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Copper-catalyzed electrosynthesis of 1-acyl-2,2-diphenyl-cyclopropanes and their behaviour in acidic medium

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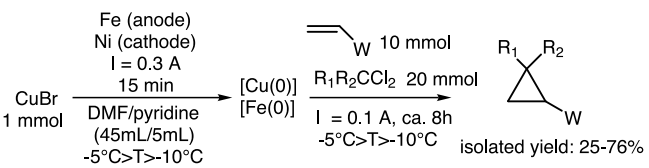
Abstract—The formation of 1-acyl-2,2-diphenylcyclopropanes is performed under mild electrochemical conditions. These cyclopropane derivatives, through acid-catalyzed ring-opening, lead to γ,γ-diphenyl-β,γ-unsaturated carbonyl compounds which evolve into either substituted naphthalenes, or β-benzhydryl-α,β-cycloalkenones depending on the acyclic or cyclic nature of the intermediate allyl ketone.

1. Introduction

We have previously investigated the synthesis of cyclopropanes by direct electroreductive cyclocondensation between α,α,α-trichloro or *gem*-dihalo compounds and α,β-unsaturated carboxylic esters. This method, however, only applies to activated olefins which are more easily reduced than the polyhalo compound.[1a] We have more recently found a way to get round this limitation by setting up a method involving the indirect electrochemical activation of the halo compound, through either a Fe/Ni catalyst in the case of non-activated *gem*-dibromocompounds[1b] (dibromomethane, 2,2-dibromopropane, 1,1-dibromoethane) or a Fe/Cu catalyst in the case of activated α,α,α-trichloro or *gem*-dichlorocompounds[1c] (methyltrichloroacetate, α,α,α-trichlorotoluene, benzal chloride, dichlorodiphenylmethane). A brief description of these most recent results is given in Equation (1a).



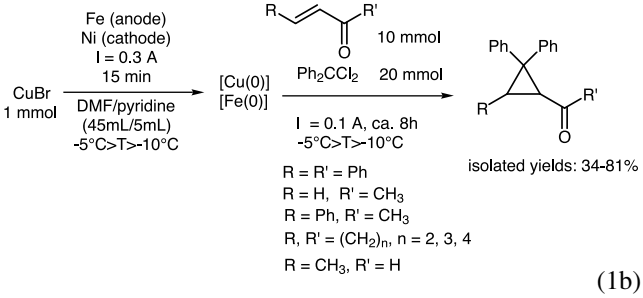
(1a)

In this paper, we develop the synthesis of 1-acyl-2,2-diphenylcyclopropanes, based on the same electroreductive coupling process, now applied to α,β-unsaturated ketones or aldehydes and dichlorodiphenylmethane. It has already been shown that nucleophilic ring opening of acylcyclopropanes is a useful route to prepare 1,4-difunctional compounds.[2a,b] In this study, we have found that, under acidic treatment, 1-acyl-2,2-diphenylcyclopropanes can be converted into allyl ketones which are new routes to substituted naphthalenes or to β-benzhydryl-α,β-cycloalkenones.

2. Results and discussion

2.1. Cyclopropane formation

The cyclocondensations (Eq. (1b)) are conducted, as previously described,[1c] in an undivided cell fitted with an XC10 iron rod (iron containing 0.1% of carbon) as the anode and a nickel foam as the cathode. A solution of copper bromide (1 mmol) and Bu_4NBr (300 mg) in DMF (45 mL) and pyridine (5 mL) is first electrolyzed at constant current intensity (0.3 A) during 15 min at $-5 > T > -10$°C. Then the α,β-unsaturated ketone or aldehyde (10 mmol) and dichlorodiphenylmethane (20 mmol) are added, and the



(1b)

Keywords: acyl cyclopropanes; β-benzhydryl-α,β-cycloalkenones; substituted naphthalenes; electro-organic synthesis; benzannulation.

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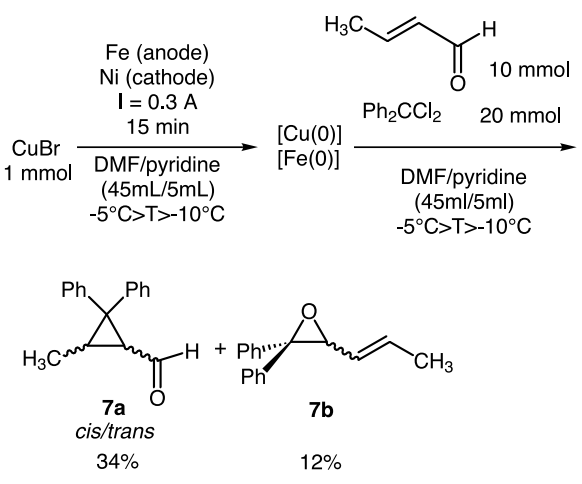
solution is electrolyzed (0.1 A) until complete consumption of the carbonyl compound (about 8 h).

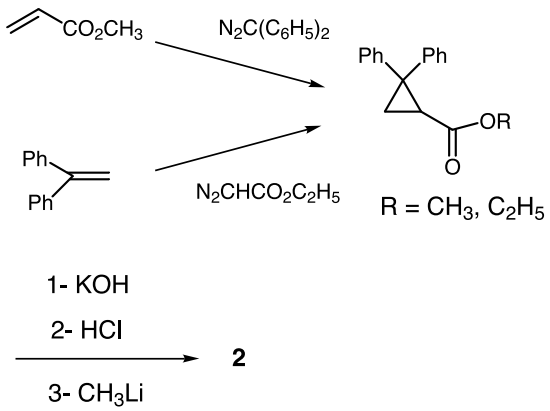
Our results are listed in Table 1. The by-products are reduction or dimerisation derivatives of dichlorodiphenylmethane, i.e. diphenylmethane, benzhydryl chloride, and tetraphenylethylene. As for the couple dimethylitaconate–dichlorodiphenylmethane selected as model reagents in Ref. 1c, the influence of several parameters on the yield and selectivity of the cyclopropanation has been examined on the cyclohexenone–dichlorodiphenymethane model system (Table 1, entry 4), i.e. the reagents ratio, the reaction temperature, the DMF-pyridine ratio, the current intensity during the electrolysis, the CuBr-reagents ratio, and the charge required for the formation of Cu(0) and, possibly, Fe(0) during the pre-electrolysis. Only the two last parameters led to some effects in regard to the previous results. Thus, on the one hand, in the absence of CuBr, the cyclopropane yield was down to 51% instead of 76% (Table 1, entry 4), but tetraphenylethylene, benzhydryl chloride and diphenylmethane remain minor products while they previously became major products in Ref. 1c (traces of cyclopropane). On the other hand, when the pre-electrolysis was carried on beyond 15 min (Table 1, entry 4), the yield of cyclopropane was slightly increased (+4%). Consequently, we examined the effect of the duration of the pre-electrolysis for every model, and found that the cyclopropane yield increased significantly only for the mixture chalcone-dichlorodiphenylmethane (from 25 to 41%, Table 1, entry 1). With the optimized conditions, isolated yields are in the range of 34–81% (Table 1, entries 1–7).

