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Decarbonylative Addition

Rh-Catalyzed Decarbonylative Addition of Salicylaldehydes with Vinyl Ketones: Synthesis of Taccabulins A–E

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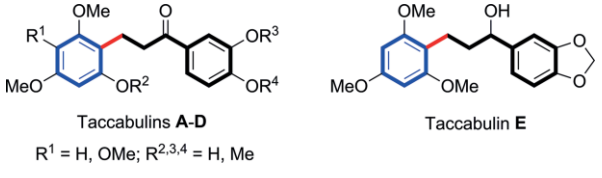
Abstract: A rhodium-catalyzed decarbonylative addition of salicylaldehydes with vinyl ketones was developed to synthesize *o*-hydroxydihydrochalcones (2-hydroxyphenethyl ketones). These decarbonylative addition reactions afforded various functionalized *o*-hydroxydihydrochalcones in moderate to good yields with broad functional group tolerance and selectivity. This method was also applied further in the divergent synthesis of dihydrochalcone derived taccabulins **A**–**E**.

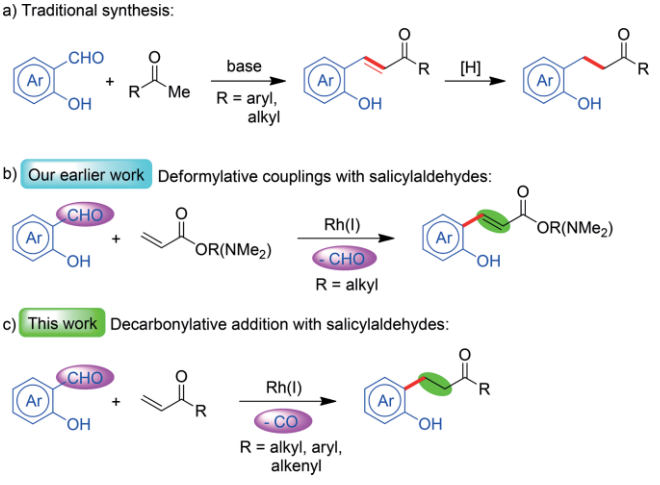
Introduction

Dihydrochalcones are valuable synthons possessing several biological applications.[1] In particular, molecules with *o*-hydroxydihydrochalcone (HDHC) as a core have been studied in various biological studies (Scheme 1).[2] Importantly, a family of taccabulins extracted from *Tacca* species were found to show antiproliferative activity against various cancer cell lines.[2a] For instance, taccabulin **A** possesses microtubule-destabilizing activity.[2b] The antiproliferative activity of taccabulins **A** and **D** in HeLa cells showed IC_{50} values of 0.6 μM and 28.9 μM respectively. Whereas, taccabulins **B**, **C** and **E** exhibited IC_{50} values greater than 50 μM in HeLa cells. Further, the structure-activity relationship studies of taccabulin family indicated improved antiproliferative activity with dihydrochalcones containing additional hydroxy group.[2a]



Scheme 1. Taccabulin family of natural products.

Taccabulins can be synthesized from the corresponding *o*-hydroxychalcones (Scheme 2a).[3] This approach in general, is problematic as the preparation of *o*-hydroxychalcones involves tedius synthetic procedures often with low yields due to the presence of free phenolic group.[3a] Further, synthesis of *o*-hydroxydihydrochalcones with direct use of salicylaldehydes was also reported with protection/deprotection synthetic manoeuvring to obtain improved yields.[3]



Scheme 2. Salicylaldehydes in the synthesis of *o*-hydroxydihydrochalcones.

Other methods such as Pd-catalyzed Heck reaction of *o*-iodophenols with allylic alcohols[4] and C–H alkylation of *N*-phenoxyacetamides with allylic alcohols under Rh-catalysis also provide HDHCs.[5] Thus, synthetic methods with the direct use of salicylaldehydes in the preparation of HDHCs under metal-catalyzed conditions are rare. There is a dire need to explore for such a possibility keeping in view the significance of HDHCs.

Simple aldehydes in decarbonylative addition reactions are known with olefins,[6] while salicylaldehydes react in hydroacylation process with olefins.[7] However, salicylaldehydes reactivity in decarbonylative addition reactions are scant.[8] In this context, we recently reported the decarbonylative coupling of salicylaldehydes with acrylates and acrylamides to synthesize functionaly important *o*-hydroxycinnamates and *o*-hydroxycinnamamides (Scheme 2b).[9] In literature the competition between β-hydride elimination and conjugate addition of alkyl rhodium intermediates was reported in reaction with acrylates and vinyl ketones respectively.[10] Thus, vinyl ketones are known to predominently deliver saturated products while acrylates gave unsaturated products.[11] Hence, it was of interest to explore the decarbonylative addition reactivity of salicylaldehydes

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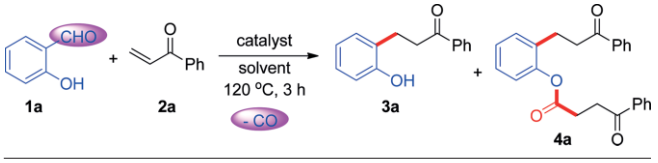
with vinyl ketones under rhodium catalysis and its possible application in the synthesis of taccabulin natural products containing HDHCs. This attempt provided an opportunity for the direct synthesis of *o*-hydroxydihydrochalcones from salicylaldehydes and vinyl ketones under Rh-catalyzed conditions (Scheme 2c). Further the developed method was also applied in the synthesis of taccabulin natural products as elaborated below.

Results and Discussion

The coupling of salicylaldehyde **1a** with phenyl vinyl ketone **2a** (4 equiv.) was investigated (Table 1) initially with catalytic $Rh(CO)_2(acac)$ in DMF at 120 °C for 3 h (entry 1). This resulted in the formation of *o*-hydroxydihydrochalcone **3a** in 53 % yield along with **4a** as a side product in 25 % yield (entry 1). Evidently, product **4a** arose from **3a** through carbonylative Michael addition[12] involving vinyl ketone **2a**. With the aim to improve the yield of **3a**, this reaction was further done with reduced amounts of **2a** (cf. entry 2 and 3). To some extent this helped in improving the yield of **3a** up to 61 % with the use of 2 equiv. of vinyl ketone (entry 2). Further optimization with different Rh-catalysts and solvent conditions did not improve the yield (entries 4–8). Lowering the reaction temperature also gave poor yield (entry 9). Thus, from this optimization study, the protocol comprising phenyl vinyl ketone (2 equiv.), $Rh(CO)_2(acac)$ (0.05 equiv.) in DMF at 120 °C for 3 h proved to be more efficient and it was considered as an optimal one for our further study (entry 2).

Table 1. Optimization studies.[a]



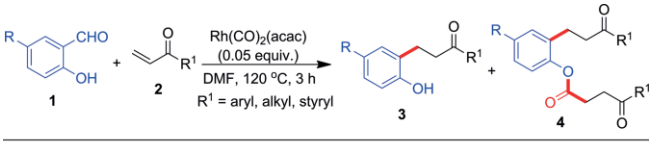
Entry	Catalyst	Solvent	**3a** [%]	**4a** [%]
1	$Rh(CO)_2(acac)$	DMF	53	25[b]
2	$Rh(CO)_2(acac)$	DMF	61	21
3	$Rh(CO)_2(acac)$	DMF	46	21[c]
4	$RhCl_3/PPh_3$	DMF	20	9
5	$RhCl(PPh_3)_3$	DMF	33	17
6	$RhCl(CO)(PPh_3)_2$	DMF	37	8
7	$Rh(CO)_2(acac)$	DMA	39	16
8	$Rh(CO)_2(acac)$	NMP	46	16
9	$Rh(CO)_2(acac)$	DMF	28	30[d]

[a] Conditions: **1a** (0.5 mmol, 1 equiv.), **2a** (1 mmol, 2 equiv.), catalyst (0.025 mmol, 0.05 equiv.), solvent (2 mL), 120 °C, 3 h. [b] **2a** (2 mmol, 4 equiv.). [c] **2a** (0.5 mmol, 1 equiv.). [d] Reaction was carried out at 100 °C.

The above study thus established the direct synthesis of *o*-hydroxydihydrochalcone (HDHC) from readily available salicylaldehyde and vinyl ketone under Rh-catalyzed conditions. Additionally, this method ensured protecting-group free coupling and direct utilization of vinyl ketones as reactant. With these advantages in hand, further exploration for general reactivity was explored.

First the optimized Rh-catalyzed conditions was tested with various functionalized salicylaldehydes and vinyl ketones. These results are given in Table 2. From this study, it was clear that the desired decarbonylative addition underwent smoothly with electronically different salicylaldehydes **1a**–**1e** in reaction with vinyl ketone **2a** delivering the corresponding HDHCs (**3a**–**3e**) in moderate yields along with **4** as a minor side product in some cases.

Table 2. Scope of functionalized salicylaldehydes and vinyl ketones.[a]



Entry	Salicylaldehyde	Vinyl ketone	Product **3**	Product **4**
1	**1a** R = H	R^1 = phenyl **2a**	**3a** R = H 61%	**4a**, 21%
2	**1b** R = Me		**3b** R = Me 52%	**4b**, 24%
3	**1c** R = F		**3c** R = F 59%	--
4	**1d** R = Br		**3d** R = Br 54%	--
5	**1e** R = Ac		**3e** R = Ac 54%	--
6	**1a**	**2b** R^1 = *p*-tolyl	**3f** R = Me 60%	**4f**, 10%
7		**2c** R^1 = *p*-anisyl	**3g** R = OMe 62%	**4g**, 14%
8	**1f**	R^1 = *p*-anisyl **2c**	**3h**, 68%	--
9	**1a** R = H	R^1 = *p*-Clphenyl **2d**	**3i** R = H 54%	**4i**, 15%
10	**1b** R = Me		**3j** R = Me 48%	**4j**, 17%
11	**1c** R = F		**3k** R = F 54%	**4k**, 13%
12	**1a**	R^1 = *β*-naphthyl **2e**	**3l**, 57%	--
13	**1e** R = Ac	R^1 = Me **2f**	**3m** R = Ac 73%	--
14	**1g** R = CO_2Me		**3n** R = CO_2Me 71%	--
15	**1b** R = Me	R^1 = styryl **2g**	**3o** R = Me 57%	**4o**, 18%
16	**1c** R = F		**3p** R = F 58%	**4p**, 18%
17	**1g** R = CO_2Me		**3q** R = CO_2Me 52%	**4q**, --

[a] Conditions: **1a**–**1g** (0.5 mmol, 1 equiv.), **2a**–**2g** (1 mmol, 2 equiv.), $Rh(CO)_2(acac)$ (0.025 mmol, 0.05 equiv.), DMF (2 mL), 120 °C, 3 h.

