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Catalyzed addition of acid chlorides to alkynes by unmodified nano-powder magnetite: synthesis of chlorovinyl ketones, furans, and related cyclopentenone derivatives

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In memory of Professor Robert E. Gawley

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ABSTRACT

Inexpensive and commercially available nano-powder magnetite is an excellent catalyst for the addition of acid chlorides to internal and terminal alkynes, yielding the corresponding chlorovinyl ketones in good yields. The process has been applied to the synthesis of 5-chloro-4-arylcyclopent-2-enones, 3-aryl-1*H*-cyclopenta[*a*]naphthalen-1-ones, and (*E*)-3-alkylidene-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ones, just by changing the nature of the starting acid chloride or the alkyne. All tested processes elapse with an acceptable or excellent regio- and stereo-selectivity. Moreover, the use of the iridium impregnated on magnetite catalyst permits the integration of the chloroacylation process with a second dehydrochlorination–annulation process to yield, in one-pot, 1-aryl-2,4-dialkylfurans in good yields, independently of the nature of the starting reagents, and including the heteroaromatic ones.

1. Introduction

The design of catalysts able to perform the heteroatom-acylation of alkynes, forming in a regio-, stereo-selective and simultaneous manner a carbon–carbon and a carbon–heteroatom bonds, is extremely challenging.[1] The interest of this reaction is not only a matter of the intrinsic process but also of the final products. Thus, the addition of acid chlorides to alkynes gives β-chlorovinyl ketones,[2] which are a class of compounds very useful for the synthesis of a variety of other compounds.

The initial use of stoichiometric amounts of aluminum derivatives, as Lewis acids, for the Friedel–Crafts addition of acyl chlorides to alkynes showed a very low selectivity, with the *E*-isomer being the major product.[3] The replacement of the aluminum catalyst to silver perchlorate,[4] gallium trichloride,[5] or zinc oxide[6] did not change so much the initial picture of this process. This fact favored the introduction of typical transition metal complexes, such as those derived from rhodium[7] or iridium.[8] These new complexes permitted the reduction of the catalyst amount from stoichiometric to 5–1 mol %, obtaining only the *Z*-chlorovinyl ketone isomer. However, these catalysts have new drawbacks, such as their inherent toxicity, their handling difficulty, their instability, high price, the CO extrusion from reagents depending on the catalyst, and their no-reactivity with internal alkynes.

Very recently, different iron salts ($FeBr_2$[9] and $FeCl_3$[10]) have been introduced as a convenient, inexpensive, environmentally friendly, and practical catalyst alternative. In our ongoing project on the use of magnetite as an efficient catalyst for different organic reactions,[11] we anticipated that it could be a new and sustainable alternative for this process. Herein, we wish to describe its use as valuable catalyst for the addition of acid chlorides to poor reactive internal alkynes leading to the formation of chlorovinyl ketones, cyclopenta[*a*]naphthalen-1-ones, 5-chloro-4-arylcyclopent-2-enones, and 2,3,5-trisubstituted furans, depending on the nature of the substrates.

2. Results and discussion

2.1. Chloroacylation process

Since the reaction with internal alkynes is either unknown using rhodium, iridium, gallium trichloride, and iron dibromide derivatives or yields a very low isomeric ratio for the iron trichloride-catalyzed reaction[10] (with the *E*/*Z* ratio being 2.2/1), the addition of benzoyl chloride (**1a**) to dec-5-yne (**2a**) was chosen as model (Table 1). The first trial was carried out in absence of any catalyst to

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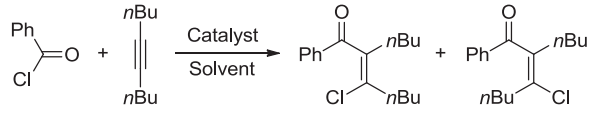
Table 1
Optimization of the reaction conditions[a]



1a 2a 3a 4a

Entry	Cat. (mol %)	T (°C)	Solvent	t (h)	**3a** (%)[b]	**4a** (%)[b]
1		70	PhMe	7	0	0
2	Fe_3O_4[c] (65)	70	PhMe	0.25	62	20
3	Fe_3O_4[d] (65)	70	PhMe	0.25	72	19
4	Fe_3O_4[d] (33)	70	PhMe	0.25	83	11
5	Fe_3O_4[d] (13)	70	PhMe	0.25	64	18
6	Fe_3O_4[d] (130)	70	PhMe	0.25	66	16
7	Fe_3O_4[d] (33)	110	PhMe	0.25	55	22
8	Fe_3O_4[d] (33)	25	PhMe	7	44	23
9[e]	Fe_3O_4[d] (33)	70	PhMe	0.25	73	21
10[f]	Fe_3O_4[d] (33)	70	PhMe	0.25	59	13
11	Fe_3O_4[d] (33)	70	—	0.25	61	21
12	Fe_3O_4[d] (33)	70	Dioxane	0.25	0	0
13	Fe_3O_4[d] (33)	70	MeCN	0.25	0	0
14	Fe_3O_4[d] (33)	70	DMF	0.25	0	0
15	Fe_3O_4[d] (33)	70	$CHCl_3$	0.25	61	28
16	Fe_3O_4[d] (33)	70	$(ClCH_2)_2$	0.25	60	30
17	FeO (33)	70	PhMe	1	24	8
18	Fe_2O_3 (33)	70	PhMe	0.25	74	21
19	$FeCl_2$ (33)	70	PhMe	1	20	8
20	$FeCl_3$ (33)	70	PhMe	0.25	69	24

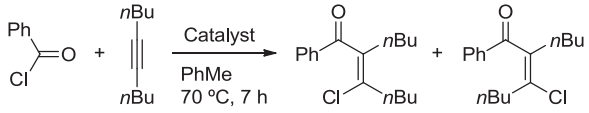
[a] Reaction carried out using **1a** (1.5 mmol) and **2a** (1.0 mmol) in the corresponding solvent (2.5 mL) under an argon atmosphere.
[b] Isolated yield after column chromatography.
[c] Powder<5 μm.
[d] Powder<50 nm.
[e] Reaction performed using **1a** (2 mmol) and **2a** (1.0 mmol).
[f] Reaction performed using **1a** (1.0 mmol) and **2a** (2.0 mmol).

prove the real activity of iron oxide (entry 1), and after several hours the reaction failed recovering the unchanged alkyne **2a**. However, a similar reaction but conducted in the presence of a substoichiometric amount of micro-particles of magnetite (65% of the stoichiometric gram atomic mass of iron) gave a mixture of isomers (*Z*)-**3a** and (*E*)-**4a** after only 15 min at 70 °C (entry 2). Both isomers could be isolated by column chromatography and fully characterized. Once the activity of unmodified commercial magnetite was proved, the size of the particles was tested, finding that the related nano-particle gave even better yield and *Z*/*E* ratio (3.8/1, entry 3). Then, the influence of the amount of catalyst was studied (entries 3–6), as well as the temperature (entries 6–8), the reagent's ratios (entries 9 and 10), and the solvent (entries 11–16), with the best condition being described in the entry 4.

After finding the activity of nano-particles of magnetite, we studied the activity of other iron sources, such as iron(II) and (III) as catalyst (entries 17 and 18), with nano-particles of Fe_2O_3 having a similar activity to magnetite. The necessity of a slight excess of acyl chloride to complete the reaction made us suspect that the magnetite function was to form a soluble iron chloride species, and to prove this fact we performed the reaction using $FeCl_2$ and $FeCl_3$, and, as in the case of oxides, the iron(III) salt gave a better result than iron(II). However, the results were significantly inferior to that obtained using magnetite (compare entries 4, 19, and 20), and with the price of iron chloride being also another small disadvantage. It should be pointed out that the recycled magnetite had a lower activity rendering, in a second trial, a mixture of compounds in lower yield (72%), and dropping to 47% in the third run. To understand this fact, we studied by ICP-MS analysis the resulting reaction solution mixture after the first cycle, finding that 1.1% of initial amount of iron of the catalyst was leached to the solution. This leaching phenomenon could explain the decrease of the obtained yield.

Recently, we have developed a new, simple, and robust method to immobilize different transition metal oxides onto micro-particles of magnetite,[12] and we studied these catalysts, as well as new ones, such as rhodium, silver, tungsten, and gold derivatives (see Supplementary data) as possible promoters of the process. However, in all cases the results (Table 2) were similar to those obtained using only the magnetite support (entry 1).

Table 2
Optimization of the catalyst[a]



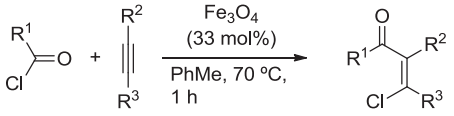
1a 2a 3a 4a

Entry	Catalyst (mol %)	**3a** (%)[b]	**4a** (%)[b]
1	Fe_3O_4[c] (65)	62	20
2	CoO–Fe_3O_4 (1.4)	56	18
3	NiO–Fe_3O_4 (1.4)	58	29
4	CuO–Fe_3O_4 (1.3)	64	24
5	Ru_2O_3–Fe_3O_4 (1.4)	64	23
6	Rh_2O_3–Fe_3O_4 (0.8)	58	26
7	PdO–Fe_3O_4 (1.4)	8	4
8	Ag_2O/Ag–Fe_3O_4 (1.3)	66	20
9	WO_3–Fe_3O_4 (0.6)	66	16
10	IrO_2–Fe_3O_4 (0.14)	67	19
11	PtO/PtO_2–Fe_3O_4 (0.6)	59	17
12	Au_2O_3/Au–Fe_3O_4 (0.1)	65	21
13	NiO/CuO–Fe_3O_4 (0.9/1.1)	60	25
14	PdO/CuO–Fe_3O_4 (1.5/0.8)	9	6

[a] Reaction carried out using **1a** (1.5 mmol) and **2a** (1.0 mmol) in toluene (2.5 mL) under an argon atmosphere.
[b] Isolated yield after column chromatography.
[c] Powder<5 μm.

As the nano-particle of magnetite was the best catalyst, the scope of the reaction was studied (Table 3). The reaction gave the expected *Z*-isomers **3** as the main product after only a 1 h reaction. The reaction gave similar results independently of the side chain of internal alkyne (entries 1–3). In the case of using ethynylbenzene

Table 3
Preparation of β-chlorovinyl ketones[a]



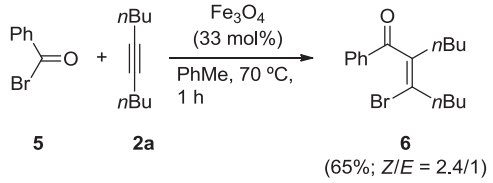
1 2 3

Entry	R^1	R^2	R^3	Z/E ratio[b]	No.	Yield (%)[c]
1	Ph	^{n}Bu	^{n}Bu	7.5/1	**3a**	83
2	Ph	Et	Et	7.5/1	**3b**	89
3	Ph	^{n}C_5H_{11}	^{n}C_5H_{11}	5.7/1	**3c**	82
4	Ph	H	Ph	>20/1	**3d**	63
5	4-ClC_6H_4	^{n}Bu	^{n}Bu	3.5/1	**3e**	70
6	4-^{t}BuC_6H_4	^{n}Bu	^{n}Bu	3.5/1	**3f**	75
7	4-$MeOC_6H_4$	^{n}Bu	^{n}Bu	15/1	**3g**	91[d]
8	2-$MeOC_6H_4$	^{n}Bu	^{n}Bu	2.2/1	**3h**	58
9	4-$FC_{10}H_6$[e]	^{n}Bu	^{n}Bu	15/1	**3i**	89
10	2-Thienyl	^{n}Bu	^{n}Bu	4.1/1	**3j**	74
11	4-$MeOC_6H_4$	Ph	Ph	4/1	**3k**	72
12	Ph$(CH_2)_2$	^{n}Bu	^{n}Bu	3/1	**3l**[f]	77

[a] Reaction carried out using **1** (1.5 mmol) and **2** (1.0 mmol) in toluene (2.5 mL) under an argon atmosphere.
[b] Determined by ^{1}H NMR from the crude mixture.
[c] Isolated yield after column chromatography.
[d] The relate indenone derivative was detected from the crude reaction medium by GC–MS (<3%).
[e] 4-$FC_{10}H_6$ denotes for 4-fluoronaphth-1-yl.
[f] The compound **3l** could not be separated from the mixture of both isomers (*Z*)-**3l**/(*E*)-**3l**.

