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Triflic Acid Promoted Transformations of Linear-Conjugated Enynones and their Reactions with Arenes. Synthesis of Dihydropyranones, Conjugated Dienones, and Indanes

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Linear-conjugated enynones,1,5-diarylpent-4-en-2-yn-1-ones [Ar^2–CH=CH–C≡C–C(=O)Ar^1], have been cyclized into 2,6-diaryl-2,3-dihydropyran-4-ones in triflic acid TfOH (CF_3SO_3H). Reactions of these enynones with arenes Ar^3H in TfOH have afforded, at first stage, products of hydroarylation of the acetylene bond, 1,3,5-triarylpent-2,4-dien-1-ones [Ar^2–CH=CH–C(Ar^3)=CH–C(=O)Ar^1], which have been further cyclized into alkylidene indanes. Plausible reaction mechanisms have been proposed. According to quantum chemical calculations by DFT method, initial key reactive intermediates are vinyl type dications [Ar^2–CH=CH–C^+=CH–C(=O^+H)Ar^1], generated under the protonation of carbonyl oxygen and acetylene bond of starting enynones in TfOH.

Introduction

Nowadays, different linear- and cross-conjugated enynones are widely used in organic synthesis (see recent reviews[1–5] on this topic). However, among all enynone structures, the linear-conjugated pent-4-en-2-yn-1-ones [>C=C(R)–C≡C–C(R′)=O] still remain sparsely investigated. One of the reasons of that is a difficult synthesis of such compounds. There are just a few examples of reactions of these enynones with nucleophiles,[6–7] and their intramolecular cyclization into various carbocycles.[8] Based on our recent studies on reactions of other types of linear- and cross-conjugated enynones under the superelectrophilic activation conditions[9–12] and on our short preliminary communication on the cyclization of 1-aryl-5-phenylpent-4-en-2-yn-1-ones into 6-aryl-2-phenyl-2,3-dihydropyran-4-ones in triflic acid TfOH (CF_3SO_3H),[13] we undertook a special investigation on TfOH-promoted transformations of the series of 1,5-diarylpent-4-en-2-yn-1-ones.

Protonation of enynones **1** in Brønsted acids may give rise to various cationic species (Scheme 1). First protonation of carbonyl oxygen affords cations **A**. The second consequent protonation of triple or double carbon-carbon bonds may result in the formation of dications **B** or **C** correspondingly. The species **A**, **B** and **C** exist in several mesomeric forms having delocalized positive charge on carbon atoms C1, C3 and C5, that can be reactive electrophilic centers. Hypothetically, the protonation of carbonyl oxygen and both unsaturated carbon-carbon bonds leads to trications **D**, which can be considered as three electrophilic synthons generated from enynones **1**.

The main goal of this work was to investigate transformations of 1,5-diarylpent-4-en-2-yn-1-ones under superelectrophilic activation conditions in Brønsted superacid TfOH, including reactions with aromatic nucleophiles. Apart from that, a quantum chemical calculation study of electronic characteristics and reactivity of intermediate cations generated from these enynones was performed by DFT method.

Results and discussion

Starting 1,5-diarylpent-4-en-2-yn-1-ones **1a–i** used in this study are shown in Figure 1 (see their synthesis and characterization in Experimental part and SI).

In the beginning of this study, we undertook theoretical quantum chemical calculations of intermediate cations **A**, **B**, **C** and **D** (see Scheme 1) derived under protonation of enynones **1** in order to estimate electrophilic properties and reactivity of these species. Gibbs energies ΔG_{298} of protonation reactions **1**→**A**→**B**→**C**→**D**, electronic and orbital characteristics (charge distribution, HOMO/LUMO energies, contribution of atomic orbitals into LUMO, global electrophilicity index ω[14]) of cations

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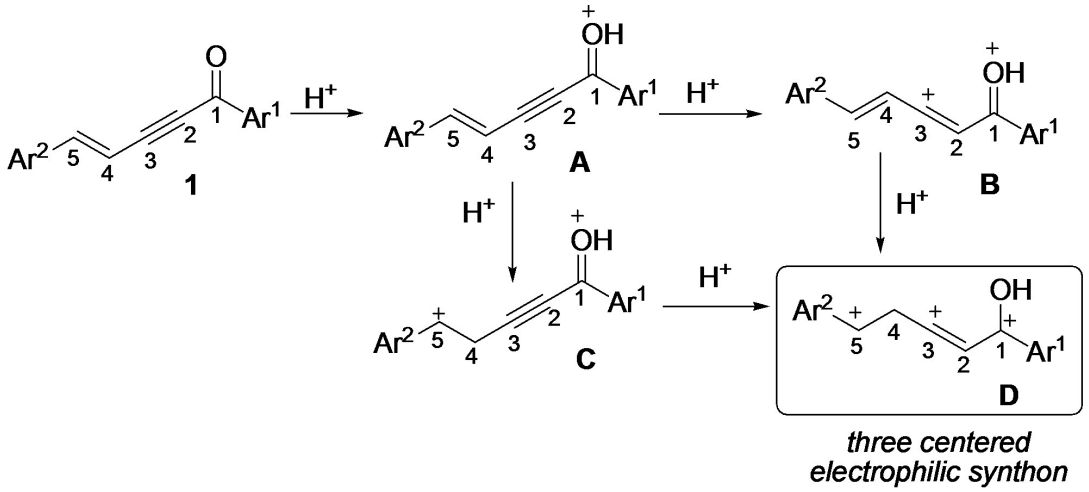


Scheme 1. Generating of various cationic species from linear-conjugated enynones **1** under the protonation in Brønsted acids.

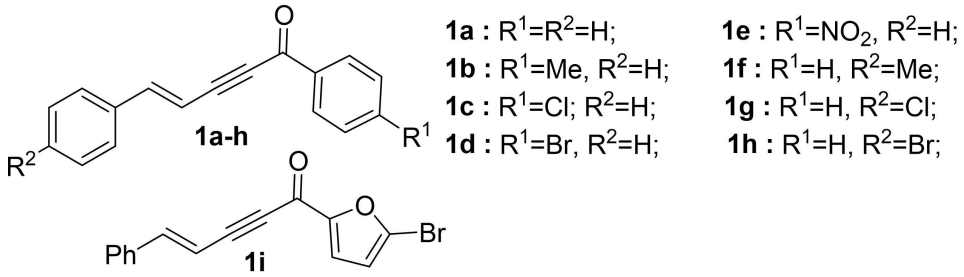
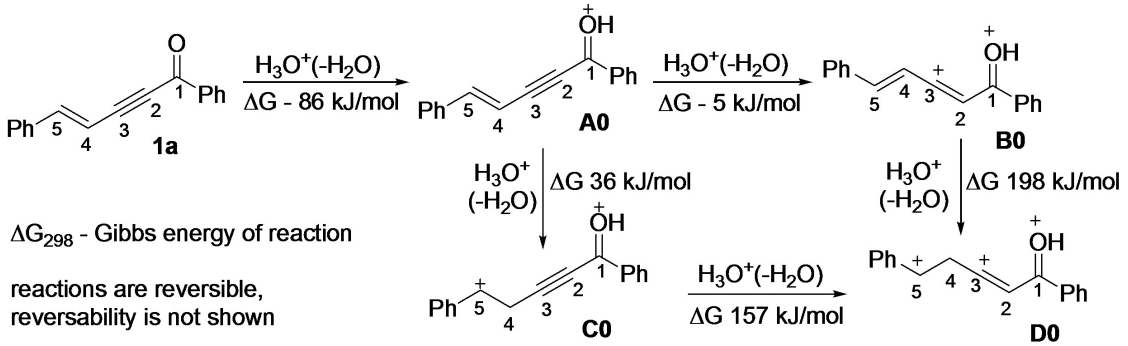


Figure 1. Starting 1,5-diarylpent-4-en-2-yn-1-ones **1a–i** used in this study.

A, **B**, **C**, **D** were calculated using DFT method. Cations **A0**–**A7**, **B0**–**B7**, **C0**–**C7**, **D0**–**D7** generated from enynones **1a**, **1f**, **1g**, **1h**, **1e**, **1b**, **1c**, **1d** correspondingly were studied. As an example, see data for species **A0**–**D0** generated from **1a** in Table 1. Calculation for other cations **A1**–**D7** are presented in Table S12 in SI.

Table 1. Selected electronic characteristics (DFT calculations) of cations **A0**, **B0**, **C0, D0** 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] [%]
A0	−7.00	−4.18	5.5	0.48	0.19	−0.02	25.5	17.2	14.5
B0	−8.20	−4.99	6.8	0.61	0.36	0.12	2.1	15.5	22.2
C0	−8.17	−4.92	6.6	0.53	0.24	0.21	8.0	10.6	9.5
D0	−8.61	−6.06	10.5	0.61	0.66	0.16	10.5	38.2	2.1

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

Calculations of Gibbs energies of protonation reactions showed that the first protonation onto carbonyl oxygen leading to species **A0**–**A7** was thermodynamically very favorable. The ΔG_{298} values of this step are −86–−57 kJ/mol (see scheme in Table 1, and Table S12 in SI). The formation of dications **B** from **A** by protonation of atom C2 of carbon-carbon triple bond is also thermodynamically favorable; the corresponding ΔG_{298}values of protonation reactions **A0**–**A7**→**B0**–**B7** are −28–−5 kJ/mol. Alternative protonation of atom C4 of carbon-carbon double bond in species **A** leading to dications **C** is much more unfavorable (values of$\Delta G_{298}$for reactions **A0**–**A7**→**C0**–**C7** are 18–47 kJ/mol), compared to the formation of dications **B0**–**B7**. The third protonation of both **B** and **C** affording trications **D** is completely impossible due to the very high ΔG_{298} values of the corresponding protonation reactions **B0**–**B7**→**D0**–**D7** (190–211 kJ/mol) and **C0**–**C7**→**D0**–**D7** (144–158 kJ/mol) (see Table 1, and Table S12 in SI). Thus, the thermodynamical calculations pointed out that a generating of dications **B0**–**B7** is highly likely.

Calculations of electrophilic properties of species **A**, **B**, **C** showed that dications **B** and **C** had higher values of electrophilicity index ω 6.3–7.1 eV and 6.0–6.9 eV, respectively, compared to cations **A** with ω 5.4–6.4 eV (see Table 1, and Table S12 in SI). Cations **A**, **B** and **C** have positive charge localization mainly on all three carbons C1, C3 and C5, which may behave as reactive electrophilic centers (see Scheme 1). Investigation of charge distribution revealed that the largest positive charge was localized on atom C1: 0.42–0.48 e in **A0**–**A7**, 0.58–0.62 e in **B0**–**B7**, 0.52–0.55 e in **C0**–**C7**. However, contribution of C1 atomic orbital into LUMO is rather low in **B0**–**B7** (1.8–5.5%) and **C0**–**C7** (0.9–8%) that pointed out a weak orbital control in reactivity of this electrophilic center.

In species **A0**–**A7**, carbon C1 is the most reactive electrophilic center, since other carbons bear less charge (−0.30–0.21 e for C3; −0.49–0.01 e for C5) and give less contribution into LUMO (14.0–17.2% for C3; 12.4–14.5% for C5, compared to 21.8–25.5% for C1). However, no reactions took place at carbon C1 (see below data on chemical transformations of enynones **1** in Brønsted acids), therefore it is unlikely that cations **A** may be reactive species.

Concerning dications **C0**–**C7**, they have large positive charges on carbons C3 and C5, 0.23–0.27 e and 0.18–0.21 e, respectively. However, these carbons have low contributions into LUMO: 3.0–11.2% for C3 and 8–31.3% for C5, that reveals low orbital control. There is no coincidence in charge and orbital controls for reactivity of atoms C3 and C5 in species **C**. Thus, their participation in reactions has low probability.

Electronic properties of vinyl type dications **B0**–**B7** show that these species may have reactive electrophilic centers both on carbon C3 and C5. Atom C3 possesses a big positive charge 0.15–0.36 e and gives a substantial contribution (12.1–15.5%) into LUMO. Carbon C5 have a wide charge value from −0.14 to 0.86 e, depending on substituents in aromatic rings; and this carbon gives a big contribution into LUMO, 17.0–22.2% (see Table 1, and Table S12 in SI). To clarify this point, which of carbons C3 or C5 would be a reactive center, we conducted reactions of enynones **1** in TfOH (*vide infra*).

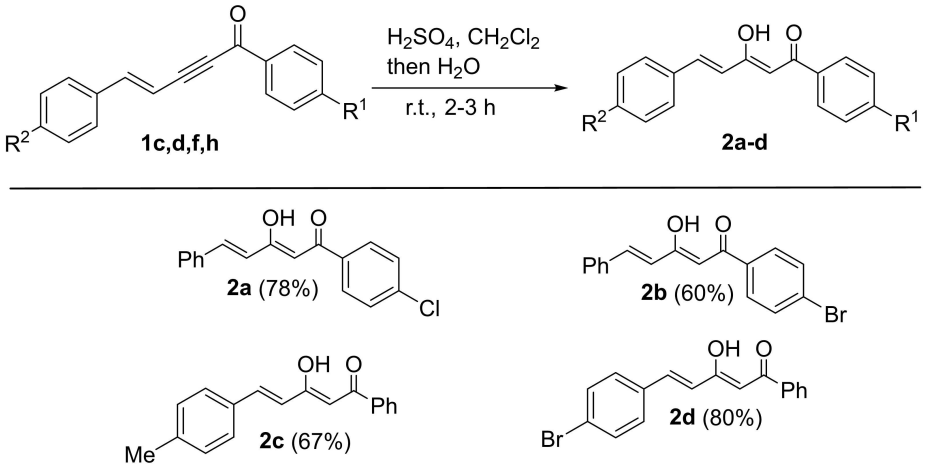
Thus, based on DFT calculations, taking into account thermodynamical data on the most favorable formation of vinyl dications **B**, and their electronic and orbital characteristics, one may expect that these species should be key electrophilic intermediates in reactions of enynones **1** in Brønsted superacids.

Then, reactions of enynones **1** in the superacid TfOH were carried out. Analogously to transformations of other types of linear-[9] and cross-[11] conjugated enynones in TfOH, one would expect a formation of the corresponding vinyl triflates, as product of addition of TfOH to the acetylenic bond of enynones **1**. We run reactions of several enynones **1** with 1.5 equiv. of TfOH in CH_2Cl_2 at room temperature for 0.5–1 h and obtained complex mixture of reaction products containing just traces of vinyl triflates according to ^1H, ^{19}F and ^{13}C NMR data. These vinyl triflates were found to be unstable and were easily hydrolyzed into the corresponding enolic forms of 1,3-diketones, which were also detected among the reaction products in TfOH. However, the enols **2a**–**d** were obtained in good yields in reactions of compounds **1c**, **1d**, **1f**, **1h** with H_2SO_4 (Scheme 2). Structure of compound **2a** was confirmed by X-ray analysis (see SI). It should be specially mentioned that such 1,5-diaryl-3-hydroxypent-2,4-diene-1-ones are very important substances. They not only exhibit antiproliferative effect,[15] but also they are precursors for the preparation of various pharmaceutically significant drugs. In particular, they are used in the synthesis of 2-styrylchromones.[16]

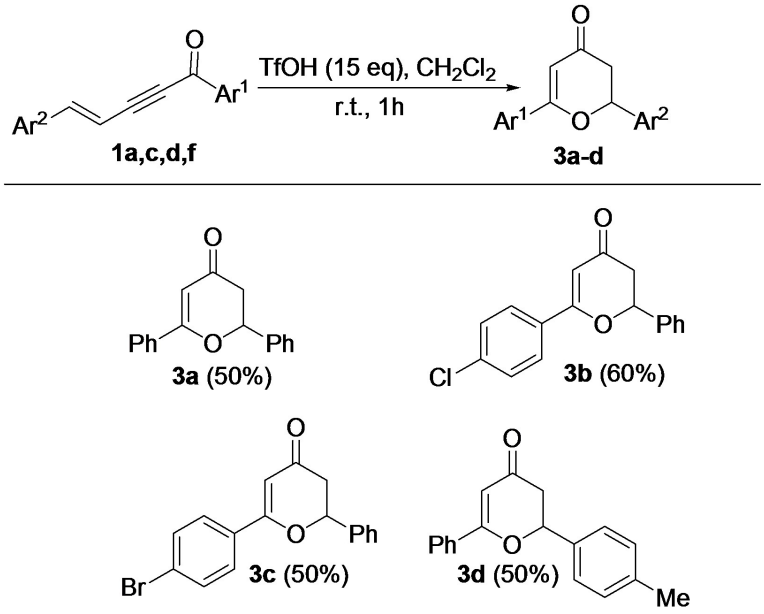
It was found that enynones **1a**, **f**, **c**, **d** were cyclized into 2,3-dihydropyran-4-ones **3a**–**d** correspondingly in excess of TfOH at room temperature for 1 h (Scheme 3, see also our preliminary communication[13]). The position of the double bond in dihydropyranone structures **3a**–**d** was confirmed by NOESY correlations between vinyl proton and *ortho*-protons of neighbor aromatic system (see SI). The same dihydropyranones were obtained from enynones **1** in H_2SO_4; however, the reaction proceeded much longer (2-3 days), compared to TfOH (1 h).

