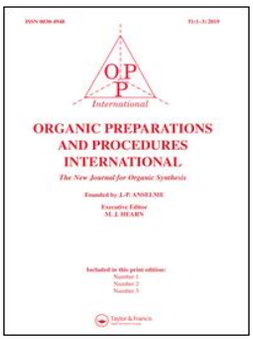

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Synthesis of Quinolines, Spiro[4*H*-pyran-oxindoles] and Xanthenes Under Solvent-Free Conditions

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Green multi-component domino reactions (MCRs)[1–7] for the synthesis of fine chemicals have attracted much recent interest.[8–9] Quinolines, spiro[4*H*-pyran-oxindoles] and xanthenes are reported as having a wide range of medicinal properties.[10–17] Quinolines are found to undergo hierarchical self assembly into a variety of nano-structures and meso structures with enhanced electronic and photonic functions.[18] Xanthenes have been widely used as pH sensitive fluorescent materials for visualization of biomolecules,[19] laser technology,[20] luminescent dyes[21] and sensitizers in photodynamic therapy.[22] (*Figure 1*).

A number of methodologies for preparation of these compounds have been reported that include such catalysts as Fe_3O_4@SiO_2-imid-PMAn,[23] SBNPTT,[24] NO_2−FePc/C,[25] nano-alumina sulfuric acid[26] and many others.[27–55] However, some of these methods suffer from such disadvantages as low yields, long reaction times, harsh reaction conditions, tedious work-up or excess amounts of reagents or catalysts. As part of our ongoing research program on the development of green methodologies, we now report a clean and facile one-pot synthesis of polysubstituted quinolines,[56] spiro[4*H*-pyran] derivatives, 12-aryl-tetrahydrobenzo[α]xanthene-11-ones and 14-aryl-14*H*-dibenzo[α,*j*]xanthenes, in the presence of catalytic amounts of citric acid under solvent-free conditions.

Initial screening studies confirmed that the solvent-free technique is optimal for the preparation of quinolines **3a-g** (*Scheme 1*, *Table 1*). Thus, the cyclocondensation of 2-aminobenzophenone (1.0 mmol) and dimedone (1.0 mmol) was carried out with citric acid (15 mol %) as catalyst at 90 °C for 15 min under solvent-free conditions to give a yield of 92% (*Table 1*, Entry 4). The efficiency of citric acid was demonstrated by synthesizing a variety of polysubstituted quinolines at 90 °C under solvent-free conditions, as shown in *Table 2*.

We explored citric acid as an environmentally friendly catalyst for the synthesis of spiro[4*H*-pyran-oxindoles] through the coupling of isatin/acenaphthequinone (**4**, 1.0 mmol), malononitrile (**5,** 1.0 mmol) and 1,3-dicarbonyl compounds (**6,** 1.0 mmol). Isatin, malononitrile and dimedone were selected as the model substrates and reacted with different experimental variants (*Scheme 2*). The results are summarized in *Table 3*.

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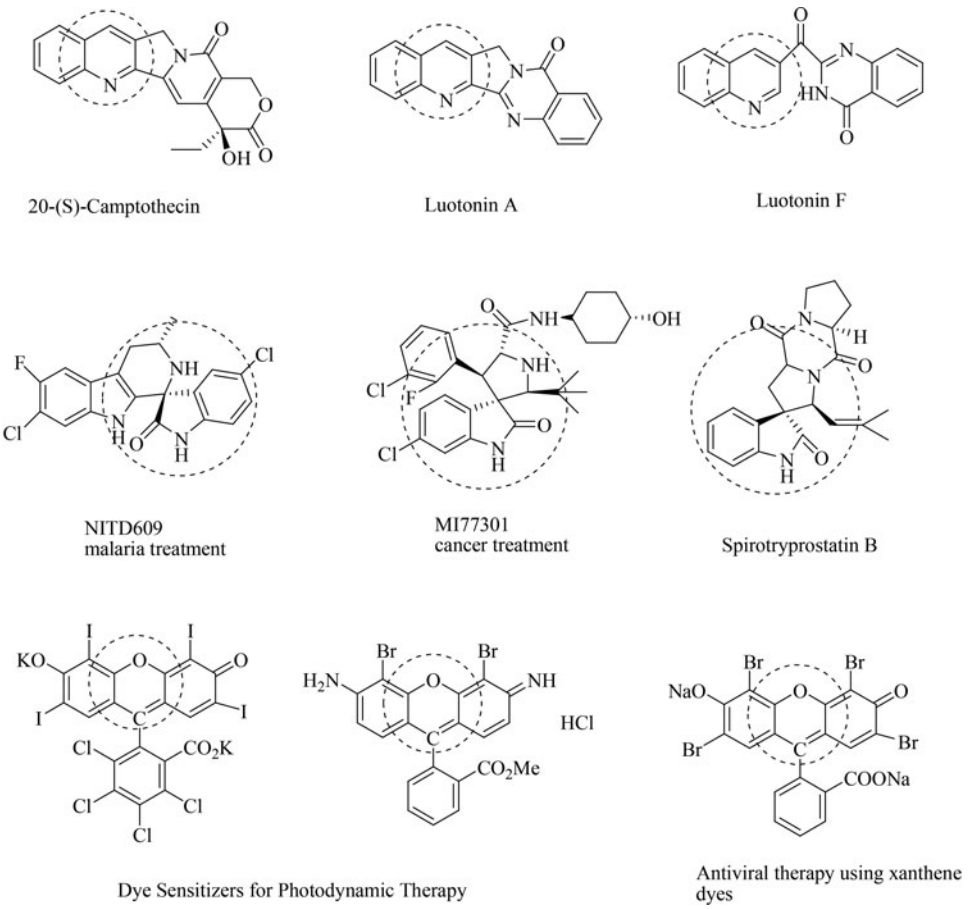
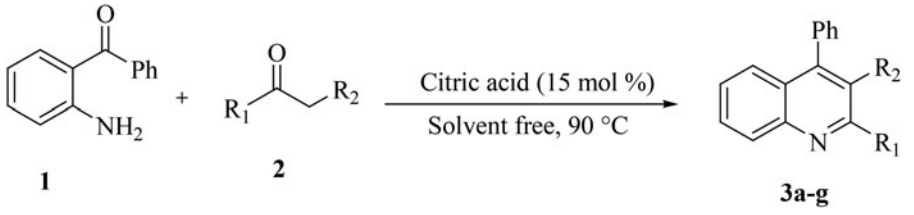


