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Rh-Catalyzed Cyclization of 3-Aryloxycarbonyldiazonaphthoquinones for the Synthesis of β-Phenylnaphthalene Lactones and Formal Synthesis of Pradimicinone

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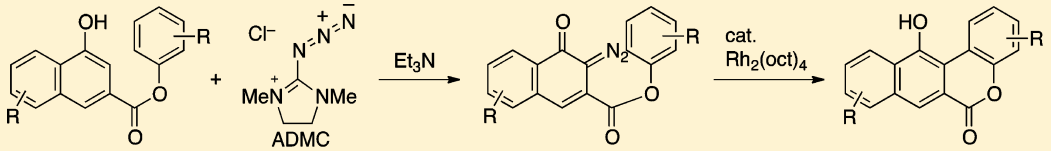
Supporting Information



ABSTRACT: In this study, we developed a novel method for the synthesis of β-phenylnaphthalene lactones. The diazo-transfer reactions of 2-azido-1,3-dimethylimidazolinium chlorides to 3-aryloxycarbonyl-1-naphthols proceeded smoothly to give corresponding 3-aryloxycarbonyldiazonaphthoquinones in high yields. These intermediates were further transformed to β-phenylnaphthalene lactones through a Rh-catalyzed intramolecular formal C−H insertion reaction. This method of lactone formation was efficiently applied to the formal total synthesis of pradimicinone.

Rh(II)-catalyzed intramolecular C−H insertion reactions are an efficient synthetic method for the formation of 5-membered carbocyclic/heterocyclic compounds.[1] In the particular case of diazocarbonyl compounds that do not have the required C−H bond for the formation of 5-membered rings, the various formed products are dependent on the reaction conditions and substrates. For example, the Rh-catalyzed reactions of *N*-benzyl-2-diazoacetamides give either a 4-membered C−H insertion product or a 7-membered ring product. These reactions proceed through aromatic cyclo-addition and a successive expansion of a phenyl ring (Büchner reaction).[2] The formation of a 6-membered formal C−H insertion product has also been reported for the Rh-catalyzed reaction of 1-diazo-4-aryl-2-butanone via the Büchner reaction intermediate.[3]

β-Phenylnaphthalene lactones (6*H*-benzo[*b*]naphtho[2,3-*d*]-pyran-6-one derivatives and 5*H*-benzo[*d*]naphtho[2,3-*b*]pyran-5-one derivatives) are often found in bioactive natural products (Figure 1).[4] These compounds are widely used as intermediates for the synthesis of natural products such as polyketides and biaryl compounds.[5−7] Although several synthetic methods have been reported for the formation of β-phenylnaphthalene lactones,[8] the most efficient method involves the Pd-catalyzed intramolecular biaryl coupling of halogenated aryl carboxylic acid aryl esters.[9] This reaction is even applicable for the formation of bulky ortho-tetra-substituted biaryl bonds. However, this method can occasionally encounter several problems such as a limited accessibility of starting haloaryl compounds, the reproducibility of the reaction, and the harsh, high-temperature reaction conditions.

Herein, we report a new synthetic method for the formation of β-phenylnaphthalene lactones **2** via a Rh-catalyzed intramolecular 6-membered cyclization of 3-aryloxycarbonyl-2-diazonaphthoquinones **1** (Scheme 1). We also address the application of this synthetic methodology to the formal synthesis of pradimicinone.

Diazonaphthoquinones **1** were readily prepared from the corresponding naphthols **3** through a regioselective, one-step

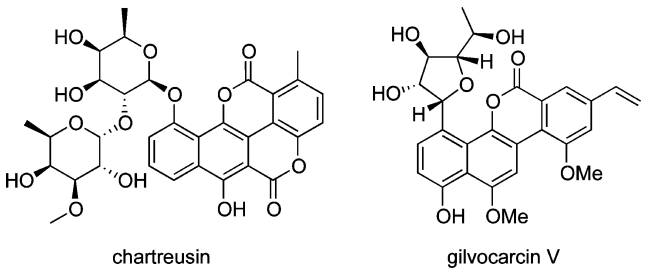
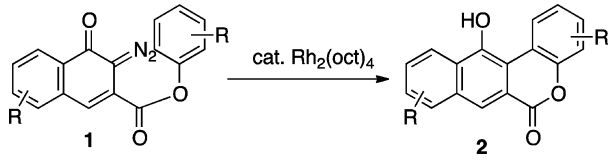


Figure 1. Natural products with the β-phenylnaphthalene lactone.

Scheme 1. Rh-Catalyzed Synthesis of β-Phenylnaphthalene Lactone 2 from 3-Aryloxycarbonyldiazonaphthoquinone 1



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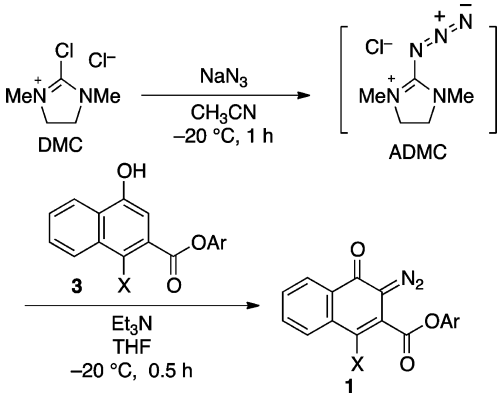
reaction. This was accomplished using our recently developed diazo-transfer method with 2-azido-1,3-dimethylimidazolinium chloride (ADMC), which was prepared by reacting 2-chloro-1,3-dimethylimidazolinium chloride (DMC) and sodium azide (Table 1).[10,11] We reported that the addition of 15-crown-5