Then NMR study of intermediate cationic species generated from enynones **1** was carried out. Dissolving of enynones **1c**, **d** in H_2SO_4 directly in NMR tube showed the formation of the corresponding O-protonated forms of vinyl sulfates **Ea**, **b** at room temperature in 3 h (see selected ^1H and ^{13}C NMR chemical shifts in Scheme 4, and full spectral data in SI). Extending these reactions in NMR tubes till 3 days afforded O-protonated forms of dihydropyranones **Fa**, **b** (Scheme 4, and see spectral data in SI). Similar protonated dihydropyranones, generated from cross-conjugated enynones (1,5-diarylpent-1-en-4-yn-3-ones), were observed by ourselves previously.[11] We also took NMR spectra of enynones **1** in neat TfOH, however these spectra had more complex character, they contained impurities of oligomeric products of transformations of these compounds in the superacid.

The data obtained on the formation of vinyl sulfates (triflates) **Ea**, **b** (Scheme 4) and enols **2** (Scheme 2), and their cyclization into dihydropyranones **3** (Scheme 3 and 4) have allowed proposing plausible reaction mechanisms of the formation of these compounds (Scheme 5). Protonation of carbonyl oxygen and acetylene bond of **1** gives rise to dication



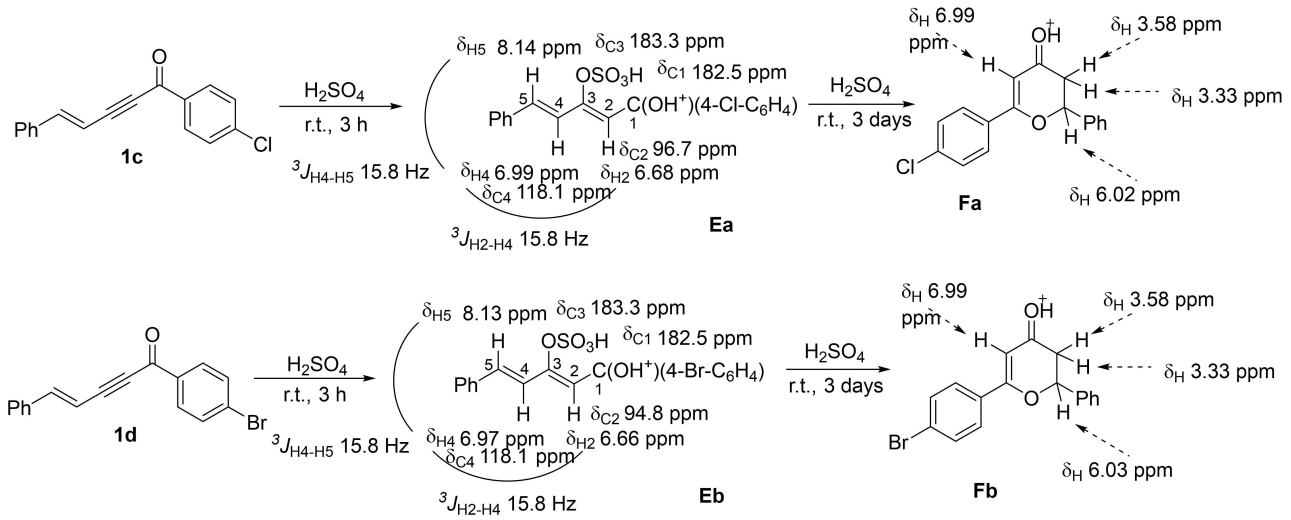
Scheme 2. Transformation of enynones **1 c**, **d**, **f**, **h** into enols **2 a**–**d** correspondingly in H_2SO_4.



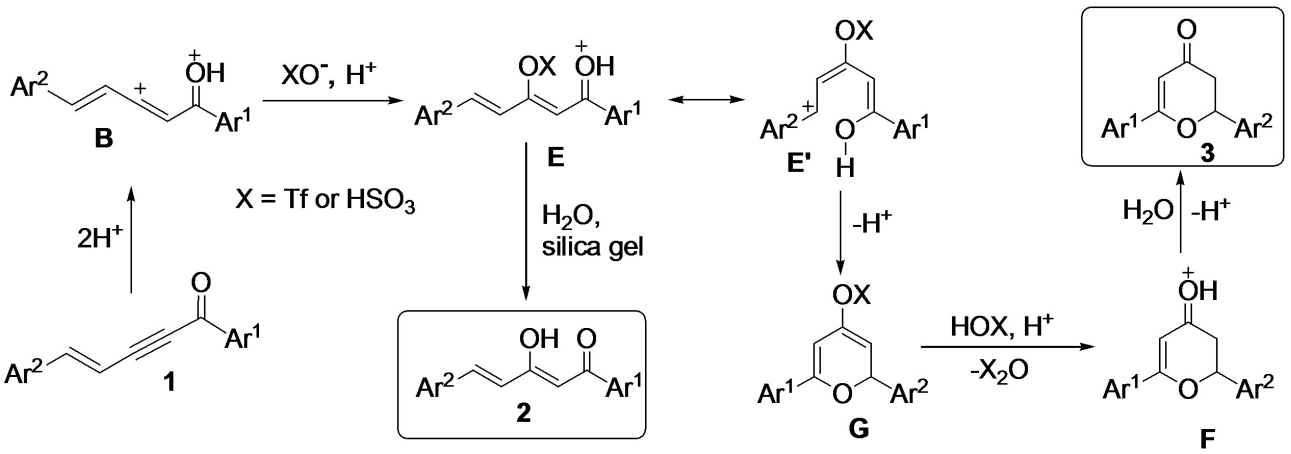
Scheme 3. Cyclization of enynones**1 a**, **f**, **c**, **d** into dihydropyranones **3 a**–**d** correspondingly in TfOH.

B, which interacts with acid counter anions (HSO_4^- or TfO^-) leading to the corresponding O-protonated forms of vinyl sulfates or triflates **E**. Hydrolysis (or transformation on silica gel for vinyl triflates) of the later at this early reaction stage results enols **2**. Longer reaction time has finally led to cyclization of species **E** (in its resonance form **E′**) into dihydropyranones **3** through an intermediate formation of species **G** and **F**. See also a detailed discussion on mechanism of such dihydropyranone formation in our previous studies[11,13] and in works.[17,18]

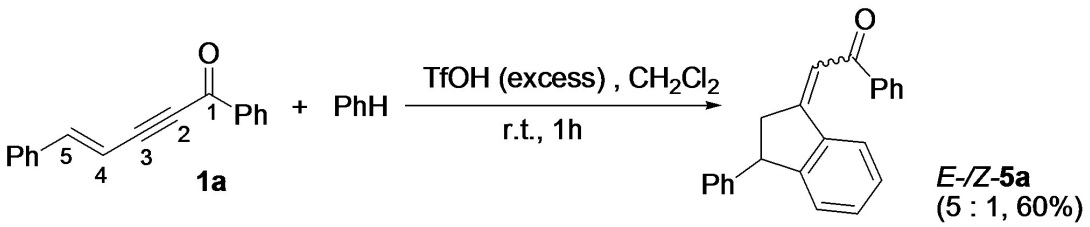
The next step of this study was investigation of reactions of enynones **1** with arenes in TfOH. It was found that reaction of **1 a** with benzene in the excess of TfOH and CH_2Cl_2, as co-solvent, furnished a mixture of isomeric alkylidene indanes *Z-/E*-**5 a** (Scheme 6). Taking into account that a key reactive intermediate could be dication **B0** (see data of DFT calculations in Table 1), it was not clear how the indane **5 a** was formed. Namely, which carbon C3 or C5 in the species **B0** participated in the first stage of electrophilic aromatic substitution with benzene. In other words, at which carbon C3 or C5 phenyl moiety was attached in interaction with species **B0**; the next stage was cyclization into indane. To clarify this point, we run the series of reactions of enynones **1 a**–**d** with polymethylated arenes, mesitylene (1,3,5-trimethylbenzene), durene (1,2,4,5-tetramethylbenzene), and *para*-xylene (1,4-dimethylbenzene), under the action of TfOH (1.5 equiv.) in CH_2Cl_2 at room temperature for 0.5 h (Scheme 7). These sterically hindered arenes, giving *ortho*-methyl substituted aryl ring upon their electrophilic substitution, were chosen to avoid a consequent cyclization into indane after the first step of the reaction. These reactions afforded dienones **4 a**–**h**, that unambiguously re-



Scheme 4. NMR study on the formation of O-protonated forms vinyl sulfates **Ea**, **b** and dihydropyranones **Fa**, **b** generated from enynones **1 c**, **d** in H_2SO_4.



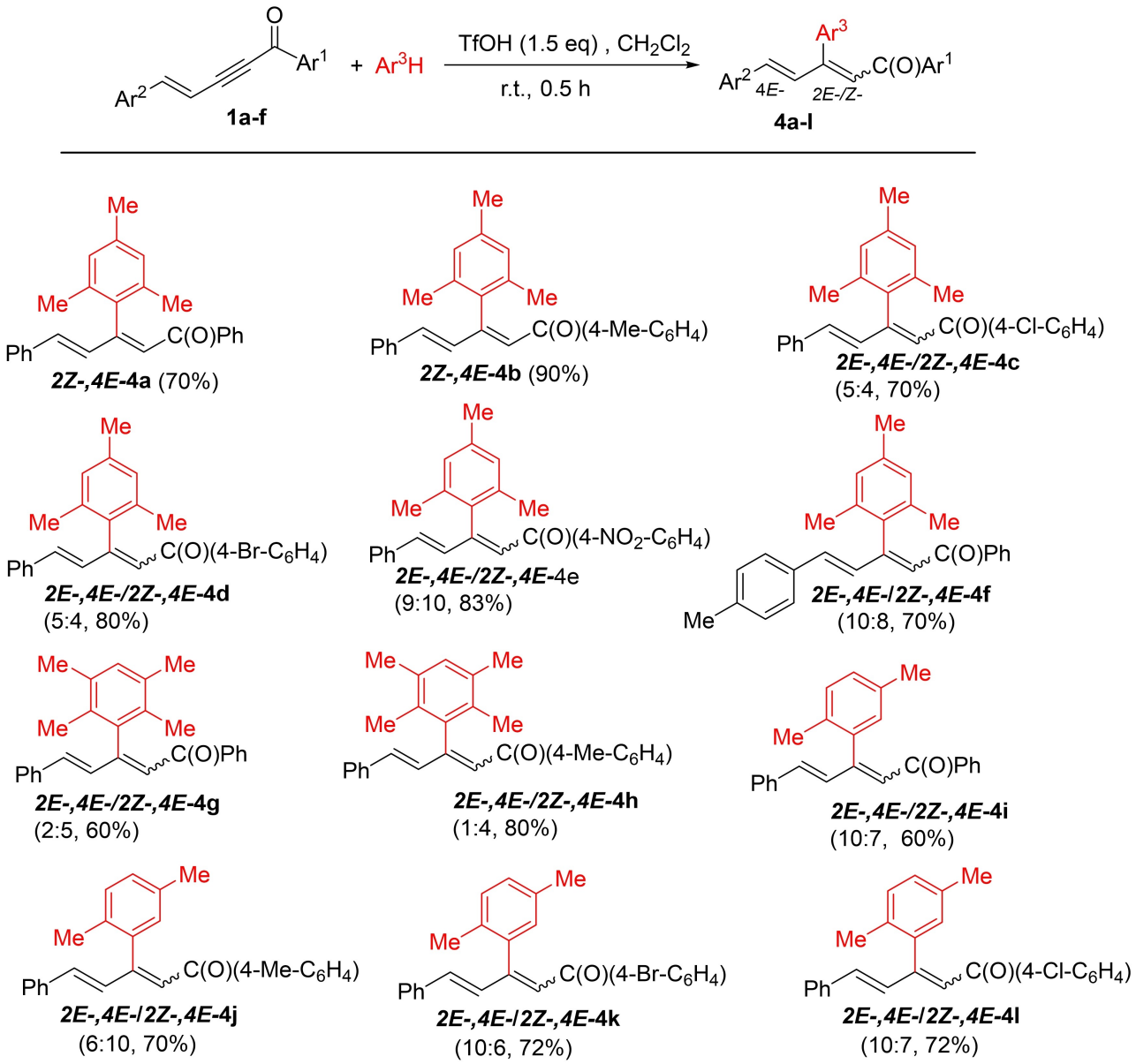
Scheme 5. Plausible reaction mechanism for transformations of enynones**1** in TfOH and H_2SO_4 leading to enols **2** and dihydropyranones **3**.



Scheme 6. Reaction of enynone **1 a** with benzene in TfOH leading to *E-/Z*-indanes **5 a**.

vealed a hydroarylation of the acetylene bond in compounds **1** and participation of electrophilic center C3 of species **B** (see Table 1) in reaction with aromatic molecules.

The obtained dienones **4** have 4-E-configuration of $C^4{=}C^5$ double bond and 2-E-or 2-Z-configuration of $C^2{=}C^3$ bond. Structure of **4 e** was confirmed by X-ray analysis (see SI). Stereochemical configuration of both carbon-carbon bonds in compounds **4** was determined by H–H NOESY correlations between vinyl protons of diene system with methyl groups and protons of neighbor aryl rings (see spectra in SI). Dienones **4 a**, **b** were obtained as pure 2Z-isomers, other compounds **4 c**–**h** were mixtures of 2E-/Z-isomers. It should be noted that, in ^{1}H NMR spectra, signals of vinyl protons H4 (~7.20 ppm) and H5 (~6.33 ppm) with $^3J_{H4\text{-}H5}$ ~15.8 Hz for 2Z-isomers of **4** have been down field shifted in comparison with the same signals for 2E-

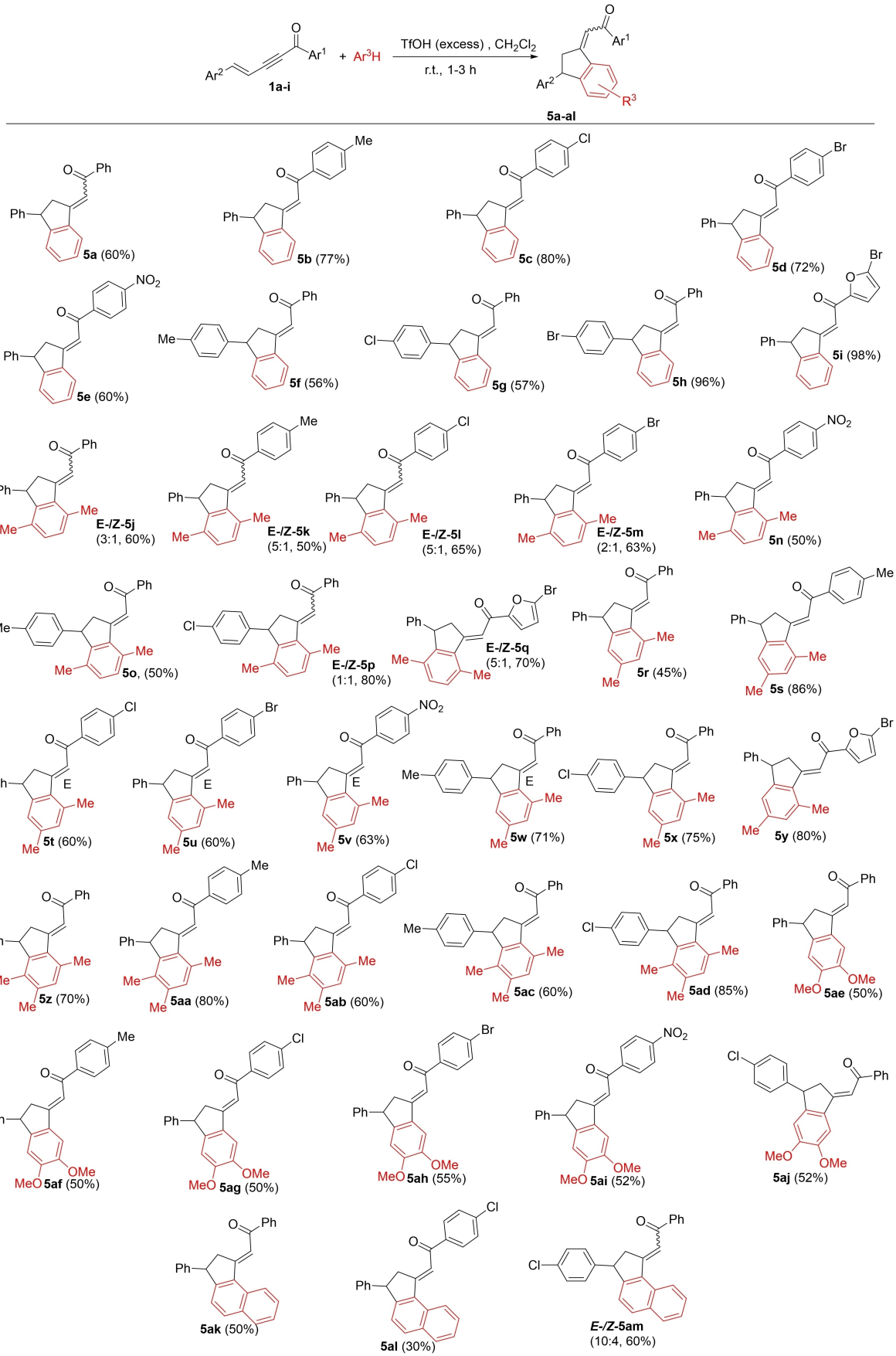


Scheme 7. Hydroarylation of enynones **1a–f** by arenes in TfOH leading to dienones **4a–l**.