(entry 4) practically only one regio- and stereo-isomer was obtained, as it was previously found for other ruthenium, iridium or iron complexes. The presence of electron-withdrawing or electron-donating groups at the *para*-position of aromatic ring did not have a significant effect on the results (entries 5–7). However, the presence of a group located at *ortho*-position (entry 8) of the acid chloride gave worse results, in terms of chemical yield and isomeric ratio. This fact could be a proof of a possible steric hindrance in the transition state. Other acyl derivatives, such as 4-naphthyl or thienyl, were used without finding any difference with the model reagents (compare entries 1, 9, and 10). The reaction of 4-methoxybenzoyl chloride with 1,2-diphenylethyne gave the expected product **3k** (entry 11). It should be pointed out that the reaction using aliphatic 3-phenylpropanoyl chloride gave the expected mixture of products (*Z*)-**3l** and (*E*)-**4l**, with the main isomer **3l** not being possible to be separated from the isomer **4l**; contrary to other aromatic examples, in which isomer **3** could be isolated but not the related **4**.

The above protocol could be used not only for acyl chlorides (**1**) but also for the related bromides. Thus, the addition of benzoyl bromide (**5**) to dec-5-yne (**2a**) using nano-particles of magnetite (Scheme 1) gave the expected bromovinyl ketone **6**, with similar yield and isomeric ratio to the case of using the related chlorine reagent.



5 **2a** **6** (65%; *Z*/*E* = 2.4/1)

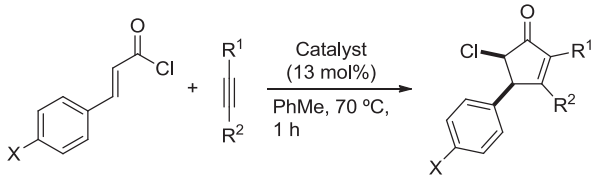
Scheme 1. Preparation of a β-bromovinyl ketone.

2.2. Nazarov-type cyclization processes

The mechanistic considerations of this reaction have proposed the formation of a vinyl cation[3c,4,5,10] intermediate, which is captured by the chloride ion through an intra- or intermolecular process. With this proposed catalytic mechanism in mind, we thought that the cationic intermediate could be trapped to form a cyclic compound by using the adequate olefinic reagent in a Nazarov-type process.[13] So, the reaction of the alkyne **2a** with cinnamoyl chloride (**7a**, X=H) yielded, after only one hour at 70 °C, the expected 5-chlorocyclopent-2-enone **8a** in good yield and as a single isomer (Table 4, entry 1).

Then, we studied the influence of the amount of nano-magnetite (entries 1–3), the source of iron oxides (entries 4 and 5), and different iron chlorides (entries 6 and 7). As in the case of the chlorovinylation process, nano-magnetite gave even better results than iron(III) oxide or chloride. The reaction was performed with similar results with other symmetrically substituted alkynes (entries 8 and 9). In the case of using 4,4-dimethylpent-2-yne (**2f**), the reaction was regioselective, rendering only the corresponding 2-methyl-3-*tert*-butylcyclopentenone **8d** with good yield (entry 10). However, only in this case both diastereomeric *cis*/*trans* isomer were detected and isolated. The assignation of relative configuration was performed in basis of the constant coupling between both hydrogen of cyclopentenone ring. The minor isomer showed a *J*=2.8 Hz, and it was assumed that it was the *cis*-**8d**. Meanwhile the major isomer showed a *J*=1.0 Hz, and it was assumed that it was the *trans*-**8d′**. These constant coupling for all compounds **8** were always higher than 2.5 Hz and they were assigned as *cis*-ones. The reaction using a *para*-substituted cinnamoyl chloride gave the expected product **8** with similar results to previous trials, independently of the electron-nature of the group (entries 11 and 12).

Table 4
Preparation of 5-chloro-4-arylcyclopent-2-enones[a]



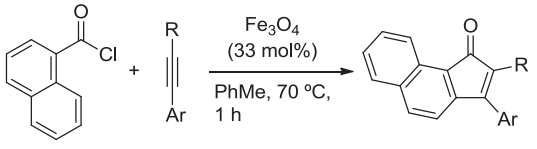
7 **2** **8**

Entry	Catalyst	X	R^1	R^2	No.	Yield (%)[b]
1	Fe_3O_4[c,d]	H	^{n}Bu	^{n}Bu	**8a**	78
2	Fe_3O_4[c]	H	^{n}Bu	^{n}Bu	**8a**	77
3	Fe_3O_4[c,e]	H	^{n}Bu	^{n}Bu	**8a**	58
4	FeO	H	^{n}Bu	^{n}Bu	**8a**	29
5	Fe_2O_3	H	^{n}Bu	^{n}Bu	**8a**	67
6	$FeCl_2$	H	^{n}Bu	^{n}Bu	**8a**	34
7	$FeCl_3$	H	^{n}Bu	^{n}Bu	**8a**	69
8	Fe_3O_4[c]	H	Et	Et	**8b**	89
9	Fe_3O_4[c]	H	^{n}C_5H_{11}	^{n}C_5H_{11}	**8c**	91
10	Fe_3O_4[c]	H	Me	^{t}Bu	**8d**	91[f]
11	Fe_3O_4[c]	F	^{n}Bu	^{n}Bu	**8e**	67
12	Fe_3O_4[c]	MeO	^{n}Bu	^{n}Bu	**8f**	83

[a] Reaction carried out using **7** (1.5 mmol) and **2** (1.0 mmol) in toluene (2.5 mL) under an argon atmosphere.
[b] Isolated yield after column chromatography.
[c] Power<50 nm.
[d] Reaction performed using 33 mol %.
[e] Reaction performed using 7 mol %.
[f] Mixture of isolated isomers (*cis*-**8d**/*trans*-**8d′**: 3/88%).

After the success in the cyclization process, we rationalized that the stabilization of the vinyl cation intermediate could give us a chance to carry out an intramolecular aromatic electrophilic substitution, yielding fused bicyclic ketones.[3c,7a] For this purpose, we carried out the model reaction of 2-naphthalenecarbonyl chloride (**1j**) with the unsymmetrical 1-phenylpentyne (**9a**) and, after only one hour, the corresponding 3-phenyl-2-methyl-1*H*-cyclopenta[*a*]naphthalen-1-one (**10a**) was obtained in excellent yield and regioselectivity (entry 1 in Table 5), with the other regioisomer not being detected. The structure of compounds **10** was unambiguously assigned according to NOESY, HSQC- and HMBC-NMR experiments, as well as X-ray data for compound **10a** (see Fig. 1). The reaction with other 1-arylalkynes gave, in all cases, the corresponding products **10** (entries 2 and 3) with the reaction pathway starting with the regioselective addition of acyl cation to form the most stable 1-arylvinyl cation.

Table 5
Preparation of 3-aryl-1*H*-cyclopenta[*a*]naphthalen-1-ones[a]



1j **9** **10**

Entry	Ar	R	No.	**4a** (%)[b]
1	Ph	Me	**10a**	91
2	Ph	^{n}Bu	**10b**	87
3	4-MeC_6H_4	Me	**10c**	79

[a] Reaction carried out using **1j** (1.5 mmol) and **9** (1.0 mmol) in toluene (2.5 mL) under an argon atmosphere.
[b] Isolated yield after column chromatography.

Then, we tried to extend the scope of the reaction to simple alkynes of type **2**, in which the postulated cationic intermediate is less stable. The reaction between the acid chloride **1j** and hex-3-yne (**2b**) did not produce the expected cyclopenta[*a*]naphthlen-1-ones of type **10**, but yielded the product **11a** (Table 6, entry 1)

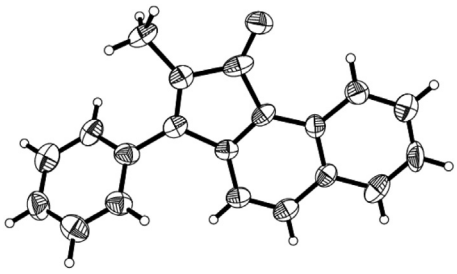
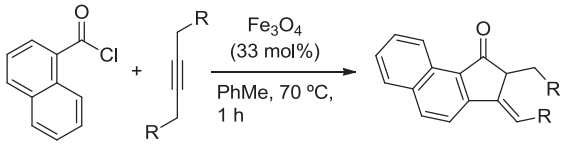


Fig. 1. ORTEP drawing of compound **10a**.

Table 6
Preparation of (*E*)-3-alkylidene-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ones[a]



1j **2** **11**

Entry	R	No.	Yield (%)[b]
1	Me	**11a**	85
2	^{n}Pr	**11b**	87[c,d]
3	^{n}Bu	**11c**	84

[a] Reaction carried out using **1j** (1.5 mmol) and **2** (1.0 mmol) in toluene (2.5 mL) under an argon atmosphere.
[b] Isolated yield after column chromatography.
[c] Reaction performed during 4 h.
[d] A 5% of chlorovinyl ketone of type **3m** was isolated.

with a good chemical yield. To the best of our knowledge, this type of compound has been synthesized for the first time, and its formation could be explained by a simple isomerization, in the reaction media, from the α,β-unsaturated ketone of type **10** to the corresponding conjugated stryryl unit **11**. We do not have any clear explanation of the driving force for this process. The structure of compound **11** was unambiguously assigned according to NOESY, HSQC- and HMBC-NMR experiments, as well as X-ray data for compound **11a** (see Fig. 2). The reaction seems to be general, obtaining similar results for all tested aliphatic-substituted internal alkynes (entries 2 and 3).

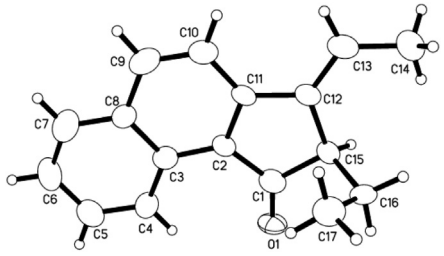
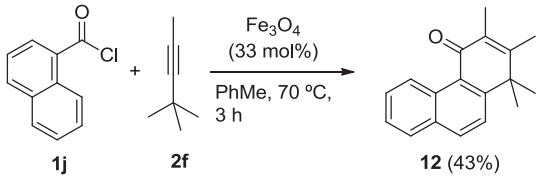


Fig. 2. ORTEP drawing of compound **11a**.

To avoid the formation of an *exo*-cyclic double bond in compounds **11**, we repeated the reaction with alkyne **2f** (Scheme 2). However, in this case, a 1,2-shift methyl migration took place, after the vinyl cation formation to give the more stable allylic

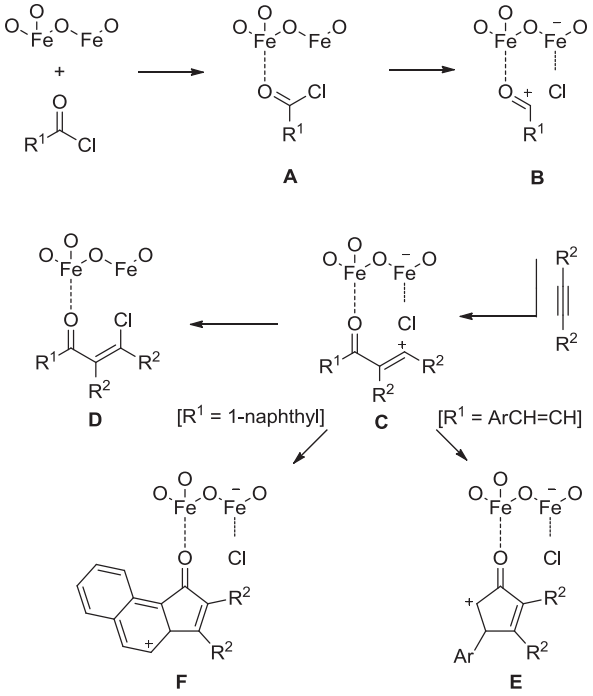


1j **2f** **12** (43%)

Scheme 2. Preparation of compound **12**.

intermediate, which, then cyclized to yield compound **12**. This behavior was previously described for other Lewis acid catalysts.[3c,14]

The hypothetic mechanism pathway is depicted in Scheme 3. The adsorption of acyl chloride on the surface of the magnetite with a debilitation of the corresponding chlorine carbon bond in **A** is the first step of the process. The addition to the alkyne reagent would generate the key vinyl cation **C**. This intermediate **C** renders different intermediates depending on the nature of the substituent R^1 of the starting acyl chloride. So, the usual pathway was the reaction with chloride in a *syn*-manner (**D**). However, if the R^1 group has a carbon–carbon double bond (R^1=ArCH=CH) the vinyl cation **C** suffers a cyclization process to give intermediate **E**, or if the R^1 group has the possibility of suffering electrophilic aromatic substitution (R^1=1-naphthyl) the intermediate yielded cation **F**.