The cyclopropane adducts are obtained from the α,β-unsaturated ketones with high stereoselectivity. With acyclic enones no *cis*-1-acyl-2,2-diphenylcyclopropane was detected by GC–MS, (Table 1, entry 1 and 3). As expected, also, no *trans*-cyclopropane derivative was formed with cyclic enones (Table 1, entries 4–6). Within these two series, the cyclisation is also regiospecific as no oxirane was formed. On the contrary, with crotonaldehyde (Table 1, entry 7 and Eq. (2)), the cyclocondensation gave a 74/26 mixture of cyclopropane and oxirane and, in addition, the cyclopropanation gave a *cis/trans* ratio of 45/55. The oxirane **7b** was characterized by GC–MS and NMR.



(2)

These electrosyntheses are a good alternative to the photocondensation of diphenyldiazomethane with α,β-unsaturated ketones,[2c] or to its 1,3-dipolar addition followed by a ring-contraction of the pyrazolines.[3a,b,4,9] Surprisingly, in the literature, 1-acetyl-2,2-diphenylcyclopropane **2** is prepared in three steps via methyl[6] or ethyl[8] 2,2-diphenylcyclopropane carboxylate and subsequent treatment with KOH, HCl and methyllithium[7,8] (Eq. (3)). Diphenyldiazomethane is possibly basic enough to deprotonate methylvinylketone.

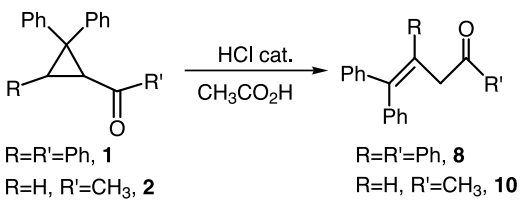


(3)

2.2. Acid-catalyzed ring-opening

Subsequent acid catalyzed isomerization to γ,γ-diphenyl-β,γ-unsaturated ketones was carried out as follows: to a solution of 1-acyl-2,2-diphenylcyclopropane (250 mg in 25 mL glacial acetic acid) was added 0.5 mL of 12N hydrochloric acid. The reaction was monitored by GC analysis. In the case of slow isomerization, the reaction mixture was heated at reflux.

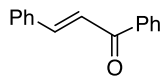
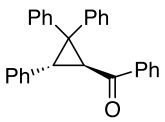
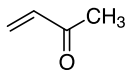
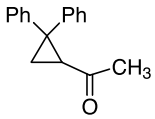
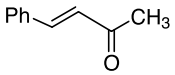
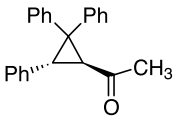
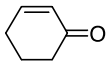
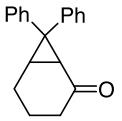
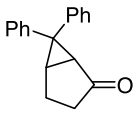
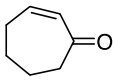
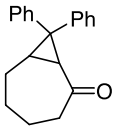
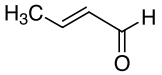
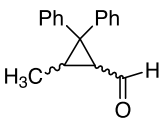
Our results, in agreement with the work of Lutz et al.[2c] about the preparation of 1,3,4,4-tetraphenylbut-3-en-1-one **8** from 1-benzoyl-2,2,3-triphenylcyclopropane **1** in acidic medium are reported in Table 2, entries 1 and 3: γ,γ-Diphenyl-β,γ-unsaturated ketones **8** and **10** are obtained by acid-catalyzed isomerization of 1-acyl-2,2-diphenylcyclopropanes **1** (AcOH, reflux) and **2** (AcOH, rt), respectively (Eq. (4)).



(4)

When 1-acetyl-2,2,3-triphenylcyclopropane **3** (Table 2, entry 5) or 1-formyl-3-methyl-2,2-diphenylcyclopropane **7** (Table 2, entry 7) was treated at room temperature, the expected γ,γ-diphenyl-β,γ-unsaturated carbonyl compound was actually formed, as indicated by GC–MS analysis, but another product was also observed, which became the only product after heating at reflux. These products were characterized as naphthalene derivatives, i.e. 1,2-diphenyl-4-methylnaphthalene **13** and 2-methyl-1-phenylnaphthalene **15** (Table 2, entries 6 and 8). By similar treatment, the γ,γ-diphenyl-β,γ-unsaturated ketones **8** and **10** also lead to respectively 1,2,4-triphenylnaphthalene **9** and

Table 1. 1-Acyl-2,2-diphenylcyclopropane formation by copper catalyzed indirect electroreductive coupling of activated olefins and dichlorodiphenylmethane

Entry	Olefin	1-Acyl-2,2-diphenyl-cyclopropane	Nr	Isolated yield (%)	CAS RN	Melting point (°C)	Melting point °C, yield% in literature
1			**1**	25 41[a]	[10266-31-6]	125–126	100–103,[4] 35[4] 125–127,[2c] 20[2c]
2			**2**	40	[27067-40-9]	58–59	58–59,[5] 38[6,7] $bp_{2,5}$=159–160,[7,8] 53[8]
3			**3**	41	New compound	136–138	New compound
4			**4**	76 80[a] 51[b]	New compound	94–95	New compound
5			**5**	81	[22524-16-9]	108–109	105–106,[9] 25[9]
6			**6**	51	New compound	67–68	New compound
7			**7**	34	New compounds *cis*/*trans*: 55/45	*cis*: 94–96 *trans*: not isolated	New compounds

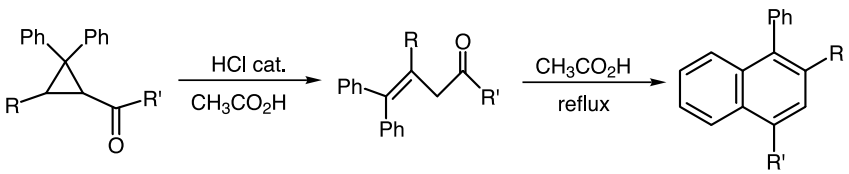
[a] Pre-electrolysis: 30 mn, 0.3 A.
[b] Pre-electrolysis without CuBr.