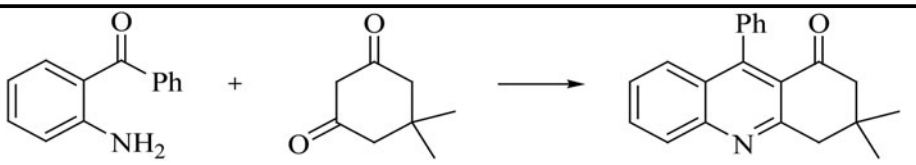
Figure 1. Pharmaceutically active compounds with quinoline, spirocyclic oxindole and xanthene units.



Scheme 1. Synthesis of polysubstituted quinolines.

The condensation of isatin, malononitrile and dimedone was best catalyzed by 20 mol % citric acid at 80 °C (*Table 3*, entry 5). In the absence of catalyst only a trace of product was observed (*Table 3*, entry 1). To ascertain the scope and limitation of the present protocol, a number of reactions were examined, and the results are summarized in *Table 4*. We were pleased to find that all substrates were converted to the corresponding products in good to excellent yields (82-93%).

Table 1
Optimization of the Reaction Conditions for the Synthesis of **3a**[a]



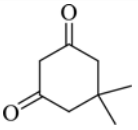
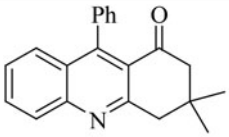
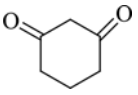
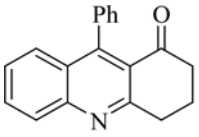
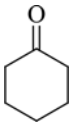
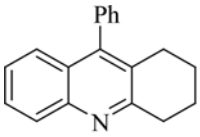
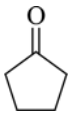
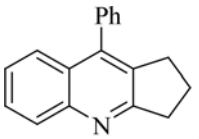
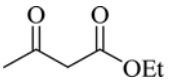
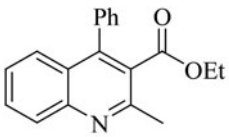
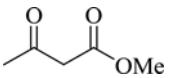
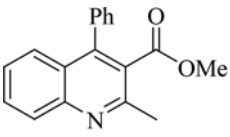
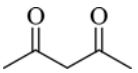
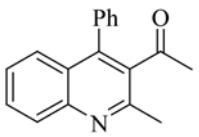
Entry	Citric acid (mol %)	Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	90	420	No product
2	5	90	40	58
3	10	90	25	74
4	**15**	**90**	**15**	**92**
5	15	rt	420	trace
6	15	40	55	36
7	15	60	35	67
8	15	80	25	83
9	15	100	15	92
10	20	90	15	94

[a]Reaction conditions: 2-aminobenzophenone (1, 1.0 mmol), carbonyl compound (2, 1.0 mmol) and citric acid heated at specified various temperatures for the times listed.

We were further interested in the preparation of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones and the influence of a catalytic amount of citric acid on this type of reaction (*Scheme 3*). To obtain the optimized reaction conditions, the condensation of *β*-naphthol (1.0 mmol), benzaldehyde (1.0 mmol) and dimedone (1.0 mmol) was selected as a model. This reaction gave the desired 12-(phenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[α]xanthene-11-one and was studied in the presence of different molar ratios of citric acid at rt-90 °C under solvent-free conditions; the respective results are summarized in *Table 5*. The best results were obtained when the reaction was carried out using 20 mol % of the catalyst at 80 °C (*Table 5*, entry 5). To assess the efficiency and generality of the catalyst, *β*-naphthol (**8**, 1.0 mmol) was reacted with aromatic aldehyde derivatives (**9**, 1.0 mmol) and dimedone (**10**, 1.0 mmol). The results are displayed in *Table 6*. As *Table 6* indicates, aldehydes with both electron-donating substituents and electron-attracting substituents rings afforded the desired products in high yields and short reaction times.

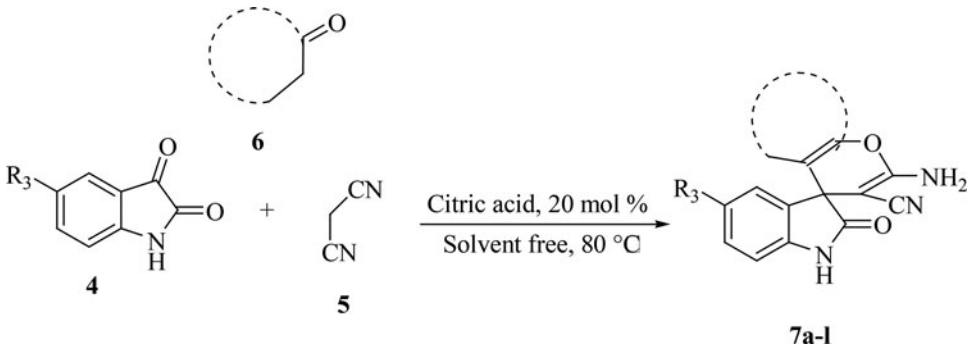
We were also interested in the preparation of 14-aryl-14*H*- dibenzo[α,*j*]xanthenes from the reaction between *β*-naphthol (**8**, 2.0 mmol) and aromatic aldehyde derivatives (**9**, 1.0 mmol) in the present of citric acid under thermal and solvent-free conditions (*Scheme 4*). For optimization of the reaction conditions, the reaction of *β*-naphthol (2.0 mmol) and benzaldehyde (1.0 mmol) was chosen as the model, carried out in the presence of different catalytic amounts of citric acid and at various temperatures. The best result was obtained for the reaction of 2.0 mmol of *β*-naphthol with 1.0 mmol of benzaldehyde in the presence of 20 mol % citric acid at 80 °C, which gave 14-phenyl-14*H*-dibenzo[α,*j*]xanthene in 95% yield after 10 min (*Table 7*, entry 5). The model reaction was performed in the absence of catalyst, which led to only a trace of product after

