Efficient One-Pot Syntheses of 7-Alkyl-6*H*,7*H*-naphtho[1,2:5,6]pyrano-[3,2-*c*]chromen-6-ones by 1-Methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium Chloride

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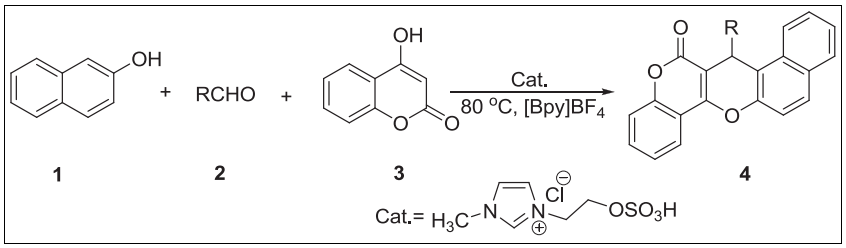

An efficient synthesis of 7-alkyl-6*H*,7*H*-naphtho-[10,20:5,6]pyrano[3,2-*c*]chromen-6-ones by three-component condensation reaction of β-naphthol, aromatic aldehydes, and 4-hydroxycoumarin catalyzed by 1-methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride is reported in good to excellent yields and short reaction times.

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INTRODUCTION

Chromenes constitute a major class of naturally occurring compounds [1–7], and interest in their chemistry continues unabated because of their wide range of biological and therapeutic properties such as antioxidant [8,9], antibacterial [10,11], cytotoxic [12], anticancer [13,14], and antihypertensive activity [15]. Considering the aforementioned reports, development of new and simple synthetic methods for efficient preparation of new chromenes is an interesting challenge.

Recently, 1-methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride (MSI) was emerged as a promising catalyst for an acid catalyzed in our lab, such as 14-aryl or alkyl-14*H*-dibenzo[*a,j*] xanthenes [16]. This catalyst is safe, easy to handle, and environmentally benign, and presents fewer disposal problems.

To research its new application, herein we describe an MSI-catalyzed facile synthesis of 7-alkyl-6*H*,7*H*-naphtho [1,2:5,6]pyrano-[3,2-*c*]chromen-6-ones via a three-component reaction of β-naphthol, aromatic aldehydes, and 4-hydroxycoumarin (Scheme 1).

RESULTS AND DISCUSSION

To choose optimum conditions, the effect of temperature and solvent on the rate of the reaction was studied for the preparation of 7-phenyl-6*H*,7*H*-naphtho[1,2:5,6]pyrano[3,2-*c*] chromen-6-one (**4a**) by three-component condensation reaction of β-naphthol (**1**), benzaldehyde(**2a**), and 4-hydroxycoumarin (**3**) in the presence of MSI in [Bpy]BF_4 (Table 1). At 80 °C (Table 1, entries 9–12); the reaction proceeded smoothly and gave short reaction time and high yield. The increase in temperature did not enhance the yield of the product. Therefore, we kept the reaction temperature at 80°C. Then, it was shown that when common organic solvents and water were used as solvents, the yields were very low (Table 1, entries 1–5). It may be that in these organic solvents, this reaction could only give some cross-aldol condensation products, and these low-boiling organic solvents cannot offer enough energy to afford desired product, which may be a thermodynamic controlled ones. Meanwhile, water may be making the equilibrium toward the reactants. However, when three kinds of ionic liquids were used as reaction medium, the yield of **4a** increased to 85–90% surprisingly (Table 1, entries 6–8). [Bpy]BF_4 gave the highest yield because of its strongest basicity among these ionic liquids.

According to Table 2, it was found that MSI was the most efficient catalyst (Table 2, entries 1–7). The important role of MSI may be attributed to its fitting acidity, stability, and nonvolatility. Then, the study set out to determine the optimal amount of MSI (Table 2, entries 7–12). The best yield was obtained when 4 mol% of MSI was loading. Further increasing the amount of MSI had no significant effect on the yield.

Under the optimized reaction condition, the scope and efficiency of these procedures were explored for the synthesis of 7-alkyl-6*H*,7*H*-naphtho[1,2:5,6]pyrano[3,2-*c*]chromen-6-ones. As shown in Table 3, the direct three-component

Scheme 1. One-pot synthesis of 7-alkyl-6*H*,7*H*-naphtho[1,2:5,6]pyrano-[3,2-*c*]chromen-6-ones catalyzed by 1-methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride.