4-methyl-1-phenylnapthalene **11** (Table 2, entries 2 and 4). This acid catalyzed isomerization followed by a benzannulation is, to our knowledge, a new route to naphthalene derivatives (Eq. (5)).

The formation of 4-methyl-1,2-diphenylnapthalene **13** (new compound) from **3** can be explained as shown in Equation (6). The intermediate **12** is very likely formed, but rapidly transformed via its protonated form.

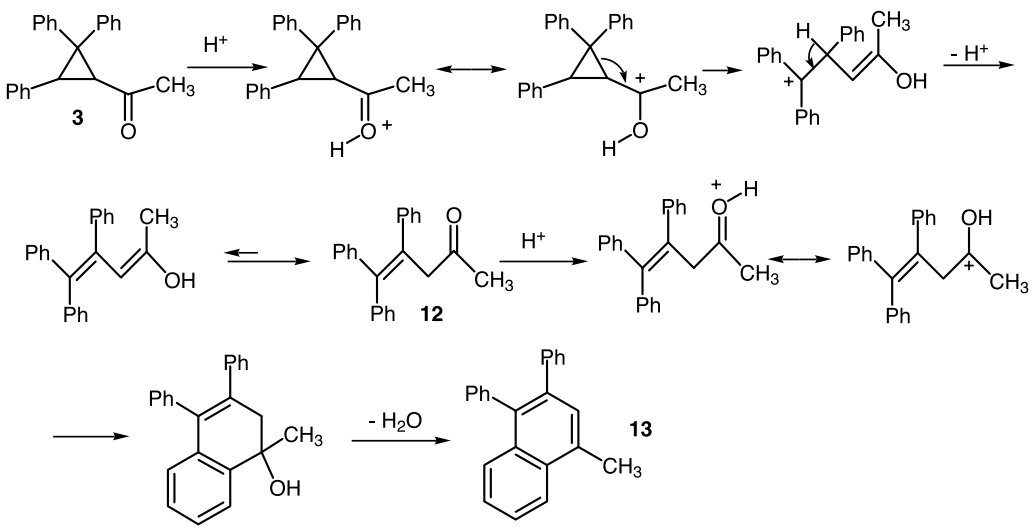
These naphthalene compounds are usually prepared either by multistep syntheses (**11**,[13,14,19,20] **15**[21]), or by nickel-catalyzed coupling of Grignard reagents with naphthylbromide derivative (**15**[16]), or by palladium-catalyzed annulation of internal alkynes by arene-containing vinyl iodides (**9**[11]).

The acid catalyzed isomerization of the two bicyclic ketones **4** and **5** leads respectively to 3-benzhydrylcyclohex-2-enone **17** and to 3-benzhydrylcyclopent-2-enone **19** via the expected γ,γ-diphenyl-β,γ-unsaturated ketones **16** and **18** which are thermodynamically less stable as they have an



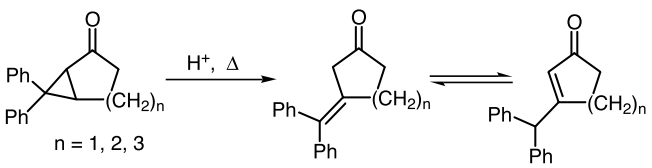
R=Ph, R'=CH_3, **3**	**12**, not isolated	**13**
R=CH_3, R'=H, **7**	**14**, not isolated	**15**
R=R'=Ph, **1**	**8**	**9**
R=H, R'=CH_3, **2**	**10**	**11**

(5)



(6)

exocyclic double bond (Table 2, entries 9–12). In the case of 8,8-diphenylbicyclo[5.1.0]octan-2-one **6** (Table 2, entry 13) the two isomeric *exo*/*endo* enones **20** and **21** are obtained in 73/27 ratio, this ratio did not change even after prolonged heating, though the yields decrease, respectively, to 44 and 16% instead of 61 and 24% (Eq. (7)).

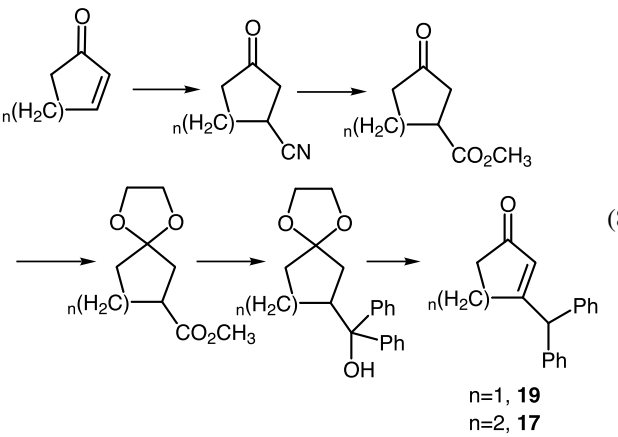


n=1, **5**	**18**, not isolated	**19**
n=2, **4**	**16**, not isolated	**17**
n=3, **6**	**20**	**21**

(7)

No naphthalenic compounds are formed, likely because the rigidity of the cyclic β,γ-unsaturated ketones should prevent it to get the appropriate geometry for the benzannulation reaction. In brief, the acyclic allyl ketones, in acidic medium, are converted into substituted naphthalenes and the cyclic allyl ketones in β-benzhydryl-α,β-cycloalkenones via the corresponding 3-benzhydrylidenecycloalkanones. Our results are listed in Table 2.

