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Hydroarylation of unsaturated carbon–carbon bonds in cross-conjugated enynones under the action of superacid CF_3SO_3H or acidic zeolite HUSY. Reaction mechanism and DFT study on cationic intermediate species†

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Reactions of cross-conjugated enynones,1,5-diarylpent-1-en-4-yn-3-ones, with arenes in the system TfOH-pyridine or under the action of acidic zeolite HUSY lead regioselectively to products of hydroarylation of the acetylene bond only,1,1,5-triarylpent-1,4-dien-3-ones, in yields up to 98%. These dienones add one more arene molecule to the double carbon–carbon bond in neat TfOH forming 1,1,5,5-tetraarylpent-1-en-3-ones in high yields. Cationic reaction intermediates have been studied by means of DFT calculations to elucidate plausible reaction mechanisms.

Introduction

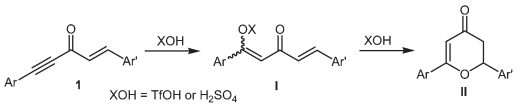
Various conjugated enynones are widely used in organic synthesis. The presence of three reaction centers in the structure of these compounds, namely, carbon atoms of double and triple bonds and carbonyl group, allows the construction of various carbo- or heterocycles[1–3] and analogues of natural compounds.[4,5] In particular, addition of S-nucleophiles to cross-conjugated enynones takes place mainly at the acetylene bond, which further leads to the formation of substituted thiopyranes.[6] These enynones have a great synthetic utility for medicinal chemistry research.[7]

Very recently we have shown that cross-conjugated enynones, 1,5-diarylpent-1-en-4-yn-3-ones **1**, undergo addition of triflic acid (CF_3SO_3H, TfOH) or sulfuric acid (H_2SO_4) to the acetylene bond with the formation of vinyl triflates or sulfates **I**, correspondingly, which are further cyclized into 2,6-diaryldihydropyran-4-ones **II** under the acidic reaction conditions (Scheme 1).[8]

Based on previous work[8] and our general research on superelectrophilic activation of alkynes, alkenes and allenes,[9] we undertook a special study on reactions of 1,5-diarylpent-1-en-4-yn-3-ones **1** with arenes under the action of acids. At the acid promoted interaction of enynones **1** with arenes, one may expect a hydroarylation of both triple and double carbon–carbon bonds leading to the formation of various compounds (Scheme 2).

The main goals of this work were the investigation of regio- and stereo-selectivities of hydroarylation of 1,5-diarylpent-1-en-4-yn-3-ones **1** by arenes under the action of Brønsted acids or acidic zeolite and the study of the reaction cationic intermediates by quantum chemical calculations (DFT method).

It should be specially mentioned that acidic zeolites are widely and effectively explored as electrophilic activators in reactions of organic compounds.[10] Compared to the conventional Brønsted (super)acids (H_2SO_4, TfOH, FSO_3H, HF, *etc.*), the use of zeolites is much more ecologically friendly and they are easily recyclable.[10]



Scheme 1 Brønsted acid-promoted cyclization of 1,5-diarylpent-1-en-4-yn-3-ones **1** into 2,6-diaryldihydropyran-4-ones **II** through the intermediate formation of vinyl triflates or sulfates **I** (data from ref. 8).

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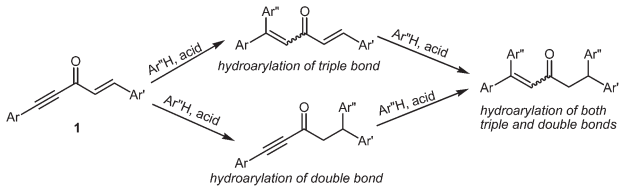
†Electronic supplementary information (ESI) available: Copies of ^1H, ^{13}C, ^{19}F NMR spectra of compounds; X-ray data; data of DFT calculations. CCDC 1847444, 1847451, 1847452, 1847453, 1847454 and 1847456. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ob01985a



Scheme 2 Possible ways of acid promoted hydroarylation of triple and double bonds in enynones **1**.

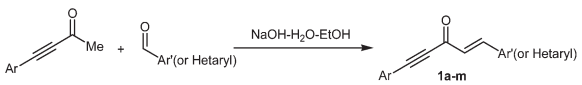
Results and discussion

Starting cross-conjugated pent-1-en-4-yn-3-ones **1a–m** bearing aryl or hetaryl rings with various donor–acceptor substituents were synthesized by Claisen–Schmidt condensation of the corresponding 4-arylbut-3-yn-2-ones and aromatic (or hetero-aromatic) aldehydes (Table 1).

First we considered possible ways of protonation of 1,5-diphenylpent-1-en-4-yn-3-one **1a**. The protonation of **1a** may proceed in several consecutive steps (Table 2 and scheme in it). A first proton is bonded to the more basic carbonyl oxygen that affords cation **A1**. Then, protonation of the carbon–carbon triple or double bonds may take place leading to species **B1** or **C1**, respectively, both of which may be further protonated to trication **D1**. Calculations of Gibbs free energies of these protonation reactions showed that the formation of cation **A1** is very favorable energetically with ΔG_{298} −94.3 kJ mol^{-1} (see reaction ΔG_{298} values in scheme in Table 2). The second protonation, which leads to species **B1** and **C1**, is unfavourable. However, the formation of cation **B1** is less unfavourable. Formation of **B1** in two protonation steps is thermodynamically possible with a value of ΔG_{298} = −94.3 + 22.8 = −71.5 kJ mol^{-1}. For **C1**, this value is higher, ΔG_{298} = −94.3 + 48.4 = −45.9 kJ mol^{-1}. Trication **D1** is very high in energy (see high positive ΔG_{298} values of the corresponding reactions). From these data, one may conclude that the second protonation, most probably, should rather take place on the triple bond than on the double one for cross-conjugated enynones.

Charge distribution, contribution of the atomic orbital to the LUMO and global electrophilicity indices ω (ref. 11) of species **A1**, **B1**, **C1**, and **D1** were calculated by the DFT method. Compared to cation **A1**, dication **B1** and **C1** have

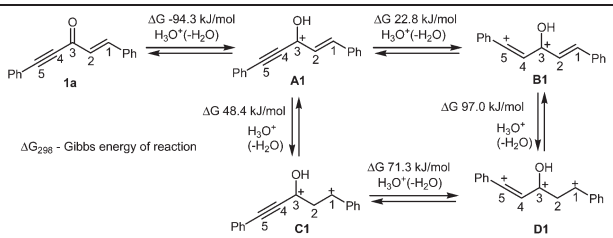
Table 1 Synthesis of starting cross-conjugated enynones **1a–m** used in this study



Enynone	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
Ar	Ph	4-MeC_6H_4	4-MeOC_6H_4	Ph	Ph	Ph	Ph	Ph
Ar′(or Hetaryl)	Ph	Ph	Ph	4-MeC_6H_4	4-$NO_2C_6H_4$	4-ClC_6H_4	4-FC_6H_4	3-FC_6H_4

Enynone	**1i**	**1j**	**1k**	**1l**	**1m**
Ar	Ph	Ph	Ph	Ph	Ph
Ar′(or Hetaryl)	2-FC_6H_4	2,4-$F_2C_6H_3$	5-Bromofuran-2-yl	Thiophen-2-yl	4-MeOC_6H_4

Table 2 Selected electronic characteristics (DFT calculations) of cations **A1**, **B1**, **C1**, and **D1** derived from protonation of enynone **1a**, and calculated Gibbs energies ΔG_{298} of protonation reactions



Cation	E_{HOMO}, eV	E_{LUMO}, eV	ω^a, eV	q (C^1)^b, e	q (C^3)^b, e	q (C^5)^b, e	k (C^1)$_{LUMO}$ ^{c}, %	k (C^3)$_{LUMO}$ ^{c}, %	k (C^5)$_{LUMO}$ ^{c}, %
1a	−7.02	−2.75	2.8	−0.06	0.49	0.08	18.3	14.6	14.5
A1	−7.41	−4.04	4.9	0.04	0.23	−0.33	21.7	24.0	15.3
B1	−8.05	−4.93	6.8	0.09	0.54	0.43	0.5	5.8	18.4
C1	−8.25	−4.78	6.1	0.20	0.34	−0.24	25.2	5.5	3.2
D1	−9.04	−5.92	6.7	0.18	0.74	0.54	0.5	11.2	19.8

^{a} Global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})^2/8(E_{LUMO} - E_{HOMO})$. ^{b} Natural charges. ^{c} Contribution of the atomic orbital to the molecular orbital.