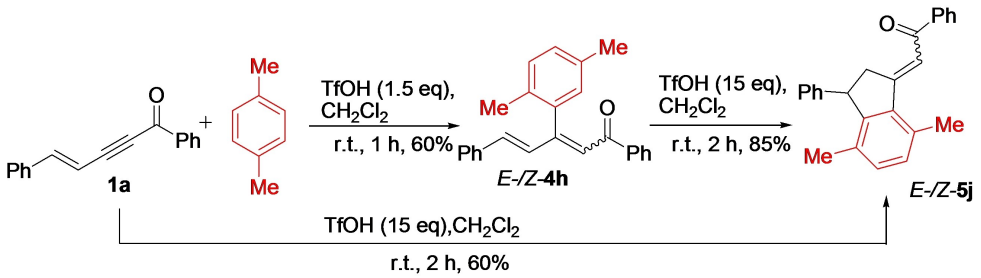
isomers, H4 (~8.64 ppm) and H5 (~6.41 ppm) with $^{3}J_{H4\text{-}H5}$ ~16.0 Hz (see spectra in SI).

Then, reactions of enynones **1a–i** with other arenes [benzene, xylenes (dimethylbenzenes), pseudocumene (1,2,4-trimethylbenzene), veratrole (1,2-dimethoxybenzene), naphthalene] in the excess of TfOH resulting alkylidene indanes **5a–5am** in good yields were performed (Scheme 8). Yields of compounds **5ae–al** that were obtained in reactions with good electron-donating arenes, veratrole and naphthalene, were moderate 30–55%, perhaps, due to secondary electrophilic reactions of the obtained electron rich indanes under super-acidic conditions leading to oligomeric compounds. Structures of **5b**, **c**, **d**, **w**, **xz**, **aa**, **ab**, **ac** were confirmed by X-ray analysis (see SI). In general, the reaction proceeded highly stereo-selectively with the predominant formation of indanes **5** having *E*-configuration of alkylidene exocyclic double bond, the stereo-chemistry of that was unambiguously determined by H–H NOESY correlations between vinyl proton with CH_2 group of indane ring (for *Z*-isomers) or aromatic protons (for *E*-isomers) (see spectra in SI). *E*-Stereochemistry may be explained by spatial factors. *Trans*-orientation of 3-aryl-3-oxopropylidene group to aryl moiety of indane may be more favorable, especially, for indanes **5j–z**, **5aa–ae** having substituents in position 7 (*peri*-position to propylidene group).

To have additional proof on intermediate formation of dienones **4** in the synthesis of indanes **5**, the consequent formation of *E-/Z*-dienones **4h** and *E-/Z*-indanes **5j** from enynone **1a** and *para*-xylene in TfOH was carried out (Scheme 9). Compounds *E-/Z*-**4h** were obtained from **1a** and *para*-xylene in reaction with 1.5 equiv. of TfOH. Then *E-/Z*-**4h**



Scheme 8. Reaction of enynones **1a–i** with arenes inTfOH leading to indanes**5a–al**.



Scheme 9. Consequent formation ofdienone **4h** and indane **5j** from enynone **1a** and *para*-xylene in TfOH.

were transformed into *E-/Z*-**5j** in the excess of TfOH (15 equiv.). Apart from that, running reaction of **1a** and *para*-xylene in the excess of TfOH resulted directly *E-/Z*-**5j**.

Summarizing all the data obtained on the synthesis of dienones **4** and indanes **5** (Schemes 6–9), one may propose a plausible reaction mechanism of the formation of these compounds (Scheme 10). Interaction of dication **B** with arene affords O-protonated form of dienone **H**, hydrolysis of which results in the formation of dienone **4**. In the excess of TfOH, species **H** may be protonated at carbon-carbon bond giving dication **I**, which is finally cyclized into indane **5**. The formation of indanes **5** reveals that enynones **1** in reactions with arenes in TfOH behave as 1,3-dielectrophile **J** (Scheme 10; see also Scheme 1 in Introduction).

It should be noted that synthesis of indanes and indenes is very important since these compounds have a lot of practical applications, as functional materials, biologically active substances, pharmaceuticals, ligands for metal complexes (see recent reviews[19–21] on synthesis and properties of indanes and indenes). However, in this field, synthesis of alkylideneindanes has not been very much developed. These indane derivatives are still hardly available compounds.[22–24]

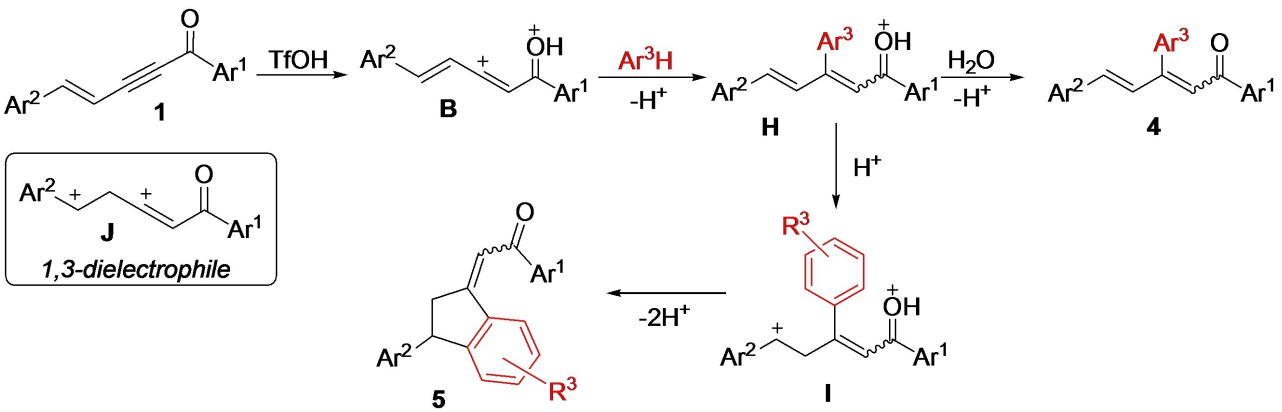
Conclusions

Novel methods of synthesis of compounds of the series of 2,3-dihydropyran-4-ones, conjugated dienones, alkylidene indanes, have been developed on the basis of transformations of linear-conjugated enynons, 1,5-diarylpent-4-en-2-yn-1-ones, under superelectrophilic activation conditions in Brønsted superacid TfOH.

Experimental Section

General information. The NMR spectra of solutions of compounds in $CDCl_3$ were recorded on Bruker AVANCE III 400 (at 400and 100 MHz for ^{1}Hand ^{13}C NMR spectra respectively) spectrometer at 25 °C. The residual proton-solvent peak $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR spectra and the carbon signal of $CDCl_3$ (δ 77.0 ppm) for ^{13}C NMR spectra were used as references. HRMS was carried out at instruments Bruker maXis HRMS-ESI-QTOF and Varian 902-MS MALDI Mass 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 eluation.

X-Ray analysis. Single crystal X-ray analysis was performed at single crystal diffractometer Agilent Technologies (Oxford Diffraction) «Supernova». A suitable crystal was selected and studied on the diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2[25] the structure was solved with the ShelXS[26] structure solution program using Direct Methods and



Scheme 10. A plausible reaction mechanism of the formation of dienones **4** and indanes **5** from enynones **1** and arenes in TfOH.

refined with the ShelXL refinement package using Least Squares minimisation. **DFT calculations**. All computations were carried out at the DFT/HF hybrid level of theory using hybrid exchange functional B3LYP by using GAUSSIAN 2009 program packages.[27] The geometries optimization were performed using the 6-311+G(2d,2p) basis set (standard 6-311G 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, solvent = water).

Preparation and characterization of compounds

General procedure for synthesis of starting1,5-diarylpent-4-en-2-yn-1-ones 1 a–i. Synthesis was carried out according to literature procedure.[28] Mixture of $Pd(OAc)_2$ (0.03 mmol) and PPh_3 (0.07 mmol) and CuI (0.17 mmol) in THF (20 ml) was stirred in argon atmosphere at room temperature for 15 min. Then benzoic acid chloride (1.6 mmol), 1-aryl-but-1-en-3-yne (1.9 mmol) and triethylamine (1.6 mmol) were consequently added. Reaction mixture was stirred at room temperature for 3 h. Then solvent was removed in vacuo, the obtained residue was subjected to column chromatography on silica gel [eluent: petroleum ether (fraction with bp 40–70 °C) – ethyl acetate].

(*E*)-1,5-Diphenylpent-4-en-2-yn-1-one (1 a):[28] Light yellow needles, mp 64–65 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, *J* = 16.3 Hz, 1H), 7.36 (d, *J* = 16.3 Hz, 1H), 7.38–7.41 (m, 3H), 7.47–7.49 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.60–7.64 (m, 1H), 8.18–8.20 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 89.10, 93.06, 105.49, 127.15, 128.71, 129.10, 129.67, 130.24, 134.13, 135.32, 137.08, 147.99, 178.01. HRMS (ESI) calcd. For $C_{17}H_{13}O^+$ $[M+H]^+$ 233.0961; found 233.0966.

(*E*)-5-Phenyl-1-(4-methylphenyl)pent-4-en-2-yn-1-one (1 b):[28] Light yellow needles, mp 56.5–57.5 °C.^{1}H NMR ($CDCl_3$, 500 MHz) δ, ppm: 2.32 (s, 3H), 6.25 (d, *J* = 16.3 Hz, 1H), 7.18–7.22 (m, 3H), 7.26–7.35 (m, 5H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.99 (d, *J* = 7.9 Hz, 2H).^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 88.9, 92.2, 105.1, 126.7, 128.7, 128.7, 129.4, 129.8, 134.4, 134.9, 144.8, 147.3, 177.2. HRMS (ESI) calcd. For $C_{18}H_{15}O^+$ $[M+H]^+$ 247.1117; found 247.1123.

(*E*)-1-(4-Chlorophenyl)-5-phenylpent-4-en-2-yn-1-one (1 c):[28] Brown oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, *J* = 16.3 Hz, 1H), 7.36 (d, *J* = 16.3 Hz, 1H), 7.38–7.41 (m, 3H), 7.47–7.49 (m, 4H), 8.11 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 88.78, 93.62, 105.24, 127.19, 129.08, 129.12, 130.36, 130.96, 135.21, 135.49, 140.71, 148.39, 176.62.HRMS (ESI) calcd. For $C_{17}H_{12}ClO^+$ $[M+H]^+$ 267.0571; found 267.0576.

(*E*)-1-(4-Bromophenyl)-5-phenylpent-4-en-2-yn-1-one (1 d): Yellow needles, mp 89–90 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, *J* = 16.1 Hz, 1H), 7.36 (d, *J* = 16.1 Hz, 1H), 7.38–7.41 (m, 3H), 7.47–7.50 (m, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 8.03 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 88.78, 93.68, 105.25, 127.21, 129.14, 129.57, 130.39, 131.05, 132.09, 135.23, 135.90, 148.44, 176.84. HRMS (ESI) calcd. For $C_{17}H_{12}BrO^+$ $[M+H]^+$ 311.0066; found 311.0075.

(*E*)-1-(4-Nitrophenyl)-5-phenylpent-4-en-2-yn-1-one (1 e): Brownish oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ, ppm: 6.41 (d, *J* = 16.3 Hz, 1H), 7.41–7.43 (m, 4H), 7.49–7.51 (m, 2H), 7.34–7.36 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 88.7, 95.5, 104.8, 123.9, 127.3, 129.2, 130.5, 130.7, 135.0, 141.2, 149.5, 151.0, 175.8. HRMS (ESI) calcd. for $C_{17}H_{12}NO_3^+$ $[M+H]^+$ 278.0812; found 278.0817.

(*E*)-1-Phenyl-5-(4-Methylphenyl)pent-4-en-2-yn-1-one (1 f): Light yellow needles, mp 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 6.34 (d, *J* = 16.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 16.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.49–7.53 (m, 2H), 7.60–7.64 (m, 2H), 8.17–8.20 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 21.60, 89.03, 93.62, 104.33, 127.16, 128.71, 129.68, 129.84, 132.68, 134.07, 137.17, 140.72, 148.16, 178.06. HRMS (ESI) calcd. for $C_{18}H_{15}O^+$ $[M+H]^+$ 247.1117; found 247.1112.

(*E*)-5-(4-Chlorophenyl)-1-phenylpent-4-en-2-yn-1-one (1 g): Light yellow needles, mp 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (d, *J* = 16.3 Hz, 1H), 7.29 (d, *J* = 16.3 Hz, 1H), 7.34–7.40 (m, 4 H), 7.49–7.53 (m, 2H), 7.60–7.65 (m, 1H), 8.16–8.18 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 89.39, 92.44, 106.17, 128.28, 128.74, 129.38, 129.68, 133.81, 134.22, 136.12, 137.01, 146.40, 177.94. HRMS (ESI) calcd. for $C_{17}H_{12}ClO^+$ $[M+H]^+$ 267.0571; found 267.0578.

(*E*)-5-(4-Bromophenyl)-1-phenylpent-4-en-2-yn-1-one (1 h): Light yellow needles, mp 101–102 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (d, *J* = 16.3 Hz, 1H), 7.27 (d, *J* = 16.3 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.49–7.53 (m, 4H). 7.60–7.64 (m, 1H), 8.16–8.18 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 89.43, 92.40, 106.30, 124.43, 128.50, 128.75, 129.68, 132.35, 134.23, 137.01, 146.45, 177.94. HRMS (ESI) calcd. for $C_{17}H_{12}BrO^+$ $[M+H]^+$ 311.0066; found 311.0061

(*E*)-1-(5-Bromofuran-2-yl)-5-phenylpent-4-en-2-yn-1-one (1 i): Light yellow plates, mp 97–98 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (d, *J* = 16.3 Hz, 1H), 6.54 (d, *J* = 3.6 Hz, 1H), 7.30 (d, *J* = 3.6 Hz, 1H), 7.33 (d, *J* = 16.3 Hz, 1H), 7.38–7.40 (m, 3H), 7.46–7.48 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.79, 92.64, 105.09, 114.90, 122.33, 127.21, 129.13, 130.41, 130.53, 135.19, 148.59, 154.90, 163.33. HRMS (ESI) calcd. for $C_{17}H_{12}BrO^+$ $[M+H]^+$ 300.9859; found 300.9854.

General procedure for synthesis of (*2Z,4E*)-3-hydroxy-1,5-diarylpenta-2,4-dien-1-ones 2 a–d from enynones 1 in H_2SO_4. H_2SO_4 (0.1 ml, 1.9 mmol) was added with vigorous stirring at room temperature to a solution of enynone**1** (0.086 mmol) in CH_2Cl_2 (0.1 ml).The mixture was stirred for 2–3 h. Then the reaction mixture was poured into H_2O (50 ml), extracted with $CHCl_3$ (3×25 ml). The combined extracts were consequently washed with H_2O (50 ml), saturated aqueous solution of$NaHCO_3$(25 ml), again with H_2O (25 ml) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the product was isolated by preparative TLC on LS 5/40 μm silica gel plates, eluent-petroleum ether-EtOAc, 95:5 vol. The separated fractions were washed off from the sorbent with CH_2Cl_2.

(*2Z,4E*)-1-(4-Chlorophenyl)-3-hydroxy-5-phenylpenta-2,4-dien-1-one (2 a): Yield 17 mg (78%). Yellow crystals. M.p. 100–102 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 6.30 (s, 1H), 6.64 (d, ^3J = 15.8 Hz, 1H), 7.38–7.42 (m, 3H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.56–7.58 (m, 2H), 7.70 (d, ^3J = 15.8 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 16.06 (bsr, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 97.6, 123.2, 128.2, 128.9, 129.1, 130.3, 134.5, 135.1, 139.0, 140.6, 179.7, 188.3 HRMS (ESI) calcd. for $C_{17}H_{14}ClO_2^+$ $[M+H]^+$ 285.0677; found 285.0680.

