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PAPER

NHC Brønsted base-catalyzed transformations of isochromene derivatives: regulation of products by the structures of carbene catalysts†

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Two different transformations of α-(isochromen-1-yl)ketones catalyzed by NHC Brønsted bases are reported. In the presence of a triazole carbene, α-(isochromen-1-yl)ketones isomerized into β-(2-(aroylmethylene)phenyl)-α,β-unsaturated ketones in 38–88% yields, while the same reaction catalyzed by an imidazole carbene produced 1-aroylnaphthalene derivatives in 90–99% yields. This work not only provides a new method for the synthesis of a novel type of α,β-unsaturated ketone and multi-substituted naphthalene derivatives, but also advances the application of NHC catalysts in the field of Brønsted base-catalysis.

Introduction

N-Heterocyclic carbenes (NHCs) have remarkable scope as organocatalysts.[1] The majority of NHC-catalyzed reactions were initiated from nucleophilic additions of carbene catalysts to carbonyl compounds, which led to the umpolung reactivity of carbonyl groups. These umpolung reactions were exemplified by benzoin reactions,[1,2] Stetter reactions,[1,3] the reactions of homoenolates derived from enals,[1,4] and the cycloadditions of ketenes,[5] *etc.* The umpolung of electron-deficient alkenes has also been achieved by the nucleophilic addition of NHCs to Michael acceptors,[6] while acid esters and acid fluorides could be activated, but without umpolung of the carbonyls, by nucleophilic addition of NHCs to these carboxylic derivatives.[7] Although *N*-heterocyclic carbene catalysts have been demonstrated to have moderate nucleophilicity but high Lewis and Brønsted basicity,[8] their catalysis as Brønsted bases remains very limited. The main application of NHC Brønsted base-catalysis is the promotion of transesterification reactions,[9] in which NHCs activate the reaction by deprotonation of alcohols. NHCs have also been utilized as Brønsted base catalysts in the Michael addition of alcohols or amines to α,β-unsaturated ketones.[10] Very few examples of the NHC-catalyzed deprotonation of *ortho*-protons of carbonyl compounds have been reported, which lead to the formation of enol ethers[11] or the intramolecular Michael addition.[12] Compared to the numerous studies on NHC-mediated catalysis based on the nucleophilicity or Lewis basicity of NHCs, the Brønsted base activations of NHCs have been largely unexplored. We considered that the mild NHCs-catalysis might attenuate unwanted side reactions that could take place under anionic base catalysis conditions. Therefore, the development of NHCs as efficient Brønsted base catalysts is of great importance.

We have been interested in the reactivity and synthetic applications of *N*-heterocyclic carbenes for many years.[13] Recently, our attention was drawn to NHC-catalyzed reactions.[14] During our study on the NHC-catalyzed condensation of carbonyl compounds, we discovered two different transformations of α-(isochromen-1-yl)ketones. Herein, we reported the NHC Brønsted base-catalyzed transformations of isochromene derivatives, which leads to the formation of β-(2-(aroylmethylene)phenyl)-α,β-unsaturated ketones or 1-aroylnaphthalenes and is regulated by the structures of the NHC catalysts.

Results and discussion

In this work, the reactants α-(3-arylisochromen-1-yl) substituted ketones **3** were prepared from the reaction of 2-(arylethynyl)-benzaldehydes **1** with ketones **2** catalyzed by $PdCl_2$ (See ESI†). Initially, the 1-(3-phenylisochromen-1-yl)propan-2-one **3a** was stirred with 10 mol% of different NHC precursors **4** and DBU in acetonitrile for 6–12 h at room temperature. It was found that 1-(3-phenylisochromen-1-yl)propan-2-one **3a** was transformed into (*E*)-4-(2-(benzoylmethylene)phenyl)-3-buten-2-one **5a** in 20–28% yields in the presence of triazole carbenes **4a′–4c′**, while **3a** catalyzed by imidazole carbenes **4d′** and **4e′** was converted to 1-benzoyl-2-methylnaphthalene **6a** in 33–37% yields (Table 1, entries 1–5). Under the same conditions, thiazole carbene **4f′** was totally inefficient for these transformations. When the reaction was operated in refluxing acetonitrile, 49% of