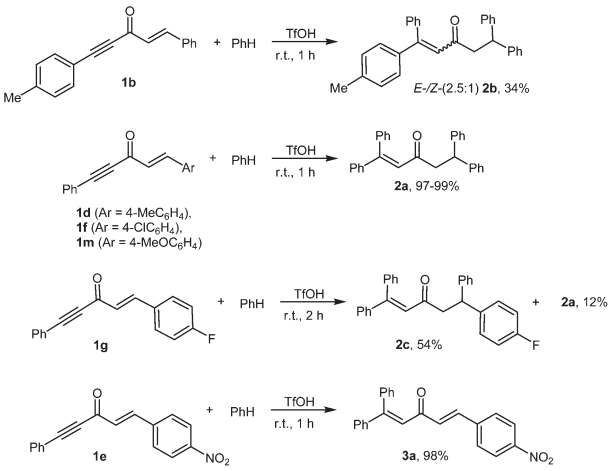
higher values of electrophilicity indices and they may be considered as strong electrophiles.[12,13]

The comparison of the charge distributions in species **A1**, **B1**, and **C1** reveals that carbon C^3 bears a large part of positive charge (Table 2). Among these three species, dication **B1** has the largest charge on C^5 (0.43*e*) and the highest contribution (18.4%) in the LUMO as well. These data show a coincidence of charge and orbital control in the reactivity of carbon C^5 in species **B1**. Thus, both calculated thermodynamic parameters (ΔG_{298} of reactions) and electronic characteristics (Table 2) indicate that vinyl type dications **B**, with an electrophilic centre on carbon C^5, are presumably the reactive species derived from cross-conjugated enynones **1** under their protonation in Brønsted superacids.

Then, reactions of enynone **1a** with benzene promoted by different Brønsted and Lewis acids were explored (Table 3). The reaction with an excess of benzene (11 equiv.) in TfOH for 1 h afforded quantitatively compound **2a** as a product of hydrophenylation of both triple and double bonds of **1a** (entry 1), while the use of 1 equiv. of benzene gave a more complex mixture of products (entry 2). The use of H_2SO_4 was not effective to obtain hydrophenylation product **2a** in high yield: the main reaction products were **Ia** and **IIa** (entries 3 and 4), which formation was already observed and discussed in our previous work.[8] Also, Lewis acid $AlCl_3$ did not give good results (entries 5 and 6). Thus, TfOH was found to be the best acid for carrying out hydroarylation of unsaturated bonds in enynones **1**.

Then, reactions of other compounds **1** with benzene in TfOH were carried out (Scheme 3). Enynone **1b** gave the addition product of benzene to each unsaturated bond as a mixture of *E*-/*Z*-isomers of enone **2b** in a yield of 34%. Reactions of enynones **1d,f,m** bearing 4-methyl, 4-chloro, or 4-methoxy groups in the aryl ring at the double bond resulted in the quantitative formation of compound **2a**. The latter one was formed by addition of benzene to both triple and double bonds followed by exchange of the aryl group for a phenyl one. The same exchange was observed previously by us for reactions of other arylalkenes in Brønsted superacids.[14,15]

4-Fluorophenyl substituted enynone **1g** gave the product of exhaustive hydrophenylation *E*-/*Z*-**2c** along with the aryl group exchange product **2a** (Scheme 3). In this case, the electron withdrawing 4-fluorophenyl group hampers, to some extent, this exchange. However, reaction took 2 h to achieve complete conversion of starting **1g**. On the other hand, enynone **1e** having a powerful acceptor 4-nitrophenyl ring at the double bond afforded only a product of addition to the triple bond, dienone **3a** (Scheme 3). No addition of benzene to such deactivated double bonds occurred.

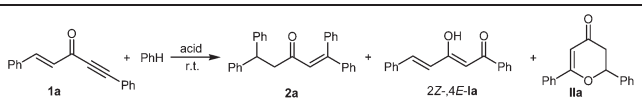


Scheme 3 Reactions of enynones **1b,d,e,f,g, and m** with benzene in TfOH at room temperature.

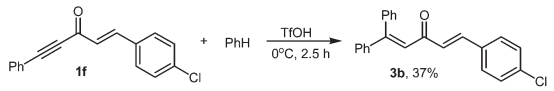
Based on our experience on suppression of such aryl group exchange,[14,15] we tried to avoid this process in reactions of enynones **1** by lowering the reaction temperature. However, decreasing temperature down to −40 °C in TfOH for enynones **1d,m** bearing strong donating substituents (4-MeC_6H_4 and 4-$MeOC_6H_4$, respectively) did not help to suppress the exchange of aryl groups. In these cases, only compound **2a** was obtained with incomplete conversion of starting **1d,m**; the exchange went too fast.

In the case of 4-chlorophenyl enynone **1f**, carrying out reaction at 0 °C for 2.5 h resulted in the formation of dienone **3b** as a product of mono-hydrophenylation of the acetylene bond with an incomplete conversion of **1f** (Scheme 4). For this particular reaction, increasing reaction time or temperature again led to the formation of the aryl group exchange product **2a**.

Table 3 Reactions of **1a** with benzene under the action of different acids at room temperature



Entry	Acid	Equiv. of benzene	Time	Reaction products, yield %
1	TfOH	11	1 h	**2a**, 98%
2	TfOH	1	1 h	Complex mixture
3	H_2SO_4	11	1 h	**2a**, 25% + 2*Z*-,4*E*-**Ia**, 60%
4	H_2SO_4	11	72 h	**2a**, 32% + **IIa**, 62%
5	$AlCl_3$ (5 equiv.) in CH_2Cl_2 (solvent)	11	12 h	Complex mixture
6	$AlCl_3$ (5 equiv.) in PhH (solvent)	Solvent	12 h	Complex mixture



Scheme 4 Reaction of enynone **1f** with benzene in TfOH at 0 °C (incomplete conversion of **1f**, ~50%).

Reactions of 3-fluorophenyl (**1h**, Table 4) and 2-fluorophenyl (**1i**, Table 5) enynones with benzene in TfOH afforded products of mono-hydrophenylation of the triple bond (**3c** and **3d** correspondingly) and exhaustive hydrophenylation (**2d** and **2e** correspondingly). Increasing the reaction time led to the increase of the yields of **2d** and **2e** and to the decrease of the yields of **3c** and **3d**, respectively (see Tables 4 and 5). This reveals that enynones **1** give at first mono-hydroarylation adducts **3**, which are further converted into products of double hydroarylation **2**. It should be mentioned that increasing reaction time up to 12–24 h led to the lowering yields of **2d** and **2e**, and the formation of oligomeric materials was detected. The presence of electron withdrawing 2-(or 3-)fluorophenyl substituents in enones **2d** and **2e** does not allow exchange of these aryl groups with phenyl ones (no formation of **2a**).

Reactions of enynone **1a** with other arenes (toluene, anisole, veratrole, and *o*-, *m*-, *p*-xylenes) in TfOH at room temperature for 1 h led to complex inseparable mixtures of regio- and stereo-isomers of products of exhaustive hydroarylation of triple and double bonds in **1a**.

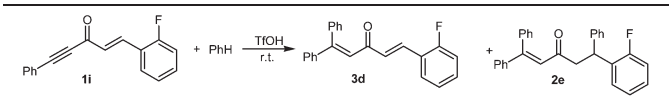
Summarizing the data obtained and discussed above, one may state that solely addition of arenes to the acetylene bond of enynones **1** proceeds in TfOH for the compounds having strong electron withdrawing substituents (4-NO_2, 2-F, 3-F) in the aryl ring at the double bond. For other enynones **1**, hydroarylation occurs at both triple and double carbon–carbon bonds, and this reaction may be complicated by aryl group exchange.

Taking into account the data on the formation of compounds **3a–d** and **2a–e** (Schemes 3, 4, and Tables 4, 5), one may conclude that the first hydroarylation step of enynones **1** takes place at the acetylene bond, and then the second hydroarylation goes onto the double bond.

A plausible reaction mechanism is presented in Scheme 5. Protonation of enynones **1** in TfOH gives consequently cations **A**, and then vinyl type dications **B** (see data on DFT calculations of these species in Table 2). Both species may take part in electrophilic aromatic substitution with arenes, leading to cations **E**, deprotonation of which during aqueous quenching of the reaction results in dienones **3**.

Most probably the addition of the second arene molecule to the double bond of dienones **3** in TfOH leads to the formation of *O*,*C*-diprotonation species **F**, since the nitro substituted enynone **1e** does not give products of hydroarylation of the double bond, it forms **3a** only (see Scheme 3). For such a deactivated substrate as **3a**, the presence of the acceptor nitro group should give the corresponding *O*-protonated (on carbonyl oxygen) species an enhanced electrophilicity (compared to other substituents), while preventing protonation of the double bond. Since no reaction proceeds at the double bond, we assume that protonation is necessary and that species **F** are involved. Interaction of cations **F** with arenes furnishes enones **2** (Scheme 5). Exchange of aryl groups may take place in compounds **2** in the presence of arenes under superacidic reaction conditions. This exchange may proceed in two ways. First one is protonation of electron donating aryl ring Ar′ followed by

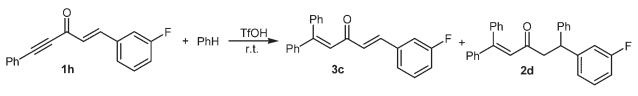
Table 5 Reactions of enynone **1i** with benzene in TfOH at room temperature



Entry	Reaction time	Reaction products, yield %[a] 3d	2e	Unreacted recovered starting **1i**, yield %[a]
1	3 min	30	—	61
2	10 min	72	—	26
3	45 min	91	7	—
4	1 h	52	40	—
5	4 h	28	74	—
6	9 h	9	78	—

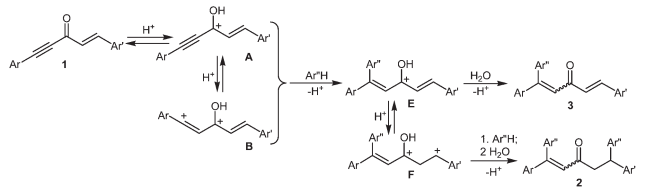
[a] Yields were determined by NMR.