Up to now, only multistep syntheses of **17** and **19** are described in the literature, as shown in Equation (8).[17,18]

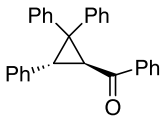
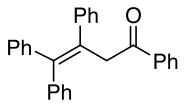
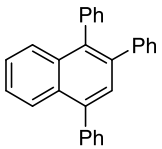
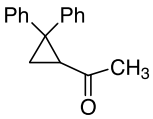
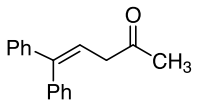
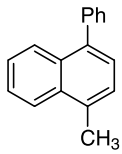
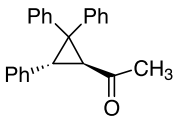
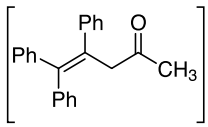
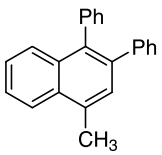
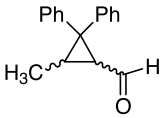
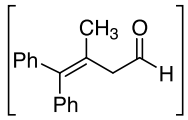
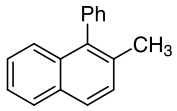


(8)

3. Conclusion

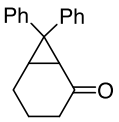
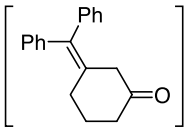
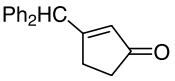
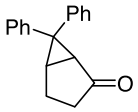
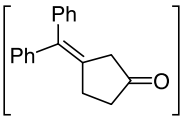
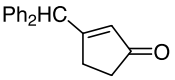
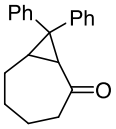
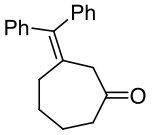
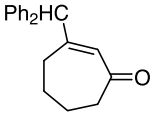
This paper presents an interesting method of formation of 1-acyl-2,2-diphenylcyclopropanes under mild electrochemical reaction conditions. The monocyclic compounds obtained proved to be new synthons of naphthalene derivatives through acid catalyzed sequential ring-opening/

Table 2. Acidic transformations of 1-acyl-2,2-diphenylcyclopropanes

Entry	1-Acyl-2,2-diphenyl-cyclopropane	Nr	Reaction time, temperature	Product	Nr	Isolated yield%	CAS RN	Melting point (°C)	Melting point °C in literature
1		**1**	3 h, 120°C		**8**	81	[53449-11-9]	195–196	193.5–198[2c]
2		**1**	48 h, 120°C		**9**	20	[806-58-6]	158–160	159–161[11]
3		**2**	30 min, rt		**10**	51	[55004-95-0]	50–51	51–52[12a]
4		**2**	15 h, 120°C		**11**	60	[13280-69-8]	37–38	38.5–39[13]
5		**3**	4 h, rt		**12**	Not isolated[a]	[7593-09-1]		147.5–148.5[15]
6		**3**	3 h, 120°C		**13**	72	New compound	139–140	New compound
7		**7**			**14**	Not isolated[a]			
8		**7**	4 h 15 min, 120°C		**15**	33	[29304-63-0]	43–44	44[16a]

(*continued on next page*)

Table 2 (*continued*)

Entry	1-Acyl-2,2-diphenyl-cyclopropane	Nr	Reaction time, temperature	Product	Nr	Isolated yield%	CAS RN	Melting point (°C)	Melting point °C in literature
9		**4**	3 h, rt		**16**	Not isolated[b]			
10		**4**			**17**	67	[21086-47-5]	Oil	$bp_{0.2}$: 170–180[17]
11		**5**	25 h, rt		**18**	Not isolated[b]			
12		**5**			**19**	58	[70239-00-8]	68–69	68.5–69.5[18]
13		**6**	30 min, 120°C		**20**	61 44[c]	New compound	74–75	New compound
					**21**	24 16[c]	New compound	91–92	New coumpound

[a] The γ,γ-diphenyl-β,γ-unsaturated ketone or aldehyde undergoes a very fast cyclisation leading to the substituted naphthalene and, therefore, cannot be isolated.
[b] The γ,γ-diphenyl-β,γ-unsaturated ketone presents an exocyclic double bond and is rapidly converted into the stable isomer with the endocyclic double bond.
[c] 120°C, 7 h.

benzannulation. In the case of bicyclic derivatives, the acid-catalyzed ring-opening leads to the corresponding 3-benzhydrylidene-5-, 6-, or 7-membered-cycloalkanone. These compounds, which have an exocyclic double bond, are completely (the two first cases) or partially (last case) converted into endocyclic double bond isomers. Therefore, the two consecutive reactions (cyclopropanation and acid catalyzed isomerization) can efficiently replace a Heck type reaction in the preparation of β-benzhydryl-α,β-cycloalkenones.

The cyclopropanation may result from a conjugated addition followed by SN_i or may involve a metallocarbene species. This remains to be elucidated by electrochemical analyses. We are now investigating the formation of oxiranes by copper indirect electroreductive coupling of aldehydes or ketones and activated *gem*-dichlorocompounds, which was observed as a side reaction in the presence of crotonaldehyde.

4. Experimental

4.1. General information

Melting points were determined with an Electrothermal IA 9100 digital melting point apparatus. ^1H, ^{13}C NMR spectra were recorded on a Bruker AC-200 (200, 50 MHz respectively) or Bruker AM-300 (300, 75 MHz respectively) spectrometer. Mass spectra (electron impact) were obtained on a GCQ Thermoquest spectrometer equipped with a DB 5MS capillary column. Infrared spectra were recorded on a Perkin–Elmer Spectrum BX FT-IR spectrometer. High-resolution mass spectral analyses and

elemental analyses were carried out at 'Service Central d'Analyse du CNRS', Vernaison, France. Gas chromatography was performed on a Varian 3300 chromatograph fitted with a SIL-5 CP capillary column. Solvents and chemicals were used as received. The XC10 Fe rod (iron with 0.1% of carbon) is purchased from Weber Métaux.

