3-Unsubstituted 1,5-Diaryl-2,4-pentanediones and -4-methoxy-2-pentanones: Synthesis via Corresponding 3-Hydroxy Ketones Generated from 2-Isoxazolines

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Aryl acetaldoximes are reacted with allylarenes in the presence of sodium hypochlorite to give 3,5-bis(arylmethyl)-2-isoxazolines which are then converted to 1,5-diaryl-4-hydroxy-2-pentanones by a reductive hydrogenation in the presence of water. These intermediate aldols can then be either oxidized with Corey−Kim reagent to stable dimethylsulfonium 1-(arylacetyl)-2-oxo-3-arylpropylides followed by zinc−acetic acid reduction to give 1,5-diaryl-2,4-pentanediones, or converted to 1,5-diaryl-4-methoxy-2-pentanones by refluxing in methanol in the presence of hydrochloric acid. A detailed study of this general route is reported here.

1,3-Diketones are an important class of compounds because of their high synthetic utility and ability to form stable complexes. These enolizable compounds can act as binding sites to both metal ions[1] and nonmetallic elements[2] and are therefore used as subunits in supramolecular host molecules.[3] 3-Unsubstituted 2,4-pentanediones and 4-methoxy-2-pentanones with aromatic groups at 1,5-positions have very flexible structures due to negligible rotational barriers of the skeletal bonds. Having a binding site for a cation, they could act, for example, as templates in artificial allosteric systems. Despite the simplicity of the title compounds, general routes leading to them have not been reported yet. Only a few papers describe synthesis of the diketones **7** with two similar aromatic groups at the opposite ends of the same molecule,[4] and methods for the methoxy ketones **5** are previously unpublished.

There are mainly two straightforward approaches for the synthesis of 1,3-diketones. The traditional way is an acylation reaction of a methyl ketone with a carboxylic acid derivative.[5] However, in our case the methyl ketone would have been an arylacetone which tends to undergo acylation at the methylene rather than the methyl group.[5a] This was also proved by our unsuccesful efforts to make diketones **7** by an acylation using NaH or LDA as the base. Even the kinetically controlled acylation of the dianion of an arylacetone gave the same result. Furthermore, we made several attempts to produce the diketones from malonyl chloride and benzyllithium, from dichloromethane and lithium salts of the ethylene dithiolane or ethylene acetal of phenyl acetaldehyde, and by an acylation reaction of diethyl malonate with an aryl acetyl chloride, but they also were unsuccessful. On the other hand, 1,3-diketones can be prepared using a 1,3-dipolar cycloaddition of acetylenic derivatives with nitrile oxides to build up isoxazoles, which are then converted to β-enamino ketones by reductive ring opening followed by acidic hydrolysis to β-diketones.[6] Nevertheless, this method is rather limited because of the somewhat difficult accessibility of the acetylenic compounds,[6c] and the idea of using it was therefore dismissed.

3-Methoxy ketones can be prepared *via* 3-hydroxy ketones which also give an entry to the corresponding 1,3-diketones. The synthesis of 3-hydroxy ketones is usually carried out either by using an aldol condensation of carbonyl compounds with aldehydes[7] or by preparing an 2-isoxazoline[6b,c,8] which can then be converted to the corresponding aldol with a catalytic hydrogenation.[9] Because the methylene carbon of the precursor ketone is activated, the aldol condensation method would fail in the present case for the same reason as the acylation did. Therefore, we decided to use the second method.

We reported earlier a general route to the title compounds[10] which is based on using a nitrile oxide − olefin [3 + 2] cycloaddition reaction to build up the five-carbon skeleton of the molecules. The cycloaddition product, a 2-isoxazoline, is readily hydrogenated in the presence of water to a 3-hydroxy ketone, which can be either oxidized *via* stable dimethylsulfonium methylide to a 1,3-diketone[11] or converted to a 3-methoxy ketone with a one flask synthesis (Scheme 1). We wish to report here a more detailed study which, to the best of our knowledge, is the first general route to the title compounds having different aromatic groups and using the same precursor to produce both the diketones **7** and the methoxy ketones **5**.

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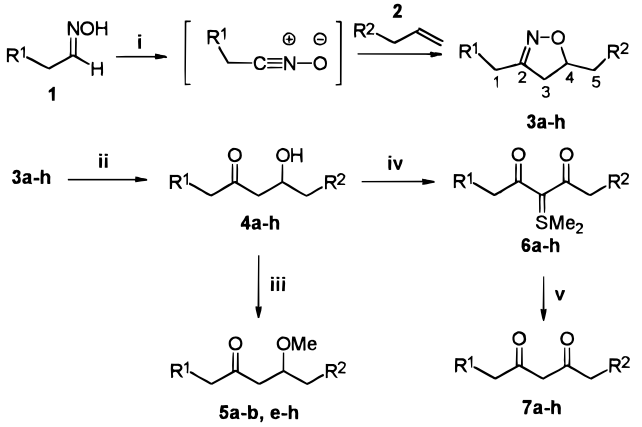
Scheme 1



i: NaOCl, Pyridine, $CHCl_3$, 0 °C, 36-92%; ii: H_2, Raney Ni, H_2O, AcOH, MeOH or THF, RT, 71-95%; iii: HCl, MeOH, refl., 32-82%; iv: Me_2S, NCS, Et_3N, CH_2Cl_2, -70 °C, 43-94%; v: Zn, AcOH, CH_2Cl_2, RT, 68-93%.

	R^1	R^2		R^1	R^2
a	Ph	Ph	**e**	Ph	F_5-Ph
b	Ph	2-MeO-Ph	**f**	1-Napht	1-Napht
c	Ph	4-MeO-Ph	**g**	2-Napht	1-MeO-2-Napht
d	Ph	3,4-Di-MeO-Ph	**h**	2-Napht	3-MeO-2-Napht

Results and Discussion

Preparation of 3,5-Bis(arylmethyl)-2-isoxazolines 3. 2-Isoxazolines are usually prepared by treating a nitrile oxide, generated from an aldoxime or a primary nitro compound, with an equimolar amount of olefin in the presence of a catalytic amount of an organic base, but in our case using equimolar quantities of the aryl acetaldoxime **1** and the allylarene **2** gave only poor yields and most of **2** remained unreacted. After optimizing the amount of **1** as well as the reaction conditions by varying the base, the solvent, and reaction temperature, we ended up with a procedure where compounds **3a**−**h** were obtained by reacting a two-fold excess of **1** with 5% sodium hypochlorite solution in a two-phase system in the presence of **2** at 0 °C using a catalytic amount of pyridine as the base in chloroform. Except for **3g** and **3h**, the yields were high.

Preparation of 1,5-Diaryl-4-hydroxy-2-pentanones 4. The isoxazolines **3** were smoothly converted to the corresponding hydroxy ketones **4** by a catalytic reduction with Raney nickel under hydrogen atmosphere in the presence of water and acetic acid at room temperature in high yields. In the case of the precursors **3a**−**e**, methanol was successfully used as a solvent. However, the solubility of the isoxazolines **3f**−**h** having bulky nonpolar naphthyl groups in methanol was significantly weaker and manifested itself in long reaction times and poor yields. When methanol was replaced with tetrahydrofuran, which dissolved the isoxazolines easier and was also miscible with the water needed for the hydrolysis of the labile hydroxyimine intermediate resulting from the N−O bond cleavage of the isoxazoline ring, the reaction occurred easily giving high yields.

Preparation of 1,5-Diaryl-4-methoxy-2-pentanones 5. The methoxy ketones **5** were easily achieved with a one flask synthesis by refluxing **4** in methanol overnight in the presence of concentrated hydrochloric acid, usually giving satisfactory yields. Only in the case of **4c** and **4d**, with 4-methoxyphenyl and 3,4-dimethoxyphenyl groups, respectively, the reaction led to unidentified mixtures. According to our NMR studies of the reaction mixtures of **4a**, the first step of the reaction is an acid-catalyzed dehydration of the alcohol **4** leading to α,β- and β,γ-unsaturated ketones which are readily attacked by HCl producing a 3-chloro ketone. If the reaction is quenched too soon, this intermediate is found to be the main product in the crude mixture which also includes small amounts of the both unsaturated ketones. The last step of the reaction is a nucleophilic substitution of chlorine with methoxyl ion which leads to **5**.