Table 4 Reactions of enynone **1h** with benzene in TfOH at room temperature



Entry	Reaction time	Reaction products, yield %[a] 3c	2d	Unreacted recovered starting **1h**, yield %[a]
1	15 min	72	—	20
2	45 min	90	2	3
3	1 h	84	13	—
4	6 h	60	29	—

[a] Yields were determined by NMR.



Scheme 5 A plausible mechanism of hydroarylation of the triple and double carbon–carbon bonds in cross-conjugated enynones **1** by arenes in Brønsted superacid TfOH.

elimination of arene molecules with the formation of the corresponding benzyl type cation (alike to species **F**), which reacts with arene Ar″H giving the product of aryl group exchange. In an alternative way, the same benzyl type cation may be formed at the protonation of the carbon–carbon bond C(H)–C(Ar′) in the superacid with the leaving of arene molecule Ar′H.

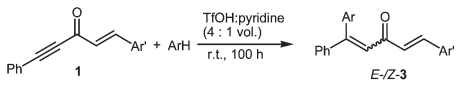
DFT calculations of electronic and thermodynamic characteristics of various protonated forms **E1**, **F1**, **G1**, and **H1** derived from dienone **3e** are presented in Table 6. Comparison of dications **F1** and **G1** shows that **F1** has higher electrophilicity properties, ω value, positive charge and LUMO coefficient on the reactive center C^1, although its formation is less favorable from a thermodynamic point of view (see values of ΔG_{298} of protonation reactions in the scheme in Table 6). So, species **F** may act as electrophilic intermediates in reactions of enynones **1** in superacids (see the mechanism in Scheme 5). We also tried to register NMR spectra of the protonated form of **3e** in TfOH, but obtained a rather complex and ambiguous ^{1}H NMR spectrum.

To achieve regioselective hydroarylation at the acetylene bonds of enynones **1**, we decided to carry out this reaction in the system TfOH–pyridine (4 : 1 vol.), which has less acidity than neat TfOH. We have already used this system to achieve selective addition of TfOH to acetylene bonds of enynones.[8] In this system, hydroarylation occurred at the acetylene bond solely, leading to dienones **3**, but it needed long time 100 h at room temperature (Table 7).

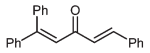
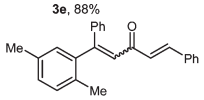
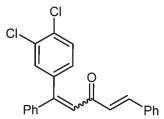
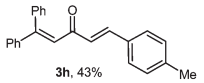
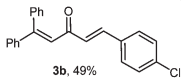
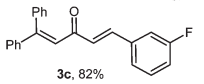
Then, reactions of enynones **1** with arenes were carried out under the action of acidic zeolite HUSY (CBV-720) in a high pressure glass tube at high temperature of 85–180 °C for 2–8 h. It was found that hydroarylation of the triple bond only took place with the formation of dienones **3** (Table 8). The double bond of enynones **1** remained unreactive with zeolite CBV-720.

The *E*-/*Z*-Configuration of the newly formed double bond (former acetylenic one) in substances **3** (see Tables 7 and 8) was unambiguously determined by ^{1}H–^{1}H NOESY correlations between vinyl and aromatic protons (see the ESI†).

Table 7 Reactions of enynones **1** with arenes in the system TfOH–pyridine (4 : 1 vol.) at room temperature for 100 h

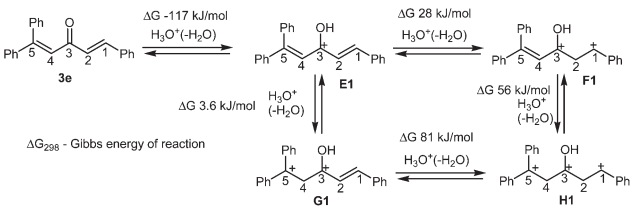


1 *E*-/*Z*-**3**

Entry	Enynone	ArH	Reaction product, yield %
1	**1a** Ar′ = Ph	Benzene	 **3e**, 88%
2	**1a** Ar′ = Ph	*p*-Xylene	 *E*-/*Z*-(5:1) **3f**, 82%
3	**1a** Ar′ = Ph	1,2-Dichlorobenzene	 *E*-/*Z*-(1.25:1) **3g**, 75%
4	**1d** Ar′ = 4-MeC_6H_4	Benzene	 **3h**, 43%
5	**1f** Ar′ = 4-ClC_6H_4	Benzene	 **3b**, 49%
6	**1h** Ar′ = 3-FC_6H_4	Benzene	 **3c**, 82%

Additionally, structures of compounds **3b**, **3d**, **3e**, **3l**, and **3p** were confirmed by X-ray data (see the ESI†). Hydroarylation of the triple bond in enynones **1** with zeolite CBV-720 was efficiently achieved with the following arenes: benzene, *p*-xylene, and 1,2-dichlorobenzene. Other arenes, for instance, *o*-xylene (entry 3, Table 8), gave a complex mixture of inseparable regio- and stereo-isomers. It should be also mentioned that triarylsubstituted dienones **3** are hardly available compounds. They have been synthesized recently by the

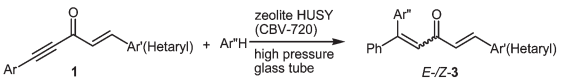
Table 6 Selected electronic characteristics (DFT calculations) of cations **E1**, **F1**, **G1**, and **H1** derived from protonation of compound **3e**, and calculated Gibbs energies ΔG_{298} of protonation reactions

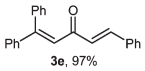
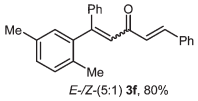
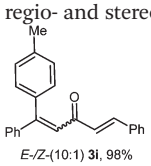
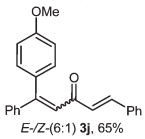
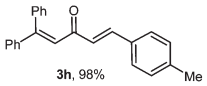
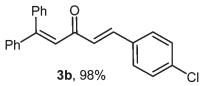
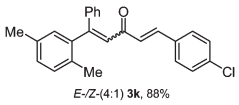
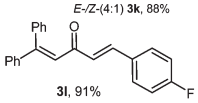
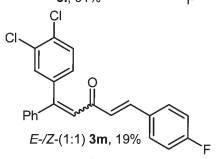
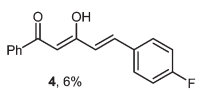
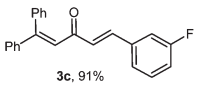
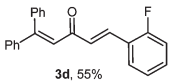
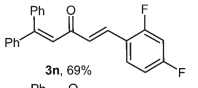
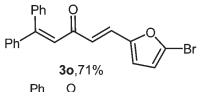
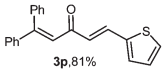
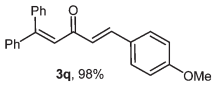


Cation	E_{HOMO}, eV	E_{LUMO}, eV	ω^a, eV	q (C^1)^b, e	q (C^3)^b, e	q (C^5)^b, e	k (C^1)$_{LUMO}$ ^{c}, %	k (C^3)$_{LUMO}$ ^{c}, %	k (C^5)$_{LUMO}$ ^{c}, %
E1	−7.17	−3.89	4.7	−0.02	0.50	−0.05	19	17	12
F1	−8.00	−4.64	5.9	0.21	0.59	0.23	17	7	4
G1	−8.01	−4.54	5.7	0.08	0.60	0.31	19	9	25
H1	−8.51	−4.96	6.4	0.18	0.80	0.26	16	6	10

^{a} Global electrophilicity index $\omega = (E_{HOMO} + E_{LUMO})^2/8(E_{LUMO} - E_{HOMO})$. ^{b} Natural charges. ^{c} Contribution of the atomic orbital to the molecular orbital.

