APPENDIX

Appendix

DABCO Catalyzed Synthesis of β-Hydroxy Ketones Derived from α-Methyl Ketones and Ninhydrin under Microwave Irradiations

Introduction

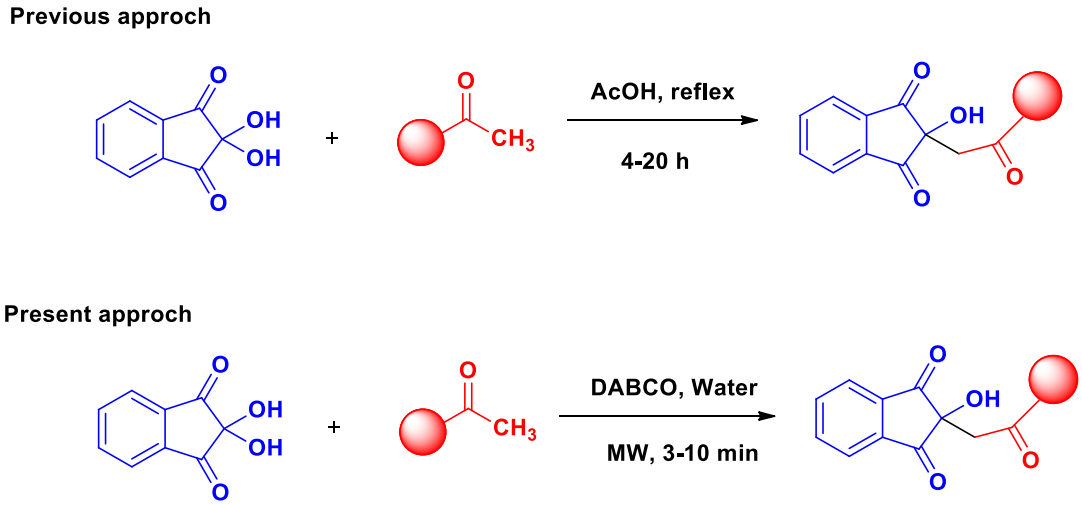
Ninhydrin is a privileged structural constituent which is involved as intermediates for the synthesis of an extensive range of pharmaceutically and biologically active compounds (Ziarani et al. 2015). Ninhydrin have highly activated carbonyl at C-2 position which readily reacts with carbon, nitrogen, oxygen and sulfur nucleophiles which results in the formation of C-C, C-N, C-O and C-S bonds respectively (Etman et al. 2011, Naskar et al. 2010, Mohammadizadeh et al. 2016, Ukhin et al. 2013, Chen et al. 2016). There are ample of name reactions for C-C bond construction but among them cross aldol condensation are most widely used. Isatin undergoes cross aldol reaction with ketones to give many biologically and pharmaceutically active products (Lu et al. 2015, Gao et al. 2012, Tiwari et al. 2016). In 2017, Hao and et al. reported β–hydroxyl ketones as a precursor for the synthesis of indole derivatives (Lan et al. 2017). It inspired us to carry out the cross aldol condensation reaction of ninhydrin with alkyl/ aryl methyl ketones to synthesis β–hydroxyl ketones. The literature survey reveals that only two reports are available for the reaction of ninhydrin with alkyl methyl ketones in glacial acetic acid (Carotti et al. 1985, Kneubuehler et al. 1995).

However, there are some shortcomings of these reported methods like harsh reaction condition, high reaction temperature, longer reaction time, tedious workup, low yield and use of a hazardous solvent. Thus the development of a new facial and rapid protocol for the synthesis of β-hydroxyl ketones is still in demand and challenging.

Recently, a great deal of attention has been paid to the development of simple and efficient methodologies for the synthesis of organic compounds in water. Water is environmentally and economically favorable; it is the most abundant solvent on earth and also, its unique and unusual physical and chemical properties enhance its reactivity and selectivity compared to organic solvents (Nagaraju et al. 2017, Shaabani et al. 2018, Gawande et al. 2013, Khazaei et al. 2015, Guo et al. 2019, Yang et al. 2018, Zhang et al. 2018, Rostami et al. 2018, Li et al. 2017). Water has advantages over many traditional organic solvents for being non-toxic, easily available, the reactions occur under mild conditions and usually easy to handle in workup processes.

Organocatalyst has emerged as a valuable and attractive tool for the synthesis of molecules through construction of new bonds. Organocatalytic formation of carbon-carbon bond provides a convenient methodology for constructing basic molecular frameworks and valuable building blocks. Recently, nitrogen-based oganocatalyst like bicyclic Lewis bases 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triazabicyclodecene (TBD) etc. have found extensive applications in organic transformations. DABCO has emerged as a base (Shi et al. 2008, Bhagat et al. 2017, Wen

et al. 2014), catalyst (Biswas et al. 2016, Keyume et al. 2014, Chong et al. 2014, Zhang et al. 2017) acts as a nucleophile (Chung et al. 2011, Meshram et al. 2012) and bulky ligand (Li et al. 2004, Han et al. 2011) for various organic reactions. DABCO is an inexpensive, easily available, non-toxic and exceedingly soluble in water so it is easy to separate from the product.