The couplings of the functionalized aryl vinyl ketones (**2b**–**2e**) with different salicylaldehydes (**1a**–**c** and **1f**) also furnished the corresponding HDHCs (**3f**–**3l**) in moderate to good yields. Further couplings using aliphatic variant such as methyl vinyl ketone **2f** with salicylaldehydes (**1e** and **1g**) also gave the corresponding functionalized HDHCs (**3m** and **3n**) in good yields.

Additional curiosity check was carried out with styryl vinyl ketone **2g** in combination with functionalized salicylaldehydes **1b**, **1c** and **1g**. In these cases, the respective functionaly loaded

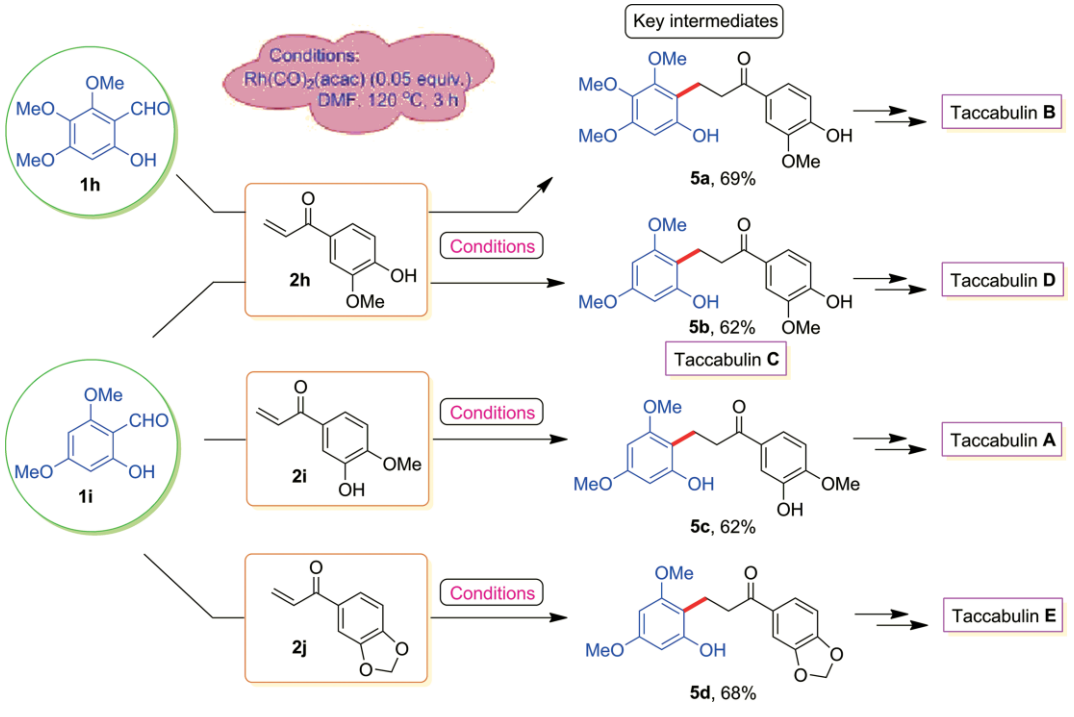
(*E*)-5-(2-hydroxyphenyl)-1-phenylpent-1-en-3-ones (**3o**–**3q**) were obtained in moderate yields. The direct synthesis of these multifunctional products in a one-pot operation involving decarbonylative addition is synthetically advantageous process. Importantly, the product **3p** is known for its antiproliferative activity,[2c] and it was earlier synthesized from benzaldehyde involving multi-step sequence.[13] Importantly, the present decarbonylative addition of salicylaldehydes to vinyl ketones has hitherto not been reported in the literature. It is to be noted that in most cases, the side product **4** (**4a**, **4b**, **4f**, **4g**, **4i**–**k**, **4o** and **4p**) was formed in minor amount as carbonylative Michael addition[12] of product **3** with vinyl ketone (**2**).

To demonstrate synthetic application of the present protocol, we considered the preparation of taccabulins **A**–**E** that are known for their numerable biological activities.[2] A concise plan was envisaged for the preparation of taccabulins **A**–**E** with salicylaldehydes (**1h** and **1i**) in combination with vinyl ketones (**2h**, **2i** and **2j**).

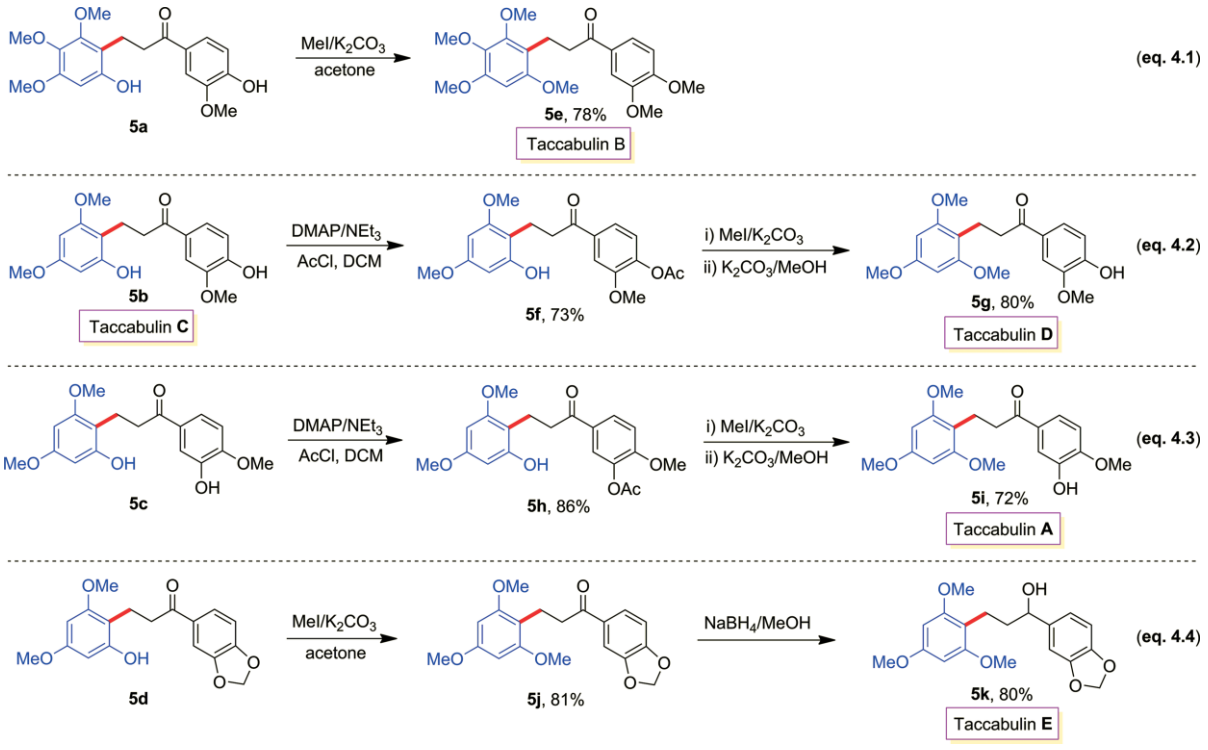
Accordingly, the first synthetic application was started with the synthesis of taccabulin **C** employing salicylaldehyde **1i** and vinyl ketone **2h** under Rh-catalyzed conditions (Scheme 3). Our method thus proved to be very useful as the desired coupling underwent smoothly without protection of the phenolic group in salicylaldehyde **1i** and vinyl ketone **2h**.[3] This directly afforded taccabulin **C** (**5b**) in 62 % yield. The key intermediates **5a**, **5c** and **5d** required for the synthesis of other taccabulins were also synthesized in 62–69 % yields similary using salicylaldehydes **1h** and **1i** with vinyl ketones **2h**–**2j**. Clearly the present protocol further demonstrated the tolerance for *o*-sterics as in **1h** and **1i**. In elaboration, the reaction of salicylaldehyde **1h** with vinyl ketone **2h** afforded **5a**, a precursor for taccabulin **B**, in 69 % yield. Reactions of salicylaldehyde **1i** with the vinyl ketones **2i** and **2j** gave intermediates **5c** and **5d** which are precursors for taccabulins **A** and **E** in 62 % and 68 % yields respectively. Importantly, taccabulin **C** is also a precursor for taccabulin **D**. Evidently the present Rh-catalyzed protocol thus smoothly afforded these different intermediates required for the synthesis of the taccabulins **A**–**E** in a synthetically viable and advantage manner (Scheme 4).

