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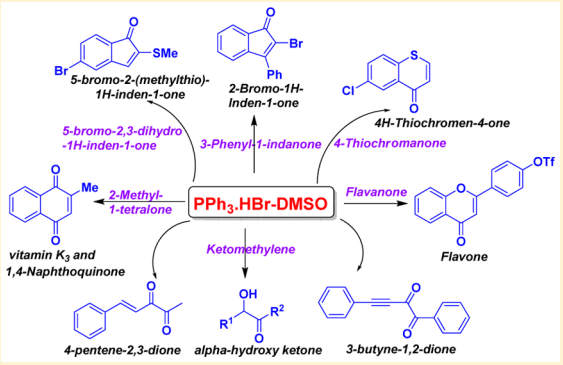
PPh_3·HBr−DMSO: A Reagent System for Diverse Chemoselective Transformations

Kanchan Mal,[‡] Amanpreet Kaur,[‡] Fazle Haque, and Indrajit Das*

Chemistry Division, CSIR-Indian Institute of Chemical Biology, 4, Raja S. C. Mullick Road, Jadavpur, Kolkata 700 032, India

Supporting Information

ABSTRACT: The broad applicability of the hitherto unexplored reagent combination PPh_3·HBr−DMSO is exemplified with multiple highly diverse one-step transformations to synthetically useful building blocks, such as flavones, 4*H*-thiochromen-4-ones, α-hydroxy ketones, 1,4-naphthoquinones (including vitamin K_3), 2-bromo-3-substituted-1*H*-1-indenones, 2-methylthio-1*H*-1-indenones, 3-butyne-1,2-dione, and 4-pentene-2,3-diones. The simple and mild reaction conditions make the reagent superior in terms of yield and substrate scope in comparison with the existing alternatives.



INTRODUCTION

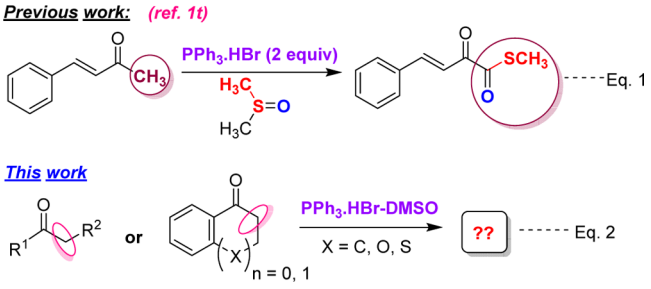
The oxidative bromination, with in situ generation of an active brominating species/molecular bromine from hydrobromic acid (HBr)/bromide salts and hydrogen peroxide, is regarded as an efficient and viable alternative to the existing procedures utilizing molecular bromine for the synthesis of bromide derivatives.[1a−k] Currently, depending on this concept, several elegant approaches have been documented in the literature.[1e−k] However, HBr-mediated oxidative bromination suffers from environmental, health, and safety issues due to its hazardous nature.

On the other hand, dimethyl sulfoxide (DMSO), an inexpensive and less toxic solvent than other members of this category, such as *N*,*N*-dimethylformamide (DMF) and hexamethylphosphoramide (HMPA), is extensively employed as an effective oxidant in traditional named reactions, such as Swern oxidation and its variants, and as a useful oxygen source in Kornblum oxidation as well as hydroxylation reaction.[1l,m] Moreover, the combination of HBr or Br_2 with DMSO is generally pertinent in a variety of oxidative brominations followed by DMSO-based oxidation reactions.[1n−s] Despite its wide applicability in chemical transformations, this reagent combination fails to circumvent the aforementioned issues. However, PPh_3·HBr−DMSO is such a reagent system, which eliminates the ecological and operational concerns.

Herein, we report the PPh_3·HBr−DMSO-mediated highly diverse and chemoselective one-step transformation of ketomethylene derivatives into flavones, 4*H*-thiochromen-4-ones, α-hydroxy ketones, 1,4-naphthoquinones, 2-bromo-3-substituted-1-indenones, 2-methylthio-1-indenones, ynedione, and enediones. The present method involving simple reaction conditions and the readily available and relatively green reagent combination make these transformations more convenient than the reported ones. Furthermore, the in situ generation of bromine by using PPh_3·HBr−DMSO eliminates the need to handle highly corrosive and toxic bromine.

In our previous work with PPh_3·HBr−DMSO, we transformed α,β-unsaturated ketomethyl derivatives to γ-substituted β,γ-unsaturated α-ketomethyl thioesters (Scheme 1, eq 1).[1t]

Scheme 1. Synthesis of α-Ketothioesters from Ketomethyl Derivatives by Using PPh_3·HBr−DMSO



Importantly, we did not observe any bromination at the aromatic ring or at the alkenyl/alkynyl olefinic bond. Intrigued by this finding and to further explore the potential of the PPh_3·HBr−DMSO reagent system, we initiated a systematic study with compounds containing the ketomethylene group (Scheme 1, eq 2).

RESULTS AND DISCUSSION

Based on our previous report,[1t] we began the investigation for optimal reaction conditions with **1f** using 2.0 equiv of PPh_3·HBr

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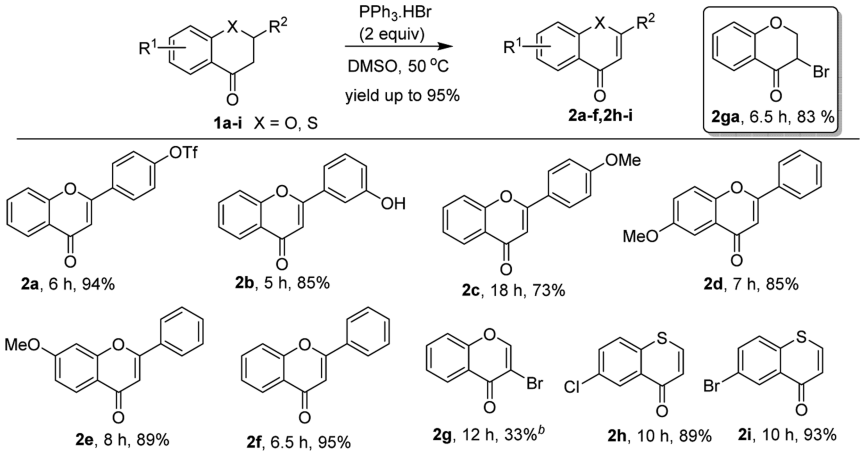
Table 1. Dehydrogenation Using PPh_3·HBr–DMSO[a]

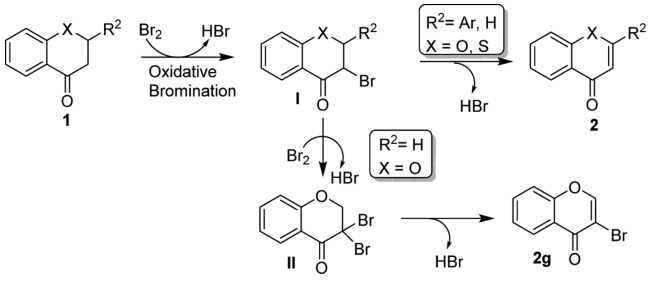


[a]By stirring a mixture of **1** (0.05 g, 1.0 equiv) and PPh_3·HBr (2.0 equiv) in dry DMSO (2.0 mL) under an Ar atmosphere at 50 °C, employing time as noted, isolated yield. [b]The reaction was carried out at 100 °C. In addition to product **2g**, other unidentified products were isolated.

in DMSO at 50 °C. We are pleased to isolate **2f** in 95% yield, resulting from the dehydrogenation of **1f**. When the amount of PPh_3·HBr was decreased to 1.0 equiv, the corresponding isolated yield decreased to 79% after 13 h. The yield was further lowered (13 h, 51%) with a catalytic amount of PPh_3·HBr (0.5 equiv). Besides, in both cases (1 equiv and 0.5 equiv PPh_3·HBr), 10–25% starting materials were isolated even after the reaction was conducted for several hours. Further, the use of 2.5 equiv of PPh_3·HBr failed to improve the yield (6.5 h, 81%) of the reaction significantly (see also Table 2 for optimization studies, vide infra). Consequently, we decided to carry out all of the reactions with 2.0 equiv of PPh_3·HBr in DMSO at 50 °C. As shown in Table 1, several substituted flavanones (**1a–f**) and 4-thiochromanones (**1h–i**) underwent smooth dehydrogenation to produce the corresponding flavones (**2a–f**) and 4*H*-thiochromen-4-ones (**2h,i**) in good to excellent yields,[2a,b,e] but under the standard reaction conditions, 4-chromanone was converted to only 3-bromochroman-4-one (**2ga**), and raising the temperature to 100 °C produced the corresponding 3-bromo-4*H*-chromen-4-one (**2g**).[2c,d] Flavones and (thio)chromones, being biologically active molecules, remain enthralling targets for synthetic chemists, and the methods developed so far mostly utilize expensive metal catalysts.[2a–k]

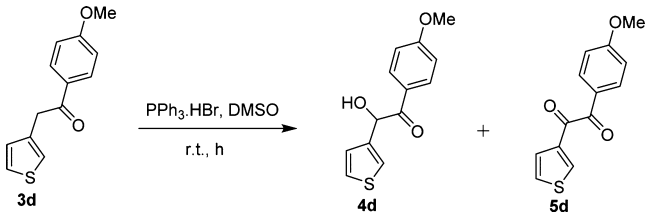
Based on the results obtained in Table 1, we propose a plausible mechanism as in Scheme 2. We presume that PPh_3·HBr in the presence of DMSO would generate Br_2, Ph_3PO, $(CH_3)_2S$, and H_2O through an oxidation–reduction cycle.[1t] The initial oxidative bromination of **1** could then lead to the intermediate **I**, followed by either immediate elimination of HBr to generate product **2** or further bromination to **II**, which upon elimination of HBr produces **2g** (Scheme 2).

Scheme 2. Proposed Reaction Mechanism



Inspired by the above results, we investigated the substrate scope and generality for this transformation using a broad range of compounds containing α-methylene and α-methine ketones. To optimize the reaction conditions, we initiated a systematic study of **3d** with PPh_3·HBr in DMSO under different reaction conditions. As shown in Table 2, we observed that a catalytic amount of PPh_3·HBr proved insufficient to drive the reaction to completion (entry 1). The use of PPh_3·HBr in stoichiometric ratios (entries 2–4) accelerated the transformation. We isolated

Table 2. Optimization of the Reaction Conditions[a]



entry	PPh_3·HBr (equiv)	t (h)	recovered (%) **3d**	yield (%) of **4d**	yield (%) of **5d**
1	0.5	50	10	73	trace
2	1.0	48	8	78	trace
3	1.5	30	18	77	trace
4	2.0	23	trace	90	9
5	3.0	21		65	28
6	5.0	18		65	32
7[b]	2.0	30	100		
8[c]	2.0	36	14	80	trace
9[d]	2.0	40	92	trace	
10[e]	2.0	3		67	20
11[f]	2.0	8		67	17
12[g]	2.0	36	14	56	trace

[a]By stirring a mixture of **3d** (0.05 g, 0.215 mmol, 1.0 equiv) and PPh_3·HBr (equiv) in dry DMSO (2 mL) under an Ar atmosphere at room temperature (30–35 °C), with times as noted. Yields are of isolated products. [b]0.050 g of 3 Å molecular sieves was used. [c]10.0 equiv of H_2O was used. [d]100.0 equiv of H_2O was used. [e]Reaction was performed at 50 °C. [f]Reaction was conducted at 50 °C with 10.0 equiv of H_2O. [g]DMSO was used without drying.