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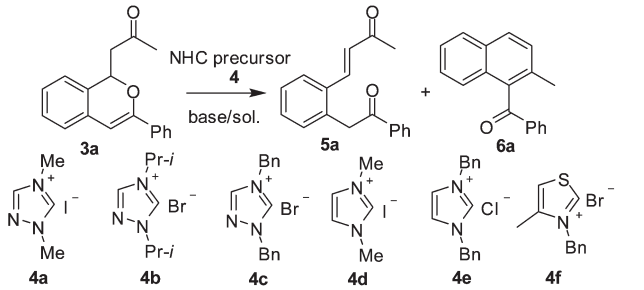
† Electronic supplementary information (ESI) available: The preparation and characterization of α-(3-arylisochromen-1-yl)ketones **3**, copies of ^{1}H NMR and ^{13}C NMR spectra of compounds **3**, **5** and **6** are available. CCDC 895476, 895477 and 895478 [**3a**, **3f-II** and **5f**]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob26622a

Table 1 NHC-catalyzed transformations of 1-(3-phenylisochromen-1-yl)propan-2-one **3a** under different conditions



Entry	Reaction conditions: Cat. (mol %)	Base[a]	Sol.	*T* (°C)	*T* (h)	Yield (%): **5a**	**6a**
1	**4a** (10)	DBU	CH_3CN	rt	6	20	—
2	**4b** (10)	DBU	CH_3CN	rt	6	17	—
3	**4c** (10)	DBU	CH_3CN	rt	6	28	—
4	**4d** (10)	DBU	CH_3CN	rt	6	7	33
5	**4e** (10)	DBU	CH_3CN	rt	6	8	37
6	**4f** (10)	DBU	CH_3CN	rt	12	—	—
7	**4c** (10)	DBU	CH_3CN	Reflux	10	49	—
8	**4e** (10)	DBU	CH_3CN	Reflux	10	—	89
9	**4c (20)**	**DBU**	**CH_3CN**	**Reflux**	**6**	**55**	—
10	**4e (20)**	**DBU**	**CH_3CN**	**Reflux**	**2**	—	**98**
11	**4c** (20)	DBU	Dioxane	80	6	33	—
12	**4c** (20)	DBU	Benzene	80	6	22	—
13	**4c** (20)	DBU	$ClCH_2CH_2Cl$	80	6	23	—
14	**4c** (20)	*t*-BuOK	CH_3CN	Reflux	6	35	23
15	**4c** (20)	NaH	CH_3CN	Reflux	6	28	67
16	—	DBU	CH_3CN	Reflux	6	6	—

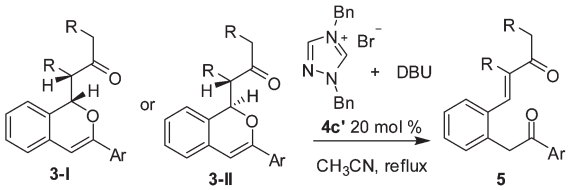
[a] The mol% of bases are equal to the mol% of carbene catalysts.

5a or 89% of **6a** was obtained from 1-isochromenylpropanone **3a** by using 10 mol% of *N,N*-dibenzyltriazole carbene **4c′** or *N,N*-dibenzylimidazole carbene **4e′** as the catalyst, respectively. In refluxing acetonitrile, the catalyst loading of triazole carbene **4c′** or imidazole carbene **4e′** was then increased to 20 mol% and the yield of **5a** or **6a** was improved to 55% or 98%, respectively (Table 1, entries 9 and 10). To improve the yield of α,β-unsaturated ketone **5a**, the reaction conditions were further optimized by varying the solvent and base utilized to generate the carbene catalyst. However, under the catalysis of triazole carbene **4c′** and at a similar temperature as the refluxing acetonitrile, the reactions in 1,4-dioxane, benzene and 1,2-dichloroethane all led to a diminishing of the yield of product **5a** (Table 1, entries 11–13). The use of strong bases *t*-BuOK or NaH to generate the carbene catalyst decreased the selectivity in the formation of products **5a** and **6a** (Table 1, entries 14–15).