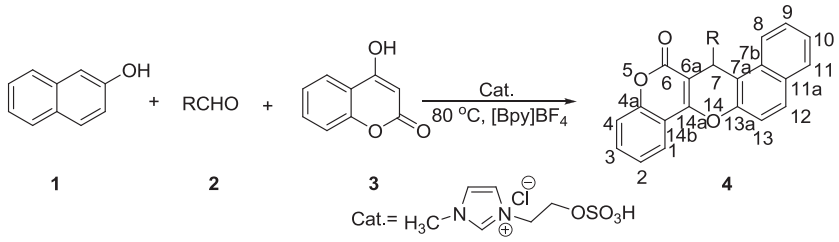


Table 1

Optimization of reaction conditions.[a]

Entry	Solvent	X (mol%)	T (°C)	Yield (%)
1	C_2H_5OH	4	80	30
2	THF	4	66	NP
3	DMF	4	100	42
4	H_2O	4	95	NP
5	Ethyl acetate	4	80	NP
6	$[Bmim]BF_4$	4	80	85
7	[Bpy]Br	4	80	81
8	$[Bpy]BF_4$	4	80	90
9	$[Bpy]BF_4$	4	90	90
10	$[Bpy]BF_4$	4	100	85
11	$[Bpy]BF_4$	4	70	75
12	$[Bpy]BF_4$	4	60	52

[a]All reactions were carried out in the scale of 2.0 mmol of β-naphthol (**1**), 2.0 mmol of aromatic aldehyde (**2**), and 2.0 mmol of 4-hydroxycoumarin (**3**) in 2 h.

Table 2

Optimization of the catalyst for the synthesis of 7-phenyl-6*H*,7*H*-naphtho [1,2:5,6]pyrano[3,2-*c*]chromen-6-one.[a]

Entry	Catalyst	X (mol%)	Time (h)	Yield (%)
1	H_2SO_4	4	2	14
2	SSA	4	2	31
3	TsOH	4	2	70
4	HCl	4	2	17
5	SiO_2	4	2	NP
6	HOAc	4	2	24
7	MSI	1	2	64
8	MSI	2	2	72
9	MSI	3	2	83
10	MSI	4	2	90
11	MSI	5	2	90
12	MSI	6	2	88

SSA, silica sulfuric acid; MSI, 1-methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride.

[a]All reactions were carried out in the scale of 2.0 mmol of β-naphthol (**1**), 2.0 mmol of aromatic aldehyde (**2**), and 2.0 mmol of 4-hydroxycoumarin (**3**) in 2 h.

reaction worked well with a variety of aromatic aldehydes. The electronic and steric effects of substituents in aromatic aldehydes had no significant effect on the yields. Aromatic aldehydes bearing electron-withdrawing or electron-donating groups such as Me, Cl, F, CN, and NO_2 worked well (Table 3, entries **4d**, **4f**, **4b**, **4j**, and **4p**).

We also investigated the reusability of catalyst together with $[Bpy]BF_4$. The result indicated that the combination of catalyst and solvent was successfully reused for four cycles without significant loss of activity (Table 3, entry **4a**).

The suggested mechanism of the MSI-catalyzed transformations is shown in Scheme 2. The reaction likely proceeds initial formation of ortho-quinone methide **5**. The oxonium species **6** is then formed on reaction with 4-hydroxycoumarin, which then undergoes dehydration to afford the desired product **4**. In β-naphthol, the electron density at the benzylic C-1 position (which is in conjugation with the aromatic ring) is higher than that at the C-3 position. Thus, regioselective formation of the ortho-quinone methide from this compound involving the C-1 and C-2 positions is favored. In simple phenolic compounds and 1-naphthol (which are weaker nucleophiles compared with β-naphthol), the electron density at the ortho-position of the hydroxyl group is not sufficient for the reaction of these compounds with the aldehydes, leading to the formation of the corresponding ortho-quinone methides.