(*2Z,4E*)-1-(4-Bromophenyl)-3-hydroxy-5-phenylpenta-2,4-dien-1-one (2 b): Yield 13 mg (60%). Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 6.30 (s, 1H), 6.64 (d, ^3J = 15.8 Hz, 1H), 7.39–7.41 (m, 3H), 7.55–7.58 (m, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.70 (d, ^3J = 15.8 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 16.06 (bsr, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 97.6, 123.3, 127.6, 128.2, 129.0, 129.1, 130.3, 132.1, 135.1, 135.3, 140.6, 179.8, 188.3.HRMS (ESI) calcd. for $C_{17}H_{14}BrO_2^+$ $[M+H]^+$ 329.0172; found 329.0177.

(*2Z,4E*)-3-Hydroxy-5-(4-methylphenyl)-1-phenyl-penta-2,4-dien-1-one (2 c): Yield 14 mg (60%). Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.39 (s, 3H), 6.34 (s, 1H), 6.62 (d, ^3J = 15.8 Hz, 1H), 7.21 (d, *J* =

7.8 Hz, 2H), 7.46–7.49 (m, 4H), 7.53–7.57 (m, 1H), 7.68 (d, ^3J= 15.8 Hz, 1H), 7.94–7.97 (m, 2H), 16.20 (bsr, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 21.6, 97.6, 122.5, 127.5, 128.2, 128.8, 129.8, 132.5, 132.6, 136.5, 140.3, 140.6, 180.1, 189.1 HRMS (ESI) calcd. for $C_{18}H_{17}O_2^+$ $[M+H]^+$ 265.1223; found 265.1227.

(*2Z,4E*)-5-(4-Bromophenyl)-3-hydroxy-1-phenylpenta-2,4-dien-1-one (2 d): Yield 17 mg (80 %). Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 6.34 (s, 1H), 6.63 (d, J=15.8 Hz, 1H), 7.42 (d, J=8.5 Hz, 2H), 7.46–750 (m, 2H), 7.52–7.57 (m, 3H), 7.61 (d, J=15.8 Hz, 1H), 7.94–7.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 98.0, 124.1, 124.3, 127.5, 128.8, 129.5, 132.3, 132.8, 134.2, 136.4, 138.7, 178.9, 189.9. HRMS (ESI) calcd. for $C_{17}H_{14}BrO_2^+$ $[M+H]^+$ 329.0172; found 329.0180.

General procedure for synthesis of 2,6-diaryl-2,3-dihydro-4*H*-pyran-4-ones 3 a–d from enynones1 in TfOH. TfOH (0.1 ml, 1.29 mmol) was added with vigorous stirring at room temperature to a solution of enynone **1** (0.086 mmol) in CH_2Cl_2 (0.1 ml).The mixture was stirred for 1 h. Then reaction mixture was poured into H_2O (50 ml), extracted with $CHCl_3$ (3×25 ml). The combined extracts were consequently washed with H_2O (50 ml), saturated aqueous solution of $NaHCO_3$(25 ml), again with H_2O (25 ml) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the product was isolated by preparative TLC on LS 5/40 μm silica gel plates, eluent-petroleum ether-EtOAc, 95:5 vol. The separated fractions were washed off from the sorbent with CH_2Cl_2.

2,6-Diphenyl-2,3-dihydro-4H-pyran-4-one (3 a):[11] Yield 11 mg (50 %). Pale-yellow solid. Mp 94–95°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.75 (ddd, ^2J=16.9, ^3J=3.4, ^4J=0.8 Hz, 1H), 2.97 (dd, ^2J=16.9, ^3J=14.1 Hz, 1H), 5.59 (dd, ^3J=14.1, ^3J=3.4 Hz, 1H), 6.13 (d, 4 J= 0.8 Hz, 1H), 7.41–7.47 (m, 4H), 7.48–7.52 (m, 3H), 7.77–7.80 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 43.1, 81.2, 102.5, 126.3, 126.8, 128.9, 129.0, 131.9, 132.7, 138.5, 170.5, 193.1. HRMS (ESI) calcd. for $C_{17}H_{15}O_2^+$ $[M+H]^+$ 251.1067; found 251.1073.

6-(4-Chlorophenyl)-2-phenyl-2,3-dihydro-4H-pyran4-one (3 b): Yield 13 mg (60 %). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.75 (ddd, ^2J=16.9, ^3J=3.4, ^4J=0.9, 1H), 2.96 (dd, ^2J=16.9, ^3J=14.1, 1H), 5.58 (dd, ^3J=14.1, ^3J=3.4 Hz, 1H), 6.09 (d, ^4J=0.9 Hz, 1H), 7.41 (d, J=8.8 Hz, 2H), 7.44–7.48 (m, 5H), 7.71 (d, J=8.8, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 43.1, 81.4, 102.6, 126.4, 128.1, 129.0, 129.1, 129.2, 131.2, 138.1, 138.3, 169.2, 192.8. HRMS (ESI) calcd. for $C_{17}H_{14}ClO_2^+$ $[M+H]^+$ 285.0677; found 285.0683.

6-(4-Bromophenyl)-2-phenyl-2,3-dihydro-4H-pyran4-one (3 c): Yield 10 mg (50 %). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.75 (ddd, ^2J=17.0, ^3J=3.4, ^4J=0.9 Hz, 1H), 2.96 (dd, ^2J=17.0, ^3J= 14.1 Hz, 1H), 5.58 (dd, ^3J=14.1, ^3J=3.4 Hz, 1H), 6.10 (d, ^4J=0.9 Hz, 1H), 7.42–7.50 (m, 5H), 7.57 (d, J=8.8 Hz, 2H), 7.64 (d, J=8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 43.0, 81.4, 102.6, 126.4, 126.6, 128.3, 129.1, 132.2, 138.2, 169.4, 192.9. HRMS (ESI) calcd. for $C_{17}H_{14}BrO_2^+$ $[M+H]^+$ 329.0172; found 329.0180.

6-(4-Methylphenyl)-2-phenyl-2,3-dihydro-4H-pyran4-one (3 d): Yield 10 mg (50 %). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.40 (s, 3H), 2.73 (ddd, ^2J=16.9, ^3J=3.4, ^4J=0.9 Hz, 1H), 2.96 (dd, ^2J=16.9, ^3J=14.1 Hz, 1H), 5.56 (dd, ^3J=14.1, ^3J=3.4 Hz, 1H), 6.12 (d, ^4J=0.9 Hz, 1H), 7.25–7.27 (m, 2H), 7.39 (d, J=8.0 Hz, 2H), 7.42–7.44 (m, 2H), 7.47–7.51 (m, 2H), 7.76–7.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 21.4, 43.0, 81.2, 102.4, 126.4, 126.8, 128.8, 129.7, 131.9, 132.8, 135.4, 139.0, 170.6, 193.3. HRMS (ESI) calcd. for $C_{18}H_{17}O_2^+$ $[M+H]^+$ 265.1223; found 265.1230.

General procedure for synthesis of 1,3,5-triarylpenta-2,4-dien-1-one 4 a- from enynones 1 in TfOH. TfOH (0.129 mmol) was added with vigorous stirring at room temperature to a solution of enynone **1** (0.086 mmol), arene (0.103 mmol) in CH_2Cl_2 (0.1 ml).The mixture was stirred for 0.5 h. Then reaction mixture was poured into H_2O (50 ml), extracted with $CHCl_3$ (3×25 ml). The combined extracts were consequently washed with H_2O (50 ml), saturated aqueous solution of $NaHCO_3$(25 ml), again with H_2O (25 ml) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the product was isolated by preparative TLC on LS 5/40 μm silica gel plates, eluent petroleum ether-EtOAc, 95:5, vol. The separated fractions were washed off from the sorbent with CH_2Cl_2.

(*2Z,4E*)-3-(2,4,6-Trimethylphenyl)-1,5-diphenylpenta-2,4-dien-1-one (4 a): Yield 21 mg (70 %). Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.11 (s, 6H), 2.34 (s, 3H), 6.39 (d, J=15.7 Hz, 1H), 6.92 (s, 2H), 7.20 (d, J=15.7 Hz, 1H), 7.29–7.36 (m, 4H), 7.43–7.46 (m, 4H), 7.51–7.54 (m, 1H), 7.95–7.97 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm: 19.8, 21.4, 124.8, 127.4, 128.2, 128.3, 128.6, 128.8, 128.9, 130.7, 132.6, 133.7, 134.8, 136.5, 136.6, 137.5, 138.9, 154.2, 189.6. HRMS (ESI) calcd. for $C_{26}H_{25}O^+$ $[M+H]^+$ 353.1900, found 353.1903.

(*2Z,4E*)-3-(2,4,6-Trimethylphenyl)-5-phenyl-1-(4-methylphenyl) penta-2,4-dien-1-one (4 b): Yield 26 mg (90 %). Green oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.10 (s, 6H), 2.34 (s, 3H), 2.41 (s, 3H), 6.37 (d, J=15.7 Hz, 1H), 6.91 (s, 2H), 7.18 (d, J=15.7 Hz, 1H), 7.23–7.26 (m, 3H), 7.28–7.35 (m, 3H), 7.43 (d, J=7.2 Hz, 2H), 7.87 (d, J=8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm: 19.8, 21.4, 21.7, 124.9, 127.4, 128.1, 128.5, 128.8, 129.3, 130.8, 133.7, 134.8, 136.3, 136.5, 136.6, 137.2, 143.3, 153.8, 189.2. HRMS (ESI) calcd. for $C_{27}H_{27}O^+$ $[M+H]^+$ 367.2056, found 367.2058.

(*2E-,4E-*)/(*2Z-,4E-*)-1-(4-Chlorophenyl)-3-(2,4,6-trimethylphenyl)-5-phenylpenta-2,4-dien-1-one (4 c): *2E-,4E-*/*2Z-,4E-* in a ratio of 5:4. General yield of 20 mg (70 %).

***2Z-,4E-*4c:** ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.09 (s, 6H), 2.35 (s, 3H), 6.40 (d, J=15.6 Hz, 1H), 6.93 (s, 2H), 7.19 (d, J= 15.6 Hz, 1H), 7.20 (s, 1H), 7.29–7.36 (m, 3H), 7.40–7.45 (m, 4H), 7.89 (d, J=8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ, ppm: 19.8, 21.4, 124.2, 127.5, 128.2, 128.9, 129.7, 129.7, 130.5, 133.5, 134.7, 136.4, 136.7, 137.2, 138.0, 138.9, 154.9, 188.3. ***2E-,4E-*4c**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.22 (s, 6H), 2.38 (s, 3H), 6.46 (d, J=16.0 Hz, 1H), 6.68 (s, 1H), 6.98 (s, 2H), 7.28–7.34 (m, 3H), 7.44 (d, J=8.6 Hz, 2H), 7.48–7.50 (m, 2H), 7.92 (d, J=8.6 Hz, 2H), 8.61 (d, J=16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), selected signals δ, ppm: 20.0, 21.2, 122.5, 126.0, 127.9, 128.4, 128.8, 129.0, 129.2, 129.8, 135.7, 136.5, 137.2, 140.1, 156.0, 189.9. HRMS (ESI) calcd. for $C_{26}H_{24}ClO^+$ $[M+H]^+$: 387.1510, found 387.1513.

(*2E-,4E-*)/(*2Z-,4E-*)-1-(4-Bromophenyl)-3-(2,4,6-trimethylphenyl)-5-phenylpenta-2,4-dien-1-one (4 d): (*2E,4E*)/(*2Z-,4E-*)- in a ratio of 5:4. General yield of 22 mg (80 %). ***2Z-,4E-*4 d:** ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.07 (s, 6H), 2.37 (s, 3H), 6.39 (d, J= 15.6 Hz, 1H), 6.91 (s, 2H), 7.17 (d, J=15.6 Hz, 1H), 7.18 (s, 1H), 7.28–7.35 (m, 3H), 7.42–7.44 (m, 2H), 7.57 (d, J=8.5 Hz, 2H), 7.80 (d, J= 8.5 Hz, 2H).

***2E-,4E-*4 d:** ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm:2.21 (s, 6H), 2.37 (s, 3H), 6.44 (d, J=16.0 Hz, 1H), 6.66 (s, 1H), 6.97 (s, 2H), 7.28–7.35 (m, 3H), 7.47–7.49 (m, 2H), 7.60 (d, J=8.6 Hz, 2H), 7.83 (d, J=8.6 Hz, 2H), 8.59 (d, J=16.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm (for mixture of ***(2E-,4E-)*/(*2Z-,4E-*)**-isomers): 19.8, 20.0, 21.2, 21.4, 122.4, 124.1, 126.1, 127.5, 127.6, 127.8, 128.0, 128.2, 128.4, 128.8, 128.9, 129.1, 129.2, 129.8, 129.9, 130.5, 131.9, 132.0, 133.5, 134.7, 135.7, 136.4, 136.5, 136.7, 136.8, 137.4, 137.6, 138.1, 138.5, 140.2, 155.0, 156.1, 188.5, 190.0. HRMS (ESI) calcd. for $C_{26}H_{23}BrNaO$[M+Na]: 453.0830, found 453.0835.

(*2E-,4E-*)/(*2Z-,4E-*)-3-(2,4,6-Trimethylphenyl)-1-(4-nitrophenyl)-5-phenylpenta-2,4-dien-1-one (4 e): (*2E,4E*)/(*2Z-,4E-*)- in a ratio of 9:10. General yield of 24 mg (83 %). ***(2Z,4E)*-4 e**: Green crystals. M.p.

146–148 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.09 (s, 6H), 2.34 (s, 3H), 6.46 (d, J = 15.8 Hz, 1H), 6.92 (s, 2H), 7.20 (s, 1H), 7.21 (d, J = 15.8 Hz, 1H), 7.31–7.37 (m, 3H), 7.44–7.46 (m, 2H), 8.04 (d, J = 8.8 Hz, 2H), 8.27 (d, J = 8.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ, ppm: 19.8, 21.3, 123.8, 127.6, 128.3, 128.9, 129.1, 130.2, 134.7, 139.3, 149.9, 156.7, 188.1. **(*2E,4E*)-4 e**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.22 (s, 6H), 2.38 (s, 3H), 6.53 (d, J = 16.0 Hz, 1H), 6.70 (s, 1H), 6.98 (s, 2H), 7.19 (s, 1H), 7.31–7.37 (m, 3H), 7.50–7.52 (m, 2H), 8.10 (d, J = 8.8 Hz, 2H), 8.31 (d, J = 8.8 Hz, 2H), 8.66 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ, ppm: 20.0, 21.2, 121.7, 125.8, 158.0, 189.2.^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm (for mixture of **(*2E,4E*)/(*2Z-,4E-*)**-isomers): 19.8, 20.0, 21.2, 21.3, 121.7, 123.7, 123.8, 123.9, 125.8, 127.6, 128.1, 128.3, 128.5, 128.9, 129.0, 129.1, 129.3, 129.4, 129.6, 130.2, 133.1, 134.7, 135.6, 136.2, 136.5, 137.1, 137.6, 139.3, 141.6, 143.7, 144.5, 149.9, 156.7, 158.0, 188.1. HRMS (ESI) calcd. for $C_{26}H_{23}NNaO_3$ [M + Na]: 420.1576, found 420.1570.

(*2E-,4E-*)/(*2Z-,4E-*)-3-(2,4,6-Trimethylphenyl)-5-(4-methylphenyl)-1-phenylpenta-2,4-dien-1-one (4 f): (*2E-,4E-*)/(*2Z-,4E-*)- in a ratio of 10 : 8. General yield of 70 %. Green oil. ***(2E,4E)*-4 f**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.22 (3, 6H), 2.34 (s, 3H), 2.36 (s, 3H), 6.41 (d, J = 16.1 Hz, 1H), 6.70 (s, 1H), 6.97 (s, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.10–7.57 (m, 5H), 7.97–8.00 (m, 2H), 8.59 (d, J = 16.1 Hz, 1H). **(*2Z,4E*)-4 f**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.09 (3, 6H), 2.34 (s, 3H), 2.35 (s, 3H), 6.36 (d, J = 15.8 Hz, 1H), 6.91 (s, 2H), 7.23 (s, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.09–7.57 (m, 6H), 7.92–7.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm (for mixture of **(*2E,4E*)/(*2Z-,4E-*)**-isomers): 191.33, 189.60, 155.68, 154.63, 139.81, 139.78, 139.34, 139.17, 138.98, 137.64, 137.18, 136.76, 136.54, 135.77, 134.77, 134.07, 133.82, 133.80, 132.61, 132.50, 129.76, 129.60, 129.51, 128.69, 128.59, 128.38, 128.32, 128.30, 128.15, 127.91, 127.40, 125.30, 124.23, 122.70, 21.50, 21.47, 21.37, 21.22, 20.01, 19.79. HRMS (ESI) calcd. for $C_{27}H_{27}O^+$ [M + H] $^+$ 367.2056, found 367.2061.