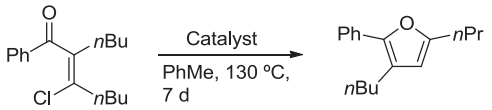
Scheme 3. Proposed mechanism for the addition of acid chloride to alkynes and further evolution.

2.3. Furan cyclization

Very recently, the Tsuji research group has found a new entry to the direct synthesis of 2,5-disubstituted furans starting from acid chlorides and terminal alkynes, in moderate yields for phenyl derivatives and low yields for thienyl ones.[8a] The possible catalytic pathway involved the dehydrochlorination of the corresponding chlorovinyl ketone followed by cyclization of formed allenic ketone. Since zinc chloride, in combination with an amine, has been introduced as a catalyst for this elimination process,[15] we studied the activity of other Lewis acid catalysts for this tandem dehydrochlorination–cyclization process (Table 7), with the idea in mind to integrate all processes starting from internal alkynes to yield 1,2,5-trisubstituted furans.

The reaction of chlorovinyl ketone **3a** with nano-power magnetite did not yield the expected furan **13a** after 7 days at 130 °C. However, the same process but using rhodium trichloride gave the product **13a** in a moderate yield. Then other transition salts were tested, with palladium and iridium giving excellent results (entries 3 and 4). Finally, the same process was conducted with the related transition metal oxides impregnated on magnetite (entries 5–7). From the comparison of the results from both types of catalysts

Table 7
Cyclization of β-chlorovinyl ketone **3a**[a]



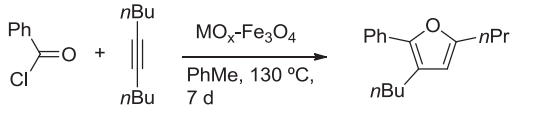
3a **13a**

Entry	Catalyst (mol %)	Yield **13a** (%)[b]
1	Fe_3O_4[c] (65)	0
2	$RhCl_3$ (10)	54
3	$PdCl_2$ (10)	89
4	$IrCl_3$ (10)	87
5	Rh_2O_3–Fe_3O_4 (0.8)	75
6	PdO–Fe_3O_4 (1.4)	82
7	IrO_2–Fe_3O_4 (0.07)	95

[a] Reaction carried out using **3a** (1 mmol) in toluene (2.5 mL) under an argon atmosphere.
[b] Isolated yield after column chromatography.
[c] Powder<5 μm.

could be concluded that the heterogeneous catalysts gave better results than homogenous ones, since with amounts around 1 mol % of heterogeneous catalysts it was possible to obtain similar results to the reached using homogenous ones at 10 mol % loading.

Once we found that the dehydrochlorination–cyclization process was catalyzed by different metallic oxides impregnated on magnetite (Table 7) and that the magnetite could catalyze the addition of acid chlorides to internal alkynes, we tried to perform the whole integrated process. The reaction of chloride **1a** with the alkyne **2a** gave the expected product **13a** after seven days at 130 °C. However, the chemical yield was moderate, independently of the catalyst used (Scheme 4). Then, we carried out the reaction with IrO_2–Fe_3O_4 at 70 °C during 1 h (chloroacylation process) and, after that, the temperature was increased up to 130 °C, with the yield of compound **13a** and **3a** being 59 and 30%, respectively.



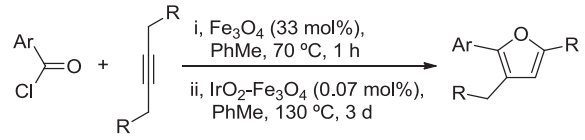
1a **2a** **13a**

MO_x (mol%)	Yield (%)
Rh_2O_3 (0.8)	38
PdO (1.4)	7
IrO_2 (0.07)	45

Scheme 4. Direct Synthesis of Furan **13a**.

We believed that the main reason for this behavior was that the excess of acid chloride decomposed the catalyst, and formed the corresponding less active and soluble transition metal chloride. To prove this hypothesis we perform a two-step one-pot process (Table 8). After carrying out the standard reaction of chloride **1a** with alkyne **2a** catalyzed by nano-powder magnetite, this catalyst was removed by a magnet and $RhCl_3$ (1 mol %, entry 1), $PdCl_2$ (1 mol %, entry 2), or $IrCl_3$ (1 mol %, entry 3) was added to this mixture giving in all cases better results than the strategy showed in Scheme 3. Instead of homogenous salt, we, then, studied the same process but using the impregnated catalyst. After removing the magnetite by the magnet, the corresponding palladium impregnated on magnetite catalyst was added (1.2 mol %, entry 4) obtaining a similar result to the obtained one using the homogenous catalyst. The protocol using iridium impregnated catalyst (0.07 mol %) gave an excellent result (entry 5, 88%), since the same reaction but using $IrCl_3$ (0.07 mol %) yielded 43% of compound **13a**. Then, the scope of the reaction using IrO_2–Fe_3O_4 was tested finding that the length of the alkyne side chain did not influence the result

Table 8
One-pot synthesis of 1-aryl-2,4-dialkylfurans[a]



1 **2** **13**

Entry	Ar	R	No.	Yield (%)[b]
1	Ph	^{n}Pr	**13a**	62[c,d]
2	Ph	^{n}Pr	**13a**	87[c,e]
3	Ph	^{n}Pr	**13a**	90[c,f]
4	Ph	^{n}Pr	**13a**	70[g]
5	Ph	^{n}Pr	**13a**	88 (51)
6	Ph	Me	**13b**	91 (68)
7	4-ClC_6H_4	^{n}Pr	**13c**	76 (55)
8	4-$MeOC_6H_4$	^{n}Pr	**13d**	94 (69)
9	2-Thienyl	^{n}Pr	**13e**	74 (41)

[a] Reaction carried out using **1** (1.5 mmol) and **2** (1.0 mmol) in toluene (2.5 mL) under an argon atmosphere.
[b] Isolated yield after column chromatography; In the parenthesis appear the results using Rh_2O_3–Fe_3O_4 (0.8 mol %) as catalyst for the step ii.
[c] Reaction performed during 7 d.
[d] In the step ii, only $RhCl_3$ (1 mol %) was used as catalyst.
[e] In the step ii, only $PdCl_2$ (1 mol %) was used as catalyst.
[f] In the step ii, only $IrCl_3$ (1 mol %) was used as catalyst.
[g] In the step ii, only PdO–Fe_3O_4 (1.2 mol %) was used as catalyst.

(entry 6). Even, quite similar results were obtained independently of the presence of electron-withdrawing or -donating groups in the ring of acyl chloride (entries 7 and 8). Finally, it should be pointed out that the protocol rendered similar result in the special case of the thienyl derivative (entry 9), which was a challenging example for the construction of more simple 2,5-disubstituted furans.[8a]

3. Conclusion

In conclusion, we have demonstrated that simple and commercially available magnetite is a good catalyst for the chloroacylation of internal alkynes, as well as terminal ones, yielding the corresponding chlorovinyl ketones with good yields. The process could be applied to the synthesis of 5-chloro-4-arylcyclopent-2-enones, 3-aryl-1*H*-cyclopenta[*a*]naphthalen-1-ones, and (*E*)-3-alkylidene-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-ones, just by changing either the starting acyl chloride or alkyne. The acceptable to excellent regio- and stereo-selectivity of the process, together with the low price of catalyst and the simplicity of the process could anticipate a good future for the process shown in this study not only in the laboratory but also in industry. Moreover, the use of iridium impregnated on magnetite into an integrated process allowed us the one-pot synthesis of 1-aryl-2,4-dialkylfurans with good yields, independently of the nature of the starting regents, including heteroaromatic ones, with the low catalyst loading being an important issue.

4. Experimental section

4.1. General information

XPS analyses were carried out on a VG-Microtech Multilab. TEM images were obtained on a JEOL, model JEM-2010 equipped with an X-ray detector OXFORD INCA Energy TEM 100 for microanalysis (EDS). XRF analyses were obtained on a PHILIPS MAGIX PRO (PW2400) X-ray spectrometer equipped with a rhodium X-ray tube and a beryllium window. BET isotherms were carried out on a AUTOSORB-6 (Quantachrome), using N_2. Melting points were obtained with a Reichert Thermovar apparatus. NMR spectra were recorded on a Bruker AC-300 (300 MHz for ^{1}H and 75 MHz for ^{13}C)

using $CDCl_3$ as a solvent and TMS as internal standard for ^1H and ^{13}C; chemical shifts are given in δ (parts per million) and coupling constants (J) in Hertz. FT-IR spectra were obtained on a JASCO 4100LE (Pike Miracle ATR) spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a Himazdu QP-5000 spectrometer, giving fragment ions in m/z with relative intensities (%) in parentheses. HRMS spectra were obtained with a Finnigan High-resolution Mass Spectrometer (MAT95S model). Single-Crystal XRD analyses were obtained on a Bruker CCD-Apex equipped with an X-ray tube with Mo anode. Crystallographic data for compounds **10a** (CCDC 910476) and **11a** (CCDC 910475) can be obtained free of charge from Cambridge Crystallographic Data Centre. Thin layer chromatography (TLC) was carried out on Schleicher & Schuell F1400/LS 254 plates coated with a 0.2 mm layer of silica gel; detection by UV_{254} light, staining with phosphomolybdic acid [25 g phosphomolybdic acid, 10 g $Ce(SO_4)_2$ $4H_2O$, 60 mL of concentrated H_2SO_4, and 940 mL H_2O]. Column chromatography was performed using silica gel 60 of 35–70 mesh. All reagents were commercially available (Acros, Aldrich, Fluorochem) and were used as received.

4.2. General procedure for the preparation of catalysts

To a stirred solution of the corresponding metal salt MCl_x (1 mmol) in deionized water (150 mL) was added commercial available Fe_3O_4 (4 g, 17 mmol, powder <5 μm, BET area: 9.86 m^2/g). After 10 min at room temperature, the mixture was slowly basified with NaOH (1 M) until pH around 13. The mixture was stirred during one day at room temperature in air. After that, the catalyst was filtered and washed several times with deionized water (3×10 mL). The solid was dried at 100 °C during 24 h in a standard glassware oven obtaining the expected catalyst. The rhodium catalyst gave an incorporation of rhodium of 1.7% according to XRF; by XPS the rhodium on the surface was determined as 17.5%; the BET area surface was 8.4 m^2/g. The silver catalyst gave an incorporation of silver of 2.7% according to XRF; by XPS the silver on the surface was determined as 6.2%; the BET area surface was 7.4 m^2/g. The tungsten catalyst gave an incorporation of tungsten of 2.1% according to XRF; by XPS the tungsten on the surface was determined as 13.6%; the BET area surface was 7.7 m^2/g. The gold catalyst gave an incorporation of gold of 1.5% according to XRF; by XPS the gold on the surface was determined as 14.8%; the BET area surface was 7.9 m^2/g.

4.3. General procedure for the addition reactions

To a stirred solution of alkyne (**2** or **9**, 1 mmol) in dry toluene (2.5 mL) under argon atmosphere were added Fe_3O_4 (25 mg or 10 mg) and the corresponding acid derivative (**1**, **5** or **7**, 1.5 mmol). The resulting mixture was stirred at 70 °C during one hour. The catalyst was removed by a magnet and the resulting mixture was quenched with water (5 mL) and extracted with EtOAc (3×5 mL). The organic phases were dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The product was usually purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding products **3**, **4**, **6**, **8**, **10**, **11**, and **12**. Physical and spectroscopic data, as well as literature for known compounds, follow:

*4.3.1. (Z)-2-Butyl-3-chloro-1-phenylhept-2-en-1-one (**3a**).* Brown oil; R_f=0.77 (hexane/ethyl acetate 4:1); t_R 14.3; IR (cm^{-1}): 1668, 1637, 1596, 1579, 1465, 1448, 1313, 1268, 1212, 935, 719, 689; ^1H NMR (300 MHz, $CDCl_3$): δ 0.77 (t, J=7.3 Hz, 3H, $ClCCH_2CH_2CH_2CH_3$), 0.86 (t, J=7.1 Hz, 3H, $ClCCCH_2CH_2CH_2CH_3$), 1.1–1.2, 1.25–1.45, 1.45–1.55 (3m, 2, 4 and 2H, respectively, CH_2 ×4), 2.18 (t, J=7.3 Hz, 2H, $ClCCH_2$), 2.5 (t, J=7.1 Hz, 2H, $ClCCCH_2$), 7.4–7.5 (m, 2H, OCCCHCH ×2), 7.55–7.65 (m, 1H, OCCCHCHCH), 7.85–7.95 (m, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.7, 21.7, 22.5, 29.6, 29.7, 32.3, 36.9, 128.7 (2C), 129.4 (2C), 133.6, 136.4, 137, 137.1, 197.5; EIMS m/z: 278 (M^+, 10%), 243 (25), 237 (10), 235 (28), 187 (10), 179 (23), 145 (11), 105 (100), 77 (46). HRMS calcd for $C_{17}H_{23}ClO$: 278.1437; found: 278.1434.