Scheme 1 An illustration of the previous and present reports for synthesis of 2- substituted-2-hydroxy-indan-1,3-diones

Herein, we disclose a simple, greener, environment friendly and highly efficient microwave induced synthesis of 2-substituted-2-hydroxy-indan-1,3-diones using water as a solvent and catalyzed by DABCO through the cross aldol condensation in good to excellent yields. A comparison of the previous and present strategies is illustrated in **Figure 1**.

Results and Discussion

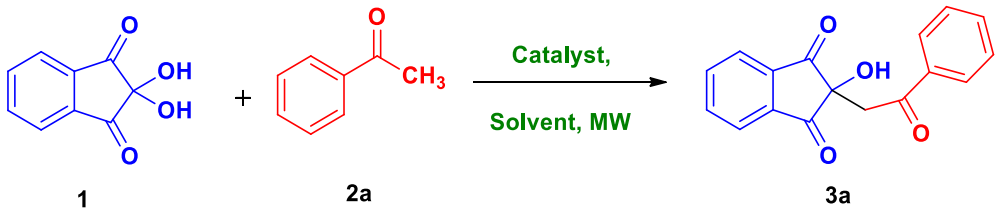
In order to achieve the optimized reaction conditions, various parameters like the effect of solvent, catalyst and mol% of the catalyst were examined in detail by choosing the model reaction of ninhydrin (**1**) and acetophenone (**2a**). To begin with, the model reaction was undertaken by conventional heating at 80 ^{0}C in acetonitrile without using any catalyst and as expected no product was obtained even after 24 h. The model reaction was then carried out with 10 mol% of DABCO as a catalyst, 40% of the product was observed in 2.5h. Just to avoid the solvent, reaction was tried with 10 mol% of DABCO at 80 ^{0}C without solvent and by grinding at room temperature for 1h but unfortunately no product was observed. It shows that solvent has a notable impact on the yield of the product. To our surprise when the reaction was carried out in the presence of DABCO (10 mol%) in acetonitrile under microwave irradiation (300W, 80 ^{0}C) the product yield was increased to 70% in 10 min (**Table 1, entry 1**). A further increase in reaction time and amount of the catalyst did not improve the yield. Microwave irradiation gave the best result in short span of time so all further optimization were carried out under microwave irradiations.

To investigate the effect of different solvents the model reaction was undertaken in various solvents under microwave irradiation using with10 mol% of DABCO as a catalyst. In the presence of non-polar solvents like toluene, xylene (**Table 1, entries 5-6**) no product was obtained while in polar solvents like methanol, ethanol and water provided good yield of product (**Table 1, entries 2-4**), among all tested solvents water and ethanol gave 100%

conversion. From the environment benign green synthesis point of view volatile organic solvents (VOS) should be replaced by green solvents so we preferred water than ethanol.

Further different catalysts were also screened for this transformation, the model reaction was microwave irradiated for 60 min with 10 mol% of Et_3N, piperidine, urea, Cs_2CO_3, *p*-TSA in water gave the desired product in low yield (40-60%), (**Table 1, entries 7-11**) while C_2H_5ONa, TiO_2, K-10 (**Table 1, entries 12-14**) didn't give any trace of the product. Among all the tested catalysts, DABCO gave the best result in lesser time. The catalyst loading was also optimized with DABCO concentration i.e. 0, 2, 5, 7 and 8 mol% (**Table 1, entries 15-19**) the results show that 8 mol% catalyst loading is optimum for the reaction, a decrease in the mol% of the catalyst amount resulted in diminished yield and any further increase of catalyst amount did not show any significant improvement in rate of the reaction and yield. The formation of product (**3a**) was confirmed by IR and NMR spectra. IR spectrum shows peaks at 3354 and 1749, 1710, 1674 cm^{-1} for OH and carbonyl groups respectively. In ^1H NMR ($CDCl_3$) shows a singlet at δ 3.43 (1H, D_2O exchangeable) for 2-hydroxyl and a singlet at 3.93 (2H) for β-methylenic protons. Appearance of singlet for methelynic protons shows that they are in same magnetic environment and are orthogonal to the indandione ring.