Preparation of Dimethylsulfonium 1-(Arylacetyl)-2-oxo-3-arylpropylides 6. Using the procedure previously described by Katayama et al.,[11] the hydroxy ketones **4** were converted to sulfur ylides **6** which were isolated and characterized as stable intermediates before conversion to the corresponding dicarbonyl compounds **7**. The reaction of **4** with a five-fold excess of the Corey-Kim reagent (*S*,*S*-dimethylsuccinimidosulfonium chloride)[12] under argon at −70 °C afforded **6**, the yields being 43−94%.

Preparation of 1,5-Diaryl-2,4-pentanediones 7. The diketones **7** were released with excellent yields from S-ylides **6** by a reductive desulfurization with zinc in the presence acetic acid at room temperature.[11a] The NMR measurements established the tautomeric behavior of the diketones **7**, as both the diketone and the enol structures were evident in the spectra. As expected, the energetically favorable enol tautomer was the dominating form in all cases. The percentage of the diketone form was only 12−20% in chloroform.

In summary we have presented the first general route to produce 3-unsubstituted 1,5-diaryl-2,4−pentanediones and -4-methoxy-2-pentanones having different aromatic groups in the same structure. The method is based on a [3 + 2] nitrile oxide−olefin cycloaddition which leads to a 2-isoxazoline **3**. This intermediate is converted to the corresponding 3-hydroxy ketone **4** which may be used as a precursor to both title compounds. All intermediates and products are characterized by means of NMR and mass spectrometry studies, and except for **7a**,[4c] they are previously unreported.

Experimental Section

General Methods. All moisture sensitive reactions were performed under a positive pressure of argon in oven-dried glassware equipped with rubber septa. Melting points were measured with Stuart Scientific SMP2 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra (TMS/$CDCl_3$) were recorded on a Bruker AM 400 WB spectrometer operating at 400 and 101 MHz, respectively. All coupling constants are given in Hz. Mass spectra were obtained on a Varian VG 70-250SE spectrometer. Column chromatography was performed with silica gel 60 (SiO_2, 70−230 mesh).

Materials. In all the experiments involving the Corey-Kim reagent, solvents and liquid reagents were dried, distilled, stored under argon, and transferred using a syringe flushed with argon. Aryl acetaldoximes **1** were synthesized from the corresponding aldehydes and hydroxylamine hydrochloride.[8b] Phenyl acetaldehyde was a commercial product and distilled prior to use. 1- and 2-Naphthyl acetaldehydes were prepared from the corresponding arylacetyl chlorides[13] which were obtained by reacting the corresponding carboxylic acids with a slight excess of thionyl chloride. Allyl arenes **2** were either commercial products or synthesized by allylating a phenol or

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a naphthol via Claisen rearrangement to the corresponding β-allyl product[14] and then converting the hydroxyl group to the methoxyl.[15]

Synthesis of 3,5-Bis(arylmethyl)-2-isoxazolines 3. To a stirred solution of oxime **1** (20 mmol), alkene **2** (10 mmol), and pyridine (4 mmol) in 100 mL of $CHCl_3$ at 0 °C was added 5% NaOCl solution (40 mmol) during 1.5 h. The organic layer was separated and washed with 2 M HCl, saturated $NaHCO_3$, and water and evaporated to give the product as an oil which was purified by column chromatography using CH_2Cl_2 as an eluent.

3,5-Dibenzyl-2-isoxazoline (3a): yield 82%, mp 57.0−57.5 °C; ^{1}H NMR δ 7.29−7.09 (m, 10 H), 4.75 (m, 1 H), 3.62, 3.57 (2 d, 2 H, J = 14.9), 2.95 (dd, 1 H, J = 13.8, 5.9), 2.73 (dd, 1 H, J = 17.1, 10.2), 2.72 (dd, 1 H, J = 13.8, 7.1), 2.48 (dd, 1 H, J = 17.1, 7.5); ^{13}C NMR δ 157.8, 136.9, 135.9 (3 s), 129.4, 128.8, 128.8, 128.5, 127.0, 126.6, 81.0 (7 d), 40.8, 40.6, 34.2 (3 t); MS m/z (%) 251 (M^+) (3), 160 (13), 91 (100); HRMS Calcd for $C_{17}H_{17}NO$: (M^+) 251.13101. Found: (M^+) 251.13101

3-Benzyl-5-[(2-methoxyphenyl)methyl]-2-isoxazoline (3b): yield 78%, a pale brown oil; ^{1}H NMR δ 7.36−7.16 (m, 6 H), 7.04 (d, 1 H, J = 7.4), 6.85 (td, 1 H, J = 7.4, 1.1), 6.79 (d, 1 H, J = 8.2), 4.85 (m, 1 H), 3.72 (s, 3 H), 3.68, 3.61 (2 d, 2 H, J = 14.9), 3.03 (dd, 1 H, J = 13.4, 5.7), 2.73 (dd, 1 H, J = 13.4, 7.7), 2.72 (ddt, 1 H, J = 17.1, 10.1, 0.9), 2.54 (ddt, 1 H, J = 17.1, 7.1, 0.8); ^{13}C NMR δ 157.8, 157.4, 136.0 (3 s), 131.2, 128.8, 128.7, 127.9, 126.9 (5 d), 125.3 (s), 120.5, 110.3, 79.9 (3 d), 55.1 (q), 40.5, 35.3, 34.2 (3 t); MS m/z (%) 281 (M^+) (5), 160 (12), 121 (60), 91 (100); HRMS Calcd for $C_{18}H_{19}NO_2$: (M^+) 281.14158. Found: (M^+) 281.14158.

3-Benzyl-5-[(4-methoxyphenyl)methyl]-2-isoxazoline (3c): yield 86%, a pale yellow oil; ^{1}H NMR δ 7.31−7.23 (m, 3 H), 7.14−7.10 (m, 2 H), 7.03 (m, 2 H), 6.78 (m, 2 H), 4.72 (m, 1 H), 3.75 (s, 3 H), 3.63, 3.56 (2 d, 2 H, J = 14.9), 2.88 (dd, 1 H, J = 14.0, 5.8), 2.74 (ddt, 1 H, J = 17.0, 10.2, 0.9), 2.69 (dd, 1 H, J = 14.0, 6.8), 2.48 (ddt, 1 H, J = 17.0, 7.6, 0.8 Hz); ^{13}C NMR δ 158.4, 157.7, 135.9 (3 s), 130.4 (d), 128.9 (s), 128.8, 128.7, 127.0, 113.9, 81.2 (5 d), 55.2 (q), 40.4, 39.8, 34.2 (3 t); MS m/z (%) 281 (M^+) (5), 160 (5), 121 (100), 91 (42); HRMS Calcd for $C_{18}H_{19}NO_2$: (M^+) 281.14158. Found: (M^+) 281.14158.

3-Benzyl-5-[(3,4-dimethoxyphenyl)methyl]-2-isoxazoline (3d): yield 81%, a pale yellow oil; ^{1}H NMR δ 7.29−7.18 (m, 3 H), 7.15−7.08 (m, 2 H), 6.72 (d, 1 H, J = 8.1), 6.66 (d, 1 H, J = 2.0), 6.64 (dd, 1 H, J = 8.1, 2.0), 4.74 (m, 1 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 3.63, 3.53 (2 d, 2 H, J = 14.9), 2.85 (dd, 1 H, J = 14.0, 5.9), 2.75 (ddt, 1 H, J = 17.0, 10.3, 0.8), 2.69 (dd, 1 H, J = 14.0, 6.4), 2.48 (ddt, 1 H, J = 17.0, 7.4, 0.7); ^{13}C NMR δ 157.7, 148.9, 147.8, 135.9, 129.4 (5 s), 128.7, 128.7, 126.9, 121.4, 112.8, 111.3, 81.0 (7 d), 55.8, 55.8 (2 q), 40.3, 40.2, 34.0 (3 t); MS m/z (%) 311 (M^+) (28), 160 (16), 151 (100), 91 (52); HRMS Calcd for $C_{19}H_{21}NO_3$: (M^+) 311.15214. Found: (M^+) 311.15214.