Table 2
Citric Acid Catalyzed Synthesis of Polysubstituted Quinolines

Entry	Ketone/Ketoester	Product	Time (min)	Isolated Yields (%)	Mp°C	Lit. Mp°C ref
1		 **3a**	15	92	191-193	192-194[27]
2		 **3b**	10	93	155-157	157-159[23]
3		 **3c**	15	89	154-156	153-154[27]
4		 **3d**	15	87	128-130	129-131[27]
5		 **3e**	15	91	99-101	98-99[23]
6		 **3f**	15	94	105-107	107-108[23]
7		 **3g**	10	92	114-116	113-114[23]

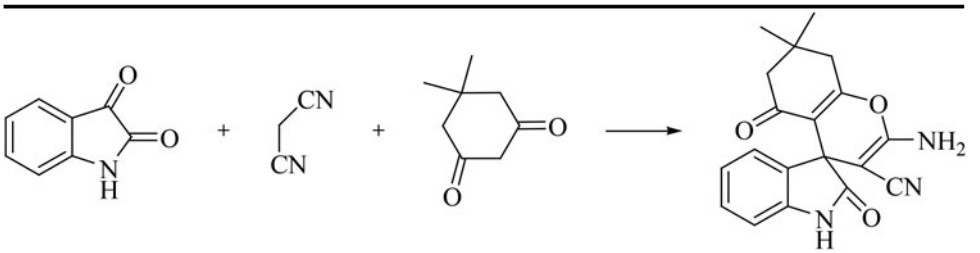
7 hours. Different aldehydes and β-naphthol were reacted under the optimized reaction conditions to afford the corresponding products (*Scheme 4*, *Table 8*, entries 1-13). As shown in *Table 8*, both electron-donating and electron-withdrawing substituents in the benzaldehydes satisfactorily reacted with β-naphthol in good to excellent yields.

Comparisons of catalytic abilities reported in the literature for the synthesis of polysubstituted quinolines, spiro[4*H*-pyran-oxindoles], 12-aryl-tetrahydrobenzo[α]xanthene-11-ones and 14-aryl-14*H*-dibenzo[α,*j*]xanthenes are shown in *Tables 9*, *10*, *11* and *12*.



Scheme 2. Synthesis of spiro[4*H*-pyran-oxindoles].

Table 3
Optimization of the Reaction Conditions for the Synthesis of **7a**[a]

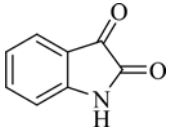
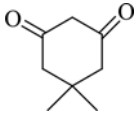
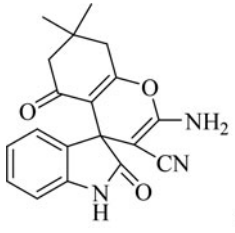
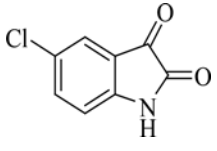
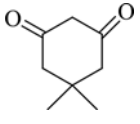
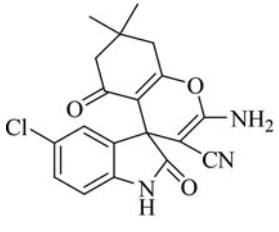
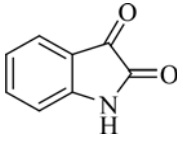
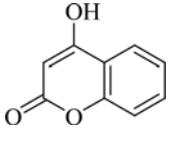
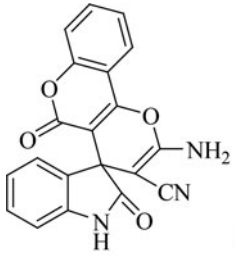


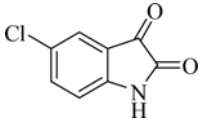
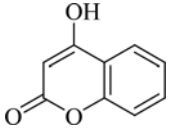
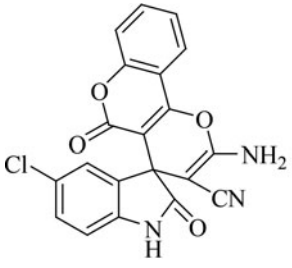
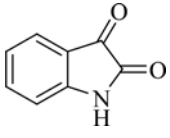
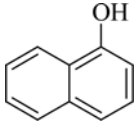
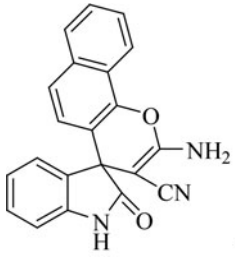
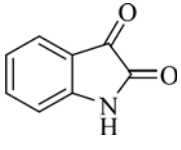
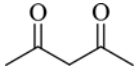
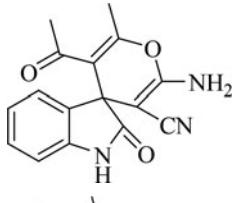
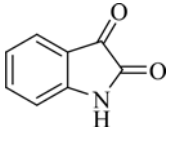
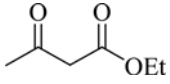
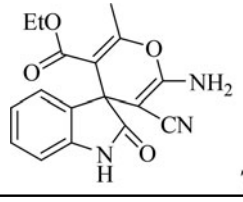
Entry	Citric acid (mol %)	Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	80	420	trace
2	5	80	75	63
3	10	80	65	76
4	15	80	50	94
5	**20**	**80**	**40**	**91**
6	20	rt	420	trace
7	20	40	70	35
8	20	60	55	57
9	20	70	45	76
10	20	90	10	93
11	25	80	40	92

[a]Reaction conditions: isatin (4, 1.0mmol); malononitrile (5, 1.0 mmol), dimedone (6, 1.0 mmol) and citric acid heated at specified temperatures for the appropriate times.