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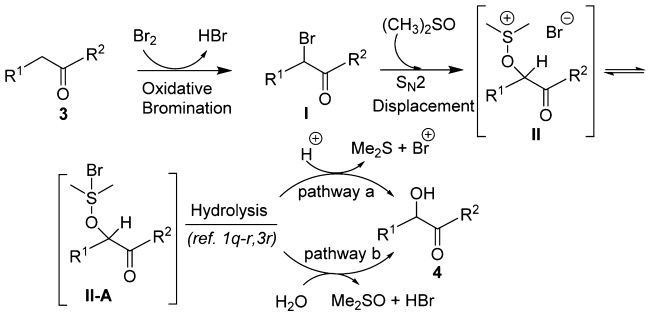
4d in excellent yield (90%, entry 4) when 2 equiv of PPh_3·HBr was used, along with a minor amount of **5d** (9%). Moreover, the yield of **4d** was further lowered when an excess of reagents was used (entries 5 and 6) or the reaction was conducted either at 50 °C (entry 10) or with DMSO that hadn't been dried (entry 12). In all cases (entries 5, 6, and 10), **5d** was also isolated in 20−32% yields. Furthermore, in order to rationalize the influence of water that was expected to be generated in situ through the "oxidation−reduction cycle", we conducted the experiment with 3 Å molecular sieves. In this case, only starting material was recovered (entry 7), as 3 Å molecular sieves are known to remove the water from the reaction medium. On the other hand, conducting the experiment with 10.0 equiv of H_2O at room temperature (entry 8) or at 50 °C (entry 11) produced **4d** in 67−80% yields; however, the use of 100.0 equiv of H_2O completely prevented the formation of product, and the starting material was recovered (entry 9). The exact role of water in the proposed reaction mechanism is not very clear at the moment (Scheme 3).

Scheme 3. Proposed Reaction Mechanism



We presume that, initially, it could help to enolize the ketomethyl group and subsequent oxidative bromination to generate the corresponding α-bromo derivative (**I**, Scheme 3). In addition, water might help to regenerate HBr from bromide ion in the proposed reaction mechanism. As shown in Table 3, the reactions proceeded smoothly to afford the corresponding unsymmetrical α-hydroxy ketones in moderate to excellent yields (**4a**−**r**).[3a−m]

To expand the realm of this methodology, acyclic β-diketones were treated under the standard reaction conditions, and the product was isolated as a mixture of vicinal triketones and its hydrated form (**4t**,**u**, Table 3),[3o,p] whereas a β-diketone with a methine in between produced only the corresponding α-bromo derivative (**4s**, Table 3).[3n] Besides, in few cases, the corresponding 1,2-diketo derivatives (**5**, see the Experimental Section for details), through Kornblum oxidation of intermediate **II**, were isolated in minor quantities along with α-hydroxy ketones as the major components.[3q] However, we observed the change in selectivity for unsaturated ketomethylene groups leading to the predominant formation of unsaturated 1,2-diketones compared to their hydroxy ketones (Schemes 6 and 7).

On the basis of the above investigations and the reported literature,[1q,r,3r] a plausible mechanism for α-hydroxylation is outlined in Scheme 3. We believe that initial oxidative bromination of **3** could generate **I**, which undergoes S_N2 displacement by DMSO to produce **II**, and afterward formation of **II-A**. Subsequently, intermediate **II-A** could be hydrolyzed either by pathway a or pathway b to yield **4**.[3s,t]

Consequently, the scope of 2-methyl-1-tetralone (**6a**) as a substrate was explored under the standard PPh_3−HBr−DMSO reaction conditions. Pleasingly, this led to the formation of vitamin K_3 or menadione (**7a**, Table 4).[4a] The reaction is believed to proceed through the initial oxidative bromination of **6a** to produce intermediate **I** followed by elimination of HBr to generate alkene (**II**), which undergoes rapid isomerization to give substituted 1-naphthol (**II-A**). Subsequent oxidative bromination at the 4-position (more active and less hindered side) would furnish **III**, which through Kornblum oxidation (**IV**) yields **7a** (Scheme 4). Similarly, when we used other substituted α-methyl (**6b**,**c**), α-bromo-α′-methyl (**6d**), and α-unsubstituted (**6e**) 1-tetralones, respective substituted 1,4-naphthoquinones (**7b**−**e**, Table 4) were isolated.[4b,c] It is noteworthy that syntheses of such 1,4-naphthoquinones, which serve as scaffolds for therapeutic compounds, mainly rely on selective oxidation of hydroxylated aromatics and substituted naphthalenes.[4d,e]

Next, we examined the scope and viability of the PPh_3·HBr−DMSO system with substituted 1-indanones (Table 5) since functionalized indanones and indenones exhibit diverse arrays of pharmacological applications.[5a,b] Interestingly, under the standard reaction conditions, 3-phenyl/3-methyl-1-indanones (**8a**,**b**) underwent smooth conversion to 2-bromo-3- phenyl/3-methyl-1*H*-inden-1-ones (**9a**,**b**),[5c] whereas 5-Br/6-OMe-1-indanones without any substitution at C-3 (**8c**−**d**) produced the corresponding 2-methylsulfanyl-1*H*-inden-1-ones (**10a**,**b**), along with minor amounts of monobromo- and dibromo-1-indanone derivatives (see the Experimental Section for details) and other unidentified compounds.[5d−f] The lower yields (**10a**,**b**) obtained in these reactions were thought to be due to the formation of substituted indan-1,2-diones (**IV**) from the corresponding α-bromo (**I**) intermediates through DMSO-based Kornblum oxidation (Scheme 5). However, no such derivatives (**IV**) were isolated. The structure of **10a** was established by single-crystal X-ray diffraction analysis (Table 5).[5g] The distinct behavior exhibited by substituted 1-indanones could be explained on the basis of consecutive oxidative bromination of **8** to yield **II**, followed either by elimination of HBr to produce **9** or by displacement of the bromine atom by dimethylsulfide (to form **III**), and final dehydrobromination to generate **10** (Scheme 5). It must be mentioned here, after the formation of α,α′-dibromo intermediates **II**, if the oxygen atom in DMSO acts as a nucleophile to some extent rather than dimethyl sulfide, the corresponding indan-1,2-diones (**IV**) should be formed. As discussed previously, we have not isolated any such derivatives.

To observe the effect of the PPh_3·HBr−DMSO reagent system on conjugated ketomethylene groups, we conducted the experiment with α,β-alkenyl ketones (**11**) as substrates. Interestingly, this yielded α-oxo-β,γ-unsaturated ketomethyl derivatives (**12a**,**b**, Scheme 6) in moderate yields.[6a] Subsequently, we examined the reaction of α,β-alkynyl ketones (**13**) with PPh_3·HBr−DMSO, which afforded the substituted ynedione (**14**, Scheme 6) in good yield.[6b] These dramatic selectivity changes for unsaturated ketomethylene groups (Scheme 6) in contrast to the saturated ketomethylene groups (Table 3 and Scheme 3, vide supra) may be explained by the presence of extended conjugation in **11** and **13**, which makes the α-H of intermediate bromo derivative (**II**, Scheme 7) more acidic and resulting in rapid abstraction of proton by bromide anion to produce α-diketones as the predominant products **12**/**14** (Scheme 7) rather than hydrolyzed products. It is interesting to note that syntheses of such derivatives (enedione and ynedione) are very rare in the literature, though they are useful as medicinally active compounds.[6c−h] On the other hand, an

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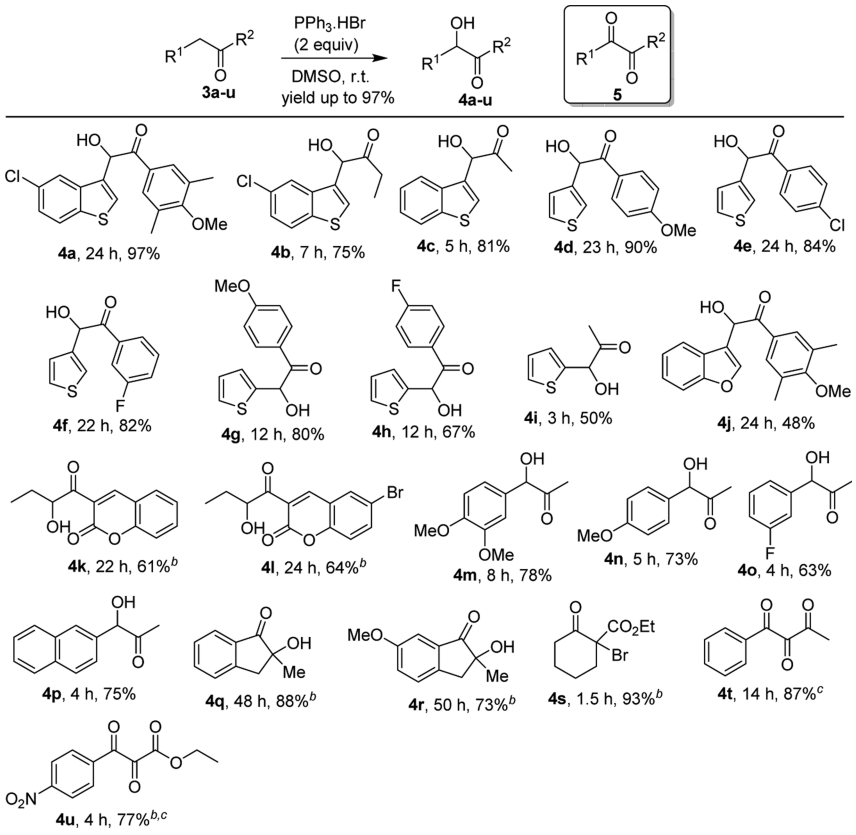
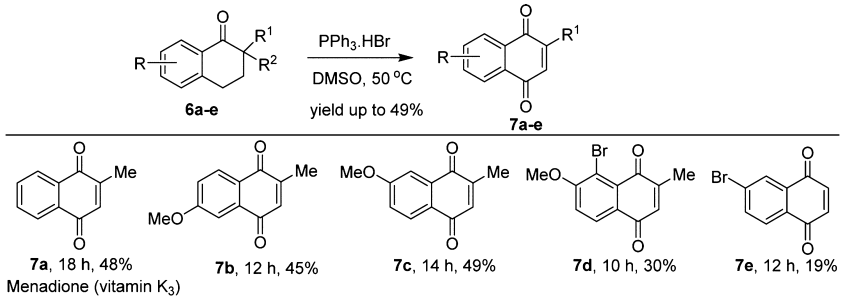
Table 3. α-Hydroxylation Using PPh_3·HBr−DMSO[a]



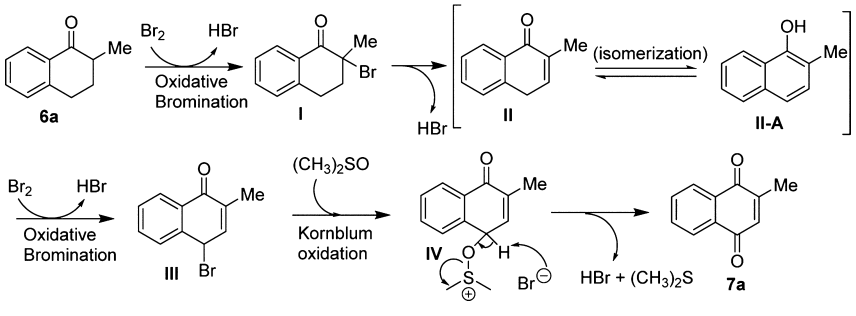
[a]Unless otherwise noted, reactions were carried out at rt (30−35 °C) under the reaction conditions in Table 1, isolated yield. Minor amounts of diketo derivatives were isolated in a few cases; see the Experimental Section. [b]The reaction was carried out at 50 °C. [c]Isolated as a mixture of vicinal tricarbonyl and its hydrated form.