Under the same conditions as that of the reaction catalyzed by 20 mol% of **4c**, the reaction of **3a** catalyzed by DBU alone only yielded 6% of product **5a** and 88% of reactant **3a** was recovered (Table 1, entry 16), which confirmed that the catalysis is due to the *N*-heterocyclic carbenes.

The 4-(2-(benzoylmethylene)phenyl)-3-buten-2-one **5a** represents a novel skeleton of β-(2-(aroylmethylene)phenyl)-α,β-unsaturated ketones that has never been reported before. To assess the generality for the preparation of β-(2-(aroylmethylene)-phenyl)-α,β-unsaturated ketones **5** from isochromenyl substituted ketones, a variety of α-(3-arylisochromen-1-yl)ketones **3** was surveyed under the catalysis of triazole carbene **4c′** in refluxing acetonitrile. As shown in Table 2, the aryls and alkyls attached to

Table 2 Triazole carbene-catalyzed transformation of α-(3-aryl-isochromen-1-yl)ketones **3** under optimized conditions



Entry	Reactant **3**	*T* (h)	Product **5**	Yield (%)[a]
1	**3a**	6	**5a**	**5a**: 55
2	**3b**	6	**5b**	**5b**: 88
3	**3c**	6	**5c**	**5c**: 66
4	**3d**	6	**5d**	**5d**: 38
5	**3e-II**	6	**5e**	**5e**: 41
6	**3f-I**	1	**5f**	**5f**: 81
7	**3f-II**	1	**5f**	**5f**: 83
8	**3g-I** + **3g-II**	6	**5g**	**5g**: 53

[a] 4%–14% of 6 were also isolated.

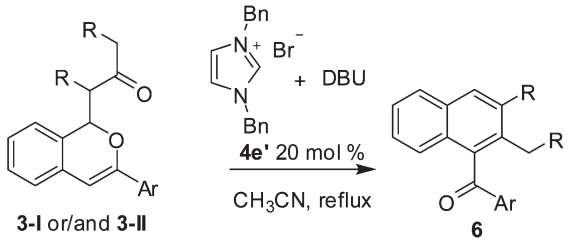
both the isochromene rings and the α-positions of the carbonyls of **3** have influence on the outcomes of the reactions. For example, the electron-donating *p*-anisyl or *p*-tolyl substituted isochromenylpropanones **3b** or **3c** afforded a yield of product **5b** or **5c** higher than isochromenylpropanones **3a** and **3d** attached by phenyl and *p*-chlorophenyl, respectively (Table 2, entries 1–4). On the other hand, among α-(3-phenylisochromen-1-yl)-cyclopentanone **3f**, -propanone **3a**, -pentanone **3e** and -cyclohexanone **3g**, cyclopentanone **3f** was the most reactive one and produced the highest yield of product **5f** (Table 2, entries 1, 5–8). Except for α-(3-arylisochromen-1-yl)propanones **3a–3d**, other reactants including α-(isochromen-1-yl)pentanone **3e**, α-(isochromen-1-yl)cyclopentanone **3f** and α-(isochromen-1-yl)cyclohexanone **3g** have a pair of diastereoisomers **3-I** and **3-II**. Both *cis*-isomers **3-I** and *trans*-isomers **3-II** were obtained from the $PdCl_2$-catalyzed reaction of 2-(arylethynyl)benzaldehydes with ketones (See ESI†). It was found that the *cis* and *trans* isomers produced the same products in very similar yields under the same conditions (Table 2, entries 6 and 7). Thus, all *cis*-isomers **3-I**, *trans*-isomers **3-II**, or a mixture of two diastereoisomers **3-I** and **3-II** could be used as the starting materials.