In summary, an efficient protocol for one-pot preparation of 7-alkyl-6*H*,7*H*-naphtho[1,2:5,6]pyrano[3,2-*c*]chromen-6-ones by three-component condensation reaction of β-naphthol (**1**), aromatic aldehydes (**2**), and 4-hydroxycoumarin (**3**) using MSI as catalyst is described; 19 products were synthesized. The reactions were carried out under $[Bpy]BF_4$ in short reaction time and produced the corresponding products in good to excellent yields. Also, the $[Bpy]BF_4$ and MSI could be successfully recovered and recycled at least for three runs without significant loss in activity.

EXPERIMENTAL

General information. Commercial solvents and reagents were used as received. Melting points are uncorrected. IR spectra were recorded on Varian F-1000 spectrometer in KBr with absorptions in cm^{-1}. ^1H NMR were determined on Varian 400-MHz spectrometer in DMSO-d_6 (J values are in Hz). Chemical shifts are expressed in parts per million downfield from internal standard TMS.

The synthesis of methyl-3-(2-(sulfooxy)ethyl)-1*H*-imidazol-3-ium chloride was followed by literature method [16].

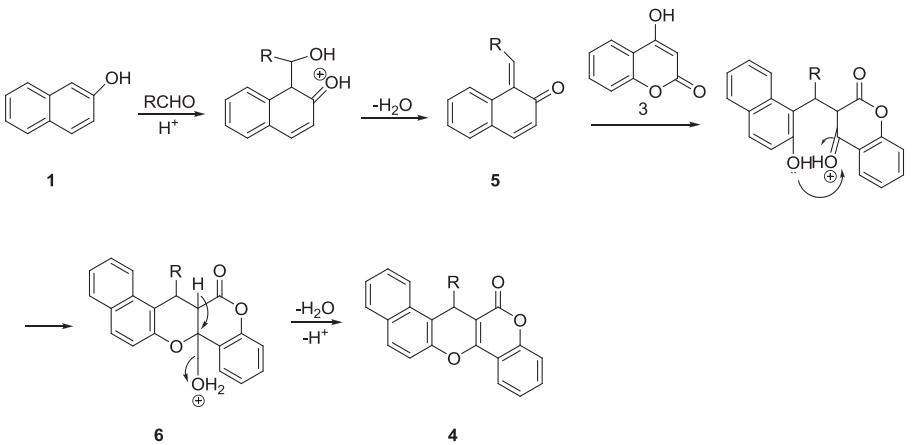
Table 3

Preparation of 7-alkyl-6*H*,7*H*-naphtho[1,2:5,6]pyrano-[3,2-*c*]chromen-6-one.[a]

Entry	R	Time (h)	Yield (%)	Mp (°C)	
				Found	Reported
4a	C_6H_5	2	90(90, 90, 89)[b]	199–200	281–282 [17]
4b	3-FC_6H_4	2	87	216–217	
4c	4-OH-3-$NO_2C_6H_3$	2	89	298–299	
4d	2,3-$(CH_3)_2C_6H_3$	2	90	267–268	
4e	2,3-$(OCH_3)_2C_6H_3$	3	88	266–267	
4f	2,4-$Cl_2C_6H_4$	2	86	239–240	267–268 [17]
4g	3,4,5-$(OCH_3)_3C_6H_2$	3	84	196–197	
4h	4-BrC_6H_4	2	88	281–282	
4i	4-ClC_6H_4	2	90	262–263	267–268 [17]
4j	4-CNC_6H_4	1	91	241–242	
4k	4-IC_6H_4	1	92	282–283	
4l	4-$CHOC_6H_4$	3	85	242–243	
4m	4-$OCH_3C_6H_4$	2	90	211–212	
4n	4-FC_6H_4	2	91	245–246	253–254 [17]
4o	3-BrC_6H_4	2	90	206–207	
4p	3-$NO_2C_6H_4$	1	87	237–238	249–250 [17]
4q	2-ClC_6H_4	1	85	240–241	
4r	2-$OCH_3C_6H_4$	2	91	211–212	
4s	4-OHC_6H_4	3	90	299–300	

[a]All reactions were carried out in the scale of 2.0 mmol of β-naphthol (**1**), 2.0 mmol of aromatic aldehyde (**2**), and 2.0 mmol of 4-hydroxycoumarin (**3**).
[b]Yields after recovery of $[Bpy]BF_4$.

Scheme 2. Proposed mechanism for the synthesis of 7-alkyl-6*H*,7*H*-naphtho[10,20:5,6]pyrano-[3,2-*c*]chromen-6-one.