Table 4. Synthesis of 1,4-Naphthoquinones by PPh_3·HBr−DMSO[a]



[a]Unless otherwise noted, reactions were carried out at 50 °C under the conditions in Table 1, isolated yield.

Scheme 4. Proposed Reaction Mechanism



isopropyl derivative (**15a**) produced merely the corresponding α'-Br derivative (**16**, Scheme 6) due to the lack of α-H for further oxidation,[6i] and *trans*-chalcone (**15b**) gave no conversion due to the lack of enolizable proton.

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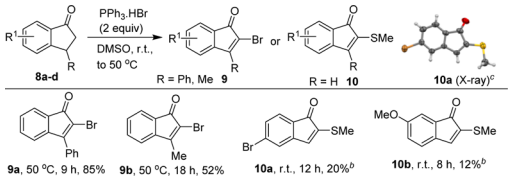
Table 5. Synthesis of Substituted 1*H*-Inden-1-ones by PPh_3·HBr−DMSO[a]



[a]Unless otherwise noted, reactions were carried under the reaction conditions in Table 1, isolated yield. [b]Minor amounts of monobromo- and dibromo-1-indanone derivatives were isolated; see the Experimental Section. [c]The thermal ellipsoids are shown in 50% probability level (X-ray structure; **10a**).

To demonstrate the potential utility of the developed intermediates, we undertook the synthesis of substituted 2-alkynylated 1*H*-inden-1-ones (**17a,b**) from **9a** under Pd-$(PPh_3)_2Cl_2$/CuI-catalyzed standard Sonogashira coupling reaction conditions (Scheme 8).[5b] Moreover, when we treated **14** with $AuCl_3$ (2 mol %) and BnOH in CH_2Cl_2 at room temperature, the corresponding substituted 3(2*H*)-furanone **18**, a key structural unit in many biologically active natural products, was isolated (Scheme 8).[6c,j]

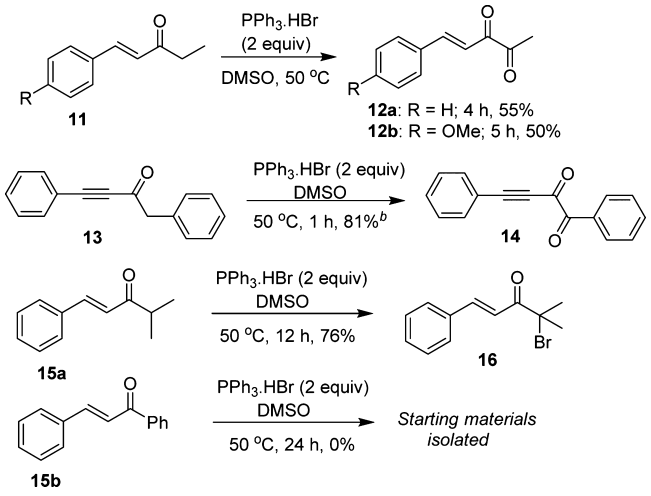
CONCLUSION

In conclusion, we have demonstrated PPh_3·HBr−DMSO-mediated efficient and chemoselective transformations of ketomethylene derivatives into flavones, 4*H*-thiochromen-4-ones, α-hydroxy ketones, 1,4-naphthoquinones, substituted-1*H*-1-indenones, ynedione, and enediones. The operationally simple reaction conditions and ready availability of reactants make these transformations more practical than the reported ones. Additionally, $AuCl_3$-catalyzed efficient access to 3(2*H*)-furanone and $Pd(PPh_3)_2Cl_2$/CuI-catalyzed Sonogashira coupling to produce highly substituted 2-alkynylated 1*H*-inden-1-ones is described. Further applications of this reagent system are in progress.

EXPERIMENTAL SECTION

General Information. Melting points were determined in open-end-capillary tubes and are uncorrected. TLC was performed on silica gel plates (Merck silica gel 60, f_{254}), and the spots were visualized with UV light (254 and 365 nm) or by charring the plate dipped in 5% H_2SO_4−MeOH or vanillin charring solution. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solvent using TMS as the internal standard. HRMS (*m*/*z*) were measured using EI (magnetic sector, positive ion) and ESI (Q-TOF, positive ion) techniques. Infrared (IR) spectra were recorded on Fourier transform infrared spectroscopy; only intense peaks were reported. All of the PPh_3·HBr−DMSO-mediated reactions and the workup were performed in a well-ventilated fume hood; as the volatile byproduct, dimethyl sulfide (Me_2S) having an obnoxious odor formed in the reaction medium.

Scheme 6. Synthesis of Enediones and Ynedione by PPh_3·HBr−DMSO[a]

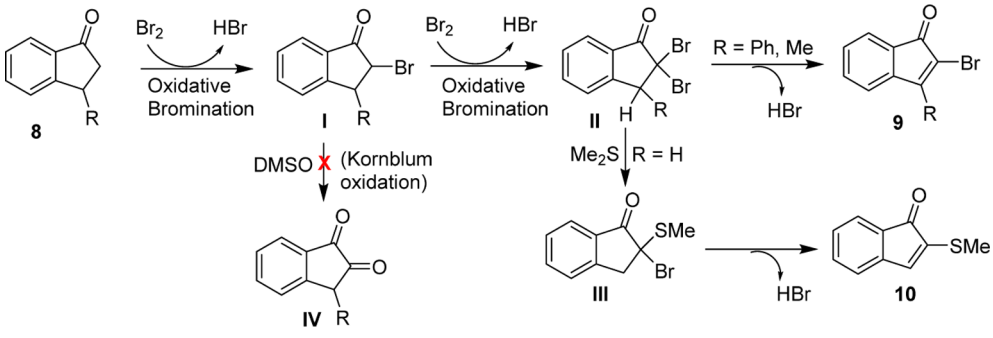


[a]Unless otherwise noted, reactions were carried out at 50 °C under the reaction conditions in Table 1, isolated yield. [b]Small amount of hydroxyketo derviative was formed, see the Experimental Section.

General Procedure for the Synthesis of 2a−i, 4a−u, 7a−e, 9a,b, 10a,b, 12a,b, 14, and 16. PPh3·HBr (2 equiv/mmol) was taken in a 25 mL two-necked round-bottom flask under Ar atmosphere with condenser. Dry DMSO (2 mL) was added dropwise. The corresponding starting materials **1**, **3**, **6**, **8**, **11**, **13**, and **15a** (0.05 g, 1 equiv) were introduced separately into the reaction mixtures at room temperature, and the mixtures were stirred at the same temperature or heated with stirring for the time indicated. After completion of the reaction (TLC), saturated ammonium chloride solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to get a residue. The crude residue was purified over silica gel column chromatography [230−400; eluent: ethyl acetate/*n*-hexane] to obtain **2a−i**, **4a−u**, **5b−p**, **7a−e**, **9a,b**, **10a,b**, **12a,b**, **14**, and **16**.

*4-(4-Oxo-4H-chromen-2-yl)phenyl Trifluoromethanesulfonate (**2a**).* Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.0467 g, 94%; white solid; mp 95−97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.25 (dd, J = 1.5, 8.1 Hz, 1 H), 8.04 (d, J = 9.0 Hz, 2 H), 7.72−7.77 (m, 1 H), 7.59 (d, J = 8.4 Hz, 1 H), 7.26−7.48 (m, 3 H), 6.83 ppm (s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 178.0, 161.2, 156.1, 151.3, 134.1, 132.1, 128.3 (2 CH), 125.8, 125.5, 123.8, 122.1 (2 CH), 112.3−125.1 (m, 1 C, CF_3), 118.0, 108.4 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1642, $\tilde{\nu}_{C=C}$ = 1502, $\tilde{\nu}_{max}$ = 1422, 1376, 1217, 1138, 880, 754, 618; HRMS (EI) *m*/*z* calcd for

Scheme 5. Proposed Reaction Mechanism



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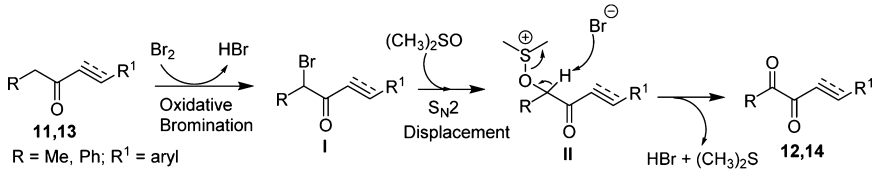
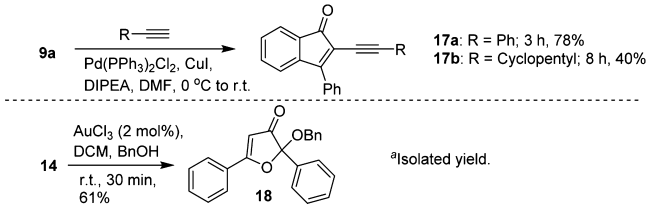
Scheme 7. Proposed Reaction Mechanism



Scheme 8. Synthetic Applications[a]



$C_{16}H_9F_3O_5S$ $[M]^+$ 370.0123, found 370.0097. Anal. Calcd for $C_{16}H_9F_3O_5S$: C, 51.90; H, 2.45. Found: C, 51.83; H, 2.72.

*2-(3-Hydroxyphenyl)-4H-chromen-4-one (**2b**).*[2a] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (30%); isolated yield = 0.042 g, 85%; white solid; ^{1}H NMR (600 MHz, DMSO-d_6) δ = 9.90 (br. s., 1 H), 8.04 (dd, J = 1.8, 7.8 Hz, 1 H), 7.81−7.84 (m, 1 H), 7.75−7.76 (m, 1 H), 7.48−7.52 (m, 2 H), 7.43 (t, J = 2.4 Hz, 1 H), 7.36 (t, J = 8.4 Hz, 1 H), 6.99 (dd, J = 1.8, 8.4 Hz, 1 H), 6.91−6.92 ppm (m, 1 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 178.5, 164.2, 159.3, 157.1, 135.8, 133.9, 131.7, 127.0, 126.2, 124.8, 120.3, 120.0, 118.7, 114.3, 108.4 ppm. (Analytical data are consistent with previously reported values.)

*2-(4-Methoxyphenyl)-4H-chromen-4-one (**2c**).*[2b] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.036 g, 73%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.22 (dd, J = 1.8, 8.4 Hz, 1 H), 7.88−7.90 (m, 2 H), 7.68 (ddd, J = 1.8, 7.2, 8.6 Hz, 1 H), 7.54−7.56 (m, 1 H), 7.39−7.42 (m, 1 H), 7.01−7.04 (m, 2 H), 6.75 (s, 1 H), 3.89 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 179.4, 164.4, 163.4, 157.2, 134.6, 129.0 (2 CH), 126.7, 126.1, 125.0, 124.9, 119.0, 115.5 (2 CH), 107.2, 56.5 ppm. (Analytical data are consistent with previously reported values.)