3-Benzyl-5-[(pentafluorophenyl)methyl]-2-isoxazoline (3e): yield 92%, mp 77−79 °C; ^{1}H NMR δ 7.34−7.19 (m, 5 H), 4.77 (m, 1 H), 3.70, 3.63 (2 d, 2 H, J = 14.9), 2.97 (ddt, 1 H, J = 13.9, 7.1, $^4J_{HF}$ = 1.3), 2.93 (dd, 1 H, J = 17.4, 10.2), 2.84 (ddt, 1 H, J = 13.9, 6.0, $^4J_{HF}$ =1.4), 2.52 (dd, 1 H, J = 17.4, 7.5); ^{13}C NMR δ 157.6 (s), 145.4, 140.2 (2 d), 137.5 (d), 135.5 (s), 128.9, 128.7 (2 d), 127.3 (d), 110.4 (s), 78.2 (d), 41.1, 34.1, 27.9 (3 t); MS m/z (%) 341 (M^+) (1), 181 (13), 160 (15), 91 (100); HRMS Calcd for $C_{17}H_{12}F_5NO$: (M^+) 341.08389. Found: (M^+) 341.08391.

3,5-Bis-(1-naphthylmethyl)-2-isoxazoline (3f): yield 84%, a pale yellow oil; ^{1}H NMR δ 8.16 (d, 1 H, J = 8.3), 7.90−7.78 (m, 4 H), 7.66 (d, 1 H, J = 8.3), 7.58−7.49 (m, 2 H), 7.45−7.38 (m, 3 H), 7.31 (d, 1 H, J = 7.0), 7.23 (dd, 1 H, J = 8.3, 7.0), 6.91 (dd, 1 H, J = 7.0, 1.2), 4.91 (m, 1 H), 4.18, 4.06 (2 d, 2 H, J = 15.2), 3.46 (dd, 1 H, J = 14.0, 5.7), 2.93 (dd, 1 H, J = 14.0, 8.3), 2.63 (ddt, 1 H, J = 17.1, 10.0, 1.0), 2.44 (ddt, J = 14.0, 6.8, 0.8); ^{13}C NMR δ 158.1, 134.0, 133.8, 132.8, 132.0, 131.9, 131.8 (7 s,) 128.8, 128.8, 128.1, 127.4, 127.3, 127.3, 126.6, 126.1, 126.0, 125.6, 125.5, 125.4, 123.7, 123.4, 80.2 (15 d), 40.9, 37.7, 32.1 (3 t); MS m/z (%) 351 (M^+) (21), 210 (3), 141 (100), 115 (27); HRMS Calcd for $C_{25}H_{21}NO$: (M^+) 351.16231. Found: (M^+) 351.16231.

3-(2-Naphthylmethyl)-5-[(1-methoxy-2-naphthyl)methyl]-2-isoxazoline (3g): yield 62%, a pale brown oil; ^{1}H NMR δ 7.96 (d, 1 H, J = 8.4), 7.76−7.68 (m, 3 H), 7.62 (d, 1 H, J = 8.7), 7.57 (s, 1 H), 7.46 (d, 1 H, J = 8.6), 7.44−7.39 (m, 4 H), 7.23 (d, 1 H, J = 8.5), 7.18 (dd, 1 H, J = 8.4, 1.9), 4.88 (m, 1 H), 3.75 (d, 1 H, J = 14.8), 3.75 (s, 3 H), 3.70 (d, 1 H, J = 14.8), 3.13 (dd, 1 H, J = 13.6, 5.8), 2.94 (dd, 1 H, J = 13.6, 7.2), 2.72 (ddt, 1 H, J = 17.1, 10.1, 0.8), 2.60 (ddt, 1 H, J = 17.1, 7.3, 0.7); ^{13}C NMR δ 157.9, 154.1, 134.2, 133.5, 133.3, 132.4 (6 s), 128.6, 128.5, 128.0 (3 d), 127.9 (s), 127.6, 127.5, 127.4, 126.7, 126.2, 125.9, 125.7, 125.7 (8 d), 125.2 (s), 124.1, 122.0, 80.6 (3 d), 61.8 (q), 40.7, 34.7, 34.3 (3 t); MS m/z (%) 381 (M^+) (25), 210 (7), 171 (65), 141 (100); HRMS Calcd for $C_{26}H_{23}NO_2$: (M^+) 381.17288. Found: (M^+) 381.17288.

3-(2-Naphthylmethyl)-5-[(3-methoxy-2-naphthyl)methyl]-2-isoxazoline (3h): yield 36%, mp 144.5−145.0 °C; ^{1}H NMR δ 7.81−7.72 (m, 4 H), 7.68 (d, 1 H, J = 8.0), 7.64 (d, 1 H, J = 9.0), 7.63 (s, 1 H), 7.44 (m, 2 H), 7.32 (dd, 1 H, J = 8.4, 1.8), 7.22 (ddd, 1 H, J = 8.0, 6.8, 1.3), 7.16 (ddd, 1 H, J = 8.5, 6.8, 1.5), 7.09 (d, 1 H, J = 9.0), 4.93 (m, 1 H), 3.86, 3.70 (2 d, 2 H, J = 14.6), 3.61 (s, 3 H), 3.36 (dd, 1 H, J = 13.4, 5.6), 3.31 (dd, 1 H, J = 13.4, 8.8), 2.67 (ddt, 1 H, J = 17.1, 6.0, 0.7), 2.60 (ddt, 1 H, J = 17.1, 9.7, 0.7); ^{13}C NMR δ 157.9, 154.9, 133.6, 133.5, 133.3, 132.5, 129.1 (7 s), 128.6, 128.5, 128.5, 127.6, 127.6, 127.4, 126.9, 126.6, 126.3, 125.8, 123.3, 123.0 (12 d), 117.7 (s), 112.8, 80.2 (2 d), 56.0 (q), 40.4, 34.4, 29.8 (3 t); MS m/z (%) 381 (M^+) (25), 210 (2), 171 (100), 141 (81); HRMS Calcd for $C_{26}H_{23}NO_2$: (M^+) 381.17288. Found: (M^+) 381.17288.

Synthesis of 1,5-Diaryl-4-hydroxy-2-pentanones 4. A solution of isoxazoline **3** (10 mmol), AcOH (0.1 mol) and water (1.0 mol), in 100 mL of MeOH (with **3e**−**h**, 200 mL of THF was used as the solvent) was stirred under H_2 at rt overnight in the presence of Raney Ni (1.5 g). The catalyst was removed by filtering through Celite and the filtrate extracted by CH_2Cl_2. The extracts were washed with saturated $NaHCO_3$ and water and evaporated to give the pure product.

1,5-Diphenyl-4-hydroxy-2-pentanone (4a): yield 89%, a pale yellow oil; ^{1}H NMR δ 7.35−7.15 (m, 10 H), 4.26 (m, 1 H), 3.68 (s, 2 H), 3.29 (s, 1 H), 2.79 (dd, 1 H, J = 13.6, 7.3) 2.69 (dd, 1 H, J = 13.6, 6.0), 2.58 (d, 1 H, J = 4.8), 2.57 (d, 1 H, J = 7.2); ^{13}C NMR δ 208.9, 137.9, 133.6 (3 s), 129.5, 129.4, 128.8, 128.5, 127.2, 126.6, 68.8 (7 d), 50.8, 47.6, 42.9 (3 t); MS m/z (%) 254 (M^+) (1), 236 ($M^+ - H_2O$) (15), 121 (64), 119 (35), 91 (100); HRMS Calcd for $C_{17}H_{16}O$: ($M^+ - H_2O$) 236.12011. Found: ($M^+ - H_2O$) 236.12012.

