Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201801058

Link to VoR: http://dx.doi.org/10.1002/adsc.201801058

10.1002/adsc.201801058

FULL PAPER

DOI: 10.1002/adsc.201

Synthesis of Enones and Enals via Dehydrogenation of Saturated Ketones and Aldehydes

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Received:

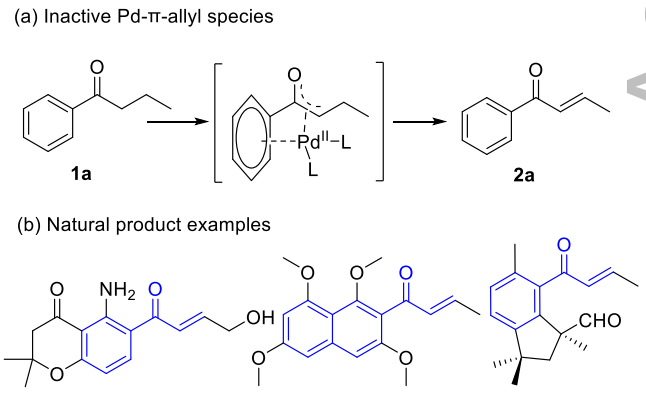
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract: A general, efficient and economic palladium-catalyzed dehydrogenation to form enones or enals has been developed. The approach possesses extremely broad substrate scope including various linear or cyclic saturated ketones and aldehydes. The protocol is ligand-free, and molecular oxygen is used as the sole clean oxidant in the reaction. Due to mild reaction conditions, good functional group compatibility, and versatile utilities of enones and enals, the method can be applied in the late-stage synthesis of natural products, pharmaceuticals and fine chemicals.

Keywords: dehydrogenation; enones; enals; palladium catalysis; synthetic methods

Introduction

α,*β*-Unsaturated carbonyl structural motif is embedded in numerous natural products, drug molecules and bulk chemicals.[1] *α*,*β*-Unsaturated carbonyl compounds are also versatile synthetic intermediates for diverse organic transformations, such as Michael addition, Diels-Alder reaction and Heck reaction.[2] Classically, besides aldol-like condensations,[3] the general methods to prepare such compounds include *α*-substitution (e.g. *α*-bromination[4], *α*-selenyiation[5] and *α*-sulfenylation[6]) of carbonyl compounds and subsequent elimination or palladium(II)-mediated dehydrosilylation of silyl enol ethers (namely, Saegusa oxidation).[7] Compared to these methods, the approaches of direct *α*,*β*-dehydrogenative oxidations of the corresponding saturated carbonyl compounds offer a straightforward and atom-economical pathway. In this regard, earlier studies utilized stiochiometric strong oxidants, such as SeO_2[8a,8b] or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[8c-e] to fulfill the direct *α*,*β*-dehydrogenation of ketones and aldehydes.[8] The reaction conditions are harsh, and the reactions suffer from limited functional group compatibility. Later, Nicolaou et al. developed a general and mild method with stoichiometric *o*-iodoxybenzoic acid (IBX) as the oxidant to accomplish the transformation.[9] Recently, Stahl,[10] Li and Wang,[11] Qu and Kang,[12] and Huang[13] et al. reported elegant palladium-catalyzed aerobic *α*,*β*-dehydrogenations of ketones and aldehydes to produce enones and enals.[14,15] The catalytic approaches undoubtedly provided an appealing access to enones and enals. However, there are some issues constraining the synthetic utility of the methods: 1) costly ligand (e.g. 4,5-diazafluorenone[10c]) or co-catalyst (e.g. amines,[11] ^{t}BuONO[12]) required for the dehydrogenations of linear ketone and aldehyde substrates, which obviously increased the cost of the reaction and impeded large-scale production; 2) limited substrate scope, for example, propyl phenyl ketone (**1a**), a kind of special and challenging substrate, affording the enone in only 20% yield in previous literature.[10c] The low yield likely ascribed to the deactivation of palladium catalyst by formation of an inactive Pd-π-allyl species (Scheme 1a). More recently, Newhouse and co-workers disclosed a palladium-catalyzed direct dehydrogenation to synthesize cyclic enones



Scheme 1. Alkenyl aryl ketones.

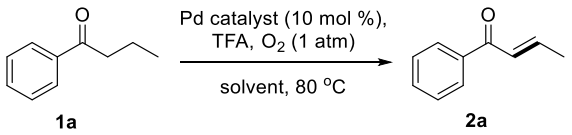
via a zinc enolate intermediate using allyl acetate as the terminal oxidant.[16] Similarly, the dehydrogenation conditions were also ineffective for ketone **1a**. The two cases evidenced this kind of alkyl aryl ketone was difficult substrate for the direct *α,β*-dehydrogenative approach. Nevertheless, the alkenyl aryl ketone is a key structural unit in some natural products and bioactive molecules (Scheme 1b).[1a,c,d] Therefore, the development of a facile, economic and efficient catalytic *α,β*-dehydrogenation of saturated ketones and aldehydes to produce enones and enals with a broad substrate scope is still highly desirable but challenging.

Results and Discussion

To overcome these limitations, we envisioned that a more active catalytic system should be exploited. Initially, we chose difficult **1a** as the model substrate to commence our study. Considering the two factors: one is that trifluoroacetic acid (TFA) and $Pd(OAc)_2$ can facilitate the generation of more catalytic active $[Pd(II)O_2CCF_3]^+$ species;[17] the other is that TFA could coordinate with palladium thereby diminishing above Pd-π coordination, we introduced TFA into the $Pd(OAc)_2$-catalyzed system. To our delighted, **1a** underwent smoothly dehydrogenation in the reaction conditions of $Pd(OAc)_2$ (10 mol %) and TFA (20 mol %) with DMSO as the solvent under an oxygen atmosphere (oxygen balloon) at 80 °C for 12 h to produce enone **2a** in good yield (56%, Table1, entry 1). Then we set about optimizing the reaction conditions. Changing the solvent (entries 2 - 6) and other palladium sources (entries 7, 8) did not enhance the reactivity. By investigating the amount of TFA, we found that 1.0 equiv of TFA was the optimal amount to afford the desired product in 75% yield, and in the absence of TFA, the reaction would hardly proceed (entries 9-17). Using anhydrous DMSO, the yield of **2a** was improved slightly (entry 18). Interestingly, replacing $Pd(OAc)_2$ with $Pd(OTFA)_2$, and using AcOH (1.0 equiv) as the additive in anhydrous DMSO, the yield of **2a** was only 18% (entry 19). And with Stahl's reaction conditions,[10b] the yield of **2a** was 20% (entry 20). Accordingly, the reaction conditions were optimized as follows: $Pd(OAc)_2$ (10 mol %), TFA (1.0 equiv) under oxygen atmosphere in dry DMSO at 80 °C.