Further, *o*-hydroxydihydrochalcone **5a** was first methylated to obtain taccabulin **B** in 78 % yield (Equation 4.**1**, Scheme 4). Synthesis of taccabulin **A** and **D** required the protection and deprotection sequence to achieve the selective methylations. The selective acetylation of taccabulin **C** (**5b**) was initially carried out to obtain monoacetylated product **5f** in 73 % yield. It was then methylated followed by deacetylation to afford taccabulin **D** (**5g**) in 80 % combined yield (Equation 4.**2**, Scheme 4). Similarly, selective acetylation of *o*-hydroxydihydrochalcone **5c** afforded monoacetylated product **5h** in 86 % yield. Further methylation and deacetylation sequence gave taccabulin **A** (**5i**) in 72 % combined yield (Equation 4.**3**, Scheme 4). Additionally, taccabulin **E** (**5k**) was obtained from *o*-hydroxydihydrochalcone **5d** involving methylation (**5j**) and reduction protocol in 80 % yield (Equation 4.**4**, Scheme 4). Overall, these efforts thus demonstrated a facile synthetic procedure for the synthesis of *o*-hydroxydihydrochalcones containing taccabulin (**A**–**E**) natural products. The selective monoacetylation strategy adopted in the synthesis of taccabulin **A** and **D** enriched the overall synthetic yields in a concise manner.

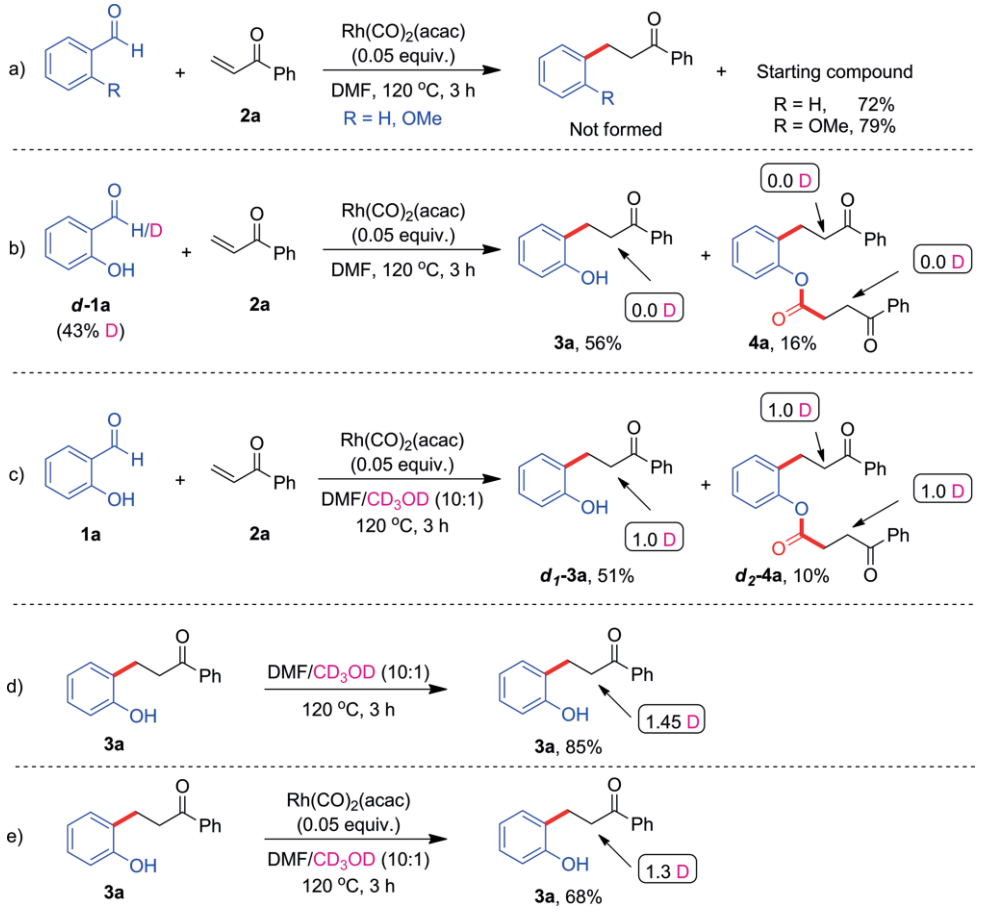
To gain insights into the reaction mechanism a few control reactions were carried out as given in Scheme 5. First, the role of the hydroxy group was investigated with benzaldehyde and 2-methoxybenzaldehyde (Scheme 5a). In these cases, the corresponding dihydrochalcones were not formed and starting alde-



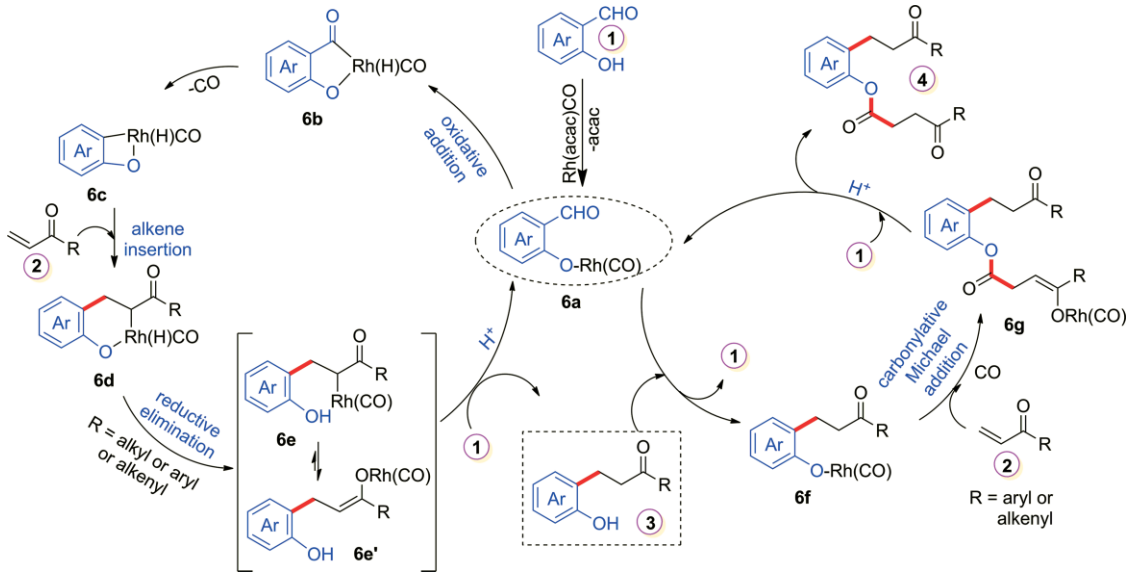
Scheme 3. Synthesis of taccabulin C and other key intermediates.



Scheme 4. Synthesis of taccabulin natural products.



Scheme 5. Mechanistic study.



Scheme 6. Proposed mechanistic cycle.

hydes were recovered. This indicates the necessity of the presence of hydroxy group. Further, the reaction of partially deuterated salicylaldehyde (***d*-1a**) with vinyl ketone **2a** gave *o*-hydroxydihydrochalcone (**3a**) in 56 % yield along with **4a** in 16 % yield (Scheme 5b) without incorporation of deuterium in the products. This shows that aldehydic proton is not involved for protonation during the catalytic cycle and the absence of H/D exchange between aldehyde and phenol during the reaction course. Importantly, deuterium exchange between phenolic group of salicylaldehyde and CD_3OD was known to give salicylaldehyde with deuterium incorporation at phenolic group.[14] This was proven with the reaction of salicylaldehyde (**1a**) with vinyl ketone (**2a**) in DMF/CD_3OD solvent mixture (Scheme 5c) delivering mono-deuterated product (***d*$_1$-3a**) in 51 % yield along with di-deuterated product (***d*$_2$-4a**) in 10 % yield. Additional two control experiments with product **3a** using DMF/CD_3OD solvent combination without (Scheme 5d) and with Rh-catalyst (Scheme 5e) also delivered partial deuterium exchange at alfa carbon of carbonyl group confirming the possibility of acidic proton exchange after the product formation. However, the mono-deuterations in equal proportion found both in products **3** and **4** (Scheme 5c) clearly indicates their direct formation through catalytic cycle and not after acidic proton exchange (as seen in Scheme 5d and Scheme 5e).

Based on the above experimentation, the probable mechanistic cycle for the formation of product (**3**) along with minor product (**4**) is given in Scheme 6. The initial ligand exchange of the rhodium catalyst with salicylaldehyde (**1**) would form the aryloxyrhodium **6a**. It undergoes oxidative addition to give the aroylrhodium hydride intermediate **6b** followed by decarbonylation gives arylrhodium hydride **6c**. This in turn undergoes insertion of vinyl ketone (**2**) generates alkylrhodium **6d** which upon reductive elimination provides **6e**/**6e′**. Further protonation involving salicylaldehyde provides product *o*-hydroxydihydrochalcone **3** with the regeneration of **6a**. The formation of minor product **4** could be due to the further involvement of preformed product **3** in ligand exchange with **6a** giving the intermediate **6f** followed by its Michael addition[12] to vinyl ketone generating **6g.** This upon protonation involving salicylaldehyde forms product **4**. The formation of mono-deuterated product (***d*$_1$-3a**) and di-deuterated product (***d*$_2$-4a**) confirms the formation of product **4** with the involvement of preformed product **3** as proposed in the catalytic cycle. The proposed carbonylation in the formation of **6g** also further confirms the initial decarbonylation step during the formation of **6c**.

Conclusions

In conclusion, we have developed a simple and straight forward catalytic method for the decarbonylative addition of salicylaldehydes to vinyl ketones for the synthesis of *o*-hydroxydihydrochalcones. This protecting-group free and step-economic method provides the direct preparation of *o*-hydroxydihydrochalcones in moderate to good yields. This method was further applied in the Rh-catalyzed first time synthesis of the taccabulin natural products which are important scaffolds with antiproliferative activity against various cancer cell lines and other biological activities.