1-Phenyl-5-(2-methoxyphenyl)-4-hydroxy-2-pentanone (4b): yield 75%, a greenish brown viscous oil; ^{1}H NMR δ 7.32−7.13 (m, 6 H), 7.08 (dd, 1 H, J = 7.4, 1.8), 6.87 (td, 1 H, J = 7.4, 1.1), 6.83 (dd, 1 H, J = 8.2, 1.1), 4.30 (m, 1 H), 3.77 (s, 3 H), 3.66 (s, 2 H), 2.82 (dd, 1 H, J = 13.4, 6.8), 2.77 (dd, 1 H, J = 13.4, 6.0), 2.59 (d, 1 H, J = 6.1), 2.59 (d, 1 H, J = 5.8); ^{13}C NMR δ 208.9, 157.6, 133.9 (3 s), 131.4, 129.5, 128.7, 128.0, 127.1 (5 d), 126.2 (s), 120.6, 110.5, 67.9 (3 d), 55.3 (q), 50.7, 48.0, 37.5 (3 t); MS m/z (%) 266 ($M^+ - H_2O$) (100), 193 (8), 175 (24), 163 (13), 121 (11), 91 (9); HRMS Calcd for $C_{18}H_{20}O_3$: (M^+) 284.14124. Found: (M^+) 284.14124.

1-Phenyl-5-(4-methoxyphenyl)-4-hydroxy-2-pentanone (4c): yield 76%, a pale yellow oil; ^{1}H NMR δ 7.32−7.23 (m, 3 H), 7.16−7.12 (m, 2 H), 7.05 (m, 2 H), 6.80 (m, 2 H), 4.19 (m, 1 H), 3.74 (s, 3 H), 3.65 (s, 2 H), 2.69 (dd, 1 H, J = 13.7, 7.2), 2.61 (dd, 1 H, J = 13.7, 6.0), 2.59 (dd, 1 H, J = 17.4, 4.5), 2.55 (dd, 1 H, J = 17.4, 7.5); ^{13}C NMR δ 208.8, 158.3, 133.7 (3 s), 130.3 (d), 129.9 (s), 129.5, 128.7, 127.1, 114.0, 68.9 (5 d), 55.2 (q), 50.7, 47.6, 42.0 (3 t); MS m/z (%) 284 (M^+) (8), 266 ($M^+ - H_2O$) (100), 175 (11), 147 (37), 134 (27), 121 (13), 91 (5); HRMS Calcd for $C_{18}H_{20}O_3$: (M^+) 284.14124. Found: (M^+) 284.14124.

1-Phenyl-5-(3,4-dimethoxyphenyl)-4-hydroxy-2-pentanone (4d): yield 90%, a yellow oil; ^{1}H NMR δ 7.34−7.23 (m, 3 H), 7.17−7.14 (m, 2 H), 6.80−6.66 (m, 3 H), 4.22 (m. 1 H), 3.84 (s, 3 H), 3.83 (s, 3 H), 3.68 (s, 2 H), 2.70 (dd, 1 H, J = 13.7, 7.3), 2.63 (dd, 1 H, J = 13.7, 5.9), 2.61 (d, 1 H, J = 4.2),

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2.60 (d, 1 H, J = 7.7); ^{13}C NMR δ 208.9, 149.0, 147.8, 133.6, 130.4 (5 s), 129.5, 128.8, 127.2, 121.4, 112.6, 111.4, 68.8 (7 d), 55.9, 55.9 (2 q), 50.8, 47.7, 42.5 (3 t); MS m/z (%) 314 (M^+) (10), 298 ($M^+ - H_2O$) (1), 205 (7), 181 (7), 151 (42), 91 (100); HRMS Calcd for $C_{19}H_{22}O_4$: (M^+) 314.15181. Found: (M^+) 314.15181.

1-Phenyl-5-(pentafluorophenyl)-4-hydroxy-2-pentanone (4e): yield 88%, mp 68.5−69.0 °C; ^{1}H NMR δ 7.35−7.16 (m, 5 H), 4.24 (m, 1 H), 3.72, (s, 2 H), 2.99 (d, OH, J = 4.2, coupled due to strong hydrogen bonding), 2.88 (ddt, 1 H, J = 13.8, 7.9, $^4J_{HF}$ = 1.6), 2.76 (ddt, 1 H, J = 13.8, 5.3, $^4J_{HF}$ = 1.6), 2.70 (dd, 1 H, J = 17.9, 3.4), 2.63 (dd, 1 H, J = 17.9, 8.2); ^{13}C NMR δ 208.68 (s), 145.5, 140.0, 137.5 (3 d), 133.3 (s), 129.5, 128.9, 127.4 (3 d), 111.5 (s), 66.7 (d), 50.8, 47.3, 29.1 (3 t); MS m/z (%) 344 (M^+) (3), 326 ($M^+ - H_2O$) (5), 253 (29), 235 (58), 211 (63), 181 (43), 91 (100); HRMS Calcd for $C_{17}H_{13}F_5O_2$: (M^+) 344.08356. Found: (M^+) 344.08357.

1,5-Di(1-naphthyl)-4-hydroxy-2-pentanone (4f): yield 93%, a pale brown viscous oil; ^{1}H NMR δ 8.00−7.96 (m, 1 H), 7.84−7.77 (m, 3 H), 7.75, 7.69 (2 d, 2 H, J = 8.2), 7.48−7.41 (m, 4 H), 7.36, 7.30 (2 dd, 2 H, J = 8.2, 7.0), 7.24, 7.18 (2 dd, 2 H, J = 7.0, 1.2), 4.36 (m, 1 H), 4.05, 4.02 (2 d, 2 H, J = 16.1), 3.11 (d, 2 H, J = 6.7), 2.63 (dd, 1 H, J = 17.5, 8.1), 2.61 (dd, 1 H, J = 17.5, 3.8); ^{13}C NMR δ 209.2, 134.0, 134.0, 133.9, 132.2, 132.1, 130.4 (7 s), 128.9, 128.8, 128.3, 128.2, 127.6, 127.5, 126.6, 126.1, 126.0, 125.7, 125.5, 125.4, 123.9, 123.7, 68.2 (15 d), 48.9, 47.5, 40.0 (3 t); MS m/z (%) 354 (M^+) (5), 336 ($M^+ - H_2O$), 213 (5), 183 (5), 153 (21), 141 (100); HRMS Calcd for $C_{25}H_{22}O_2$: (M^+) 354.16198. Found: (M^+) 354.16198.

1-(2-Naphthyl)-5-(1-methoxy-2-naphthyl)-4-hydroxy-2-pentanone (4g): yield 71%, a pale brown oil; ^{1}H NMR δ 8.04 (d, 1 H, J = 8.3), 7.79−7.69 (m, 4 H), 7.56 (s, 1 H), 7.51−7.40 (m, 5 H), 7.22 (dd, 1 H, J = 8.3, 2.1), 7.22 (d, 1 H, J = 8.5), 4.36 (m, 1 H), 3.85 (s, 3 H), 3.81, 3.76 (2 d, 2 H, J = 15.4), 2.99 (dd, 1 H, J = 13.5, 6.8), 2.94 (dd, 1 H, J = 13.5, 6.3), 2.65 (d, 1 H, J = 6.6), 2.65 (d, 1 H, J = 5.2); ^{13}C NMR δ 209.1, 154.0, 134.2, 133.5, 132.4, 131.2 (6 s), 128.8, 128.3, 128.3, 128.1 (4 d), 127.9 (s), 127.7, 127.6, 127.5 (3 d), 126.2 (s), 126.2, 126.0, 125.8, 125.8, 124.2, 122.0, 68.6 (7 d), 61.8 (q), 50.7, 47.6, 36.9 (3 t); MS m/z (%) 384 (M^+) (10), 366 ($M^+ - H_2O$) (13), 225 (11), 183 (10), 171 (25), 141 (100); HRMS Calcd for $C_{26}H_{24}O_3$: (M^+) 384.17254. Found: (M^+) 384.17254.

