, $J=1.6$, 8.3, 1 H); 7.53 (*s*, 1 H); 7.29 (*dd*, $J=4.2$, 8.3, 1 H); 4.56 (*q*, $J=7.1$, 2 H); 2.95–2.99 (*m*, 4 H); 1.86–1.91 (*m*, 4 H); 1.47 (*t*, $J=7.14$, 3 H). ^{13}C-NMR (100 MHz): 169.7; 150.2; 143.9; 136.8; 136.3; 134.9; 132.7; 127.5; 126.2; 120.8; 61.4; 30.0; 27.0; 22.6; 22.5; 14.4. HR-ESI-MS: 266.1153 ($[M+Na]^+$, $C_{15}H_{17}NNaO_2^+$; calc. 266.1153).

1-(Chloromethyl)-3-phenylnaphthalene (**2l**). Yield: 83%. Pink solid. M.p. 72°. R_f (AcOEt/hexane 1:20) 0.50. IR (NaCl, $CHCl_3$): 2974, 1595, 1448, 761, 698. ^{1}H-NMR (400 MHz): 8.18 (*d*, $J=8.4$, 1 H); 8.06 (*s*, 1 H); 7.96 (*d*, $J=8.4$, 1 H); 7.82 (*d*, $J=1.6$, 1 H); 7.73 (*d*, $J=7.2$, 2 H); 7.50–7.64 (*m*, 4 H); 7.40–7.44 (*m*, 1 H); 5.13 (*s*, 2 H). ^{13}C-NMR (100 MHz): 140.4; 138.0; 134.3; 133.6; 130.3; 129.2; 128.9; 127.7; 127.5; 127.4; 127.38; 126.8; 126.6; 123.6; 44.7. HR-ESI-MS: 253.0788 ($[M+H]^+$, $C_{17}H_{14}{}^{35}Cl^+$; calc. 253.0784).

1-Methyl-3-phenylnaphthalene (**2m**). Yield: 88%. Yellow oil. R_f (AcOEt/hexane 1:40) 0.66. IR (NaCl, neat): 3026, 1597, 1496, 1440, 875, 761, 696. ^{1}H-NMR (400 MHz): 8.06 (*d*, $J=5.6$, 1 H); 7.95–7.98 (*m*, 2 H); 7.78–7.80 (*m*, 2 H); 7.67 (*s*, 1 H); 7.53–7.59 (*m*, 4 H); 7.42–7.46 (*m*, 1 H); 2.82 (*s*, 3 H). ^{13}C-NMR (100 MHz): 141.2; 138.2; 134.8; 133.9; 131.8; 128.82; 128.78; 127.4; 127.2; 126.3; 126.0; 125.8; 124.2; 124.0; 19.5. HR-ESI-MS: 219.1174 ($[M+H]^+$, $C_{17}H_{15}^+$; calc. 219.1174).

1-Benzyl-3-phenylnaphthalene (**2n**). Yield: 80%. Yellow solid. M.p. 92°. R_f (AcOEt/hexane 1:40) 0.33. IR (NaCl, $CHCl_3$): 3016, 1597, 1494, 1450, 1220, 779, 669. ^{1}H-NMR (400 MHz): 8.03–8.07 (*m*, 2 H);

7.96 (*d*, *J* = 8.0, 1 H); 7.76 – 7.78 (*m*, 2 H); 7.67 (*s*, 1 H); 7.49 – 7.55 (*m*, 4 H); 7.42 – 7.44 (*m*, 1 H); 7.25 – 7.33 (*m*, 5 H); 4.57 (*s*, 2 H). ^{13}C-NMR (100 MHz): 141.0; 140.5; 138.1; 137.2; 134.3; 131.3; 129.0; 128.8; 128.7; 128.5; 127.4; 127.3; 127.1; 126.1; 126.02; 126.0; 125.0; 124.2; 39.2. HR-ESI-MS: 295.1489 ($[M+H]^+$, $C_{23}H_{19}^+$; calc. 295.1487).

1,2,3,4-Tetrahydro-9-methylanthracene (**2o**). Yield: 77%. Off-white paste. R_f (AcOEt/hexane 1:20) 0.66. IR (NaCl, $CHCl_3$): 2912, 2854, 2252, 906, 732. ^{1}H-NMR (400 MHz): 8.04 (*d*, *J* = 8.4, 1 H); 7.75 (*d*, *J* = 7.2, 1 H); 7.39 – 7.49 (*m*, 3 H); 3.02 (*t*, *J* = 6.4, 2 H); 2.95 (*t*, *J* = 6.4, 2 H); 2.60 (*s*, 3 H); 1.95 (*d*, *J* = 5.6, 2 H); 1.87 (*d*, *J* = 5.6, 2 H). ^{13}C-NMR (100 MHz): 135.9; 133.6; 131.9; 131.3; 131.1; 127.7; 125.2; 124.7; 124.5; 123.6; 31.0; 27.8; 23.8; 22.9; 13.9. HR-ESI-MS: 197.1329 ($[M+H]^+$, $C_{15}H_{17}^+$; calc. 197.1330).

9-Benzyl-1,2,3,4-tetrahydroanthracene (**2p**). Yield: 63%. Yellow solid. M.p. 106°. R_f (AcOEt/hexane 1:20) 0.75. IR (NaCl, $CHCl_3$): 3012, 2854, 2252, 1597, 1448, 1384, 906, 779. ^{1}H-NMR (400 MHz): 7.89 (*d*, *J* = 8.0, 1 H); 7.73 (*d*, *J* = 7.6, 1 H); 7.54 (*s*, 1 H); 7.31 – 7.37 (*m*, 2 H); 7.18 – 7.24 (*m*, 2 H); 7.12 – 7.15 (*m*, 1 H); 7.04 – 7.06 (*m*, 2 H); 4.46 (*s*, 2 H); 3.00 (*t*, *J* = 6.0, 2 H); 2.86 (*t*, *J* = 6.0, 2 H); 1.82 – 1.83 (*m*, 4 H). ^{13}C-NMR (100 MHz): 140.0; 136.3; 134.9; 132.9; 132.2; 131.6; 128.4; 128.1; 127.8; 126.4; 125.8; 125.2; 124.7; 124.1; 33.5; 30.9; 27.4; 23.7; 22.9. HR-ESI-MS: 273.1645 ($[M+H]^+$, $C_{21}H_{21}^+$; calc. 273.1643).

1,2,3,4-Tetrahydroanthracene (**2q**). Yield: 60%. Pale yellow solid. M.p. 97°. R_f (AcOEt/hexane 1:20) 0.66. IR (NaCl, $CHCl_3$): 3014, 2931, 1220, 761. ^{1}H-NMR (400 MHz): 7.73 (*dd*, *J* = 3.3, 6.1, 2 H); 7.56 (*s*, 2 H); 7.37 (*dd*, *J* = 3.2, 6.2, 2 H); 2.99 (*s*, 4 H); 1.89 (*dd*, *J* = 3.2, 6.4, 4 H). ^{13}C-NMR (100 MHz): 136.2; 132.1; 127.0; 126.7; 124.9; 29.8; 23.4. HR-ESI-MS: 183.1175 ($[M+H]^+$, $C_{14}H_{15}^+$; calc. 183.1174).

cis-*2,3,3a,8a-Tetrahydrocyclopenta[*a*]inden-8(1*H*)-one* (**3**). Yield: 98%. Pale yellow oil. R_f (AcOEt/hexane 1:10) 0.26. IR (NaCl, $CHCl_3$): 2958, 2252, 1704, 1265, 908, 735. ^{1}H-NMR (400 MHz): 7.64 (*d*, *J* = 7.6, 1 H); 7.58 (*td*, *J* = 7.6, 1.2, 1 H); 7.45 (*dd*, *J* = 0.8, 7.6, 1 H); 7.31 (*t*, *J* = 7.6, 1 H); 3.74 (*t*, *J* = 7.6, 1 H); 3.03 (*ddd*, *J* = 2.2, 6.8, 9.7, 1 H); 1.80 – 2.02 (*m*, 4 H); 1.56 – 1.58 (*m*, 1 H); 1.05 – 1.18 (*m*, 1 H). ^{13}C-NMR (100 MHz): 210.3; 158.7; 137.3; 135.1; 127.3; 125.9; 123.0; 52.3; 43.9; 33.1; 30.8; 24.7. HR-ESI-MS: 173.0965 ($[M+H]^+$, $C_{12}H_{13}^+$; calc. 173.0966).