4.2. General procedure

Method a, indirect electrochemical process with Fe anode in the presence of CuBr. The reactions are conducted in an undivided cell fitted with an Fe rod as the anode and a nickel foam as the cathode (area: ca. 40 cm^2). A solution of CuBr (144 mg, 1 mmol) and Bu_4NBr (300 mg) in DMF (45 mL) and pyridine (5 mL) is electrolysed at constant current intensity (0.3 A) during 15 min at $-5>T>-10$°C. Then, the activated olefin (10 mmol) and the dichlorodiphenylmethane (20 mmol) are added and electrolysed (0.1 A) until the complete consumption of the olefin (about 8 h). The DMF is evaporated under reduced pressure. The reaction mixture is poured into a cold mixture of 1 M HCl (50 mL) and diethyl ether (50 mL). The layers are separated and extracted with diethyl ether (three portions of 25 mL). The combined ethereal extracts are washed with a saturated solution of ammonium chloride and brine, dried over $MgSO_4$. Products are isolated either by column chromatography on silica gel (230–400 mesh) or aluminium oxide (70–230 mesh) using pentane-ether as eluent or by flash chromatography on aluminium oxide (70–230 mesh) using pentane–dichloromethane as eluent.

Method b, chemical isomerization and benzannulation process. The reactions are performed in a two-necked round bottom flask fitted with a condenser. To 250 mg of 1-acyl-2,2-diphenylcyclopropane is added a mixture of glacial acetic acid (2.5 mL) and hydrochloric acid 37% (0.5 mL). The solution is stirred at rt (products **10**, **17**, **19**) or at 120°C (products **8**, **9**, **11**, **13**, **15**, **20**, **21**). The isomerization and the benzannulation reactions are monitored by GC analysis (see reaction time in Table 2). When reaction time is longer than 5 h at 120°C, small amounts of acetic acid and HCl must be added, from time to time, in order to maintain the acidic conditions (pH 1). The mixture is diluted in water and the products are extracted with diethyl ether (three portions of 25 mL). The combined ethereal extracts are washed with a saturated solution of sodium hydrogenocarbonate and brine, dried over $MgSO_4$. The products are isolated using the procedure described in method a.

4.3. Isolated products

4.3.1. *trans*-1-Benzoyl-2,2,3-triphenylcyclopropane 1. ($C_{28}H_{22}O$); MW: 374.483; CAS RN: 10266-31-6. Pentane/ether: (99/1)–(90/10); obtained: 1.55 g (yield: 41%, method a); mp: 125–126°C; ^{1}H NMR[4] (200 MHz, $CDCl_3$) δ 8.25 (H_{ortho}, 1H, d, J=1.3 Hz), 8.20 (H_{ortho}, 1H, d, J=1.8 Hz), 7.75–7.10 (Ph, 18H, m), 4.25 (H-3, 1H, d, J=6.2 Hz), 4.20 (H-1, 1H, d, J=6.2 Hz), for the couple H-3/H-1 ($\Delta\nu/J$= 1.6 Hz AB system). ^{13}C NMR (50 MHz, $CDCl_3$) δ: *C*O: 195.0; C(Ph): 141.0, 140.5, 138.5, 136.4, 132.7, 129.4, 129.3, 128.5, 128.1, 128.0, 127.9, 127.7, 126.7, 126.4, 126.1; C-2: 51.7; C-1, C-3: 36.7, 36.1. EI-MS *m*/*z*: 374, 270, 269 (base peak), 268, 192, 191, 165, 105, 91, 77, 65, 50. IR[4] ν (cm^{-1}) (CCl_4) 3075, 3035, 1675, 1600, 1580, 1495, 1445.

4.3.2. 1-Acetyl-2,2-diphenylcyclopropane 2. ($C_{17}H_{16}O$); MW: 236.314; CAS RN: 27067-40-9. Pentane (aluminium oxide—90 active, neutral (activity I)); obtained: 0.945 g (yield: 40%, method a); mp: 58–59°C. ^{1}H NMR[8] (200 MHz, $CDCl_3$) δ 7.40–7.00 (Ph, 10H, m), 2.80 (H-1, 1H, dd, J=7.9, 6.3 Hz), 2.25 (H-3a, 1H, dd, J=6.3, 4.2 Hz), 2.10 (CH_3, 3H, s), 1.50 (H-3b, 1H, dd, J=7.9, 4.2 Hz). ^{13}C NMR[8] (50 MHz, $CDCl_3$) δ *C*O: 203.7; C(Ph): 145.0, 139.4, 129.9, 129.4, 128.4, 128.3, 128.2, 127.5, 127.2, 127.0, 126.5; C-2: 42.7; C-1, *C*H_3: 37.1, 31.1; C-3: 21.0. EI-MS *m*/*z*: 236, 221, 194, 193 (base peak), 179, 178, 166, 165, 116, 115; IR[8] ν (cm^{-1}) (CH_2Cl_2) 3060, 2990, 1705, 1605, 1585, 1500, 1460, 1440, 1430.

4.3.3. *trans*-1-Acetyl-2,2,3-triphenylcyclopropane 3 (new compound). ($C_{23}H_{20}O$); MW: 312.412; Anal. calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45; O, 5.12. Found: C, 88.21; H, 6.36; O, 5.15. Pentane/ether: (99/1)–(95/5); obtained: 1.28 g (yield: 41%, method a); mp: 136–138°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50–7.00 (Ph, 15H, m), 3.90 (H-3, 1H, d, J=6.3 Hz), 3.50 (H-1, 1H, d, J=6.3 Hz), 2.40 (CH_3, 3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 203.4; C(Ph): 141.3, 140.4, 136.3, 129.8, 129.2, 128.5, 128.2, 128.0, 127.9, 127.4, 127.0, 126.6, 126.3; C-2: 51.1; C-1, C-3, *C*H_3: 40.8, 35.6, 31.4. EI-MS *m*/*z* 270, 269, 192, 191 (base peak), 190, 189, 165, 91; IR ν (cm^{-1}) (CH_2Cl_2) 3060, 2990, 1705, 1605, 1585, 1500, 1450.