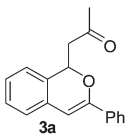
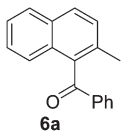
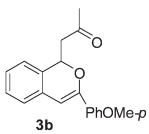
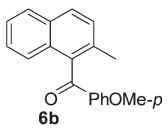
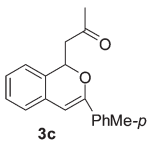
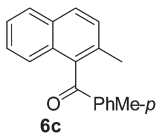
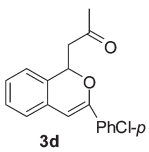
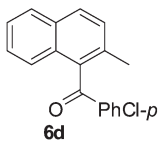
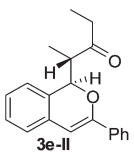
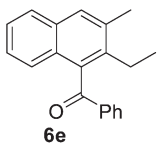
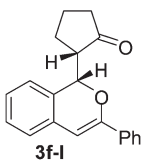
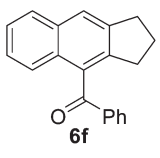
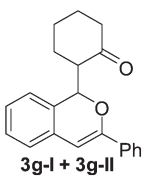
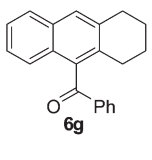
To develop a new method for the synthesis of multi-substituted naphthalene derivatives, the reaction of α-(3-arylisochromen-1-yl)ketones **3** catalyzed by an imidazole carbene was then examined in refluxing acetonitrile. In the presence of *N,N*-dibenzylimidazole carbene **4e′**, all α-(3-arylisochromen-1-yl)-ketones **3a–3g** with different aryls and alkyls attached to the isochromene rings and the α-positions of the carbonyls reacted efficiently to afford 1-aroylnaphthalenes **6** in almost quantitative yields (Table 3).

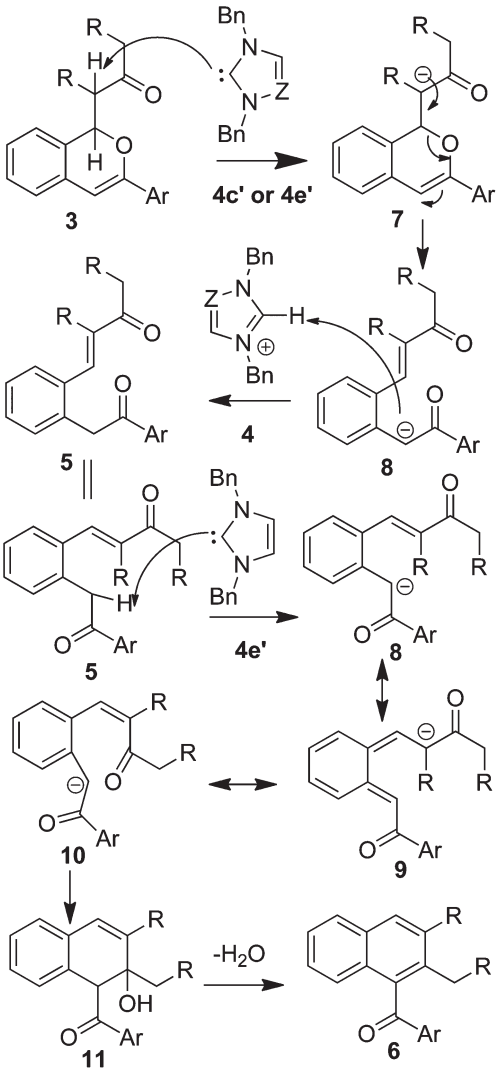
The structures of all products **5** and **6** were ascertained by spectroscopic methods. Theoretically, the transformation of α-(isochromen-1-yl)ketones **3** to α,β-unsaturated ketones **5** could form a pair of *Z*- and *E*-isomers. However, no *Z*-configured isomers of **5** were detected in any reactions. The coupling constants (^3J) of the two vinyl protons of 4-(2-(aroylmethylene)-phenyl)-3-buten-2-ones **5a–5d** were around 16 Hz, which are in agreement with the *E*-configuration of carbon–carbon double bonds. The configuration of the trisubstituted C=C bonds of **5e–5g** cannot be assigned using coupling constants of the vinyl protons. To determine the configurations of **5e–5g** beyond doubt, single crystal X-ray diffraction analysis of **5f** was performed,[15] which confirmed unambiguously that **5f** is (*E*)-2-(2-(benzoylmethylene)benzylidene)cyclopentanone.†