1-(2-Naphthyl)-5-(3-methoxy-2-naphthyl)-4-hydroxy-2-pentanone (4h): yield 95%, a brown oil; ^{1}H NMR δ 7.96 (d, 1 H, J = 8.7), 7.73−7.63 (m, 5 H), 7.47 (s, 1 H), 7.42−7.34 (m, 3 H), 7.28 (ddd, 1 H, J = 8.1, 6.8, 1.1), 7.14 (dd, 1 H, J = 8.5, 1.7), 7.10 (d, 1 H, J = 9.1), 4.39 (m, 1 H), 3.71 (s, 3 H), 3.68, 3.64 (2 d, 2 H, J = 15.7), 3.26 (d, 1 H, J = 7.0), 3.26 (d, 1 H, J = 6.6), 2.68 (dd, 1 H, J = 17.5, 8.0), 2.56 (dd, 1 H, J = 17.5, 3.9); ^{13}C NMR δ 209.2, 154.8, 133.4, 133.4, 132.3, 131.3, 129.2 (7 s), 128.5, 128.5, 128.2, 128.2, 127.6, 127.5, 127.5, 126.6, 126.1, 125.7, 123.3, 123.3 (12 d), 119.0 (s), 112.9, 68.3 (2 d), 56.1 (q), 50.6, 48.1, 31.9 (3 t); MS m/z (%) 384 (M^+) (10), 366 ($M^+ - H_2O$) (9), 197 (14), 171 (34), 165 (22), 141 (100); HRMS Calcd for $C_{26}H_{24}O_3$: (M^+) 384.17254. Found: (M^+) 384.17254.

Synthesis of 1,5-Diaryl-4-methoxy-2-pentanones 5. To a stirred solution of hydroxy ketone **4** (1 mmol) in 25 mL of MeOH was added dropwise concd HCl (0.2 mL) at 0 °C, and the mixture was refluxed overnight. Then the solution was taken up with CH_2Cl_2, washed with saturated $NaHCO_3$ and water, and evaporated. The residue was purified by column chromatography using chloroform as an eluent to afford the pure product.

1,5-Diphenyl-4-methoxy-2-pentanone (5a): yield 78%, a pale yellow oil; ^{1}H NMR δ 7.34−7.14 (m, 10 H), 3.90 (m, 1 H), 3.65 (s, 2 H), 3.28 (s, 3 H), 2.84 (dd, 1 H, J = 13.7, 6.0), 2.70 (dd, 1 H, J = 13.7, 6.4), 2.64 (dd, 1 H, J = 16.3, 7.5), 2.44 (dd, 1 H, J = 16.3, 4.9); ^{13}C NMR δ 207.0, 138.2, 134.2 (3 s), 129.8, 129.8, 128.9, 128.6, 127.3, 126.6, 78.6 (7 d), 57.7 (q), 51.3, 46.5, 40.2 (3 t); MS m/z (%) 268 (M^+) (1), 236 (M^+ − MeOH) (54), 177 (49), 135 (82), 119 (66), 117 (48), 91 (100); HRMS Calcd for $C_{18}H_{20}O_2$: (M^+) 268.14632. Found: (M^+) 268.14633.

1-Phenyl-5-(2-methoxyphenyl)-4-methoxy-2-pentanone (5b): yield 52%, a pale yellow oil; ^{1}H NMR δ 7.30−7.10 (m, 6 H), 7.08 (ddd, 1 H, J = 7.4, 1.8, 0.4), 6.85 (td, 1 H, J = 7.4, 1.1), 6.81 (dd, 1 H, J = 8.2, 1.1), 3.97 (m, 1 H), 3.77 (s, 3 H), 3.67, 3.62 (2 d, 2 H, J = 15.9), 3.31 (s, 3 H), 3.01 (dd, 1 H, J = 13.3, 5.4), 2.63 (dd, 1 H, J = 16.0, 8.4), 2.62 (dd, 1 H, J = 13.3, 7.4), 2.43 (dd, 1 H, J = 16.0, 4.0); ^{13}C NMR δ 206.9, 157.6, 134.2 (3 s), 131.3, 129.6, 128.6, 127.8, 126.9 (5 d), 126.3 (s), 120.5, 110.4, 77.3 (3 d), 57.3, 55.2 (2 q), 50.8, 46.7, 34.5 (3 t); MS m/z (%) 266 (M^+ − MeOH) (40), 175 (16), 147 (36), 121 (38), 119 (26), 91 (100); HRMS Calcd for $C_{19}H_{22}O_3$: (M^+) 298.15689. Found: (M^+) 298.15693.

1-Phenyl-5-(pentafluorophenyl)-4-methoxy-2-pentanone (5e): yield 75%, a pale yellow oil; ^{1}H NMR δ 7.34−7.12 (m, 5 H), 3.92 (m, 1 H), 3.70 (s, 2 H), 3.30 (s, 3 H), 2.88 (m, 2 H), 2.73 (dd, 1 H, J = 16.8, 7.5), 2.44 (dd, 1 H, J = 16.8, 5.1); ^{13}C NMR δ 205.9 (s), 145.5, 140.0, 137.4 (3 d), 133.7 (s), 129.5, 128.8, 127.2 (3 d), 111.2 (s), 75.9 (d), 57.7 (q), 50.9, 46.0, 26.5 (3 t); MS m/z (%) 358 (M^+) (9), 267 (16), 225 (100), 181 (14), 177 (23); HRMS Calcd for $C_{18}H_{15}F_5O_2$: (M^+) 358.09921. Found: (M^+) 358.09920.

1,5-Di(1-naphthyl)-4-methoxy-2-pentanone (5f): yield 40%, a pale brown oil; ^{1}H NMR δ 8.04 (d, 1 H, J = 8.1), 7.86−7.78 (m, 3 H), 7.75 (d, 1 H, J = 8.3), 7.71 (d, 1 H, J = 8.2), 7.52−7.42 (m, 4 H), 7.37 (dd, 1 H, J = 8.3, 7.0), 7.33 (dd, 1 H, J = 8.2, 7.0), 7.26 (d, 2 H, J = 7.0), 4.09 (d, 1 H, J = 16.2), 4.06 (m, 1 H), 4.04 (d, 1 H, J = 16.2), 3.29 (dd, 1 H, J = 13.9, 6.6), 3.21 (s, 3 H), 3.08 (dd, 1 H, J = 13.9, 6.4), 2.75 (dd, 1 H, J = 16.3, 7.3), 2.49 (dd, 1 H, J = 16.3, 5.0); ^{13}C NMR δ 207.1, 134.2, 133.9, 133.9, 132.3, 132.2, 130.7 (7 s), 128.8, 128.7, 128.3, 128.0, 127.9, 127.2, 126.4, 126.0, 125.8, 125.5, 125.5, 125.4, 123.9, 123.8, 78.0 (15 d), 57.7 (q), 49.3, 46.4, 37.5 (3 t); MS m/z (%) 368 (M^+) (2), 336 (M^+ − MeOH) (14), 200 (27), 184 (16), 167 (26), 153 (53), 141 (100); HRMS Calcd for $C_{26}H_{24}O_2$: (M^+) 368.17763. Found: (M^+) 368.17763.