*6-Methoxy-2-phenyl-4H-chromen-4-one (**2d**).*[2b] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.042 g, 85%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.91−7.93 (m, 2 H), 7.60 (d, J = 3.0 Hz, 1 H), 7.50−7.55 (m, 4 H), 7.29 (dd, J = 3.0, 9.0 Hz, 1 H), 6.82 (s, 1 H), 3.91 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 179.3, 164.2, 158.0, 152.1, 132.9, 132.5, 130.0 (2 CH), 127.2 (2 CH), 125.6, 124.8, 120.5, 107.9, 105.8, 57.0 ppm. (Analytical data are consistent with previously reported values.)

*7-Methoxy-2-phenyl-4H-chromen-4-one (**2e**).*[2b] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (25%); isolated yield = 0.0444 g, 89%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.14 (d, J = 9.0 Hz, 1 H), 7.90−7.91 (m, 2 H), 7.51−7.53 (m, 3 H), 6.97−6.99 (m, 2 H), 6.76 (s, 1 H), 3.93 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 178.9, 165.2, 164.0, 159.0, 132.9, 132.4, 130.0 (2 CH), 128.1, 127.2 (2 CH), 118.9, 115.4, 108.6, 101.4, 56.8 ppm. (Analytical data are consistent with previously reported values.)

*2-Phenyl-4H-chromen-4-one (**2f**).*[2b] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (20%); isolated yield = 0.047 g, 95%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.24 (d, J = 7.8 Hz, 1 H), 7.93−7.95 (m, 2 H), 7.69−7.72 (m, 1 H), 7.51−7.58 (m, 4 H), 7.41−7.44 (m, 1 H), 6.83−6.84 ppm (m, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 179.5, 164.4, 157.3, 134.8, 132.8, 132.6, 130.1 (2 CH), 127.3 (2 CH), 126.7, 126.2, 125.0, 119.1, 108.6 ppm. (Analytical data are consistent with previously reported values.)

*3-Bromo-4H-chromen-4-one (**2g**).*[2c] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (4%); isolated yield = 0.025 g, 33%; light yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.28 (dd, J = 1.2, 7.8 Hz, 1 H), 8.24 (s, 1 H), 7.69−7.75 (m, 1 H), 7.44−7.51 ppm (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.1, 156.0, 153.7, 134.0, 126.4, 125.8, 123.1, 118.0, 110.6 ppm. (Analytical data are consistent with previously reported values.)

*3-Bromochroman-4-one (**2ga**).*[2d] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (3%); isolated yield = 0.064 g, 83%; white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.96 (dd, J = 1.8, 8.1 Hz, 1 H), 7.53−7.58 (m, 1 H), 7.09 (dd, J = 7.2, 14.4 Hz, 1 H), 7.05 (d, J = 8.4 Hz, 1 H), 4.57−4.71 ppm (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 185.2, 160.6, 136.7, 128.2, 122.3, 118.7, 117.9, 71.2 (CH_2), 45.4 ppm. (Analytical data are consistent with previously reported values.)

*6-Chloro-4H-thiochromen-4-one (**2h**).*[2e] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.044 g, 89%; white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.53 (s, 1 H), 7.84 (d, J = 10.5 Hz, 1 H), 7.58 (s, 2 H), 7.03 ppm (d, J = 10.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 178.4, 137.8, 135.6, 134.3, 133.3, 131.8, 128.2, 128.1, 125.6 ppm. (Analytical data are consistent with previously reported values.)

*6-Bromo-4H-thiochromen-4-one (**2i**).*[2e] Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (10%); isolated yield = 0.046 g, 93%; white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.69 (d, J = 2.4 Hz, 1 H), 7.85 (d, J = 10.8 Hz, 1 H), 7.72 (dd, J = 2.1, 8.4 Hz, 1 H), 7.51 (d, J = 8.7 Hz, 1 H), 7.04 ppm (d, J = 10.5 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 178.3, 137.9, 136.2, 134.5, 133.5, 131.3, 128.3, 125.8, 122.2 ppm. (Analytical data are consistent with previously reported values.)

*2-(5-Chlorobenzo[b]thiophene-3-yl)-2-hydroxy-1-(4-methoxy-3,5-dimethylphenyl)ethanone (**4a**).* Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (20%); 0.051 g, 97%; white solid; mp 112−113 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.95 (d, J = 1.8 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 1 H), 7.62 (s, 2 H), 7.33 (dd, J = 1.8, 8.4 Hz, 2 H), 6.21 (d, J = 6.0 Hz, 1 H), 4.44 (d, J = 6.0 Hz, 1 H), 3.71 (s, 3 H), 2.23 ppm (s, 6 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.5, 162.3, 138.8, 138.6, 133.9, 131.7, 131.1, 130.1 (2 CH), 128.9, 128.1, 125.4, 123.8 (2 C), 122.1, 70.3, 59.6, 16.3 ppm (2 CH_3); IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3414, $\tilde{\nu}_{C=O}$ = 1671, $\tilde{\nu}_{C=C}$ = 1598, $\tilde{\nu}_{max}$ = 1320, 1306, 1213, 1158, 1106, 1009, 832, 815, 804; HRMS (EI) m/z calcd for $C_{19}H_{17}ClO_3S$ $[M]^+$ 360.0587, found 360.0585. Anal. Calcd for $C_{19}H_{17}ClO_3S$: C, 63.24; H, 4.75. Found: C, 63.58; H, 5.05;

*1-(5-Chlorobenzo[b]thiophene-3-yl)-1-hydroxybutan-2-one (**4b**) and 1-(5-Chlorobenzo[b]thiophene-3-yl)butane-1,2-dione (**5b**).* Prepared according to the general procedure discussed above. **4b**: eluent, EtOAc/*n*-hexane (20%); 0.040 g, 75%; yellow gum. **5b**: EtOAc/*n*-hexane (5%); 0.008 g, 15%; yellow solid; mp 85−86 °C. **4b**: ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.03 (d, J = 8.7 Hz, 1 H), 7.92 (d, J = 1.8 Hz, 1 H), 7.86 (s, 1 H), 7.40 (dd, J = 2.1, 8.7 Hz, 1 H), 6.19 (d, J = 4.5 Hz, 1 H), 5.50 (d, J = 4.2 Hz, 1 H), 2.45−2.58 (m, 2 H), 0.86 ppm (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 210.3, 138.6, 138.5, 134.2, 129.4, 127.8, 124.6, 124.6, 122.4, 74.7, 30.3 (CH_2), 7.6 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3421, $\tilde{\nu}_{C=O}$ = 1719, $\tilde{\nu}_{C=C}$ = 1643, $\tilde{\nu}_{max}$ = 1384, 1077, 970, 832, 796; HRMS (ESI) m/z calcd for $C_{12}H_{11}ClO_2SNa$ $[M + Na]^+$ 277.0066, found 277.0050. Anal. Calcd for $C_{12}H_{11}ClO_2S$: C, 56.58; H, 4.35. Found: C, 56.92; H, 4.42. **5b**: ^{1}H NMR (600 MHz, DMSO-d_6) δ = 9.10 (s, 1 H), 8.56 (d, J = 1.8 Hz, 1 H), 8.19 (d, J = 8.4 Hz, 1 H), 7.55 (dd, J = 1.8, 8.4 Hz, 1 H), 2.96 (q, J = 6.6, 14.4 Hz, 2 H), 1.06 ppm (t, J = 6.6 Hz, 3 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 202.6, 185.7, 147.8, 138.3, 138.2, 131.9, 128.1, 126.3, 125.4, 123.9, 31.1, 7.3 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1713, $\tilde{\nu}_{C=C}$ = 1642, $\tilde{\nu}_{max}$ = 1420, 1096, 1076, 1023, 800; HRMS (ESI) m/z calcd for $C_{12}H_9ClO_2SNa$ $[M + Na]^+$ 274.9910, found 274.9912.

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*1-Benzo[b]thiophene-3-yl-1-hydroxypropan-2-one (**4c**) and 1-Benzo[b]thiophene-3-ylpropane-1,2-dione (**5c**).* Prepared according to the general procedure discussed above. **4c**: eluent, EtOAc/*n*-hexane (15%); 0.044 g, 81%; yellow gum. **5c**: EtOAc/*n*-hexane (3%); 0.008 g, 15%; yellow gum. **4c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87−7.90 (m, 1 H), 7.71−7.74 (m, 1 H), 7.52 (s, 1 H), 7.37−7.41 (m, 2 H), 5.46 (s, 1 H), 4.26 (br s, 1 H), 2.11 ppm (s, 3 H); ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.97−8.00 (m, 1 H), 7.85−7.88 (m, 1 H), 7.77 (s, 1 H), 7.37−7.39 (m, 2 H), 6.16 (d, J = 4.5 Hz, 1 H), 5.44 (d, J = 4.5 Hz, 1 H), 2.10 ppm (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 207.8, 140.0, 137.1, 134.4, 125.4, 124.5, 124.2, 123.0, 122.9, 75.3, 25.1 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3439, $\tilde{\nu}_{C=O}$ = 1717, $\tilde{\nu}_{max}$ = 1428, 1356, 1102, 763, 735; HRMS (EI) m/z calcd for $C_{11}H_{10}O_2S$ $[M]^+$: 206.0402; found: 206.0404. **5c:** ^{1}H NMR (600 MHz, DMSO-d_6) δ = 9.01 (s, 1 H), 8.57−8.58 (m, 1 H), 8.12−8.14 (m, 1 H), 7.54−7.56 (m, 1 H), 7.49 (td, J = 1.8, 8.4 Hz, 1 H), 2.49 ppm (s, 3 H); ^{13}C NMR (150 MHz, DMSO-d_6) δ = 200.3, 185.5, 145.9, 139.5, 137.0, 128.6, 126.6, 126.2, 124.7, 123.6, 26.1 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1627, $\tilde{\nu}_{max}$ = 1422, 1056, 750; HRMS (ESI) m/z calcd for $C_{11}H_8O_2SNa$ $[M + Na]^+$ 227.0143, found 227.0150.