The transformations of α-(3-arylisochromen-1-yl)ketones **3** to α,β-unsaturated ketones **5** and naphthalene derivatives **6** can be explained by the deprotonation of ketones **3** under the catalysis of NHCs. As shown in Scheme 1, the triazole or imidazole carbene acts as Brønsted base to deprotonate the α-protons of ketones **3**, which leads to the formation of carbon anion intermediates **7**. Isomerization of **7** to anions **8** followed by protonation of **8** affords products **5**. In the presence of an imidazole carbene, the intramolecular aldol condensation of bisketones **5** forms the dihydronaphthalen-2-ols **11**, which produce products **6** after dehydration. During the formation of naphthalene rings, the isomerization of the *E*-configuration of α,β-unsaturated ketones **5** to the *Z*-configuration probably proceeds *via* the resonance of anions **8** with **9** and **10**. According to the study of Herbert Mayr and co-workers,[8] imidazole carbenes have stronger basicity than the corresponding triazole carbenes due to the electron-withdrawing effect of the additional nitrogen atom of the triazole ring. Therefore, the different transformations of α-isochromenylketones **3** under the catalysis of imidazole carbene and triazole carbene can be explained by the stronger basicity of the imidazole carbene which promotes the intramolecular aldol condensation of product **5**. In refluxing acetonitrile, product **5a** catalyzed by imidazole carbene **4e′** was almost totally converted into **6a** in 1 h, which supported our mechanism.

Table 3 Imidazole carbene-catalyzed reaction of α-(3-arylisochromen-1-yl)ketones **3** under optimized conditions



Entry	Reactant **3**	*T* (h)	Product **5**	Yield (%)
1	 **3a**	2	 **6a**	**6a**: 98
2	 **3b**	2	 **6b**	**6b**: 99
3	 **3c**	4	 **6c**	**6c**: 97
4	 **3d**	2	 **6d**	**6d**: 97
5	 **3e-II**	2	 **6e**	**6e**: 91
6	 **3f-I**	2	 **6f**	**6f**: 96
7	 **3g-I + 3g-II**	2	 **6g**	**6g**: 90



Scheme 1 Proposed mechanism.

Conclusions

In summary, the NHC-catalyzed transformations of α-(isochromen-1-yl)ketones were studied. In the presence of a triazole carbene, α-(isochromen-1-yl)ketones isomerized into β-(2-(aroylmethylene)phenyl)-α,β-unsaturated ketones in moderate to good yields, while the same reaction catalyzed by an imidazole carbene produced 1-aroylnaphthalene derivatives in excellent yields. Both reactions were initiated by the deprotonation of the α-protons of the ketones with a NHC catalyst. This work not only provides a new method for the synthesis of novel α,β-unsaturated ketones and multi-substituted naphthalene derivatives, but also advances the application of NHC catalysts in the field of Brønsted base-catalysis.

Experimental section

1. General procedure for the preparation of β-(2-(aroylmethylene)phenyl)-α,β-unsaturated ketones 5 from α-(3-arylisochromen-1-yl)ketones 3

Under a nitrogen atmosphere, α-(isochromen-1-yl)ketones **3** (1 mmol) and *N,N*-benzyl-1,2,4-triazolium salt **4c** (0.2 mmol) were dissolved in acetonitrile (20 mL), and then DBU (0.2 mmol) was added using a microliter syringe. The reaction mixture was refluxed for 1–6 h. The solvent was removed under vacuum and the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (20 : 1 to 10 : 1) to afford β-(2-(aroylmethylene)phenyl)-α,β-unsaturated ketones **5** in 38–88% yields.