Table 1 Effect of the solvents, catalysts on the yield of the product 3a[a]



Entry	Solvent	Catalyst	Loading of the catalyst (mol%)	Time(min)	% Yield[b]
1	Acetonitrile	DABCO	10	10	70
2	Methanol	DABCO	10	5	80
3	Ethanol	DABCO	10	3	93
4	Water	DABCO	10	3	95
5	Toluene	DABCO	10	60	NR
6	Xylene	DABCO	10	60	NR
7	Water	Triethylamine	10	60	40
8	Water	Piperdine	10	60	40
9	Water	Urea	10	60	60
10	Water	Cs_2CO_3	10	60	60
11	Water	p-TSA	10	60	50
12	Water	C_2H_5ONa	10	60	NR
13	Water	TiO_2	10	60	NR
14	Water	K-10	10	60	NR

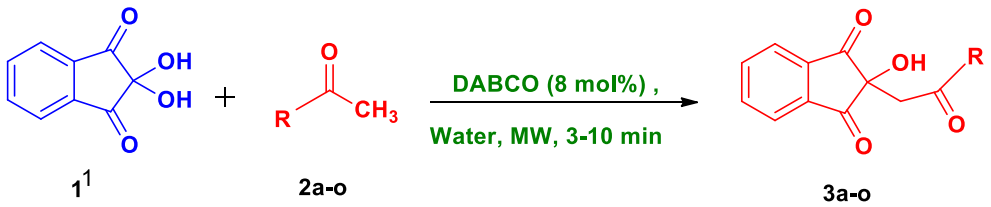
15	Water	-	0	60	NR
16	Water	DABCO	2	3	20
17	Water	DABCO	5	3	60
18	Water	DABCO	7	3	75
19	Water	DABCO	8	3	95

[a]**Reaction conditions**: Ninhydrin (**1**) (1.0 mmol), acetophenone (**2a**) (1.0 mmol) and catalyst in 5 mL of solvent were irradiated in microwave.[b]Isolated yield.

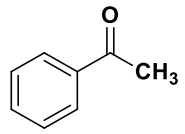
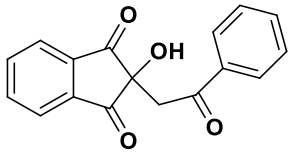
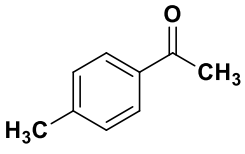
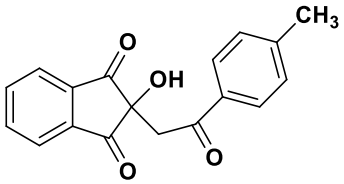
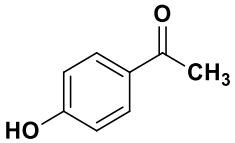
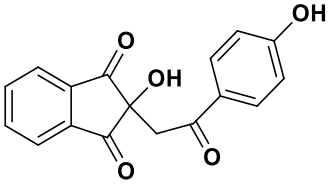
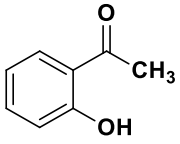
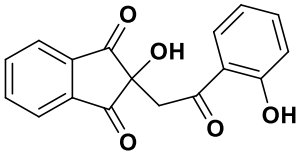
With these encouraging results and having the optimized reaction conditions, the scope and the applicability of this methodology was examined on various aromatic and aliphatic α-methyl ketones (**2**) with ninhydrin (**1**). Acetophenones (**1a**), 4-methyl acetophenones (**1b**), 4-hydroxy acetophenones (**1c**), 2-hydroxy acetophenones (**1d**), 2- naphthalenones (**1e**), 4-amino acetophenones (**1f**) 4-fluoro acetophenones (**3g**), 4-chloro acetophenones (**3h**), 4-bromo acetophenones (**3i**), 3-nitro acetophenones (**3j**), 2-acetyl thiophene (**3k**), 2-acetyl pyridine (**3l**), acetyl cyclopropene (**3m**) gives 2-Hydroxy-2-(2'-oxo-2'-phenylethyl)indan-1,3-dione (**3a**), 2-Hydroxy-2-(2'-oxo-2'-(4-tolyl)ethyl)indan-1,3-dione (**3b**), 2-Hydroxy-2-(2'-(4-hydroxyphenyl)-2'-oxoethyl)indan-1,3-dione (**3c**), 2-Hydroxy-2-(2-(2-hydroxyphenyl)-2-oxoethyl)-1H-indene-1,3(2H)-dione (**3d**), 2-Hydroxy-2-(2-(naphthalen-1-yl)-2-oxoethyl)-1H-indene-1,3(2H)-dione (**3e**), 2-(2-(4-Aminophenyl)-2-oxoethyl)-2-hydroxy-1H-indene-1,3(2H)-dione (**3f**), 2-(2-(4-Fluorophenyl)-2-oxoethyl)-2-hydroxy-1H-indene-1,3(2H)-dione (**3g**), 2-(2-(4-Cholrophenyl)-2-oxoethyl)-2-hydroxy-1H-indene-1,3(2H)-dione (**3h**), 2-(2-(4-