After identifying the optimized conditions, we then moved on to examine the substrate scope. We were pleased with the generality of this approach. Firstly, the different substituted phenylbutan-1-ones were investigated. The results were summarized in Scheme 2. The substrates possessing either electron-withdrawing groups or electron-donating groups on aromatic ring all reacted smoothly providing corresponding enones in good to excellent yields (72-91%, **2b**-**2g**). A series of important functional groups, including methyl, methoxy, hydroxy group (-OH) and halides (F, Cl and Br) were compatible with this procedure, and could be versatile handles for further

Table 1. Optimization of the reaction conditions[a]



1a **2a**

Entry	Catalyst (10 mol %)	TFA (equiv)	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	0.2	DMSO	56
2	$Pd(OAc)_2$	0.2	DMF	20
3	$Pd(OAc)_2$	0.2	DMA	5
4	$Pd(OAc)_2$	0.2	CH_3CN	50
5	$Pd(OAc)_2$	0.2	1,4-ioxane	20
6	$Pd(OAc)_2$	0.2	THF	20
7	$Pd(OTFA)_2$	0.2	DMSO	35
8	$PdCl_2$	0.2	DMSO	16
9	$Pd(OAc)_2$	0.1	DMSO	30
10	$Pd(OAc)_2$	0.4	DMSO	65
11	$Pd(OAc)_2$	0.6	DMSO	70
12	$Pd(OAc)_2$	0.8	DMSO	72
13	$Pd(OAc)_2$	1.0	DMSO	75
14	$Pd(OAc)_2$	1.2	DMSO	75
15	$Pd(OAc)_2$	1.5	DMSO	58
16	$Pd(OAc)_2$	2.0	DMSO	51
17	$Pd(OAc)_2$	-	DMSO	trace
18[c]	$Pd(OAc)_2$	1.0	DMSO	78
19[c]	$Pd(OTFA)_2$	AcOH (1.0)	DMSO	18
20[10b]	$Pd(OTFA)_2$	DMSO (0.1)	AcOH	20

[a] Reaction conditions: Unless otherwise noted, the reaction was carried out with **1a** (0.5 mmol), [Pd] (10 mol %) in solvent (5 mL) under O_2 (1 atm) atmosphere at 80 °C, 12 h.
[b] Isolated yields.
[c] Dry DMSO was used.

transformations. Di- and tri-substituted aromatic substrates were also suitable for the reaction to give the corresponding products (**2h**-**2k**) in good yields. Substitution at the *α*-, and *β*-sites of the carbonyl group did not hinder the reaction (**2l**-**2o**). Interestingly, other aromatic substrates, such as 1-naphthyl propyl ketone, 2-naphthyl propyl ketone and 1-(5-bromothiophen-2-yl)butan-1-one, also reacted successfully providing **2p**-**2r** in 76%, 78% and 75% yields, respectively. The structures of products **2g** were confirmed by X-ray crystallography analysis.

Next, we investigated another kind of ketones, 4-arylbutan-2-ones (Scheme 3, **4a**-**4n**). To our surprised,

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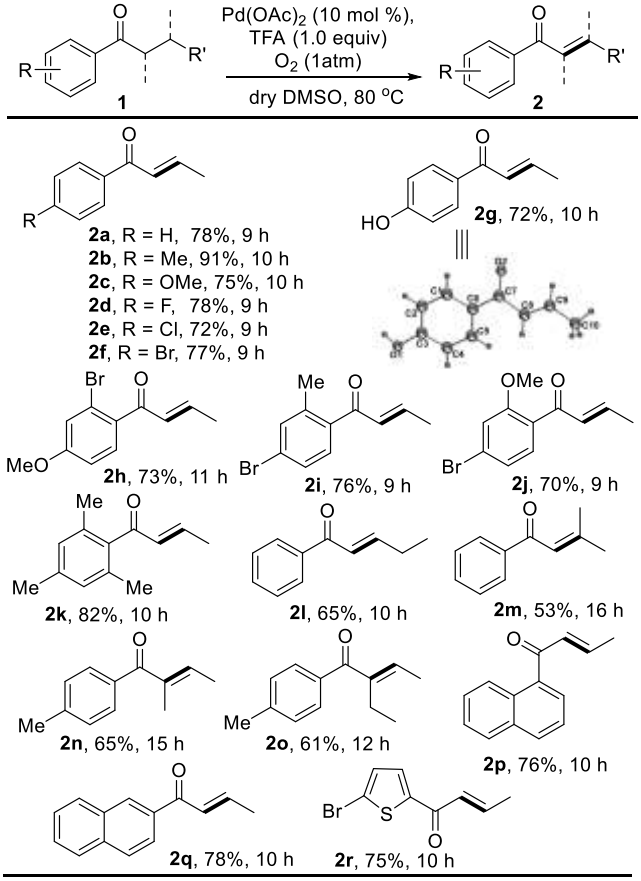
the reaction conditions were extremely efficient for this kind of substrates, and for various substituted substrates almost quantitative yields were obtained. Again the reaction showed good functional group

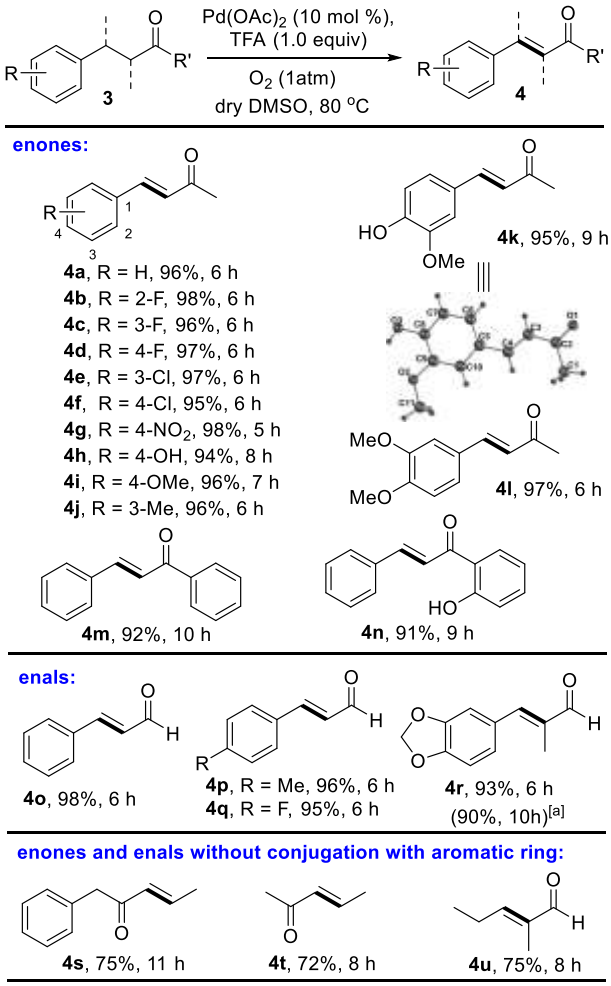


Scheme 2. Dehydrogenation of substituted arylbutan-1-ones. Reaction conditions: **1** (0.5 mmol), $Pd(OAc)_2$ (10 mol %), TFA (1.0 equiv), Under O_2 (1 atm) in DMSO (5 ml) at 80 °C. All yields given are those for the isolated products.

compatibility. Furthermore, the position of the substituted group on the phenyl ring did not affect the reactivity (**4b**-**4d**). In addition, 1,3-diphenylpropan-1-ones were treated with this catalyst system giving corresponding chalcones in excellent yields (**4m**, **4n**). The structures of products **4k** were confirmed by X-ray crystallography analysis.