(*2E-,4E-*)/(*2Z-,4E-*)-1,5-Diphenyl-3-(2,3,5,6-tetramethylphenyl) penta-2,4-dien-1-one (4 g): (*2E-,4E-*)/(*2Z-,4E-*)- in a ratio of 2 : 5. General yield of 60 %. Green oil. ***(2Z,4E)*-4 g**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm:2.00 (s, 6H), 2.24 (s, 6H), 6.33 (d, J = 15.7 Hz, 1H), 6.96 (s, 1H), 7.20 (d, J = 15.7 Hz, 1H), 7.24 (s, 1H), 7.27–7.35 (m, 3H), 7.41–7.46 (m, 4H), 7.48–7.52 (m, 1H), 7.90–7.93 (m, 2H).^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 16.4, 20.2, 155.2, 190.0. ***(2E,4E)*-4 g**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.13 (s, 6H), 2.29 (s, 6H), 6.41 (d, J = 16.0 Hz, 1H), 8.64 (d, J = 16.0 Hz,1H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 16.8, 20.2, 156.6, 191.4. ^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm (for mixture of **(*2E,4E*)/(*2Z-,4E-*)**-isomers): 123.3, 125.0, 126.6, 127.4, 127.9, 128.3, 128.4, 128.5, 128.7, 128.8, 128.9, 129.0, 129.1, 130.8, 130.9, 131.4, 131.7, 132.5, 132.7, 133.2, 133.9, 136.5, 136.6, 136.9, 137.8, 139.0, 140.0. HRMS (ESI) calcd. for $C_{27}H_{27}O^+$ [M + H]$^+$ 367.2056, found 367.2061.

(*2E-,4E-*)/(*2Z-,4E-*)-1-(4-Methylphenyl)-5-phenyl-3-(2,3,5,6-tetramethylphenyl)-penta-2,4-dien-1-one (4 h). (*2E-,4E-*)/(*2Z-,4E-*)- in a ratio of 1 : 4. General yield of 25 mg (80 %). Green oil. **(*2Z,4E*)-4 h**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.01 (s, 6H), 2.25 (s, 6H), 2.40 (s, 3H), 6.32 (d, J = 15.7 Hz, 1H), 7.19 (d, J = 15.8 Hz, 1H), 7.22 (s, 1H), 7.25–7.36 (m, 5H), 7.42–7.45 (m, 2H), 7.84 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), selected signals δ, ppm: 16.4, 20.2, 21.7, 125.1, 127.4, 128.4, 128.80, 128.82, 129.3, 130.8, 131.2, 133.1, 136.4, 136.6, 136.7, 137.5, 143.2, 154.7, 189.5.

(*2E,4E*)-4 h: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.13 (s, 6H), 2.30 (s, 6H), 2.42 (s, 3H), 6.39 (d, J = 16.1 Hz, 1H), 6.70 (s, 1H), 7.27–7.33 (m, 5H), 7.89 (d, J = 8.2 Hz, 2H), 8.64 (d, J = 16.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), selected signals δ, ppm: 16.8, 20.2, 21.8, 123.5, 126.6, 127.4, 127.9, 128.6, 128.7, 129.0, 129.4, 130.9, 131.7, 133.9, 136.9, 137.2, 139.62, 139.64, 143.4, 156.0, 191.0. HRMS (ESI) calcd. for $C_{28}H_{28}NaO$ [M + Na] 403.2038, found 403.2043.

(*2E-,4E-*)/(*2Z-,4E-*)-3-(2,5-Dimethylphenyl)-1,5-diphenylpenta-2,4-dien-1-one (4 i): Green oil. **(*2E-,4E-*)/(*2Z-,4E-*)**- in a ratio of 10 : 7. General yield of 17 mg (60 %). **(*2Z,4E*)-4 i**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.16 (s, 3H), 2.33 (s, 3H), 6.39 (d, J = 15.8 Hz, 1H), 6.85 (s, 1H), 7.16 (s, 1H), 7.20 (d, J = 15.8 Hz, 1H), 7.30–7.36 (m, 4H), 7.43–7.47 (m, 4H), 7.50 (d, J = 8.0 Hz, 2H), 7.93–7.95 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), selected signals δ, ppm: 19.2, 19.5, 21.1, 21.2, 122.9, 124.9, 126.8, 127.4, 127.8, 128.4, 128.5, 128.7, 128.8, 128.9, 129.0, 129.1, 129.8, 129.9, 130.2, 131.6, 132.5, 132.7, 134.9, 135.3, 136.5, 136.8, 136.9, 138.7, 139.1, 139.7, 139.9, 140.9, 154.5, 156.0, 190.3, 191.4. **(*2E,4E*)-4 i**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.27 (s, 3H), 2.40 (s, 3H), 6.47 (d, J = 16.1 Hz, 1H), 6.78 (s, 1H), 7.15 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 8.60 (d, J = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), selected signals δ, ppm: 19.2, 19.5, 21.1, 21.2, 122.9, 124.9, 126.8, 127.4, 127.8, 128.4, 128.5, 128.7, 128.8, 128.9, 129.0, 129.1, 129.8, 129.9, 130.2, 131.6, 132.5, 132.7, 134.9, 135.3, 136.5, 136.8, 136.9, 138.7, 139.1, 139.7, 139.9, 140.9, 154.5, 156.0, 190.3, 191.4. HRMS (ESI) calcd. for $C_{25}H_{23}O^+$ [M + H]$^+$ 339.1743, found 339.1748.

(*2E-,4E-*)/(*2Z-,4E-*)-1-(4-methylphenyl)-3-(2,5-dimethylphenyl)-5-phenylpenta-2,4-dien-1-one (4 j): (*2E-,4E-*)/(*2Z-,4E-*)- in a ratio of 6 : 10. General yield of 70 %. Green oil. **(*2Z,4E*)-4 j**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.13 (s, 3H), 2.30 (s, 3H), 2.40 (s, 3H), 6.34 (d, J = 15.7 Hz, 1H), 6.83 (s, 1H), 7.05–7.08 (m, 1H), 7.11–7.36 (m, 8H), 7.42 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H). **(*2E,4E*)-4 j**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.24 (s, 3H), 2.38 (s, 3H), 2.42 (s, 3H), 6.42 (d, J = 16.1 Hz, 1H), 6.74 (s, 1H), 7.05 (s, 1H), 7.12–7.36 (m, 7H), 7.48 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 8.56 (d, J = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm (for mixture of **(*2E,4E*)/(*2Z-,4E-*)**-isomers): 19.2, 19.5, 21.1, 21.2, 21.7, 21.8, 123.1, 125.0, 126.9, 127.3, 127.8, 128.5, 128.6, 128.8, 128.9, 129.3, 129.4, 129.7, 129.9, 130.2, 131.8, 132.5, 132.8, 134.9, 135.3, 136.5, 136.6, 136.9, 137.0, 137.1, 138.4, 140.0, 140.5, 143.3, 191.0, 143.5, 147.7, 154.0, 154. 9, 155.6, 189.8. HRMS (ESI) calcd. for $C_{26}H_{25}O^+$ [M + H]$^+$ 353.1900, found 353.1905.

(*2E-,4E-*)/(*2Z-,4E-*)-1-(4-Bromophenyl)-3-(2,5-dimethylphenyl)-5-phenylpenta-2,4-dien-1-one (4 k): (*2E-,4E-*)/(*2Z-,4E-*)- in a ratio of 10 : 6. General yield of 72 %. Green oil. **(*2E,4E*)-4 k**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.23 (s, 3H), 2.37 (s, 3H), 6.47 (d, J = 16.1 Hz, 1H), 6.69 (s, 1H), 7.03 (s, 1H), 7.05–7.37 (m, 5H), 7.46–7.50 (m, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 8.57 (d, J = 16.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), selected signals δ, ppm: 19.5, 21.1, 122.0, 126.7, 127.4, 127.9, 128.8, 130.0, 132.0, 132.7, 135.4, 136.7, 138.4, 139.8, 141.5, 156.9, 190.1. **(*2Z,4E*)-4 k**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.12 (s, 3H), 2.30 (s, 3H), 6.37 (d, J = 15.8 Hz, 1H), 6.80 (s, 1H), 7.37–7.06 (m, 7H), 7.44–7.39 (m, 2H), 7.55 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), selected signals δ, ppm: 19.1, 21.2, 124.2, 127.6, 127.8, 128.7, 128.8, 129.1, 129.8, 131.4, 132.4, 135.0, 136.4, 136.6, 137.8, 139.3, 155.2, 189.3. HRMS (ESI) calcd. for $C_{25}H_{22}BrO^+$ [M + H]$^+$ 417.0849, found 417.0854.

(*2E-,4E-*)/(*2Z-,4E-*)-1-(4-Chlorophenyl)-3-(2,5-dimethylphenyl)-5-phenylpenta-2,4-dien-1-one (4 l): (*2E-,4E-*)/(*2Z-,4E-*)- in a ratio of 10 : 7. General yield of 40 %. **(*2E,4E*)-4 l**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.23 (s, 3H), 2.37 (s, 3H), 6.46 (d, J = 16.1 Hz, 1H), 6.69 (s, 1H), 7.03 (s, 1H), 7.42–7.05 (m, 5H), 7.44 (d, J = 8.6 Hz, 2H), 7.46–7.50 (m, 2H), 7.93 (d, J = 8.6 Hz, 2H), 8.57 (d, J = 16.1 Hz, 1H). **(*2Z,4E*)-4 l**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.12 (s, 3H), 2.30 (s, 3H), 6.37 (d, J = 15.7 Hz, 1H), 6.80 (s, 1H), 7.05–7.52 (m, 9H), 7.39 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ, ppm (for mixture of **(*2E,4E*)/(*2Z-,4E-*)**-isomers): 19.2, 19.5, 21.1, 21.2, 122.1, 124.3, 126.7, 127.4, 127.9, 128.8, 128.9,

129.0, 129.1, 129.2, 129.8, 129.8, 130.3, 131.4, 132.4, 132.7, 135.0, 135.4, 136.4, 136.7, 136.7, 137.4, 138.0, 138.9, 139.1, 139.2, 139.8, 141.4, 155.1, 156.8, 189.1, 189.9. HRMS (ESI) $C_{25}H_{22}ClO^+$ $[M+H]^+$ calcd. for 373.1354, found 373.1359.

General procedure for synthesis of 1-aryl-2-(3-aryl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-ones 5a-am from enynones1 in TfOH. TfOH (0.1 ml, 1.29 mmol) was added with vigorous stirring at room temperature to a solution of enynone**1** (0.086 mmol), arene (0.103 mmol) in CH_2Cl_2 (0.1 ml), the mixture was stirred for 1–3 h. The reaction mixture was poured into H_2O (50 ml), extracted with $CHCl_3$ (3×25 ml). The combined extracts were consequently washed with H_2O (50 ml), saturated aqueous solution of $NaHCO_3$(25 ml), again with H_2O (25 ml) and dried with Na_2SO_4. The solvent was removed under reduced pressure, the product was isolated by preparative TLC on LS 5/40 μm silica gel plates, eluent petroleum ether-EtOAc, 95:5, vol. The separated fractions were washed off from the sorbent with CH_2Cl_2.

1-Phenyl-2-(3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5a): ***E*-/*Z*-5a** in a ratio of5:1. General yield of 16 mg (60%). Yellow oil. ***E*-5a**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 3.44 (ddd, ^4J=2.5, ^3J=4.0, ^2J=20.3 Hz, 1H), 4.07 (ddd, ^4J=2.5, ^3J=8.2, ^2J=20.3 Hz, 1H), 4.55 (dd, ^3J=4.0, ^3J=8.21 Hz, 1H), 7.13–7.15 (m, 2H), 7.19–7.24 (m, 1H), 7.26–7.33 (m, 3H), 7.34–7.42 (m, 2H), 7.47–7.52 (m, 2H), 7.54–7.58 (m, 2H), 7.82–7.84 (m, 1H), 8.04–8.06 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 43.4, 49.6, 111.9, 121.6, 126.5, 126.7, 127.6, 127.8, 128.1, 128.7, 128.8, 131.8, 132.4, 139.8, 140.6, 145.0, 153.1, 162.8, 190.8. ***Z*-5a**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 3.55 (ddd, ^2J=17.2, ^3J=8.0, ^4J=1.9 Hz, 1H), 4.47 (dd, ^3J=5.2, ^3J=8.0 Hz, 1H), 7.00 (t, ^4J=1.9 Hz, 1H). HRMS (ESI) calcd. for $C_{23}H_{19}O^+$ $[M+H]^+$ 311.1430; found 311.1433.

(*E*)-1-(4-Methylphenyl)2-(3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)-ethan-1-one (5b): Yield 20 mg (77%). Yellow crystals. M.p. 133–135 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.43 (s, 3H), 3.43 (ddd, ^4J=2.5, ^3J=3.9, ^2J=20.2 Hz, 1H), 4.06 (ddd, ^4J=2.5, ^3J=8.2, ^2J=20.2 Hz, 1H), 4.55 (dd, ^3J=3.9, ^3J=8.2 Hz, 1H), 7.13–7.15 (m, 2H), 7.17–7.23 (m, 2H), 7.27–7.31 (m, 4H), 7.32–7.40 (m, 2H), 7.55 (t, ^4J=2.5 Hz, 1H), 7.82–7.84 (m, 1H), 7.94–7.97 (d, J=8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 21.7, 43.4, 49.6, 112.0, 121.6, 126.5, 126.7, 127.5, 127.8, 128.2, 128.8, 129.4, 131.7, 137.3, 140.6, 143.0, 145.1, 152.9, 162.3, 190.4. HRMS (ESI) calcd. for $C_{24}H_{21}O^+$ $[M+H]^+$ 325.1587, found 325.1590.

(*E*)-1-(4-Chlorophenyl)-2-(3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5c): Yield 21 mg (80%).Yellow crystals. M.p. 159–161 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.42 (ddd, ^4J=2.5, ^3J=3.8, ^2J=20.3 Hz, 1H), 4.04 (ddd, ^4J=2.5, ^3J=8.1, ^2J=20.3 Hz, 1H), 4.55 (dd, ^3J=3.8, ^3J=8.1 Hz, 1H), 7.12–7.14 (m, 2H), 7.18–7.24 (m, 2H), 7.27–7.31 (m, 2H), 7.34–7.42 (m, 2H), 7.47 (d, J=8.6 Hz, 2H), 7.50 (t, ^4J=2.5 Hz,1H), 7.82 (d, J=7.1 Hz, 1H), 7.98 (d, J=8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 43.6, 49.6, 111.4, 121.7, 126.6, 126.8, 127.6, 127.8, 128.8, 129.0, 129.6, 132.1, 138.2, 138.7, 140.4, 144.9, 153.3, 163.6, 189.4. HRMS (MALDI) calcd. for $C_{23}H_{18}ClO^+$ $[M+H]^+$ 345.1041 found 345.1044.

(*E*)-1-(4-Bromophenyl)-2-(3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5d): Yield 18 mg (72%). Yellow crystals. M.p. 132–135 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.41 (ddd, ^4J=2.5, ^3J=3.8, ^2J=20.3 Hz, 1H), 4.04 (ddd, ^4J=2.5, ^3J=8.1, ^2J=20.3 Hz, 1H), 4.55 (dd, ^3J=3.8, ^3J=8.1 Hz, 1H), 7.12–7.14 (m, 2H), 7.18–7.23 (m, 2H), 7.27–7.31 (m, 2H), 7.36–7.40 (m, 2H), 7.49 (t, ^4J=2.5 Hz, 1H), 7.63 (d, J=8.6 Hz, 2H), 7.81–7.83 (m, 1H), 7.90 (d, J=8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 43.6, 49.6, 111.4, 121.7, 126.6, 126.8, 127.6, 127.8, 128.8, 129.0, 129.6, 132.1, 138.2, 138.7, 140.4, 144.9, 153.3, 163.6, 189.4. HRMS (ESI) calcd. for $C_{23}H_{18}BrO^+$ $[M+H]^+$ 389.0536, found 389.0539.

(*E*)-1-(4-Nitrophenyl)-2-(3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene) ethan-1-one (5e): Yield 15 mg (60%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.43 (ddd, ^4J=2.4, ^3J=3.6, ^2J=20.5 Hz, 1H), 4.07 (ddd, ^4J=2.4, ^3J=8.0, ^2J=20.5 Hz, 1H), 4.57 (dd, ^3J=3.6, ^3J=8.0 Hz, 1H), 7.12–7.14 (m, 2H), 7.21–7.25 (m, 2H), 7.28–7.32 (m, 2H), 7.36–7.48 (m, 2H), 7.51 (t, J^4=2.4 Hz, 1H), 8.16 (d, J=8.8 Hz, 2H), 8.34 (d, J=8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 43.8, 49.5, 111.1, 121.8, 123.9, 126.7, 126.9, 127.7, 127.8, 128.9, 129.1, 132.6, 140.1, 144.6, 144.7, 149.9, 153.7, 165.6, 188.8. HRMS (ESI) calcd. for $C_{23}H_{18}NO_3^+$ $[M+H]^+$ 356.1281; found 356.1286.