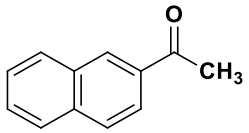
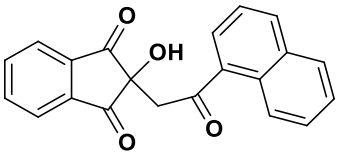
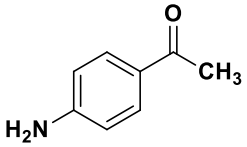
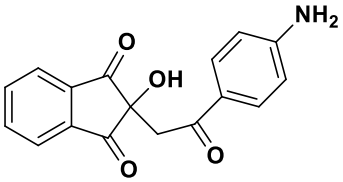
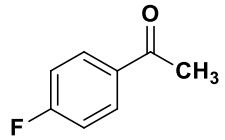
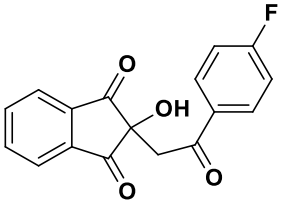
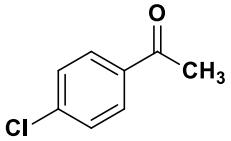
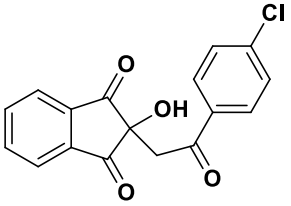
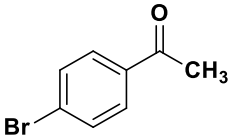
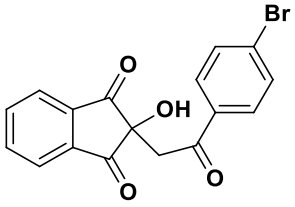
Bromophenyl)-2-oxoethyl)-2-hydroxy-1H-indene-1,3(2H)-dione (**3i**), 2-Hydroxy-2-(2-(3-nitrophenyl)-2-oxoethyl)-1H-indene-1,3(2H)-dione (**3j**), 2-Hydroxy-2-(2-oxo-2-(thiophen-2-yl)ethyl)-1H-indene-1,3(2H)-dione (**3k**), 2-Hydroxy-2-(2-oxo-2-(pyridin-2-yl)ethyl)-1H-indene-1,3(2H)-dione (**3l**), 2-(2-Cyclopropyl-2-oxoethyl)-2-hydroxy-1H-indene-1,3(2H)-dione (**3m**), 2-Hydroxy-2-(2-oxobutyl)-1H-indene-1,3(2H)-dione (**3n**), 2-Hydroxy-2-(4-methyl-2-oxopentyl)-1H-indene-1,3(2H)-dione (**3o)**. Acetophenones with electron withdrawing group e.g. flouro, chloro, bromo and nitro (**Table 2, entries 7-10**) provided slightly higher yields in lesser time than electron releasing groups like alkyl, hydroxyl and amino (**Table 2, entries 2-6**). Higher rate of reaction in case of electron withdrawing substituents may be due to better stabilization of the enolate ions and makes it better nucleophile. We have employed the *o*-hydroxyl acetophenone as the ketone substrate (2d), but no annulated product was observed. Further under optimized conditions 2-acetyl thiophene and 2-acetyl pyridine (**Table 2, entries 11 and 12**) also gave desired product in good to excellent yields, on the other hand aliphatic and cyclic ketones also gave the products in good yields but took longer reaction time 7-10 min (**Table 2, entries 13-15**). The structures of all the synthesized compounds (**3a-o**) were characterized by CHN analysis, ^{1}H and ^{13}C NMR spectroscopy.

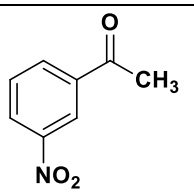
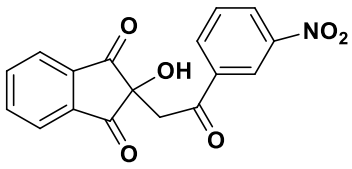
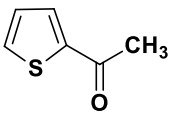
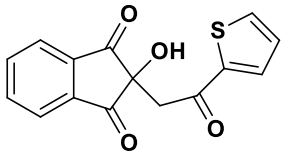
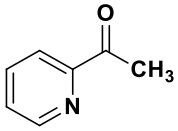
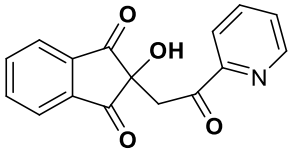
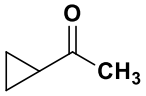
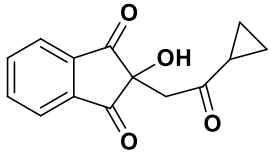
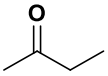
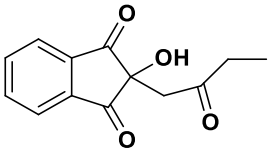
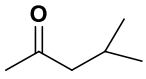
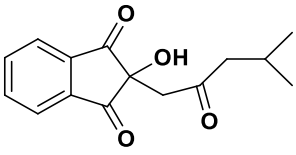
Table 2 Synthesis of **3a-o** under microwave irradiation method[a]