Procedure for the synthesis of 7-alkyl-6*H*,7*H*-naphtho [1,2:5,6]pyrano[3,2-*c*]chromen-6-ones. A mixture of aldehyde (2 mmol), β-naphthol (2 mmol), 4-hydroxycoumarin (2 mmol), ionic liquid $[Bpy]BF_4$ (2 mL), and MSI (0.06 mmol) was stirred at 80°C for 1–3 h (monitored by TLC). The resulting solid was washed with water and dried in vacuum. The crude product was purified by recrystallization from ethanol and DMF to give target products.

The spectral data of new products are given as follows.

7-(3-Fluorophenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c] chromen-6-ones (4b). mp 216–217°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (t, J = 7.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.34–7.42 (m, 2H), 7.24–7.34 (m, 4H), 7.09–7.15 (m, 2H), 6.58 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.64, 162.41, 162.28, 152.32, 151.98, 141.08, 133.89, 132.01, 130.46, 128.96, 128.80, 128.65, 127.90, 127.16, 126.59, 123.89, 123.51, 123.23, 122.78, 122.60, 118.70, 116.12, 112.54, 98.65, 35.67; IR (KBr, ν, cm^{-1}): 3023, 2938, 1680, 1605, 1533, 1436, 1374, 1246, 1026, 942, 806, 739; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{26}H_{15}FO_3$: 395.1101; found: 395.1161.

7-(4-Hydroxy-3-nitrophenyl)-6H,7H-naphtho[1,2:5,6]pyrano [3,2-c]chromen-6-ones(4c). mp 298–299°C, yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.84 (s, 1H), 7.98–8.11 (m, 5H), 7.82 (t, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.49–7.57 (m, 4H), 6.96 (d, J = 8.8 Hz, 1H), 6.01 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.01, 165.09, 164.71, 152.16, 148.50, 147.08, 132.16, 131.82, 123.83, 123.72, 118.84, 117.90,

115.94, 111.57, 111.32, 104.38, 99.10, 35.59; IR (KBr, ν, cm^{-1}): 3123, 3042, 1716, 1640, 1572, 1468, 1304, 1277, 1071, 926, 834, 744, 674; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{26}H_{15}NO_6$: 438.1069; found: 438.1057.

7-(2,3-Dimethylphenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4d). mp 267–268°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 9.2 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.31–7.36 (m, 2H), 7.09 (d, J = 8.8 Hz, 1H), 7.02–7.04 (m, 3H), 6.59 (s, 1H), 2.18 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 176.73, 162.95, 151.80, 139.13, 136.45, 134.11, 133.69, 132.19, 129.09, 128.77, 127.89, 126.93, 125.22, 124.06, 123.35, 122.94, 122.60, 119.34, 118.40, 116.15, 116.07, 112.72, 105.59, 98.79, 36.08, 20.40, 15.04; IR (KBr, ν, cm^{-1}): 3058, 3027, 1689, 1630, 1573, 1539, 1488, 1344, 1271, 1075, 942, 819, 754; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{28}H_{20}O_3$: 404.1410; found: 404.1414.

7-(2,3-Dimethoxyphenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4e). mp 266–267°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (s, 1H), 8.36 (d, J = 7.6 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.93–7.98 (m, 3H), 7.71 (t, J = 7.2 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.44–7.53 (m, 4H), 6.81 (d, J = 7.6 Hz, 1H), 5.97 (s, 1H), 3.70 (s, 3H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.37, 162.59, 152.49, 146.72, 143.28, 134.20, 131.43, 131.14, 130.59, 130.18, 130.06, 128.72, 127.62, 125.78, 125.58, 125.03, 123.73, 119.74, 117.83, 116.76, 116.48, 112.72, 98.93, 56.86, 55.26, 35.21; IR (KBr, ν, cm^{-1}): 3012, 2932, 1716, 1651, 1576, 1483, 1372, 1251, 1035, 932, 818, 759, 660; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{28}H_{20}O_5$: 437.1344; found: 437.1354.