Table 8 Reactions of enynones **1** with arenes under the action of acidic zeolite HUSY (CBV-720)



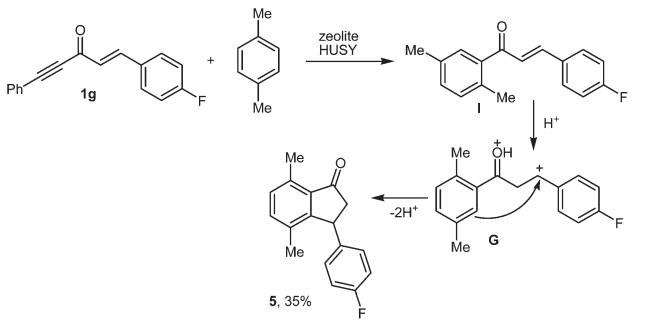
Entry	Enynone	Arene, Ar″H	Reaction conditions: temperature, time	Reaction product, yield %
1	**1a** Ar = Ar′ = Ph	Benzene	85 °C, 2 h	 **3e**, 97%
2	**1a** Ar = Ar′ = Ph	*p*-Xylene	140 °C, 2 h	 *E*-/*Z*-(5:1) **3f**, 80%
3	**1a** Ar = Ar′ = Ph	*p*-Xylene	145 °C, 2 h	Complex mixture of inseparable regio- and stereo-isomers, 75%
4	**1b** Ar = 4-MeC$_6$H$_4$ Ar′ = Ph	Benzene	100 °C, 2 h	 *E*-/*Z*-(10:1) **3i**, 98%
4	**1c** Ar = 4-MeOC$_6$H$_4$ Ar′ = Ph	Benzene	85 °C, 2 h	 *E*-/*Z*-(6:1) **3j**, 65%
5	**1d** Ar = Ph Ar′ = 4-MeC$_6$H$_4$	Benzene	100 °C, 2 h	 **3h**, 98%
6	**1f** Ar = Ph Ar′ = 4-ClC$_6$H$_4$	Benzene	85 °C, 2 h	 **3b**, 98%
7	**1f** Ar = Ph Ar′ = 4-ClC$_6$H$_4$	*p*-Xylene	140 °C, 2 h	 *E*-/*Z*-(4:1) **3k**, 88%
8	**1g** Ar = Ph Ar′ = 4-FC$_6$H$_4$	Benzene	85 °C, 2 h	 **3l**, 91%
9	**1g** Ar = Ph Ar′ = 4-FC$_6$H$_4$	1,2-Dichlorobenzene	180 °C, 2 h	 *E*-/*Z*-(1:1) **3m**, 19% +  **4**, 6%
10	**1h** Ar = Ph Ar′ = 3-FC$_6$H$_4$	Benzene	85 °C, 8 h	 **3c**, 91%
11	**1i** Ar = Ph Ar′ = 2-FC$_6$H$_4$	Benzene	85 °C, 8 h	 **3d**, 55%
12	**1j** Ar = Ph Ar′ = 2,4-F$_2$C$_6$H$_3$	Benzene	85 °C, 2 h	 **3n**, 69%
13	**1k** Ar = Ph Hetaryl = 5-bromofuran-2-yl	Benzene	85 °C, 2 h	 **3o**,71%
14	**1l** Ar = Ph Hetaryl = thiophen-2-yl	Benzene	85 °C, 2 h	 **3p**,81%
15	**1m** Ar = Ph Ar′ = 4-MeOC$_6$H$_4$	Benzene	100 °C, 2 h	 **3q**, 98%

Pd-catalyzed reaction of complex arylethynyl cyclopropanoles with iodoarenes.[16]

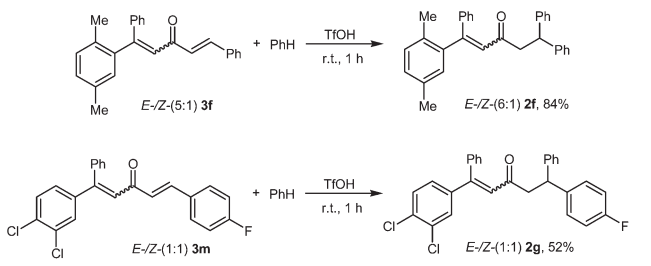
Apart from the main product *E*-/*Z*-**3m**, enynone **1g** in reaction with 1,2-dichlorobenzene gave the minor compound **4**, which was formed as a result of hydration of the acetylene bond in **1g** by residual water in the reaction system (entry 9, Table 8). The enolic form of **4** was confirmed by X-ray data (see the ESI†). The structure of such aryl diketones was described recently.[17]

One more unusual direction was found in reaction of **1g** and *p*-xylene with zeolite; in this case, indanone **5** was obtained (Scheme 6). Most probably the acylation of *p*-xylene by 4-fluorocinnamic acid with formation of enone **I** takes place. This cinnamic acid along with acetophenone may be formed in the retro aldol reaction from the corresponding product of hydration of the acetylene bond of **1g**. Protonation (activation on zeolite acidic sites) of *I* affords dication **G**, which is cyclized into the final product **5** (Scheme 6). The same cyclization of 1-phenyl-2-propen-1-ones into indanones using H-zeolite was found to proceed through intermediate *O*,*C*-diprotonated forms of enones, alike species **G**.[18]

Having in hand the procedures for the synthesis of dienones **3** (Tables 7 and 8), one may carry out a second hydroarylation of the double bond in these compounds by another arene. It allows conducting one by one addition of two different arenes to the triple and double bonds of starting enynones **1**. To demonstrate this approach, we performed hydrophenylation of dienones *E*-/*Z*-**3f,m** that resulted in the formation of compounds *E*-/*Z*-**2f,g** correspondingly (Scheme 7). It should be noted that compounds **2** are hardly available and they could be promising Michael acceptors in organic synthesis.



Scheme 6 Zeolite promoted reaction of **1g** with *p*-xylene leading to indanone **5**.



Scheme 7 Reactions of **3f** and **m** with benzene in TfOH leading to **2f** and **g** correspondingly.

Conclusions

We have developed a method for the regio-selective hydroarylation of the acetylene bond in cross-conjugated enynones by arenes in the system TfOH-pyridine or under the action of HUSY acidic zeolite. A further hydroarylation step of the double bond in cross-conjugated enynones proceeds in neat TfOH; however, this reaction may be complicated by exchange of aryl groups under the superacidic reaction conditions.

Experimental section

The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on a Bruker AVANCE III 400 (at 400, 376 and 100 MHz for ^1H, ^{19}F and ^{13}C NMR spectra respectively) spectrometer at 25 °C. The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for ^1H NMR spectra and the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra were used as references. ^{19}F NMR spectra were indirectly referenced to the signal of $CFCl_3$ (δ 0.0 ppm). HRMS (ESI-TOF) was carried out on Bruker maXis-ESI-QTOF Mass Spectrometer instruments. IR spectra of compounds were recorded with a Bruker spectrometer. The preparative reactions were monitored by thin-layer chromatography carried out on silica gel plates (Alugram SIL G/UV-254), using UV light for detection. Preparative TLC was performed on silica gel Chemapol L 5/40 with petroleum ether-ethyl acetate mixture elution.

X-ray diffraction study

A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2[19] the structure was solved with the ShelXS[20] structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization. CCDC 1847444 – (**3b**), 1847451 – (**3d**), 1847452 – (**3e**), 1847453 – (**3l**), 1847454 – (**3p**), 1847456 – (**4**).†

DFT calculations

All computations were carried out at the DFT/HF hybrid level of theory using hybrid exchange functional M06 by using GAUSSIAN 2009 program packages.[21] The geometry optimization were performed using the M06/6-311+G(2d,2p) basis set (standard 6-311 basis set added with polarization (d,p) and diffuse functions). Optimizations were performed on all degrees of freedom and solvent-phase optimized structures were verified as true minima with no imaginary frequencies. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima and to estimate the thermodynamic parameters.

Solvent-phase calculations used the Polarizable Continuum Model (PCM), and the solvent was water.

The following enynones were previously obtained and characterized by us:[8] 1,5-diphenylpent-1-en-4-yn-3-one (**1a**), 5-(4-methoxyphenyl)-1-phenyl-pent-1-en-4-yn-3-one (**1c**), 1-(4-methylphenyl)-5-phenylpent-1-en-4-yn-3-one (**1d**), 1-(4-nitrophenyl)-5-phenylpent-1-en-4-yn-3-one (**1e**), 1-(4-chlorophenyl)-5-phenyl-pent-1-en-4-in-3-one (**1f**), and 1-(4-methoxyphenyl)-1-phenylpent-1-en-4-yn-3-one (**1m**).

5-(4-Methylphenyl)-1-phenylpent-1-en-4-yn-3-one (1b). White crystals. M.p. 79–80 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 2.41 (c, 3H), 6.90 (d, J = 16.1 Hz, 1H), 7.24–7.32 (m, 2H), 7.44–7.48 (m, 3H), 7.57–7.65 (m, 4H), 7.93 (d, J = 16.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ ppm: 21.8, 86.5, 92.2, 117.1, 128.6, 128.7, 129.1, 129.5, 131.1, 133.0, 134.2, 141.3, 148.0, 178.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{18}H_{14}ONa$: 269.0937; found 269.0949.