(1Z)-1-Benzylidene-1,4-dihydrospiro[2-benzopyran-3,1′-cyclohexane] (**4p**). Yield: 52%. Yellow oil. R_f (AcOEt/hexane 1:9) 0.26. IR (NaCl, neat): 2940, 2252, 1707, 907, 732, 651. ^{1}H-NMR (400 MHz): 7.83 (*d*, *J* = 7.6, 2 H); 7.70 – 7.72 (*m*, 1 H); 7.33 (*t*, *J* = 7.6, 2 H); 7.09 – 7.24 (*m*, 4 H); 6.22 (*s*, 1 H); 2.88 (*s*, 2 H); 1.25 – 1.88 (*m*, 10 H). ^{13}C-NMR (100 MHz): 148.8; 136.8; 132.1; 128.9; 128.7; 128.2; 127.9; 126.5; 125.5; 123.5; 103.9; 76.1; 39.9; 35.7; 25.8; 22.1. HR-ESI-MS: 291.1746 ($[M+H]^+$, $C_{21}H_{23}^+$; calc. 291.1749).

2-Chloro-3-methylnaphthalene (**6a**) [16] and *3-methylnaphthalen-1-ol* (**7a**) [17] were known compounds obtained as a *ca.* 4:1 mixture. NMR Spectra obtained were in agreement with those in the literatures.

2-Chloro-3-phenylnaphthalene (**6b**) is a known compound, and NMR spectra were in agreement with those in [18].

1,2,3,4-Tetrahydrotetracene (**9a**). Yield: 68%. Yellow solid. M.p. 233°. R_f (AcOEt/hexane 1:20) 0.66. IR (NaCl, $CHCl_4$): 3019, 2922, 2399, 1429, 921, 898, 669. ^{1}H-NMR (400 MHz): 8.28 (*s*, 2 H); 7.94 (*dd*, *J* = 3.2, 6.5, 2 H); 7.71 (*s*, 2 H); 7.39 (*dd*, *J* = 3.2, 6.6, 2 H); 3.02 (*s*, 2 H); 1.88 – 1.91 (*m*, 2 H). ^{13}C-NMR (100 MHz): 136.4; 131.3; 131.0; 128.1; 126.1; 124.9; 124.7; 30.0; 23.4. HR-ESI-MS: 233.1330 ($[M+H]^+$, $C_{18}H_{17}^+$; calc. 233.1330).

1,2,3,4-Tetrahydro-5-methyltetracene (**9b**). Yield: 49%. Yellow oil. R_f (CH_2Cl_2/hexane 1:20) 0.66. IR (NaCl, neat): 3019, 2922, 2399, 1429, 1597, 1448, 1384, 906, 650. ^{1}H-NMR (400 MHz): 8.55 (*s*, 1 H); 8.28 (*s*, 1 H); 8.01 (*dd*, *J* = 3.7, 6.0, 1 H); 7.95 (*dd*, *J* = 3.2, 6.0, 1 H); 7.62 (*s*, 1 H); 7.41 (*dd*, *J* = 3.1, 6.5, 2 H); 2.98 – 3.05 (*m*, 4 H); 2.70 (*s*, 3 H); 1.84 – 1.97 (*m*, 4 H). ^{13}C-NMR (100 MHz): 136.1; 133.3; 131.2; 130.9; 130.7; 130.6; 130.3; 128.6; 127.7; 125.4; 124.8; 124.7; 124.6; 122.0; 31.3; 28.0; 23.9; 22.9; 14.2. HR-ESI-MS: 247.1486 ($[M+H]^+$, $C_{19}H_{19}^+$; calc. 247.1487).

6,7-Dihydropentaphene (**11a**). Yield: 52%. Yellow solid. M.p. 140°. R_f (AcOEt/hexane 1:20) 0.50. IR (NaCl, $CHCl_3$): 3019, 2956, 2872, 1668, 1462, 883, 669. ^{1}H-NMR (400 MHz): 8.40 (*s*, 2 H); 7.93 (*dd*, *J* = 6.0, 3.4, 2 H); 7.80 (*dd*, *J* = 6.0, 3.4, 2 H); 7.72 (*s*, 2 H); 7.45 – 7.48 (*m*, 4 H); 3.13 (*s*, 4 H). ^{13}C-NMR (100 MHz): 136.5; 133.2; 133.12; 133.09; 128.1; 127.1; 126.05; 125.99; 125.5; 123.2; 30.1. HR-ESI-MS: 281.333 ($[M+H]^+$, $C_{22}H_{17}^+$; calc. 281.330).

6,7-Dihydro-13,14-Dimethylpentaphene (**11b**). Yield: 40%. Yellow solid. M.p. 191°. R_f (AcOEt/hexane 1:10) 0.84. IR (NaCl, $CHCl_3$): 3016, 2945, 2399, 1463, 1436, 1024, 669. ^{1}H-NMR (400 MHz):

8.13–8.15 (*m*, 2 H); 7.85–7.87 (*m*, 2 H); 7.67 (*s*, 2 H); 7.52–7.57 (*m*, 4 H); 3.06 (*d*, *J* = 9.6, 2 H); 2.81 (*d*, *J* = 9.6, 2 H); 2.59 (*s*, 6 H). ^{13}C-NMR (100 MHz): 139.8; 133.1; 132.7; 132.6; 132.5; 127.6; 125.8; 125.2; 125.0; 122.8; 32.6; 18.0. HR-ESI-MS: 309.1646 ($[M+H]^+$, $C_{24}H_{21}^+$; calc. 309.1643).

6,7-Dihydro-13,14-dioctylpentaphene (**11c**). Yield: 21%. Clear crystal (CH_2Cl_2/hexanes). M.p. 62°. R_f (AcOEt/hexane 1:20) 0.75. IR (NaCl, $CHCl_3$): 2926, 2852, 1500, 1463, 1261, 1076, 908, 734. ^{1}H-NMR (400 MHz): 8.12–8.14 (*m*, 2 H); 7.82–7.85 (*m*, 2 H); 7.62 (*s*, 2 H); 7.47–7.50 (*m*, 4 H); 3.34–3.36 (*m*, 2 H); 3.16–3.19 (*m*, 2 H); 3.02 (*d*, *J* = 9.8, 2 H); 2.73 (*d*, *J* = 9.6, 2 H); 0.75–1.46 (*m*, 34 H). ^{13}C-NMR (100 MHz): 139.6; 136.5; 133.3; 133.0; 131.5; 127.9; 125.3; 124.7; 122.8; 32.8; 31.6; 30.8; 29.3; 29.1; 29.0; 28.6; 22.5; 14.0. HR-ESI-MS: 505.3830 ($[M+H]^+$, $C_{38}H_{49}^+$; calc. 505.3834). The structure was confirmed by X-ray crystallographic analysis (CCDC-893291).