Experimental Section

General: All the NMR (^1H and ^{13}C) spectra were recorded on a JEOL-Lambda (400 MHz and 500 MHz) spectrometer in $CDCl_3$ solvent. IR spectra were recorded with a Perkin-Elmer FT/IR spectrometer. HRMS spectra were recorded with a Waters GCT Premier-CAB155 and Waters-Q-Tof Premier-HAB213 instruments. Melting points were determined using a Yamato melting point apparatus. All the coupling reactions were performed in dry Schlenk tube under nitrogen atmosphere conditions. Standard procedures were followed to dry various solvents used in coupling reactions. Methyl vinyl ketone (**2f**) was purchased commercially and used without further purification. Salicylaldehyde (**1a**), 5-bromosalicylaldehyde (**1d**) and 2-hydroxy-1-

naphthaldehyde (**1f**) were purchased from commercial suppliers. The other substituted salicylaldehydes (**1b**,[15a] **1c**,[15a] **1e**,[15b] **1g**,[15c] **1h**,[15d] **1i**[15d] and ***d*-1a**[7b]) were prepared by known procedures.

General procedure for the synthesis of vinyl ketones (2): The substituted aryl vinyl ketones were prepared from the corresponding acetophenones by α-methylenation of carbonyls known in literature.[16] In an oven-dried 150 mL R.B flask, acetophenone was taken in dry THF and paraformaldehyde (2 equiv.), diisopropylammonium 2,2,2-trifluoroacetate (1 equiv.), TFA (50 mol-%) were added. The reaction mixture was stirred at reflux for 2 h in an open atmosphere. The mixture will become clear, then the reaction mixture is cooled down to room temperature and paraformaldehyde (2 equiv.) was added. Next, the reaction mixture was stirred at reflux for an additional 16 h. The reaction mixture was cooled to r.t. and the solvent was removed under reduced pressure, extracted with DCM and washed with 1 N HCl, 1 N NaOH and brine solution. The organic contents were dried with anhydrous $MgSO_4$ and the solvents evaporated to dryness. The crude was purified by silica gel column chromatography.

The characterization data for vinyl ketones (**2a**–**2e** and **2g**–**2j**) is given below.

1-Phenylprop-2-en-1-one (2a):[16] Colourless liquid (2.4 g, 44 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96–7.94 (m, 2H), 7.60–7.55 (m, 1H), 7.50–7.46 (m, 2H), 7.16 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.44 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.93 (dd, *J* = 10.6, 1.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 137.4, 133.1, 132.5, 130.4, 128.8, 128.8 ppm.

1-*p*-Tolylprop-2-en-1-one (2b):[17a] Colourless liquid (3.3 g, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.2 Hz, 2H), 7.28 (dd, *J* = 8.6, 0.6 Hz, 2H), 7.16 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.43 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.90 (dd, *J* = 10.6, 1.8 Hz, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 144.0, 134.9, 132.5, 129.9, 129.5, 129.0, 21.8 ppm.

1-(4-Methoxyphenyl)prop-2-en-1-one (2c):[17b] Colourless liquid (2.3 g, 42 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 9.0 Hz, 2H), 7.17 (dd, *J* = 17.1, 10.5 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.42 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.87 (dd, *J* = 10.5, 1.8 Hz, 1H), 3.87 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 189.4, 163.7, 132.3, 131.2, 130.4, 129.4, 114.0, 55.6 ppm.

1-(4-Chlorophenyl)prop-2-en-1-one (2d):[18a] Colourless liquid (3.16 g, 58 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.11 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.44 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.94 (dd, *J* = 10.6, 1.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.9, 139.6, 135.7, 132.1, 130.8, 130.2, 129.1 ppm.

1-(Naphthalen-2-yl)prop-2-en-1-one (2e):[17b] Colourless liquid (1.41 g, 26 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1H), 8.04 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.98–7.88 (m, 3H), 7.63–7.54 (m, 2H), 7.33 (dd, *J* = 17.1, 10.6 Hz, 1H), 6.51 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.98 (dd, *J* = 10.6, 1.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0, 135.7, 134.7, 132.6, 132.5, 130.5, 130.2, 129.7, 128.7, 128.6, 127.9, 127.0, 124.6 ppm.

(*E*)-1-Phenylpenta-1,4-dien-3-one (2g):[16] Colourless liquid (1.68 g, 31 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 16.0 Hz, 1H), 7.60–7.57 (m, 2H), 7.41–7.40 (m, 3H), 7.01 (d, *J* = 16.0 Hz, 1H), 6.72 (dd, *J* = 17.4, 10.6 Hz, 1H), 6.39 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.89 (dd, *J* = 10.6, 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.7, 144.1, 135.6, 134.7, 130.7, 129.1, 128.7, 128.5, 124.2 ppm.

1-(4-Hydroxy-3-methoxyphenyl)prop-2-en-1-one (2h):[18b] Colourless liquid (2.65 g, 49 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.54 (m, 2H), 7.18 (dd, *J* = 17.0, 10.6 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.43 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.87 (dd, *J* = 10.5, 1.8 Hz, 1H), 5.56 (s, 1H), 3.95 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.3, 150.7, 147.0, 132.0, 130.2, 129.4, 124.2, 114.0, 110.6, 56.2 ppm. IR (KBr): $\tilde{\nu}$ = 3378, 2936, 1659, 1588, 1515, 1464, 1427, 1275, 1201, 1172, 1024, 785 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{10}H_{10}O_3$ $[M]^+$ 178.0630, found 178.0638.

1-(3-Hydroxy-4-methoxyphenyl)prop-2-en-1-one (2i): Colourless liquid (0.18 g, 33 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.54 (m, 2H), 7.15 (dd, *J* = 17.0, 10.5 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 6.42 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.87 (dd, *J* = 10.5, 1.8 Hz, 1H), 5.72 (s, 1H), 3.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.5, 150.8, 145.7, 132.1, 131.1, 129.6, 122.5, 114.9, 110.1, 56.2 ppm. IR (KBr): $\tilde{\nu}$ = 3393, 2939, 2844, 1660, 1611, 1582, 1513, 1440, 1276, 1176, 1017, 890, 782 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{10}H_{11}O_3$ $[M + H]^+$ 179.0708, found 179.0702.

1-(Benzo[d][1,3]dioxol-5-yl)prop-2-en-1-one (2j):[18c] Colourless liquid (0.42 g, 19 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.46 (d, *J* = 1.7 Hz, 1H), 7.12 (dd, *J* = 17.2, 10.7 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.41 (dd, *J* = 17.2, 1.8 Hz, 1H), 6.05 (s, 2H), 5.87 (dd, *J* = 10.7, 1.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.0, 152.0, 148.4, 132.2, 129.6, 125.2, 108.6, 108.1, 102.0 ppm. IR (KBr): $\tilde{\nu}$ = 3080, 2906, 1666, 1600, 1445, 1253, 1038, 779 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{10}H_9O_3$ $[M + H]^+$ 177.0552, found 177.0558.

Representative procedure for decarbonylative addition reactions: The decarbonylative addition reaction was performed by charging a dry Schlenk tube with salicylaldehyde (**1a**) (61 mg, 0.5 mmol), phenyl vinyl ketone (**2a**) (132 mg, 1 mmol), $Rh(CO)_2(acac)$ (6.4 mg, 0.025 mmol) and DMF (2 mL) solvent. This mixture was stirred in an oil bath at 120 °C for 3 h. In the end, the contents were brought to r.t., quenched with dil. HCl and extracted with ethyl acetate (30 mL). The organic extract was washed with water (15 mL), brine (15 mL), dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane as an eluent. The product **3a** and **4a** were obtained in 61 % (69 mg) and 21 % (40 mg) respectively.

The characterization data of all the products is given below.

3-(2-Hydroxyphenyl)-1-phenylpropan-1-one (3a):[19] Colourless solid (69 mg, 61 %), m.p. 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.96 (m, 2H), 7.60–7.55 (m, 1H), 7.47–7.42 (m, 2H), 7.14–7.09 (m, 2H), 6.93–6.84 (m, 2H), 3.47–3.43 (m, 2H), 3.06–3.03 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 154.6, 136.2, 133.9, 130.7, 128.8, 128.5, 128.1, 127.9, 120.8, 117.6, 40.5, 23.5 ppm. IR (KBr): $\tilde{\nu}$ = 3355, 3064, 2926, 1670, 1596, 1490, 1449, 1365, 1235, 1207, 1098, 754, 741, 688 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1072, found 227.1075.

3-(2-Hydroxy-5-methylphenyl)-1-phenylpropan-1-one (3b): Colourless liquid (62 mg, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.59–7.54 (m, 1H), 7.47–7.42 (m, 2H), 6.93–6.89 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 3.46–3.42 (m, 2H), 3.02–2.98 (m, 2H), 2.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 152.3, 136.2, 133.9, 131.2, 129.9, 128.8, 128.6, 128.5, 127.6, 117.4, 40.6, 23.5, 20.6 ppm. IR (KBr): $\tilde{\nu}$ = 3354, 3060, 2924, 1671, 1597, 1504, 1449, 1363, 1262, 1206, 1110, 815, 759, 689 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1229, found 241.1234.

3-(5-Fluoro-2-hydroxyphenyl)-1-phenylpropan-1-one (3c): Colourless solid (73 mg, 59 %), m.p. 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.1 Hz, 2H), 7.86 (s, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 6.87–6.77 (m, 3H), 3.47–3.43 (m, 2H), 3.03–2.99 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.92,

157.17 (d, J_{C-F} = 239.0 Hz), 150.65, 136.05, 134.11, 129.29 (d, J_{C-F} = 6.9 Hz), 128.87, 128.50, 118.67 (d, J_{C-F} = 8.3 Hz), 116.51 (d, J_{C-F} = 22.5 Hz), 114.44 (d, J_{C-F} = 22.8 Hz), 40.39, 23.54 ppm. IR (KBr): $\tilde{\nu}$ = 3346, 3063, 1671, 1598, 1509, 1498, 1449, 1364, 1243, 1206, 1185, 971, 813, 759, 688 cm^{-1}. HRMS (EI^+): calcd. for $C_{15}H_{13}FO_2$ $[M]^+$ 244.0900, found 244.0900.