1-(2-Naphthyl)-5-(1-methoxy-2-naphthyl)-4-methoxy-2-pentanone (5g): yield 32%, a pale brown oil; ^{1}H NMR δ 8.06 (d, 1 H, J = 8.2), 7.82−7.70 (m, 4 H), 7.56 (s, 1H), 7.52 (d, 1 H, J = 8.3), 7.52−7.40 (m, 4 H), 7.29 (d, 1 H, J = 8.4), 7.22 (dd, 1 H, J = 8.8, 1.7), 4.07 (m, 1 H), 3.88 (s, 3 H), 3.81 (s, 2 H), 3.32 (s, 3 H), 3.11 (dd, 1 H, J = 13.5, 5.8), 2.88 (dd, 1 H, J = 13.5, 6.6), 2.72 (dd, 1 H, J = 16.4, 7.3), 2.57 (dd, 1 H, J = 16.4, 5.1); ^{13}C NMR δ 206.8, 154.1, 134.1, 133.5, 132.4, 131.6 (6 s), 129.0, 128.3, 128.2, 128.0 (4 d), 128.0 (s), 127.6, 127.6, 127.6 (3 d), 126.4 (s), 126.1, 125.9, 125.7, 125.7, 124.0, 122.1, 78.0 (7 d), 61.9, 57.4 (2 q), 51.0, 46.4, 33.9 (3 t); MS m/z (%) 398 (M^+), (22), 366 (M^+ − MeOH) (31), 257 (5), 225 (29), 197 (40), 171 (66), 141 (100); HRMS Calcd for $C_{27}H_{26}O_3$: (M^+) 398.18819. Found: (M^+) 398.18819.

1-(2-Naphthyl)-5-(3-methoxy-2-naphthyl)-4-methoxy-2-pentanone (5h): yield 83%, a brown viscous oil; ^{1}H NMR δ 7.98 (d, 1 H, J = 8.7), 7.78−7.68 (m, 5 H), 7.50 (s, 1 H), 7.46−7.40 (m, 3 H), 7.30 (ddd, 1 H, J = 8.0, 6.8, 1.1), 7.17 (d, 1 H, J = 9.0), 7.16 (dd, 1 H, J = 8.4, 1.8), 4.10 (m, 1 H), 3.82 (s, 3 H), 3.72 (s, 2 H), 3.43 (dd, 1 H, J = 13.4, 5.6), 3.36 (s, 3 H), 3.16 (dd, 1 H, J = 13.4, 8.2), 2.79 (dd, 1 H, J = 16.3, 8.6), 2.43 (dd, 1 H, J = 16.3, 3.8); ^{13}C NMR δ 207.1, 155.0, 133.5, 133.4, 132.4, 131.7, 129.2 (7 s), 128.5, 128.4, 128.2, 128.1, 127.6, 127.6, 127.6, 126.5, 126.0, 125.7, 123.3, 123.3 (12 d), 119.1 (s), 113.0, 77.7 (2 d), 57.5, 56.2 (2 q), 50.9, 47.1, 29.3 (3 t); MS m/z (%) 398 (M^+) (43), 366 (M^+ − MeOH) (38), 257 (12), 215 (12), 201 (16), 197 (38), 183 (19), 171 (90), 141 (100); HRMS Calcd for $C_{27}H_{26}O_3$: (M^+) 398.18819. Found: (M^+) 398.18819.

Synthesis of Dimethylsulfonium 1-(Arylacetyl)-2-oxo-3-arylpropylides 6. To a stirred suspension of NCS (20 mmol) in 60 mL of anhydrous CH_2Cl_2 was added dropwise dimethyl sulfide (40 mmol) at −70 °C under argon and stirring was continued for 1 h. Then a solution of hydroxy ketone **4** (4.0 mmol) in 6 mL of CH_2Cl_2 was added, maintaining the same temperature, and the solution was stirred for 1 h. Triethylamine (60 mmol) was then added and after 1 h the reaction mixture was treated with saturated brine (20 mL). This mixture was extracted with ether and the organic layer washed with saturated brine and evaporated. The residue was purified by column chromatography using 95:5 chloroform−acetone as an eluent to give **6**.

Dimethylsulfonium 1-(phenylacetyl)-2-oxo-3-phenylpropylide (6a): yield 80%, a pale yellow viscous oil; ^{1}H NMR δ 7.30−7.18 (m, 10 H), 4.07 (br s, 4 H), 2.63 (s, 6 H); ^{13}C NMR

δ 191.4, 137.1 (2 s), 129.5, 128.4, 126.3 (3 d), 85.4 (s), 48.7 (t), 26.5 (q); MS *m*/*z* (%) 312 (M^+) (17), 250 (21), 221 (86), 206 (18), 91 (100); HRMS Calcd for $C_{19}H_{20}O_2S$: (M^+) 312.11839. Found: (M^+) 312.11840.

Dimethylsulfonium 1-(phenylacetyl)-2-oxo-3-(2-methoxyphenyl)propylide (6b): yield 75%, a pale yellow viscous oil; ^{1}H NMR δ 7.30−7.24 (m, 4 H), 7.21−7.16 (m, 2 H), 7.08 (dd, 1 H, *J* = 7.4, 1.5), 6.86 (td, 1 H, *J* = 7.4, 1.1), 6.83 (dd, 1 H, *J* = 7.9, 1.1), 4.10, 4.00 (2 br s, 4 H), 3.74 (s, 3 H) 2.63 (s, 6 H); ^{13}C NMR δ 191.5, 157.3, 137.4 (3 s), 130.8, 129.5, 128.2, 127.7, 126.1 (5 d), 126.0 (s), 120.5, 110.5 (2 d), 85.7 (s), 55.4 (q), 48.4, 42.8 (2 t), 26.5, 26.5 (2 q); MS *m*/*z* (%) 342 (M^+) (17), 251 (18), 221 (65), 121 (79), 91 (100); HRMS Calcd for $C_{20}H_{22}O_3S$: (M^+) 342.12897. Found: (M^+) 342.12897.

Dimethylsulfonium 1-(phenylacetyl)-2-oxo-3-(4-methoxyphenyl)propylide (6c): yield 56%, a pale yellow viscous oil; ^{1}H NMR: δ 7.30−7.16 (m, 5 H), 7.13, 6.81 (2 m, 4 H), 4.06, 3.99 (2 br s, 4 H), 3.76 (s, 3 H) 2.62 (s, 6 H); ^{13}C NMR δ 191.7, 158.4, 137.4 (3 s), 130.6, 129.7 (2 d), 129.4 (s), 128.6, 126.5, 114.1 (3 d), 85.7 (s), 55.5 (q), 48.8, 47.9 (2 t), 26.7 (q); MS *m*/*z* (%) 342 (M^+) (3), 280 (10), 251 (3), 221 (12), 121 (100); HRMS Calcd for $C_{20}H_{22}O_3S$: (M^+) 342.12897. Found: (M^+) 342.12897.

Dimethylsulfonium 1-(phenylacetyl)-2-oxo-3-(3,4-dimethoxyphenyl)propylide (6d): yield 94%, a pale brown viscous oil; ^{1}H NMR δ 7.30−7.16 (m, 5 H), 6.81−6.78 (m, 3 H), 4.06, 4.02 (2 br s, 4 H), 3.85, 3.82 (2 s, 6 H), 2.66 (s, 6 H); ^{13}C NMR δ 192.2, 191.1, 148.9, 147.6, 137.1, 129.6 (6 s), 129.4, 128.4, 126.3, 121.6, 112.6, 111.2 (6 d), 85.4 (s), 55.9, 55.9 (2 q), 48.6, 48.1 (2 t), 26.5, 26.5 (2 q); MS *m*/*z* (%) 372 (M^+) (10), 310 (59), 221 (37), 191 (56), 151 (100); HRMS Calcd for $C_{21}H_{24}O_4S$: (M^+) 372.13953. Found: (M^+) 372.13953.