(*E*)-4-(2-(Benzoylmethylene)phenyl)-3-buten-2-one 5a

55%, mp 87–88 °C; IR ν (cm^{-1}) 1680, 1655, 1619, 1597, 1581; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 7.98 (d, J = 7.1 Hz, 2H), 7.64 (d, J = 16.3 Hz, 1H), 7.63 (d, J = 5.9 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.3 Hz, 2H), 7.21–7.26 (m, 3H), 6.54 (d, J = 16.1 Hz, 1H), 4.56 (s, 2H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ (ppm) 198.2, 197.8, 141.4, 137.8, 136.5, 135.5, 134.1, 132.8, 130.9, 129.6, 129.5, 129.2, 128.3, 127.4, 43.7, 27.5; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{18}H_{16}O_2Na$: 287.1048; found: 287.1053.

(*E*)-4-(2-(*p*-Methoxybenzoylmethylene)phenyl)-3-buten-2-one 5b

88%, mp 68–69 °C; IR ν (cm^{-1}) 1672, 1646, 1624, 1602, 1577; ^{1}H NMR (400 MHz, CD_3COCD_3) δ (ppm) 8.00 (d, J = 8.7 Hz, 2H), 7.71 (d, J = 16.1 Hz, 1H), 7.63 (d, J = 7.4 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 6.62 (d, J = 16.0 Hz, 1H), 4.40 (s, 2H), 3.87 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.4, 195.5, 163.9, 140.8, 135.1, 134.3, 131.5, 130.8, 130.4, 129.5, 129.0, 127.8, 127.0, 114.0, 55.6, 43.0, 27.7; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{19}H_{19}O_3$: 295.1334; found: 295.1335. Anal. Calcd for $C_{19}H_{18}O_3$: C 77.53, H 6.16; found: C 77.38, H 6.00.

(*E*)-4-(2-(*p*-Methylbenzoylmethylene)phenyl)-3-buten-2-one 5c

66%, mp 79–80 °C; IR ν (cm^{-1}) 1676, 1647, 1608; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 16.0 Hz, 1H), 7.56 (dd, J = 7.3, 1.2 Hz, 1H), 7.24–7.31 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.17 (dd, J = 7.6, 1.3 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 4.36 (s, 2H), 3.35 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 196.5, 144.4, 140.7, 134.8, 134.3, 134.0, 131.4, 130.3, 129.4, 129.0, 128.5, 127.7, 126.9, 43.1, 27.6, 21.7; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{19}H_{19}O_2$: 279.1385; found: 279.1387. Anal. Calcd for $C_{19}H_{18}O_2$: C 81.99, H 6.52; found: C, 81.70, H 6.35.

(*E*)-4-(2-(*p*-Chlorobenzoylmethylene)phenyl)-3-buten-2-one 5d

38%, mp 113–114 °C; IR ν (cm^{-1}) 1680, 1643, 1619; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 16.2 Hz, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.1 Hz, 1H), 7.22 (d, J = 7.0 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 4.42 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 195.7, 140.3, 140.0, 134.7, 134.2, 131.3, 130.4, 129.8, 129.1, 128.9, 127.9, 127.0, 43.2, 27.7; HRMS (TOF-ESI): $[M + Na]^+$ calcd for

$C_{18}H_{15}ClO_2Na$: 321.0658; found: 321.0663. Anal. Calcd for $C_{18}H_{15}ClO_2$: C 72.36, H 5.06; found: C, 72.12, H 4.67.

(*E*)-2-Methyl-1-(2-(benzoylmethylene)phenyl)pent-1-en-3-one 5e

41%, mp 52–53 °C; IR ν (cm^{-1}) 1677, 1668, 1636; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.94 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.51 (s, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.27–7.33 (m, 3H), 7.22 (dd, J = 5.2, 4.2 Hz, 1H), 4.28 (s, 2H), 2.66 (q, J = 7.3 Hz, 2H), 1.81 (d, J = 1.2 Hz, 3H), 1.06 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.9, 197.2, 139.0, 137.2, 136.0, 133.5, 133.3, 130.7, 129.2, 128.7, 128.4, 128.3, 127.1, 43.7, 30.8, 13.0, 8.6; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{20}H_{20}O_2Na$: 315.1361; found: 315.1358. Anal. Calcd for $C_{20}H_{20}O_2$: C 82.16, H 6.89; found: C, 82.20, H 6.88.