3-(5-Bromo-2-hydroxyphenyl)-1-phenylpropan-1-one (3d): Colourless solid (82 mg, 54 %), m.p. 93–95 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H), 7.99–7.96 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48–7.44 (m, 2H), 7.24–7.18 (m, 2H), 6.80 (d, J = 8.6 Hz, 1H), 3.47–3.44 (m, 2H), 3.01–2.97 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 154.0, 135.9, 134.2, 133.2, 131.0, 130.2, 128.9, 128.5, 119.7, 112.6, 40.5, 23.3 ppm. IR (KBr): $\tilde{\nu}$ = 3346, 2934, 1670, 1596, 1493, 1448, 1362, 1271, 1235, 1208, 1111, 815, 743, 687 cm^{-1}. HRMS (EI^+): calcd. for $C_{15}H_{13}BrO_2$ $[M]^+$ 304.0099, found 304.0092.

3-(5-Acetyl-2-hydroxyphenyl)-1-phenylpropan-1-one (3e): Colourless solid (72 mg, 54 %), m.p. 132–134 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.87 (s, 1H), 8.00–7.97 (m, 2H), 7.82 (d, J = 2.2 Hz, 1H), 7.74 (dd, J = 8.4, 2.3 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 6.95 (d, J = 8.4 Hz, 1H), 3.51–3.47 (m, 2H), 3.09–3.05 (m, 2H), 2.53 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.6, 197.3, 159.7, 135.8, 134.3, 131.7, 130.3, 129.6, 128.9, 128.6, 127.9, 117.5, 40.5, 26.5, 23.4 ppm. IR (KBr): $\tilde{\nu}$ = 3347, 3062, 1760, 1682, 1597, 1449, 1359, 1278, 1208, 1130, 690 cm^{-1}. HRMS (EI^+): calcd. for $C_{17}H_{16}O_3$ $[M]^+$ 268.1099, found 268.1099.

3-(2-Hydroxyphenyl)-1-*p*-tolylpropan-1-one (3f): Colourless solid (73 mg, 60 %), m.p. 122–124 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1H), 7.88 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.13–7.09 (m, 2H), 6.93–6.83 (m, 2H), 3.44–3.41 (m, 2H), 3.05–3.01 (m, 2H), 2.40 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.8, 154.7, 144.9, 133.8, 130.7, 129.5, 128.6, 128.1, 128.0, 120.8, 117.7, 40.5, 23.5, 21.8 ppm. IR (KBr): $\tilde{\nu}$ = 3349, 2935, 1667, 1605, 1456, 1361, 1235, 1180, 975, 809, 755 cm^{-1}. HRMS (EI^+): calcd. for $C_{16}H_{16}O_2$ $[M]^+$ 240.1150, found 240.1150.

3-(2-Hydroxyphenyl)-1-(4-methoxyphenyl)propan-1-one (3g): Yellow solid (79 mg, 62 %), m.p. 58–60 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 1H), 7.96 (d, J = 9.0 Hz, 2H), 7.13–7.08 (m, 2H), 6.93–6.89 (m, 3H), 6.85 (td, J = 7.4, 1.2 Hz, 1H), 3.86 (s, 3H), 3.42–3.38 (m, 2H), 3.04–3.00 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 164.2, 154.8, 130.8, 130.7, 129.2, 128.12, 128.06, 120.7, 117.7, 113.9, 55.6, 40.2, 23.6 ppm. IR (KBr): $\tilde{\nu}$ = 3329, 2935, 1656, 1599, 1510, 1457, 1261, 1172, 1028, 839, 755 cm^{-1}. HRMS (EI^+): calcd. for $C_{16}H_{16}O_3$ $[M]^+$ 256.1099, found 256.1093.

3-(2-Hydroxynaphthalen-1-yl)-1-(4-methoxyphenyl)propan-1-one (3h): Colourless solid (105 mg, 68 %), m.p. 128–130 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 1H), 7.95 (d, J = 8.92 Hz, 2H), 7.89 (d, J = 8.56 Hz, 1H), 7.78 (d, J = 7.92 Hz, 1H), 7.66 (d, J = 8.84 Hz, 1H), 7.54–7.49 (m, 1H), 7.35–7.31 (m, 1H), 7.23 (d, J = 8.8 Hz, 1H), 6.88 (d, J = 8.92 Hz, 2H), 3.84 (s, 3H), 3.59–3.56 (m, 2H), 3.46–3.43 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.9, 164.3, 152.7, 133.1, 130.9, 129.6, 129.07, 129.05, 128.6, 126.5, 122.9, 122.1, 120.3, 118.9, 113.9, 55.6, 38.7, 18.6 ppm. IR (KBr): $\tilde{\nu}$ = 3241, 2936, 2840, 1656, 1598, 1512, 1250, 1230, 1171, 1027, 817, 749 cm^{-1}. HRMS (ESI^+): calcd. for $C_{20}H_{19}O_3$ $[M + H]^+$ 307.1334, found 307.1333.

1-(4-Chlorophenyl)-3-(2-hydroxyphenyl)propan-1-one (3i): Colourless solid (71 mg, 54 %), m.p. 138–140 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.6 Hz, 2H), 7.62 (s, 1H), 7.42 (d, J = 8.6 Hz, 2H), 7.13–7.09 (m, 2H), 6.91–6.84 (m, 2H), 3.42–3.38 (m, 2H), 3.05–3.01 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.8, 154.5, 140.4, 134.6, 130.7, 129.9, 129.1, 128.2, 127.7, 120.9, 117.5, 40.5, 23.6 ppm. IR (KBr): $\tilde{\nu}$ = 3357, 2917, 2849, 1672, 1589, 1489, 1457, 1401, 1267, 1235, 1093, 1013, 832, 755 cm^{-1}. HRMS (EI^+): calcd. for $C_{15}H_{13}ClO_2$ $[M]^+$ 260.0604, found 260.0608.

1-(4-Chlorophenyl)-3-(2-hydroxy-5-methylphenyl)propan-1-one (3j): Colourless solid (66 mg, 48 %), m.p. 68–70 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92–7.89 (m, 2H), 7.43–7.39 (m, 2H), 6.91 (d, J = 7.4 Hz, 2H), 6.80 (d, J = 8.5 Hz, 1H), 3.40–3.37 (m, 2H), 3.01–2.97 (m, 2H), 2.24 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 152.2, 140.3, 134.6, 131.2, 130.0, 129.8, 129.1, 128.6, 127.4, 117.3, 40.5, 23.6, 20.6 ppm. IR (KBr): $\tilde{\nu}$ = 3362, 2924, 1672, 1589, 1503, 1401, 1263, 1205, 1092, 1013, 960, 817 cm^{-1}. HRMS (EI^+): calcd. for $C_{16}H_{15}ClO_2$ $[M]^+$ 274.0761, found 274.0760.

1-(4-Chlorophenyl)-3-(5-fluoro-2-hydroxyphenyl)propan-1-one (3k): Colourless solid (75 mg, 54 %), m.p. 104–106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.90 (m, 2H), 7.65 (s, 1H), 7.45–7.42 (m, 2H), 6.87–6.77 (m, 3H), 3.43–3.39 (m, 2H), 3.02–2.98 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.60, 157.18 (d, J_{C-F} = 236.5 Hz), 150.52, 140.62, 134.39, 129.88, 129.21, 129.06 (d, J_{C-F} = 7.1 Hz), 118.56 (d, J_{C-F} = 8.0 Hz), 116.54 (d, J_{C-F} = 22.5 Hz), 114.50 (d, J_{C-F} = 22.4 Hz), 40.29, 23.57 ppm. IR (KBr): $\tilde{\nu}$ = 3374, 2917, 2849, 1673, 1589, 1497, 1401, 1265, 1203, 1092, 1013, 819, 739 cm^{-1}. HRMS (EI^+): calcd. for $C_{15}H_{12}ClFO_2$ $[M]^+$ 278.0510, found 278.0518.

3-(2-Hydroxyphenyl)-1-(naphthalen-2-yl)propan-1-one (3l): Colourless solid (79 mg, 57 %), m.p. 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1H), 8.03 (dd, J = 8.6, 1.8 Hz, 1H), 7.95–7.85 (m, 4H), 7.63–7.53 (m, 2H), 7.17–7.10 (m, 2H), 6.94 (dd, J = 8.1, 1.2 Hz, 1H), 6.87 (td, J = 7.4, 1.3 Hz, 1H), 3.61–3.58 (m, 2H), 3.12–3.09 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.1, 154.7, 136.0, 133.6, 132.5, 130.8, 130.5, 129.8, 129.0, 128.7, 128.2, 127.9, 127.1, 123.9, 120.9, 117.6, 40.7, 23.7 ppm. IR (KBr): $\tilde{\nu}$ = 3342, 3060, 2934, 1667, 1627, 1594, 1490, 1456, 1372, 1230, 1184, 1125, 862, 822, 755, 475 cm^{-1}. HRMS (ESI^+): calcd. for $C_{19}H_{17}O_2$ $[M + H]^+$ 277.1229, found 277.1223.

4-(5-Acetyl-2-hydroxyphenyl)butan-2-one (3m): Yellow liquid (75 mg, 73 %). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.71 (m, 3H), 6.93–6.90 (m, 1H), 2.94–2.91 (m, 2H), 2.87–2.83 (m, 2H), 2.53 (s, 3H), 2.19 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.2, 197.3, 159.6, 131.5, 130.3, 129.6, 127.7, 117.3, 45.2, 29.8, 26.4, 23.3 ppm. IR (KBr): $\tilde{\nu}$ = 3268, 2999, 2931, 1712, 1672, 1596, 1425, 1360, 1280, 1164, 1116, 1086, 931, 827 cm^{-1}. HRMS (ESI^+): calcd. for $C_{12}H_{15}O_3$ $[M + H]^+$ 207.1021, found 207.1023.