(*E*)-2-(3-(4-Methylphenyl)-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenyl-ethan-1-one (5f): Yield 15 mg (56%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 2.32 (s, 3H), 3.41 (ddd, ^4J=2.5, ^3J=3.9, ^2J=20.3 Hz, 1H), 4.04 (ddd, ^4J=2.5, ^3J=8.1, ^2J=20.3 Hz, 1H), 4.51 (dd, ^3J=3.9, ^3J=8.1 Hz, 1H), 6.84 (s, 1H), 7.03 (d, J=8.0 Hz, 2H), 7.10 (d, J=8.0 Hz, 2H), 7.17–7.19 (m, 1H), 7.33–7.40 (m, 2H), 7.50 (d, J=7.6 Hz, 2H), 7.54–7.56 (m, 2H), 7.81–7.83 (m, 1H), 8.02–8.04 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 21.0, 43.4, 49.1, 111.7, 121.4, 126.4, 127.3, 127.6, 128.7, 128.0, 128.5, 129.3, 131.7, 132.2, 136.1, 139.7, 140.4, 141.9, 153.2, 162.8, 190.7. HRMS (ESI) calcd. for $C_{24}H_{21}O^+$ $[M+H]^+$ 325.1587, found 325.1592.

(*E*)-2-(3-(4-Chlorophenyl)-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenylethan-1-one (5g): Yield 15 mg (57%).Green oil.^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.40 (ddd, ^4J=2.5, ^3J=3.9, ^2J=20.2 Hz, 1H), 4.05 (ddd, ^4J=2.5, ^3J=8.2, ^2J=20.2 Hz, 1H), 4.52 (dd, ^3J=3.9, ^3J=8.2 Hz, 1H), 7.06 (d, J=8.4 Hz, 2H), 7.17–7.22 (m, 1H), 7.26 (d, J=8.4 Hz, 2H), 7.36–7.40 (m, 2H), 7.50–7.55 (m, 3H), 7.56 (t, ^4J=2.5 Hz, 1H) 7.82–7.84 (m, 1H), 8.03–8.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 43.3, 48.9, 112.1, 121.7, 126.4, 127.8, 128.1, 128.7, 129.0, 129.2, 131.9, 132.4, 132.5, 139.7, 140.5, 143.6, 152.5, 162.3, 190.8. HRMS (MALDI) calcd. for $C_{23}H_{18}ClO^+$ $[M+H]^+$ 345.1041 found 345.1044.

(*E*)-2-(3-(4-Bromophenyl)-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenylethan-1-one (5h): Yield 24 mg (96%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.40 (ddd, ^4J=2.5, ^3J=3.9, ^2J=20.2 Hz, 1H), 4.05 (ddd, ^4J=2.5, ^3J=8.2, ^2J=20.2 Hz, 1H), 4.52 (dd, ^3J=3.9, ^3J=8.2 Hz, 1H), 7.06 (d, J=8.4 Hz, 2H), 7.17–7.22 (m, 1H), 7.26 (d, J=8.4 Hz, 2H), 7.36–7.40 (m, 2H), 7.50–7.55 (m, 3H), 7.56 (t, ^4J=2.5 Hz, 1H) 7.82–7.84 (m, 1H), 8.03–8.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 43.3, 48.9, 112.1, 121.7, 126.4, 127.8, 128.1, 128.7, 129.0, 129.2, 131.9, 132.4, 132.5, 139.7, 140.5, 143.6, 152.5, 162.3, 190.8. HRMS (MALDI) calcd. for $C_{23}H_{18}BrO^+$ $[M+H]^+$ 389.0536 found 389.0541.

(*E*)-1-(5-Bromofuran-2-yl)-2-(3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5i): Yield 25 mg (98%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ, ppm: 3.41 (ddd, ^4J=2.5, ^3J=3.7, ^2J=20.4 Hz, 1H), 4.05 (ddd, ^4J=2.5, ^3J=8.1, ^2J=20.4 Hz, 1H), 4.53 (dd, ^3J=3.7, ^3J=8.1 Hz, 1H), 6.51 (d, ^3J=3.5 Hz, 1H), 7.11–7.13 (m, 2H), 7.17–7.19 (m, 1H), 7.19 (d, ^3J=3.5 Hz, 1H), 7.21–7.23 (m, 1H), 7.27–7.30 (m, 2H), 7.34–7.41 (m, 3H), 7.84–7.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ, ppm: 43.4, 49.6, 110.7, 114.6, 117.9, 122.0, 126.5, 126.8, 127.0, 127.6, 127.8, 128.8, 132.1, 140.3, 144.9, 153.3, 156.6, 163.8, 177.8. HRMS (ESI) calcd. for $C_{21}H_{16}BrO_2^+$ $[M+H]^+$ 379.0328, found 379.0332.

2-(4,7-Dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenylethan-1-one (5j): ***E*-/*Z*-5** in a ratio of 3:1. General yield of 20 mg (60%). Yellow oil. ***E*-5j**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 1.99 (s, 3H), 2.7 (s, 3H), 3.50 (dt, ^4J=2.2, ^3J=2.2, ^2J=19.8 Hz, 1H), 3.90 (ddd, ^4J=2.2, ^3J=8.6, ^2J=19.8, Hz, 1H), 4.52 (dd, ^3J=8.6,

^3J = 2.2 Hz, 1H), 7.59 (t, ^4J = 2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 18.9, 22.5, 44.5, 48.6, 116.2, 126.3, 127.4, 128.1, 128.7, 128.7, 131.0, 132.22, 132.4, 133.4, 133.6, 138.9, 140.2, 145.2, 151.9, 164.6, 191.1. ***Z*-5 j**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.30 (s, 3H), 2.71 (s, 3H), 3.40–3.46 (m, 1H), 4.01–4.09 (m, 1H), 4.41–4.44 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 21.5, 22.4, 44.1, 49.1, 115.1, 124.5, 126.5, 127.8, 128.6, 131.5, 132.0, 140.1, 141.4, 145.3, 154.6, 154.6, 164.0. HRMS (ESI) $C_{25}H_{23}O^+$ $[M+H]^+$calcd. for 339.1743, found 339.1748.

***(E)*-2-(4,7-Dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)-1-(4-methylphenyl)ethan-1-one (5 k): *E*-/*Z*-5 k** in a ratio of 5:1. General yield of 14 mg (50%). Yellow oil. ***E*-5 k**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 1.98 (s, 3H), 2.42 (s, 3H), 2.73 (s, 3H), 3.44 (dt, ^4J = 2.3, ^3J = 2.3, ^2J = 19.7 Hz, 1H), 3.89 (ddd, ^4J = 2.3, ^3J = 8.6, ^2J = 19.7 Hz, 1H), 4.51 (dd, ^3J = 2.3, ^3J = 8.6 Hz, 1H), 6.99–7.01 (m, 2H), 7.08–7.10 (m, 1H), 7.12–7.16 (m, 2H), 7.19–7.3 (m, 2H), 7.26–7.28 (m, 2H), 7.57 (t, ^4J = 2.3 Hz, 1H), 7.89 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 18.9, 21.7, 22.4, 44.4, 48.6, 116.3, 126.3, 127.4, 128.3, 128.7, 129.4, 131.0, 132.3, 133.3, 133.6, 137.6, 138.9, 142.9, 151.3, 151.8, 164.1, 190.9. HRMS (ESI) $C_{26}H_{25}O^+$ $[M+H]^+$calcd. for 353.1900, found 353.1903. ***Z*-5 k**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 3.42 (m, 1H), 4.04 (m, 1H), 4.42 (m, 1H), 7.57 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 21.6, 22.5, 44.1, 49.3, 115.4. HRMS (ESI) $C_{26}H_{25}O^+$ $[M+H]^+$ calcd. for 353.1900, found 353.1903.

1-(4-Chlorophenyl)-2-(4,7-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one 5 l:. *E*-/*Z*-5 l in a ratio of 5:1. General yield of 18 mg (65%). Yellow oil. ***E*-5 l**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm:1.98 (s, 3H), 2.72 (s, 3H), 3.48 (dt, ^4J = 2.3, ^3J = 2.3, ^2J = 19.7 Hz, 1H), 3.88 (ddd, ^4J = 2.3, ^3J = 8.6, ^2J = 19.7 Hz, 1H), 4.51 (dd, ^3J = 2.3, ^3J = 8.6 Hz, 1H), 6.98–7.00 (m, 2H), 7.09–7.11 (m, 2H), 7.13–7.17 (m, 1H), 7.20–7.23 (m, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.52 (t, ^4J = 2.3 Hz, 1H), 7.91 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 18.9, 22.5, 44.5, 48.5, 115.6, 126.4, 127.4, 128.7, 128.9, 129.5, 131.1, 132.6, 133.5, 133.7, 138.4, 138.7, 142.9, 145.1, 152.0, 165.5, 189.7. **(*Z*)-5 l**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 2.05 (s, 3H), 2.70 (s, 3H), 3.38–3.44 (m, 1H), 4.03 (ddd, ^3J = 2.1, ^3J = 8.2, ^2J = 19.6 Hz, 1H), 4.41–4.45 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 18.5, 22.3, 44.3, 48.2, 164.9, 190.8. HRMS (MALDI) calcd. for $C_{25}H_{22}ClO^+$ $[M+H]^+$ 373.1354, found 373.1356.

1-(4-Bromophenyl)-2-(4,7-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 m): *E*-/*Z*-5 m in a ratio of 5:1. General yield of 17 mg (65%). Yellow oil. ***E*-5 m**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm:1.98 (s, 3H), 2.71 (s, 3H), 3.48 (dt, ^4J = 2.3, ^3J = 2.3, ^2J = 19.8 Hz, 1H), 3.88 (ddd, ^4J = 2.3, ^3J = 8.5, ^2J = 19.8 Hz, 1H), 4.51 (dd, ^3J = 2.3, ^3J = 8.5 Hz, 1H), 6.98–7.00 (m, 2H), 7.10–7.11 (m, 2H), 7.12–7.17 (m, 1H), 7.20–7.23 (m, 2H), 7.51 (t, ^4J = 2.3 Hz, 1H), 7.61 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 18.9, 22.5, 44.6, 48.5, 115.6, 126.4, 127.4, 128.7, 129.7, 131.1, 132.0, 132.6, 133.5, 133.7, 138.7, 138.9, 145.1, 152.1, 165.6, 189.9.

***Z*-5 m**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 3.38–3.44 (m, 1H), 4.03 (ddd, ^4J = 2.2, ^3J = 8.1, ^2J = 19.6 Hz, 1H), 4.43 (dd, ^3J = 4.2, ^3J = 8.1 Hz, 1H), 7.46 (t, ^4J = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ, ppm: 21.7, 44.3, 48.5, 114.6. HRMS (MALDI) calcd. for $C_{25}H_{22}BrO^+$ $[M+H]^+$ 417.0849, found 417.0852.

(*E*)1-(4-Nitrorophenyl)-2-(4,7-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 n): Yield 14 mg (50%). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.98 (s, 3H), 2.73 (s, 3H), 3.50 (dt, ^4J = 2.3, ^3J = 2.0, ^2J = 20.0 Hz, 1H), 3.91 (ddd, ^4J = 2.3, ^3J = 8.6, ^2J = 20.0 Hz, 1H), 4.54 (dd, ^3J = 2.3, ^3J = 8.6 Hz, 1H), 6.98–7.00 (m, 2H), 7.09–7.11 (m, 2H), 7.13 (s, 1H), 7.16–7.18 (m, 2H), 7.21–7.24 (m, 2H), 7.54 (t, ^4J = 2.3 Hz, 1H), 8.10 (d, J = 8.8 Hz, 2H), 8.32 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 18.9, 22.5, 44.9, 48.5, 115.2, 124.0, 126.5, 127.4, 128.8, 129.0, 131.3, 133.2, 133.7, 133.9, 138.4, 144.9, 145.1, 149.8, 152.5, 167.6, 189.1. HRMS (ESI) $C_{25}H_{21}NNaO_3^+$ $[M+Na]$ calcd. for 406.1419, found 406.1412.

(*E*)-2-(4,7-Dimethyl-3-(4-methylphenyl)-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenylethan-1-one (5 o): Yield 20 mg (70%). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.00 (s, 3H), 2.29 (s, 3H), 2.73 (s, 3H), 3.49 (dt, ^4J = 2.0, ^3J = 2.4, ^2J = 19.7 Hz, 1H), 3.89 (ddd, ^4J = 2.4, ^3J = 8.5, ^2J = 19.7 Hz, 1H), 4.49 (dd, ^3J = 2.0, ^3J = 8.5 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.08–7.13 (m, 2H), 7.46–7.50 (m, 2H), 7.52–7.56 (m, 2H), 7.59 (t, J^4 = 2.4 Hz, 1H), 7.98–8.00 (m, 2H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ, ppm: 18.9, 21.1, 22.4, 44.6, 48.1, 116.2, 127.3, 128.1, 128.6, 129.3, 130.9, 132.2, 132.4, 133.4, 133.6, 135.7, 138.8, 140.2, 142.2, 152.0, 164.8, 191.1. HRMS (ESI) $C_{26}H_{25}O^+$ $[M+H]^+$calcd. for 353.1900, found 353.1905.

2-(3-(4-Chlorophenyl)-4,7-dimethyl-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenylethan-1-one (5 p):*E*-/*Z*-5 p in a ratio of 5:1. General yield of 18 mg (66%). Green oil. ***E*-5 p**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 1.98 (s, 3H), 2.72 (s, 3H), 3.46 (dt, ^4J = 2.1, ^3J = 2.1, ^2J = 19.6 Hz, 1H), 3.88 (ddd, ^4J = 2.1, ^3J = 8.6, ^2J = 19.6 Hz, 1H), 4.49 (dd, ^3J = 2.1, ^3J = 8.6 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 7.07–7.14 (m, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.46–7.50 (m, 2H), 7.53–7.55 (m, 1H), 7.59 (t, ^4J = 2.3 Hz, 1H), 7.97–7.99 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 18.9, 22.4, 44.3, 47.9, 116.4, 128.1, 128.7, 128.8, 128.9, 129.1, 131.2, 132.3, 132.5, 133.5, 133.6, 138.8, 140.1, 143.8, 151.3, 164.0, 191.2. ***Z*-5 p**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm:1.94 (s, 3H), 2.70 (s, 3H), 3.35–3.41 (m, 1H), 4.03 (ddd, ^3J = 2.5, ^3J = 8.5, ^2J = 19.6 Hz, 1H), 4.39–4.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ, ppm: 18.5, 22.3, 44.3, 47.6, 120.0, 191.9. HRMS (MALDI) cald. for $C_{25}H_{22}ClO^+$ $[M+H]^+$ 373.1354, found 373.1356.

(*E*)-1-(5-Bromofuran-2-yl)-2-(4,7-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 q): *E*-/*Z*-5 q in a ratio of 5:1. General yield of 16 mg (70%). Green oil. ***E*-5 q**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 1.98 (s, 3H), 2.72 (s, 3H), 3.51 (dt, ^4J = 2.3, ^3J = 1.8, ^2J = 19.9 Hz, 1H), 3.87 (ddd, (^4J = 2.3, ^3J = 8.5, ^2J = 19.8 Hz, 1H), 4.50 (dd, ^3J = 1.8, ^3J = 8.5 Hz, 1H), 6.48 (d, ^3J = 3.5 Hz, 1H), 6.97–7.00 (m, 2H), 7.10 (d, J = 3.4 Hz, 2H), 7.12 (d, ^3J = 3.5 Hz, 1H), 7.14–7.17 (m, 1H), 7.19–7.23 (m, 2H), 7.43 (t, ^4J = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ, ppm: 18.9, 22.3, 44.4, 48.59, 114.5, 114.7, 117.6, 126.3, 127.4, 128.7, 128.8, 131.1, 132.7, 133.6, 133.8, 138.6, 145.1, 152.1, 156.8, 165.6, 178.1. ***Z*-5 q**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 1.98 (s, 3H), 2.73 (s, 3H), 3.42 (ddd, ^4J = 2.3, ^3J = 4.0, ^2J = 19.8 Hz, 1H), 4.04 (ddd, ^3J = 2.3, ^3J = 8.1, ^2J = 19.8 Hz, 1H), 4.42 (dd, ^3J = 4.0, ^3J = 8.1 Hz, 1H), 7.38 (t, ^4J = 2.3 Hz, 1H). HRMS (MALDI) cald. for $C_{23}H_{20}BrO^+$ $[M+H]^+$ 407.0641, found 407.0646.

(*E*)-2-(5,7-Dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenylethan-1-one (5 r): Yield 11 mg (45%). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.30 (s, 3H), 2.70 (s, 3H), 3.43 (ddd, ^4J = 2.5, ^3J = 4.0, ^2J = 20.3 Hz, 1H), 4.07 (ddd, ^4J = 2.5, ^3J = 8.2, ^2J = 20.3 Hz, 1H), 4.55 (dd, ^3J = 4.0, ^3J = 8.21 Hz, 1H), 6.83 (s, 1H), 6.97 (s, 1H), 7.12–7.14 (m, 2H), 7.21–7.23 (m, 1H), 7.27–7.28 (m, 2H), 7.47–7.56 (m, 4H), 7.98–8.00 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6, 22.5, 44.2, 49.3, 115.3, 124.7, 126.6, 128.0, 128.1, 128.7, 128.7, 131.7, 132.2, 135.9, 136.0, 140.3, 141.6, 145.4, 154.8, 164.1, 191.2. HRMS (ESI) $C_{25}H_{23}O^+$ $[M+H]^+$calcd. for 339.1743, found 339.1746.