*4.3.2. (Z)-3-Chloro-2-ethyl-1-phenylpent-2-en-1-one (**3b**).*[10] Yellow oil, R_f=0.7 (hexane/ethyl acetate 4:1); t_R 12.4; IR (cm^{-1}): 1666, 1638, 1596, 1449, 1285, 1242, 822, 711, 689; ^1H NMR (300 MHz, $CDCl_3$): δ 1.03 (t, J=7.6 Hz, 3H, $ClCCCH_2CH_3$), 1.04 (t, J=7.3 Hz, 3H, $ClCCH_2CH_3$), 2.2 (q, J=7.3 Hz, 2H, $ClCCH_2$), 2.53 (q, J=7.6 Hz, 2H, $ClCCCH_2$), 7.45–7.5 (m, 2H, OCCCHCH ×2), 7.55–7.65 (m, 1H, OCCCHCHCH), 7.85–7.95 (m, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.8, 12.3, 25.7, 30.6, 128.7 (2C), 129.3 (2C), 133.6, 136.4, 137.3, 137.4, 197.3; EIMS m/z: 222 (M^+, 10%), 187 (59), 159 (32), 158 (13), 105 (100), 77 (67).

*4.3.3. (Z)-3-Chloro-2-pentyl-1-phenyloct-2-en-1-one (**3c**).* Yellow oil; R_f=0.73 (hexane/ethyl acetate 4:1); t_R 15.5; IR (cm^{-1}): 1669, 1596, 1465, 1448, 1314, 1259, 719, 689; ^1H NMR (300 MHz, $CDCl_3$): δ 0.79, 0.84 (2t, J=7.1 and 7 Hz, respectively, 3H each one, CH_3 ×2), 1.05–1.2, 1.2–1.35, 1.35–1.6 (3m, 4H each one, CH_2 ×6), 2.18 (t, J=7.3 Hz, 2H, $ClCCH_2$), 2.49 (t, J=7.6 Hz, 2H, $ClCCCH_2$), 7.4–7.5 (m, 2H, OCCCHCH ×2), 7.55–7.65 (m, 1H, OCCCHCHCH), 7.85–7.95 (m, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 13.9, 22.2, 22.3, 27.1, 27.3, 30.8, 31.5, 32.6, 37.1, 128.7 (2C), 129.4 (2C), 133.6, 136.4, 137, 137.1, 197.4; EIMS m/z: 270 (7%), 227 (14), 105 (100), 77 (34). HRMS calcd for $C_{19}H_{27}ClO$–HCl: 270.1984; found: 270.1995.

*4.3.4. (Z)-3-Chloro-1,3-diphenylprop-2-en-1-one (**3d**).*[10] Pale yellow oil; R_f=0.37 (hexane/ethyl acetate 4:1); t_R 16.3; IR (cm^{-1}): 1662, 1597, 1574, 1446, 1234, 1206, 1016, 756, 687; ^1H NMR (300 MHz, $CDCl_3$): δ 7.35 (s, 1H, ClCCH), 7.4–7.5, 7.55–7.6, 7.7–7.8, 7.95–8.05 (4m, 5, 1, 2 and 2H, respectively, Ph ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 121.4, 127.1 (2C), 128.6 (2C), 128.6 (2C), 128.7 (2C), 130.5, 133.3, 137.3, 137.7, 143.3, 189.8; EIMS m/z: 244 (M^++2, 15%), 243 (M^++1, 39), 242 (M^+, 46), 241 (100), 179 (18), 178 (19), 167 (10), 165 (31), 105 (61), 102 (58), 101 (17), 89 (16), 77 (96).

*4.3.5. (Z)-2-Butyl-3-chloro-1-(4-chlorophenyl)hept-2-en-1-one (**3e**).* Yellow oil; R_f=0.73 (hexane/ethyl acetate 4:1); t_R 15.6; IR (cm^{-1}): 1670, 1586, 1465, 1399, 1266, 1211, 1091, 1013, 932, 846, 771, 757; ^1H NMR (300 MHz, $CDCl_3$): δ 0.8, 0.88 (2t, J=7.3 and 7.1 Hz, respectively, 3H each one, CH_3 ×2), 1.1–1.25, 1.3–1.45, 1.45–1.55 (3m, 2, 4 and 2H, respectively, CH_2 ×4), 2.19 (t, J=7.4 Hz, 2H, $ClCCH_2$), 2.5 (t, J=7.2 Hz, 2H, $ClCCCH_2$), 7.48 (d, J=8.5 Hz, 2H, ClCCH ×2), 7.86 (d, J=8.5 Hz, 2H, ClCCHCH ×2),; ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.7, 21.7, 22.5, 29.6, 29.7, 32.3, 37, 129.2 (2C), 130.8 (2C), 134.7, 136.7, 137.3, 140.2, 196.2; EIMS m/z: 277 (11%), 141 (34), 140 (9), 139 (100), 111 (27). HRMS calcd for $C_{17}H_{22}Cl_2O$–Cl: 277.1359; found: 277.1340.

*4.3.6. (Z)-2-Butyl-1-(4-[tert-butyl]phenyl)-3-chlorohept-2-en-1-one (**3f**).* Yellow oil; R_f=0.77 (hexane/ethyl acetate 4:1); t_R 16.4; IR (cm^{-1}): 1667, 1603, 1463, 1268, 1188, 1107, 933, 852, 780, 719; ^1H NMR (300 MHz, $CDCl_3$): δ 0.77, 0.87 (2t, J=7.3 and 7.1 Hz, respectively, 3H each one, CH_3 ×2), 1.1–1.2, 1.25–1.45, 1.45–1.6 (3m with s at 1.36, 9, 2, 4 and 2H, respectively, CH_2 ×4 and $C(CH_3)_3$), 2.19 (t, J=7.3 Hz, 2H, $ClCCH_2$), 2.51 (t, J=7.1 Hz, 2H, $ClCCCH_2$), 7.5 (d, J=8.5 Hz, 2H, OCCCHCH ×2), 7.84 (d, J=8.5 Hz, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 13.7, 21.7, 22.5, 29.6, 29.7, 31 (3C), 32.3, 35.2, 36.9, 125.7 (2C), 129.4 (2C), 133.8, 136.4, 137.2, 157.5, 197.1; EIMS m/z: 298 (12%), 283 (11), 269 (12), 162 (12), 161 (100). HRMS calcd for $C_{21}H_{31}ClO$–HCl: 298.2297; found: 298.2312.

*4.3.7. (Z)-2-Butyl-3-chloro-1-(4-methoxyphenyl)hept-2-en-1-one (**3g**).* Yellow oil; R_f=0.43 (hexane/ethyl acetate 4:1); t_R 16.2; IR

(cm^{-1}): 1659, 1597, 1255, 1215, 1159, 1030, 845; ^1H NMR (300 MHz, $CDCl_3$): δ 0.73, 0.82 (2t, J=7.3 and 7.1 Hz, respectively, 3H each one, CH_3 ×2), 1.05–1.2, 1.2–1.35, 1.35–1.5 (3m, 2, 4 and 2H, respectively, CH_2 ×4), 2.15 (t, J=7.4 Hz, 2H, $ClCCH_2$), 2.45 (t, J=7.1 Hz, 2H, $ClCCCH_2$), 3.84 (s, 3H, OCH_3), 6.92 (d, J=8.8 Hz, 2H, OCCCHC*H* ×2), 7.84 (d, J=8.8 Hz, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 13.6, 21.6, 22.4, 29.5, 29.6, 32.3, 36.8, 55.3, 113.9 (2C), 129.2, 131.7 (2C), 135.7, 137, 163.9, 195.8; EIMS m/z: 272 (9%), 243 (10), 135 (100), 77 (10). HRMS calcd for $C_{18}H_{25}ClO_2$–HCl: 272.1776; found: 272.1780.

*4.3.8. (Z)-2-Butyl-3-chloro-1-(2-methoxyphenyl)hept-2-en-1-one (**3h**).* Pale yellow oil; R_f=0.47 (hexane/ethyl acetate 4:1); t_R 15.1; IR (cm^{-1}): 1656, 1597, 1484, 1463, 1435, 1288, 1246, 1162, 1024, 931, 754; ^1H NMR (300 MHz, $CDCl_3$): δ 0.81, 0.86 (2t, J=7.3 and 7.2 Hz, respectively, 3H each one, CH_3 ×2), 1.15–1.25, 1.25–1.35, 1.35–1.45, 1.45–1.55 (4m, 2H each one, CH_2 ×4), 2.35 (t, J=7.5 Hz, 2H, $ClCCH_2$), 2.46 (t, J=7.5 Hz, 2H, $ClCCCH_2$), 3.86 (s, 3H, OCH_3), 6.96 (d, J=8.3 Hz, 1H, CH_3OCCH), 7.02 (td, J=7.6 Hz, ^4J=0.7 Hz, 1H, $CH_3OCCCHCH$), 7.49 (td, J=8.2, Hz, ^4J=1.7 Hz, 1H, $CH_3OCCHCH$), 7.62 (dd, J=7.6 Hz, ^4J=1.7 Hz, 1H, CH_3OCCCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.8, 21.9, 22.5, 29.7, 29.9, 31.8, 36.6, 55.6, 111.7, 120.5, 127.9, 131.1, 133.8, 139.5, 139.8, 158.6, 196.5; EIMS m/z: 308 (M^+, 0.1%), 135 (100), 77 (12). HRMS calcd for $C_{18}H_{25}ClO_2$: 308.1543; found: 308.1515.

*4.3.9. (Z)-2-Butyl-3-chloro-1-(4-fluoronaphthalen-1-yl)hept-2-en-1-one (**3i**).* Orange oil; R_f=0.77 (hexane/ethyl acetate 4:1); t_R 18.3; IR (cm^{-1}): 1661, 1627, 1599, 1463, 1424, 1243, 1214, 1050, 769; ^1H NMR (300 MHz, $CDCl_3$): δ 0.76, 0.89 (2t, J=7.3 and 7.2 Hz, respectively, 3H each one, CH_3 ×2), 1.1–1.25, 1.3–1.4, 1.45–1.6 (3m, 2, 2 and 4H, respectively, CH_2 ×4), 2.30 (t, J=7.4 Hz, 2H, $ClCCH_2$), 2.58 (t, J=7.6 Hz, 2H, $ClCCCH_2$), 7.19 (dd, $^3J_{(H,F)}$=9.6 Hz, J=8.3 Hz, 1H, FCCH), 7.6–7.7 (m, 1H, FCCCHC*H*), 7.73 (ddd, J=8.6 and 6.8 Hz, ^4J=1.1 Hz, 1H, FCCCHCHC*H*), 7.9 (dd, J=8.3 Hz, $^4J_{(H,F)}$=, 5.6 Hz, FCCHC*H*), 8.2 (d, J=8.3 Hz, 1H, FCCCH), 8.96 (d, J=8.6 Hz, 1H, FCCCCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 13.8, 21.8, 22.5, 29.9 (2C), 32.6, 37, 108.2 (d, $^2J_{(C,F)}$=21 Hz), 120.9 (d, $^3J_{(C,F)}$=6.4 Hz), 124.2 (d, $^2J_{(C,F)}$=15.7 Hz), 125.8 (d, $^4J_{(C,F)}$=2 Hz), 127 (d, $^4J_{(C,F)}$=1.6 Hz), 129.5, 130.3 (d, $^4J_{(C,F)}$=4.2 Hz), 132.3 (d, $^3J_{(C,F)}$=10.1 Hz), 132.7 (d, $^3J_{(C,F)}$=5.6 Hz), 138.9, 139.8, 161.7 (d, $^1J_{(C,F)}$=261.5 Hz), 197.9; EIMS m/z: 346 (M^+, 0.4%), 311 (22), 310 (100), 268 (40), 267 (90), 255 (11), 254 (32), 253 (18), 239 (13), 226 (31), 225 (80), 213 (14), 212 (47), 211 (67), 209 (16), 207 (22), 197 (36), 196 (47), 183 (32), 170 (11). HRMS calcd for $C_{21}H_{24}ClFO$: 346.1500; found: 346.1474.