1[1] 2a-o 3a-o

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1	 2a	 3a	3	95
2	 2b	 3b	5	85
3	 2c	 3c	6	82
4	 2d	 3d	6	84

5	 2e	 3e	5	85
6	 2f	 3f	5	86
7	 2g	 3g	3	96
8	 2h	 3h	4	92
9	 2i	 3i	4	90

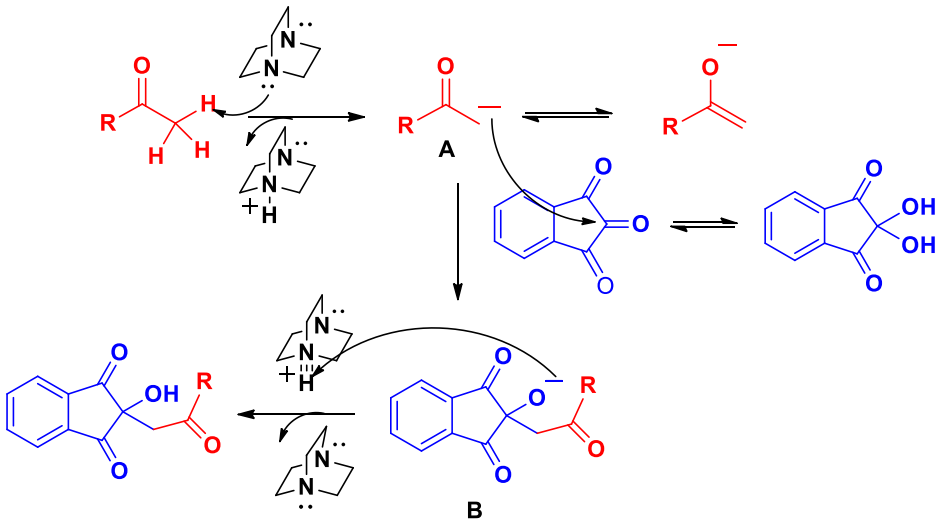
10	 2j	 3j	5	92
11	 2k	 3k	8	89
12	 2l	 3l	8	88
13	 2m	 3m	7	82
14	 2n	 3n	10	85
15	 2o	 3o	10	85

[a]**Reaction conditions:** Ninhydrin (1.0 mmol), aryl/alkyl methyl ketone (1.0 mmol) and DABCO (8 mol %) in 5 mL of water were irradiated in microwave. [b]Isolated yield.

A plausible mechanism for the DABCO catalyzed cross aldol condensation reaction shown in Scheme 1. DABCO abstracts acidic proton from α-methyl ketones and from

enolate (**A**) followed by attack at the C-2 position of ninhydrin and from (**B**) which subsequently abstract proton from protonated DABCO and from desired products.

To demonstrate the potential synthetic application of this protocol the synthesis of (**3a**) was carried out on gram scale with 5g (0.028 mol) of ninhydrin and 3.26 ml (0.028) mol of acetophenone using 8 mol% DABCO in water under microwave irradiation gave 3a in (7.22 g) 92% yield and also comparable to the yield obtained in mg scale (**Table 2, entry 1**).



Scheme 1 Plausible mechanism of the cross-aldol reaction

Experimental section

General procedure for the preparation 2-susbtituted-2-hydroxy indan-1,3-dione derivatives (3a-o)

A mixture of ninhydrin **1** (1.0 mmol), aryl/alkyl methyl ketone **2** (1.0 mmol) and DABCO (8 mol %) in water (5 mL) was placed in round bottom flask and irradiated in microwave oven at 300 W, 80 ^{0}C. The progress of reaction was monitored by TLC using *n*-hexane/ethyl acetate and after the completion of reaction, solvent was evaporated under vaccum. The crude products were purified by silica gel column chromatography using ethyl acetate- hexane solvent system to afford the pure β–hydroxy ketones (3a-o).

Analytical data

2-Hydroxy-2-(2'-oxo-2'-phenylethyl)indan-1,3-dione (3a)

Yield 95%; Light yellow; m.p. 107-108 ^{0}C; **^{1}H NMR** ($CDCl_3$) δ (ppm): 8.05-8.04 (m, 2H), 7.90-7.89 (m, 2H), 7.84-7.82 (d, 2H), 7.57-7.54 (t, 1H), 7.43-7.40 (t, 2H), 3.91 (s, 2H), 3.41 (s, 1H, OH); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.47, 197.57, 140.91, 136.88, 135.01, 134.34, 129.05, 128.61, 124.80, 124.56, 73.66, 44.49; **Elemental analysis**: Calc. (%) for $C_{17}H_{12}O_4$ (280.27): C 72.85, H 4.32; Found (%): C 72.50, H 4.72.