In summary, a green synthetic route to the facile preparation of polysubstituted quinolines, spiro[4*H*-pyran-oxindoles], 12-aryl-tetrahydrobenzo[α]xanthene-11-ones and 14-aryl-14*H*-dibenzo[α,*j*]xanthenes has been developed using citric acid as a catalyst under solvent-free reaction conditions. All reactions are completed in a short period of time and the products are obtained in good to excellent yields. The salient features of this green approach are easy work-up, the absence of organic solvents and the use of a readily available green catalyst.

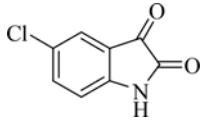
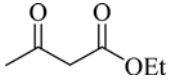
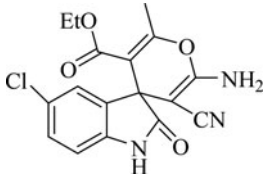
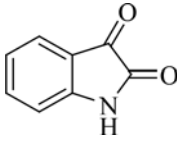
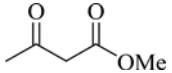
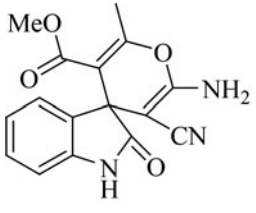
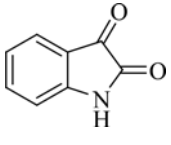
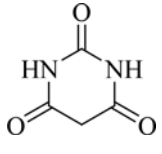
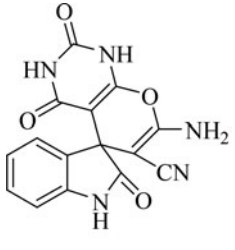
Table 4
Citric Acid Catalyzed Synthesis of Spiro[4*H*-pyran-oxindoles]

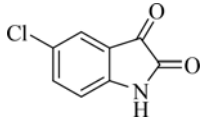
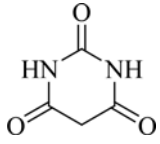
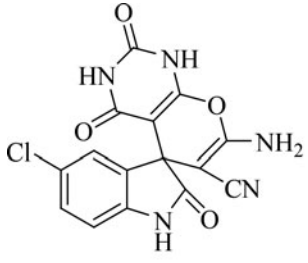
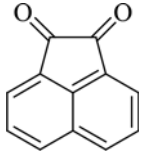
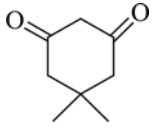
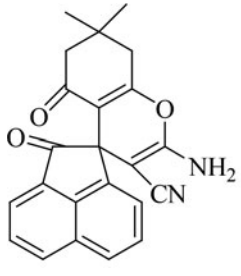
Entry	4	6	Product	Time (min)	Yields (%)	Mp°C	Lit. Mp°C [ref]
1			 **7a**	40	91	298-300	Mp > 300[40]
2			 **7b**	45	87	289-291	289-291[40]
3			 **7c**	55	85	284-286	283-285[40]

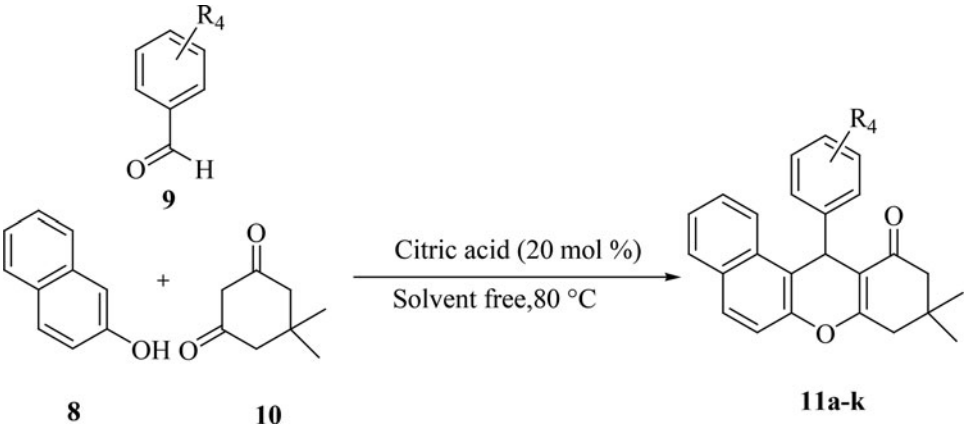
4			 **7d**	55	82	300-302	Mp > 300[40]
5			 **7e**	50	88	236-238	238-240[33]
6				35	93	243-245	242-243[34]
7			 **7g**	40	92	260-262	260-262[35]

(*Continued*)

Table 4
(Continued).

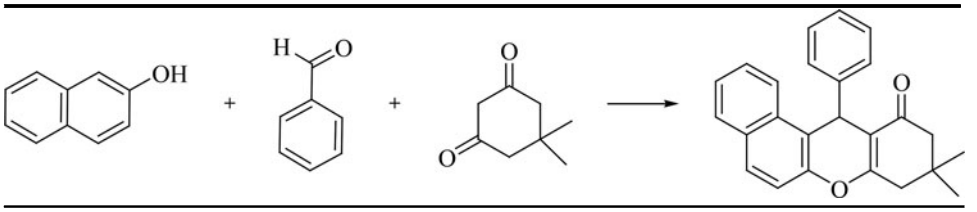
Entry	4	6	Product	Time (min)	Yields (%)	Mp°C	Lit. Mp°C [ref]
8				50	86	253-255	255-257[35]
9			 **7i**	35	89	278-280	280-281[34]
10			 **7j**	45	84	275-277	276-278[24]

11			 **7k**	55	85	240-242	237-240[24]
12			 **7l**	60	83	266-268	268-270[36]



Scheme 3. Synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones.