1-(4-Fluorophenyl)-5-phenylpent-1-en-4-yn-3-one (1g). White crystals. M.p. 85 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 6.89 (d, J = 16.3 Hz, 1H), 6.88–6.99 (m, 2H), 7.40–7.50 (m, 3H), 7.59–7.67 (m, 4H), 8.03 (d, J = 16.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ ppm: 86.6, 91.6, 116.3 (d, J = 22.3 Hz), 120.2, 128.3 (d, J = 2.3 Hz), 128.7, 130.3 (d, J = 3.4 Hz), 130.6 (d, J = 3.6 Hz), 132.9, 146.8, 164.4 (d, J = 252.8 Hz), 177.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −107.90. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{17}H_{11}FONa$ 273.0686; found 273.0692.

1-(3-Fluorophenyl)-5-phenylpent-1-en-4-yn-3-one (1h). Yellow crystals. M.p. 95–96 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 6.97 (d, J = 16.3 Hz, 1H), 7.14–7.30 (m, 2H), 7.41–7.54 (m, 4H), 7.61–7.61 (m, 3H), 8.14 (d, J = 16.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ, ppm: 86.6, 92.0, 114.7 (d, J = 21.7 Hz), 117.9 (d, J = 21.7 Hz), 120.1, 124.6 (d, J = 2.8 Hz), 128.7, 129.6, 130.6 (d, J = 8.28 Hz), 130.7, 133.0, 136.3 (d, J = 7.71 Hz), 146.5 (d, J = 2.40 Hz), 161.8 (d, J = 247.3 Hz), 177.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ, ppm: −114.08. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd 273.0686; found 273.0689.

1-(2-Fluorophenyl)-5-phenylpent-1-en-4-yn-3-one (1i). White crystals. M.p. 90–91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 6.87 (d, J = 16.1 Hz, 1H), 7.14–7.19 (m, 1H), 7.31–7.33 (m, 1H), 7.56–7.38 (m, 5H), 7.71–7.62 (m, 2H), 7.88 (d, J = 16.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ ppm: 86.5, 92.1, 116.4 (d, J = 21.9 Hz), 120.1, 124.67 (d, J = 3.6 Hz), 122.3 (d, J = 11.5 Hz), 128.7, 128.9 (d, J = 2.33 Hz), 130.4 (d, J = 5.68 Hz), 130.7, 132.7 (d, J = 8.94 Hz), 133.1, 140.5 (d, J = 3.63 Hz), 161.5 (d, J = 254.7 Hz), 178.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −112.07. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{17}H_{11}FONa$ 273.0686, found 273.0694.

1-(2,4-Difluorophenyl)-5-phenylpent-1-en-4-yn-3-one (1j). Yellow crystals. M.p. 95–96 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 6.89 (d, J = 16.3 Hz, 1H), 6.88–6.99 (m, 2H), 7.40–7.50 (m, 3H), 7.59–7.67 (m, 3H), 8.03 (d, J = 16.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ ppm: 86.4, 92.2, 112.4 (dd, J = 22.0, 3.7 Hz), 120.1 (t, J = 25.5 Hz), 128.7, 130.1, 130.2, 130.3, 130.7, 130.8, 133.0, 139.4 (m), 164.5 (d, J = 255.9 Hz), 164.6 (d, J = 255.3 Hz), 178.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −109.46 (d, J = 9.93 Hz), −104.17 (d, J = 9.93 Hz). HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{17}H_{10}F_2ONa$ 291.0592; found 291.0598.

1-(5-Bromofuran-2-yl)-5-phenylpent-1-en-4-yn-3-one (1k). Grey crystals. M.p. 122–124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 6.48 (d, J = 3.5 Hz, 1H), 6.73 (d, J = 3.5 Hz, 1H), 6.75 (d, J = 15.9 Hz, 1H), 7.43–7.53 (m, 5H), 7.62 (d, J = 15.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ ppm: 86.7, 91.4, 114.9, 118.7, 120.2, 126.3, 127.0, 128.7, 130.6, 131.9, 132.9, 152.5, 177.2. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{15}H_9BrNaO_2$ 322.9678; found 322.9688.

5-Phenyl-1-(thiophen-2-yl)pent-1-en-4-yn-3-one (1l).[22] Grey crystals. M.p. 79–81 °C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ ppm: 6.69 (d, J = 15.7 Hz, 1H), 7.12 (t, J = 5.0, 3.7 Hz, 1H), 7.44 (m, 5H), 7.69–7.61 (m, 2H), 8.00 (d, J = 15.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ ppm: 86.6, 91.2, 120.4, 127.0, 128.6, 129.9, 130.6, 132.4, 132.9, 139.4, 140.2, 177.4. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{15}H_{10}NaOS$ 261.0345; found 261.0340.

General procedure for reactions of enynones 1 or dienones 3 with arenes in TfOH or in the system TfOH–pyridine (4 : 1 vol.)

Enynone **1** (0.08 mmol) was added to a mixture of TfOH (1 mL) [or TfOH (0.8 mL) and absolute pyridine (0.2 mL)] and benzene (0.2 mL) or another arene (0.22 mol) and stirred at room temperature and for the time indicated in Schemes 3, 4, 7 and Tables 4, 5, 7 for each compound **1** or **3**. The reaction mixture was poured into water (10 mL), extracted with CH_2Cl_2 (4 × 10 mL), washed with a saturated aqueous solution of $NaHCO_3$ (2 × 10 mL) and water (10 mL), and dried with Na_2SO_4. The organic solvent was distilled off under reduced pressure, if necessary the reaction products were isolated by preparative thin-layer chromatography (eluent: petroleum ether–ethyl acetate, 9 : 1 vol.).

General procedure for reactions of enynones 1 with arenes under the action of acidic zeolite HUSY (CBV-720)

A mixture of enynone (0.08 mmol), 5 mL of arene and 250 mg of HUSY zeolite CBV-720 (commercially available material) pre-calcined at 400–450 °C for 2 h was heated in the high pressure glass tube at 85–140 °C for 2–8 h (exact temperature and time for each compound are indicated in Table 8) with vigorous stirring. The reaction mixture was then cooled down to room temperature. The zeolite was filtered on a glass filter and washed several times with MeOH (4 × 10 mL). Organic solutions in benzene and in methanol were combined. The solvents were distilled off under reduced pressure, if necessary the reaction products were isolated by preparative thin-layer chromatography (eluent: petroleum ether–ethyl acetate, 9 : 1 vol.).

1,1,5,5-Tetraphenylpent-1-en-3-one (2a). Yield 98%. Yellow crystals. M.p. 231 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 3.01 (d, 2H, J = 8 Hz), 4.54 (t, 1H, J = 8 Hz), 6.44 (s, 1H), 7.07–7.35 (m, 20 H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 46.7, 49.2, 126.4, 127.0, 127.9, 128.5, 128.5, 128.6, 128.8, 129.5, 129.7, 139.0, 141.0, 144.0, 153.7, 200.3. IR (KBr) cm^{-1}: 1683 (C═O); HRMS (ESI-TOF) m/z $[M + H]^+$: calcd for $C_{29}H_{24}NaO$ 411.1725; found 411.1719.

***1-E-/Z-*1-(4-Methylphenyl)-1,5,5-triphenylpent-1-en-3-one (2b).** Yield 34%. ***E-/Z-*2b** 3 : 1. Yellow oil. ***E-*2b**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ ppm: 2.35 (s, 3H), 2.98 (d, J = 7.7 Hz, 2H), 6.42 (s, 1H). ^{13}C NMR (101 Hz, $CDCl_3$): selected signals δ ppm: 21.3, 46.6, 49.1, 144.0, 153.7, 200.0. ***Z-*2b**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals δ ppm: 2.39 (s, 3H), 3.00 (d, J = 7.7 Hz, 2H), 4.52 (t, J = 7.7 Hz, 1H), 6.38 (c, 1H). ^{13}C NMR (101 Hz $CDCl_3$) selected signals δ ppm: 21.4, 29.7, 44.3, 153.8, 200.3. ***E-/Z-*2b** (for mixture of isomers) ^{1}H NMR δ ppm: 7.05–7.24 (m, 21H), 7.27–7.39 (m, 6H). ^{13}C NMR (101 Hz, $CDCl_3$): δ ppm: 126.1, 126.2, 126.3, 126.7, 126.9, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5, 128.6, 128.7, 129.0, 129.3, 129.4, 129.6, 136.0, 138.1, 138.7, 139.0, 139.1, 139.7, 141.2, 143.9. HRMS (ESI-TOF) (for mixture of isomers) m/z $[M + Na]^+$: calcd for $C_{30}H_{26}OCl$ 425.1876; found 425.1869.