2-Hydroxy-2-(2'-oxo-2'-(4-tolyl)ethyl)indan-1,3-dione (3b)

Yield 85%; White solid; m.p. 140-142 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.03-8.01 (m, 2H), 7.88-7.86 (m, 2H), 7.22-7.70 (d, 2H), 7.19-7.18 (d, 2H), 3.89 (s, 2 H), 3.65 (s, 1H,

OH), 2.36 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.71, 197.14, 145.08, 140.99, 136.03, 132.69, 129.38, 128.40, 124.15, 73.48, 43.47, 21.18; **Elemental analysis**: Calc. (%) for $C_{18}H_{14}O_4$ (294.30): C 73.46, H 4.79; Found (%): C 73.85, H 4.74.

2-Hydroxy-2-(2'-(4-hydroxyphenyl)-2'-oxoethyl)indan-1,3-dione (3c)

Yield 82%; White solid; m.p. 138-140 ^{0}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.54 (s, 1H, OH), 8.02 (s, 4H), 7.77-7.76 (d, 2H), 6.83-6.81 (d, 2H), 6.77 (s, 1H, OH), 3.84 (s, 2H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm): 199.50, 195.71, 163.08, 141.04, 136.38, 131.08, 126.56, 123.71, 115.61, 72.72, 43.91; **Elemental analysis**: Calc. (%) for $C_{17}H_{12}O_5$ (296.27): C 68.91, H 4.08; Found (%): C 68.52, H 4.19.

2-Hydroxy-2-(2'-(2-hydroxyphenyl)-2'-oxoethyl)indan-1,3-dione (3d)

Yield 84%; Yellowish solid; m.p. 131-132 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 11.21 (s, 1H, OH), 8.05-8.03 (m, 2H), 7.92-7.90 (m, 2H), 7.70 (s, 1H), 7.47-7.41(t, 1H), 6.90-6.83 (m, 2H), 3.95 (s, 2H), 3.37 (s, 1H, OH); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 202.06, 197.86, 162.32, 140.90, 137.32, 136.26, 130.22, 124.26, 119.33, 118.63, 72.14, 43.63; **Elemental analysis**: Calc. (%) for $C_{17}H_{12}O_5$ (296.27): C 68.91, H 4.08; Found (%): C 68.50, H 4.03.

2-Hydroxy-2-(2'-(naphthalen-1-yl)-2'-oxoethyl)indan-1,3-dione (3e)

Yield 85%; Yellowish solid; m.p. 110-112 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.39 (s, 1H), 8.05 (s, 2H), 7.89 (s, 3H), 7.80 (s, 3H), 7.58-7.52 (d, 2H), 4.06 (s, 2H), 3.54 (s, 1H,

OH); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.26, 197.01, 141.01, 136.19, 135.91, 132.46, 132.27, 130.63, 129.68, 128.99, 128.63, 127.78, 126.99, 124.21, 123.31, 73.57, 44.01; **Elemental analysis**: Calc. (%) for $C_{21}H_{14}O_4$ (330.33): C 76.35, H 4.27; Found (%): C 75.98, H 4.24.

2-(2'-(4-Aminophenyl)-2'-oxoethyl)-2-hydroxy-indan-1,3-dione (3f)

Yield 86%; Pale Yellow; m.p. 160-162 ^{0}C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ (ppm): 8.00 (s, 4H), 7.57-7.56 (d, 2H), 6.68 (s, 1H), 6.53-6.51 (d, 2H), 6.21 (s, 2H), 3.75 (s, 2H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ (ppm): 198.88, 193.48, 153.98, 140.41, 135.51, 130.20, 122.93, 121.83, 112.02, 72.10, 43.00; **Elemental analysis**: Calc. (%) for $C_{17}H_{13}NO_4$ (295.29): C 69.14, H 4.43; Found (%): C 68.74, H 4.48.

2-(2'-(4-Fluorophenyl)-2'-oxoethyl)-2-hydroxy-indan-1,3-dione (3g)

Yield 96%; Brown solid; m.p. 114-115 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.05-8.03 (m, 2H), 7.91-7.89 (m, 2H), 7.87-7.84 (m, 2H), 7.09-7.06 (t, 2H), 3.89 (s, 2H), 3.51 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.17, 195.43, 167.28, 165.24, 140.95, 136.24, 131.07, 131.00, 124.20, 116.04, 115.86, 73.33, 43.85; **Elemental analysis**: Calc. (%) for $C_{17}H_{11}FO_4$ (298.27): C 68.46, H 3.72; Found (%): C 68.09, H 3.66.