7-(3,4,5-Trimethoxyphenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4g). mp 196–197°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (t, J = 8.0 Hz, 2H), 8.07 (d, J = 9.2 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.72–7.77 (m, 2H), 7.48–7.56 (m, 4H), 6.67 (d, J = 9.6 Hz, 2H), 5.78 (s, 1H), 3.64 (s, 6H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.58, 159.60, 152.53, 147.62, 146.87, 145.76, 135.06, 134.24, 131.45, 130.45, 129.76, 128.76, 127.79, 125.79, 123.75, 122.97, 121.81, 117.83, 116.79, 115.78, 98.49, 56.88, 56.34, 56.25, 35.89; IR (KBr, ν, cm^{-1}): 3080, 2958, 1721, 1646, 1573, 1465, 1304, 1265, 1067, 923, 842, 755, 686; HRMS (ESI) *m/z*: Calcd for $[M+Na]^+$ $C_{29}H_{22}O_6$: 489.1416; found: 489.1406.

7-(4-Bromophenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4h). mp 281–282°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.18 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.84–7.89 (m, 2H), 7.66 (t, J = 8.0 Hz, 1H), 7.45–7.52 (m, 4H), 7.40 (t, J = 7.6 Hz, 1H), 7.30–7.36 (m, 4H), 6.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.50, 159.62, 152.51, 149.14, 146.78, 134.26, 132.23, 131.43, 130.31, 129.50, 128.75, 127.71, 125.82, 125.02, 123.66, 122.44, 118.55, 117.84, 116.79, 115.87, 109.50, 98.46, 35.69; IR (KBr, ν, cm^{-1}): 3058, 3027, 1692, 1634, 1554, 1482, 1361, 1259, 1027, 966, 875, 776; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{26}H_{15}BrO_3$: 454.0205; found: 454.0212.

7-(4-Cyanophenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4j). mp 241–242°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.07 (t, J = 8.8 Hz, 2H), 8.01 (t J = 8.4 Hz, 2H), 7.83 (t, J = 8.0 Hz, 1H), 7.64–7.83 (m, 6H), 7.49–7.57 (m, 3H), 6.11 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.89, 158.63, 152.55, 147.63, 146.88, 145.77, 135.07, 134.26, 131.46, 130.08, 129.77, 128.77, 127.80, 125.81, 125.05, 123.77, 122.98, 122.07, 121.82, 117.85, 116.81, 115.80, 112.76, 98.51, 35.33; IR (KBr, *v*, cm^{-1}): 3023, 2229, 1680, 1617, 1571, 1466, 1264, 1171, 1070, 926, 810, 761, 685; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{27}H_{15}NO_3$: 402.1167; found: 402.1178.

7-(4-Iodophenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4k). mp 282–283°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98–8.06 (m, 4H), 7.82 (t, J = 8.4 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.48–7.57 (m, 5H), 7.24 (d, J = 8.0 Hz, 2H), 5.95 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.51, 159.37, 152.64, 146.26, 143.37, 134.49, 131.25, 130.20, 129.66, 128.17, 128.11, 127.58, 126.72, 125.89, 125.01, 123.43, 122.87, 117.41, 116.73, 101.43, 98.34; IR (KBr, ν, cm^{-1}): 3077, 3042, 1715, 1640, 1571, 1468, 1304, 1276, 1005, 926, 815, 754, 674; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{26}H_{15}IO_3$: 503.0219; found: 503.0229.

7-(4-Formylphenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4l). mp 242–243°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 8.07–8.10 (m, 2H), 8.00 (t, J = 8.4 Hz, 2H), 7.82 (t, J = 8.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 3H), 7.65–7.71 (m, 3H), 7.48–7.56 (m, 3H), 6.10 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.50, 159.47, 152.47, 146.69, 143.70, 136.99, 134.18, 131.41, 130.73, 130.18, 130.03, 128.71, 127.60, 125.77, 125.56, 125.02, 123.70, 122.50, 117.82, 116.74, 116.44, 98.92, 92.69, 35.12; IR (KBr, ν, cm^{-1}): 3031, 1698, 1638, 1573, 1466, 1304, 1235, 1071, 926, 819, 748, 687; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{27}H_{16}O_4$: 405.1170; found: 405.1189.