(*E*)-2-(2-(Benzoylmethylene)benzylidene)cyclopentanone 5f

83%, mp 126–127 °C; IR ν (cm^{-1}) 1707, 1680, 1614, 1595; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (dd, J = 7.6, 1.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.44–7.48 (m, 4H), 7.33 (t, J = 4.0 Hz, 1H), 7.31 (t, J = 4.3 Hz, 1H), 7.23 (dd, J = 5.7, 4.1 Hz, 1H), 4.42 (s, 2H), 2.66 (td, J = 7.2, 2.6 Hz, 2H), 2.37 (t, J = 7.8 Hz, 2H), 1.96 (quintet, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 207.7, 197.0, 138.2, 136.7, 135.5, 135.2, 133.4, 131.1, 129.4, 129.3, 129.2, 128.8, 128.5, 127.2, 43.1, 38.1, 29.3, 20.5; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{20}H_{18}O_2Na$: 313.1204; found: 313.1201. Anal. Calcd for $C_{20}H_{18}O_2$: C 82.73, H 6.25; found: C, 82.47, H 5.97.

(*E*)-2-(2-(Benzoylmethylene)benzylidene)cyclohexanone 5g

53%, mp 169–170 °C; IR ν (cm^{-1}) 1676, 1593, 1580, 1566; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.40 (s, 1H), 7.37 (dd, J = 7.3, 1.5 Hz, 2H), 7.16–7.23 (m, 3H), 7.12 (dd, J = 6.3, 2.4 Hz, 1H), 4.42 (s, 2H), 2.50 (td, J = 7.0, 1.8 Hz, 2H), 2.34 (t, J = 6.7 Hz, 2H), 1.79 (quintet, J = 5.4 Hz, 2H), 1.59 (quintet, J = 5.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.0, 197.2, 139.4, 136.8, 135.6, 134.5, 133.5, 133.3, 130.7, 129.4, 128.8, 128.6, 128.4, 126.9, 43.2, 40.7, 28.8, 24.1, 23.8; HRMS (TOF-ESI): $[M + Na]^+$ calcd for $C_{21}H_{20}O_2Na$: 327.1361; found: 327.1363. Anal. Calcd for $C_{21}H_{20}O_2$: C 82.86, H 6.62; found: C, 82.81, H 6.23.

2. General procedure for the preparation of 1-aroylnaphthalenes 6 from α-(3-arylisochromen-1-yl)ketones 3

Under a nitrogen atmosphere, α-(isochromen-1-yl)ketones **3** (1 mmol) and *N,N*-benzylimidazole salt **4e** (0.2 mmol) were dissolved in acetonitrile (20 mL), and then DBU (0.2 mmol) was added. The reaction mixture was refluxed for 2–4 h. After removal of solvent under vacuum, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (20 : 1) to give 1-aroylnaphthalenes **6** in 90–99% yields.

(2-Methylnaphthalen-1-yl)(phenyl)methanone 6a

98%, mp 71–72 °C (lit.[16] mp 74–75 °C); IR ν (cm^{-1}) 1667, 1594, 1578; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 7.4 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 7.6Hz, 3H), 7.37 (d, J = 8.5 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.3, 137.5, 135.9, 133.8, 132.2, 131.6, 130.6, 129.7, 128.9, 128.8, 128.5, 128.1, 126.7, 125.4, 124.9, 19.7; MS (ESI): 247 $[M + H]^+$.