2-(2'-(4-Cholrophenyl)-2'-oxoethyl)-2-hydroxy-indan-1,3-dione (3h)

Yield 92%; Brown solid; m.p. 180-181 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.03-8.02 (d, 2H), 7.90-7.89 (d, 2H), 7.76-7.74 (d, 2H), 7.38-7.36 (d, 2H), 3.88 (s, 2H), 3.54 (s, 1H,

OH); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.14, 195.86, 140.94, 136.26, 133.43, 131.51, 129.66, 129.08, 124.21, 73.32, 43.88; **Elemental analysis**: Calc. (%) for $C_{17}H_{11}ClO_4$ (314.72): C 64.88, H 3.52; Found (%): C 65.28, H 3.55.

2-(2'-(4-Bromophenyl)-2'-oxoethyl)-2-hydroxy-indan-1,3-dione (3i)

Yield 90%; Yellow solid; m.p. 150-152 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.98-7.97 (d, 2H), 7.84-7.83 (d, 2H), 7.64-7.63 (d, 2H), 7.49-7.47 (d, 1H), 3.90 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.47, 196.10, 140.91, 136.15, 133.68, 131.95, 129.69, 129.31, 124.10, 73.19, 44.01; **Elemental analysis**: Calc. (%) for $C_{17}H_{11}BrO_4$ (359.17): C 56.85, H 3.09; Found (%): C 56.52, H 3.15.

2-Hydroxy-2-(2'-(3-nitrophenyl)-2'-oxoethyl)indan-1,3-dione (3j)

Yield 92%; White solid; m.p. 160-162 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.67 (s, 1H), 8.43-8.41 (d, 1H), 8.17- 8.15 (d, 1H), 8.07- 8.05 (m, 2H), 7.94-7.92 (m, 2H), 7.66 - 7.63 (t, 1H), 3.95 (s, 2H), 3.31 (s, 1H, OH); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 197.75, 194.71, 148.55, 140.80, 136.45, 133.67, 130.27, 127.74, 124.39, 123.41, 73.24, 43.93; **Elemental analysis**: Calc. (%) for $C_{17}H_{11}NO_6$ (325.27): C 62.77, H 3.40; Found (%): C 62.36, H 3.37.

2-Hydroxy-2-(2'-oxo-2'-(thiophen-2-yl)ethyl)indan-1,3-dione (3k)

Yield 89%; Yellow solid; m.p. 144-145 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.03 (s, 1H), 7.88-7.83 (t, 4H), 7.56-7.54 (d, 1H), 7.42-7.41 (d, 1H), 4.14 (s, 1H, OH), 3.99 (s,

2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.51, 197.06, 140.95, 136.08, 134.97, 133.97, 128.63, 128.24, 124.10, 73.32, 44.08; **Elemental analysis**: Calc. (%) for $C_{15}H_{10}O_4S$ (286.30): C 62.92, H 3.52; Found (%): C 62.52, H 3.46.

3.1.2-Hydroxy-2-(2'-oxo-2'-(pyridin-2-yl)ethyl)indan-1,3-dione (3l)

Yield 88%; White solid; m.p. 108-110 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 8.67-8.66 (d, 1H), 8.04-7.99 (m, 3H), 7.90-7.88 (m, 2H), 7.56-7.54 (t, 1H), 7.33 (s, 1H), 3.61 (s, 2H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 198.87, 197.51, 151.98, 148.35, 139.96, 138.03, 136.51, 127.82, 124.18, 122.77, 74.75, 44.79; **Elemental analysis**: Calc. (%) for $C_{16}H_{11}NO_4$ (281.26): C 68.32, H 3.94; Found (%): C 67.94, H 3.88.

2-(2'-Cyclopropyl-2'-oxoethyl)-2-hydroxy-indan-1,3-dione (3m)

Yield 82%; White solid; m.p. 116-118 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.94-7.82 (d, 4H), 4.21 (s, 1H), 3.43 (s, 2H), 1.86 (s, 1H), 0.91-0.87 (s, 4H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 208.13, 198.52, 140.76, 136.07, 123.96, 72.99, 47.57, 20.38, 11.62; **Elemental analysis**: Calc. (%) for $C_{14}H_{12}O_4$ (244.24): C 68.84, H 4.95; Found (%): C 69.25, H 4.93.

2-Hydroxy-2-(2'-oxobutyl)indan-1,3-dione (3n)

Yield 85%; White solid; m.p. 128-129 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.98 -7.93 (t, 2H), 7.86-7.84 (t, 2H), 3.26 (s, 1H), 3.21 (s, 2H), 2.16 (d, 2H), 1.42-1.41 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 210.78, 198.20, 140.58, 136.11, 123.91, 75.55, 51.23,

28.93, 11.09; **Elemental analysis**: Calc. (%) for $C_{13}H_{12}O_4$ (232.23): C 67.23, H 5.20; Found (%): C 67.60, H 5.23.