Table 5
Optimization of the Reaction Conditions for the Synthesis of **11a**[a]



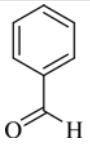
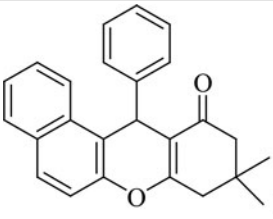
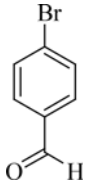
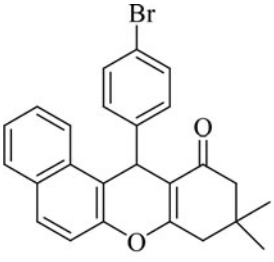
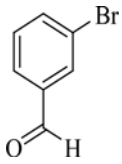
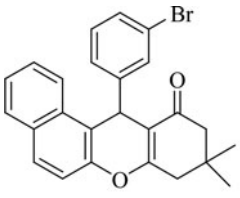
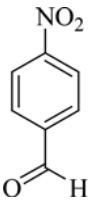
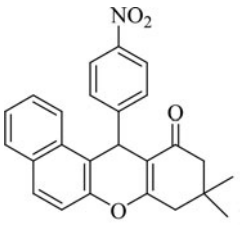
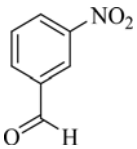
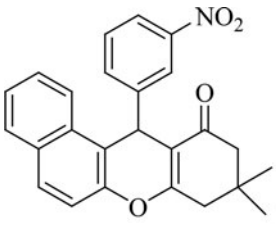
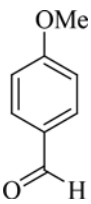
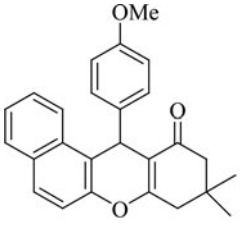
Entry	Citric acid (mol %)	Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	80	420	trace
2	5	80	45	49
3	10	80	35	65
4	15	80	20	81
5	**20**	**80**	**10**	**93**
6	20	rt	420	trace
7	20	40	55	37
8	20	60	45	59
9	20	70	20	74
10	20	90	10	93
11	25	80	10	92

[a]Reaction conditions: β-naphthol (8, 1.0 mmol), benzaldehyde (9, 1.0 mmol), dimedone (10, 1.0 mmol) and citric acid heated at specified temperatures for the appropriate times.

Experimental Section

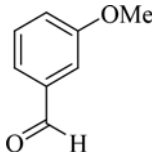
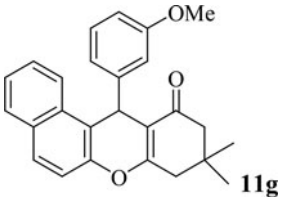
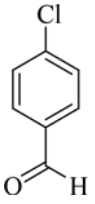
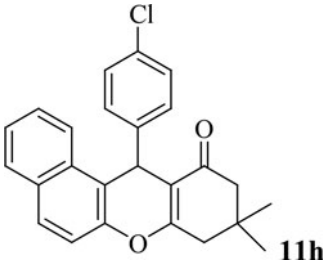
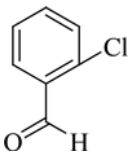
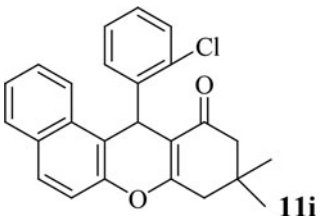
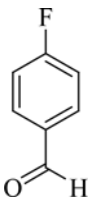
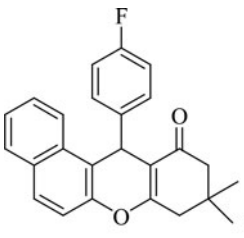
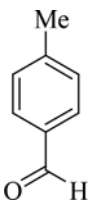
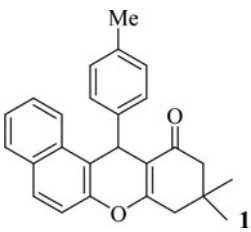
Melting points of all compounds were determined using an Electro thermal 9100 apparatus and are uncorrected ^{1}H NMR spectra were recorded on a Bruker DRX-400 Avance instrument with $CDCl_3$ or DMSO-d_6 as solvents. All reagents and solvents were

Table 6
Citric Acid Catalyzed Synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones

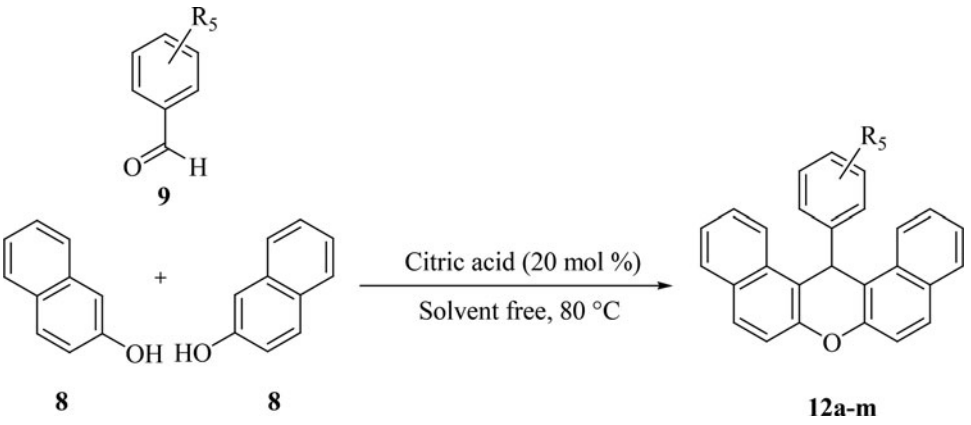
Entry	Aldehyde	Product	Time (min)	Yields (%)	Mp°C	Lit. Mp°C ref
1		 **11a**	10	93	148-150	148-150[43]
2		 **11b**	25	84	182-184	184-186[43]
3		 **11c**	25	85	163-165	161-164[44]
4		 **11d**	15	94	177-179	175-178[44]
5		 **11e**	15	95	165-167	167-169[45]
6		 **11f**	20	87	204-206	202-204[43]

(*Continued*)

Table 6
(Continued).