7-(4-Methoxyphenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4m). mp 211–212°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 8.0 Hz, 1H), 7.98–8.05 (m, 3H), 7.80 (t, J = 8.4 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.48–7.55 (m, 3H), 7.32 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 5.94 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.51, 159.57, 152.38, 146.65, 143.75, 137.02, 134.81, 131.93, 131.13, 130.22, 130.04, 128.61, 127.62, 126.77, 125.76, 125.03, 123.74, 122.55, 117.61, 116.47, 116.12, 101.87, 99.56, 35.62; IR (KBr, ν, cm^{-1}): 3074, 1708, 1632, 1510, 1408, 1304 1264, 1032, 923, 812, 753, 686; HRMS (ESI) *m/z*: Calcd for $[M+Na]^+$ $C_{27}H_{18}O_4$: 429.1160; found: 429.1162.

7-(3-Bromophenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4o). mp 206–207°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.05–8.11 (m, 3H), 8.01 (t, J = 8.4 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.70 (t, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 7.18 (t, J = 8.4 Hz, 1H), 6.02 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.97, 156.02, 153.22, 147.45, 144.07, 135.10, 131.41, 129.61, 128.26, 127.72, 126.87, 125.30, 125.09, 123.79, 122.82, 118.18, 117.53, 116.46, 101.75, 35.89; IR (KBr, ν, cm^{-1}): 3067, 1711, 1644, 1568, 1461, 1265, 1066, 926, 808, 742, 684; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{26}H_{15}BrO_3$: 454.0215; found: 454.0232.

7-(2-Chlorophenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4q). mp 240–241°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, J = 8.4 Hz, 2H), 7.76–7.87 (m, 3H), 7.68 (d, J = 8.0 Hz, 1H), 7.47–7.54 (m, 3H), 7.39 (d, J = 7.6 Hz, 1H), 7.31–7.36 (m, 3H), 7.23 (t, J = 8.8 Hz, 1H), 6.34 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.20, 165.64, 162.28, 156.39, 152.96, 149.09, 142.38, 140.25, 135.61, 133.58, 131.11, 130.54, 129.00, 128.71, 127.38, 126.60, 125.89, 123.72, 122.52, 121.44, 116.13, 112.99, 99.86, 35.22; IR (KBr, ν, cm^{-1}): 3071, 1711, 1639, 1573, 1466, 1352, 1237, 1072, 983, 827, 759, 683; HRMS (ESI) *m/z*: Calcd for $[M+H]^+$ $C_{26}H_{15}ClO_3$: 411.0850; found: 411.0855.

7-(2-Methoxyphenyl)-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4r). mp 211–212°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.60 (t, J = 8.4 Hz, 1H), 7.37–7.44 (m, 2H), 7.27–7.34 (m, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 8.8 Hz, 1H), 6.68 (s, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.73, 159.77, 156.21, 152.48, 146.57, 143.36, 137.10, 134.49, 131.35, 130.25, 130.00, 128.14, 127.29, 125.33, 125.12, 125.02, 123.64, 122.32, 117.08, 116.84, 116.61, 112.49, 98.89, 35.80; IR (KBr, ν, cm^{-1}): 3023, 2939, 1681, 1632, 1578, 1489, 1388, 1251, 1032, 949, 819, 755; HRMS (ESI) *m/z*: Calcd for $[M + Na]^+$ $C_{27}H_{18}O_4$: 429.1168; found: 429.1160.

7-(4-Hydroxyphenyl-6H,7H-naphtho[1,2:5,6]pyrano[3,2-c]chromen-6-ones(4s). mp 299–300°C, white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.29 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.08 (t. J = 8.0 Hz, 2H), 8.02 (d, J = 8.0 Hz, 3H), 7.97 (d, J = 8.0 Hz, 3H), 7.81 (t, J = 8.0 Hz, 1H), 7.69–7.73 (m, 3H), 7.61 (d, J = 9.2 Hz, 1H), 5.88 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.03, 162.41, 156.28, 152.32, 151.98, 149.08, 140.63, 140.11, 135.27, 131.52, 131.01, 130.87, 130.13, 128.57, 128.13, 127.29, 126.88, 123.72, 123.03, 122.82, 118.91, 116.12, 112.53, 98.76, 35.46; IR (KBr, ν, cm^{-1}): 3293, 3023, 1712, 1648, 1562, 1467, 1311, 1226, 1051, 918, 835, 756, 690; HRMS (ESI) *m/z*: Calcd for $[M + H]^+$ $C_{26}H_{16}O_4$: 393.1178; found: 393.1188.

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