Dimethylsulfonium 1-(phenylacetyl)-2-oxo-3-(pentafluorophenyl)propylide (6e): yield 92%, mp 127−129 °C; ^{1}H NMR δ 7.34−7.21 (m, 5 H), 4.33, 3.92 (2 br s, 4 H), 2.71 (s, 6 H); ^{13}C NMR δ 190.0, 188.6 (2 s), 145.5, 139.9, 137.3 (3 d), 136.6 (s), 129.2, 128.8, 126.7 (3 d), 111.3, 85.2 (2s), 48.4, 36.2 (2 t), 26.7 (q); MS *m*/*z* (%) 402 (M^+) (3), 311 (22), 181 (36), 118 (17), 91 (100); HRMS Calcd for $C_{19}H_{15}F_5O_2S$: (M^+) 402.07128. Found: (M^+) 402.07129.

Dimethylsulfonium 1-(1-naphthylacetyl)-2-oxo-3-(1-naphthyl)propylide (6f): yield 72%, mp 69−70 °C, ^{1}H NMR δ 7.94, 7.82, 7.72 (3 m, 6 H), 7.47−7.35 (m, 8 H), 4.53 (br s, 4 H), 2.42 (s, 6 H); ^{13}C NMR δ 191.7, 133.8, 133.8, 132.4 (4 s), 128.6, 127.7, 127.2, 126.0, 125.6, 125.4, 124.3 (7 d), 86.3 (s), 46.3 (t), 26.4 (q); MS *m*/*z* (%) 412 (M^+) (1), 350 (11), 271 (9), 141 (100), 115 (30); HRMS Calcd for $C_{27}H_{24}O_2S$: (M^+) 412.14970. Found: (M^+) 412.14970.

Dimethylsulfonium 1-(2-naphthylacetyl)-2-oxo-3-(1-methoxy-2-naphthyl)propylide (6g): yield 43%, a pale brown viscous oil, ^{1}H NMR δ 8.07 (d, 1 H, *J* = 8.2), 7.81−7.72 (m, 5 H), 7.50−7.41 (m, 6 H), 7.24 (d, 1 H, *J* = 8.5), 4.30, 4.24 (2 br s, 4 H), 3.88 (s, 3 H), 2.59 (s, 6 H); ^{13}C NMR δ 191.8, 191.2, 153.4, 134.8, 134.1, 133.6, 132.2 (7 s), 128.6, 128.1, 128.0, 128.0 (4 d), 128.0 (s), 127.8, 127.6, 127.6 (3 d), 126.0 (s), 125.9, 125.8, 125.7, 125.3, 124.0, 122.0 (6 d), 85.8 (s), 61.8 (q), 48.7, 42.8 (2 t), 26.6 (q); MS *m*/*z* (%) 442 (M^+) (1), 380 (8), 285 (6), 271 (10), 243 (14), 169 (57), 141 (100); HRMS Calcd for $C_{28}H_{26}O_3S$: (M^+) 442.16027. Found: (M^+) 442.16027.

Dimethylsulfonium 1-(2-naphthylacetyl)-2-oxo-3-(3-methoxy-2-naphthyl)propylide (6h): yield 54%, a pale brown viscous oil; ^{1}H NMR δ 7.82−7.73 (m, 6 H), 7.50−7.41 (m, 3 H), 7.35−7.25 (m, 4 H), 4.63, 4.25 (2 br s, 4 H), 3.90 (s, 3 H), 2.62 (s, 6 H); ^{13}C NMR δ 192.8, 190.9, 155.0, 134.9, 133.8, 133.7, 132.2, 129.3 (8 s), 128.4, 128.4, 127.7, 127.6, 127.6, 127.6, 127.6 (7 d), 126.3 (s), 125.9, 125.4, 123.7, 123.7, 125.2, 113.7 (6 d), 85.9 (s), 56.9 (q), 48.6, 38.6 (2 t), 26.8 (q); MS *m*/*z* (%) 442 (M^+) (1), 301 (10), 171 (100), 141 (88); HRMS Calcd for $C_{28}H_{26}O_3S$: (M^+) 442.16027. Found: (M^+) 442.16027.

Synthesis of 1,5-Diaryl-2,4-pentanediones 7. To a stirred suspension of ylide **6** (1.5 mmol) and Zn powder (30 mmol) in 25 mL of CH_2Cl_2 was added AcOH (30 mmol) at 0 °C, and stirring was continued at rt overnight. The mixture was filtered through Celite and the filtrate washed with saturated $NaHCO_3$ and water, eluted with CH_2Cl_2 through a short column of Florisil (100−200 mesh), and evaporated. The crude product was crystallized from methanol.

1,5-Diphenyl-2,4-pentanedione (7a): yield 88%, mp 64−65 °C (lit. mp 65.2−66.5 °C);[4c] enol form (85%): ^{1}H NMR δ 15.27 (br, OH), 7.32−7.19 (m, 10 H), 5.42 (s, 1 H), 3.55 (s, 4 H); ^{13}C NMR δ_C 192.3, 135.1 (2 s), 129.4, 128.7, 127.1, 99.6 (4 d), 45.1 (t); diketone form (15%): ^{1}H NMR δ_H 7.27−7.11 (m, 10 H), 3.68 (s, 4 H), 3.55 (s, 2 H); ^{13}C NMR δ 201.8, 133.3 (2 s), 129.7, 129.0, 127.4 (3 d), 54.8, 50.7 (2 t); MS *m*/*z* (%) 252 (M^+) (5), 161 (99), 133 (6), 119 (8), 91 (100); HRMS: Calcd for $C_{17}H_{16}O_2$: (M^+) 252.11502. Found: (M^+) 252.11503.

1-Phenyl-5-(2-methoxyphenyl)-2,4-pentanedione (7b): yield 82%, a pale yellow oil; enol form (80%): ^{1}H NMR δ 15.29 (br, OH), 7.30−7.10 (m, 7 H), 6.89 (td, 1 H, *J* = 7.4, 1.1), 6.83 (dd, 1 H, *J* = 8.2, 0.9), 5.39 (s, 1 H), 3.71 (s, 3 H), 3.55, 3.50 (2 s, 4 H); ^{13}C NMR δ 194.3, 190.2, 157.4, 135.3 (4 s), 131.0, 129.3, 128.8, 128.6, 126.9 (5 d), 123.6 (s), 120.6, 110.6, 99.3 (3 d), 55.3 (q), 44.5, 39.8 (2 t); diketone form (20%): ^{1}H NMR δ 7.31−7.10 (m, 6 H), 7.06 (dd, 1 H, *J* = 7.7, 1.4 Hz), 6.90 (td, 1 H, *J* = 7.4, 1.1 Hz), 6.84 (dd, 1 H, *J* = 8.2, 0.9 Hz), 3.73 (s, 3 H), 3.67, 3.61, 3.52 (3 s, 6 H); ^{13}C NMR δ 202.4, 202.0, 157.3, 133.5 (4 s), 131.4, 129.6, 128.9, 128.6, 127.2 (5 d), 122.6 (s), 120.8, 110.5 (2 d), 55.3 (q), 54.7, 50.3, 45.5 (3 t); MS *m*/*z* (%) 282 (M^+) (3), 191 (10), 161 (24), 148 (10), 121 (38), 91 (100); HRMS Calcd for $C_{18}H_{18}O_3$: (M^+) 282.12559. Found: (M^+) 282.12559.

1-Phenyl-5-(4-methoxyphenyl)-2,4-pentanedione (7c): yield 77%, mp 66−67 °C; enol form (88%): ^{1}H NMR δ 15.29 (br, OH), 7.32−7.17 (m, 5 H), 7.10 (m, 2 H), 6.83 (m, 2 H), 5.41 (s, 1 H), 3.76 (s, 3 H), 3.53, 3.47 (2 s, 4 H); ^{13}C NMR δ 192.7, 192.2, 158.7, 135.0 (4 s), 130.3, 129.3, 128.6, 127.0 (4 d), 127.0 (s), 114.1, 99.4 (2 d), 55.2 (q), 45.0, 44.1 (2 t); diketone form (12%): ^{1}H NMR δ 7.32−7.17 (m, 7 H), 7.01 (m, 2 H), 3.75 (s, 3 H), 3.67, 3.60, 3.52 (3 s, 6 H); ^{13}C NMR δ 202.2, 201.9, 158.7, 133.3 (4 s), 130.6, 129.6, 128.6, 127.3 (4 d), 125.2 (s), 114.3 (d), 55.2 (q), 54.5, 50.6, 49.7 (3 t); MS *m*/*z* (%) 282 (M^+) (5), 191 (14), 161 (48), 148 (21), 121 (100); HRMS Calcd for $C_{18}H_{18}O_3$: (M^+) 282.12559. Found: (M^+) 282.12559.