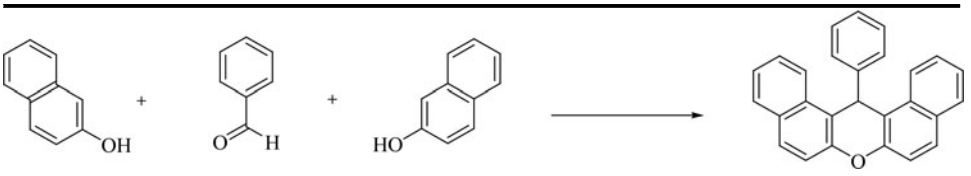
Entry	Aldehyde	Product	Time (min)	Yields (%)	Mp°C	Lit. Mp°C [ref]
7		 **11g**	20	90	205-207	204-205[46]
8		 **11h**	25	86	175-177	176-178[43]
9		 **11i**	25	87	180-182	179-180[47]
10		 **11j**	10	96	182-184	184-185[45]
11		 **11k**	10	94	172-174	171-173[43]

purchased from Merck, Fluka and Acros chemical companies and were used without further purification. TLC was done on silica gel plates, using solvents specified in individual procedures.



Scheme 4. Synthesis of 14-aryl-14*H*-dibenzo[α,j]xanthenes.

Table 7
Optimization of the Reaction Conditions for the Synthesis of **12a**[a]



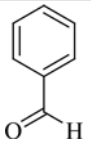
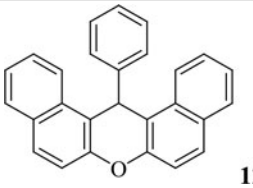
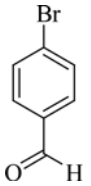
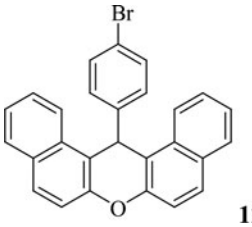
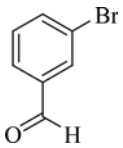
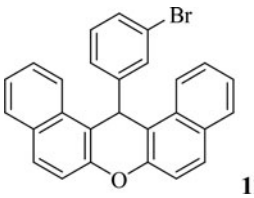
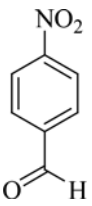
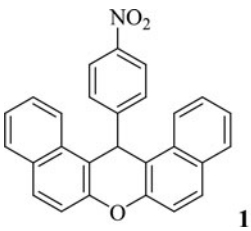
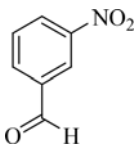
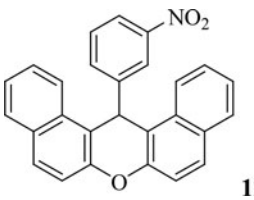
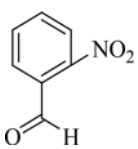
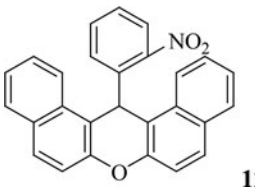
Entry	Citric acid (mol %)	Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	80	420	trace
2	5	80	50	47
3	10	80	35	68
4	15	80	15	83
5	**20**	**80**	**10**	**95**
6	20	rt	420	trace
7	20	40	55	51
8	20	60	30	67
9	20	70	20	79
10	20	90	10	94
11	25	80	10	95

[a]Reaction conditions: β-naphthol (8, 2.0 mmol), benzaldehyde (9, 1.0 mmol) and citric acid heated at specified temperatures for the appropriate times.

General Procedures for Preparation of Polysubstituted Quinolines, Spiro[4H-pyran-oxindoles], 12-aryl-tetrahydrobenzo[α]xanthene-11-ones and 14-aryl-14H-dibenzo[α,j]xanthenes

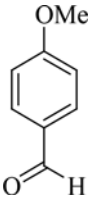
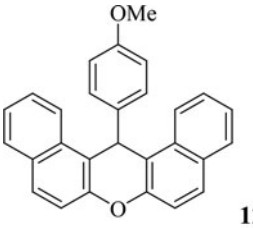
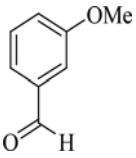
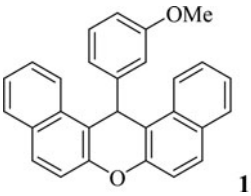
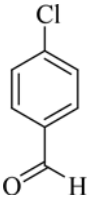
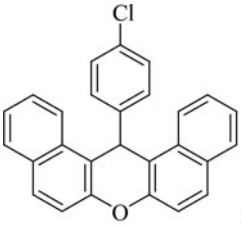
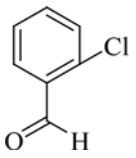
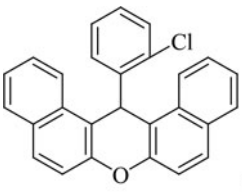
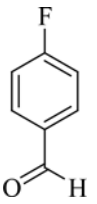
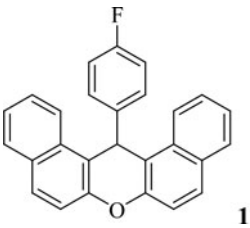
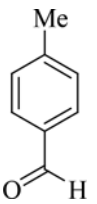
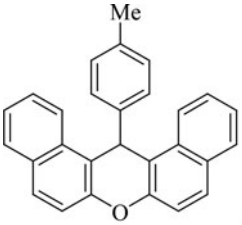
*Synthesis of polysubstituted quinolines (**3**):* A mixture of 2-aminobenzophenone (**1**, 1.0 mmol), ketone/ketoester (**2**, 1.0 mmol) and citric acid (15 mol %) was heated at 90 °C for the appropriate time. After completion of the reaction (TLC using ethylacetate/n-hexane

Table 8
Citric Acid Catalyzed Synthesis of 14-aryl-14*H*-dibenzo[α,*j*]xanthenes

Entry	Aldehyde	Product	Time (min)	Yields (%)	Mp°C	Lit. Mp°C [ref]
1		 **12a**	10	95	182-184	183-184[51]
2		 **12b**	20	87	295-297	297-298[43]
3		 **12c**	20	88	190-192	191-193[45]
4		 **12d**	10	91	306-308	308-309[52]
5		 **12e**	10	93	213-215	212-213[52]
6		 **12f**	10	93	211-213	213-214[52]

(*Continued*)

Table 8
(Continued).