2-Hydroxy-2-(4'-methyl-2'-oxopentyl)indan-1,3-dione (3o)

Yield 85%; White solid; m.p. 165-166 ^{0}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.99-7.98 (d, 2H), 7.86-7.85 (d, 2H), 3.76 (s, 1H, OH), 3.26 (s, 2H), 2.24-2.23 (d, 2H), 2.00-1.96 (m, 1H), 0.82-0.81 (d, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ (ppm): 208.52, 198.35, 140.80, 136.22, 124.12, 73.14, 51.42, 47.27, 24.52, 22.34; **Elemental analysis**: Calc. (%) for $C_{15}H_{16}O_4$ (260.29): C 68.22, H 6.20; Found (%): C 68.82, H 6.23.

Spectral data of product (3a)

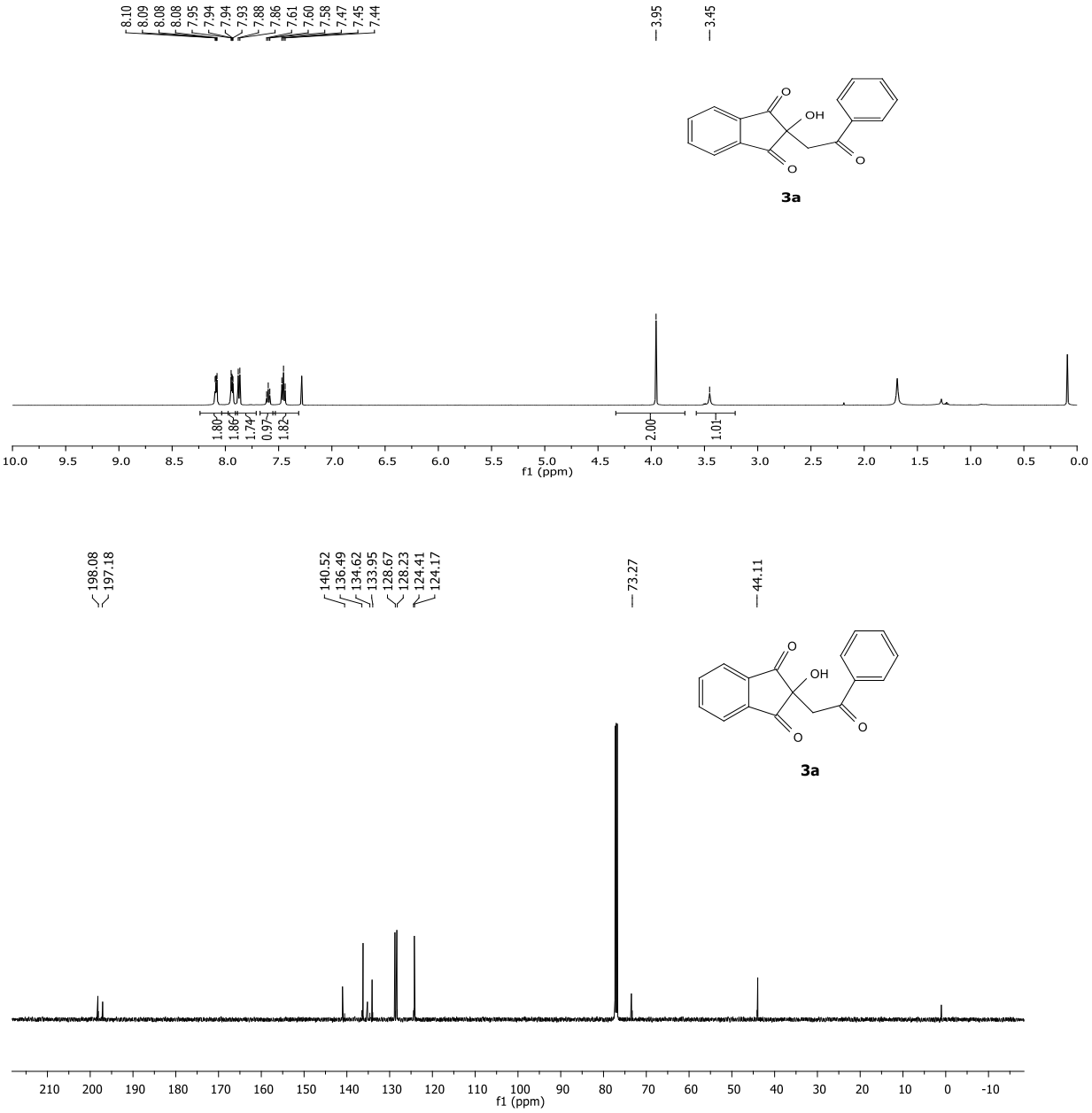


Figure ^{1}H and ^{13}C NMR of 2-Hydroxy-2-(2'-oxo-2'-phenylethyl)indan-1,3-dione (3a)