5-(4-Fluorophenyl)-1,1,5-triphenylpent-1-en-3-one (2c). Yield 52%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.01 (dd, J = 15.9, 7.6 Hz, 2H), 4.55 (t, J = 7.5 Hz, 1H), 6.47(s, 1H). NMR ^{13}C (101 MHz, $CDCl_3$): δ ppm: 45.7, 49.1, 115.2 (d, J = 20.9 Hz), 126.3, 126.4, 126.8, 127.78 (d, J = 13.4 Hz), 128.3, 128.4, 128.5, 128.6, 129.6, 139.7 (d, J = 3.1 Hz), 140.9, 153.8, 161.4 (d, J = 244.4 Hz), 199.8. ^{19}F$\{^1$H$\}$ NMR (376 MHz, $CDCl_3$), δ ppm: −116.36. HRMS (ESI-TOF) m/z $[M + H]^+$: calcd for $C_{29}H_{24}OF$ 407.1806; found 407.1820. m/z $[M + Na]^+$: calcd for $C_{29}H_{24}ONa$ 411.1719, found 411.1736.

5-(3-Fluorophenyl)-1,1,5-triphenylpent-1-en-3-one (2d). Yield 29%. Obtained in a yellow oil mixture with **3c**. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm (selected signals): 2.99 (d, J = 7.6 Hz, 2H), 4.56 (t, J = 7.6 Hz, 1H), 6.46 (s, 1H). ^{19}F$\{^1$H$\}$ NMR (376 MHz, $CDCl_3$): δ ppm: −113.11.

5-(2-Fluorophenyl)-1,1,5-triphenylpent-1-en-3-one (2e). Yield 78%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 3.07 (dd, J = 7.7, 2.05 Hz, 2H), 4.85 (t, J = 7.7 Hz, 1H), 6.51(s, 1H), 7.10–7.45 (m, 19H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 40.0, 47.9, 115.7 (d, J = 22.6 Hz), 124.1 (d, J = 3.8 Hz), 126.5 (d, J = 12.4 Hz), 127.8, 128.0 (d, J = 8.4 Hz), 128.4, 128.5, 128.7, 128.9 (d, J = 4.6 Hz), 129.4, 129.6, 138.9, 140.9, 142.7, 153.7, 160.6 (d, J = 246.2 Hz), 199.6. ^{19}F $\{^1$H$\}$ NMR (376 MHz, $CDCl_3$), δ ppm: −116.36. HRMS (ESI-TOF) m/z $[M + H]^+$: calcd for $C_{29}H_{24}OF$ 407.1806; found 407.1833.

***E-/Z-*1-(2,5-Dimethylphenyl)-1,5,5-triphenylpent-1-en-3-one (2f).** Yield 84%. ***E-/Z-*2f** 6 : 1. Colorless oil. ***E-*2f**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals, δ ppm: 1.94 (s, 3H), 2.30 (s, 3H), 2.90 (d, J = 7.4 Hz, 2H), 4.53 (t, J = 7.4 Hz, 1H), 6.62 (s, 1H), 6.82 (s, 1H). ^{13}C NMR (101 Hz $CDCl_3$) selected signals, δ ppm: 19.1, 20.9, 45.9, 49.3, 130.3, 132.7, 135.4, 138.4, 143.8, 153.7, 199.2. ***Z-*2f**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals, δ ppm: 1.89 (s, 3H), 3.07 (d, J = 7.4 Hz, 2H), 6.05 (c, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ ppm: 19.8, 47.1, 49.3, 130.6, 133.0, 135.1, 139.0, 141.5, 144.2, 154.1, 201.3. ***E-/Z-*2f** (for a mixture of isomers) ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 7.01–7.24 (m, 16H), 7.28–7.33 (m, 4H). ^{13}C NMR (101 Hz, $CDCl_3$), δ ppm: 126.2, 126.4, 127.0, 127.5, 127.7, 127.9, 128.2, 128.4, 128.5, 128.6, 128.8, 129.0, 129.1, 129.3, 129.4, 129.7. HRMS (ESI-TOF) (for a mixture of isomers) m/z $[M + Na]^+$: calcd for $C_{31}H_{28}O$ 439.2032; found 439.2031.

***E-/Z-*1-(3,4-Dichlorophenyl)-5-(4-fluorophenyl)-1,5-diphenylpent-1-en-3-one (2g).** Yield 52%. ***E-/Z-*2g** 1 : 1. Colorless oil. ***E-*2g**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals δ ppm: 2.95 (dd, J = 7.6, 1.7 Hz, 2H), 4.48 (t, J = 7.7 Hz, 1H), 6.35 (c, 1H), 6.77 (dd, J = 8.2, 2.0 Hz, 1H). ^{19}F$\{^1$H$\}$ NMR (376 MHz, $CDCl_3$), δ ppm: −116.51. ^{13}C NMR (101 Hz, $CDCl_3$): selected signals δ ppm: 43.7, 68.2, 115.4, 122.9, 125.8, 127.7, 128.2, 128.6, 143.2, 157.5, 189.6. ***Z-*2g**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals δ ppm: 3.17 (dd, J = 7.6, 1.7 Hz, 2H), 4.57 (t, J = 7.7 Hz, 1H), 6.55 (c, 1H). ^{19}F$\{^1$H$\}$ NMR (376 MHz, $CDCl_3$): δ ppm −116.69. ***E-/Z-*2g** (for a mixture of isomers) ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 6.90–7.07 (m, 17H), 7.32–7.43 (m, 20H). HRMS (ESI-TOF) (for a mixture of isomers) m/z $[M + Na]^+$: calcd for $C_{29}H_{21}Cl_2FO$ 497.0846; found 497.0861.

(4*E*)-5-(4-Nitrophenyl)-1,1-diphenylpenta-1,4-dien-3-one (3a). Yield 98%. Orange crystals. M.p. 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 6.42 (d, 1H, J = 15.8 Hz), 6.78 (s, 1H), 7.26–7.33 (m, 4H), 7.39–7.46 (m, 9H), 7.50 (d, 2H, J = 8.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm: 123.9, 127.6, 128.4, 128.5, 128.6, 128.7, 129.4, 129.7, 129.8, 130.4, 137.9, 139.0, 140.6, 141.3, 148.2, 155.5, 190.6. IR (KBr) cm^{-1}: 1651 (C═O). HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{23}H_{17}NaNO_3$: 378.1106; found 378.1101.

(4*E*)-5-(4-Chlorophenyl)-1,1-diphenylpenta-1,4-dien-3-one (3b). Yield 88%. Yellow crystals. M.p. 100–102 °C. The structure was confirmed by X-ray analysis (see ESI†). ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 6.36 (d, J = 15.8 Hz, 1H), 6.77 (s, 1H), 7.14–717 (m, 2H), 7.26–7.31 (m, 3H), 7.37–7.43 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 126.8, 127.6, 128.4, 128.5, 128.9, 129.0, 129.2, 129.6, 130.3, 133.5, 135.6, 139.1, 140.1, 140.9, 154.5, 191.2. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{23}H_{17}OClNa$ 367.0860; found 367.0843.

(4*E*)-5-(3-Fluorophenyl)-1,1-diphenylpenta-1,4-dien-3-one (3c). Yield 91%. Red oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm: 6.34 (d, J = 15.8 Hz, 1H), 6.78 (s, 1H), 6.86 (dr, 9.93, 2.94 Hz, 1H), 7.22–7.30 (m, 4H), 7.37–7.44 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 114.1 (d, J = 21.9 Hz), 116.9 (d, J = 21.4 Hz), 124.3 (d, J = 2.9 Hz), 127.4 (d, J = 10.8 Hz), 128.5, 128.7, 129.2, 129.7, 130.2, 130.3, 137.3 (d, J = 7.4 Hz), 139.1, 140.23 (d, J = 2.9 Hz), 140.8, 155.0, 162.9 (d, J = 246.5 Hz), 191.0. ^{19}F$\{^1$H$\}$ NMR (376 MHz, $CDCl_3$), δ ppm: −112.84. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{23}H_{17}OFNa$ 351.1156, found 351.1160.

(4*E*)-5-(2-Fluorophenyl)-1,1-diphenylpenta-1,4-dien-3-one (3d). Yield 55%. Yellow crystals. M.p. 91–95 °C. The structure was confirmed by X-ray analysis (see ESI†). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm: 6.50 (d, J = 16.0 Hz, 1H), 6.77 (s, 1H), 6.99–7.06 (m, 2H), 7.26–7.28 (m, 4H), 7.36–7.40 (m, 8H), 7.64 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm: 116.0 (d, J = 22.0 Hz), 123.0 (d, J = 11.7 Hz), 124.2 (d, J = 3.6 Hz), 127.8, 128.7 (d, J = 2.9 Hz), 128.4, 128.7, 129.0, 129.5, 130.1, 131.4 (d, J = 8.6 Hz), 134.2 (d, J = 2.9 Hz), 139.1, 141.0, 154.3, 161.4 (d, J = 254.0 Hz), 190.7. ^{19}F$\{^1$H$\}$ NMR (376 MHz, $CDCl_3$), δ ppm: −114.29. HRMS (ESI-TOF) m/z $[M + Na]^+$: calcd for $C_{23}H_{17}OFNa$ 351.1156; found 351.1167.