Entry	Aldehyde	Product	Time (min)	Yields (%)	Mp°C	Lit. Mp°C ref
7		 **12g**	15	89	204-206	204-205[43]
8		 **12h**	10	90	171-173	172-173[52]
9		 **12i**	20	86	290-292	289-290[51]
10		 **12j**	20	89	213-215	212-213[51]
11		 **12k** **12k**	10	94	241-243	240-242[53]
12		 **12l**	10	92	226-228	227-228[43]

(*Continued*)

Table 8
(Continued).

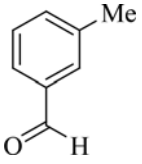
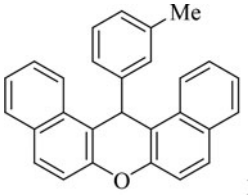
Entry	Aldehyde	Product	Time (min)	Yields (%)	Mp°C	Lit. Mp°C [ref]
13		 **12m**	10	94	195-197	197-198[52]

Table 9
Comparison of Catalytic Ability of Catalysts Reported in the Literature for Synthesis of Polysubstituted Quinolines[a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	DSIMHS	Solvent-free, 70 °C	25 min/89	[27]
2	$FeCl_2{\cdot}2H_2O$-RiHA	Solvent-free,90 °C	35 min/86	[28]
3	Cellulose sulfuric acid	Solvent-free, 100 °C	35 min/70	[29]
4	Starch sulfuric acid	Solvent-free, 100 °C	45 min/75	[29]
5	Amberlyst-15	EtOH, Reflux	210 min/72	[30]
6	P_2O_5/SiO_2	Solvent-free, 80 °C	35 min/94	[31]
7	Citric acid	Solvent-free, 90 °C	15 min/92	This work

[a]Based on reaction of 2-aminobenzophenone (1.0 mmol) and dimedone (1.0 mmol).

Table 10
Comparison of Catalytic Ability of Catalysts Reported in the Literature for Synthesis of Spiro[4*H*-pyran-oxindoles][a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	SBNPTT	H_2O, Reflux	H_2O, Reflux	[24]
2	Silica-Sulfuric acid NPs	EtOH, Reflux	EtOH, Reflux	[33]
3	Carbon-SO_3H	EtOH, Reflux	EtOH, Reflux	[37]
4	L-Proline	H_2O, 80 °C	H_2O, 80 °C	[38]
5	$Mg(ClO_4)_2$	EtOH/H_2O,50 °C	EtOH/H_2O,50 °C	[39]
6	Sodium stearate	H_2O, 60 °C	H_2O, 60 °C	[40]
7	MgO nanocrystalline	H_2O, 80 °C	H_2O, 80 °C	[41]
8	$InCl_3$	CH_3CN, Reflux	CH_3CN, Reflux	[42]
9	Citric acid	Solvent-free, 80 °C	Solvent-free, 80 °C	This work

[a]Based on three-component reaction of isatin (1.0mmol), malononitrile (1.0mmol) and dimedone (1.0mmol)

(3:6) as eluent), 3 ml EtOH was added. The mixture was poured into cold water (10 mL) and the resulting precipitate was recrystallized from ethanol to give pure product (**3a-g**).

Table 11
Comparison of Catalytic Ability of Catalysts Reported in the Literature for Synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones[a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	NO2 – FePc/C	EtOH, Reflux	30 min/91%	[25]
2	DSIMHS	Solvent-free, 55 °C	20 min/93	[43]
3	Fe_3O_4@SiO_2-SO_3H	Solvent-free, 110 °C	30 min/95	[45]
4	$NaHSO_4/SiO_2$	CH_2Cl_2, Reflux	300 min/91	[48]
5	CAN	Microwave irradiation, 120 °C	120 min/85	[49]
6	$Sr(OTf)_2$	1,2-Dichloroethane, 80 °C	300 min/85	[50]
7	Citric acid	Solvent-free, 80 °C	10 min/93	This work

[a]Based on the three-component reaction of β-naphthol (1.0 mmol), benzaldehyde (1.0 mmol) and dimedone (1.0 mmol).

Table 12
Comparison of Catalytic Ability of Catalysts Reported in the Literature for Synthesis of 14-aryl-14*H*-dibenzo[α,*j*]xanthenes[a]

Entry	Catalyst	Conditions	Time/Yield (%)	References
1	[BMim][BF_4]	$Mg(BF_4)_2$, 80 °C	15 min/95	[35]
2	DSIMHS	Solvent-free, 90 °C	3 min/94	[43]
3	Fe_3O_4@SiO_2-SO_3H	Solvent-free, 110 °C	30 min/94	[45]
4	Diatomite-SO_3H	Solvent-free, 90 °C	10 min/93	[51]
5	[H-NMP][HSO_4]	Solvent-free, 110 °C	12 min/94	[52]
6	SFP	Solvent-free, 90 °C	30 min/98	[54]
7	SiO_2-Pr-SO_3H	Solvent-free, 125 °C	20 min/98	[55]
8	Citric acid	Solvent-free, 80 °C	10 min/95	This work