Diethyl 6,13-Dihydropentacene-5,12-dicarboxylate (**12d**). Yield: 19%. Yellow crystals (CH_2Cl_2/hexanes). M.p. 104°. R_f (AcOEt/hexane 1:3) 0.63. IR (NaCl, $CHCl_3$): 3024, 2985, 2304, 1714, 1035, 669. ^{1}H-NMR (300 MHz): 7.79–7.88 (*m*, 6 H); 7.45–7.50 (*m*, 4 H); 4.64 (*q*, *J* = 7.1, 4 H); 4.26 (*s*, 4 H); 1.54 (*t*, *J* = 7.5, 12 H). ^{13}C-NMR (75 MHz): 169.3; 134.4; 133.3; 132.1; 129.0; 128.8; 127.73; 127.66; 126.6; 126.0; 124.6; 61.6; 35.1; 14.6. HR-ESI-MS: 425.1760 ($[M+H]^+$, $C_{28}H_{25}O_4^+$; calc. 425.1753). Structure was confirmed by X-ray crystallographic analysis (CCDC-893292).

2-Alkenylbenzaldehydes **1f** [19], **1q**, and **1s** [20] are known compounds and were prepared from 2-bromobenzaldehyde *via* a *Wittig* reaction, followed by formylation under the conditions described in [19].

2-Alkenylphenyl Ketones **1c**–**1e**, **1i**, **1j**, **1m**–**1p**, **8b**, **10b**, and **10c** were prepared from the corresponding 2-alkenylbenzaldehydes and the respective *Grinard* reagents (1.1 equiv. for **1** and **8**, 2.5 equiv. for **10**) or organolithium reagents (1.1 equiv. for **1i**) in THF at 0°, followed by oxidation using pyridinium chlorochromate (PCC; 1.5 equiv. for **1** and **8**, 3.0 equiv. for **10**) in CH_2Cl_2 at r.t.

1-[2-(2-Methylprop-1-en-1-yl)phenyl]ethanone (**1c**). Yield: 70% in two steps. Pale yellow oil. R_f (AcOEt/hexane 1:9) 0.60. IR (NaCl, neat): 2974, 2912, 1681, 1595, 1215, 758. ^{1}H-NMR (400 MHz): 7.62 (*d*, *J* = 7.6, 1 H); 7.42 (*t*, *J* = 7.6, 1 H); 7.28 (*t*, *J* = 7.6, 1 H); 7.22 (*d*, *J* = 7.6, 1 H); 6.49 (*s*, 1 H); 2.51 (*s*, 3 H); 1.91 (*s*, 3 H); 1.67 (*s*, 3 H). ^{13}C-NMR (100 MHz): 202.8; 138.9; 137.8; 136.2; 131.0; 130.9; 128.4; 126.3; 124.6; 30.1; 26.2; 19.3. HR-ESI-MS: 175.1122 ($[M+H]^+$, $C_{12}H_{15}O^+$; calc. 175.1123).

[2-(2-Methylprop-1-en-1-yl)phenyl](phenyl)methanone (**1d**). Yield: 64% in two steps. Yellow oil. R_f (AcOEt/hexane 1:9) 0.66. IR (NaCl, neat): 3059, 2972, 1718, 1664, 1448, 1286, 929. ^{1}H-NMR (400 MHz): 7.73 (*dd*, *J* = 8.2, 1.1, 1 H); 7.53 (*t*, *J* = 7.4, 1 H); 7.39–7.45 (*m*, 4 H); 7.27–7.31 (*m*, 2 H); 6.13 (*s*, 1 H); 1.65 (*dd*, *J* = 3.5, 1.2, 6 H). ^{13}C-NMR (100 MHz): 198.7; 138.7; 137.9; 137.5; 137.0; 132.8; 130.2; 129.9; 129.8; 128.3; 128.2; 125.9; 123.5; 25.9; 19.3. HR-ESI-MS: 237.1278 ($[M+H]^+$, $C_{17}H_{17}O^+$; calc. 237.1279).

1-[2-(2-Methylprop-1-en-1-yl)phenyl]nonan-1-one (**1e**). Yield: 63% in two steps. Pale yellow oil; R_f (AcOEt/hexane 1:20) 0.40. IR (NaCl, neat): 2926, 2854, 1687, 1442, 756. ^{1}H-NMR (500 MHz): 7.51 (*dd*, *J* = 7.6, 1.1, 1 H); 7.39 (*td*, *J* = 7.6, 1.2, 1 H); 7.26 (*t*, *J* = 9.3, 1 H); 7.20 (*d*, *J* = 7.6, 1 H); 6.42 (*s*, 1 H); 2.80 (*t*, *J* = 7.4, 2 H); 1.89 (*d*, *J* = 1.2, 3 H); 1.66 (*d*, *J* = 1.2, 3 H); 1.61–1.64 (*m*, 2 H); 1.26–1.30 (*m*, 10 H); 0.88 (*t*, *J* = 1.0, 3 H). ^{13}C-NMR (125 MHz): 206.2; 139.6; 137.2; 136.2; 130.7; 130.3; 127.6; 126.2; 124.2; 42.3; 31.8; 29.4; 29.3; 29.1; 26.1; 24.4; 22.6; 19.3; 14.0. HR-ESI-MS: 273.2219 ($[M+H]^+$, $C_{19}H_{29}O^+$; calc. 273.2218).

(3-Bromothiophen-2-yl)[2-(2-methylprop-1-en-1-yl)phenyl]methanone (**1i**). Yield: 62% in two steps. Yellow oil. R_f (AcOEt/hexane 1:20) 0.40. IR (NaCl, neat): 3103, 2970, 2908, 1651, 1487, 1402, 1292, 871, 744. ^{1}H-NMR (400 MHz): 7.51 (*d*, *J* = 5.2, 1 H); 7.42–7.47 (*m*, 2 H); 7.31 (*d*, *J* = 7.4, 1 H); 7.25–7.28 (*m*, 1 H); 7.06 (*d*, *J* = 5.2, 1 H); 6.20 (*s*, 1 H); 1.72 (*s*, 3 H); 1.69 (*s*, 3 H). ^{13}C-NMR (100 MHz): 190.0; 138.8; 138.3; 137.8; 137.5; 133.1; 132.1; 130.4; 130.2; 128.0; 126.2; 122.7; 115.5; 26.1; 19.6. HR-ESI-MS: 320.9933 ($[M+H]^+$, $C_{15}H_{14}{}^{79}BrOS^+$; calc. 320.9949).

[(2-Methylprop-1-en-1-yl)phenyl](thiophen-2-yl)methanone (**1j**). Yield: 86% in two steps. Yellow oil. R_f (AcOEt/hexane 1:20) 0.43. IR (NaCl, neat): 2908, 1643, 1633, 1409, 1296, 1047, 837. ^{1}H-NMR (300 MHz): 7.68 (*dd*, *J* = 1.1, 4.9, 1 H); 7.42–7.47 (*m*, 2 H); 7.37 (*dd*, *J* = 1.1, 3.8, 1 H); 7.29–7.32 (*m*, 2 H); 7.08 (*dd*, *J* = 3.8, 4.9, 1 H); 6.28 (*s*, 1 H); 1.76 (*d*, *J* = 1.2, 3 H); 1.70 (*d*, *J* = 1.2, 3 H). ^{13}C-NMR (100 MHz): 190.4; 144.9; 138.7; 137.2; 137.0; 135.2; 134.5; 130.3; 129.9; 127.9; 127.8; 125.7; 123.0; 26.2; 19.5. HR-ESI-MS: 243.0848 ($[M+H]^+$, $C_{15}H_{15}OS^+$; calc. 243.0844).

1-[2-(2-Phenylprop-1-en-1-yl)phenyl]ethanone (**1m**). Yield: 64% in two steps. Yellow oil. R_f (AcOEt/hexane 1:40) 0.26. IR (NaCl, neat): 2974, 1681, 1595, 1562, 1477, 1440, 1354, 1249, 954, 765.