*4.3.10. (Z)-2-Butyl-3-chloro-1-(thiophen-2-yl)hept-2-en-1-one (**3j**).* Pale yellow oil; R_f=0.67 (hexane/ethyl acetate 4:1); t_R 14.9; IR (cm^{-1}): 1644, 1514, 1409, 1274, 1049, 722; ^1H NMR (300 MHz, $CDCl_3$): δ 0.79, 0.88 (2t, J=7.3 and 7.2 Hz, respectively, 3H each one, CH_3 ×2), 1.15–1.25, 1.3–1.4, 1.4–1.45, 1.45–1.55 (4m, 2H each one, CH_2 ×4), 2.26 (t, J=7.2 Hz, 2H, $ClCCH_2$), 2.52 (t, J=7.4 Hz, 2H, $ClCCCH_2$), 7.15 (dd, J=4.9 and 3.8 Hz, 1H, SCHC*H*), 7.63 (dd, J=3.8 Hz, ^4J=1.1 Hz, 1H, SCCH), 7.72 (dd, J=4.9 Hz, ^4J=1.1 Hz, 1H, SCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.8, 21.7, 22.5, 29.7, 29.8, 32.4, 37.1, 128.3, 134.3, 135.2, 137, 137.1, 144, 189.7; EIMS m/z: 284 (M^+, 9%), 253 (19), 251 (57), 241 (12), 111 (100). HRMS calcd for $C_{15}H_{21}ClOS$: 284.1002; found: 284.1028.

*4.3.11. (Z)-3-Chloro-1-(4-methoxyphenyl)-2,3-diphenylprop-en-1-one (**3k**).* Orange oil; R_f=0.33 (hexane/ethyl acetate 4:1); t_R 22.5; IR (cm^{-1}): 1604, 1509, 1346, 1249, 1175, 1028, 753, 696; ^1H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H, OCH_3), 6.92 (d, J=8.9 Hz, 2H, OCCH ×2), 7.15–7.4 (m, 12H, Ph ×2 and OCCHCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 114.1 (2C), 121.2, 122.7, 127.5 (2C), 128 (2C), 129.8 (2C), 130.2 (2C), 131, 131.1, 131.6, 133.2 (2C), 145.1, 155.1, 160.4, 196.4; EIMS m/z: 313 (25%), 312 (100), 311 (24), 281 (22), 268 (11), 240 (10), 239 (29). HRMS calcd for $C_{22}H_{17}ClO_2$–HCl: 312.1150; found: 312.1113.

*4.3.12. (Z)-4-Butyl-5-chloro-1-phenylnon-4-en-3-one and (E)-4-butyl-5-chloro-1-phenylnon-4-en-3-one [(Z)-**3l**/(E)-**4l**: 3/1].* Brown oil; R_f=0.73 (hexane/ethyl acetate 4:1); t_R 15.6; IR (cm^{-1}): 1697, 1603, 1496, 1454, 747, 698; ^1H NMR (300 MHz, $CDCl_3$): δ 0.85–1 (m, 8H, CH_3 ×4), 1.2–1.6 (m, 11H, CH_2 ×8), 2.15–2.45 (m, 5H, CH_2 ×4), 2.85–3 (m, 5H, CH_2 ×4), 7.2–7.35 (m, 7H, Ph ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.8, 13.9, 13.9, 21.9, 22, 22.4, 22.5, 29.5, 29.7, 29.8, 29.8, 29.9, 30.2, 30.6, 30.9, 34.6, 36.6, 43.9, 44.6, 126, 126.2, 128.3 (2C), 128.4 (2C), 128.4 (2C), 128.5 (2C), 132, 138.8, 139.2, 140.1, 140.8, 141.1, 204.2 (C=O, *Z*), 206.2 (C=O, *E*); EIMS m/z: 270 (19%), 241 (42), 180 (13), 179 (100), 166 (12), 137 (39), 105 (66), 91 (63). HRMS calcd for $C_{19}H_{27}ClO$–HCl: 270.1984; found: 270.1973.

*4.3.13. (Z)-2-Butyl-3-chloro-1-(naphthalen-1-yl) hept-2-en-1-one (**3m**).* Orange oil; R_f=0.73 (hexane/ethyl acetate 4:1); t_R 18.8; IR (cm^{-1}): 1699, 1582, 1519, 1458, 1259, 1069, 1019, 822, 797; ^1H NMR (300 MHz, $CDCl_3$): δ 0.96, 1.01 (2t, J=7.2 and 7.3 Hz, respectively, 3H each one, CH_3 ×2), 1.35–1.45, 1.45–1.55, 1.6–1.7 (3m, 2, 4 and 2H, respectively, CH_2 ×4), 2.28, 2.59 (2t, J=7.2 and 7.5 Hz, respectively, 2H each one, CCH_2 ×2), 7.25–7.35, 7.45–7.5, 7.7–7.75, 7.85–7.9, 8.65–8.7 (5m, 3, 1, 1, 1 and 1H, respectively, ArH ×7); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14, 22.6, 22.8, 23, 25.9, 30, 31.7, 117.7, 122.8, 123.5, 125.3, 128.2, 128.8 (2C), 133.4, 133.9, 134, 147, 155.6, 200.8; EIMS m/z: 293 (M^+–Cl, 22%), 292 (94), 250 (39), 249 (100), 236 (20), 235 (19), 221 (11), 208 (23), 207 (79), 202 (11), 195 (18), 194 (52), 193 (85), 191 (19), 190 (10), 189 (19), 179 (49), 178 (62), 177 (11), 176 (15), 165 (41), 152 (16). HRMS calcd for $C_{21}H_{25}ClO$–HCl: 292.1827; found: 292.1834.

*4.3.14. (E)-2-Butyl-3-chloro-1-phenylhept-2-en-1-one (**4a**).* Pale yellow oil; R_f=0.73 (hexane/ethyl acetate 4:1); t_R 14.6; IR (cm^{-1}): 1668, 1636, 1596, 1579, 1465, 1448, 1268, 1213, 935, 720, 690; ^1H NMR (300 MHz, $CDCl_3$): δ 0.89, 0.99 (2t, J=7.6 and 7.3 Hz, respectively, 3H each one, CH_3 ×2), 1.3–1.55, 1.6–1.7 (2m, 6 and 2H, respectively, CH_2 ×4), 2.35–2.4, 2.45–2.5 (2m, 2H each one, CCH_2 ×2), 7.45–7.5 (m, 2H, OCCCHC*H* ×2), 7.55–7.65 (m, 1H, OCCCHCHC*H*), 7.85–7.95 (m, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.9, 22.2, 22.6, 29.6, 30.5, 31.4, 34.5, 128.7 (2C), 129.4 (2C), 133.4, 135.7, 136.6, 137, 197.3; EIMS m/z: 280 (M^++2, 11%), 279 (M^++1, 10), 278 (M^+, 33), 277 (11), 243 (32), 235 (17), 201 (11), 199 (12), 187 (11), 179 (18), 145 (14), 105 (100), 77 (50). HRMS calcd for $C_{17}H_{23}ClO$: 278.1437; found: 278.1428.

*4.3.15. (Z)-3-Bromo-2-butyl-1-phenylhept-2-en-1-one (**6**).* Brown oil; R_f=0.77 (hexane/ethyl acetate 4:1); t_R 14.3; IR (cm^{-1}): 1668, 1631, 1596, 1580, 1463, 1449, 1313, 1264, 1211, 934, 716, 688; ^1H NMR (300 MHz, $CDCl_3$): δ 0.68, 0.78 (2t, J=7.3 and 7.1 Hz, respectively, 3H each one, CH_3 ×2), 1.1–1.15, 1.15–1.35, 1.35–1.5 (3m, 2, 4 and 2H, respectively, CH_2 ×4), 2.20 (t, J=7.3 Hz, 2H, $ClCCH_2$), 2.41 (t, J=7.2 Hz, 2H, $ClCCCH_2$), 7.35–7.45 (m, 2H, OCCCHC*H* ×2), 7.45–7.55 (m, 1H, OCCCHCHC*H*), 7.8–7.85 (m, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 13.7, 21.6, 22.4, 29.4, 30.6, 35.3, 38.9, 128.7 (2C), 129.4 (2C), 130.4, 133.7, 136, 139.8, 197.1; EIMS m/z: 243 (1%), 242 (5), 213 (12), 105 (100), 77 (29). HRMS calcd for $C_{17}H_{23}BrO$: 322.0932; found: 322.0910.

*4.3.16. cis-2,3-Dibutyl-5-chloro-4-phenylcyclopent-2-enone (**8a**).* Yellow oil; R_f=0.63 (hexane/ethyl acetate 4:1); t_R 16.5; IR (cm^{-1}): 1714, 1632, 1603, 1496, 1455, 1346, 751, 700; ^1H NMR (300 MHz, $CDCl_3$): δ 0.76 (t, J=7.1 Hz, 3H, $OCCCH_2CH_2CH_2CH_3$), 0.86 (t, J=7.2 Hz, 3H, $OCCCCH_2CH_2CH_2CH_3$), 1.1–1.45 (m, 8H, CH_2 ×4), 1.9 (ddd, ^2J=14 Hz, J=8.7 and 5.3 Hz, 1H, $OCCCCH_2$), 2.15–2.3 (m, 2H, $OCCCH_2$), 2.41 (ddd, ^2J=14 Hz, J=9.4 and 6.2 Hz, 1H, $OCCCCH_2$), 3.90

(d, *J*=2.7 Hz, 1H, OCCHC*H*), 3.98 (d, *J*=2.7 Hz, 1H, OCCH), 7–7.05 (m, 2H, ClCHCHCC*H* ×2), 7.15–7.3 (m, 3H, ClCHCHCCHC*H* ×2 and ClCHCHCCHCHC*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 13.8, 22.5, 22.6, 23.3, 28.5, 29.1, 30.6, 57.7, 62.1, 127.5 (2C), 127.8, 129.1 (2C), 138.9, 139.9, 172.6, 201.1; EIMS *m*/*z*: 306 (M^++2, 18%), 305 (M^++1, 12), 304 (M^+, 54), 277 (24), 276 (14), 275 (71), 270 (21), 269 (100), 247 (13), 227 (13), 185 (11), 183 (11), 155 (14), 153 (10), 141 (21), 129 (17), 128 (14), 115 (17), 103 (12), 91 (32), 77 (13). HRMS calcd for $C_{19}H_{25}ClO$: 304.1594; found: 304.1645.

*4.3.17. cis-5-Chloro-2,3-diethyl-4-phenylcyclopent-2-enone (**8b**).* Yellow oil; R_f=0.37 (hexane/ethyl acetate 4:1); t_R 14.5; IR (cm^{-1}): 1713, 1633, 1603, 1495, 1455, 1354, 760, 728, 700; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, *J*=7.6 Hz, 3H, OCCCCH$_2$C*H*$_3$), 1.1 (t, *J*=7.6 Hz, 3H, OCCCH$_2$C*H*$_3$), 2.02 (dq, ^2J=14.5 Hz, *J*=7.6 Hz, 1H, OCCCCH$_2$), 2.35 (q, *J*=7.6 Hz, 2H, OCCCH$_2$), 2.53 (dq, ^2J=14.5 Hz, *J*=7.6 Hz, 1H, OCCCCH$_2$), 4.01 (d, *J*=2.7 Hz, 1H, OCCHC*H*), 4.08 (d, *J*=2.7 Hz, 1H, OCCH), 7.1–7.15 (m, 2H, ClCHCHCC*H* ×2), 7.3–7.4 (m, 3H, ClCHCHCCHC*H* ×2 and ClCHCHCCHCHC*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.7, 13.1, 16.8, 21.9, 57.4, 62.2, 127.5 (2C), 127.8, 129.1 (2C), 138.7, 140.7, 173.4, 201; EIMS *m*/*z*: 250 (M^++2, 14%), 248 (M^+, 42), 219 (11), 214 (16), 213 (100), 185 (16), 143 (14), 141 (12), 129 (28), 128 (15), 115 (17), 91 (16), 77 (14). HRMS calcd for $C_{15}H_{17}ClO$: 248.0968; found: 248.0930.