(4*E*)-1,1,5-Triphenylpenta-1,4-dien-3-one (3e).[16] Yield 97%. Yellow crystals. M.p. 62–65 °C. The structure was confirmed by

X-ray analysis (see ESI†). ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 6.45 (d, J = 15.9 Hz, 1H), 6.80 (s, 1H), 7.25–7.33 (m, 7H), 7.39–7.43 (m, 8H), 7.53 (d, J = 15.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 126.5, 127.6, 128.1, 128.4, 128.5, 128.6, 128.7, 129.0, 129.5, 130.1, 130.2, 134.9, 139.1, 141.1, 141.9, 154.2, 191.5. HRMS (ESI-TOF) m/z [M + Na]$^+$: calcd for$C_{23}H_{18}NaO$ 333.1250, found 333.1263.

(1*E*/*Z*),(4*E*)-1-(2,5-Dimethylphenyl)-1,5-diphenylpenta-1,4-dien-3-one (3f). Yield 82%. ***E*-/*Z*-3f** 5 : 1. Yellow oil. ***E*-3f**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.07 (s, 3H), 2.30 (s, 3H), 6.44 (d, J = 15.8 Hz, 1H), 6.91 (s, 1H), 6.97 (s, 1H), 7.48 (d, J = 15.8 Hz, 1H). ^{13}C NMR (101 Hz $CDCl_3$): selected signals, δ, ppm: 19.4, 20.9, 125.9, 127.7, 128.1, 128.6, 141.7, 153.9, 190.7. ***Z*-3f**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals, δ ppm: 2.06 (s, 3H), 2.36 (s, 3H), 6.40 (c, 1H), 6.49 (d, J = 16.0 Hz, 1H), 7.54 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 Hz $CDCl_3$): selected signals, δ ppm: 20.0, 126.8, 142.0, 154.5, 192.4. ***E*-/*Z*-3f** (for a mixture of isomers) ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 7.09–7.39 (m, 15H). ^{13}C NMR (101 Hz $CDCl_3$): δ ppm: 128.2, 128.7, 128.8, 128.9, 129.1, 129.3, 129.5, 129.6, 129.8, 130.0, 130.1, 130.3, 130.5, 130.7, 133.0, 135.0, 138.4, 140.0. HRMS (ESI-TOF) (for a mixture of isomers) m/z [M + Na]$^+$: calcd for $C_{25}H_{22}ONa$ 361.1563; found 361.1580.

(1*E*/*Z*),(4*E*)-1-(3,4-Dichlorophenyl)-1,5-diphenylpenta-1,4-dien-3-one (3g). Yield 75%. ***E*-/*Z*-3g** 1.25 : 1. Colorless oil. ***E*-3g**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals, δ ppm: 6.43 (d, 1H, J = 16.0 Hz), 6.74 (s, 1H), 7.22 (dd, 1H, J = 8.0 Hz, 2.0 Hz), 7.26–7.47 (m, 12H), 7.52 (d, 1H, J = 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) selected signals, δ, ppm: 126.1, 126.9, 127.7, 128.2, 128.2, 128.5, 128.7, 128.8, 129.4, 130.0, 130.4, 131.5, 132.8, 134.6, 138.0, 140.2, 142.5, 151.3, 191.0. ***Z*-3g**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals, δ, ppm: 6.43 (d, 1H, J = 16 Hz), 6.88 (s, 1H), 7.14 (dd, 1H, J = 8.0 Hz, 2.0 Hz), 7.26–7.47 (m, 12H), 7.59 (d, 1H, J = 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), selected signals, δ, ppm: 126.1, 126.9, 128.3, 128.4, 128.7, 128.7, 128.9, 129.2, 129.9, 130.3, 130.5, 132.6, 133.6, 134.7, 139.1, 141.1, 143.2, 151.8, 190.1. HRMS (ESI-TOF) (for a mixture of isomers) m/z [M + Na]$^+$: calcd for $C_{23}H_{16}Cl_2ONa$ 401.0470; found 401.0470.

(4*E*)-5-(4-Methylphenyl)-1,1-diphenylpenta-1,4-dien-3-one (3h). Yield 98%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 2.34 (s, 3H), 6.39 (d, J = 15.9 Hz, 1H), 6.76 (s, 1H), 7.09–7.16 (m, 4H), 7.26–7.29 (m, 2H), 7.37–7.39 (m, 8H), 7.48 (d, J = 15.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 21.4, 125.6, 128.1, 128.4, 128.4, 128.6, 129.5, 130.2, 139.1, 140.5, 141.1, 142.0, 153.9, 191.6. HRMS (ESI-TOF) m/z [M + Na]$^+$: calcd for $C_{24}H_{20}ONa$ 347.1406; found 347.1422.

(1*E*/*Z*),(4*E*)-1-(4-Methylphenyl)-1,5-diphenylpenta-1,4-dien-3-one (3i). Yield 98%. ***E*-/*Z*-3i** 10 : 1. Orange crystals. ***E*-3i**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals, δ ppm: 2.41 (s, 3H), 6.44 (d, 1H, J = 15.8 Hz), 6.79 (s, 1H), 7.09–7.24 (m, 5H), 7.36–7.40 (m, 9H), 7.52 (d, 1H, J = 15.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) selected signals, δ ppm: 21.3, 126.5, 126.8, 128.1, 128.4, 128.7, 129.2, 130.2, 135.0, 138.2, 139.8, 141.5, 154.5, 191.3. ***Z*-3i**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals, δ, ppm: 2.40 (s, 3H), 6.43 (d, 1H, J = 15.8 Hz), 6.76 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), selected signals, δ, ppm: 128.1, 128.5, 128.7, 128.8, 129.9, 141.2. HRMS (ESI-TOF) (for a mixture of isomers) m/z [M + H]$^+$: calcd for $C_{24}H_{20}NaO$ 347.1412; found 347.1412.

(1*E*/*Z*),(4*E*)-1-(4-Methoxyphenyl)-1,5-diphenylpenta-1,4-dien-3-one (3j). Yield 65%. ***E*-/*Z*-3j** 6 : 1. Yellow oil. ***1*–3j**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals δ ppm: 3.84 (s, 1H), 6.83 (d, J = 15.85 Hz, 1H), 6.75 (s, 1H), 7.47 (d, J = 15.85 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) selected signals, δ, ppm: 113.9, 120.3, 154.5, 183.7. **2–3j**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals, δ, ppm: 3.79 (s, 1H), 6.73 (d, J = 15.9 Hz, 1H), 6.67 (s, 1H). 7.50 (d, J = 15.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$), selected signals, δ, ppm: 113.8, 119.8, 153.7, 182.3. ***E*-/*Z*-3j** (for a mixture of isomers) ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 7.42–7.46 (m 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 125.9, 126.4, 126.6, 126.7, 128.1, 128.4, 128.5, 128.7, 128.8, 128.9, 129.9, 130.1, 130.2, 130.5, 130.6, 131.3, 131.4, 131.9, 132.0, 132.1, 133.5, 134.7, 137.8, 141.3. HRMS (ESI-TOF) (for a mixture of isomers) m/z [M + H]$^+$: calcd for $C_{24}H_{20}O_2$ 341.1536; found 341.1549, m/z [M + Na]$^+$: calcd for $C_{24}H_{19}O_2Na$ 363.1356; found 363.1371, m/z [M + K]$^+$: $C_{24}H_{19}O_2K$ 379.1095; found 379.1126.

(1*E*/*Z*),(4*E*)-5-(4-Chlorophenyl)-1-(2,5-dimethylphenyl)-1-phenylpenta-1,4-dien-3-one (3k). Yield 88%. ***E*-/*Z*-3k** 4 : 1. Yellow oil. ***E*-3k**: ^{1}H NMR (400 MHz, $CDCl_3$) selected signals, δ ppm: 2.07 (s, 3H), 2.30 (s, 3H), 6.44 (d, J = 15.8 Hz, 1H), 6.91 (s, 1H), 6.97 (s, 1H), 7.48 (d, J = 15.8 Hz, 1H). ^{13}C NMR (101 Hz $CDCl_3$) selected signals, δ ppm: 19.3, 20.9, 126.3, 127.7, 128.3, 128.7, 128.9, 129.2, 154.3, 190.5. ***Z*-3k**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals, δ ppm: 2.06 (s, 3H), 2.36 (s, 3H), 6.40 (s, 1H), 6.49 (d, J = 16.0 Hz, 1H), 7.54 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 Hz $CDCl_3$) selected signals, δ ppm: 19.2, 21.0, 155.0, 192.1. ***E*-/*Z*-3k** (for a mixture of isomers) ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 7.09–7.39 (m, 15H). ^{13}C NMR (101 Hz $CDCl_3$) δ ppm: 127.1, 127.3, 127.7, 127.9, 129.0, 129.3, 129.4, 129.6, 129.7, 129.8, 130.4, 130.7, 131.1, 133.1, 133.4, 133.6, 135.3, 135.6, 135.7, 135.8, 135.9, 138.4, 139.9, 140.0, 140.2 HRMS (ESI-TOF) (for a mixture of isomers) m/z [M + H]$^+$: calcd for $C_{25}H_{21}OClNa$ 395.1173; found 395.1158.