*2-Hydroxy-1-(4-methoxyphenyl)-2-(thiophene-3-yl)ethanone (**4d**) and 1-(4-Methoxyphenyl)-2-(thiophene-3-yl)ethane-1,2-dione (**5d**).* Prepared according to the general procedure discussed above. **4d**: eluent, EtOAc/*n*-hexane (20%); 0.048 g, 90%; white solid; mp 119−122 °C. **5d**: EtOAc/*n*-hexane (7%); 0.005 g, 9%; yellow solid; mp 65−67 °C. **4d**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.93 (d, J = 9.0 Hz, 2 H), 7.25−7.27 (m, 2 H), 6.99−7.00 (m, 1 H), 6.90 (d, J = 8.7 Hz, 2 H), 6.02 (d, J = 6.6 Hz, 1 H), 4.47 (d, J = 6.6 Hz, 1 H), 3.85 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.7, 164.2, 140.3, 131.5 (2 CH), 126.7, 126.3, 123.8, 114.0 (2 CH), 70.9, 55.5 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3443, $\tilde{\nu}_{C=O}$ = 1667, $\tilde{\nu}_{C=C}$ = 1603, $\tilde{\nu}_{max}$ = 1266, 1231, 1192, 1091, 975, 864, 777; HRMS (ESI) m/z calcd for $C_{13}H_{12}O_3SNa$ $[M + Na]^+$ 271.0405, found 271.0439. Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.89; H, 4.87. Found: C, 62.94; H, 4.59. **5d**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.21 (dd, J = 1.2, 3.0 Hz, 1 H), 7.99 (dt, J = 3.0, 9.0 Hz, 2 H), 7.66 (dd, J = 1.2, 5.4 Hz, 1 H), 7.39 (dd, J = 3.0, 5.4 Hz, 1 H), 6.98 (dt, J = 3.0, 9.0 Hz, 2 H), 3.89 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 192.9, 188.7, 166.0, 139.3, 137.9, 133.6 (2 CH), 128.2, 128.0, 126.7, 115.3 (2 CH), 56.6 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1651, $\tilde{\nu}_{C=C}$ = 1601, $\tilde{\nu}_{max}$ = 1508, 1166, 1262, 1232, 834, 738, 609; HRMS (ESI) m/z calcd for $C_{13}H_{10}O_3SNa$ $[M + Na]^+$ 269.0249, found 269.0247.

*1-(4-Chlorophenyl)-2-hydroxy-2-(thiophene-3-yl)ethanone (**4e**) and 1-(4-Chlorophenyl)-2-(thiophene-3-yl)ethane-1,2-dione (**5e**).* Prepared according to the general procedure discussed above. **4e**: eluent, EtOAc/*n*-hexane (20%); 0.045 g, 84%; white solid; mp 97−99 °C. **5e**: EtOAc/*n*-hexane (4%); 0.008 g, 15%; yellow solid; mp 85−87 °C. **4e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.26−7.29 (m, 2 H), 6.96−6.98 (m, 1 H), 6.03 (d, J = 6.0 Hz, 1 H), 4.32 ppm (d, J = 6.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.3, 140.6, 139.4, 131.8, 130.4 (2 CH), 129.1 (2 CH), 127.1, 126.1, 124.2, 71.4 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3451, $\tilde{\nu}_{C=O}$ = 1682, $\tilde{\nu}_{C=C}$ = 1590, $\tilde{\nu}_{max}$ = 1266, 1226, 1088, 976, 865, 826, 782, 673; HRMS (ESI) m/z calcd for $C_{12}H_9ClO_2SNa$ $[M + Na]^+$ 274.9910, found 274.9941. Anal. Calcd for $C_{12}H_9ClO_2S$: C, 57.03; H, 3.59. Found: C, 57.25; H, 3.60. **5e**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.24 (dd, J = 1.8, 3.0 Hz, 1 H), 7.97 (dt, J = 2.4, 8.4 Hz, 2 H), 7.67 (dd, J = 1.2, 5.4 Hz, 1 H), 7.49 (dt, J = 2.4, 9.0 Hz, 2 H), 7.42 ppm (dd, J = 3.0, 5.4 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 191.7, 186.5, 141.5, 137.8, 137.3, 131.5 (2 CH), 131.1, 129.3 (2 CH), 127.3, 127.2 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1657, $\tilde{\nu}_{C=C}$ = 1583, $\tilde{\nu}_{max}$ = 1403, 1225, 1168, 1087, 821, 701; HRMS (EI) m/z calcd for $C_{12}H_7ClO_2S$ $[M]^+$ 249.9855, found 249.9849.

*1-(3-Fluorophenyl)-2-hydroxy-2-(thiophene-3-yl)ethanone (**4f**) and 1-(3-Fluorophenyl)-2-(thiophene-3-yl)ethane-1,2-dione (**5f**).* Prepared according to the general procedure discussed above. **4f**: eluent, EtOAc/*n*-hexane (20%); 0.044 g, 82%; white solid; mp 102−104 °C. **5f**: EtOAc/*n*-hexane (5%); 0.008 g, 15%; yellowish white solid; mp 82−84 °C. **4f**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.70 (dt, J = 1.2, 7.8 Hz, 1 H), 7.61−7.63 (m, 1 H), 7.41 (td, J = 5.4, 7.8 Hz, 1 H), 7.24−7.29 (m, 3 H), 6.97−6.99 (m, 1 H), 6.04 (d, J = 6.6 Hz, 1 H), 4.29 ppm (d, J = 6.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 197.4, 162.7 (d, J_{C-F} = 246.0 Hz, 1 C), 139.2, 135.5 (d, J_{C-F} = 6.0 Hz, 1 C), 130.5 (d, J_{C-F} = 7.5 Hz, 1 C), 127.2, 126.1, 124.8 (d, J_{C-F} = 1.5 Hz, 1 C), 124.3, 121.1 (d, J_{C-F} = 21.0 Hz, 1 C), 115.8 (d, J_{C-F} = 22.5 Hz, 1 C), 71.6 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3456, $\tilde{\nu}_{C=O}$ = 1684, $\tilde{\nu}_{C=C}$ = 1586, $\tilde{\nu}_{max}$ = 1486, 1433, 1266, 1075, 990, 898, 792, 680; HRMS (ESI) m/z calcd for $C_{12}H_9FO_2SNa$ $[M + Na]^+$ 259.0205, found 259.0185. **5f**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.24 (dd, J = 1.2, 3.0 Hz, 1 H), 7.79 (dt, J = 1.2, 7.8 Hz, 1 H), 7.72−7.74 (m, 1 H), 7.68 (dd, J = 1.2, 5.4 Hz, 1 H), 7.50 (td, J = 5.4, 7.8 Hz, 1 H), 7.42 (dd, J = 3.0, 5.4 Hz, 1 H), 7.36 ppm (tdd, J = 1.2, 2.4, 8.4 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 191.7, 186.3, 162.8 (d, J = 247.5 Hz, 1 C), 137.7, 137.3, 134.7 (d, J = 6.0 Hz, 1 C), 130.7 (d, J = 7.5 Hz, 1 C), 127.3, 127.2, 126.2 (d, J = 3.0 Hz, 1 C), 121.9 (d, J = 21.0 Hz, 1 C), 116.4 (d, J = 22.5 Hz, 1 C) ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1658, $\tilde{\nu}_{C=C}$ = 1585, $\tilde{\nu}_{max}$ = 1442, 1237, 1143, 730, 661; HRMS (EI) m/z calcd for $C_{12}H_7FO_2S$ $[M]^+$ 234.0151, found 234.0149.

*2-Hydroxy-1-(4-methoxyphenyl)-2-(thiophene-2-yl)ethanone (**4g**) and 1-(4-Methoxyphenyl)-2-(thiophene-2-yl)ethane-1,2-dione (**5g**).* Prepared according to the general procedure discussed above. **4g**: eluent, EtOAc/*n*-hexane (20%); 0.043 g, 80%; yellow gum. **5g**: EtOAc/*n*-hexane (7%); 0.010 g, 19%; yellow solid; mp 52−53 °C. **4g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.97 (d, J = 9.0 Hz, 2 H), 7.25−7.26 (m, 1 H), 6.90−6.98 (m, 4 H), 6.16 (d, J = 6.6 Hz, 1 H), 4.55 (d, J = 6.9 Hz, 1 H), 3.86 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.6, 164.3, 142.6, 131.6 (2 CH), 127.2, 126.3 (2 CH), 126.0, 114.0 (2 CH), 70.2, 55.5 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3447, $\tilde{\nu}_{C=O}$ = 1671, $\tilde{\nu}_{C=C}$ = 1599, $\tilde{\nu}_{max}$ = 1262, 1172, 1073, 1028, 969, 838, 709, 607; HRMS (EI) m/z calcd for $C_{13}H_{12}O_3S$ $[M]^+$ 248.0507, found 248.0504. Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.89; H, 4.87. Found: C, 63.21; H, 4.98. **5g**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.03 (d, J = 9.0 Hz, 2 H), 7.80−7.83 (m, 2 H), 7.18 (t, J = 4.2 Hz, 1 H), 6.98 (d, J = 9.0 Hz, 2 H), 3.90 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 190.6, 186.0, 165.0, 140.1, 136.6 (2 CH), 132.7 (2 CH), 128.7, 125.6, 114.3 (2 CH), 55.6 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1650, $\tilde{\nu}_{C=C}$ = 1596, $\tilde{\nu}_{max}$ = 1411, 1169, 1265, 1226, 1169, 1025, 729, 605; HRMS (EI) m/z calcd for $C_{13}H_{10}O_3S$ $[M]^+$ 246.0351, found 246.0341.

*1-(4-Fluorophenyl)-2-hydroxy-2-(thiophene-2-yl)ethanone (**4h**) and 1-(4-Fluorophenyl)-2-(thiophene-2-yl)ethane-1,2-dione (**5h**).* Prepared according to the general procedure discussed above. **4h**: eluent, EtOAc/*n*-hexane (20%); 0.036 g, 67%; yellow solid; mp 80−81 °C. **5h**: EtOAc/*n*-hexane (5%); 0.014 g, 26%; yellow solid; mp 55−57 °C. **4h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.99−8.03 (m, 2 H), 7.26−7.29 (m, 1 H), 7.12 (t, J = 8.4 Hz, 2 H), 6.92−6.98 (m, 2 H), 6.17 (d, J = 6.6 Hz, 1 H), 4.43 ppm (d, J = 6.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.8, 166.2 (d, J_{C-F} = 255.7 Hz, 1 C), 141.7, 131.9 (d, J_{C-F} = 9.7 Hz, 2 C), 129.6 (d, J_{C-F} = 3.0 Hz, 1 C), 127.3, 126.7, 126.6, 116.1 (d, J_{C-F} = 21.7 Hz, 2 C), 70.6 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3427, $\tilde{\nu}_{C=O}$ = 1681, $\tilde{\nu}_{C=C}$ = 1598, $\tilde{\nu}_{max}$ = 1508, 1269, 1235, 1154, 1066, 970, 840, 705, 636; Anal. Calcd for $C_{12}H_9FO_2S$: C, 61.01; H, 3.84. Found: C, 60.90; H, 4.02; HRMS (EI) m/z calcd for $C_{12}H_9FO_2S$ $[M]^+$ 236.0307, found 236.0287. **5h**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.08−8.13 (m, 2 H), 7.83−7.86 (m, 2 H), 7.17−7.26 ppm (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 190.2, 185.0, 166.8 (d, J_{C-F} = 257.2 Hz, 1 C), 139.7, 136.9 (d, J_{C-F} = 19.5 Hz, 2 C), 133.2, 133.1, 129.1, 128.8, 116.3 (d, J_{C-F} = 21.7 Hz, 2 C) ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1670, 1644, $\tilde{\nu}_{C=C}$ = 1596, $\tilde{\nu}_{max}$ = 1505, 1409, 1233, 1161, 843, 723, 603; HRMS (EI) m/z calcd for $C_{12}H_7FO_2S$ $[M]^+$ 234.0151, found 234.0138.