Besides the synthesis of *α,β*-unsaturated ketones, the method is also efficient for the synthesis of *α,β*-unsaturated aldehydes (Scheme 3, **4o**-**4r**). All *α,β*-unsaturated aldehydes bearing different substituted *β*-aryl groups were produced in excellent yields, and the highly active aldehyde group remained intact indicating that the oxidative dehydrogenation conditions were mild. Simple enones and enals without conjugation with aromatic ring could also be accessed conveniently from corresponding saturated ketones and aldehydes by the direct catalytic dehydrogenation approach (Scheme 3, **4s**-**4u**).

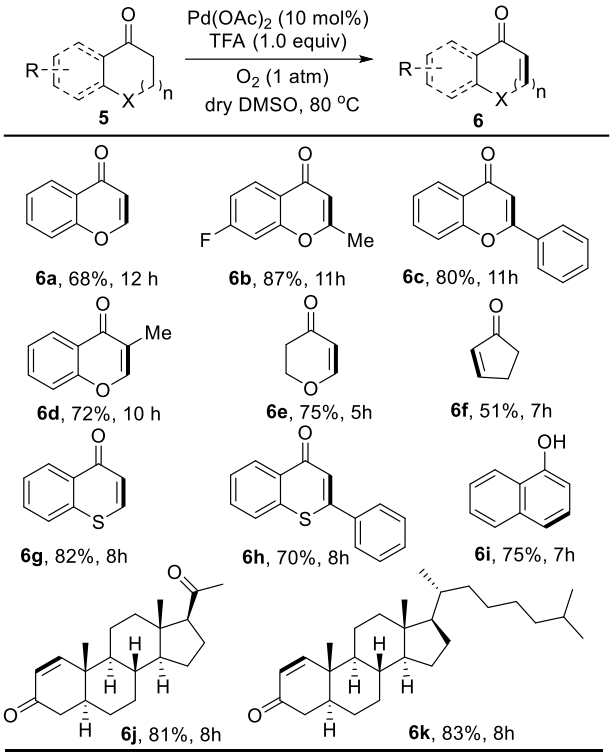
Cyclic enones are interesting structural units found in many natural products and biologically active compounds. Chromones and flavones, two kind of natural products, possessing the backbone of benzopyran-4-one, have important biological activity and widely utilized as pharmaceutical ingredients.[18] They were easily prepared by the palladium-



Scheme 3. Dehydrogenation of ketones and aldehydes. Reaction conditions: **3** (0.5 mmol), $Pd(OAc)_2$ (10 mol %), TFA (1.0 equiv), Under O_2 (1 atm) in DMSO (5 ml) at 80 °C. All yields given are those for the isolated products. [a] The yield for gram scale.

catalyzed dehydrogenation of dihydrobenzopyranones in good to excellent yields (Scheme 4, **6a**-**6d**). Simple tetrahydro-4H-pyran-4-one was also able to be dehydrogenated to give dihydro-pyran-4-one (**6e**) in 75% yield. The lower reactivity of cyclopentantone was also suitable substrate affording cyclopentenone (**6f**) in 51% yield. It is worthwhile to note that thiochroman-4-one (**5g**) and 2-phenylthiochroman-4-one (**5h**) each contained a sulfur atom which could usually poison palladium catalyst or was prone to oxidation under aerobic conditions, but they were also smoothly converted into their corresponding thiochromone (**6g**) and thioflavone (**6h**) in good yields, once again testifying

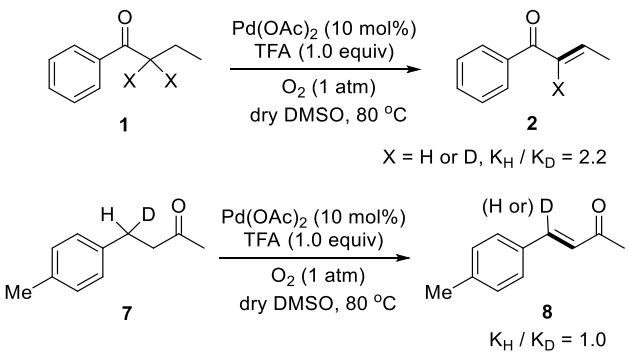
the advantage of this palladium catalytic system. 1-Tetralone underwent the dehydrogenation to give 1-naphthol (**6i**) in 75% yield. Additionally, two steroid derivatives were desaturated regioselectively under the standard conditions providing the less substituted enones in 81% (**6j**) and 83% yields (**6k**), respectively. These cases demonstrated that the palladium-catalyzed dehydrogenative protocol can be used into



Scheme 4. Dehydrogenation of cycloketones. Reaction conditions: **5** (0.5 mmol), $Pd(OAc)_2$ (10 mol %), TFA (1.0 equiv), Under O_2 (1 atm) in DMSO (5 ml) at 80°C. All yields given are those for the isolated products.

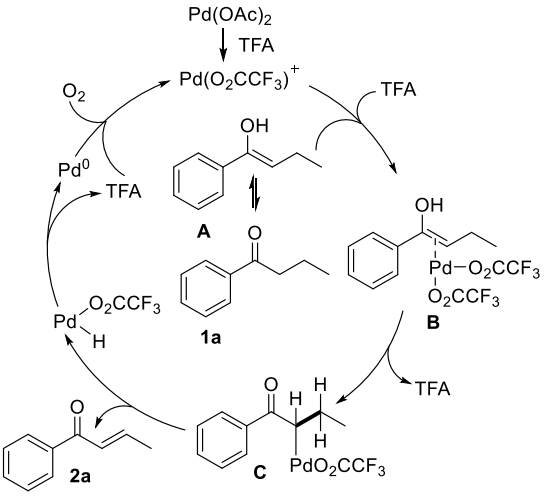
the late-stage construction of enone or enal unit of complex active molecules.

To test the practicality of the method, a gram-scale experiment has been carried out. With above standard reaction conditions, **3r** (1.9 g) was converted into the desired enal **4r** (1.7 g) in 90% yield. Furthermore, when the catalyst loading was reduced to 5 mol%, although more reaction time was required, the yield was not decreased.