(4*E*)-5-(4-Fluorophenyl)-1,1-diphenylpenta-1,4-dien-3-one (3l). Yield 91%. Brown crystals. M.p. 85–87 °C. The structure was confirmed by X-ray analysis (see the ESI†). ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 6.29 (d, J = 15.8 Hz, 1H), 6.75 (s, 1H), 6.95 (t, J = 8.6 Hz, 2H), 7.18–7.22 (m, 2H), 7.26–7.29 (m, 2H), 7.36 (m, 8H), 7.42–7.46 (d, J = 15.8 Hz, 1H). ^{19}F $\{^1$H$\}$ NMR (376 MHz, $CDCl_3$): δ ppm: −109.81. ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 115.3 (d, J = 62.3 Hz), 126.2, 127.6, 128.4, 128.48, 128.65, 129.526, 129.9 (d, J = 8.4 Hz), 130.2, 131.2 (d, J = 3.1 Hz), 138.9, 140.4, 141.0, 154.3, 162.5 (d, J = 252 Hz), 191.3. HRMS (ESI-TOF) m/z [M + Na]$^+$: calcd for $C_{23}H_{17}OFNa$ 351.1156; found 351.1163.

(1*E*/*Z*),(4*E*)-1-(3,4-Dichlorophenyl)-5-(4-fluorophenyl)-1-phenylpenta-1,4-dien-3-one (3m). Yield 19%. ***E*-/*Z*-3m** 1 : 1. Yellow oil. ***E*-3m**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals, δ ppm: 6.30 (d, J = 15.8 Hz, 1H), 6.70 (s, 1H), 7.11 (dd, J = 8.2, 2.1 Hz, 1H). ^{13}C NMR (101 Hz $CDCl_3$) selected signals, δ ppm: 141.0,

161.0 (d, J = 241.5 Hz), 189.9. ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −109.02. ***Z*-3m**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals, δ ppm: 6.54 (d, J = 15.9 Hz, 1H), 6.84 (s, 1H), 7.51 (d, J = 15.9 Hz, 1H). ^{13}C NMR (101 Hz $CDCl_3$), selected signals, δ ppm: 141.84, 160.1 (d, J = 241.5 Hz), 190.8. ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −109.41. ***E*-/*Z*-3m**: (for a mixture of isomers) ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 6.96–7.08 (m, 5H), 7.18–7.23 (m, 5H), 7.32–7.45 (m, 14 H). ^{13}C NMR (101 Hz $CDCl_3$), δ ppm: 115.8, 116.0, 122.4, 126.9, 127.9, 129.4, 129.7, 129.9, 130.1, 130.3, 130.5, 131.5. HRMS (ESI-TOF) (for a mixture of isomers) m/z [M + Na]$^+$: calcd for $C_{23}H_{15}Cl_2FONa$ 419.0376; found 419.0356.

(4*E*)-5-(2,4-Difluorophenyl)-1,1-diphenylpenta-1,4-dien-3-one (3n). Yield 69%. Orange crystals. M.p. 58–59 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 6.41 (d, J = 16.0 Hz, 1H), 6.75 (s, 1H), 6.88–6.68 (m, 2H), 7.19–7.04 (m, 1H), 7.31–7.21 (m, 2H), 7.37 (m, 8H), 7.56 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm: 104.1 (t, J = 25.7 Hz), 111.7 (dd, J = 18.7, 3.7 Hz), 119.9 (dd, J = 10.9, 4.2 Hz), 127.3, 128.4, 128.5, 128.7, 129.0, 129.6, 129.7 (dd, J = 12.02, 4.5 Hz), 130.2, 133.0, 140.0, 140.9, 154.7, 160.3 (dd, J = 210, 9.9 Hz), 162.9 (dd, J = 210, 9.9 Hz). ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −106.34 (d, J = 9.2 Hz), −109.81 (d, J = 9.2 Hz). HRMS (ESI-TOF) m/z [M + Na]$^+$: calcd for $C_{23}H_{16}F_2ONa$ 369.1061; found 369.1057.

(4*E*)-5-(5-Bromofuran-2-yl)-1,1-diphenylpenta-1,4-dien-3-one (3o). Yield 71%. Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 6.34 (d, J = 15.5 Hz, 2H), 6.34 (d, J = 3.4 Hz, 1H), 6.43 (d, J = 3.4 Hz, 1H), 6.73 (s, 1H), 6.73 (s, 1H), 7.13 (d, J = 15.5 Hz, 1H), 7.28–7.21 (m, 2H), 7.37 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 114.2, 116.8, 124.7, 125.2, 126.8, 127.8, 128.3, 128.4, 128.6, 129.0, 129.6, 130.0, 138.9, 141.0, 153.4, 154.6, 190.3. HRMS (ESI-TOF) m/z [M + Na]$^+$: calcd for $C_{21}H_{15}BrO_2Na$ 401.0148; found 401.0152.

(4*E*)-1,1-Diphenyl-5-(thiophen-2-yl)penta-1,4-dien-3-one (3p). Yield 81%. Brownish crystals. The structure was confirmed by X-ray analysis (see ESI†). ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 6.20 (d, J = 15.5 Hz, 1H), 6.73 (s, 1H), 6.97 (dd, J = 5.0, 3.6 Hz, 1H), 7.11 (d, J = 3.6 Hz, 1H), 7.26 (m, 3H), 7.36–7.41 (m, 8H), 7.60 (d, J = 15.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 125.4, 127.5, 128.1, 128.4, 128.5, 128.6, 129.1, 129.5, 130.1, 131.1, 134.2, 139.0, 140.5, 141.1, 154.3, 190.7. HRMS (ESI-TOF) m/z [M − Na]$^+$: calcd for $C_{21}H_{16}NaOS$ 339.0814; found 339.0811.

(4*E*)-5-(4-Methoxyphenyl)-1,1-diphenylpenta-1,4-dien-3-one (3q). Yield 98%. Colorless oil. ^{1}H NMR (400 M Hz, $CDCl_3$), δ ppm: 3.83 (s, 3H), 6.36 (d, 1H, J = 15.6 Hz), 6.78 (s, 1H), 7.20–7.31 (m, 10H), 7.36–7.42 (m, 4H), 7.50 (d, 1H, J = 15.6 Hz). ^{13}C NMR (100 M Hz, $CDCl_3$), δ ppm: 55.3, 114.2, 124.5, 128.3, 128.4, 128.6, 129.8, 130.1, 139.2, 141.2, 141.8, 153.7, 161.3, 191.5; HRMS (ESI-TOF) m/z [M + Na]$^+$: calcd for $C_{24}H_{20}NaO_2$ 363.1361; found 363.1361.

(2*Z*,4*E*)-5-(4-Fluorophenyl)-3-hydroxy-1-phenylpenta-2,4-dien-1-one (4). Yield 6%. Orange crystals. The structure was confirmed by X-ray analysis (see ESI†). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 6.34 (s, 1H), 6.58 (d, J = 15.8 Hz, 1H), 7.08–7.16 (m, 4H), 7.47–7.64 (m, 3H), 7.66 (d, J = 15.8 Hz, 1H), 7.94–7.97 (m, 2H), 16.15 (c, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz), δ ppm: 29.7, 97.6, 116.1 (d, J = 22.2 Hz), 123.1 (d, J = 2.0 Hz), 127.4, 128.7, 129.8 (d, J = 8.1 Hz), 132.6, 136.2, 138.7, 159.3 (d, J = 254.5 Hz), 179.3, 189.3. ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −109.96. HRMS (ESI-TOF) m/z [M + Na]$^+$: calcd for $C_{17}H_{13}FO_2Na$ 291.0792, found 273.0789.

3-(4-Fluorophenyl)-4,7-dimethylindan-1-one (5). Yield 35%. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 1.96 (s, 3H), 2.52 (dd, J = 19.0, 2.59 Hz, 1H), 2.67 (s, 3H), 3.19 (dd, J = 19.0, 8.49 Hz, 3H), 4.51 (dd, J = 8.4, 2.32 Hz, 1H), 6.92–7.00 (m, 4H), 7.10 (d, J = 7.5 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ ppm: 18.05, 18.1, 42.5, 48.0, 115.7, 128.8 (d, J = 8.1 Hz), 130.3, 133.6, 134.4, 135.9 (d, J = 8.7 Hz), 139.9 (d, J = 2.9 Hz) 155.9, 161.6 (d, J = 245.1 Hz), 207.2. ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$), δ ppm: −116.36. HRMS (ESI-TOF) m/z [M + H]$^+$: calcd for $C_{17}H_{15}FO$ 255.1180; found 255.1188.

Conflicts of interest

There are no conflicts to declare.

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