^{1}H-NMR (400 MHz): 7.58 (*d*, *J* = 7.6, 1 H); 7.14 – 7.57 (*m*, 5 H); 7.06 – 7.07 (*m*, 2 H); 6.91 (*d*, *J* = 6.8, 1 H); 6.77 (*s*, 1 H); 2.49 (*s*, 3 H) 2.25 (*s*, 3 H). ^{13}C-NMR (100 MHz): 201.7; 141.2; 138.6; 138.3; 137.9; 131.9; 130.9; 128.7; 128.6; 128.1; 126.8; 126.4; 126.2; 29.5; 25.8. HR-ESI-MS: 237.1281 ($[M+H]^+$, $C_{17}H_{17}O^+$; calc. 237.1279).

1-[2-(2-Methylprop-1-en-1-yl)phenyl]-2-phenylethanone (**1n**). Yield: 49% in two steps. White solid. M.p. 84°. R_f (AcOEt/hexane 1:40) 0.23. IR (NaCl, $CHCl_3$): 3016, 1681, 1494, 1220, 1215, 985, 761, 700, 667. ^{1}H-NMR (400 MHz): 7.60 (*d*, *J* = 7.6, 1 H); 7.31 – 7.34 (*m*, 2 H); 7.24 – 7.26 (*m*, 3 H); 7.07 – 7.16 (*m*, 5 H); 6.99 – 7.00 (*m*, 2 H); 6.85 (*d*, *J* = 7.6, 1 H); 6.71 (*s*, 1 H); 4.18 (*s*, 2 H); 2.22 (*s*, 3 H). ^{13}C-NMR (100 MHz): 201.4; 141.1; 138.9; 138.1; 138.0; 134.4; 131.9; 130.7; 129.6; 128.62; 128.60; 128.2; 128.0; 126.9; 126.8; 126.11; 126.03; 48.4; 25.8. HR-ESI-MS: 313.1594 ($[M+H]^+$, $C_{23}H_{21}O^+$; calc. 313.1592).

1-[2-(Cyclohexylidenemethyl)phenyl]ethanone (**1o**). Yield: 84% in two steps. Yellow oil. R_f (AcOEt/hexane 1:20) 0.33. IR (NaCl, neat): 2926, 2854, 1689, 1595, 1448, 1354, 1246, 759. ^{1}H-NMR (400 MHz): 7.61 (*d*, *J* = 7.6, 1 H); 7.39 – 7.43 (*m*, 1 H); 7.26 – 7.30 (*m*, 1 H); 7.18 (*d*, *J* = 7.6, 1 H); 6.42 (*s*, 1 H); 2.52 (*s*, 3 H); 2.28 (*t*, *J* = 6.0, 2 H); 2.13 (*t*, *J* = 6.0, 2 H); 1.63 – 1.67 (*m*, 2 H); 1.57 – 1.61 (*m*, 2 H); 1.48 – 1.51 (*m*, 2 H). ^{13}C-NMR (100 MHz): 202.9; 143.9; 139.2; 137.3; 131.0; 130.8; 128.2; 126.3; 121.4; 37.2; 30.4; 29.7; 28.3; 27.7; 26.6. HR-ESI-MS: 215.1436 ($[M+H]^+$, $C_{15}H_{19}O^+$; calc. 215.1436).

1-[2-(Cyclohexylidenemethyl)phenyl]-2-phenylethanone (**1p**). Yield: 41% in two steps. Clear oil. R_f (AcOEt/hexane 1:10) 0.63. IR (NaCl, $CHCl_3$): 2912, 2854, 2252, 1689, 1097, 906, 732, 650. ^{1}H-NMR (400 MHz): 7.55 (*d*, *J* = 7.6, 1 H); 7.42 (*t*, *J* = 7.6, 1 H); 7.30 – 7.34 (*m*, 2 H); 7.25 – 7.27 (*m*, 2 H); 7.20 – 7.23 (*m*, 3 H); 6.42 (*s*, 1 H); 4.18 (*s*, 2 H); 2.30 (*t*, *J* = 6.0, 2 H); 2.15 (*t*, *J* = 6.0, 2 H); 1.58 – 1.67 (*m*, 4 H); 1.51 – 1.52 (*m*, 2 H). ^{13}C-NMR (100 MHz): 203.0; 144.5; 139.2; 137.0; 134.5; 130.9; 130.5; 129.6; 128.5; 128.0; 126.8; 126.3; 121.0; 49.1; 37.3; 29.7; 28.4; 27.7; 26.6. HR-ESI-MS: 291.1750 ($[M+H]^+$, $C_{21}H_{23}O^+$; calc. 291.1749).

1-[3-(Cyclohexylidenemethyl)naphthalen-2-yl]ethanone (**8b**). Yield: 34% in two steps. White paste. R_f (AcOEt/hexane 1:20) 0.33. IR (NaCl, $CHCl_3$): 2926, 2851, 1686, 1626, 1445, 1354, 1265, 1196, 1128. ^{1}H-NMR (400 MHz): 8.13, (*s*, 1 H); 7.87 (*d*, *J* = 8.0, 1 H); 7.79 (*d*, *J* = 8.1, 1 H); 7.60 (*s*, 1 H); 7.53 (*t*, *J* = 7.1, 1 H); 7.50 (*t*, *J* = 7.7, 1 H); 6.54 (*s*, 1 H); 2.63 (*s*, 3 H); 2.34 (*t*, *J* = 5.9, 2 H); 2.22 (*t*, *J* = 6.0, 2 H); 1.54 – 1.69 (*m*, 6 H). ^{13}C-NMR (100 MHz): 202.5; 143.6; 137.9.0; 134.3; 133.8; 131.2; 129.6; 129.0; 128.7; 127.8; 127.4; 126.2; 121.4; 37.3; 30.2; 29.6; 28.4; 27.8; 26.6. HR-ESI-MS: 265.1593 ($[M+H]^+$, $C_{19}H_{21}O^+$; calc. 265.1592).

1,1′-[Cyclohexane-1,4-diylidenebis(methylylidenebenzene-2,1-diyl)]diethanone (**10b**). Yield: 76% in two steps (*cis:trans ca.* 3:2). White solid. M.p. 72 – 80, 95 – 110°. R_f (AcOEt/hexane 1:9) 0.66. IR (NaCl, $CHCl_3$): 3018, 2906, 2841, 1683, 1593, 1438, 667. ^{1}H-NMR (400 MHz): 7.65 (*dd*, *J* = 1.2, 7.8, 0.8 H); 7.63 (*dd*, *J* = 1.2, 7.8, 1.2 H); 7.44 (*td*, *J* = 7.5, 1.3, 0.8 H); 7.40 (*td*, *J* = 7.5, 1.3, 1.2 H); 7.27 – 7.34 (*m*, 2 H); 7.21 (*d*, *J* = 7.6, 0.8 H); 7.17 (*d*, *J* = 7.6, 1.2 H); 6.56 (*s*, 1.2 H); 6.53 (*s*, 0.8 H); 2.54 (*s*, 2.6 H); 2.53 (*s*, 3.4 H); 2.49 (*s*, 1.2 H); 2.32 (*s*, 1.6 H); 2.16 (*s*, 1.2 H). ^{13}C-NMR (100 MHz): 202.4; 141.7; 141.6; 138.9; 137.1; 137.08; 131.0; 130.99; 130.91; 128.5; 128.47; 126.5; 122.98; 122.95; 37.8; 37.2; 30.4; 30.2; 29.8. HR-ESI-MS: 345.1855 ($[M+H]^+$, $C_{24}H_{25}O_2^+$; calc. 345.1855).