(4-Methoxyphenyl)(2-methylnaphthalen-1-yl)methanone 6b[17]

99%, mp 101–102 °C; IR ν (cm^{-1}) 1657, 1600, 1574; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 7.6 Hz, 2H), 7.49 (d, J = 8.3 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.83 (t, J = 8.7 Hz, 1H), 6.89 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.9, 164.2, 136.4, 132.3, 132.1, 131.8, 130.9, 128.8, 128.6, 128.1, 126.7, 125.5, 125.1, 114.2, 55.6, 19.8; MS (ESI) 277 $[M + H]^+$.

(2-Methylnaphthalen-1-yl)(4-methylphenyl)methanone 6c[18]

97%, mp 104–105 °C (lit.[18] mp 106 °C); IR ν (cm^{-1}) 1658, 1601; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.77 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 8.3 Hz, 1H), 7.34 (t, J = 7.1 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 7.27 (td, J = 7.0, 1.0 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 2.33 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.9, 144.8, 136.2, 135.2, 132.1, 131.7, 130.7, 129.9, 129.5, 128.8, 128.0, 126.6, 125.4, 125.0, 21.8, 19.7; MS (ESI) 261 $[M + H]^+$.

(4-Chlorophenyl)(2-methylnaphthalen-1-yl)methanone 6d

97%, mp 106–107 °C; IR ν (cm^{-1}) 1669, 1585; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.27–7.38 (m, 6H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 140.4, 135.9, 135.4, 132.3, 131.7, 131.1, 129.2, 128.53, 128.47, 128.2, 126.9, 125.6, 124.7, 19.7; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{18}H_{14}ClO$: 281.0733; found: 281.0739. Anal. Calcd for $C_{18}H_{13}ClO$: C 77.01, H 4.67; found: C, 76.94, H 4.88.

(2-Ethyl-3-methylnaphthalen-1-yl)(phenyl)methanone 6e

91%, mp 108–109 °C; IR ν (cm^{-1}) 1660, 1592, 1578; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.36–7.43 (m, 4H), 7.27 (t, J = 8.2 Hz, 1H), 2.70 (br, 1H), 2.54 (br, 1H), 2.54 (s, 3H), 1.09 (t, J = 7.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.0, 137.5, 135.91, 135.89, 133.9, 132.8, 131.8, 129.8, 129.3, 128.9, 128.1, 127.5, 125.8, 125.5, 124.7, 30.2, 27.4, 22.9; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{20}H_{19}O$: 275.1436; found: 275.1431.

(Cyclopenta[*b*]naphthalen-4-yl)(phenyl)methanone 6f[19]

96%, mp 108–109 °C; IR ν (cm^{-1}) 1666, 1653, 1594, 1578; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.83 (d, J = 7.1 Hz, 2H), 7.81 (d, J = 7.8 Hz, 1H), 7.77 (s, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.57 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 7.2 Hz, 1H), 7.31 (t, J = 7.0 Hz, 1H), 3.08 (t, J = 7.2 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H), 2.09 (quintet, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.4, 143.2, 141.4, 137.8, 133.8, 133.1, 132.4, 130.1, 130.0, 128.9, 128.0, 125.9, 125.5, 125.2, 124.1, 32.5, 31.9, 26.1; MS (ESI): 273 $[M + H]^+$.

(Phenyl)(tetrahydroanthracen-9-yl)methanone 6g

90%, mp 147–148 °C (lit.[20] mp 158 °C); IR ν (cm^{-1}) 1657, 1593, 1578; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81 (d, J = 7.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.65 (s, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.39 (d, J = 6.4 Hz, 1H), 7.37 (t, J = 8.1 Hz, 1H), 7.26 (t, J = 8.2 Hz, 1H), 3.02 (t, J = 6.4 Hz, 2H), 2.80 (br, 1H), 2.57 (br, 1H), 1.81–1.87 (m, 2H), 1.77 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.0, 137.5, 135.91, 135.89, 133.9, 132.8, 131.8, 129.8, 129.3, 128.9, 128.1, 127.5, 125.8, 125.5, 124.7, 30.2, 27.4, 23.0, 22.9; MS (ESI): 287 $[M + H]^+$.

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