*4.3.18. cis-5-Chloro-2,3-dipentyl-4-phenylcyclopent-2-enone (**8c**).* Yellow oil; R_f=0.63 (hexane/ethyl acetate 4:1); t_R 17.5; IR (cm^{-1}): 1715, 1632, 1603, 1496, 1455, 1358, 748, 728, 700; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83, 0.91 (2t, *J*=6.9 Hz each one, 3H each one, CH_3 ×2), 1.15–1.25, 1.25–1.4, 1.4–1.55 (3m, 4H each one, CH_2 ×6), 1.98 (ddd, ^2J=13.8 Hz, *J*=9.2 and 5.3 Hz, 1H, OCCCCH$_2$), 2.2–2.4 (m, 2H, OCCCH$_2$), 2.47 (ddd, ^2J=13.8, Hz, *J*=9.4 and 6.6 Hz, 1H, OCCCCH$_2$), 3.98 (d, *J*=2.7 Hz, 1H, OCCHC*H*), 4.06 (d, *J*=2.7 Hz, 1H, OCCH), 7.1–7.15 (m, 2H, ClCHCHCC*H* ×2), 7.3–7.4 (m, 3H, ClCHCHCCHC*H* ×2 and ClCHCHCCHCHC*H*); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.9, 22.2, 22.4, 23.5, 26.6, 28.1, 28.8, 31.5, 31.7, 57.8, 62.1, 127.5 (2C), 127.8, 129.1 (2C), 138.9, 139.9, 172.6, 201.1; EIMS *m*/*z*: 334 (M^++2, 18%), 333 (M^++1, 13), 332 (M^+, 52), 298 (24), 297 (100), 291 (27), 290 (16), 289 (79), 263 (14), 261 (39), 241 (18), 185 (14), 183 (15), 165 (10), 155 (17), 153 (13), 141 (26), 129 (18), 128 (17), 115 (19), 103 (14), 91 (44), 77 (14). HRMS calcd for $C_{21}H_{29}ClO$: 332.1907; found: 332.1912.

*4.3.19. cis-3-(tert-Butyl)-5-chloro-2-methyl-4-phenylcyclopent-2-enone (**8d**).* Pale yellow oil; R_f=0.73 (hexane/ethyl acetate 4:1); t_R 14.7; IR (cm^{-1}): 1713, 1636, 1603, 1495, 1484, 1455, 1313, 1143, 1022, 966, 759, 700; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H, C(CH$_3$)$_3$), 2 (d, ^5J=0.7 Hz, 3H, CH_3), 3.79 (dd, *J*=2.8 Hz, ^5J=0.7 Hz, 1H, OCCHC*H*), 3.99 (d, *J*=2.8 Hz, 1H, OCCH), 7.1–7.15, 7.3–7.4 (2m, 2 and 3H, respectively, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3, 29.5 (3C), 34, 60.6, 62.2, 127.6 (2C), 127.9, 129.2 (2C), 139.3, 145.3, 166, 200.8; EIMS *m*/*z*: 264 (M^++2, 16%), 262 (M^+, 47), 247 (16), 228 (18), 227 (100), 200 (15), 199 (91), 185 (17), 183 (12), 169 (13), 165 (13), 157 (16), 155 (12), 153 (11), 143 (15), 142 (12), 141 (19), 129 (15), 128 (21), 115 (15), 105 (18), 103 (14), 91 (26), 77 (18). HRMS calcd for $C_{16}H_{19}ClO$: 262.1124; found: 262.1080.

*4.3.20. trans-3-(tert-Butyl)-5-chloro-2-methyl-4-phenylcyclopent-2-enone (**8d′**).* Pale yellow oil; R_f=0.67 (hexane/ethyl acetate 4:1); t_R 14.8; IR (cm^{-1}): 1712, 1649, 1602, 1494, 1479, 1465, 1241, 703; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (s, 9H, C(CH$_3$)$_3$), 2.08 (d, ^5J=1.6 Hz, 3H, CH_3), 3.83 (d, *J*=1 Hz, 1H, OCCH), 4.15–4.2 (m, 1H, OCCHC*H*), 7.05–7.15, 7.25–7.35 (2m, 2 and 3H, respectively, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 29 (3C), 36.1, 58.4, 59.5, 127.2 (2C), 127.7, 129.1 (2C), 135, 140.6, 178.4, 203.4; EIMS *m*/*z*: 262 (M^+, 21%), 247 (11), 228 (11), 227 (61), 205 (11), 169 (11), 141 (17), 128 (10), 125 (10), 124 (100), 123 (14), 115 (12), 109 (50), 103 (11), 91 (15), 81 (24), 77 (14). HRMS calcd for $C_{16}H_{19}ClO$: 262.1124; found: 262.1116.

*4.3.21. cis-2,3-Dibutyl-5-chloro-4-(4-fluorophenyl)cyclopent-2-enone (**8e**).* Yellow oil; R_f=0.67 (hexane/ethyl acetate 4:1); t_R 16.3; IR (cm^{-1}): 1715, 1633, 1605, 1508, 1464, 1458, 1348, 1227, 1159, 1097, 823, 789, 733; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, *J*=7.1 Hz, 3H, OCCCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.94 (t, *J*=7.1 Hz, 3H, OCCCCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.2–1.5 (m, 8H, CH_2 ×4), 1.96 (ddd, ^2J=13.7 Hz, *J*=8.6, 4.7 Hz, 1H, OCCCCH$_2$), 2.2–2.35 (m, 2H, OCCCH$_2$), 2.49 (ddd, ^2J=13.7 Hz, *J*=9.2 and 5.7 Hz, 1H, OCCCCH$_2$), 3.97 (d, *J*=2.8 Hz, 1H, OCCHC*H*), 4.01 (d, *J*=2.8 Hz, 1H, OCCH), 7–7.15 (m, 4H, ArH ×4); ^{13}C NMR (75 MHz, $CDCl_3$): δ 2.8, 3, 13.2, 13.3, 14.1, 20.1, 20.9, 22.6, 53.6, 59.6, 122.9 (d, $^2J_{(C,F)}$=25.3 Hz, 2C), 138.1 (d, $^3J_{(C,F)}$=9.6 Hz, 2C), 144.6 (d, $^4J_{(C,F)}$=3.8 Hz), 151.1, 177 (d, $^1J_{(C,F)}$=289.5 Hz), 188.5, 222.1; EIMS *m*/*z*: 324 (M^++2, 16%), 323 (M^++1, 10), 322 (M^+, 48), 295 (24), 294 (13), 293 (72), 288 (22), 287 (100), 265 (13), 245 (11), 203 (11), 201 (11), 159 (20), 147 (12), 146 (13), 133 (14), 109 (34), 91 (14). HRMS calcd for $C_{19}H_{24}ClFO$: 322.1500; found: 322.1489.

*4.3.22. cis-2,3-Dibutyl-5-chloro-4-(4-methoxyphenyl)cyclopent-2-enone (**8f**).* Pale yellow oil; R_f=0.53 (hexane/ethyl acetate 4:1); t_R 18.1; IR (cm^{-1}): 1713, 1631, 1611, 1511, 1463, 1249, 1176, 1033, 820; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85, 0.94 (2t, *J*=7.1 Hz each one, 3H each one, CH_2CH_3 ×2), 1.15–1.5 (m, 8H, CH_2 ×4), 1.99 (ddd, ^2J=13.8 Hz, *J*=8.8 and 5 Hz, 1H, OCCCCH$_2$), 2.2–2.4 (m, 2H, OCCCH$_2$), 2.48 (ddd, ^2J=13.8 Hz, *J*=9.3 and 6.1 Hz, 1H, OCCCCH$_2$), 3.81 (s, 3H, OCH_3), 3.93 (d, *J*=2.7 Hz, 1H, OCCHC*H*), 4.02 (d, *J*=2.7 Hz, 1H, OCCH), 6.89 (d, *J*=8.6 Hz, 2H, CH$_3$OCC*H* ×2), 7.03 (d, *J*=8.6 Hz, 2H, CH$_3$OCCHC*H* ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7, 13.9, 22.6, 22.7, 23.3, 28.5, 29.2, 30.6, 55.3, 57, 62.3, 114.6 (2C), 128.6 (2C), 130.9, 139.7, 159.2, 172.9, 201.3; EIMS *m*/*z*: 336 (M^++2, 18%), 335 (M^++1, 12), 334 (M^+, 49), 305 (19), 300 (33), 299 (100), 279 (16), 277 (47), 271 (19), 269 (14), 255 (17), 243 (11), 207 (30), 171 (11), 121 (29). HRMS calcd for $C_{20}H_{27}ClO_2$: 334.1700; found: 334.1666.

*4.3.23. 2-Methyl-3-phenyl-1H-cyclopenta[a]naphthalen-1-one (**10a**).* Orange solid; mp 117–120 °C (hexane); R_f=0.63 (hexane/ethyl acetate 4:1); t_R 19.7; IR (cm^{-1}): 1698, 1628, 1581, 1565, 1519, 1440, 1329, 1217, 1066, 834, 753, 701; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.95 (s, 3H, CH_3), 7.25 (d, *J*=8.1 Hz, 1H, OCCCC*H*CHC), 7.34 (t, *J*=8.5 Hz, 1H, OCCCCHC*H*CH), 7.45–7.6 (m, 6H, Ph and OCCCCHCHC*H*), 7.69 (d, *J*=8.3 Hz, 1H, OCCCCC*H*CHCH), 7.78 (d, *J*=8.1 Hz, 1H, OCCCCHC*H*C), 8.77 (d, *J*=8.5 Hz, 1H, OCCCC*H*CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.4, 118.8, 122.7, 123.5, 125.5, 127.9 (2C), 128.2, 128.6 (2C), 128.9 (2C), 129.1, 129.7, 132.6, 133.7, 133.9, 147, 152.7, 200.1; EIMS *m*/*z*: 271 (M^++1, 20%), 270 (M^+, 100), 269 (41), 253 (11), 242 (22), 241 (46), 240 (17), 239 (46), 226 (13), 215 (15), 120 (17). HRMS calcd for $C_{20}H_{14}O$: 270.1045; found: 270.1037. Crystal data: $C_{20}H_{14}O$, M=270.31; crystal size max=0.25, mid=0.24, min=0.03; Monoclinic, space group *P*21/c, *a*=12.714 (17), *b*=13.994 (18), *c*=8.433 (11) Å, α=90°, β=108.49° (3), γ=90°; *V*=1423 (3) Å^3; ρ_{calcd}=1.262 g/cm^3; 2θ_{max}=50.42; radiation type: Mo, λ=0.71073 Å; data collection based on three ω-scan runs (starting ω=−34°) at values Φ=0°, 120°, 240° with the detector at 2θ=−32°. An additional run of 100 frames, at 2θ=−32°, ω=−34° and Φ=0°, was acquired to improve redundancy. For each of these runs, 606 frames were collected at 0.3° intervals and 30 s per frame. *T*=25±1 °C, measured and independent reflections=2522, reflections included in refinement=10,535, $I>2/\sigma$. The diffraction frames were integrated using the program SAINT and the integrated intensities were corrected for Lorentz-polarization effects with SADABS, μ=0.076, transmission min=0.7266, transmission max=0.9977. The structure was solved by direct methods and refined to unique F^2 by full matrix least squares. No. of parameters=192. All of the hydrogen atoms were placed at idealized positions and retained as rigid

atoms. R=0.0718, wR=0.1323, residual electron density=0.519. All results were deposited at Cambridge Crystallographic Data Centre.