Methyl 4-hydroxy-3-(3-oxobutyl)benzoate (3n): Colourless solid (79 mg, 71 %), m.p. 95–96 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1H), 7.81–7.77 (m, 2H), 6.90 (d, J = 8.4 Hz, 1H), 3.86 (s, 3H), 2.95–2.92 (m, 2H), 2.86–2.84 (m, 2H), 2.19 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 212.2, 167.2, 159.2, 132.8, 130.2, 127.5, 122.6, 117.5, 52.0, 45.3, 29.8, 23.2 ppm. IR (KBr): $\tilde{\nu}$ = 3358, 3066, 2953, 1704, 1607, 1436, 1358, 1297, 1282, 1247, 1127, 993, 838, 775, 748, 634 cm^{-1}. HRMS (EI^+): calcd. for $C_{12}H_{14}O_4$ $[M]^+$ 222.0892, found 222.0897.

(*E*)-5-(2-Hydroxy-5-methylphenyl)-1-phenylpent-1-en-3-one (3o): Colourless solid (76 mg, 57 %), m.p. 96–98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 1H), 7.63 (d, J = 16.2 Hz, 1H), 7.54–7.51 (m, 2H), 7.41–7.38 (m, 3H), 6.92–6.90 (m, 2H), 6.82–6.71 (m, 2H), 3.15–3.12 (m, 2H), 2.94–2.91 (m, 2H), 2.25 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.1, 152.3, 144.2, 134.2, 131.1, 131.0, 129.9, 129.2, 128.6, 127.7, 125.4, 117.5, 42.9, 23.4, 20.6 ppm. IR (KBr): $\tilde{\nu}$ = 3332, 3057, 2919, 1651, 1606, 1504, 1450, 1265, 1090, 976, 738, 690 cm^{-1}. HRMS (EI^+): calcd. for $C_{18}H_{18}O_2$ $[M]^+$ 266.1307, found 266.1307.

(*E*)-5-(5-Fluoro-2-hydroxyphenyl)-1-phenylpent-1-en-3-one (3p): Colourless solid (78 mg, 58 %), m.p. 77–79 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.64 (d, J = 16.2 Hz, 1H), 7.54–

7.51 (m, 2H), 7.41–7.37 (m, 3H), 6.88–6.72 (m, 4H), 3.16–3.13 (m, 2H), 2.94–2.91 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.9, 157.1 (d, J_{C-F} = 236.1 Hz), 150.7 (d, J_{C-F} = 2.2 Hz), 144.6, 134.1, 131.2, 129.3 (d, J_{C-F} = 7.0 Hz), 129.2, 128.7, 125.1, 118.8 (d, J_{C-F} = 8.2 Hz), 116.5 (d, J_{C-F} = 22.3 Hz), 114.5 (d, J_{C-F} = 22.6 Hz), 42.7, 23.5 ppm. IR (KBr): $\tilde{\nu}$ = 3314, 3061, 1651, 1606, 1495, 1449, 1369, 1191, 976, 813, 750, 689 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{17}H_{15}FO_2$ [M]$^+$ 270.1056, found 270.1057.

(*E*)-Methyl 4-hydroxy-3-(3-oxo-5-phenylpent-4-enyl)benzoate (3q): Colourless solid (81 mg, 52 %), m.p. 111–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (s, 1H), 7.84–7.79 (m, 2H), 7.66 (d, J = 16.2 Hz, 1H), 7.54–7.51 (m, 2H), 7.41–7.39 (m, 3H), 6.93 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 16.2 Hz, 1H), 3.87 (s, 3H), 3.20–3.16 (m, 2H), 2.99–2.96 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 167.2, 159.4, 144.9, 134.0, 132.9, 131.3, 130.2, 129.2, 128.7, 127.7, 125.0, 122.5, 117.7, 52.0, 42.7, 23.3 ppm. IR (KBr): $\tilde{\nu}$ = 3320, 2951, 1713, 1688, 1606, 1497, 1449, 1282, 1195, 1116, 977, 772, 690 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{19}H_{18}O_4$ [M]$^+$ 310.1205, found 310.1202.

2-(3-Oxo-3-phenylpropyl)phenyl 4-oxo-4-phenylbutanoate (4a): Colourless solid (40 mg, 21 %), m.p. 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.94 (m, 2H), 7.92–7.89 (m, 2H), 7.57–7.51 (m, 2H), 7.44–7.40 (m, 4H), 7.32 (dd, J = 7.4, 1.8 Hz, 1H), 7.23 (dd, J = 7.7, 1.9 Hz, 1H), 7.18 (td, J = 7.4, 1.5 Hz, 1H), 7.08 (dd, J = 7.9, 1.4 Hz, 1H), 3.43–3.39 (m, 2H), 3.29–3.25 (m, 2H), 3.06–3.00 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 197.8, 171.9, 149.2, 137.0, 136.4, 133.6, 133.4, 133.1, 130.7, 128.73, 128.68, 128.24, 128.17, 127.6, 126.4, 122.6, 39.3, 33.6, 28.5, 24.8 ppm. IR (KBr): $\tilde{\nu}$ = 3061, 2921, 1758, 1685, 1597, 1449, 1361, 1209, 1138, 745, 690 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{25}H_{22}NaO_4$ [M + Na]$^+$ 409.1416, found 409.1411.

4-Methyl-2-(3-oxo-3-phenylpropyl)phenyl 4-oxo-4-phenylbutanoate (4b): Colourless solid (49 mg, 24 %), m.p. 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97–7.94 (m, 2H), 7.91–7.88 (m, 2H), 7.56–7.51 (m, 2H), 7.44–7.39 (m, 4H), 7.12 (d, J = 1.8 Hz, 1H), 7.03 (dd, J = 8.2, 2.1 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 3.42–3.38 (m, 2H), 3.27–3.23 (m, 2H), 3.02–2.97 (m, 4H), 2.32 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.3, 197.8, 172.1, 146.9, 137.0, 136.5, 136.0, 133.4, 133.1, 131.3, 128.70, 128.65, 128.23, 128.15, 122.3, 39.4, 33.6, 28.5, 24.7, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3060, 2921, 1755, 1687, 1597, 1498, 1449, 1360, 1196, 1140, 745, 690 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{26}H_{24}NaO_4$ [M + Na]$^+$ 423.1572, found 423.1571.

2-(3-Oxo-3-*p*-tolylpropyl)phenyl 4-oxo-4-*p*-tolylbutanoate (4f): Colourless solid (20 mg, 10 %), m.p. 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.32–7.30 (m, 1H), 7.24–7.20 (m, 5H), 7.19–7.14 (m, 1H), 7.08 (dd, J = 7.9, 1.4 Hz, 1H), 3.40–3.36 (m, 2H), 3.25–3.21 (m, 2H), 3.04–2.98 (m, 4H), 2.40 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.0, 197.4, 171.9, 149.2, 144.2, 143.8, 134.6, 134.1, 133.6, 130.7, 129.39, 129.35, 128.37, 128.30, 127.5, 126.4, 122.6, 39.2, 33.5, 28.6, 24.9, 21.79, 21.75 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 1758, 1682, 1607, 1490, 1207, 1180, 1138, 814 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{27}H_{27}O_4$ [M + H]$^+$ 415.1909, found 415.1906.

2-(3-(4-Methoxyphenyl)-3-oxopropyl)phenyl 4-(4-methoxyphenyl)-4-oxobutanoate (4g): Colourless solid (31 mg, 14 %), m.p. 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.87 (m, 4H), 7.31 (dd, J = 7.5, 1.7 Hz, 1H), 7.23 (td, J = 7.6, 1.8 Hz, 1H), 7.16 (td, J = 7.4, 1.4 Hz, 1H), 7.07 (dd, J = 7.9, 1.3 Hz, 1H), 6.89 (dd, J = 9.0, 1.0 Hz, 4H), 3.85 (s, 3H), 3.84 (s, 3H), 3.38–3.34 (m, 2H), 3.22–3.17 (m, 2H), 3.03–2.98 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.9, 196.2, 172.0, 163.7, 163.5, 149.2, 133.7, 130.7, 130.5, 130.4, 130.1, 129.6, 127.5, 126.3, 122.6, 113.83, 113.78, 55.58, 55.57, 39.0, 33.2, 28.6, 25.0 ppm. IR (KBr): $\tilde{\nu}$ = 2936, 2840, 1757, 1675, 1601, 1511, 1258, 1212, 1138, 1028, 978, 834 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{27}H_{26}NaO_6$ [M + Na]$^+$ 469.1627, found 469.1629.

2-(3-(4-Chlorophenyl)-3-oxopropyl)phenyl 4-(4-chlorophenyl)-4-oxobutanoate (4i): Colourless solid (35 mg, 15 %), m.p. 84–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.85 (m, 2H), 7.80–7.76 (m, 2H), 7.40–7.36 (m, 4H), 7.30 (dd, J = 7.4, 1.7 Hz, 1H), 7.23 (dd, J = 7.7, 1.9 Hz, 1H), 7.18 (td, J = 7.4, 1.4 Hz, 1H), 7.06 (dd, J = 7.9, 1.3 Hz, 1H), 3.38–3.35 (m, 2H), 3.24–3.19 (m, 2H), 3.05–2.98 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.1, 196.6, 171.8, 149.2, 140.0, 139.6, 135.4, 134.7, 133.4, 130.7, 129.7, 129.5, 129.1, 129.0, 127.7, 126.5, 122.6, 39.3, 33.5, 28.4, 24.7 ppm. IR (KBr): $\tilde{\nu}$ = 3355, 3063, 2918, 1757, 1686, 1590, 1489, 1401, 1208, 1174, 1141, 1092, 1013, 979, 821, 754, 524 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{25}H_{24}Cl_2NO_4$ [M + NH_4]$^+$ 472.1082, found 472.1082.