(*E*)-2-(5,7-Dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)-1-(4-methylphenyl)ethan-1-one (5 s): Yield 25 mg (86%). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.30 (s, 3H), 2.43 (s, 3H), 2.70 (s, 3H), 3.43 (ddd, ^4J = 2.2, ^3J = 4.0, ^2J = 19.6 Hz, 1H), 4.04 (ddd, ^4J = 2.2, ^3J = 8.21, ^2J = 19.6 Hz, 1H), 4.42 (dd, ^3J = 4.0, ^3J = 8. 1 Hz, 1H), 6.83 (s,

1H), 6.97 (s, 1H), 7.14 (d, J=7.6 Hz, 2H), 7.19–7.23 (m, 1H), 7.52 (t, ^4J=2.2 Hz, 1H), 7.91 (d, J=8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6, 21.7, 22.5, 44.1, 49.3, 115.4, 124.6, 126.6, 127.9, 128.2, 128.7, 129.4, 131.6, 135.8, 136.1, 137.7, 141.4, 142.8, 145.5, 154.6, 163.5,190.9. HRMS (ESI) $C_{26}H_{25}O^+$ $[M+H]^+$calcd. for 353.1900, found 353.1903.

(*E*)-1-(4-Chlorophenyl)-2-(5,7-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 t): Yield 17 mg (60 %). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.30 (s, 3H), 2.70 (s, 3H), 3.43 (ddd, ^4J=2.3, ^3J=4.1, ^2J=19.6 Hz, 1H), 4.04 (ddd, ^4J=2.3, ^3J=8.1, ^2J=19.6 Hz, 1H), 4.43 (dd, ^3J=4.1, ^3J=8.1 Hz, 1H), 6.84 (s, 1H), 6.98 (s, 1H), 7.12–7.14 (m, 2H), 7.22–7.24 (m, 1H), 7.27–7.32 (m, 2H), 7.46 (d, J=8.5 Hz, 2H), 7.47 (t, ^4J=2.3 Hz, 1H), 7.94 (d, J=8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6, 22.5, 44.3, 49.2, 114.7, 124.7, 126.7, 127.9, 128.7, 128.9, 129.5, 131.7, 135.8, 138.5, 138.6, 141.8, 141.6, 145.3, 155.0, 164.9, 189.8. HRMS (MALDI) $C_{25}H_{22}ClO^+$ $[M+H]^+$ calcd. for 373.1354, found 373.1356.

(*E*)-1-(4-Bromophenyl)-2-(5,7-dimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 u): Yield 16 mg (60 %). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.30 (s, 3H), 2.70 (s, 3H), 3.42 (ddd, ^4J=2.3, ^3J=4.2, ^2J=19.7 Hz, 1H), 4.03 (ddd, ^4J=2.3, ^3J=8.1, ^2J=19.7 Hz, 1H), 4.43 (dd, ^3J=4.2, ^3J=8.1 Hz, 1H), 6.83 (s, 1H), 6.98 (s, 1H), 7.11–7.14 (m, 2H), 7.20–7.24 (m, 1H), 7.27–7.31 (m, 2H), 7.47 (t, ^4J=2.3 Hz, 1H), 7.62 (d, J=8.6 Hz, 2H), 7.86 (d, J=8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.7, 22.5, 44.3, 49.2, 114.6, 124.7, 126.7, 127.1, 127.9, 128.8, 129.7, 131.7, 131.9, 135.8, 135.9, 139.0, 141.9, 145.3, 155.0, 165.0, 190.0. HRMS (MALDI) calcd. for $C_{25}H_{22}BrO^+$ $[M+H]^+$ 417.0849, found 417.0854.

(*E*)-2-(5,7-Dimethyl-3-phenyl-2,3-dihydro-1H-inden-1-ylidene)-1-(4-nitrophenyl)ethan-1-one (5 v): Yield 17 mg (63 %). Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm.: 2.31 (s, 3H), 2.71 (s, 3H), 3.44 (ddd, ^4J=2.2, ^3J=4.0, ^2J=19.9 Hz, 1H), 4.06 (ddd, ^4J=2.2, ^3J=8.0, ^2J=19.9 Hz, 1H), 4. 45 (dd, ^3J=4.0, ^3J=8.0 Hz, 1H), 6.85 (s, 1H), 6.99 (s, 1H), 7.11–7.13 (m, 2H), 7.21–7.24 (m, 1H), 7.28–7.31 (m, 2H), 7.49 (t, J^4=2.2 Hz, 1H), 8.11 (d, J=8.8 Hz, 2H), 8.33 (d, J=8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6, 22.4, 44.5, 49.1, 114.1, 123.8, 124.7, 126.6, 127.8, 128.7, 128.8, 131.7, 135.5, 136.0, 142.4, 144.9, 145.1, 149.7, 155.4, 166.8, 188.9. HRMS (ESI) $C_{25}H_{22}NO_3^+$ $[M+H]^+$ calcd. for 384.1594, found 384.1699.

(*E*)-2-(5,7-Dimethyl-3-(p–tolyl)-2,3-dihydro-1H-inden-1-ylidene)-1-phenylethan-1-one (5 w): Yield 20 mg (71 %). Yellow crystals. M.p. 157–160 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.31 (s, 3H), 2.34 (s, 3H), 2.71 (s, 3H), 3.42 (ddd, ^4J=2.2, ^3J=4.2, ^2J=19.5 Hz, 1H), 4.05 (ddd, ^4J=2.2, ^3J=8.1, ^2J=19.5 Hz, 1H), 4.41 (dd, ^3J=4.2, ^3J=8.1 Hz, 1H), 6.84 (s, 1H), 6.97 (s, 1H), 7.04 (d, J=7.9 Hz, 2H), 7.11 (d, J=7.9 Hz, 2H), 7.48–7.57 (m, 4H), 8.01 (d, J=7.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.2, 21.6, 22.5, 44.2, 48.9, 115.2, 124.6, 127.8, 128.0, 128.7, 129.4, 131.6, 132.1, 135.8, 136.0, 136.1, 140.3, 141.5, 142.4, 155.0, 164.2, 191.2. HRMS (ESI) $C_{26}H_{25}O^+$ $[M+H]^+$calcd. for 353.1900, found 353.1903.

(*E*)-2-(3-(4-Chlorophenyl)-5,7-dimethyl-2,3-dihydro-1H-inden-1-ylidene)-1-phenylethan-1-one (5 x): Yield 21 mg (75 %). Yellow crystals. M.p. 169–172 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.31 (s, 3H), 2.70 (s, 3H), 3.38 (ddd, ^4J=2.3, ^4J=4.2, ^2J=19.6 Hz, 1H), 4.04 (ddd, ^4J=2.3, ^3J=8.2, ^2J=19.6 Hz, 1H), 4.40 (dd, ^3J=4.2, ^3J=8.2 Hz, 1H), 6.79 (s, 1H), 6.98 (s, 1H), 7.06 (d, J=8.4 Hz, 2H), 7.24–7.26 (m, 2H), 7.47–7.55 (m, 4H), 7.98–8.00 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.6, 22.5, 44.1, 48.6, 115.4, 124.6, 128.1, 128.7, 128.9, 129.3, 131.9, 132.3, 132.4, 135.9, 136.0, 140.2, 141.7, 144.0, 154.2, 163.6, 191.2. HRMS (MALDI) $C_{25}H_{22}ClO^+$ $[M+H]^+$calcd. for 373.1354, found 373.1356.

(*E*)-1-(5-Bromofuran-2-yl)-2-(5,7-dimethyl-3-phenyl-2,3-dihydro-1H-inden-1-ylidene)ethan-1-one (5 y): Yield 21 mg (80 %). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.29 (s, 3H), 2.70 (s, 3H), 3.42 (ddd, ^4J=2.3, ^3J=4.1, ^2J=19.8 Hz, 1H), 4.04 (ddd, ^4J=2.3, ^3J=8.2, ^2J=19.8 Hz, 1H), 4.42 (dd, ^3J=4.1, ^3J=8.2 Hz, 1H), 6.49 (d, ^3J=3.6 Hz, 1H), 6.82 (s, 1H), 6.97 (s, 1H), 7.11–7.13 (m, 2H), 7.14 (d, ^3J=3.6 Hz, 1H), 7.19–7.23 (m, 1H), 7.27–7.30 (m, 2H), 7.38 (t, ^4J=2.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.7, 22.3, 44.1, 49.3, 113.7, 114.5, 117.6, 124.6, 126.6, 126.8, 127.9, 128.7, 131.7, 135.7, 136.2, 142.0, 145.3, 155.0, 156.9, 165.1, 178.1. HRMS (ESI) cald. for $C_{23}H_{20}BrO^+$ $[M+H]^+$ 407.0641, found 407.0644.

(*E*)-1-Phenyl-2-(4,5,7-trimethyl-3-phenyl-2,3-dihydro-1H-inden-1-ylidene)ethan-1-one (5 z):Yield 21 mg (70 %). Yellow crystals. M.p. 128–130 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.93 (s, 3H), 2.27 (s, 3H), 2.70 (s, 3H), 3.52 (dt, ^4J=2.3, ^3J=2.3, ^2J=19.7 Hz, 1H), 3.89 (ddd, ^4J=2.3, ^3J=8.61, ^2J=19.7 Hz, 1H), 4.55 (dd, ^3J=2.3, ^3J=8.61 Hz, 1H), 6.98–7.00 (m, 2H), 7.02 (s, 1H), 7.12–7.16 (m, 1H), 7.19–7.23 (m, 2H), 7.45–7.49 (m, 2H), 7.51–7.55 (m, 2H), 7.97–7.99 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 15.5, 20.1, 22.3, 44.8, 48.7, 115.3, 126.2, 127.4, 128.1, 128.6, 128.7, 132.0, 132.1, 133.0, 133.1, 136.9, 140.3, 140.4, 145.8, 152.3, 165.0, 191.1. HRMS (ESI) $C_{26}H_{25}O^+$ $[M+H]^+$calcd. for 353.1900, found 353.1904.

(*E*)-1-(4-Methylphenyl)-2-(4,5,7-trimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 aa):Yield 24 mg (80 %). Yellow crystals. M.p. 135–137 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.92 (s, 3H), 2.27 (s, 3H), 2.42 (s, 3H), 2.70 (s, 3H), 3.51 (dt, ^4J=2.3, ^3J=2.3, ^2J=19.6, 1H), 3.87 (ddd, ^4J=2.3, ^3J=8.6, ^2J=19.6 Hz, 1H), 4.55 (dd, ^3J=2.0, ^3J=8.6 Hz, 1H), 6.98–7.99 (m, 2H), 7.02 (s, 1H), 7.11–7.15 (m, 1H), 7.19–7.22 (m, 2H), 7.26–7.28 (m, 2H), 7.52 (t, ^4J=2.3 Hz, 1H), 7.89 (d, J=8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 15.5, 20.05, 21.71, 22.3, 44.7, 48.7, 115.4, 126.2, 127.4, 128.2, 128.7, 129.3, 131.9, 132.9, 133.0, 137.0, 137.7, 140.2, 142.7, 145.8, 152.1, 164.4, 190.8. HRMS (ESI) $C_{27}H_{27}O^+$ $[M+H]^+$cald. for 367.2056, found 367.2060.

(E)-1-(4-Chlorophenyl)-2-(4,5,7-trimethyl-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 ab):Yield 17 mg (60 %). Yellow crystals. M.p. 171–174 °C. The structure was confirmed by X-ray analysis.^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.92 (s, 3H), 2.27 (s, 3H), 2.70 (s, 3H), 3.49 (dt, ^4J=2.3, ^3J=2.3, ^2J=19.7, 1H), 3.87 (ddd, ^4J=2.3, ^3J=8.5, ^2J=19.7 Hz, 1H), 4.55 (dd, ^3J=2.3, ^3J=8.5 Hz, 1H), 6.97–7.00 (m, 2H), 7.02 (s, 1H), 7.12–7.15 (m, 1H), 7.19–7.22 (m, 2H), 7.43 (d, J=8.6 Hz, 2H), 7.47 (t, ^4J=2.3 Hz, 1H), 7.91 (d, J=8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 15.5, 20.1, 22.3, 44.9, 48.7, 114.7, 126.2, 127.3, 128.7, 128.9, 129.5, 132.1, 133.0, 133.1, 136.7, 138.4, 138.6, 140.6, 145.7, 152.4, 165.8, 189.7. HRMS (ESI) $C_{26}H_{24}ClO^+$ $[M+H]^+$calcd. for 387.1510, found 387.1512.

(*E*)-1-Phenyl-2-(4,5,7-trimethyl-3-(4-methylphenyl)-2,3-dihydro-1H-inden-1-ylidene)ethan-1-one (5 ac):Yield 18 mg (60 %). Yellow crystals. M.p. 173–175 °C. The structure was confirmed by X-ray analysis. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.95 (s, 3H), 2.28 (s, 3H), 2.29 (s, 3H), 2.70 (s, 3H), 3.51 dt (^4J=2.7, ^3J=1.8, ^2J=19.6 Hz, 1H), 3.87 ddd (^4J=2.7, ^3J=8.5, ^2J=19.6 Hz, 1H), 4.53 (dd, ^3J=1.8, ^3J=8.5 Hz, 1H), 6.89 (d, J=8.0 Hz, 2H), 7.02–7.04 (m, 3H), 7.45–7.49 (m, 2H), 7.51–7.55 (m, 2H), 7.97–8.00 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 15.5, 20.0, 21.1, 22.3, 44.9, 48.2, 115.3, 127.3, 128.1, 128.6, 129.3, 131.9, 132.0, 132.9, 133.0, 135.6, 136.8, 140.2, 140.3, 142.7, 152.4, 165.1, 191.0. HRMS (ESI) $C_{27}H_{27}O^+$ $[M+H]^+$cald. for 367.2056, found 367.2061.

(*E*)-2-(3-(4-Chlorophenyl)-4,5,7-trimethyl-2,3-dihydro-1H-inden-1-ylidene)-1-phenylethan-1-one (5 ad):Yield 23 mg (85 %). Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 1.92 (s, 3H), 2.27 (s, 3H), 2.70 (s, 3H), 3.49 (dt, ^4J=2.3, ^3J=2.3, J^2=19.6 Hz, 1H), 3.87 (ddd, ^4J=2.3, ^3J=8.6, ^2J=19.6 Hz, 1H), 4.55 (dd, ^3J=2.3, ^3J=8.6 Hz, 1H), 6.92 (d, J=8.4 Hz, 2H), 7.03 (s, 1H), 7.18 (d, J=8.4 Hz, 2H), 7.45–7.52 (m, 3H),

7.54 (t, ^4J = 2.3 Hz, 1H), 7.97–7.99 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 15.6, 20.1, 22.2, 44.6, 47.9, 115.5, 128.1, 128.6, 128.7, 128.8, 131.8, 131.9, 132.2, 133.1, 133.3, 136.8, 140.2, 140.5, 144.3, 151.6, 164.4, 191.1. HRMS (ESI) calcd. for $C_{26}H_{24}ClO^+$ $[M+H]^+$: 387.1510, found 387.1513.

***(E)*-2-(5,6-Dimethoxy-3-phenyl-2,3-dihydro-1H-inden-1-ylidene)-1-phenylethan-1-one (5 ae):**Yield 16 mg (50%). Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.40 (ddd, ^4J = 2.2, ^3J = 3.1, ^2J = 20.2 Hz, 1H), 3.82 (s, 3H), 4.00 (s, 3H), 4.05 (ddd, ^4J = 2.2, ^3J = 7.9, ^2J = 20.2 Hz, 1H), 4.48 (dd, ^3J = 3.1, ^3J = 7.9 Hz, 1H), 6.63 (s, 1H), 7.10–7.15 (m, 2H), 7.19 −7.24 (m, 2H), 7.27–7.32 (m, 2H), 7.35 (t, ^4J = 2.2 Hz, 1H), 7.46–7.56 (m, 3H), 8.00–8.06 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.4, 49.5, 56.2, 56.3, 102.9, 107.8, 109.7, 126.7, 127.7, 128.04, 128.6, 128.8, 132.1, 133.0, 140.2, 145.1, 147.5, 149.6, 153.4, 163.7, 190.6. HRMS (ESI) calcd. for $C_{25}H_{23}O_3^+$ $[M+H]^+$ 371.1642, found 371.1647.