4.3.4. 7,7-Diphenylbicyclo[4.1.0] heptan-2-one 4 (new compound). ($C_{19}H_{18}O$); MW: 262.352; Anal. calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91; O, 6.10. Found: C, 87.15; H, 7.13; O, 6.21. Pentane/ether: (98/2)–(95/5); obtained: 2.10 g (yield: 80%, method a); mp: 94–95°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60–7.20 (Ph, 10H, m), 2.70–2.10 (3H, m), 1.90–1.60 (5H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 209.0; C(Ph): 146.6, 139.0, 130.5, 129.1, 128.6, 127.4, 127.2, 126.5; C-7: 43.9; C-3: 39.3; C-1: 37.4; C-6: 29.0; C-4, C-5: 22.1, 20.1. EI-MS *m*/*z* 262, 244, 234, 219, 218, 208, 206 (base peak), 205, 204, 203, 192, 191, 189, 178, 165, 128, 92, 91. IR ν (cm^{-1}) ($CHCl_3$) 1678, 1600, 1580, 1495.

4.3.5. 6,6-Diphenylbicyclo[3.1.0]hexan-2-one 5. ($C_{18}H_{16}O$); MW: 248.325; CAS RN: 22524-16-9. Pentane/ether: (95/5)–(85/15); obtained: 2.01 g (yield: 81%, method a); mp: 108–109°C. ^{1}H NMR[9] (200 MHz, $CDCl_3$) δ 7.32–7.00 (Ph, 10H, m), 2.67 (cyclopropyl, 1H, pseudo t, J=5.7 Hz), 2.47 (cyclopropyl, 1H, d, J=5.7 Hz), 2.30–1.70 (methylene, 3H, m), 0.87 (methylene, 1H, dt, J=8.7, 19.3 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 214.0; C(Ph): 144.2, 137.5, 129.9, 128.9, 128.3, 127.2, 126.7, 126.3; C-1: 43.6; C-6: 42.5; C-5: 35.4; C-3: 35.3; C-4: 21.4. EI-MS[9] *m*/*z* 248, 220, 219, 207, 206 (base peak), 205, 204, 203, 202, 192, 191, 190, 189, 178, 165, 129, 128, 115, 91. IR[9] ν (cm^{-1}) ($CHCl_3$) 1716, 1600, 1495, 1430.

4.3.6. 8,8-Diphenylbicyclo[5.1.0]octan-2-one 6 (new compound). ($C_{20}H_{20}O$); MW: 276.379. Anal. calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29; O, 5.79. Found: C, 86.59; H, 7.34; O, 5.63. Pentane/ether: (100/0)–(80/20); obtained:

1.4 g (yield: 51%, method a); mp: 67–68°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45–7.10 (Ph, 10H, m), 2.45–1.15 ($H_{aliphatic}$, 10H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 209.3; C(Ph): 146.9, 138.2, 131.1, 128.3, 127.3, 126.8, 126.2; C-8: 43.7; C-3: 41.6; C-1: 41.0; C-7: 28.8; C-4, C-5, C-6: 24.8, 24.7, 21.8. EI-MS *m/z* 276, 258, 248, 232, 219, 217, 207, 206, 205 (base peak), 204, 203, 202, 193, 192, 191, 190, 189, 180, 179, 178, 170, 167, 166, 165, 152, 141, 129, 128, 115, 91. IR ν (cm^{-1}) ($CHCl_3$) 1700, 1665, 1600, 1500, 1430.

4.3.7. 3-Methyl-2,2-diphenylcyclopropane-1-carboxaldehyde 7a *cis/trans*, (new compounds). ($C_{17}H_{16}O$); MW: 236.314. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83; O, 6.77. Found: C, 86.27; H, 6.69; O, 6.52.

7a *cis/trans*: flash chromatography pentane/CH_2Cl_2: (80/20)–(0/100); obtained: 0.80 g (yield: 34%, method a); mixture of *cis/trans* 55/45 crystallised. ^{1}H NMR (200 MHz, $CDCl_3$) δ *cis*, [*trans*] 9.07 (CHO, 1H, d, *J*=6.9 Hz), [8.52 (CHO, 1H, d, *J*=6.9 Hz)], 7.72–6.99 (Ph, 20H (*cis/trans*), m), 2.30–2.11 (H-1, H-3, [H-1], 3H, m), [2.55–2.43 (H-3, 1H, m (d after homodecoupling of methyl at 0.95 ppm, *J*=5.1 Hz)], 1.36 (CH_3, 3H, d, *J*=6.4 Hz), [0.95 (CH_3, 3H, d, *J*=6.3 Hz)]. ^{13}C NMR (50 MHz, $CDCl_3$) δ mixture of *cis/trans* 55/45 δ *cis*, [*trans*] *C*O: 201.3, [200.7]; C(Ph): 145.6, 141.3, 140.3, 136.6, 131.0, 129.1, 129.0, 128.6, 128.3, 127.1, 126.8, 126.5; C-2: 45.8, [46.4]; C-1, C-3, CH_3, 39.8, 28.5, 12.0, [41.9, 25.0, 14.2];. EI-MS *m/z cis* 236, 221, 208, 207, 206, 205, 192, 191, 189, 179, 178, 166, 165, 130, 129 (base peak), 128, 115, 91, *trans* 236, 221, 208, 207, 206, 205, 192, 191, 189, 179, 178, 165, 130, 129 (base peak), 128, 115, 91. IR ν (cm^{-1}) (CCl_4/$CHCl_3$) 3060, 3020, 2960, 2940, 2870, 2770, 1705, 1690, 1600, 1580.

4.3.8. 1,1-Diphenyl-2-(prop-1-enyl)oxirane 7b. ($C_{17}H_{16}O$); MW: 236.314. Characterized by ^{1}H NMR, ^{13}C NMR, EI-Ms but not isolated (purity: 88%). Flash chromatography Pentane/CH_2Cl_2: (80/20); obtained: 0.29 g (yield: 12%, method a); oil. ^{1}H NMR (200 MHz, $CDCl_3$) 7.34–7.10 (Ph, 10H, m), 5.87 (H-2′, 1H, dq, *J*=15.5, 6.6 Hz), 4.83 (H-1′, 1H, ddq, *J*=15.5, 8.8, 1.5 Hz), 3.64 (H-2, 1H, d, *J*=8.8 Hz), 1.54 (CH_3, 3H, dd, *J*=6.6, 1.5 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ C(Ph), Csp^2: 141.0, 137.4, 133.5, 128.3, 128.1, 127.7, 126.7; C-1, C-2: 67.1; *C*H_3: 18.0. EI-MS *m/z*: 236, 235, 207, 167, 166, 165 (base peak), 164, 129, 105.