*1-Hydroxy-1-(thiophene-2-yl)propan-2-one (**4i**)*[3a] *and 1-(Thiophene-2-yl)propane-1,2-dione (**5i**).*[3b] Prepared according to the general procedure discussed above. **4i**: eluent, EtOAc/*n*-hexane (20%); 0.0275 g, 50%; yellow liquid. **5i**: EtOAc/*n*-hexane (8%); 0.0119 g, 21%; yellow solid. **4i**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33 (d, J = 4.8 Hz, 1 H), 7.10 (d, J = 3.0 Hz, 1 H), 7.02 (dd, J = 3.6, 5.4 Hz, 1 H), 5.37 (s, 1 H), 4.24 (br s, 1 H), 2.18 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 206.7, 141.8, 128.2, 127.6, 127.5, 76.4, 26.0 ppm. **5i**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.11 (dd, J = 1.2, 4.2 Hz, 1 H), 7.80 (dd, J = 1.2, 4.8 Hz, 1 H), 7.18 (dd, J = 3.6, 4.8 Hz, 1 H), 2.52 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 199.5, 181.7, 138.6, 138.3, 138.0, 129.6, 26.3 ppm. (Analytical data are consistent with previously reported values.)

*2-(Benzofuran-3-yl)-2-hydroxy-1-(4-methoxy-3,5-dimethylphenyl)ethan-1-one (**4j**).* Prepared according to the general

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procedure discussed above: eluent, EtOAc/*n*-hexane (15%); 0.025 g, 48%; colorless gum; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.67 (s, 2 H), 7.61−7.64 (m, 1 H), 7.58 (s, 1 H), 7.45 (d, J = 7.5 Hz, 1 H),7.22−7.32 (m, 2 H), 6.18 (d, J = 6.0 Hz, 1 H), 4.43 (d, J = 6.3 Hz, 1 H), 3.71 (s, 3 H), 2.25 ppm (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.4, 162.3, 155.5, 143.4, 131.6 (2 × C), 130.0 (2 × CH), 128.7, 125.5, 124.9, 123.1, 120.3, 119.6, 111.6, 67.5, 59.6, 16.3 ppm (2 CH_3); IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3419, $\tilde{\nu}_{C=O}$ = 1677, $\tilde{\nu}_{C=C}$ = 1595, $\tilde{\nu}_{max}$ = 1452, 1312, 1156, 1084, 1009, 750; HRMS (ESI) m/z calcd for $C_{19}H_{18}O_4Na$ $[M + Na]^+$ 333.1103, found 333.1114.

*3-(2-Hydroxybutanoyl)-2H-chromen-2-one (**4k**) and 1-(2-Oxo-2H-chromen-3-yl)butane-1,2-dione (**5k**).* Prepared according to the general procedure discussed above. **4k**: eluent, EtOAc/*n*-hexane (10%); 0.033 g, 61%; white solid; mp 110−112 °C. **5k**: EtOAc/*n*-hexane (20%); 0.005g, 9%; light yellow solid; mp 98−100 °C. **4k**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.63 (s, 1 H), 7.68−7.74 (m, 2 H), 7.36−7.43 (m, 2H), 5.23−5.26 (m, 1 H), 3.53 (d, J = 6.6 Hz, 1 H), 1.93−2.00 (m, 1 H), 1.51−1.60 (m, 1 H), 1.01 ppm (t, J = 7.5 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.7, 158.7, 155.4, 149.3, 135.0, 130.3, 125.3, 122.3, 118.1, 116.8, 76.8, 26.8 (CH_2), 9.4 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3491, $\tilde{\nu}_{C=O}$ = 1733, $\tilde{\nu}_{C=C}$ = 1608, $\tilde{\nu}_{max}$ = 1561, 1453, 1297, 1188, 1129, 1056, 971, 760; HRMS (EI) m/z calcd for $C_{13}H_{12}O_4$ $[M]^+$ 232.0736, found 232.0737. Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.33; H, 5.26. **5k**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.47 (s, 1 H), 7.68−7.72 (m, 2 H), 7.37−7.42 (m, 2 H), 2.90 (q, J = 7.2, 14.4 Hz, 2 H), 1.25 ppm (t, J = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 203.6, 192.6, 160.2, 156.5, 149.2, 136.1, 131.4, 126.4, 123.5, 119.1, 118.2, 32.0 (CH_2), 7.6 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1719, 1684, $\tilde{\nu}_{C=C}$ = 1608, $\tilde{\nu}_{max}$ = 1562, 1452, 1136, 766; HRMS (ESI) m/z calcd for $C_{13}H_{10}O_4Na$ $[M + Na]^+$ 253.0477, found 253.0473.

*6-Bromo-3-(2-hydroxybutanoyl)-2H-chromen-2-one (**4l**).* Prepared according to the general procedure discussed above: eluent, EtOAc/*n*-hexane (20%); 0.034 g, 64%; light yellow solid; mp 110−112 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.52 (s, 1 H), 7.82 (d, J = 2.4 Hz, 1 H), 7.77 (dd, J = 2.4, 9.0 Hz, 1 H), 7.29 (d, J = 9.0 Hz, 1 H), 5.22 (td, J = 4.2, 6.0 Hz, 1 H), 3.48 (d, J = 6.0 Hz, 1 H), 1.95 (dqd, J = 4.2, 7.2, 11.4 Hz, 1 H), 1.50−1.57 (m, 1 H), 1.00 ppm (t, J = 7.8 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.4, 159.0, 155.1, 148.7, 138.6, 133.3, 124.4, 120.5, 119.6, 118.8, 77.8, 27.8 (CH_2), 10.4 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3506, $\tilde{\nu}_{C=O}$ = 1714, 1686, $\tilde{\nu}_{C=C}$ = 1605, $\tilde{\nu}_{max}$ = 1552, 1197, 984, 834; HRMS (ESI) m/z calcd for $C_{13}H_{11}BrO_4Na$ $[M + Na]^+$ 332.9739, found 332.9747. Anal. Calcd for $C_{13}H_{11}BrO_4$: C, 50.19; H, 3.56. Found: C, 50.39; H, 3.71;

*1-(3,4-Dimethoxyphenyl)-1-hydroxy-propan-2-one (**4m**)[3c] and 1-(3,4-Dimethoxyphenyl)propane-1,2-dione (**5m**).[3b]* Prepared according to the general procedure discussed above. **4m**: eluent, EtOAc/*n*-hexane (30%); 0.042 g, 78%; yellow gum. **5m**: EtOAc/*n*-hexane (20%); 0.006 g, 11%; yellow solid. **4m**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.86−6.93 (m, 2 H), 6.76 (d, J = 1.8 Hz, 1 H), 5.04 (d, J = 4.2 Hz, 1 H), 4.25 (d, J = 3.9 Hz, 1 H), 3.89 (s, 3 H), 3.88 (s, 3 H), 2.09 (s, 3 H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 207.4, 149.5, 149.4, 130.4, 120.3, 111.2, 109.6, 79.8, 55.9, 55.9, 25.2 ppm. **5m**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.66 (dd, J = 1.8, 7.8 Hz, 1 H), 7.57 (d, J = 1.8 Hz, 1 H), 6.91 (d, J = 8.4 Hz, 1 H), 3.97 (s, 3 H), 3.94 (s, 3 H), 2.51 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 202.1, 191.2, 155.8, 150.4, 127.4, 125.7, 112.1, 111.3, 57.2, 57.0, 27.6 ppm. (Analytical data are consistent with previously reported values.)

*1-Hydroxy-1-(4-methoxyphenyl)propan-2-one (**4n**)[3d] and 1-(4-Methoxyphenyl)propane-1,2-dione (**5n**).[3e]* Prepared according to the general procedure discussed above. **4n**: eluent, EtOAc/*n*-hexane (20%); 0.04 g, 73%; yellow gum. **5n**: EtOAc/*n*-hexane (10%); 0.007 g, 13%; yellowish white solid. **4n**: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.23 (d, J = 8.7 Hz, 2 H), 6.91 (d, J = 8.4 Hz, 2 H), 5.04 (s, 1 H), 4.23 (d, J = 3.3 Hz, 1 H), 3.81 (s, 3 H), 2.07 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 208.4, 160.9, 131.0, 129.6 (2 CH), 115.4 (2 CH), 80.6, 56.3, 26.2 ppm. **5n**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.02 (t, J = 2.4 Hz, 1 H), 8.00 (t, J = 1.8 Hz, 1 H), 6.97 (t, J = 3.0 Hz, 1 H), 6.95 (t, J = 1.8 Hz, 1 H), 3.89 (s, 3 H), 2.50 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 201.2, 190.0, 164.8, 132.8 (2 CH), 124.6, 114.2 (2 CH), 55.6, 26.5 ppm. (Analytical data are consistent with previously reported values.)

*1-(3-Fluorophenyl)-1-hydroxypropan-2-one (**4o**)[3f] and 1-(3-Fluorophenyl)propane-1,2-dione (**5o**).[3g]* Prepared according to the general procedure discussed above: **4o:** eluent, EtOAc/*n*-hexane (15%); 0.035 g, 63%; yellow liquid. **5o**: EtOAc/*n*-hexane (5%); 0.01 g, 18%; yellow liquid. **4o**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.34−7.38 (m, 1 H), 7.13 (d, J = 7.2 Hz, 1 H), 7.04−7.05 (m, 2 H), 5.08 (br s, 1 H), 4.32 (br s, 1 H), 2.10 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 207.3, 164.1 (d, J_{C-F} = 246.0 Hz, 1 C), 141.3 (d, J_{C-F} = 7.5 Hz, 1 C), 131.6 (d, J_{C-F} = 7.5 Hz, 1 C), 124.0 (d, J_{C-F} = 3.0 Hz, 1 C), 116.8 (d, J_{C-F} = 21.0 Hz, 1 C), 115.2 (d, J_{C-F} = 21.0 Hz, 1 C), 80.5, 26.2 ppm. **5o**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82−7.83 (m, 1 H), 7.74 (ddd, J = 1.2, 2.4, 9.3 Hz, 1 H), 7.48 (td, J = 6.0, 8.1 Hz, 1 H), 7.34 (tdd, J = 1.2, 2.4, 8.1 Hz, 1 H), 2.53 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 199.6, 189.5 (d, J_{C-F} = 3.0 Hz, 1 C), 162.7 (d, J_{C-F} = 247.5 Hz, 1 C), 133.8 (d, J_{C-F} = 6.0 Hz, 1 C), 130.5 (d, J_{C-F} = 7.5 Hz, 1 C), 126.3 (d, J_{C-F} = 3.0 Hz, 1 C), 121.7 (d, J_{C-F} = 21.0 Hz, 1 C), 116.8 (d, J_{C-F} = 22.5 Hz, 1 C), 26.2 ppm. (Analytical data are consistent with previously reported values.)