*4.3.24. 2-Butyl-3-phenyl-1H-cyclopenta[a]naphthalen-1-one (**10b**).* Orange oil; R_f=0.6 (hexane/ethyl acetate 4:1); t_R 21.8; IR (cm^{-1}): 1697, 1628, 1579, 1518, 1492, 1441, 1367, 1334, 1158, 1088, 1049, 1023, 827, 799, 744, 698; ^1H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, J=7.3 Hz, 3H, CH_3), 1.25–1.4, 1.45–1.55 (2m, 2H each one, CH_2 ×2), 2.33 (t, J=7.5 Hz, 2H, CCH_2), 7.15 (d, J=8.1 Hz, 1H, OCCCC*H*CHC), 7.29 (ddd, J=8.3 and 6.8 Hz, ^4J=1.2 Hz, 1H, OCCCCHC*H*CH), 7.4–7.55 (m, 6H, Ph and OCCCCHCHC*H*), 7.65 (d, J=8.4 Hz, 1H, OCCCCC*H*CHCH), 7.74 (d, J=8.1 Hz, 1H, OCCCCHC*H*C), 8.73 (dd, J=8.3 Hz, ^4J=0.9 Hz, 1H, OCCCC*H*CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.8, 22.9, 31.6, 118.9, 122.5, 123.5, 125.5, 127.7 (2C), 128.3, 128.7 (2C), 128.9, 129, 129.1, 132.9, 133.8, 134.1, 134.3, 147.2, 153.1, 200.3; EIMS m/z: 313 (M^++1, 20%), 312 (M^+, 80), 271 (10), 270 (47), 269 (100), 268 (10), 257 (13), 256 (19), 252 (18), 251 (14), 250 (12), 241 (20), 240 (21), 239 (63), 226 (12). HRMS calcd for $C_{23}H_{20}O$: 312.1514; found: 312.1470.

*4.3.25. 2-Methyl-3-(p-tolyl)-1H-cyclopenta[a]naphthalen-1-one (**10c**).* Brown oil; R_f=0.5 (hexane/ethyl acetate 4:1); t_R 20.9; IR (cm^{-1}): 1697, 1621, 1580, 1509, 1439, 1377, 1329, 1239, 1187, 1158, 1064, 913, 825, 811, 757; ^1H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 3H, $OCCCH_3$), 2.45 (s, 3H, $CHCCH_3$), 7.29 (d, J=8.1 Hz, 1H, OCCCC*H*CHC), 7.3–7.35 (m, 3H, CH_3CCH ×2 and OCCCCHC*H*CH), 7.42 (d, J=8.2 Hz, 2H, CH_3CCHCH ×2), 7.50 (ddd, J=8.5 and 6.8 Hz, ^4J=1.3 Hz, 1H, OCCCCHCHC*H*), 7.7 (d, J=8.5 Hz, 1H, OCCCCC*H*CHCH), 7.81 (d, J=8.1 Hz, 1H, OCCCCHC*H*C), 8.75 (dd, J=8.5 Hz, ^4J=1.3 Hz, 1H, OCCCC*H*CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 8.5, 21.5, 118.9, 123, 123.7, 125.6, 128 (2C), 128.3, 129, 129.2, 129.4, 129.5, 129.4 (2C), 129.5, 129.9, 133.7, 134, 139.2, 147.3, 153, 200.4; EIMS m/z: 285 (M^++1, 23%), 284 (M^+, 100), 283 (29), 269 (38), 255 (12), 252 (10), 241 (18), 240 (15), 239 (37), 207 (17), 119 (11). HRMS calcd for $C_{21}H_{16}O$: 284.1201; found: 284.1237.

*4.3.26. (E)-2-Ethyl-3-ethylidene-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (**11a**).* Pale yellow solid; mp 94–96 °C; R_f=0.5 (hexane/ethyl acetate 4:1); t_R 16.8; IR (cm^{-1}): 1687, 1620, 1587, 1513, 1440, 1186, 815, 748; ^1H NMR (300 MHz, $CDCl_3$): δ 0.81 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.95–2.05 (m with d at 2, J=7.2 Hz, 1 and 3H, respectively, CH_2CH_3 and $CHCH_3$), 2.15–2.25 (m, 1H, CH_2CH_3), 3.3–3.35 (m 1H, $CHCH_2CH_3$), 6.45 (qd, J=7.2 Hz, ^4J=1.6 Hz, 1H, $CHCH_3$), 7.54 (ddd, J=8.1 and 7 Hz, ^4J=1.3 Hz, 1H, OCCCCHCHC*H*), 7.68 (ddd, J=8.4 and 7 Hz, ^4J=1.4 Hz, 1H, OCCCCHC*H*CH), 7.75 (d, J=8.6 Hz, 1H, $CH_3CHCCCH$), 7.87 (d, J=8.1 Hz, 1H, OCCCCC*H*CHCH), 8.01 (d, J=8.6 Hz, 1H, $CH_3CHCCCHC$*H*), 9.19 (d, J=8.4 Hz, 1H, OCCCC*H*CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.2, 15.1, 23.7, 50.2, 117.9, 120.3, 124.8, 126.6, 128, 129, 129.1, 129.5, 133, 135.7, 137.2, 152.9, 207; EIMS m/z: 236 (M^+, 36%), 209 (17), 208 (100), 193 (16), 179 (21), 178 (42), 165 (22). HRMS calcd for $C_{17}H_{16}O$: 236.1201; found: 236.1179. Crystal data: $C_{17}H_{16}O$, M=236.30; Crystal size max=0.16, mid=0.14, min=0.04; Triclinic, space group $P\bar{1}$, a=5.268 (4), b=7.674 (6), c=25.24 (2) Å, α=86.224° (13), β=84.914° (14), γ=71.474° (14); V=9630 (13) $Å^3$; ρ_{calcd}=1.222 g/cm^3; $2\theta_{max}$=50.1; radiation type: Mo, λ=0.71073 Å; data collection based on three ω-scan runs (starting ω=−34°) at values Φ=0°, 120°, 240° with the detector at 2θ=−32°. An additional run of 100 frames, at 2θ=−32°, ω=−34° and Φ=0°, was acquired to improve redundancy. For each of these runs, 606 frames were collected at 0.3° intervals and 30 s per frame. T=24±1 °C, measured and independent reflections=6371, reflections included in refinement=8052, $I>2/\sigma$. The diffraction frames were integrated using the program SAINT and the integrated intensities were corrected for Lorentz-polarization effects with SADABS, μ=0.074, transmission min=0.828, transmission max=0.997. The structure was solved by direct methods and refined to unique F^2 by full matrix least squares. No. of parameters=493 All of the hydrogen atoms were placed at idealized positions and retained as rigid atoms. R=0.0718, wR=0.1323, residual electron density=0.161. All results were deposited at Cambridge Crystallographic Data Centre.

*4.3.27. (E)-2-Butyl-3-butylidene-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (**11b**).* Orange oil; R_f=0.57 (hexane/ethyl acetate 4:1); t_R 19.1; IR (cm^{-1}): 1693, 1621, 1587, 1514, 1456, 1439, 1184, 821, 750; ^1H NMR (300 MHz, $CDCl_3$): δ 0.83, 1.05 (2t, J=7 and 7.4 Hz, respectively, 3H each one, CH_3 ×2), 1.2–1.35, 1.55–1.65 (2m, 4 and 2H, respectively, CH_2 ×3), 1.85–1.95, 2.05–2.15 (2m, 1H each one, $OCCHCH_2$), 2.25–2.45 (m, 2H, $OCCHCCHCH_2$), 3.3–3.4 (m 1H, OCCH), 6.36 (td, J=7.6 Hz, ^4J=1.5 Hz, 1H, OCCHCC*H*), 7.55 (t, J=7.5 Hz, 1H, OCCCCHCHC*H*), 7.68 (t, J=7.5 Hz, 1H, OCCCCHC*H*CH), 7.78 (d, J=8.6 Hz, 1H, OCCCC*H*CHC), 7.88 (d, J=8.2 Hz, 1H, OCCCCC*H*CHCH), 8.03 (d, J=8.6 Hz, 1H, OCCCCHC*H*C), 9.19 (d, J=8.4 Hz, 1H, OCCCC*H*CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 14, 22.8, 23, 26.9, 30.9, 31.6, 49.6, 118.1, 124.9, 125.8, 126.6, 128.1, 129.1, 129.2, 129.5, 133.1, 135.7, 136.7, 152.8, 207.1; EIMS m/z: 292 (M^+, 23%), 250 (23), 249 (17), 237 (19), 236 (100), 221 (19), 209 (11), 208 (63), 207 (28), 194 (32), 191 (12), 189 (11), 179 (31), 178 (39), 165 (26), 152 (11). HRMS calcd for $C_{21}H_{24}O$: 292.1827; found: 292.1807.

*4.3.28. (E)-2-Pentyl-3-pentylidene-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (**11c**).* Pale yellow oil; R_f=0.67 (hexane/ethyl acetate 4:1); t_R 21; IR (cm^{-1}): 1693, 1620, 1587, 1515, 1457, 1439, 1183, 822, 751; ^1H NMR (300 MHz, $CDCl_3$): δ 0.8, 0.96 (2t, J=6.9 and 7.2 Hz, respectively, 3H each one, CH_3 ×2), 1.1–1.35, 1.4–1.45, 1.5–1.55 (3m, 6, 2 and 2H, respectively, CH_2 ×5), 1.8–1.9, 2.05–2.15 (2m, 1H each one, $OCCHCH_2$), 2.3–2.4 (m, 2H, $OCCHCCHCH_2$), 3.25–3.35 (m 1H, OCCH), 6.33 (dt, J=7.6 Hz, ^4J=1.5 Hz, 1H, OCCHCC*H*), 7.53 (ddd, J=8.1 and 7.1 Hz, ^4J=1.2 Hz, 1H, OCCCCHCHC*H*), 7.65 (ddd, J=8.3 and 7.1 Hz, ^4J=1.2 Hz, 1H, OCCCCHC*H*CH), 7.76 (d, J=8.7 Hz, 1H, OCCCC*H*CHC), 7.85 (d, J=8.1 Hz, 1H, OCCCCC*H*CHCH), 8.01 (d, J=8.7 Hz, 1H, OCCCCHC*H*C), 9.15 (d, J=8.3 Hz, 1H, OCCCC*H*CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14 (2C), 22.4, 22.6, 24.4, 29.3, 31.2, 31.7, 32.1, 49.6, 118.1, 124.9, 126.1, 126.6, 128.1, 129.1, 129.2, 129.5, 133.1, 135.7, 136.6, 152.8, 207.1; EIMS m/z: 320 (M^+, 17%), 264 (19), 263 (18), 251 (12), 250 (60), 249 (10), 221 (14), 209 (18), 208 (100), 207 (24), 195 (12), 194 (31), 191 (14), 189 (13), 182 (23), 179 (35), 178 (46), 165 (29), 152 (11). HRMS calcd for $C_{23}H_{28}O$: 320.2140; found: 320.2159.

*4.3.29. 1,1,2,3-Tetramethylphenanthren-4-(1H)-one (**12**).* Pale yellow oil; R_f=0.53 (hexane/ethyl acetate 4:1); t_R 17.1; IR (cm^{-1}): 1701, 1633, 1616, 1595, 1508, 1457, 1378, 1284, 1071, 827, 757; ^1H NMR (300 MHz, $CDCl_3$): δ 1.54 (s, 6H, $C(CH_3)_2$), 2.09 (q, ^5J=0.8 Hz, 3H, $OCCCH_3$), 2.11 (q, ^5J=0.8 Hz, 3H, $OCCCCH_3$), 7.53 (ddd, J=8.1 and 6.8 Hz, ^4J=1.2 Hz, 1H, OCCCCHCHC*H*), 7.64 (ddd, J=8.3 and 6.8 Hz, ^4J=1.6 Hz, 1H, OCCCCHC*H*CH), 7.67 (d, J=8.8 Hz, 1H, OCCCC*H*CHC), 7.83 (d, J=8 Hz, 1H, OCCCCC*H*CHCH), 7.99 (d, J=8.8 Hz, 1H, OCCCCHC*H*C), 9.79 (d, J=8.3 Hz, 1H, OCCCC*H*CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.3, 16.7, 28 (2C), 40.8, 124, 124.7, 126.1, 127.7, 127.9, 128.4, 131.1, 132, 132.3, 133, 152.4, 155.1, 186.8; EIMS m/z: 251 (M^++1, 20%), 250 (M^+, 100), 236 (16), 235 (85), 222 (19), 221 (11), 220 (19), 209 (36), 208 (21), 207 (90), 193 (10), 192 (54), 191 (36), 190 (13), 189 (21), 179 (14), 178 (15), 166 (12), 165 (27), 152 (14). HRMS calcd for $C_{18}H_{18}O$: 250.1358; found: 250.1345.