4.3.9. 1,3,4,4-Tetraphenylbut-3-en-1-one 8. ($C_{28}H_{22}O$); MW: 374.483; CAS RN: 53449-11-9. Pentane/ether: (99/1)–(90/10); obtained: 0.202 g (yield: 81%, method b); mp: 195–196°C. ^{1}H NMR[10] (200 MHz, $CDCl_3$) δ 7.97–7.08 (Ph, 20H, m), 4.37 (H-2, 2H, s). ^{13}C NMR[10] (50 MHz, $CDCl_3$) δ *C*O: 197.8; C(Ph), Csp^2: 143.3, 143.0, 142.4, 142.3, 137.0, 133.3, 132.9, 130.7, 129.7, 129.2, 128.5, 128.4, 128.0, 127.9, 127.5, 127.1, 126.4, 126.2; C-2: 46.4. EI-MS[10] *m/z* 374, 270, 269 (base peak), 192, 191, 189, 165, 105, 91, 77; IR ν (cm^{-1}) (CCl_4) 3060, 3020, 1690, 1440, 1410, 1330.

4.3.10. 1,2,4-Triphenylnaphthalene 9. ($C_{28}H_{20}$); MW: 356.468; CAS RN: 806-58-6. Pentane: (100); obtained: 0.048 g (yield: 20%, method b); mp: 158–160°C. ^{1}H NMR[11] (200 MHz, $CDCl_3$) δ 7.96–7.04 (Ph, 20H, m). ^{13}C NMR[11] (50 MHz, $CDCl_3$) δ C(Ph): 141.9, 140.6, 139.8, 139.1, 137.9, 137.1, 133.1, 131.6, 131.0, 130.2, 129.4, 129.3, 128.3, 127.9, 127.6, 127.3, 126.8, 126.2, 126.1. EI-MS *m/z* 356 (base peak), 355, 339, 279, 278, 277, 276, 170, 169. IR[11] ν (cm^{-1}) (CCl_4) 3060, 3020, 1600.

4.3.11. 5,5-Diphenylpent-4-en-2-one 10. ($C_{17}H_{16}O$); MW: 236.314; CAS RN: 55004-95-0. Pentane/ether: (100/0)–(80/20); obtained: 0.128 g (yield: 51%, method b); mp: 50–51°C. ^{1}H NMR[12b] (200 MHz, $CDCl_3$) δ 7.30–7.01 (Ph, 10H, m), 6.16 (H-4, 1H, t, *J*=7.3 Hz), 3.11 (H-3, 2H, d, *J*=7.3 Hz), 1.95 (CH_3, 3H, s). ^{13}C NMR[12b] (50 MHz, $CDCl_3$) δ *C*O: 206.5; C(Ph), Csp^2: 144.7, 141.8, 139.4, 129.6, 128.3, 128.1, 127.3, 126.5; C-4: 120.5; C-3: 44.5; C-1: 29.7. EI-MS[12b] *m/z* 236, 194, 193 (base peak), 179, 178, 116, 115. IR ν (cm^{-1}) (CH_2Cl_2) 3040, 2980, 1710, 1660, 1590, 1540, 1490, 1430, 1350.

4.3.12. 1-Methyl-4-phenylnaphthalene 11. ($C_{17}H_{14}$), MW: 218.299; CAS RN: 13280-69-8. Pentane: 100; obtained: 0.138 g (yield: 60%, method b); mp: 37–38°C. ^{1}H NMR[14] (200 MHz, $CDCl_3$) δ 8.40–8.26 (Ph, 2H, m), 7.88–7.62 (Ph, 9H, m), 3.05 (CH_3, 3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ C(Ph): 141.1, 138.8, 133.8, 132.9, 131.8, 130.3, 128.3, 127.1, 126.7, 126.3, 125.7, 124.5; *C*H_3: 19.7. EI-MS *m/z* 218 (base peak), 217, 215, 204, 203, 202, 189, 165, 115, 107, 101, 95. IR ν (cm^{-1}) ($CHCl_3$) 3080, 3050, 2990, 2940, 2880, 1600, 1520.

4.3.13. 4,5,5-Triphenylpent-4-en-2-one 12. ($C_{23}H_{20}O$); MW: 312.412; CAS RN: 7593-09-1. Not isolated. EI-MS *m/z* 312, 270, 269, 192, 191 (base peak), 190, 189, 178, 165, 91.

4.3.14. 4-Methyl-1,2-diphenylnaphthalene 13 (new compound). ($C_{23}H_{18}$); MW: 294.397; HR-MS calcd for $C_{23}H_{18}$ $(M)^+$ *m/z* 294.1408, found: 294.1407. Pentane: (100); obtained: 0.17 (yield: 72%, method b); mp: 139–140°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.37 (Ph, 1H, d, *J*=8.2 Hz), 8.08 (Ph, 1H, d, *J*=8.2 Hz), 7.85–7.45 (Ph, 13H, m), 3.07 (CH_3, 3H, s). ^{13}C NMR (50 MHz, $CDCl_3$) δ C(Ph): 142.1, 139.3, 138.0, 136.0, 133.7, 132.9, 131.9, 131.6, 130.1, 129.2, 129.0, 127.8, 127.6, 126.6, 126.1, 125.9, 125.6, 124.1; *C*H_3: 19.5. EI-MS *m/z* 294 (base peak), 280, 279, 278, 277, 276, 215, 138, 132. IR ν (cm^{-1}) ($CHCl_3$) 3060, 2990, 1640, 1600, 1560.

4.3.15. 3-Methyl-4,4-diphenylbut-3-enal 14. ($C_{17}H_{16}O$); MW: 236.314. Not isolated. EI-MS *m/z* 209, 208, 207, 194, 193, 192, 191, 190, 189, 179, 178, 166, 165, 164, 152, 131, 130 (base peak), 129, 115, 91.