Scheme 5. Kinetic Isotope Effect

To gain insight into the reaction mechanism, kinetic isotope effect (KIE) experiments were performed (Scheme 5). The KIE value of two parallel competition reactions of **1a** and $[D_2]$-**1a** was found to be 2.2, and the intramolecular KIE value for the reaction of **7** was 1.0. These results implied that the cleavage of the α-C–H bond was involved in the rate-determining step while β–hydride elimination from a presumed Pd-enolate intermediate is fast.



Scheme 6. Proposed mechanism

Our current understanding of the mechanism of the reaction is show in Scheme 5. $Pd(OAc)_2$ is treated with TFA to obtain active $Pd(O_2CCF_3)^+$.[17] The ketone undergoes the formation of palladium enolate followed by β-hydride elimination to afford α,β-unsaturated ketones and Pd^{II}-hydride intermediate that eliminate a TFA and then is reoxidized to $Pd(O_2CCF_3)^+$ by O_2 in the presence of TFA to complete the catalytic cycle.[10b-d] Further investigations into a more detailed mechanism are ongoing.

Conclusion

In summary, we have developed a general, efficient and economic palladium-catalyzed dehydrogenation to form enones or enals. The method shows extremely broad substrate scope including various linear or cyclic saturated ketones and aldehydes. The protocol is ligand-free, and molecular oxygen is used as the sole clean oxidant in the reaction. Due to mild reaction conditions, good functional group compatibility, and versatile utilities of enones and enals, the approach can be found many applications in the synthesis and the late-stage functionalization of pharmaceuticals and fine chemicals.

Experimental Section

General information: All reagents were used as received unless otherwise noted. Flash chromatography was performed with silica gel (200-300 mesh). Proton nuclear magnetic resonance (^{1}H NMR) data were acquired on Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; m, multiplet, br, broad. Coupling constants *J* are quoted in Hz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 100 MHz on Bruker Ascend 400 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.1 ppm for chloroform-*d*. Infrared (IR) data were recorded as films on potassium bromide plates on a Bruker Tensor 27 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Mass spectra were acquired on a Bruker Daltonics S2 MicroTof-Q II mass spectrometer. X-ray crystal structure analyses were measured on Bruker Smart APEXIICCD instrument using Mo-Kα radiation. The structures were solved and refined using the SHELXTL software package.

General procedure for preparation of 2: A seal tube containing Ketones **1** (0.5 mmol) and $Pd(OAc)_2$ (10 mol %), was evacuated and filled with dioxygen gas using an oxygen containing balloon. Then, Dry DMSO (5 mL), trifluoroacetic acid (TFA) (1.0 mmol) were sequentially added to the system via syringe under an oxygen atmosphere. The reaction mixture was stirred at 80 °C until completion of the reaction (TLC). Then the reaction was cooled to RT and partitioned between water and ethyl acetate. The layers were separated and the organic layer was washed with aqueous saturated brine solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography afforded the **2**.

(*E*)-1-phenylbut-2-en-1-one (2a) [19] Prepared according to general procedure to afford as colorless oil (78% yield). R_f = 0.56 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 5.6, 3.9 Hz, 2H), 7.55 – 7.45 (m, 1H), 7.39 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.01 (tdd, *J* = 13.6, 7.7, 5.9 Hz, 1H), 6.90 – 6.80 (m, 1H), 1.93 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ =191.0, 145.3, 138.0, 132.7, 128.7 (4C), 127.7, 18.77.

(*E*)-1-(*p*-tolyl)but-2-en-1-one (2b) [19] Prepared according to general procedure to afford as colorless oil (91% yield). R_f = 0.56 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.97 (dt, *J* = 20.4, 6.8 Hz, 1H), 6.83 (dd, *J* = 15.3, 1.5 Hz, 1H), 2.32 (s, 3H), 1.90 (dd, *J* = 6.8, 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 144.6, 143.5, 135.4, 129.3, 128.7, 127.5, 21.7, 18.7.

(*E*)-1-(4-methoxyphenyl)but-2-en-1-one (2c) [19] Prepared according to general procedure to afford as yellow oil (75% yield). R_f = 0.45 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.8 Hz, 2H), 6.98 (dt, *J* = 13.4, 6.7 Hz, 1H), 6.92 – 6.80 (m, 3H), 3.80 (s, 3H), 1.92 (dd, *J* = 6.7, 1.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.0, 163.3, 144.0, 130.81, 130.75, 127.1, 113.7, 55.5, 18.6.

(*E*)-1-(4-fluorophenyl)but-2-en-1-one (2d) [19] Prepared according to general procedure to afford as colorless oil (78% yield). R_f = 0.45 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.14 (t, *J* = 8.7 Hz, 2H), 7.07 (dd, *J* = 14.4, 7.6 Hz, 1H), 6.89 (dd, *J* = 15.3, 1.4 Hz, 1H), 2.01 (dd, *J* = 6.8, 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2, 165.65 (d, *J* = 254.1 Hz), 145.5, 134.4, 131.2 (d, *J* = 9.2 Hz), 127.2, 115.8 (d, *J* = 21.8 Hz,), 18.8.

(*E*)-1-(4-chlorophenyl)but-2-en-1-one (2e) [19] Prepared according to general procedure to afford as colorless oil (72% yield). R_f = 0.45 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 – 7.77 (m, 2H), 7.43 – 7.31 (m, 2H), 7.02 (dq, *J* = 20.7, 6.9 Hz, 1H), 6.80 (dd, *J* = 15.3, 1.4 Hz, 1H), 1.93 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.5, 145.8, 139.2, 136.3, 130.1, 129.0, 127.2, 18.8.

(*E*)-1-(4-bromophenyl)but-2-en-1-one (2f) [20] Prepared according to general procedure to afford as yellow solid (77% yield). R_f = 0.50 (EtOAc / hexanes 1:10). m. p. =42 – 43 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.00 (dt, *J* = 13.7, 6.9 Hz, 1H), 6.78 (dd, *J* = 15.3, 1.4 Hz, 1H), 1.93 (dd, *J* = 6.9, 1.3 Hz, 3H). ^{13}C NMR (100 MHz , $CDCl_3$): δ = 189.7, 145.9, 136.7, 131.9, 130.2, 127.8, 127.1, 18.8.