1,1′-[Cyclohexane-1,4-diylidenebis(methylylidenebenzene-2,1-diyl)]dinonan-1-one (**10c**). Yield: 25% in two steps (*cis:trans ca.* 3:2). Yellow oil. R_f (AcOEt/hexane 1:9) 0.66. IR (NaCl, $CHCl_3$): 3018, 2927, 2854, 1681, 1595, 1465, 1440, 977, 667. ^{1}H-NMR (400 MHz): 7.52 – 7.57 (*m*, 2 H); 7.42 (*td*, *J* = 7.6, 1.3, 0.8 H); 7.37 (*td*, *J* = 7.5, 1.3, 1.2 H); 7.25 – 7.31 (*m*, 2 H); 7.20 (*d*, *J* = 7.6, 0.8 H); 7.16 (*d*, *J* = 7.6, 1.2 H); 6.50 (*s*, 1.2 H); 6.48 (*s*, 0.8 H); 2.81 – 2.85 (*m*, 4 H); 2.46 (*s*, 1.2 H); 2.31 – 2.32 (*m*, 1.6 H); 2.17 (*s*, 1.2 H); 1.62 – 1.65 (*m*, 4 H); 1.25 – 1.28 (*m*, 20 H); 0.84 – 0.89 (*m*, 6 H). ^{13}C-NMR (100 MHz): 205.9; 205.8; 141.9; 141.8; 139.5; 136.6; 136.5,130.9; 130.8; 130.5; 130.4; 127.81; 127.77; 126.5; 122.69; 122.66; 42.5; 37.9; 37.2; 31.8; 30.5; 29.8; 29.4; 29.35; 29.16; 24.5; 22.6; 14.1. HR-ESI-MS: 541.4042 ($[M+H]^+$, $C_{38}H_{53}O_2^+$; calc. 541.4046).

2-Chloro-1-(2-alkenylphenyl) ketones **1a**, **1b**, **1l**, **5a**, and **5b** were prepared from the corresponding 2-alkenylphenyl ketones by the following procedure (**1a** as representative): a soln. of *1-[2-(2-methylprop-1-en-1-yl)phenyl]ethanone* **1c** (1.70 g, 10.0 mmol) in anh. THF (10 ml) was added dropwise to a freshly prepared soln. of ^{i}Pr$_2$NLi (16.5 mmol) in THF at −78°, and the mixture was stirred for 2 h. Me_3SiCl (2.2 g, 20.0 mmol) was added then dropwise at 0°, and the mixture was stirred for another 6 h. Finally, *N*-chlorosuccinimide (NCS; 2.6 g, 20.0 mmol) was added in a single portion, and the mixture was stirred for

another 8 h. The reaction was quenched with H_2O, and the mixture was extracted three times with AcOEt. The combined extracts were washed with H_2O and brine, dried ($MgSO_4$), and concentrated *in vacuo*. The crude product was purified by FC (Et_2O/hexanes 1:75) to afford **1a** (1.0 g, 4.8 mmol) and *2,2-dichloro-1-[2-(2-methylprop-1-en-1-yl)phenyl]ethanone* (**1b**; 0.5 g, 2.1 mmol), in 48 and 21% yields, resp.

Data of **1a**. Yield: 48%. Pale yellow oil. R_f (AcOEt/hexanes 1:50) 0.26. IR (NaCl, neat): 2974, 2912, 1595, 1477, 1448, 1384, 1215, 758. ^{1}H-NMR (400 MHz): 7.58 (*d*, *J* = 7.6, 1 H); 7.48 (*t*, *J* = 7.6, 1 H); 7.31 (*t*, *J* = 7.6, 1 H); 7.23 (*d*, *J* = 7.6, 1 H); 6.44 (*s*, 1 H); 4.55 (*s*, 2 H); 1.92 (*s*, 3 H); 1.65 (*s*, 3 H). ^{13}C-NMR (100 MHz): 196.2; 138.3; 138.1; 136.2; 131.7; 131.0; 128.5; 126.6; 123.6; 48.5; 26.1; 19.4. HR-ESI-MS: 209.0735 ($[M+H]^+$, $C_{12}H_{14}{}^{35}ClO^+$; calc. 209.0733).

2,2-Dichloro-1-[2-(2-methylprop-1-en-1-yl)phenyl]ethanone (**1b**). Yield: 21%. Pale yellow oil. R_f (AcOEt/hexanes 1:50) 0.33. IR (NaCl, neat): 2974, 2912, 2854, 1712, 1595, 1477, 1448, 1384, 1215, 758. ^{1}H-NMR (400 MHz): 7.64 (*d*, *J* = 7.6, 1 H); 7.50 (*t*, *J* = 7.6, 1 H); 7.35 (*t*, *J* = 7.6, 1 H); 7.24 (*d*, *J* = 7.6, 1 H); 6.64 (*s*, 1 H); 6.43 (*s*, 1 H); 1.93 (*s*, 3 H); 1.62 (*s*, 3 H). ^{13}C-NMR (100 MHz): 191.5; 140.4; 138.1; 134.5; 132.2; 130.7; 129.4; 126.8; 123.0; 69.0; 26.1; 19.5. HR-ESI-MS: 243.0332 ($[M+H]^+$, $C_{12}H_{13}{}^{35}Cl_2O^+$; calc. 243.0343).

2-Chloro-1-[2-(2-phenylprop-1-en-1-yl)phenyl]ethanone (**1l**). Yield: 69%. White solid. M.p. 104°. R_f (AcOEt/hexane 1:20) 0.30. IR (NaCl, $CHCl_3$): 2974, 2912, 2854, 1689, 1595, 1477, 1448, 1384, 1215, 759. ^{1}H-NMR (400 MHz): 7.69 (*d*, *J* = 7.6, 1 H); 7.54–7.57 (*m*, 3 H); 7.34–7.41 (*m*, 4 H); 7.30–7.32 (*m*, 1 H); 7.09 (*s*, 1 H); 4.60 (*s*, 2 H); 2.07 (*d*, *J* = 1.1, 3 H). ^{13}C-NMR (100 MHz): 195.3; 142.6; 138.9; 138.3; 135.6; 132.0; 131.1; 128.9; 128.5; 127.7; 127.0; 126.03; 125.97; 48.2; 17.2. HR-ESI-MS: 271.0889 ($[M+H]^+$, $C_{17}H_{16}{}^{35}ClO^+$; calc. 271.0890).

2-Chloro-1-[2-(prop-1-en-1-yl)phenyl]ethanone (**5a**). Yield: 43% ((*Z*)/(*E*) *ca.* 3:2). Yellow oil. R_f (AcOEt/hexane 1:50) 0.23. IR (NaCl, neat): 2929, 2856, 1618, 1473, 1444, 1305, 1255, 831, 771. ^{1}H-NMR (400 MHz): 7.62 (*dd*, *J* = 7.6, 1.2, 0.8 H); 7.43–7.52 (*m*, 1.8 H); 7.26–7.36 (*m*, 1.8 H); 6.77 (*dd*, *J* = 15.6, 1.6, 0.4 H); 6.68 (*dd*, *J* = 11.6, 1.6, 0.6 H); 6.14 (*dq*, *J* = 15.6, 6.8, 0.4 H); 5.91 (*dq*, *J* = 11.6, 7.2, 0.6 H); 4.59 (*s*, 1.2 H); 4.58 (*s*,0.8 H); 1.90 (*dd*, *J* = 6.4, 1.6, 1.2 H); 1.69 (*dd*, *J* = 7.2, 2.0, 1.8 H). ^{13}C-NMR (100 MHz): 195.8; 195.7; 138.2; 136.9; 135.7; 134.3; 132.0; 131.7; 130.8; 130.6; 129.1; 128.7; 128.6; 128.5; 128.1; 127.7; 127.0; 126.7; 48.4; 48.3; 18.8; 14.4. HR-ESI-MS: 195.0585 ($[M+H]^+$, $C_{11}H_{12}{}^{35}ClO^+$; calc. 195.0577).