*1-Hydroxy-1-naphthalen-2-ylpropan-2-one (**4p**)[3a] and 1-Naphthalen-2-ylpropane-1,2-dione (**5p**).[3e]* Prepared according to the general procedure discussed above. **4p:** eluent, EtOAc/*n*-hexane (15%); 0.041 g, 75%; white solid. **5p**: EtOAc/*n*-hexane (6%); 0.009 g, 17%; yellow gum. **4p**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.84−7.88 (m, 4 H), 7.50−7.53 (m, 2 H), 7.37 (dd, J = 1.8, 8.4 Hz, 1 H), 5.27 (s, 1 H), 4.41 (br s, 1 H), 2.11 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 208.1, 136.3, 134.4, 134.3, 130.1, 129.0, 128.8, 128.2, 127.6, 127.6, 125.3, 81.3, 26.4 ppm. **5p**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.57 (s, 1 H), 8.05 (dd, J = 1.8, 9.0 Hz, 1 H), 7.97 (d, J = 8.4 Hz, 1 H), 7.93 (d, J = 8.4 Hz, 1 H), 7.89 (d, J = 8.4 Hz, 1 H), 7.65 (ddd, J = 1.2, 6.8, 8.1 Hz, 1 H), 7.58 (ddd, J = 1.2, 6.8, 8.1 Hz, 1 H), 2.59 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.8, 191.4, 136.2, 133.8, 132.3 (2 C), 130.0, 129.4, 129.0, 127.9, 127.1, 124.3, 26.6 ppm. (Analytical data are consistent with previously reported values.)

*2-Hydroxy-2-methyl-2,3-dihydro-1H-inden-1-one (**4q**).[3h]* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (20%); 0.049 g, 88%; light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (d, J = 6.4 Hz, 1 H), 7.62 (t, J = 6.0 Hz, 1 H), 7.37−7.43 (m, 2 H), 3.27 (d, J = 10.2 HZ, 1 H), 3.21 (d, J = 9.9 Hz, 1 H), 3.01 (br. s., 1 H), 1.44 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 208.1, 151.3, 135.9, 133.7, 128.0, 126.9, 125.1, 77.2, 42.4, 25.8 ppm. (Analytical data are consistent with previously reported values.)

*2-Hydroxy-6-methoxy-2-methyl-2,3-dihydro-1H-inden-1-one (**4r**).* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (20%); 0.040 g, 73%; light yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34 (d, J = 8.1 Hz, 1 H), 7.25−7.26 (m, 1 H), 7.22 (d, J = 3.0 Hz, 1 H), 3.85 (s, 3 H), 3.17 (s, 2 H), 2.55 (br. s., 1 H), 1.45 ppm (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 208.1, 159.6, 144.0, 134.5, 127.5, 125.2, 105.9, 78.1, 55.6, 41.5 (CH_2), 25.8 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{OH}$ = 3426, $\tilde{\nu}_{C=O}$ = 1713, $\tilde{\nu}_{C=C}$ = 1614, $\tilde{\nu}_{max}$ = 1492, 1281, 1239, 1026, 836, 771; HRMS (EI) m/z calcd for $C_{11}H_{12}O_3$ $[M]^+$ 192.0786, found 192.0787.

*Ethyl 1-Bromo-2-oxocyclohexane-1-carboxylate (**4s**).[3n]* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (2%); overall yield 0.068 g, 93%; yellow liquid; inseparable mixture of major and minor diastereomers. Major diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.31 (q, J = 7.2, 14.1 Hz, 2 H), 2.84−2.98 (m, 2 H), 2.42−2.51 (m, 1 H), 2.19−2.28 (m, 1 H), 1.70−1.99 (m, 4 H), 1.32 ppm (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 199.1, 167.4, 67.5, 62.9 (CH_2), 40.5 (CH_2), 38.8 (CH_2), 26.7 (CH_2), 23.1 (CH_2), 13.8 ppm. (Analytical data are consistent with previously reported values.)

*2,2-Dihydroxy-1-phenylbutane-1,3-dione and 1-Phenylbutane-1,2,3-trione (**4t**).[3o]* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (20%); overall yield 0.052 g, 87%; yellow gummy liquid. According to NMR analyses, the compound was observed mostly in hydrated form in DMSO-d_6, whereas in $CDCl_3$, as a mixtures of two (hydrated: keto form ~2.5:1): ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.02 (d, J = 7.2 Hz, 2 H), 7.63 (t, J = 7.5, 14.7 Hz, 1 H), 7.50 (t, J = 7.8, 15.3 Hz, 2 H), 7.41 (s, 2 H), 2.23 ppm (s, 3 H); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.02 (d, J = 7.5 Hz, 2 H), 7.89−7.91 (m, 1 H) 7.62−7.72 (m, 2 H), 7.45−7.56 (m, 4 H), 5.53 (br. s., 2 H), 2.56 (s, 3 H), 2.15 ppm (s, 3 H); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 205.8, 196.2,

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133.4, 133.2, 130.0, 128.4, 96.7, 24.4 ppm. (Analytical data are consistent with previously reported values.)

*Ethyl 2,2-Dihydroxy-3-(4-nitrophenyl)-3-oxopropanoate and Ethyl 3-(4-Nitrophenyl)-2,3-dioxopropanoate (**4u**).*[3p] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (25%); overall yield 0.0436 g, 77%; light yellow solid. According to NMR analyses, the compound was observed in $CDCl_3$ as a mixtures of two (hydrated: keto form ~3.6:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.25−8.34 (m, 4 H), 5.19 (br. s., 2 H), 4.24 (q, J = 7.2, 14.4 Hz, 2 H), 1.12 ppm (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 190.6, 169.0, 150.9, 136.1, 131.2 (2 CH), 123.8 (2 CH), 92.0, 63.6 (CH_2), 13.7 ppm. (Analytical data are consistent with previously reported values.)

*2-Methylnaphthalene-1,4-dione (**7a**).*[4a] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (5%); 0.026 g, 48%; red solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03−8.09 (m, 2 H), 7.70−7.72 (m, 2 H), 6.82 (d, J = 1.6 Hz, 1 H), 2.18 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.5, 184.9, 148.2, 135.7, 133.6, 133.6, 132.3, 132.2, 126.5, 126.1, 16.4 ppm. (Analytical data are consistent with previously reported values.)

*6-Methoxy-2-methylnaphthalene-1,4-dione (**7b**).*[4b] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (5%); 0.024 g, 45%; yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.03 (d, J = 9.0 Hz, 1 H), 7.47 (d, J = 3.0 Hz, 1 H), 7.17 (dd, J = 3.0, 9.0 Hz, 1 H), 6.79 (q, J = 1.8, 3.0 Hz, 1 H), 3.93 (s, 3 H), 2.17 ppm (d, J = 1.8 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.1, 185.6, 164.9, 149.5, 136.2, 135.3, 130.0, 126.7, 121.2, 110.3, 56.9, 17.5 ppm. (Analytical data are consistent with previously reported values.)

*7-Methoxy-2-methylnaphthalene-1,4-dione (**7c**).*[4b] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (5%); 0.0261 g, 49%; yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.4 Hz, 1 H), 7.52 (d, J = 3.0 Hz, 1 H), 7.18 (dd, J = 3.0, 8.4 Hz, 1 H), 6.77 (q, J = 1.2, 3.0 Hz, 1 H), 3.94 (s, 3 H), 2.17 ppm (d, J = 1.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.7, 185.2, 164.9, 148.6, 136.9, 135.1, 129.5, 126.8, 121.1, 110.9, 56.9, 17.4 ppm. (Analytical data are consistent with previously reported values.)

*8-Bromo-7-methoxy-2-methylnaphthalene-1,4-dione (**7d**).* 2,8-Dibromo-7-methoxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one was converted to **7d** according to the general procedure discussed above: EtOAc/*n*-hexane (20%); 0.012 g, 30%; yellow solid; mp 110−111 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.12 (d, J = 9.0 Hz, 1 H), 7.18 (d, J = 8.4 Hz, 1 H), 6.77 (d, J = 1.8 Hz, 1 H), 4.02 (s, 3 H), 2.20 ppm (d, J = 1.8 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 185.7, 184.0, 161.9, 150.6, 135.1, 132.1, 129.1, 128.7, 115.5, 113.5, 58.0, 18.1 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1666, $\tilde{\nu}_{C=C}$ = 1631, 1571, $\tilde{\nu}_{max}$ = 1329, 1270, 969, 718; HRMS (EI) m/z calcd for $C_{12}H_9BrO_3$ $[M]^+$ 279.9735, found 279.9740.

*6-Bromonaphthalene-1,4-dione (**7e**).*[4c] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (20%); 0.010 g, 19%; brick red solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.22 (d, J = 1.8 Hz, 1 H), 7.79 (dd, J = 1.8, 7.8 Hz, 1 H), 7.41 (d, J = 10.2 Hz, 1 H), 7.25 (d, J = 9.0 Hz, 1 H), 6.47 ppm (d, J = 9.6 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 180.9, 178.8, 145.3, 139.6, 134.4, 134.1, 133.7, 132.1, 129.2, 126.8 ppm. (Analytical data are consistent with previously reported values.)

*2-Bromo-3-phenyl-1H-inden-1-one (**9a**).*[5c] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (1%); 0.058 g, 85%; red solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.65−7.67 (m, 2 H), 7.51−7.57 (m, 4 H), 7.36 (td, J = 1.2, 7.8 Hz, 1 H), 7.25−7.28 (m, 1 H), 7.15 ppm (d, J = 7.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 190.9, 157.9, 145.5, 134.8, 132.1, 131.3, 130.9, 129.9, 129.7 (2 CH), 129.2 (2 CH), 124.7, 122.3, 119.0 ppm. (Analytical data are consistent with previously reported values.)

*2-Bromo-3-methyl-1H-inden-1-one (**9b**).* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (2%); 0.040 g, 52%; red solid; mp 77−79 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, J = 7.2 Hz, 1 H), 7.35−7.38 (m, 1 H), 7.21 (t, J = 7.6 Hz, 1 H), 7.08 (d, J = 7.2 Hz, 1 H), 2.23 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.7, 157.6, 144.9, 134.0, 129.8, 129.0, 122.8, 119.3, 119.1, 13.4 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1718, $\tilde{\nu}_{C=C}$ = 1606, 1575, $\tilde{\nu}_{max}$ = 1453, 1425, 1376, 1267, 1121, 1037, 832, 748, 696, 662; HRMS (EI) m/z calcd for $C_{10}H_7BrO$ $[M]^+$ 221.9680, found 221.9664.

*5-Bromo-2-(methylsulfanyl)inden-1-one (**10a**), 2,2,5-Tribromoindan-1-one (**10aa**),*[5d] *and 2,5-Dibromoindan-1-one (**10ab**).*[5e] Prepared according to the general procedure discussed above. **10a**: eluent, EtOAc/*n*-hexane (5%); 0.012 g, 20%; red solid; mp 130−131 °C; solvent of crystallization: dichloromethane/acetone. **10aa**: EtOAc/*n*-hexane (5%); 0.006 g, 7%; light brown solid. **10ab**: EtOAc/*n*-hexane (5%); 0.004 g, 6%; white solid; mixture of two isomers. **10a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.20−7.24 (m, 2 H), 7.04 (d, J = 1.2 Hz, 1 H), 6.72 (s, 1 H), 2.43 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 192.4, 147.7, 141.8, 132.8, 129.6, 129.5, 129.5, 124.4, 123.6, 14.0 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1706, $\tilde{\nu}_{C=C}$ = 1591, $\tilde{\nu}_{max}$ = 1443, 1257, 1046, 886, 823, 698; HRMS (EI) m/z calcd for $C_{10}H_7BrOS$ $[M]^+$ 253.9401, found 253.9400. **10aa**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.80 (d, J = 8.4 Hz, 1 H), 7.65 (dd, J = 0.6, 8.4 Hz, 1 H), 7.60 (s, 1 H), 4.26 ppm (s, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 191.6, 148.5, 132.7, 132.5, 129.3, 127.9, 127.7, 55.8, 51.9 (CH_2) ppm. **10ab**: NMR of mixtures: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68−7.71 (m, 1 H), 7.64−7.65 (m, 1 H), 7.58−7.60 (m, 1 H), 4.64 (dd, J = 3.6, 7.8 Hz, 1 H; major isomer), 4.55 (dd, J = 4.2, 7.8, Hz, 1 H; minor isomer), 3.82 (dd, J = 7.2, 18.0 Hz, 1 H; major isomer), 3.77 (dd, J = 8.4, 18.0 Hz, 1 H; minor isomer), 3.41 (dd, J = 3.0, 18.0 Hz, 1 H; major isomer), 3.29 ppm (dd, J = 4.2, 18.0 Hz, 1 H; minor isomer); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.3, 152.5, 132.4, 132.0, 131.5, 129.7, 126.2, 43.4, 37.6 (CH_2) ppm. (Analytical data are consistent with previously reported values.)