(*E*)-1-(4-hydroxyphenyl)but-2-en-1-one (2g) Prepared according to general procedure to afford as white solid (72% yield). R_f = 0.36 (EtOAc / hexanes 1:10). m. p. = 152 – 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.78 (m, 2H), 7.64 – 7.39 (br, s, 1H), 7.02 (dq, *J* = 15.1, 6.8 Hz, 1H), 6.87 (td, *J* = 4.0, 1.5 Hz, 3H), 1.92 (dd, *J* = 6.8, 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.3, 161.2, 145.2, 131.5, 130.1, 127.2, 115.7, 18.8. HRMS (ESI) for $C_{10}H_{11}O_2$ [M+H$^+$]: Calcd: 163.0754; Found: 163.0753. IR (KBr): 3394, 3189, 2958, 2922, 2854, 1658, 1584, 1450, 1263, 1096, 1025, 803 cm^{-1}.

(*E*)-1-(2-bromo-4-methoxyphenyl)but-2-en-1-one (2h) Prepared according to general procedure to afford as yellow solid (73% yield). R_f = 0.43 (EtOAc / hexanes 1:10). m. p. =192 – 193 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.1 Hz, 1H), 7.12 – 6.98 (m, 2H), 6.83 – 6.77 (m, 1H), 6.59 (d, *J* = 15.5 Hz, 1H), 3.79 (s, 3H), 1.86 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 158.4, 144.8, 132.0, 131.4, 128.1, 126.5, 123.9, 115.2, 56.1, 18.6. HRMS (ESI) for $C_{11}H_{12}BrO_2$ [M+H$^+$]: Calcd: 255.0015; Found: 255.0026. IR (KBr): 3011, 2936, 2853, 1663, 1617, 1582, 1475, 1395, 1247, 1025, 856, 805 cm^{-1}.

(*E*)-1-(4-bromo-2-methylphenyl)but-2-en-1-one (2i) Prepared according to general procedure to afford as yellow solid (76% yield). R_f = 0.46 (EtOAc / hexanes 1:10). m. p. = 188 – 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.25 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 1H), 6.70 – 6.61 (m, 1H), 6.44 – 6.35 (m, 1H), 2.28 (s, 3H), 1.88 (dd, *J* = 6.8, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.9, 147.4, 139.2, 137.8, 134.1, 132.2, 129.6, 128.5, 124.6, 20.0, 18.7. HRMS (ESI) for $C_{11}H_{12}BrO$ [M+H$^+$]: Calcd: 239.0066; Found: 239.0060. IR (KBr): 2963, 2925, 1654, 1623, 1586, 1555, 1440, 1291, 1088, 1029, 807 cm^{-1}.

(*E*)-1-(4-bromo-2-methoxyphenyl)but-2-en-1-one (2j) Prepared according to general procedure to afford as pale yellow solid (70% yield). R_f = 0.46 (EtOAc / hexanes 1:10). m. p. = 178 – 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.88

(dd, *J* = 8.5, 2.4 Hz, 1H), 6.82 – 6.72 (m, 1H), 6.51 (dd, *J* = 15.6, 1.5 Hz, 1H), 3.83 (s, 3H), 1.96 (dd, *J* = 6.8, 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 161.4, 147.0, 133.2, 131.8, 130.8, 120.9, 118.9, 113.1, 55.8, 18.7. HRMS (ESI) for $C_{11}H_{12}BrO_2$ [M+H$^+$]: Calcd: 255.0015; Found: 255.0026. IR (KBr): 2968, 2926, 1655, 1623, 1586, 1565, 1450, 1391, 1048, 1039, 806 cm^{-1}.

(*E*)-1-mesitylbut-2-en-1-one (2k) [19] Prepared according to general procedure to afford as colorless oil (82% yield). R_f = 0.55 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (s, 2H), 6.49 – 6.35 (m, 1H), 6.33 – 6.15 (m, 1H), 2.21 (s, 3H), 2.06 (s, 6H), 1.87 – 1.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 148.0, 138.3, 137.3, 134.2, 134.0, 128.3, 21.2, 19.3, 18.6. HRMS (ESI) for $C_{13}H_{17}O$ [M+H$^+$]: Calcd: 189.1274; Found: 189.1276. IR (KBr): 2958, 2922, 2857, 1653, 1440, 1274, 1095, 1064, 1024, 974, 852, 800 cm^{-1}.

(*E*)-1-phenylpent-2-en-1-one (2l) [21] Prepared according to general procedure to afford as colourless oil (65% yield). R_f = 0.39 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 – 7.80 (m, 2H), 7.52 – 7.45 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.04 (dt, *J* = 15.4, 6.4 Hz, 1H), 6.80 (dt, *J* = 15.4, 1.6 Hz, 1H), 2.45 – 2.00 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 151.5, 138.2, 132.7, 128.7, 128.6, 125.1, 26.1, 12.5.

3-methyl-1-phenylbut-2-en-1-one (2m) [27] Prepared according to general procedure to afford as colorless oil (53% yield). R_f = 0.55 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 – 7.82 (m, 2H), 7.48 – 7.43 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 6.72 – 6.64 (m, 1H), 2.14 (d, *J* = 0.9 Hz, 3H), 1.95 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 156.8, 139.4, 132.4, 128.6, 128.3, 121.3, 28.1, 21.3.

(*E*)-2-methyl-1-(p-tolyl)but-2-en-1-one (2n) [19] Prepared according to general procedure to afford as colorless oil (65% yield). R_f = 0.57 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.30 (qd, *J* = 6.9, 1.3 Hz, 1H), 2.33 (s, 3H), 1.89 (s, 3H), 1.80 (dd, *J* = 6.9, 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 141.9, 140.4, 137.7, 135.96, 129.5, 128.7, 21.51, 14.7, 12.3.

(*E*)-2-ethyl-1-(p-tolyl)but-2-en-1-one (2o) [28] Prepared according to general procedure to afford as colorless oil (61% yield). R_f = 0.56 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 6.28 (q, *J* = 7.0 Hz, 1H), 2.51 (q, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 1.90 (d, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 143.8, 142.1, 139.1, 136.5, 129.6, 128.8, 21.7, 20.0, 14.3, 13.3.

(*E*)-1-(naphthalen-1-yl)but-2-en-1-one (2p) [19] Prepared according to general procedure to afford as colorless oil (76% yield). R_f = 0.54 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 – 8.23 (m, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.90 (dd, *J* = 6.8, 2.5 Hz, 1H), 7.67 (dd, *J* = 7.0, 0.8 Hz, 1H), 7.61 – 7.47 (m, 3H), 6.88 (dq, *J* = 15.5, 6.8 Hz, 1H), 6.70 (dd, *J* = 15.6, 1.4 Hz, 1H), 1.99 (dd, *J* = 6.8, 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.3, 147.1, 137.0, 133.9, 132.9, 131.4, 130.6, 128.5, 127.4, 127.03, 126.5, 125.7, 124.5, 18.7.