2-Chloro-1-[2-(2-phenylethenyl)phenyl]ethanone (**5b**) Yield: 51% ((*Z*)/(*E*) *ca.* 1:1). White solid. M.p. 57°. R_f (AcOEt/hexane 1:50) 0.23. IR (NaCl, $CHCl_3$): 3018, 1697, 1595, 1492, 1398, 1215, 758. ^{1}H-NMR (400 MHz): 7.73 (*d*, *J* = 7.8, 0.5 H); 7.66 (*d*, *J* = 7.5, 0.5 H); 7.52–7.62 (*m*, 2 H); 7.27–7.38 (*m*, 4 H); 6.98–7.15 (*m*, 3 H); 6.88 (*d*, *J* = 12.0, 0.5 H); 6.70 (*d*, *J* = 12.0, 0.5 H); 4.64 (*s*, 1 H); 4.54 (*s*, 1 H). ^{13}C-NMR (100 MHz): 195.2; 194.3; 138.1; 136.9; 136.2; 135.2; 134.3; 132.8; 132.4; 132.3; 131.5; 131.2; 129.2; 129.1; 128.9; 128.7; 128.6; 128.2; 127.7; 127.4; 127.3; 126.9; 126.3; 48.2; 47.9. HR-ESI-MS: 257.0749 ($[M+H]^+$, $C_{16}H_{14}{}^{35}ClO^+$; calc. 257.0733).

2-(2-Alkenylphenyl) 2-*oxoacetates* **1g**, **1k**, and **10d** were prepared from the corresponding 2-alkenylphenyl bromides under the conditions described in [21].

Ethyl 2-[2-(2-Methylprop-1-en-1-yl)phenyl]-2-oxoacetate (**1g**). Yield: 69%. Yellow oil. R_f (AcOEt/hexane 1:10) 0.43. IR (NaCl, $CHCl_3$): 2980, 2912, 1734, 1685, 1595, 1197, 1020. ^{1}H-NMR (400 MHz): 7.76 (*dd*, *J* = 1.2, 7.6, 1 H); 7.53 (*ddd*, *J* = 1.2, 7.6, 7.6, 1 H); 7.36 (*ddd*, *J* = 1.2, 7.6, 7.6, 1 H); 7.20 (*dd*, *J* = 1.2, 7.6, 1 H); 6.39 (*s*, 1 H); 4.29 (*q*, *J* = 7.2, 2 H); 1.87 (*d*, *J* = 1.2, 3 H); 1.55 (*d*, *J* = 1.2, 3 H); 1.35 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (100 MHz): 189.3; 164.3; 140.1; 133.6; 133.0; 130.2; 129.9; 126.7; 123.3; 62.1; 25.8; 19.1; 13.9. HR-ESI-MS: 233.1179 ($[M+H]^+$, $C_{14}H_{17}O_3^+$; calc. 233.1178).

Ethyl 2-[3-(Cyclohexylidenemethyl)pyridin-2-yl]-2-oxoacetate (**1k**). Yield: 42%. Pale yellow solid. M.p. 39°. R_f (AcOEt/hexane 1:3) 0.59. IR (NaCl, $CHCl_3$): 3018, 2933, 2854, 1737, 1707, 1450, 1018, 987. ^{1}H-NMR (300 MHz): 8.56 (*dd*, *J* = 1.3, 4.6, 1 H); 7.62 (*d*, *J* = 7.9, 1 H); 7.39–7.44 (*m*, 1 H); 6.60 (*s*, 1 H); 4.43 (*q*, *J* = 7.1, 2 H); 2.31 (*t*, *J* = 5.4, 2 H); 2.16 (*t*, *J* = 5.6, 2 H); 1.51–1.69 (*m*, 6 H); 1.39 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (75 MHz): 188.4; 165.8; 147.4; 147.0; 146.9; 139.5; 136.5; 126.5; 117.9; 61.9; 37.5; 29.7; 28.4; 27.8; 26.5; 14.1. HR-ESI-MS: 274.1141 ($[M+H]^+$, $C_{16}H_{20}NO_3^+$; calc. 274.1443).

Diethyl 2,2′-[Cyclohexane-1,4-diylidenebis(methylylidenebenzene-2,1-diyl)]bis(2-oxoacetate) (**10d**). Prepared from **13**. Yield: 62% (*cis*/*trans ca.* 3:2). Yellow oil. R_f (AcOEt/hexane 1:3) 0.63. IR (NaCl, neat): 2958, 2937, 1747, 1732, 1651, 1595, 1454, 1195. ^{1}H-NMR (300 MHz): 7.72–7.78 (*m*, 2 H); 7.50–7.58 (*m*, 2 H); 7.33–7.41 (*m*, 2 H); 7.19–7.23 (*m*, 2 H); 6.49 (*s*, 0.8 H); 6.44 (*s*, 1.2 H); 4.27–4.36 (*m*, 4 H); 2.43

(*s*, 1.6 H); 2.19–2.21 (*m*, 4.8 H); 2.01 (*s*, 1.6 H); 1.33–1.39 (*m*, 6 H). ^{13}C-NMR (75 MHz): 189.1; 188.9; 164.2; 164.17; 144.9; 144.7; 139.3; 139.3; 133.7; 133.4; 133.1; 130.6; 130.5; 130.2; 130.1; 127.0; 126.9; 121.8; 121.7; 62.29; 62.26; 37.4; 36.5; 30.0; 29.4; 14.0; 13.98. HR-ESI-MS: 461.1962 ($[M+H]^+$, $C_{28}H_{29}O_4^+$; calc. 461.1964).

Data of trans-**10d**. Prepared from *trans*-**13**. White solid. M.p. 116°. ^{1}H-NMR (300 MHz): 7.76 (*dd*, *J* = 1.1, 7.8, 2 H); 7.55 (*td*, *J* = 1.3, 7.5, 2 H); 7.38 (*t*, *J* = 7.2, 2 H); 7.22 (*d*, *J* = 7.6, 2 H); 6.44 (*s*, 2 H); 4.30 (*q*, *J* = 7.2, 4 H); 2.19–2.21 (*m*, 8 H); 1.35 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (75 MHz): 189.1; 164.2; 144.9; 139.3; 133.7; 133.1; 130.5; 130.1; 126.9; 121.7; 62.3; 36.5; 30.0; 14.0.

2-Alkenylphenyl 2-*oxoacetates* **1h** and **1r** were prepared from **1c** and **1m**, resp., according to the procedure described in [22].

Ethyl 3-[2-(2-Methylprop-1-en-1-yl)phenyl]-3-oxopropanoate (**1h**). Yield: 71%. Yellow oil. R_f (AcOEt/hexane 1:10) 0.47. IR (NaCl, neat): 2982, 2933, 1737, 1682, 1443, 1408, 1382, 1193, 772. ^{1}H-NMR (400 MHz): 7.63 (*d*, *J* = 8.0, 0.75 H); 7.58 (*d*, *J* = 7.6, 0.25 H); 7.22–7.47 (*m*, 3 H); 6.46 (*s*, 0.75 H); 6.35 (*s*, 0.25 H); 5.36 (*s*, 0.25 H); 4.25 (*q*, *J* = 7.2, 0.5 H); 4.17 (*q*, *J* = 7.2, 1.5 H); 3.88 (*s*, 1.5 H); 2.51 (*s*, 0.25 H); 1.92 (*s*, 2.25 H); 1.90 (*s*, 0.75 H); 1.75 (*s*, 0.75 H); 1.67 (*s*, 2.25 H); 1.33 (*t*, *J* = 7.2, 0.75 H); 1.23 (*t*, *J* = 7.2, 2.25 H). ^{13}C-NMR (100 MHz): 196.7; 173.3; 172.9; 167.5; 138.1; 137.5; 137.3; 135.5; 133.5; 131.5; 131.1; 130.8; 130.7; 129.6; 128.6; 128.3; 128.1; 126.4; 126.2; 124.2; 124.0; 92.2; 61.2; 60.2; 48.6; 26.2; 26.1; 19.3; 14.3; 14.1. HR-ESI-MS: 247.1340 ($[M+H]^+$, $C_{15}H_{19}O_3^+$; calc. 247.1334).