(*E*)-2-(5,6-Dimethoxy-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)-1-(4-methylphenyl)ethan-1-one (5 af):Yield 16 mg (50%). Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 2.42 (s, 3H), 3.40 (ddd, ^4J = 2.2, ^3J = 3.1, ^2J = 20.1 Hz, 1H), 3.82 (s, 3H), 4.00 (s, 3H), 4.05 (ddd, ^4J = 2.2, ^3J = 7.8, ^2J = 20.1 Hz, 1H), 4.47 (dd, ^3J = 3.1, ^3J = 7.8 Hz, 1H), 6.62 (s, 1H), 7.12 (d, J = 7.2 Hz, 2H), 7.19–7.23 (m, 1H), 7.21 (s, 1H), 7.27–7.30 (m, 4H), 7.34 (t, ^4J = 2.2 Hz, 1H), 7.94 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 21.7, 44.3, 49.5, 56.2, 56.3, 103.9, 107.9, 109.8, 126.7, 127.8, 128.2, 128.8, 129.3, 133.1, 137.6, 142.7, 145.2, 147.3, 149.6, 153.3, 163.2, 190.3. HRMS (ESI) calcd. for $C_{26}H_{25}O_3^+$ $[M+H]^+$ 385.1798, found 385.1800.

(*E*)-1-(4-Chlorophenyl)-2-(5,6-dimethoxy-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 ag):Yield 15 mg (50%). Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.39 (ddd, ^4J = 2.4, ^3J = 3.2, ^2J = 20.2 Hz, 1H), 3.82 (s, 3H), 4.00 (s, 3H), 4.06 (ddd, ^4J = 2.4, ^3J = 7.8, ^2J = 20.2 Hz, 1H), 4.48 (dd, ^3J = 3.2, ^3J = 7.8 Hz, 1H), 6.63 (s, 1H), 7.10–7.12 (m, 2H), 7.20 (s, 1H), 7.21–7.24 (m, 1H), 7.27–7.31 (t, 1H), 7.27–7.31 (m, 3H), 7.45 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.5, 49.5, 56.3, 56.4, 103.0, 107.9, 109.2, 126.8, 127.8, 128.9, 129.5, 129.3, 132.8, 138.4, 138.5, 145.0, 147.8, 149.7, 153.7, 164.5, 189.1. HRMS (ESI) calcd. for $C_{25}H_{22}ClO_3^+$ $[M+H]^+$ 405.1252, found 405.1254.

(*E*)-1-(4-Bromophenyl)-2-(5,6-dimethoxy-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)ethan-1-one (5 ah): Yield 16 mg (55%). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.39 (dt, ^4J = 2.6, ^2J = 20.2 Hz, 1H), 3.82 (s, 3H), 4.00 (s, 3H), 4.06 (ddd, ^4J = 2.6, ^3J = 7.8, ^2J = 20.2 Hz, 1H), 4.47 (dd, ^3J = 2.6, ^3J = 7.8 Hz, 1H), 6.62 (s, 1H), 7.11 (d, J = 7.2 Hz, 2H), 7.20 (s, 1H), 7.26 (d, J = 7.3 Hz, 1H) 7.27–7.30 (m, 3H), 7.61 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.5, 49.5, 56.2, 56.3, 103.0, 107.9, 109.1, 126.8, 127.0, 127.7, 128.8, 129.6, 131.8, 132.8, 138.9, 145.0, 147.8, 149.7, 153.7, 149.82, 164.6, 189.3. HRMS (ESI) calcd. for $C_{25}H_{22}BrO_3^+$ $[M+H]^+$ 449.0747, found 449.0752.

(*E*)-2-(5,6-Dimethoxy-3-phenyl-2,3-dihydro-1*H*-inden-1-ylidene)-1-(4-nitrophenyl)ethan-1-one (5 ai): Yield 16 mg (52%). Green oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.41 (dt, ^4J = 2.6, ^2J = 20.4 Hz, 1H), 3.84 (s, 3H), 4.01 (s, 3H), 4.05 (ddd, ^4J = 2.6, ^3J = 7.7, ^2J = 20.4 Hz, 1H), 4.54 (dd, ^3J = 2.6, ^3J = 7.7 Hz, 1H), 6.64 (s, 1H), 7.11–7.13 (m, (2H), 7.21 (s, 1H), 7.23–7.25 (m, 1H), 7.28–7.32 (m, 3H), 8.15 (d, J = 8.7 Hz, 2H), 8.33 (d, J = 8.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.77, 49.51, 56.33, 56.38, 103.00, 107.89, 108.93, 123.88, 126.89, 127.74, 128.92, 128.96, 132.53, 144.77, 145.22, 148.55, 149.76, 149.82, 154.15, 166.47, 188.51. HRMS (ESI) calcd. for $C_{25}H_{22}NO_5^+$ $[M+H]^+$ 416.1492, found 416.1499.

(*E*)-2-(3-(4-Chlorophenyl)-5,6-dimethoxy-2,3-dihydro-1*H*-inden-1-ylidene)-1-phenylethan-1-one (5 aj): Yield 22 mg (72%). Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.35 (ddd, ^4J = 2.3, ^3J = 3.3, ^2J = 20.1 Hz, 1H), 3.82 (s, 3H), 4.00 (s, 3H), 4.06 (ddd, ^4J = 2.3, ^3J = 7.9, ^2J = 20.1 Hz, 1H), 4.45 (dd, ^3J = 3.3, ^3J = 7.9 Hz, 1H), 6.58 (s, 1H), 7.05 (d, J = 8.4 Hz, 2H), 7.20 (s, 1H), 7.26 (d, J = 8.4 Hz, 1H), 7.35 (t, ^4J = 2.3 Hz, 1H), 7.47–7.55 (m, 3H), 8.01–8.03 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.2, 48.9, 56.3, 56.4, 103.0, 107.7, 108.4, 109.9, 128.1, 128.6, 129.1, 132.2, 132.5, 133.0, 140.1, 143.7, 146.9, 149.8, 153.4, 163.1, 190.6. HRMS (ESI) $C_{25}H_{22}ClO_3^+$ $[M+H]^+$calcd. for 405.1252, found 405.1255.

(*E*)-1-Phenyl-2-(3-phenyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)ethan-1-one (5 ak):Yield 16 mg (50%). Brown oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.51 (ddd, ^4J = 2.3, ^3J = 4.1, ^2J = 18.8 Hz, 1H), 4.19 (ddd, ^4J = 2.3, ^3J = 7.6, ^2J = 18.8 Hz, 1H), 4.60 (dd, ^3J = 4.1, ^3J = 7.6 Hz, 1H), 7.15–7.17 (m, 2H), 7.21–7.25 (m, 2H), 7.27–7.32 (m, 2H), 7.49–7.53 (m, 2H), 7.55–7.60 (m, 2H), 7.69–7.73 (m, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 8.01 (t, ^4J = 2.3, 1H), 8.04–8.07 (m, 2H), 8.64 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.7, 50.1, 116.7, 124.0, 124.2, 126.0, 126.9, 127.5, 128.1, 128.3, 128.7, 128.8, 129.6, 129.8, 132.3, 132.9, 133.9, 135.3, 140.1, 144.7, 153.7, 163.3, 191.5. HRMS (ESI) $C_{27}H_{21}O^+$ $[M+H]^+$calcd. for 361.1587, found 361.1590.

(*E*)-1-(4-Chlorophenyl)-2-(3-phenyl-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)ethan-1-one (5 al): Yield 9 mg (30%). Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ, ppm: 3.49 (ddd, ^4J = 2.3, ^3J = 4.1, ^2J = 18.8 Hz, 1H), 4.17 (ddd, ^4J = 2.3, ^3J = 7.8, ^2J = 18.8 Hz, 1H), 4.60 (dd, ^3J = 4.1, ^3J = 7.6 Hz, 1H), 7.14–7.16 (m, 2H), 7.21–7.32 (m, 5H), 7.48 (d, J = 8.6 Hz, 2H), 7.56–7.60 (m, 1H), 7.69–7.73 (m, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.94 (t, ^4J = 2.3, 1H), 7.98 (d, J = 8.6 Hz, 2H), 8.45 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm: 44.7, 50.0, 116.0, 123.8, 124.0,126.0, 126.8,127.9, 128.2, 128.7, 128.9, 129.6, 129.7, 130.9, 133.0, 133.7, 135.0, 138.3, 138.5, 144.4, 153.8, 163.9, 189.9. HRMS (ESI) $C_{27}H_{20}ClO^+$ $[M+H]^+$calcd. for 395.1197, found 395.1202.

2-(3-(4-Chlorophenyl)-2,3-dihydro-1*H*-cyclopenta[a]naphthalen-1-ylidene)-1-phenylethan-1-one (5 am): *E*-/*Z*-5 am in a ratio of10:4. General yield of 18 mg (60%). Yellow oil. ***E*-5 am**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 3.46 (ddd, ^4J = 2.2, ^3J = 4.0, ^2J = 18.7 Hz, 1H), 4.18 (ddd, ^4J = 2.2, ^3J = 7.6, ^2J = 18.7 Hz, 1H), 4.57 (dd, ^3J = 4.0, ^3J = 7.6 Hz, 1H), 6.98–7.00 (m, 2H), 7.10–7.11 (m, 2H), 7.12–7.17 (m, 1H), 7.20–7.23 (m, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.3 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.48–7.53 (m, 2H), 7.55–7.61 (m, 2H), 7.69–7.73 (m, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 8.01 (t, ^4J = 2.2 Hz, 1H), 8.04–8.07 (m, 2H), 8.63 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz), selected signals δ, ppm: 44.6, 49.4, 162.7, 191.4

***Z*-5 am**: ^{1}H NMR (400 MHz, $CDCl_3$), selected signals δ, ppm: 3.50–3.55 (m, 1H), 4.07–4.14 (m, 1H), 4.98 (dd, ^4J = 2.2, ^3J = 8.1 Hz, 1H), 7.01 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.36–7.40 (m, 1H) .^{13}C NMR (101 MHz, $CDCl_3$) selected signals δ, ppm: 44.5, 48.2, 163.0, 190.7

^{13}C NMR ($CDCl_3$, 100 MHz) δ, ppm (for mixture of ***(E-/Z-)*-**isomers): 112.0, 116.8, 118.8, 123.7, 124.1, 125.9, 126.2, 127.1, 127.5, 128.1, 128.3, 128.4, 128.7, 128.8, 128.79, 128.95, 128.99, 129.1, 129.4, 129.5, 129.6, 129.8, 130.3, 132.3, 132.38, 132.4, 132.6, 133.1, 133.9, 135.4, 135.8, 138.8, 139.8, 140.0, 143.2, 144.1, 149.5, 153.0. HRMS (ESI) $C_{27}H_{20}ClO^+$ $[M+H]^+$calcd. for 395.1197, found 395.1200.

Spectra of cations in H_2SO_4

((*2Z,4E*)-1-(4-Chlorophenyl)-3-(hydroxysulphonyloxy)-5-phenyl-penta-2,4-dien-1-ylidene)oxonium Ea: ^{1}H NMR (H_2SO_4, CH_2Cl_2, 400 MHz, 298 K) δ, ppm: 6.68 (s, 1H), 6.99 (d, J = 15.4 Hz, 1H), 7.49 (t, J = 7.3 Hz, 2H), 7.58 (d, J = 8.4 Hz, 3H), 7.72 (d, J = 7.5 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 15.7 Hz, 1H). ^{13}C NMR (H_2SO_4, CH_2Cl_2, 101 MHz, 298 K) δ, ppm selected signals: 96.7, 118.1, 126.0, 128.1, 128.7, 129.0, 129.9, 130.1, 132.3, 143.5, 153.9, 182.5, 183.3.

((*2Z,4E*)-1-(4-Bromophenyl)-3-(hydroxysulphonyloxy)-5-phenylpenta-2,4-dien-1-ylidene)oxonium Eb: ^{1}H NMR (H_2SO_4, CH_2Cl_2, 400 MHz, 298 K) δ, ppm selected signals: 6.66 (s, 1H), 6.97 (d, J= 15.8 Hz, 1H), 8.13 (d, J=15.8 Hz, 2H). ^{13}C NMR (H_2SO_4, CH_2Cl_2, 101 MHz, 298 K) δ, ppm selected signals: 96.6, 118.1, 128.5, 129.0, 129.7, 130.1, 132.2, 132.5, 132.6, 153.9, 182.5, 183.3.

(6-(4-Chlorophenyl)-2-phenyl-2,3-dihydro-4*H*-pyran-4-ylidene) oxonium Fa:^{1}H NMR (H_2SO_4, CH_2Cl_2, 400 MHz, 298 K) δ, ppm selected signals: 3.33 (dd, J=19.0, 4.5 Hz, 1H), 3.58 (dd, J=19.0, 15.1 Hz, 1H), 6.02 (dd, J=15.1, 4.5 Hz, 1H), 6.99 (s, 1H).

(6-(4-Bromophenyl)-2-phenyl-2,3-dihydro-4*H*-pyran-4-ylidene) oxonium (Fb):^{1}H NMR (H_2SO_4, CH_2Cl_2, 400 MHz, 298 K) δ, ppm selected signals: 3.33 (dd, J=19.0, 4.5 Hz, 1H), 3.58 (dd, J=19.2, 15.2 Hz, 1H), 6.03 (dd, J=15.1, 4.6 Hz, 1H), 6.99 (s, 1H).

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Conflict of Interest

The authors declare no conflict of interest.

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[1] A. Pankova, *Chem. Heterocycl. Compd.* **2020**, *56*, 829–836.
[2] A. A. Golovanov, I. S. Odin, S. S. Zlotskii, *Russ. Chem. Rev.* **2019**, *88*, 280–318.
[3] A. A. Golovanov, D. M. Gusev, I. S. Odin, S. S. Zlotskii, *Chem. Heterocycl. Compd.* **2019**, *55*, 333–348.
[4] L. Chen, Z. Liu, S. Zhu, *Org. Biomol. Chem.* **2018**, *16*, 8884–8898.
[5] A. L. S. Kumari, A. S. Reddy, K. C. K. Swamy, *Org. Biomol. Chem.* **2016**, *14*, 6651–6671.
[6] A. A. Golovanov, D. M. Gusev, S. S. Zlotskii, *Russ. J. Org. Chem.* **2016**, *52*, 1205–1206.
[7] D. M. Gusev, A. S. Bunev, A. A. Golovanov, *Russ. J. Org. Chem.* **2020**, *90*, 217–223.
[8] A. Mondal, R. Hazra, J. Grover, M. Raghu, S. S. Ramasastry, *ACS Catal.* **2018**, *8*, 2748–2753.
[9] S. Saulnier, A. A. Golovanov, A. Yu. Ivanov, I. A. Boyarskaya, A. V. Vasilyev, *J. Org. Chem.* **2016**, *81*, 1967–1980.
[10] S. Saulnier, A. A. Golovanov, A. V. Vasilyev, *RSC Adv.* **2016**, *6*, 103546–103555.
[11] S. Saulnier, S. V. Lozovskiy, A. A. Golovanov, A. Yu. Ivanov, A. V. Vasilyev, *Eur. J. Org. Chem.* **2017**, 3635–3645.
[12] M. I. Aleksandrova, S. V. Lozovskiy, S. Saulnier, A. A. Golovanov, I. A. Boyarskaya, A. V. Vasilyev, *Org. Biomol. Chem.* **2018**, *16*, 7891–7902.
[13] A. S. Zalivatskaya, A.A. Golovanov, A. V. Vasilyev, *Chem. Heterocycl. Compd.* **2020**, *56*, 953–956.
[14] R. G. Parr, L. V. Szentpaly, S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 1922–1924.
[15] L. V. Alves, M. M. Do Canto-Cavalheiro, L. Cysne-Finkelstein, L. Leon, *Biol. Pharm. Bull.* **2003**, *26*, 453–456.
[16] J. B. Harborne, C.A Williams, *Phytochemistry* **2000**, *55*, 481–504.
[17] F. K. Mac Donald, D. J. Burnall, *J. Org. Chem.* **2009**, *74*, 6973–6979.
[18] F. Yang, K.-G. Ji, S.-C. Zhao, S. Ali, Y.-Y. Ye, X.-Y. Liu, Y.-M. Liang, *Chem. Eur. J.* **2012**, *18*, 6470–6474.
[19] A. Rinaldi, D. Scarpi, E. G. Occhiato, *Eur. J. Org. Chem.* **2019**, 7401–7419.
[20] Q. He, Z. Yin, H. Chen, Z. Zhang, X. Wang, G. Yue, *Prog. Chem.* **2016**, *28*, 801–813.
[21] C. Borie, L. Ackermann, M. Nechab, *Chem. Soc. Rev.* **2016**, *45*, 1368–1386.
[22] Y. C. Fan, O. Kwon, *Org. Lett.* **2015**, *17*, 2058–2061.
[23] S. Kesavan, J. S. Panek, J. A. Porco, *Org. Lett.* **2007**, *9*, 5203–5206.
[24] L. N. Pridgen, K. Huang, S. Shilcrat, A. Tickner-Eldridge, C. DeBrosse, R. C. Haltiwang, *Synlett* **1999**, *10*, 1612–1614.
[25] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[26] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.
[27] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr., J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox in *Gaussian 09*, *Revision C.01*, *Gaussian*, Inc., Wallingford CT, **2010**.
[28] M. Hoshi, H. Yamazaki, M. Okimoto, *Synlett.* **2010**, 2461–2464.

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