(*E*)-1-(naphthalen-2-yl)but-2-en-1-one (2q) [29] Prepared according to general procedure to afford as colorless oil (78% yield). R_f = 0.53 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H), 8.02 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.64 – 7.51 (m, 2H), 7.20 – 7.04 (m, 2H), 2.05 (d, *J* = 5.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 145.1, 135.6, 135.4, 132.7, 130.1, 129.6, 128.6, 128.4, 127.9, 127.7, 126.8, 124.68, 18.8.

(*E*)-1-(5-bromothiophen-2-yl)but-2-en-1-one (2r) Prepared according to general procedure to afford as yellow solid (75% yield). R_f = 0.40 (EtOAc / hexanes 1:10). m. p. = 260 – 261 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 4.0 Hz, 1H), 7.21 – 7.06 (m, 2H), 6.73 (ddd, *J* = 15.1, 3.2, 1.6 Hz, 1H), 1.99 (dd, *J* = 6.9, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 181.2, 146.8, 145.1, 131.9, 131.4, 126.1, 122.7, 18.7. HRMS (ESI) for C_8H_8BrOS [M+H$^+$]: Calcd: 230.9474; Found: 230.9479. IR (KBr): 3054, 2965, 2917, 2851, 1669, 1620, 1439, 1293, 969, 920, 804, 782 cm^{-1}.

General procedure for preparation of 4: A seal tube containing Ketones **3** (0.5 mmol) and $Pd(OAc)_2$ (10 mol %), was evacuated and filled with dioxygen gas using an oxygen containing balloon. Then, DMSO (5 mL), trifluoroacetic acid (TFA) (1.0 mmol) were sequentially added to the system via syringe under an oxygen atmosphere. The reaction mixture was stirred at 80 °C until completion of the reaction (TLC). Then the reaction was cooled to RT and partitioned between water and ethyl acetate. The layers were separated and the organic layer was washed with aqueous saturated brine solution, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography afforded the **4.**

(*E*)-4-phenylbut-3-en-2-one (4a) [22] Prepared according to general procedure to afford as colorless oil (96% yield). R_f = 0.54 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 – 7.41 (m, 3H), 7.31 (d, *J* = 2.8 Hz, 3H), 6.63 (d, *J* = 16.3 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 143.5, 134.5, 130.6, 129.0, 128.3, 127.2, 27.6.

(*E*)-4-(2-fluorophenyl)but-3-en-2-one (4b) [24] Prepared according to general procedure to afford as yellow oil (98% yield). R_f = 0.59 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.5 Hz, 1H), 7.58 (td, *J* = 7.6, 1.7 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.22 – 7.09 (m, 2H), 6.79 (d, *J* = 16.5 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 161.4 (d, *J* = 253.7 Hz), 135.7, 132.0 (d, *J* = 8.8 Hz), 129.2, 128.71 (d, *J* = 2.3 Hz), 124.6 (d, *J* = 3.6 Hz), 122.5 (d, *J* = 11.5 Hz,), 116.2 (d, *J* = 21.8 Hz). 27.5.

(*E*)-4-(3-fluorophenyl)but-3-en-2-one (4c) [23] Prepared according to general procedure to afford as light yellow oil (96% yield). R_f = 0.48 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 16.3 Hz, 1H), 7.33 – 7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 7.02 (t, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 16.3 Hz, 1H), 2.31 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 163.1 (d, *J* = 246.9 Hz), 142.0 (d, *J* = 2.7 Hz), 136.8 (d, *J* = 7.7 Hz), 130.6 (d, *J* = 8.3 Hz), 128.3, 124.4 (d, *J* = 2.8 Hz), 117.5 (d, *J* = 21.5 Hz), 114.5 (d, *J* = 21.9 Hz), 27.9.

(*E*)-4-(4-fluorophenyl)but-3-en-2-one (4d) [22] Prepared according to general procedure to afford as yellow oil (97% yield). R_f = 0.55 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.48 (d, *J* = 16.3 Hz, 1H), 7.09 (t, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 16.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 164.1 (d, *J* = 251.7 Hz), 142.2, 130.8, 130.7, 130.3 (d, *J* = 8.6 Hz), 127.0, 126.9, 116.3 (d, *J* = 22.0 Hz). 27.7.

(*E*)-4-(3-chlorophenyl)but-3-en-2-one (4e) [22] Prepared according to general procedure to afford as light yellow oil (97% yield). R_f = 0.51 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.14 (m, 5H), 6.62 (d, *J* = 16.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.05, 141.69, 136.35, 135.03, 130.40, 130.28, 128.22, 128.02, 126.48, 27.84.

(*E*)-4-(4-chlorophenyl)but-3-en-2-one (4f) [22] Prepared according to general procedure to afford as yellow oil (95% yield). R_f = 0.50 (EtOAc / hexanes 1:10). ^{1}H NMR (400

MHz, $CDCl_3$): δ= 7.52 – 7.41 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.68 (dd, *J* = 16.3, 0.6 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.2, 141.9, 136.5, 133.0, 129.5, 129.3, 127.5, 27.7.

(*E*)-4-(4-nitrophenyl)but-3-en-2-one (4g) [22] Prepared according to general procedure to afford as yellow solid (98% yield). R_f = 0.28 (EtOAc / hexanes 1:10). m. p. = 102 – 103 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 16.3 Hz, 1H), 6.81 (d, *J* = 16.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 148.6, 140.8, 140.2, 130.5, 128.9, 124.3, 28.1.

(*E*)-4-(4-hydroxyphenyl)but-3-en-2-one (4h) [25] Prepared according to general procedure to afford as white solid (94% yield). R_f = 0.49 (EtOAc / hexanes 1:10). m. p. = 114 – 115 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 1H), 7.44 (d, *J* = 16.2 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 16.2 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.4, 159.2, 145.1, 130.6, 126.5, 124.4, 116.3, 27.3.

(*E*)-4-(4-methoxyphenyl)but-3-en-2-one (4i) [25] Prepared according to general procedure to afford as pale yellow solid (96% yield). R_f = 0.49 (EtOAc / hexanes 1:10). m. p. = 111 – 112 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 – 7.41 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 16.3 Hz, 1H), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.0, 161.7, 143.8, 130.1, 127.0, 124.9, 114.5, 55.4, 27.3.

(*E*)-4-(m-tolyl)but-3-en-2-one (4j) [25] Prepared according to general procedure to afford as yellow solid (96% yield). R_f = 0.49 (EtOAc / hexanes 1:10). m. p. = 141 – 142 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, *J* = 16.3, 2.1 Hz, 1H), 7.38 – 7.28 (m, 2H), 7.27 (dd, *J* = 7.9, 5.6 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 6.69 (dd, J = 16.3, 2.1 Hz, 1H), 2.36 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 143.6, 138.6, 134.3, 131.4, 128.9, 128.8, 126.9, 125.5, 27.4, 21.3.