Ethyl 3-[2-(Cyclohexylidenemethyl)phenyl]-3-oxopropanoate (**1r**). Yield: 45%. Yellow oil. R_f (AcOEt/hexane 1:10) 0.47. IR (NaCl, neat): 3434, 2932, 2855, 1737, 1641, 1253, 1193, 757. ^{1}H-NMR (400 MHz): 7.61 (*d*, *J* = 7.6, 0.5 H); 7.60 (*d*, *J* = 7.6, 0.5 H); 7.18–7.45 (*m*, 3 H); 6.40 (*s*, 0.5 H); 6.28 (*s*, 0.5 H); 5.43 (*s*, 0.5 H); 4.25 (*q*, *J* = 7.2, 1 H); 4.17 (*q*, *J* = 7.2, 1 H); 3.91 (*s*, 1 H); 2.11–2.30 (*m*, 5 H); 1.48–1.67 (*m*, 5 H); 1.33 (*t*, *J* = 7.2, 1.5 H); 1.23 (*t*, *J* = 7.2, 1.5 H). ^{13}C-NMR (100 MHz): 196.9; 173.1; 167.5; 145.1; 137.8; 137.6; 131.4; 131.1; 130.8; 129.6; 128.6; 128.1; 126.4; 126.3; 121.2; 120.8; 92.2; 61.2; 48.8; 37.3; 37.2; 29.72; 29.6; 28.3; 28.3; 27.7; 27.6; 26.6; 26.5; 14.3; 14.0. HR-ESI-MS: 287.1649 ($[M+H]^+$, $C_{18}H_{23}O_3^+$; calc. 287.1647).

3-(Cyclohexylidenemethyl)naphthalene-2-carbaldehyde (**8a**) was prepared from naphthalene-2,3-dicarbaldehyde by first protecting one of its CHO groups with ethylene glycol (1.0 equiv.) in benzene with TsOH (5 mol-%) at reflux over a *Dean–Stark* setup, followed by a *Wittig* reaction with cyclohexyl (triphenyl)phosponium bromide (1.1 equiv.) with BuLi (1.1 equiv.) as base in THF, and finally deprotection with $InCl_3$ (5 mol-%) in MeOH/H_2O 3:2 at reflux. Overall yield (three steps): 50%. White solid. M.p. 76°. R_f (AcOEt/hexane 1:20) 0.33. IR (NaCl, $CHCl_3$): 3055, 3012, 2927, 2852, 1693, 1624, 1589, 1435, 1215. ^{1}H-NMR (400 MHz): 10.38 (*s*, 1 H); 8.41 (*s*, 1 H); 7.96 (*d*, *J* = 8.2, 1 H); 7.82 (*d*, *J* = 8.2, 1 H); 7.63 (*s*, 1 H); 7.58 (*t*, *J* = 8.1, 1 H); 7.51 (*t*, *J* = 7.5, 1 H); 6.66 (*s*, 1 H); 2.38 (*t*, *J* = 6.0, 2 H); 2.19 (*t*, *J* = 6.0, 2 H); 1.53–1.74 (*m*, 6 H). ^{13}C-NMR (100 MHz): 193.0; 146.2; 137.2; 136.3; 135.8; 133.7; 132.5; 131.1; 129.6; 128.7; 127.6; 126.4; 118.4; 37.3; 29.8; 28.6; 27.8; 26.6. HR-ESI-MS: 251.1438 ($[M+H]^+$, $C_{18}H_{19}O^+$; calc. 251.1436).

2,2′-(Cyclohexane-1,4-diylidenedimethylylidene)dibenzaldehyde (**10a**) was prepared from *4-bis(2-bromobenzylidene)cyclohexane* (**13**) *via* a formylation reaction with BuLi (2.1 equiv.) and DMF (3.0 equiv.) in THF at −78°. Yield: 72% (*cis*/*trans* 2:3). White solid. M.p. 104–106°. R_f (AcOEt/hexane 1:10) 0.23. IR (NaCl, $CHCl_3$): 3018, 2943, 2843, 1693, 1595, 1446, 1197, 667. ^{1}H-NMR (400 MHz): 10.25 (*s*, 1.2 H); 10.24 (*s*, 0.8 H); 7.90 (*dd*, *J* = 7.8, 1.2, 1.2 H); 7.87 (*dd*, *J* = 7.8, 1.2, 0.8 H); 7.56 (*td*, *J* = 7.5, 1.4, 1.2 H); 7.52 (*td*, *J* = 7.5, 1.4, 0.8 H); 7.37–7.41 (*m*, 2 H); 7.25 (*d*, *J* = 7.6, 1.2 H); 7.20 (*d*, *J* = 7.6, 0.8 H); 6.67 (*s*, 1.2 H); 6.63 (*s*, 1.2 H); 2.56 (*s*, 1.6 H); 2.33–2.38 (*m*, 4.8 H); 2.15 (*s*, 1.6 H). ^{13}C-NMR (100 MHz): 192.4; 144.5; 141.2; 133.9; 133.6; 133.6; 130.8; 128.3; 127.1; 119.8; 37.9; 37.0; 30.6; 29.7. HR-ESI-MS: 317.1548 ($[M+H]^+$, $C_{22}H_{21}O_2^+$; calc. 317.1542).

Data of cis-**10a**. Prepared from *cis*-**13**. White solid. M.p. 67° NMR (400 MHz): 10.25 (*s*, 2 H); 7.87 (*dd*, *J* = 7.8, 1.2, 2 H); 7.51 (*td*, *J* = 7.5, 1.4, 2 H); 7.36 (*t*, *J* = 7.5, 2 H); 7.20 (*d*, *J* = 7.6, 2 H); 6.67 (*s*, 2 H); 2.56 (*s*, 4 H); 2.15 (*s*, 4 H). ^{13}C-NMR (100 MHz): 192.4; 144.4; 141.1; 133.9; 133.6; 130.8; 128.4; 127.1; 119.8; 37.9; 29.8.

Data of trans-**10a**. Prepared from *trans*-**13**. White solid. M.p. 105° NMR (400 MHz): 10.18 (*s*, 2 H); 7.82 (*dd*, *J* = 7.6, 2 H); 7.48 (*t*, *J* = 7.2, 2 H); 7.30 (*t*, *J* = 7.5, 2 H); 7.16 (*d*, *J* = 7.6, 2 H); 6.55 (*s*, 2 H); 2.26–2.28 (*m*, 8 H). ^{13}C-NMR (100 MHz): 192.4; 144.4; 141.1; 133.9; 133.6; 130.8; 128.3; 119.7; 36.9; 30.4.

Compound **13** was prepared from cyclohexane-1,4-dione *via* a *Wittig* reaction with (2-bromobenzyl)triphenylphosphonium bromide (2.1 equiv.) with *t*BuOK (2.1 equiv.) as base, in THF at 0°. Yield: 42% (*cis*/*trans ca.* 1:1). R_f (AcOEt/hexane 1:10) 0.83. IR (NaCl): 3016, 2962, 1463, 1431, 1215, 1024, 756, 669. HR-ESI-MS: 416.9872 ($[M+H]^+$, $C_{20}H_{19}{}^{79}Br_2^+$; calc. 416.9853).