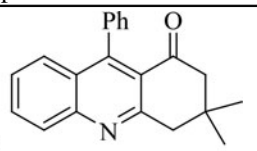
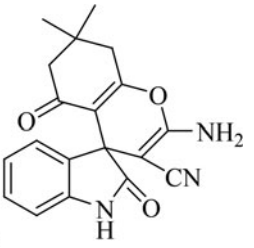
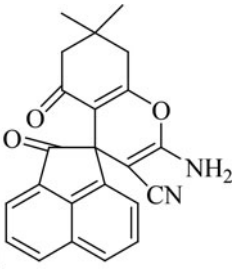
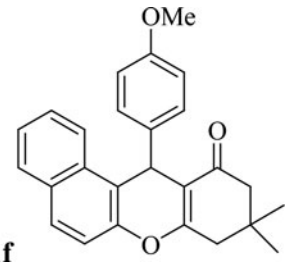
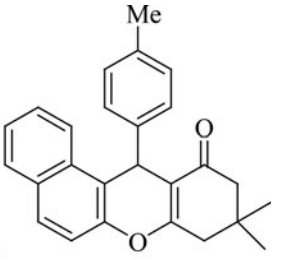
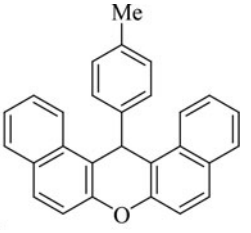
[a]Based on the three-component reaction of β-naphthol (2.0 mmol) and benzaldehyde (1.0 mmol).

*Synthesis of spiro[4H-pyran-oxindoles] (**7**):* A mixture of isatin/acenaphthequinone (**4**, 1.0 mmol), malononitrile (**5**, 1.0 mmol), and different 1,3-dicarbonyl compounds (**6**, 1.0 mmol) in the present of citric acid (20 mol %) was heated at 80 °C for the appropriate time. After completion of the reaction (TLC using ethylacetate/n-hexane (3:7) as eluent), the mixture was cooled to 25 °C, the solid products were filtered and then were recrystallized from ethanol to give the pure compounds (**7a-l**).

*Synthesis of 12-aryl-tetrahydrobenzo[α]xanthene-11-ones (**11**):* A mixture of β-naphthol (**8**, 1.0 mmol), benzaldehyde (**9**, 1.0 mmol), dimedone (**10**, 1.0 mmol) and citric acid (20 mol %) was heated at 80 °C for the appropriate time. After completion of the reaction (TLC using ethylacetate/n-hexane (3:5) as eluent), the mixture was cooled to 25 °C, ethanol was added and the precipitate was separated by filtration. The solid was recrystallized from ethanol to afford the pure products (**11a- k**).

*Synthesis of 14-aryl-14H-dibenzo[α,j]xanthenes (**12**):* A mixture of β-naphthol (**8**, 2.0 mmol), benzaldehyde (**9**, 1.0 mmol) and citric acid (20 mol %) was heated at 80 °C for the appropriate time. After completion of the reaction (TLC using ethylacetate/n-hexane (3:5) as eluent), the mixture was cooled to 25 °C and ethanol was added. The

Table 13
Spectral Data of Representative Compounds

Compound	Spectral data
 **3a**	^{1}H NMR (400 MHz, $CDCl_3$): 1.19 (6H, s, $2CH_3$), 2.59 (2H, s, CH_2), 3.33 (2H, s, CH_2),7.19-7.22 (2H, m, ArH), 7.45 (1H, t, $J = 8.0$ Hz, ArH), 7.50-7.56 (4H, m, ArH), 7.80 (1H, t, $J = 8.0$ Hz, ArH) , 8.13 (1H, brs, ArH).
 **7a**	^{1}H NMR (400 MHz, DMSO-d_6): 1.00 (3H, s, CH_3), 1.03 (3H, s, CH_3), 2.08-2.19 (2H, m, CH_2), 2.53 (2H, s, CH_2), 6.79 (1H, d, $J = 7.2$ Hz, ArH), 6.89 (1H, t, $J = 7.2$ Hz, ArH), 6.98 (1H, d, $J = 6.8$ Hz, ArH), 7.14 (1H, t, $J = 6.4$ Hz, ArH), 7.22 (2H, s, NH_2), 10.39 (1H, s, NH)
 **7l**	^{1}H NMR (400 MHz, DMSO-d_6): 1.02 (3H, s, CH_3), 1.04 (3H, s, CH_3), 2.04-2.13 (2H, m, CH_2), 2.63 (2H, s, CH_2), 7.32 (2H, s, NH_2), 7.38-8.28 (6H, m, ArH).
 **11f**	^{1}HNMR (400 MHz, $CDCl_3$): 0.99 (3H, s, CH_3), 1.12 (3H, s, CH_3), 2.16-2.35 (2H, m, CH_2), 2.58 (2H, s, CH_2), 3.71 (3H, s,OCH_3), 5.68 (1H, s, CHAr), 6.72 (2H, d, $J = 8.4$ Hz, ArH), 7.21-7.47 (5H, m, ArH), 7.85 (2H, t, $J = 9.2$ Hz, ArH), 8.01 (1H, d, $J = 8.4$ Hz, ArH).
 **11k**	^{1}H NMR (400 MHz, $CDCl_3$): 1.01 (3H, s, CH_3), 1.15 (3H, s, CH_3), 2.23 (3H, s, CH_3), 2.28 (1H, d, $J = 16.0$ Hz, CH_2), 2.34 (1H, d, $J = 16.0$ Hz, CH_2), 2.60 (2H, s, CH_2), 5.71 (1H, s, CHAr), 7.00–8.06 (10H, m, ArH).
 **12l**	^{1}H NMR (400 MHz, $CDCl_3$): 2.18 (3H, s, CH_3), 6.47 (1H, s, CHAr), 6.81(1H, d, $J = 7.6$ Hz, ArH), 6.81(1H, t, $J = 7.6$ Hz, ArH), 7.40-7.85 (12H, m, ArH), 8.42 (2H, d, $J = 8.8$ Hz, ArH).

precipitate was separated by filtration and the solid was recrystallized from ethanol to afford the pure products (**12a-m**). The products have been characterized by melting points and ^{1}H NMR spectroscopy. Spectral data of selected products are reported in *Table 13*.

Acknowledgments

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