4.4. General procedure for the synthesis of furans

To a stirred solution of alkyne (**2**, 1 mmol) in dry toluene (2.5 mL) under argon atmosphere were added Fe_3O_4 (25 mg) and the corresponding acid chloride (**1**, 1.5 mmol). The resulting mixture was stirred at 70 °C during an hour. The catalyst was removed

by a magnet and IrO_2–Fe_3O_4 (25 mg) was added. The mixture was stirred at 130 °C during three days. The catalyst was removed by a magnet and the resulting mixture was quenched with water (5 mL) and extracted with EtOAc (3×5 mL). The organic phases were dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The product was usually purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding furans **13**. Physical and spectroscopic data, as well as literature for known compound, follow:

*4.4.1. 3-Butyl-2-phenyl-5-propylfuran (**13a**).* Pale yellow oil; R_f=0.77 (hexane/ethyl acetate 4:1); t_R 14.3; IR (cm^{-1}): 1600, 1554, 1492, 1463, 1457, 1446, 801, 762, 692; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (t, J=7.3 Hz, 3H, $CCH_2CH_2CH_2CH_3$), 1.06 (t, J=7.4 Hz, 3H, $CCH_2CH_2CH_3$), 1.48 (h, J=7.3 Hz, 2H, $CCH_2CH_2CH_2CH_3$), 1.6–1.7 (m, 2H, $CCH_2CH_2CH_2CH_3$), 1.77 (h, J=7.4 Hz, 2H, $CCH_2CH_2CH_3$), 2.68, 2.69 (2t, J=7.4 Hz each one, 2H each one, CCH_2 ×2), 6.04 (s, 1H, OCCHC), 7.27 (t, J=7.4 Hz, 1H, OCCCHCHCH), 7.44 (t, J=7.4 Hz, 2H, OCCCHCH ×2), 7.64 (d, 2H, J=7.4 Hz, 2H, OCCCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 14, 21.4, 22.7, 25.7, 30.1, 32.2, 109, 122.4, 125.2 (2C), 126.2, 128.4 (2C), 132.3, 146.4, 154.9; EIMS m/z: 243 (M^++1, 10%), 242 (M^+, 55), 214 (17), 213 (100), 200 (11), 199 (20), 105 (25), 77 (20). HRMS calcd for $C_{17}H_{22}O$: 242.1671; found: 242.1691.

*4.4.2. 3-Ethyl-5-methyl-2-phenylfuran (**13b**).*[16] Colorless oil; R_f =0.63 (hexane/ethyl acetate 4:1); t_R 11.8; IR (cm^{-1}): 1600, 1557, 1492, 1444, 1071, 996, 761, 692; ^1H NMR (300 MHz, $CDCl_3$): δ 1.26 (t, J=7.5 Hz, 3H, CH_2CH_3), 2.36 (s, 3H, CCH_3), 2.68 (q, J=7.5 Hz, 2H, CH_2CH_3), 6.03 (s, 1H, OCCHC), 7.2–7.3, 7.35–7.45, 7.55–7.65 (3m, 2, 2 and 1H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.6, 14.5, 19.2, 109.2, 124, 125.2 (2C), 126.2, 128.4 (2C), 132.1, 146.3, 150.7; EIMS m/z: 187 (M^++1, 14%), 186 (M^+, 100), 172 (11), 171 (87), 143 (18), 128 (31), 115 (11), 105 (13), 77 (21).

*4.4.3. 3-Butyl-2-(4-chlorophenyl)-5-propylfuran (**13c**).* Pale yellow oil; R_f=0.83 (hexane/ethyl acetate 4:1); t_R 15.3; IR (cm^{-1}): 1568, 1549, 1487, 1464, 1094, 828; ^1H NMR (300 MHz, $CDCl_3$): δ 0.97, 1.03 (2t, J=7.2 and 7.3 Hz, respectively, 3H each one, CH_3 ×2), 1.35–1.5, 1.55–1.65, 1.7–1.8 (3m, 2H each one, CH_2 ×3), 2.62, 2.64 (2t, J=7.4 and 7.3 Hz, respectively, 2H each one, CCH_2 ×2), 6.01 (s, 1H, OCCHC), 7.37 (d, J=8.7 Hz, 2H, ClCCH ×2), 7.53 (d, J=8.7 Hz, 2H, ClCCHCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 13.9, 21.4, 22.6, 25.7, 30.1, 32.1, 109.1, 123, 126.3 (2C), 128.6 (2C), 130.7, 131.7, 145.4, 155.2; EIMS m/z: 277 (M^++1, 22%), 276 (M^+, 100), 255 (11), 253 (35), 137 (12). HRMS calcd for $C_{17}H_{21}ClO$: 276.1281; found: 276.1214.

*4.4.4. 3-Butyl-2-(4-methoxyphenyl)-5-propylfuran (**13d**).* Yellow oil; R_f=0.63 (hexane/ethyl acetate 4:1); t_R 16; IR (cm^{-1}): 1606, 1577, 1559, 1505, 1462, 1293, 1247, 1176, 1037, 830, 801; ^1H NMR (300 MHz, $CDCl_3$): δ 1.01, 1.07 (2t, J=7.3 and 7.4 Hz, respectively, 3H each one, CH_2CH_3 ×2), 1.4–1.55, 1.6–1.7, 1.7–1.85 (3m, 2H each one, CH_2 ×3), 2.65, 2.68 (2t, J=7.2 and 7.3 Hz, respectively, 2H each one, CCH_2 ×2), 3.87 (s, 3H, OCH_3), 6.03 (s, 1H, OCCHC), 7 (d, J=9 Hz, 2H, OCCHCH ×2), 7.58 (d, J=9 Hz, 2H, OCCHCH ×2); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 13.9, 21.4, 22.6, 25.6, 30.1, 32.3, 55.1, 108.6, 113.9 (2C), 120.7, 125.2, 126.7 (2C), 146.4, 154.2, 158.1; EIMS m/z: 273 (M^++1, 13%), 272 (M^+, 66), 244 (17), 243 (100), 229 (21), 135 (13). HRMS calcd for $C_{18}H_{24}O_2$: 272.1776; found: 272.1742.

*4.4.5. 3-Butyl-5-propyl-2-(thiophen-2-yl)furan (**13e**).* Pale yellow oil; R_f=0.8 (hexane/ethyl acetate 4:1); t_R 14.4; IR (cm^{-1}): 1566, 1464, 1378, 1258, 976, 848, 821, 687; ^1H NMR (300 MHz, $CDCl_3$): δ 0.99, 1.03 (2t, J=6.5 and 6.6 Hz, respectively, 3H each one, CH_3 ×2), 1.35–1.5, 1.55–1.7, 1.7–1.8 (3m, 2H each one, CH_2 ×3), 2.55-2.7 (m, 4H, CCH_2 ×2), 6 (s, 1H, OCCHC), 7.08 (dd, J=5 and 3.7 Hz, 1H, SCHCH), 7.2 (dd, J=3.7 Hz, ^4J=1.1 Hz, 1H, SCCH), 7.23 (dd, J=5 Hz, ^4J=1.1 Hz, 1H, SCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 13.9, 21.4, 22.6, 25.5, 30.1, 31.9, 108.7, 121.8, 122.1, 123, 127.2, 134.3, 142.7, 154.8; EIMS m/z: 249 (M^++1, 10%), 248 (M^+, 57), 220 (15), 219 (100), 205 (29), 111 (27). HRMS calcd for $C_{15}H_{20}OS$: 248.1235; found: 248.1228.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.06.041. These data include MOL files and InChiKeys of the most important compounds described in this article.

References and notes

1. (a) Gooβen, L. J.; Rodríguez, N.; Gooβen, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 9592–9594; (b) Fujihara, T.; Iwai, T.; Terao, J.; Tsuji, Y. *Synlett* **2010**, 2537–2548.
2. Pohland, A. E.; Benson, W. R. *Chem. Rev.* **1964**, *64*, 161–197.
3. (a) Price, C. C.; Pappalardo, J. A. *J. Am. Chem. Soc.* **1950**, *72*, 2613–2615; (b) Benson, W. R.; Pohland, A. E. *J. Org. Chem.* **1964**, *29*, 385–391; (c) Martens, H.; Janssens, F.; Hoornaert, G. *Tetrahedron* **1975**, *31*, 177–183; (d) Snelders, D. J. M.; Dyson, P. J. *Org. Lett.* **2011**, *13*, 4048–4051.
4. Manoiu, D.; Manoiu, M.; Dinulescu, I. G.; Avram, M. *Rev. Roum. Chim.* **1985**, *30*, 223–227.
5. Zhou, H.; Zeng, C.; Ren, L.; Liao, W.; Huang, X. *Synlett* **2006**, 3504–3506.
6. Hosseini-Savari, M.; Mardaneh, Z. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 778–782.
7. (a) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6941–6946; (b) Hua, R.; Shimada, S.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 12365–12366; (c) Hua, R.; Onozawa, S.-y.; Tanaka, M. *Chem.—Eur. J.* **2005**, *11*, 3621–3630; (d) Kashiwabara, T.; Kataoka, K.; Hua, R.; Shimada, S.; Tanaka, M. *Org. Lett.* **2005**, *7*, 2241–2244; (e) Kashiwabara, T.; Fuse, K.; Hua, R.; Tanaka, M. *Org. Lett.* **2008**, *10*, 5469–5472; (f) Kashiwabara, T.; Tanaka, M. *Adv. Synth. Catal.* **2011**, *353*, 1485–1490.
8. (a) Iwai, T.; Fujihara, T.; Terao, J.; Tsuji, Y. *J. Am. Chem. Soc.* **2009**, *131*, 6668–6669; (b) Iwai, T.; Fujihara, T.; Terao, J.; Tsuji, Y. *J. Am. Chem. Soc.* **2012**, *134*, 1268–1274.
9. Wang, B.; Wang, S.; Li, P.; Wang, L. *Chem. Commun.* **2010**, 5891–5893.
10. Gandeepan, P.; Parthasarathy, K.; Su, T.-H.; Cheng, C.-H. *Adv. Synth. Catal.* **2012**, *354*, 457–468.
11. (a) Martínez, R.; Ramón, D. J.; Yus, M. *Adv. Synth. Catal.* **2008**, *350*, 1235–1240; (b) Martínez, R.; Ramón, D. J.; Yus, M. *Org. Biomol. Chem.* **2009**, *7*, 2176–2181; (c) Cano, R.; Ramón, D. J.; Yus, M. *Synlett* **2011**, 2017–2020.
12. (a) Aliaga, M. J.; Ramón, D. J.; Yus, M. *Org. Biomol. Chem.* **2010**, *8*, 43–46; (b) Cano, R.; Ramón, D. J.; Yus, M. *J. Org. Chem.* **2010**, *75*, 3458–3460; (c) Cano, R.; Ramón, D. J.; Yus, M. *Tetrahedron* **2011**, *67*, 5432–5436; (d) Cano, R.; Ramón, D. J.; Yus, M. *J. Org. Chem.* **2011**, *76*, 5547–5557; (e) Cano, R.; Yus, M.; Ramón, D. J. *Tetrahedron* **2011**, *67*, 8079–8085; (f) Cano, R.; Yus, M.; Ramón, D. J. *Tetrahedron* **2012**, *68*, 1393–1400; (g) Cano, R.; Yus, M.; Ramón, D. J. *Chem. Commun.* **2012**, 7628–7630; (h) Pérez, J. M.; Cano, R.; Yus, M.; Ramón, D. J. *Eur. J. Org. Chem.* **2012**, 4548–4554.
13. (a) Denmark, S. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, UK, 1991; Vol. 5, pp 751–784; (b) Habermas, K. L.; Denmark, S. E.; Jones, T. K. In *Organic Reactions*; Paquette, L. A., Ed.; John Wiley & Sons: New York, NY, 1994; Vol. 45, pp 1–158; (c) Vaidya, T.; Eisenberg, R.; Frontier, A. J. *ChemCatChem* **2011**, *3*, 1531–1548.
14. (a) Martin, G. J.; Rabiller, C.; Mabon, G. *Tetrahedron Lett.* **1970**, 3131–3132; (b) Martin, G. J.; Rabiller, C.; Mabon, G. *Tetrahedron* **1972**, *28*, 4027–4037; (c) Rizzo, C. J.; Dunlap, N. K.; Smith, A. B. *J. Org. Chem.* **1987**, *52*, 5280–5283; (d) Fiandanese, V.; Marchese, G.; Punzi, A.; Ruggieri, G. *Tetrahedron Lett.* **1996**, *37*, 8455–8458.
15. Lee, K. Y.; Lee, M. J.; Kim, J. N. *Tetrahedron* **2005**, *61*, 8705–8710.
16. Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407–4413.