1-Phenyl-5-(3,4-dimethoxyphenyl)-2,4-pentanedione (7d): yield 68%, a pale yellow oil; enol form (85%): ^{1}H NMR δ 15.29 (br, OH), 7.32−7.20 (m, 3 H), 7.20−7.14 (m, 2 H), 6.79 (d, 1 H, *J* = 8.1), 6.72 (ddt, 1 H, *J* = 8.1, 2.0, 0.5), 6.69 (d, 1 H, *J* = 2.0), 5.42 (s, 1 H), 3.83, 3.81 (2 s, 6 H), 3.53, 3.47 (2 s, 4 H); ^{13}C NMR δ 192.7, 192.1, 149.0, 148.1, 135.0 (5 s), 129.3, 128.6 (2 d), 127.4 (s), 127.0, 121.5, 112.4, 111.3, 99.3 (5 d), 55.8, 55.8 (2 q), 45.0, 44.6 (2 t); diketone form (15%): ^{1}H NMR δ 7.24−7.17 (m, 3 H), 7.12−7.08 (m, 2 H), 6.78 (d, 1 H, *J* = 8.1), 6.65 (ddt, 1 H, *J* = 8.1, 2.0, 0.5), 6.62 (d, 1 H, *J* = 2.0), 3.83, 3.80 (2 s, 6 H), 3.66, 3.61, 3.54 (3 s, 6 H); ^{13}C NMR δ 202.2, 201.9, 149.2, 148.4, 133.2 (5 s), 129.6, 128.8 (2 d), 127.3 (s), 125.7, 121.8, 112.6, 111.5 (4 d), 55.8, 55.8 (2 q), 54.5, 50.5, 50.1 (3 t); MS *m*/*z* (%) 312 (13), 221 (6), 178 (30), 161 (68), 151 (100); HRMS Calcd for $C_{19}H_{20}O_4$: (M^+) 312.13616. Found: (M^+) 312.13616.

1-Phenyl-5-(pentafluorophenyl)-2,4-pentanedione (7e): yield 93%, mp 55−56 °C; enol form (88%): ^{1}H NMR δ 14.79 (br, OH), 7.37−7.23 (m, 5 H), 5.45 (s, 1 H), 3.70, 3.59 (2 s, 4 H); ^{13}C NMR δ 191.6, 188.5 (2 s), 145.4, 140.6, 137.5 (3 d), 134.7 (s), 129.4, 128.8, 127.3 (3 d), 108.5 (s), 98.8 (d), 43.7, 32.4 (2 t), diketone form (12%): ^{1}H NMR δ 7.32−7.20 (m, 5 H), 3.84, 3.81, 3.70 (3 s, 6 H); ^{13}C NMR δ 201.0, 197.1, 132.9 (3 s), 129.6, 129.1, 127.7 (3 d), 55.2, 50.8, 36.7 (3 t), C_6F_5 -signals not detected due to overlapping patterns; MS *m*/*z* (%) 342 (M^+) (4), 251 (100), 181 (60); HRMS Calcd for $C_{17}H_{11}F_5O_2$: (M^+) 342.06791. Found: (M^+) 342.06792.

1,5-Di(1-naphthyl)-2,4-pentanedione (7f): yield 81%, mp 80−81 °C; enol form (82%): ^{1}H NMR δ 15.29 (br, OH), 7.83−7.72 (m, 6 H), 7.45−7.39 (m, 4 H), 7.34 (dd, 1 H, *J* = 8.2, 7.0), 7.22 (d, 1 H, *J* = 6.9), 5.29 (s, 1 H), 3.92 (s, 4 H); ^{13}C NMR δ 192.4, 133.8, 132.0, 131.2 (4 s), 128.7, 128.0, 128.0, 126.3, 125.8, 125.4, 123.8, 99.7 (8 d), 42.5 (t); diketone form (18%): ^{1}H NMR δ 7.85−7.75 (m, 3 H), 7.48−7.37 (m, 4 H), 7.31 (dd, 1 H, *J* = 8.2, 7.0), 7.12 (d, 1 H, *J* = 7.1), 4.03 (s, 4 H), 3.41 (s, 2 H); ^{13}C NMR δ 202.4, 133.9 132.1, 129.9 (4 s), 128.8, 128.5, 128.3, 126.7, 126.0, 125.5, 123.7 (7 d), 53.8, 48.7 (2 t); MS *m*/*z* (%) 352 (M^+) (12), 211 (44), 183 (16), 168 (18), 141 (100); HRMS Calcd for $C_{25}H_{20}O_2$: (M^+) 352.14633. Found: (M^+) 352.14633.

1-(2-Naphthyl)-5-(1-methoxy-2-naphthyl)-2,4-pentanedione (7g): yield 86%, a pale yellow viscous oil; enol form: ^{1}H NMR δ 15.33 (br, OH), 8.13 (d, 1 H, J = 8.2), 7.88−7.78 (m, 4 H), 7.67 (s, 1 H), 7.60 (d, 1 H, J = 8.4), 7.59−7.48 (m, 4 H), 7.34 (dd, 1 H, J = 8.4, 1.7), 7.24 (d, 1 H, J = 8.5), 5.47 (s, 1 H), 3.80 (s, 3 H), 3.75, 3.63 (2 s, 4 H); ^{13}C NMR δ 193.3, 191.2, 154.1, 134.4, 133.4, 132.5, 132.4, 128.4 (8 s), 128.3, 128.2, 128.1, 128.0, 127.6, 127.6, 127.3, 126.1, 126.1, 126.0, 125.8, 124.2 (12 d), 123.5 (s), 122.1, 99.8 (2 d), 62.1 (q), 44.8, 39.2 (2 t); MS m/z (%) 382 (M^+) (1), 368 (100), 210 (16), 169 (20), 141 (100); HRMS Calcd for $C_{26}H_{22}O_3$: (M^+) 382.15689. Found: (M^+) 382.15375.

1-(2-Naphthyl)-5-(3-methoxy-2-naphthyl)-2,4-pentanedione (7h): yield 58%, mp 122−124 °C; enol form: ^{1}H NMR δ 14.96 (br, OH), 7.80 (d, 1 H, J = 8.6), 7.76−7.64 (m, 5 H), 7.49 (s, 1 H), 7.43−7.37 (m, 3 H), 7.28 (ddd, 1 H, J = 8.1, 6.8, 1.1), 7.17 (dd, 1 H, J = 8.5, 1.8), 7.13 (d, 1 H, J = 8.9), 5.32 (s, 1H), 4.12 (s, 2 H), 3.69 (s, 3 H), 3.53 (s, 2 H); ^{13}C NMR δ 195.2, 189.5, 154.8, 133.4, 133.3, 132.6, 132.3 (7 s), 129.1 (d), 129.1 (s), 128.4 (d), 128.3 (s), 128.1, 127.9, 127.6, 127.6, 126.4, 126.8, 126.0, 125.7, 123.5, 123.2, 113.0, 99.3 (12 d), 56.2 (q), 44.2, 35.3 (2 t); MS m/z (%) 382 (M^+) (13), 241 (15), 211 (15), 198 (13), 171 (100); HRMS Calcd for $C_{26}H_{22}O_3$: (M^+) 382.15689. Found: (M^+) 382.15677.

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Supporting Information Available: Discussion of spectral data and copies of ^{13}C NMR spectra (38 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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