4.3.16. 2-Methyl-1-phenylnaphthalene 15. ($C_{17}H_{14}$), MW: 218.299; CAS RN: 29304-63-0. Pentane: (100); obtained: 0.076 g (yield: 33%, method b); mp: 43–44°C. ^{1}H NMR[16b] (200 MHz, $CDCl_3$) δ 7.75–7.65 (Ph, 2H, m), 7.44–7.10 (Ph, 9H, m), 2.14 (CH_3, 3H, s). ^{13}C NMR[16b] (50 MHz, $CDCl_3$) δ C(Ph): 139.8, 138.2, 133.1, 133.0, 131.0, 130.2, 128.6, 128.4, 127.7, 127.2, 127.0, 126.2, 125.8, 124.7; CH_3: 20.8. EI-MS *m/z* 218 (base peak), 217, 215, 204, 203, 202, 189, 115, 108, 101, 95. IR[16a] ν (cm^{-1}) ($CHCl_3$) 3080, 2990, 2940, 1600, 1520.

4.3.17. 3-Benzhydrylidenecyclohexanone 16. ($C_{19}H_{18}O$), MW: 262.352. Not isolated. EI-MS *m/z* 262, 203, 184, 183 (base peak), 106, 105, 77.

4.3.18. 3-Benzhydrylcyclohex-2-en-1-one 17. ($C_{19}H_{18}O$), MW: 262.352; CAS RN: 21086-47-5. Pentane/ether: (95/5)–(85/15); obtained: 0.168 g (yield: 67%, method b); oil. ^{1}H NMR[17] (200 MHz, $CDCl_3$) δ 7.24–7.00 (Ph, 10H, m), 5.57 (H-2, 1H, s), 4.78 (H-7, 1H, s), 2.32–2.18 (CH_2, 4H, m), 1.92–1.79 (CH_2, 2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 199.7; C-3: 167.1; C(Ph), C-2: 140.1, 129.1, 128.6, 127.0; C-7: 59.0; C-4, C-6: 37.5, 30.1; C-5: 22.9. EI-MS *m/z* 262, 247, 244, 234, 233, 219, 218, 217, 215, 207, 206 (base peak), 205, 204, 203, 202, 192, 191, 190, 189, 179, 178, 171, 168, 167, 166, 165, 164, 152, 130, 129, 128, 115, 91. IR[17] ν (cm^{-1}) (CCl_4) 3080, 3060, 3020, 2940, 2860, 1680, 1620, 1490, 1450, 1430, 1360, 1340, 1320.

4.3.19. 3-Benzhydrylidenecyclopentanone 18. ($C_{18}H_{16}O$); MW: 248.325. Not isolated. EI-MS *m/z* 248 (base peak), 220, 219, 206, 205, 204, 203, 202, 192, 191, 190, 189, 178, 167, 166, 165, 129, 128, 115, 91.

4.3.20. 3-Benzhydrylcyclopent-2-en-1-one 19. ($C_{18}H_{16}O$); MW: 248.325; CAS RN: 70239-00-8. Pentane/ether: (95/5)–(85/15); obtained: 0.145 g (yield: 58%, method b); mp: 68–69°C. ^{1}H NMR[18] (200 MHz, $CDCl_3$) δ 7.28–7.06 (Ph, 10H, m), 5.71 (H-2, 1H, s), 4.92 (H-6, 1H, s), 2.53–2.50 (CH_2, 2H, m), 2.39–2.35 (CH_2, 2H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 209.5; C-3: 183.4; C(Ph): 140.5; C-2: 132.7; C(Ph): 128.2, 127.3; C-6: 55.9; C-4, C-5: 35.7, 31.2. EI-MS *m/z* 248, 220, 219, 207, 206 (base peak), 205, 204, 203, 194, 192, 191, 190, 189, 167, 166, 165, 152, 142, 141, 129, 128, 115, 91. IR[18] ν (cm^{-1}) (CCl_4) 3080, 3060, 3030, 2920, 2860, 1710, 1600, 1490, 1450, 1440, 1410.

4.3.21. 3-Benzhydrylidenecycloheptanone 20 (new compound). ($C_{20}H_{20}O$); MW: 276.379. Anal. calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29; O, 5.79. Found: C, 86.79; H, 7.19; O, 5.44. Pentane/ether: (90/10); obtained: 0.152 g (yield: 61%, method b); mp: 74–75°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25–7.00 (Ph, 10H, m), 3.20 (H-2, 2H, s), 2.55–2.50 (CH_2, 2H, m), 2.25–2.20 (CH_2, 2H, m), 1.75–1.55 (CH_2, 4H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 211.9; C(Ph), Csp^2: 142.1, 141.7, 131.7, 128.6, 128.1, 126.6, 126.4; C-2: 49.8; C-7: 43.7; C-4, C-5, C-6: 34.5, 30.1, 24.7. EI-MS *m/z* 276 (base peak), 220, 219, 218, 206, 205, 203, 194, 192, 191, 190, 189, 180, 179, 178, 167, 166, 165, 129, 115, 91. IR ν (cm^{-1}) ($CHCl_3$) 1698, 1599, 1500, 1430.

4.3.22. 3-Benzhydrylcyclohept-2-en-1-one 21 (new compound). ($C_{20}H_{20}O$); MW: 276.379. FAB-HR-MS calcd for $C_{20}H_{21}O$ $(M+H)^+$ *m/z* 277.1592, found 277.1586. Pentane/ether: (90/10); obtained: 0.06 g (yield: 24%, method b); mp: 91–92°C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25–7.00 (Ph, 10H, m), 5.60 (H-2, 1H, s), 4.80 (H-8, 1H, s), 2.50–2.45 (CH_2, 2H, m), 2.35–2.30 (CH_2, 2H, m), 1.85–1.55 (CH_2, 4H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ *C*O: 204.3; C-3: 162.7; C(Ph): 140.5; C-2: 132.2; C(Ph): 129.3, 128.6, 127.0; C-8: 61.0; C-4, C-7: 41.8, 42.8; C-5, C-6: 25.2, 21.1. EI-MS *m/z* 276, 258, 234, 233, 206, 205, 204, 193, 192, 191, 190, 185, 180, 179, 178, 168, 167 (base peak), 166, 165, 153, 152, 129, 115, 109, 91, 81, 79. IR ν (cm^{-1}) ($CHCl_3$) 1660, 1600, 1450.

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