2-(3-(4-Chlorophenyl)-3-oxopropyl)-4-methylphenyl 4-(4-chlorophenyl)-4-oxobutanoate (4j): Colourless solid (41 mg, 17 %), m.p. 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.85 (m, 2H), 7.79–7.75 (m, 2H), 7.40–7.36 (m, 4H), 7.10 (d, J = 2.0 Hz, 1H), 7.05–7.02 (m, 1H), 6.93 (d, J = 8.2 Hz, 1H), 3.37–3.33 (m, 2H), 3.22–3.18 (m, 2H), 3.00–2.95 (m, 4H), 2.31 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.1, 196.6, 172.0, 146.9, 139.9, 139.5, 136.1, 135.4, 134.8, 133.0, 131.3, 129.7, 129.5, 129.1, 129.0, 128.3, 122.3, 39.4, 33.5, 28.4, 24.7, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3356, 3061, 2920, 1753, 1686, 1590, 1498, 1401, 1203, 1143, 1092, 1013, 979, 833, 526 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{26}H_{26}Cl_2NO_4$ [M + NH_4]$^+$ 486.1239, found 486.1238.

2-(3-(4-Chlorophenyl)-3-oxopropyl)-4-fluorophenyl 4-(4-chlorophenyl)-4-oxobutanoate (4k): Brown solid (31 mg, 13 %), m.p. 64–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89–7.85 (m, 2H), 7.79–7.75 (m, 2H), 7.41–7.37 (m, 4H), 7.04–7.00 (m, 2H), 6.95–6.89 (m, 1H), 3.37–3.34 (m, 2H), 3.23–3.19 (m, 2H), 3.03–2.97 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6, 196.6, 171.9, 160.5 (d, J_{C-F} = 243 Hz), 144.9, 140.0, 139.7, 135.5 (d, J_{C-F} = 7.4 Hz), 135.2, 134.7, 129.6, 129.5, 129.1, 129.0, 123.9 (d, J_{C-F} = 8.7 Hz), 117.1 (d, J_{C-F} = 23.0 Hz), 114.3 (d, J_{C-F} = 23.1 Hz), 38.9, 33.5, 28.3, 24.7 ppm. IR (KBr): $\tilde{\nu}$ = 3070, 2921, 1757, 1686, 1590, 1491, 1401, 1206, 1178, 1139, 1092, 980, 831, 792, 527 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{25}H_{23}Cl_2FNO_4$ [M + NH_4]$^+$ 490.0988, found 490.0988.

(*E*)-4-Methyl-2-((*E*)-3-oxo-5-phenylpent-4-enyl)phenyl 4-oxo-6-phenylhex-5-enoate (4o): Colourless solid (41 mg, 18 %), m.p. 88–90 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.48 (m, 6H), 7.37 (d, J = 6.8 Hz, 6H), 7.09 (s, 1H), 7.02 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 16.2 Hz, 2H), 3.13 (t, J = 6.5 Hz, 2H), 2.97–2.91 (m, 6H), 2.31 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 197.7, 172.0, 146.8, 143.2, 142.8, 136.0, 134.7, 134.4, 133.0, 131.2, 130.7, 130.5, 129.0, 128.44, 128.40, 128.1, 126.4, 125.7, 122.2, 41.2, 35.4, 28.4, 24.8, 21.0 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2921, 1754, 1691, 1664, 1612, 1496, 1450, 1363, 1194, 1139, 1094, 977, 750, 691 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{30}H_{28}NaO_4$ [M + Na]$^+$ 475.1885, found 475.1881.

(*E*)-4-Fluoro-2-((*E*)-3-oxo-5-phenylpent-4-enyl)phenyl 4-oxo-6-phenylhex-5-enoate (4p): Brown solid (41 mg, 18 %), m.p. 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.48 (m, 6H), 7.38–7.35 (m, 6H), 7.04–6.99 (m, 2H), 6.94–6.88 (m, 1H), 6.75 (d, J = 16.4 Hz, 2H), 3.15–3.12 (m, 2H), 2.97–2.93 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.0, 197.6, 171.9, 160.4 (d, J_{C-F} = 242.8 Hz), 144.91, 144.89, 143.3, 143.0, 135.6, 135.5, 134.6, 134.4, 130.8, 130.6, 129.1, 128.5 (d, J_{C-F} = 3.0 Hz), 126.2, 125.6, 123.9 (d, J_{C-F} = 8.7 Hz), 117.0 (d, J_{C-F} = 23.0 Hz), 114.1 (d, J_{C-F} = 23.2 Hz), 40.7, 35.4, 28.3, 24.7 ppm. IR (KBr): $\tilde{\nu}$ = 3059, 2923, 1757, 1690, 1664, 1611, 1494, 1449, 1363, 1178, 1136, 1095, 976, 759, 690 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{29}H_{25}FNaO_4$ [M + Na]$^+$ 479.1635, found 479.1630.

3-(6-Hydroxy-2,3,4-trimethoxyphenyl)-1-(4-hydroxy-3-methoxyphenyl)propan-1-one (5a): Colourless solid (126 mg, 69 %), m.p. 120–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1H), 7.58 (dd, J = 8.4, 2.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.34 (s, 1H), 6.19 (s, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.39–3.36 (m, 2H), 2.93–2.90 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 152.8, 152.2, 151.19, 151.16, 146.7, 135.9, 129.1, 124.2, 114.1, 113.5, 110.1, 97.6, 60.98, 60.93, 56.2, 55.9, 39.3, 17.5 ppm. IR (KBr): $\tilde{\nu}$ = 3319, 2937, 2849, 1654, 1591, 1515, 1463, 1426, 1276, 1197, 1126, 1088, 1033, 876, 785 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{19}H_{22}NaO_7$ [M + Na]$^+$ 385.1263, found 385.1263.

1-(4-Hydroxy-3-methoxyphenyl)-3-(2-hydroxy-4,6-dimethoxyphenyl)propan-1-one (Taccabulin C, 5b):[2a] Colourless solid (104 mg, 62 %), m.p. 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (s, 1H), 7.58 (dd, J = 8.3, 2.0 Hz, 1H), 7.53 (d, J = 1.9 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.18 (d, J = 2.4 Hz, 1H), 6.04 (d, J = 2.4 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.36–3.33 (m, 2H), 2.95–2.92 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.0, 159.9, 159.1, 156.4, 151.1, 146.7, 129.2, 124.2, 114.0, 110.0, 108.8, 94.7, 91.4, 56.2, 55.6, 55.4, 38.6, 16.7 ppm. IR (KBr): $\tilde{\nu}$ = 3265, 2940, 2839, 1620, 1590, 1515, 1426, 1274, 1202, 1147, 1099, 817 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{18}H_{20}O_6$ [M]$^+$ 332.1260, found 332.1268.

3-(2-Hydroxy-4,6-dimethoxyphenyl)-1-(3-hydroxy-4-methoxyphenyl)propan-1-one (5c): Colourless solid (104 mg, 62 %), m.p. 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (s, 1H), 7.59–7.54 (m, 2H), 6.85 (d, J = 8.4 Hz, 1H), 6.18 (d, J = 2.4 Hz, 1H), 6.04 (d, J = 2.4 Hz, 1H), 5.68 (s, 1H), 3.94 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.34–3.31 (m, 2H), 2.93–2.90 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.2, 159.9, 159.1, 156.4, 151.2, 145.4, 130.0, 122.2, 114.6, 109.9, 108.9, 94.7, 91.4, 56.2, 55.6, 55.4, 38.8, 16.6 ppm. IR (KBr): $\tilde{\nu}$ = 3299, 2940, 2841, 1656, 1610, 1587, 1512, 1456, 1440, 1275, 1215, 1202, 1146, 1099, 816, 764 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{18}H_{20}NaO_6$ [M + Na]$^+$ 355.1158, found 355.1159.

1-(Benzo[d][1,3]dioxol-5-yl)-3-(2-hydroxy-4,6-dimethoxyphenyl)propan-1-one (5d): Brown solid (113 mg, 68 %), m.p. 124–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (s, 1H), 7.60 (dd, J = 8.2, 1.5 Hz, 1H), 7.44 (d, J = 1.4 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 6.18–6.03 (m, 4H), 3.79 (s, 3H), 3.74 (s, 3H), 3.32–3.29 (m, 2H), 2.93–2.91 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 159.9, 159.1, 156.4, 152.4, 148.3, 131.1, 125.1, 108.8, 108.2, 108.0, 102.1, 94.8, 91.4, 55.6, 55.4, 38.9, 16.7 ppm. IR (KBr): $\tilde{\nu}$ = 3278, 2940, 2907, 2840, 1659, 1620, 1603, 1503, 1443, 1358, 1258, 1148, 1099, 1038, 814 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{18}H_{19}O_6$ [M + H]$^+$ 331.1182, found 331.1184.

Taccabulin B (5e): Compound **5a** (25 mg, 0.069 mmol) was taken in RB flask containing 5 mL of acetone. To this potassium carbonate (95.4 mg, 0.69 mmol) and methyl iodide (0.02 mL, 0.36 mmol) were added and stirred at 50 °C for 8 h. After the reaction, RB was cooled to r.t., acetone was evaporated. The product mixture was extracted with ethyl acetate, washed with brine solution, dried with anhydrous $MgSO_4$ and concentrated. The crude was purified by column chromatography to obtain 1-(3,4-dimethoxyphenyl)-3-(2,3,4,6-tetramethoxyphenyl)propan-1-one (Taccabulin **B**, **5e**)[2a] as yellow solid (21 mg, 78 %), m.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (dd, J = 8.4, 2.0 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 6.28 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 3.11–3.07 (m, 2H), 2.99–2.95 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 153.9, 153.1, 152.6, 152.0, 149.0, 136.5, 130.4, 122.9, 115.4, 110.4, 110.1, 92.6, 61.3, 61.1, 56.3, 56.2, 56.1, 55.9, 38.9, 19.4 ppm. IR (KBr): $\tilde{\nu}$ = 2935, 2839, 1671, 1596, 1515, 1463, 1410, 1267, 1241, 1108, 1024, 805 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{21}H_{27}O_7$ [M + H]$^+$ 391.1757, found 391.1754.