Data of cis-**13**. White powder recrystallized from CH_2Cl_2. M.p. 97°. ^{1}H-NMR (400 MHz): 7.56 (*d*, *J* = 8.0, 2 H); 7.17–7.25 (*m*, 4 H); 7.07 (*t*, *J* = 7.8, 2 H); 6.29 (*s*, 2 H); 2.51 (*s*, 4 H); 2.28 (*s*, 4 H). ^{13}C-NMR (100 MHz): 142.5; 138.2; 132.5; 130.9; 127.9; 126.8; 124.3; 122.937.9; 29.8.

Data of trans-**13**. Colorless crystals from hexanes/CH_2Cl_2. M.p. 177°. ^{1}H-NMR (400 MHz): 7.59 (*dd*, *J* = 8.0, 2 H); 7.22–7.30 (*m*, 4 H); 7.10 (*t*, *J* = 7.6, 2 H); 6.27 (*s*, 2 H); 2.37–2.43 (*m*, 8 H). ^{13}C-NMR (100 MHz): 142.5; 138.1; 132.4; 130.9; 127.9; 126.8; 124.3; 122.9; 37.1; 30.5.

REFERENCES

[1] A. Rescifina, M. A. Chiacchio, A. Corsaro, E. De Clercq, D. Iannazzo, A. Mastino, A. Piperno, G. Romeo, R. Romeo, V. Valveri, *J. Med. Chem.* **2006**, *49*, 709; L. H. Mejorado, T. R. R. Pettus, *J. Am. Chem. Soc.* **2006**, *128*, 15625; A. N. Lowell, M. W. Fennie, M. C. Kozlowski, *J. Org. Chem.* **2008**, *73*, 1911.

[2] J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028; V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Oliver, R. Silbey, J.-L. Bredas, *Chem. Rev.* **2007**, *107*, 926; J. E. Anthony, *Angew. Chem., Int. Ed.* **2008**, *47*, 452; S. S. Zade, M. Bendikov, *Angew. Chem., Int. Ed.* **2010**, *49*, 4012; W. Nakanishi, T. Yoshioka, H. Taka, J. Y. Xue, H. Kita, H. Isobe, *Angew. Chem., Int. Ed.* **2011**, *123*, 5435.

[3] Y. Kuninobu, Y. Nishina, K. Takai, *Tetrahedron* **2007**, *63*, 8463; X. Jiang, W. Kong, J. Chen, S. Ma, *Org. Biomol. Chem.* **2008**, *6*, 3606; S.-G Li, X.-Q. Hu, Z.-X. Jia, P.-F. Xu, *Tetrahedron* **2010**, *66*, 8557; C. Feng, T.-P. Loh, *J. Am. Chem. Soc.* **2010**, *132*, 17710.

[4] N. Asao, K. Takahashi, S. Lee, T. Kasahara, Y. Yamamoto, *J. Am. Chem. Soc.* **2002**, *124*, 12650; N. Asao, T. Kasahara, Y. Yamamoto, *Angew. Chem., Int. Ed.* **2003**, *42*, 3504; N. Asao, H. Aikawa, Y. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 7458; H. Kusama, H. Funami, N. Iwasawa, *Synthesis* **2007**, *13*, 2014; Y. Isogai, Menggenbateer, F. N. Khan, N. Asao, *Tetrahedron* **2009**, *65*, 9575; X.-L. Fang, R.-Y. Tang, X.-G. Zhang, P. Zhong, C.-L. Deng, J.-H. Li, *J. Organomet. Chem.* **2011**, *696*, 352.

[5] S. Saito, Y. Yamamoto, *Chem. Rev.* **2000**, *100*, 2901; Y. Yamamoto, *Curr. Org. Chem.* **2005**, *9*, 503; Y. Sato, T. Tamura, A. Kinbara, M. Mori, *Adv. Synth. Catal.* **2007**, *349*, 647.

[6] W.-M. Liu, Z.-H. Liu, W.-W. Cheong, L.-Y. T. Priscilla, Y. Li, K. Narasaka, *Bull. Korean Chem. Soc.* **2010**, *31*, 563.

[7] M. Shoji, H. Imai, I. Shiina, H. Kakeya, H. Osada, Y. Hayashi, *J. Org. Chem.* **2004**, *69*, 1548; U. K. Tambar, T. Kano, B. Stoltz, *Org. Lett.* **2005**, *7*, 2413; J.-P. Lumb, D. Trauner, *Org. Lett.* **2005**, *7*, 5865.

[8] K. Kundu, J. V. McCullagh, A. T. Morehead Jr., *J. Am. Chem. Soc.* **2005**, *127*, 16042.

[9] A. K. Miller, M. R. Banghart, C. M. Beaudry, J. M. Suh, D. Trauner, *Tetrahedron* **2003**, *59*, 8919; C.-Y. Lo, C.-C. Lin, H.-M. Cheng, R.-S. Liu, *Org. Lett.* **2006**, *8*, 3153; C.-C. Lin, T.-M. Teng, A. Odedra, R.-S. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 3798.

[10] C. Hertweck, *J. Prakt. Chem.* **2000**, *342*, 316; W. He, X. Sun, A. J. Frontier, *J. Am. Chem. Soc.* **2003**, *125*, 14278; M. P. A. Lyle, N. D. Draper, P. D. Wilson, *Org. Lett.* **2005**, *7*, 901; Y. Li, Z. Yu, S. Wu, *J. Org. Chem.* **2008**, *73*, 5647; Y.-M. Pan, S.-Y. Zhao, W.-H. Ji, Z.-P. Zhan, *J. Comb. Chem.* **2009**, *11*, 103.

[11] R. Dumeunier, I. E. Markó, *Tetrahedron Lett.* **2004**, *45*, 825.

[12] T. T. Dang, F. Boeck, L. Hintermann, *J. Org. Chem.* **2011**, *76*, 9353.

[13] E. M. Cabaleiro-Lago, J. Rodríguez-Otero, A. Peña-Gallego, *J. Mol. Struct.: THEOCHEM* **2007**, *811*, 141; L. M. Bishop, J. E. Barbarow, R. G. Bergman, D. Trauner, *Angew. Chem., Int. Ed.* **2008**, *47*, 1; D. Lebœuf, L. Iannazzo, A. Geny, M. Malacria, K. P. C. Vollhardt, C. Aubert, V. Gandon, *Chem. – Eur. J.* **2010**, *16*, 8904.

[14] C. K. Bradsher, *Chem. Rev.* **1987**, *87*, 1277.

[15] J. B. Press, K. L. Sorgi, J. J. McNally, G. C. Leo, *J. Org. Chem.* **1994**, *59*, 5088.

[16] P. Müller, J.-P. Schaller, *Helv. Chim. Acta* **1989**, *72*, 1608.

[17] E. Hasegawa, Y. Ogawa, K. Kakinuma, H. Tsuchida, E. Tosaka, S. Takizawa, H. Muraoka, T. Saikawa, *Tetrahedron* **2008**, *64*, 7724.
[18] W. E. Billups, J. D. Buynak, D. Butler, *J. Org. Chem.* **1980**, *45*, 4636.
[19] M.-Y. Lin, A. Das, R.-S. Liu, *J. Am. Chem. Soc.* **2006**, *128*, 9340.
[20] C. J. Moody, G. J. Warrellow, *J. Chem. Soc., Perkin Trans. 1* **1987**, 913.
[21] B. W.-Q. Hui, S. Chiba, *Org. Lett.* **2009**, *11*, 729.
[22] H. Li, Z. He, X. Guo, W. Li, X. Zhao, Z. Li, *Org. Lett.* **2009**, 11, 4176.

Received July 26, 2012