*6-Methoxy-2-(methylsulfanyl)inden-1-one (**10b**), 2,2-Dibromo-6-methoxyindan-1-one (**10ba**),*[5f] *and 2-Bromo-6-methoxyindan-1-one (**10bb**).*[5f] Prepared according to the general procedure discussed above. **10b**: eluent, EtOAc/*n*-hexane (7%); 0.008 g, 12%; dark red solid; mp 41−43 °C. **10ba**: EtOAc/*n*-hexane (7%); 0.006 g, 6%; light brown solid. **10bb**: EtOAc/*n*-hexane (7%); 0.005 g, 7%; white solid; mixture of two isomers. **10b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.01 (d, J = 2.4 Hz, 1 H), 6.78−6.79 (m, 2 H), 6.71 (dd, J = 2.4, 7.8 Hz, 1 H), 3.79 (s, 3 H), 2.41 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 193.8, 159.5, 137.7, 137.6, 136.6, 132.8, 120.9, 117.1, 111.5, 55.7, 14.2 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1715, $\tilde{\nu}_{C=C}$ = 1608, $\tilde{\nu}_{max}$ = 1477, 1424, 1282, 1226, 1015, 839, 768; HRMS (EI) m/z calcd for $C_{11}H_{10}O_2S$ $[M]^+$ 206.0402, found 206.0395. **10ba**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.35 (d, J = 2.4 Hz, 1 H), 7.28−7.33 (m, 2 H), 4.22 (s, 2 H), 3.87 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 192.8, 160.4, 139.7, 130.2, 126.8, 126.4, 107.4, 57.2, 55.8, 51.9 (CH_2) ppm. **10bb**: (major isomer) ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.33−7.35 (m, 1 H), 7.25−7.27 (m, 2 H), 4.67 (dd, J = 3.6, 7.8 Hz, 1 H), 3.85 (s, 3 H), 3.77 (dd, J = 7.2, 17.2 Hz, 1 H), 3.35 ppm (dd, J = 3.0, 17.4 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 199.6, 160.0, 143.9, 134.7, 127.1, 125.5, 106.0, 55.7, 44.7, 37.4 (CH_2) ppm. (Analytical data are consistent with previously reported values.)

*(E)-5-Phenylpent-4-ene-2,3-dione (**12a**).*[6a] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (1%); 0.03 g, 55%; yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 (d, J = 16.2 Hz, 1 H), 7.64 (dd, J = 1.8, 7.8 Hz, 2 H), 7.46−7.41 (m, 4 H), 2.46 ppm (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 198.9, 186.8, 147.8, 134.4, 131.4, 129.1 (2 CH), 129.0 (2 CH), 117.9, 24.4 ppm. (Analytical data are consistent with previously reported values.)

*(E)-5-(4-Methoxyphenyl)pent-4-ene-2,3-dione (**12b**).* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (6%); 0.027 g, 50%; light yellow solid; mp 61−63 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 (d, J = 16.2 Hz, 1 H), 7.60 (d, J = 9.0 Hz, 2 H), 7.31 (d, J = 15.6 Hz, 1 H), 6.93 (d, J = 8.4 Hz, 2 H), 3.86 (s, 3 H), 2.45 (s, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 199.4, 186.8, 162.4, 147.7, 130.9 (2 CH), 127.3, 115.6, 114.5 (2 CH), 55.5, 24.5 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1711, 1677, $\tilde{\nu}_{C=C}$ = 1595, 1510, $\tilde{\nu}_{max}$ = 1257, 1171, 1062, 1025, 824; HRMS (EI) m/z calcd for $C_{12}H_{12}O_3$ $[M]^+$ 204.0786, found 204.0784.

*1,4-Diphenylbut-3-yne-1,2-dione (**14**)*[6b] *and 1-Hydroxy-1,4-diphenylbut-3-yn-2-one (**14a**).*[6b] Prepared according to the general procedure discussed above. **14**: EtOAc/*n*-hexane (5%); 0.043 g, 81%; yellow liquid. **14a**: EtOAc/*n*-hexane (15%); 0.006 g, 11%; light yellow solid. **14**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09−8.10 (m, 1 H), 8.08 (m, 1 H), 7.65−7.69 (m, 3 H), 7.50−7.55 (m, 3 H), 7.40−7.43 ppm (m, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 188.5, 178.5, 134.9, 133.7 (2 CH), 131.7, 131.6, 130.5 (2 CH), 128.9 (2 CH), 128.8 (2 CH), 119.2,

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99.2, 87.0 ppm. **14a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.47−7.49 (m, 2 H), 7.40−7.46 (m, 5 H), 7.35−7.38 (m, 3 H), 5.34 (s, 1 H), 4.17 ppm (br. s., 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 186.4, 137.0, 133.1 (2 CH), 131.4, 128.9, 128.8 (2 CH), 128.7 (2 CH), 127.6 (2 CH), 119.2, 98.6, 85.1, 81.1 ppm. (Analytical data are consistent with previously reported values.)

*(E)-4-Bromo-4-methyl-1-phenylpent-1-en-3-one (**16**).*[6i] Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (1%); 0.055 g, 76%; white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.78 (d, J = 15.6 Hz, 1 H), 7.62−7.61 (m, 2 H), 7.42−7.39 (m, 4 H), 1.95 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.3, 144.8, 134.4, 130.7, 128.9 (2 CH), 128.5 (2 CH), 120.2, 63.7, 29.7 ppm (2 CH_3). (Analytical data are consistent with previously reported values.)

General Procedure for the Synthesis of 17a,b. Compound **9a** (0.05 g, 0.175 mmol, 1 equiv) in dry DMF (2 mL) was placed separately into a flame-dried, two-necked, round-bottomed flask equipped with a magnetic stir bar and rubber septa. $[PdCl_2(PPh_3)_2]$ (0.06 equiv), terminal alkyne (1.2 equiv), and CuI (0.2 equiv) were added into the flask at 0 °C, and then *N*,*N*-diisopropylethylamine (DIPEA; 1.5 equiv) was added dropwise to the resulting mixtures and allowed to stir at room temperature for the required times (3−8 h). After completion of the reaction (TLC), saturated NH_4Cl solution was added, and the product was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to obtain a residue. The crude residue was purified by using silica gel column chromatography (230−400 mesh particle size; eluent: ethyl acetate/*n*-hexane) to obtain **17a,b**.

*3-Phenyl-2-(phenylethynyl)-1H-inden-1-one (**17a**).* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (5%); 0.042 g, 78%; brick red solid; mp 144−146 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89−7.91 (m, 2 H), 7.52−7.60 (m, 4 H), 7.48−7.51 (m, 2 H), 7.40−7.43 (m, 1 H), 7.35−7.37 (m, 1 H), 7.32−7.33 ppm (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ = 194.4, 161.2, 145.2, 134.7, 133.2, 132.9 (2 CH), 131.8, 131.6, 130.6, 129.7, 129.6 (2 CH), 129.4 (2 CH), 129.3 (2 CH), 124.5, 123.9, 123.1, 118.8, 100.8, 83.1 ppm; IR (KBr, cm^{-1}) $\tilde{\nu}_{C\equiv C}$ = 2211, $\tilde{\nu}_{C=O}$ = 1710, $\tilde{\nu}_{C=C}$ = 1599, $\tilde{\nu}_{max}$ = 1487, 1449, 1360, 1185, 1125, 777, 752, 712; HRMS (EI) *m*/*z* calcd for $C_{23}H_{14}O$ $[M]^+$ 306.1045, found 306.1013.

*2-(Cyclopentylethynyl)-3-phenyl-1H-inden-1-one (**17b**).* Prepared according to the general procedure discussed above: EtOAc/*n*-hexane (1%); 0.021 g, 40%; gummy red liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82−7.85 (m, 2 H), 7.50−7.55 (m, 4 H), 7.29−7.40 (m, 3 H), 2.87−2.92 (m, 1 H), 1.91−1.97 (m, 2 H), 1.61−1.73 ppm (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 194.0, 159.0, 144.3, 133.5, 132.3, 130.6, 130.2, 129.2, 128.4 (2 CH), 128.3 (2 CH), 123.3, 121.7, 118.6, 106.2, 72.4, 33.7 (2 CH_2), 31.4, 25.0 ppm (2 CH_2); IR (KBr, cm^{-1}) $\tilde{\nu}_{C\equiv C}$ = 2211, $\tilde{\nu}_{C=O}$ = 1710, $\tilde{\nu}_{C=C}$ = 1634, 1602, $\tilde{\nu}_{max}$ = 1450, 1358, 1077, 774, 710; HRMS (EI) *m*/*z* calcd for $C_{22}H_{18}O$ $[M]^+$ 298.1358, found 298.1343.

*2-(Benzyloxy)-2,5-diphenylfuran-3(2H)-one (**18**).* To a well-stirred solution of **14** (0.05 g, 0.21 mmol) in CH_2Cl_2 (4 mL) were added 2 mol % of $AuCl_3$ and benzyl alcohol (0.04 mL, 0.42 mmol) under Ar atmosphere. The resulting solution was stirred at room temperature for 30 min. After completion of the reaction, the solvent was removed under reduced pressure to obtain a residue. The resulting residue was purified over a silica gel column to afford **18**: EtOAc/*n*-hexane (7%); 0.045 g, 61%; yellow gum; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.94 (d, J = 7.2 Hz, 2 H), 7.62−7.68 (m, 3 H), 7.53−7.58 (m, 2 H), 7.30−7.40 (m, 8 H), 6.10 (s, 1 H), 4.78 (d, J = 10.8 Hz, 1 H), 4.68 ppm (d, J = 11.1 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.9, 184.4, 137.0, 134.6, 133.4, 129.5, 129.1, 128.6, 128.3, 127.9, 127.4, 126.0, 107.3, 99.3, 67.7 ppm (CH_2); IR (KBr, cm^{-1}) $\tilde{\nu}_{C=O}$ = 1708, $\tilde{\nu}_{C=C}$ = 1599, 1565, $\tilde{\nu}_{max}$ = 1450, 1355, 1130, 1050, 771, 693; HRMS (ESI) *m*/*z* calcd for $C_{23}H_{18}O_3Na$ $[M + Na]^+$ 365.1154, found 365.1153.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all new compounds; ORTEP diagram of **10a**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00846.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: (+91) 33 2473 5197. E-mail: id@csiriicb.in.

Author Contributions

‡K.M. and A.K. contributed equally.

Notes

The authors declare no competing financial interest.

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