Taccabulin D (5g): Compound **5b** (50 mg, 0.15 mmol) was taken in RB flask with 5 mL DCM. It was cooled to 0 °C and DMAP (2 mg, 0.015 mmol), triethylamine (0.02 mL, 0.15 mmol) and acetyl chloride (0.01 mL, 0.15 mmol) were added. The reaction mixture was stirred at r.t. for 12 h. It was quenched with water, extracted with DCM following the standard workup procedure. The crude product was purified by column chromatography to obtain 4-(3-(2-hydroxy-4,6-dimethoxyphenyl)propanoyl)-2-methoxyphenyl acetate (**5f**) as colourless solid (41 mg, 73 %), m.p. 115–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (s, 1H), 7.60–7.58 (m, 2H), 7.11–7.08 (m, 1H), 6.18 (d, J = 2.4 Hz, 1H), 6.05 (d, J = 2.4 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.38–3.35 (m, 2H), 2.95–2.93 (m, 2H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 168.6, 160.0, 159.1, 156.3, 151.5, 144.4, 135.1, 123.0, 122.1, 111.7, 108.5, 94.7, 91.5, 56.2, 55.6, 55.4, 39.1, 20.8, 16.7 ppm. IR (KBr): $\tilde{\nu}$ = 3311, 2926, 2853, 1768, 1671, 1621, 1599, 1507, 1465, 1414, 1369, 1279, 1154, 1099, 820, 735 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{20}H_{23}O_7$ [M + H]$^+$ 375.1444, found 375.1447.

The compound **5f** (40 mg, 0.069 mmol) was methylated to prepare compound **5f′** (35 mg, 84 %) following the procedure given in the synthesis of taccabulin **B**.

The compound **5f′** (30 mg, 0.07 mmol) was taken in RB flask with 3 mL methanol. To that, potassium carbonate (43 mg, 0.3 mmol) was added and the reaction mixture was stirred at 50 °C for 5 h. After cooled to r.t., methanol was evaporated and extracted with DCM. The organic extract was washed with brine solution, dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography to obtain 1-(4-hydroxy-3-methoxyphenyl)-3-(2,4,6-trimethoxyphenyl)propan-1-one (Taccabulin **D, 5g**)[2a] as yellow solid (25 mg, 95 %), m.p. 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (dd, J = 8.3, 1.7 Hz, 2H), 7.55 (s, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.14 (s, 2H), 3.94 (s, 3H), 3.81 (s, 3H), 3.78 (s, 6H), 3.05–3.02 (m, 2H), 2.99–2.95 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 159.7, 158.9, 150.1, 146.6, 130.2, 123.8, 113.8, 110.04, 109.99, 90.5, 56.2, 55.7, 55.5, 38.4, 18.7 ppm. IR (KBr): $\tilde{\nu}$ = 3375, 1594, 1515, 1499, 1456, 1424, 1295, 1274, 1205, 1151, 1115, 814, 788 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{19}H_{22}NaO_6$ [M + Na]$^+$ 369.1314; found 369.1319.

Taccabulin A (5i): The procedure for the synthesis of taccabulin **D** was followed with compound **5c** through sequence of monoacetylation, methylation and deacetylation reactions to obtain taccabulin **A** (**5i**).

5-(3-(2-Hydroxy-4,6-dimethoxyphenyl)propanoyl)-2-methoxyphenyl acetate (5h): Colourless solid (29 mg, 86 %), m.p. 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (s, 1H), 7.90 (dd, J = 8.7, 2.2 Hz, 1H), 7.68 (d, J = 2.2 Hz, 1H), 6.97 (d, J = 8.7 Hz, 1H), 6.17 (d, J = 2.4 Hz, 1H), 6.04 (d, J = 2.4 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 3.74 (s, 3H), 3.33–3.31 (m, 2H), 2.94–2.91 (m, 2H), 2.32 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.4, 168.9, 159.9, 159.1, 156.4, 155.9, 139.6, 129.4, 128.4, 123.4, 111.7, 108.7, 94.8, 91.4, 56.3, 55.6, 55.4, 38.8, 20.7, 16.6 ppm. IR (KBr): $\tilde{\nu}$ = 3286, 2942, 2904, 2841, 1768, 1662, 1606, 1513, 1430, 1369, 1279, 1202, 1147, 1099, 1018, 817 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{20}H_{23}O_7$ [M + H]$^+$ 375.1444; found 375.1446.

1-(3-Hydroxy-4-methoxyphenyl)-3-(2,4,6-trimethoxyphenyl)propan-1-one (Taccabulin A, 5i):[2b] Colourless solid (8 mg, 72 %), m.p. 132–134 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.57 (m, 2H), 6.87 (d, J = 8.4 Hz, 1H), 6.14 (s, 2H), 5.61 (s, 1H), 3.95 (s, 3H), 3.81 (s, 3H), 3.79 (s, 6H), 3.03–2.99 (m, 2H), 2.98–2.94 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.8, 159.7, 158.9, 150.4, 145.4, 131.0, 121.7, 114.7, 110.1, 109.9, 90.6, 56.2, 55.7, 55.5, 38.7, 18.8 ppm. IR (KBr): $\tilde{\nu}$ = 3402, 2927, 2850, 2253, 1668, 1608, 1513, 1455, 1274, 1205,

1150, 1112, 1024, 811 cm^{-1}. HRMS (ESI^+): calcd. for $C_{19}H_{22}NaO_6$ [M + Na]$^+$ 369.1314; found 369.1317.

Taccabulin E (5k): Compound **5d** (50 mg, 0.069 mmol) was methylated by following the procedure given for taccabulin **B** to obtain 1-(benzo[d][1,3]dioxol-5-yl)-3-(2,4,6-trimethoxyphenyl)propan-1-one (**5j**) as yellow solid (42 mg, 81 %), m.p. 108–110 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, J = 8.2, 1.7 Hz, 1H), 7.50 (d, J = 1.6 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.13 (s, 2H), 6.03 (s, 2H), 3.81 (s, 3H), 3.78 (s, 6H), 3.03–2.93 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1, 159.7, 158.9, 151.5, 148.1, 132.1, 124.5, 110.0, 108.3, 107.9, 101.8, 90.6, 55.7, 55.5, 38.8, 18.8 ppm. IR (KBr): $\tilde{\nu}$ = 2940, 2838, 1673, 1609, 1500, 1455, 1440, 1293, 1260, 1246, 1205, 1161, 1150, 1116, 1038, 811 cm^{-1}. HRMS (ESI^+): calcd. for $C_{19}H_{21}O_6$ [M + H]$^+$ 345.1338; found 345.1335.

The compound **5j** (30 mg, 0.087 mmol) was taken in RB flask with methanol (3 mL). It was cooled to 0 °C, $NaBH_4$ (13.2 mg, 0.35 mmol) was added portion wise and stirred for 1 h. The reaction mixture was brought to r.t. and stirred for 10 h. It was then quenched with water and extracted with chloroform and concentrated. The crude product was purified by column chromatography to obtain 1-(benzo[d][1,3]dioxol-5-yl)-3-(2,4,6-trimethoxyphenyl)propan-1-ol (Taccabulin **E, 5k**)[2a] as colourless solid (24 mg, 80 %), m.p. 102–104 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.86 (d, J = 1.6 Hz, 1H), 6.78–6.72 (m, 2H), 6.16 (s, 2H), 5.92 (s, 2H), 4.41 (dd, J = 8.3, 5.2 Hz, 1H), 3.82–3.81 (m, 9H), 3.09 (s, 1H), 2.75–2.71 (m, 2H), 1.89–1.83 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 158.9, 147.6, 146.5, 138.9, 119.3, 109.9, 108.0, 106.7, 100.9, 90.8, 72.8, 55.9, 55.5, 38.8, 18.8 ppm. IR (KBr): $\tilde{\nu}$ = 3462, 2924, 2852, 1609, 1595, 1498, 1488, 1455, 1417, 1245, 1205, 1160, 1149, 1039, 935, 811 cm^{-1}. HRMS (ESI^+): calcd. for $C_{19}H_{22}NaO_6$ [M + Na]$^+$ 369.1314; found 369.1312.

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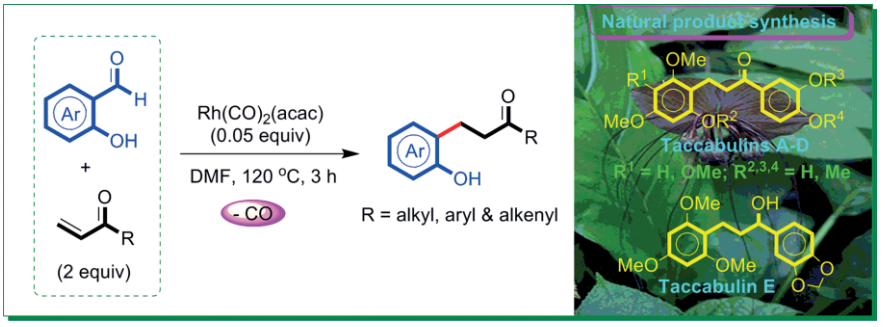
Decarbonylative Addition



A Rh-catalyzed decarbonylative addition of salicylaldehydes with vinyl ketones was developed for the synthesis of *o*-hydroxydihydrochalcones in good yields. This protocol was applied in the synthesis of taccabulin family of natural products.

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