(*E*)-4-(4-hydroxy-3-methoxyphenyl)but-3-en-2-one (4k) [10] Prepared according to general procedure to afford as yellow solid (95% yield). R_f = 0.39 (EtOAc / hexanes 1:10). m. p. = 131 – 132 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 16.2, 1.1 Hz, 1H), 7.14 – 7.03 (m, 2H), 6.94 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.59 (dd, *J* = 16.2, 1.6 Hz, 1H), 6.22 (s, 1H), 3.92 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.8, 148.5, 147.1, 144.0, 126.9, 125.0, 123.6, 115.0, 109.5, 56.0, 27.4.

(*E*)-4-(3,4-dimethoxyphenyl)but-3-en-2-one (4l) [22] Prepared according to general procedure to afford as yellow solid (97% yield). R_f = 0.48 (EtOAc / hexanes 1:10). m. p. = 78 – 80 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 16.2 Hz, 1H), 7.13 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.08 (s, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 16.2 Hz, 1H), 3.92 (s, 6H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.4, 151.4, 149.3, 143.6, 127.4, 125.3, 123.1, 111.1, 109.7, 56.1, 56.0, 27.4.

(*E*)-chalcone (4m) [19] Prepared according to general procedure to afford as yellow solid (92% yield). R_f = 0.51 (EtOAc / hexanes 1:10). m. p. = 55 – 58 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.07 – 7.97 (m, 2H), 7.81 (d, *J* = 15.7 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.60 – 7.46 (m, 4H), 7.45 – 7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 144.9, 138.3, 135.0, 132.9, 130.7, 129.1, 128.7, 128.6, 128.6, 122.2.

(*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (4n) [11] Prepared according to general procedure to afford as yellow solid (91% yield). R_f = 0.49 (EtOAc / hexanes 1:10). m. p. = 89 – 90 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 12.75 (s, 1H), 7.84 – 7.80 (m, 2H), 7.66 – 7.51 (m, 3H), 7.48 – 7.26 (m, 4H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8, 163.7, 145.6, 136.5, 134.7, 131.1, 129.8, 129.1, 128.8, 120.2, 120.1, 119.0, 118.7.

Cinnamaldehyde (4o) [26] Prepared according to general procedure to afford as yellow oil (98% yield). R_f = 0.59 (EtOAc / hexanes 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.71 (d, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.47 – 7.40 (m, 4H), 6.72 (dd, *J* = 15.9, 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.8, 152.9, 134.1, 131.4, 129.2, 128.7, 128.6.

(*E*)-3-(p-tolyl)acrylaldehyde (4p) [26] Prepared according to general procedure to afford as yellow oil (96% yield). R_f = 0.57 (EtOAc / hexanes 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.69 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.23 (m, 3H), 7.29 – 7.21 (m, 2H), 6.69 (dd, *J* = 15.9, 7.7 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.0, 153.2, 142.1, 131.4, 123.0, 128.7, 127.8, 21.7.

(*E*)-3-(4-fluorophenyl)acrylaldehyde (4q) [26] Prepared according to general procedure to afford as yellow oil (95% yield). R_f = 0.48 (EtOAc / hexanes 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.70 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.45 (d, *J* = 16.0 Hz, 1H), 7.12 (dd, *J* = 14.2, 5.7 Hz, 2H), 6.66 (dd, *J* = 16.0, 7.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 164.5 (d, *J* = 253.2 Hz), 151.5, 130.6 (d, *J* = 8.7 Hz), 130.4 (d, *J* = 3.3 Hz), 128.4 (d, *J* = 2.2 Hz), 116.5 (d, *J* = 22.1 Hz).

(*E*)-3-(benzo[d][1,3]dioxol-5-yl)-2-methylacrylaldehyde (4r) Prepared according to general procedure to afford as white solid (yield: 93%, 90% for gram scale). R_f = 0.49 (EtOAc / hexanes 1:10). m. p. = 60 – 61 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.52 (s, 1H), 7.14 (s, 1H), 7.06 (d, *J* = 10.0 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.03 (s, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 149.9, 149.0, 148.2, 136.6, 129.5, 125.9, 109.7, 108.7, 101.7, 11.0. HRMS (ESI) for $C_{13}H_{15}O_3$ [M+H$^+$]: Calcd: 219.1016. Found: 219.1016. IR (KBr): 3442, 2913, 1664, 1500, 1265, 1014, 921, 617 cm^{-1}.

(*E*)-1-phenylpent-3-en-2-one (4s) [21] Prepared according to general procedure to afford as colourless oil (75% yield). R_f = 0.47 (EtOAc / hexanes 1:10). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 7.3 Hz, 2H), 7.25 (dd, *J* = 5.8, 3.9 Hz, 1H), 7.21 (t, *J* = 6.2 Hz, 2H), 7.05 – 6.83 (m, 1H), 6.17 (dd, *J* = 15.7, 1.6 Hz, 1H), 3.81 (s, 2H), 1.87 (dd, *J* = 6.9, 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.4, 143.8, 134.7, 131.0, 129.5, 128.8, 127.0, 47.7, 18.4.

(*E*)-pent-3-en-2-one (4t) [30] Prepared according to general procedure to afford as colorless oil (72% yield). R_f = 0.65 (EtOAc / hexanes 1:30). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.92 – 6.70 (m, 1H), 6.09 (ddd, *J* = 15.9, 3.7, 1.7 Hz, 1H), 2.23 (s, 3H), 1.91 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.6, 143.7, 133.1, 26.9, 18.4.

(*E*)-2-methylpent-2-enal (4u) [31] Prepared according to general procedure to afford as colorless oil (75% yield). R_f = 0.45 (EtOAc / hexanes 1:30). ^1H NMR (400 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 6.80 (td, *J* = 7.3, 1.2 Hz, 1H) 2.69 (p, *J* = 7.5 Hz, 2H), 2.06 (s, 3H), 1.43 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 156.4, 138.9, 22.4, 12.9, 9.1.

General procedure for preparation of 6: A seal tube containing Ketones **5** (0.5 mmol) and $Pd(OAc)_2$ (10 mol %), was evacuated and filled with dioxygen gas using an oxygen containing balloon. Then, DMSO (5 mL), trifluoroacetic acid (TFA) (1.0 mmol) were sequentially added to the system via syringe under an oxygen atmosphere. The reaction mixture was stirred at 80 °C until completion of the reaction (TLC). Then the reaction was cooled to RT and partitioned between water and ethyl acetate. The layers were separated and the organic layer was washed with aqueous saturated brine solution, dried

over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash chromatography afforded the **6.**

4H-chromen-4-one (6a) [10b] Prepared according to general procedure to afford as white solid (68% yield). R_f = 0.38 (EtOAc / hexanes 1:10). m. p. = 55 – 56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 – 8.16 (m, 1H), 7.91 – 7.83 (m, 1H), 7.73 – 7.62 (m, 1H), 7.50 – 7.36 (m, 2H), 6.40 – 6.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.8, 156.5, 155.5, 133.9, 125.8, 125.3, 124.9, 118.3, 113.0.

7-fluoro-2-methyl-4H-chromen-4-one (6b) Prepared according to general procedure to afford as yellow solid (87% yield). R_f = 0.46 (EtOAc / hexanes 1:10). m. p. = 188 – 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (s, 1H), 7.49 – 7.23 (m, 2H), 6.21 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 159.6 (*J* = 246.9 Hz), 153.0, 122.3, 122.0, 120.1, 120.0, 110.7 (d, *J* = 23.6 Hz), 110.0, 20.71. HRMS (ESI) for $C_{10}H_8FO_2$ [M+H$^+$]: Calcd: 179.0503; Found: 179.0509. IR (KBr): 2963, 2925, 1654, 1623, 1586, 1555, 1440, 1291, 1088, 1029, 807 cm^{-1}.

2-phenyl-4H-chromen-4-one (6c) [10b] Prepared according to general procedure to afford as white solid (80% yield). R_f = 0.48 (EtOAc / hexanes 1:10). m. p. = 102 – 103 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 – 8.10 (m, 1H), 7.83 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.53 – 7.39 (m, 4H), 7.34 (t, *J* = 7.5 Hz, 1H), 6.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.2, 164.2, 156.4, 134.3, 132.0, 131.5, 129.2, 126.5, 125.8, 125.6, 123.6, 118.2, 107.1.

3-methyl-4H-chromen-4-one (6d) [32] Prepared according to general procedure to afford as pale yellow solid (72% yield). R_f = 0.55 (EtOAc / hexanes 1:4). m. p. = 68 – 69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (ddd, *J* = 7.9, 3.4, 1.5 Hz, 1H), 7.83 – 7.75 (m, 1H), 7.68 – 7.59 (m, 1H), 7.45 – 7.33 (m, 2H), 2.20 – 1.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4, 156.7, 151.8, 133.3, 125.9, 124.9, 123.7, 120.8, 118.1, 11.3.

2,3-dihydro-4H-pyran-4-one (6e) [19] Prepared according to general procedure to afford as colorless oil (75% yield). R_f = 0.57 (EtOAc / hexanes 1:10). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.31 (m, 1H), 5.40 (d, *J* = 6.0 Hz, 1H), 4.49 – 4.41 (m, 2H), 2.57 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.8, 164.3, 107.4, 68.2, 36.4.

cyclopent-2-en-1-one (6f) [33] Prepared according to general procedure to afford as colorless oil (51% yield). R_f = 0.39 (EtOAc / hexanes 1:30). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (dt, *J* = 5.4, 2.6 Hz, 1H), 6.36 – 6.09 (m, 1H), 2.78 – 2.62 (m, 2H), 2.49 – 2.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.9, 165.1, 134.7, 34.1, 29.1.

4H-thiochromen-4-one (6g) [10b] Prepared according to general procedure to afford as yellow solid (82% yield). R_f = 0.47 (EtOAc / hexanes 1:10). m. p. = 78 – 79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 10.5 Hz, 1H), 7.55 (d, *J* = 3.7 Hz, 2H), 7.51 – 7.42 (m, 1H), 6.95 (d, *J* = 10.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.9, 138.0, 137.7, 132.5, 131.6, 128.8, 128.0, 126.8, 126.1.

2-phenyl-4H-thiochromen-4-one (6h) [20] Prepared according to general procedure to afford as yellow solid (70% yield). R_f = 0.45 (EtOAc / hexanes 1:10). m. p. = 128 – 129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 12.5 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.39 – 7.30 (m, 1H), 7.23 – 7.13 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.9, 146.2, 135.4, 134.4, 133.7, 131.1, 130.5, 130.33, 130.30, 129.2, 127.2, 125.8, 124.0.

naphthalen-1-ol (6i) [34] Prepared according to general procedure to afford as white solid (75% yield). R_f = 0.49 (EtOAc / hexanes 1:20). m. p. = 96 – 97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 – 8.10 (m, 1H), 7.85 – 7.73 (m, 1H), 7.59 – 7.37 (m, 3H), 7.27 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 7.4 Hz, 1H), 5.39 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 134.9, 127.8, 126.5, 125.9, 125.39, 124.5, 121.6, 120.8, 108.8.

(5S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (6j) [35] Prepared according to general procedure to afford as white solid (81% yield). R_f = 0.45 (EtOAc / hexanes 1:10). m. p. = 145 – 146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, *J* = 10.2 Hz, 1H), 5.79 (d, *J* = 10.2 Hz, 1H), 2.48 (d, J = 9.0 Hz, 1H), 2.31 (dd, *J* = 17.7, 14.1 Hz, 1H), 2.16 (dd, *J* = 17.7, 4.1 Hz, 1H), 2.06 (s, 3H), 1.82 – 1.56 (m, 7H), 1.48 – 1.30 (m, 6H), 1.22 – 1.07 (m, 2H), 1.00 – 0.87 (m, 4H), 0.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.4, 200.1, 158.2, 127.5, 63.6, 56.53, 49.9, 44.3, 44.2, 40.9, 39.0, 38.8, 35.7, 31.5, 31.2, 27.5, 24.3, 22.9, 21.2, 13.6, 13.0.

(5S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-7-methyloctan-2-yl)-4,5,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (6k) [10b] Prepared according to general procedure to afford as as white solid (83% yield). R_f = 0.45 (EtOAc / hexanes 1:10). m. p. = 101 – 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, *J* = 10.2 Hz, 1H), 5.85 (d, *J* = 10.2 Hz, 1H), 2.37 (dd, *J* = 17.6, 14.1 Hz, 1H), 2.21 (dd, *J* = 17.7, 3.8 Hz, 1H), 2.05 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.97 – 1.78 (m, 2H), 1.72 (ddd, *J* = 12.9, 6.8, 3.3 Hz, 2H), 1.65 – 0.94 (m, 25H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, J = 6.6, 1.7 Hz, 6H), 0.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 158.7, 127.4, 56.5, 56.3, 50.1, 44.4, 42.8, 41.1, 39.9, 39.6, 39.1, 36.2, 35.9, 35.8, 31.4, 28.3, 28.1, 27.8, 24.2, 23.9, 22.9, 22.7, 21.4, 18.8, 13.1, 12.3.

Acknowledgements

We are grateful for financial support from National Natural Science Foundation of China (NSFC-21572178 and NSFC-21702162), Natural Science Basic Research Plan in Shaanxi Province of China (Program No. 2017JM2006), Scientific Research Program Funded by Shaanxi Provincial Education Department (Program No. 17JK0788).

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10.1002/adsc.201801058

FULL PAPER

Synthesis of Enones and Enals via Dehydrogenation of Saturated Ketones and Aldehydes

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