Table 1. Synthesis of Diazonaphthoquinones 1 from 1-Naphthols 3 by Diazo-Transfer with ADMC[a]



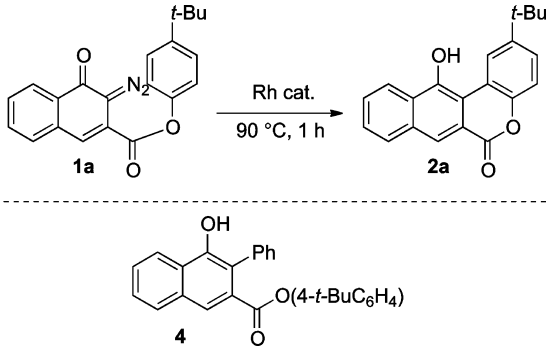
run	Ar	X	3	1	yield (%)
1	4-*t*-BuC_6H_4	H	**3a**	**1a**	92
2	Ph	H	**3b**	**1b**	97
3	4-MeC_6H_4	H	**3c**	**1c**	97
4	4-MeOC_6H_4	H	**3d**	**1d**	quant
5	4-ClC_6H_4	H	**3e**	**1e**	quant
6	4-*s*-BuC_6H_4	H	**3f**	**1f**	86
7	3-MeC_6H_4	H	**3g**	**1g**	79
8	3-MeOC_6H_4	H	**3h**	**1h**	94
9	3-ClC_6H_4	H	**3i**	**1i**	84
10	2-MeC_6H_4	H	**3j**	**1j**	97
11	2-MeOC_6H_4	H	**3k**	**1k**	97
12	2-ClC_6H_4	H	**3l**	**1l**	79
13	2-CO_2MeC_6H_4	H	**3m**	**1m**	83
14	3,5-$(MeO)_2C_6H_3$	H	**3n**	**1n**	97
15	1-naphthyl	H	**3o**	**1o**	47
16	Ph	Me	**3p**	**1p**	93
17	Ph	Ph	**3q**	**1q**	85
18	Ph	MeO	**3r**	**1r**	94

[a]Reaction conditions: **3** and Et_3N (2 equiv) were added to a solution of ADMC [prepared by the reaction between DMC (1.9 equiv) and NaN_3 (1.6 equiv) in CH_3CN at −20 °C for 1 h].

efficiently increases both the yield of the diazo-transfer products and reaction rate for the diazo-transfer conversion of ADMC to naphthols. Although all 1-naphthols were originally believed to be suitable for the diazo-transfer reaction in the presence of 15-crown-5, 1-naphthols **3** presented in Table 1 were efficiently transformed to their corresponding diazonaphthoquinones **1** in high yields without 15-crown-5.

Initially, the Rh-catalyzed reactions were examined with diazonaphthoquinone **1a** under several reaction conditions (Table 2).[12] When the reaction was performed in the presence of 3 mol % $Rh_2(OAc)_4$ in benzene (0.1 M for **1a**) at reflux (90 °C as bath temperature), **1a** was consumed after 1 h to give **2a** with a 53% yield (run 1). A lower concentration of **1a** increases the yield of **2a** (runs 1−4), and **2a** was obtained in 79% at 0.01 M (run 4). Nonpolar solvents were particularly suitable for these reactions (runs 4−9), and benzene was determined to give the best results (run 4). The amount of $Rh_2(OAc)_4$ could

Table 2. Rh-Catalyzed Cyclization of 3-Aryloxycarbonyl-2-diazonaphthoquinone 1a[a]



run	Rh cat. (mol %)	solvent	conc[b] (M)	**2a** (%)
1	$Rh_2(OAc)_4$ (3)	benzene	0.1	53
2	$Rh_2(OAc)_4$ (3)	benzene	0.06	63
3	$Rh_2(OAc)_4$ (3)	benzene	0.03	72
4	$Rh_2(OAc)_4$ (3)	benzene	0.01	79
5	$Rh_2(OAc)_4$ (3)	$(ClCH_2)_2$	0.01	63
6[c]	$Rh_2(OAc)_4$ (3)	toluene	0.01	75
7	$Rh_2(OAc)_4$ (3)	MeCN	0.01	0[d]
8	$Rh_2(OAc)_4$ (3)	DMF	0.01	0[e]
9	$Rh_2(OAc)_4$ (3)	THF	0.01	0[f]
10	$Rh_2(OAc)_4$ (1.5)	benzene	0.01	77
11	$Rh_2(oct)_4$ (1.5)[g]	benzene	0.01	92
12	$Rh_2(OCOCF_3)_4$ (1.5)	benzene	0.01	5[h]

[a]The reaction was performed at 90 °C as the bath temperature. [b]Concentration of **1a**. [c]The reaction was performed at 110 °C. [d]**1a** was recovered in 74% yield. [e]**1a** was recovered in 91% yield. [f]**1a** was recovered in 89% yield. [g]$Rh_2(OCOC_7H_{15})_4$. [h]**4** was obtained in 46% yield.

be reduced to 1.5 mol % without affecting the yield of **2a** (77%, Run 10). The yield of **2a** further increased to 92% when $Rh_2(oct)_4$ was substituted for $Rh_2(OAc)_4$. Intermolecular C−H insertion product **4** for benzene was mainly formed when $Rh_2(OCOCF)_3$ was used (run 12).

To explore the scope of the intramolecular cyclization of 3-aryloxycarbonyldiazonaphthoquinone **1**, we subjected various diazonaphthoquinones **1** to optimized reaction conditions [1.5 mol % $Rh_2(oct)_4$ in benzene (0.01 M for **1**) at reflux] (Table 3).

Phenyl ester **1b** and para-monosubstituted phenyl esters **1c**−**1f** gave their corresponding cyclic compounds **2b**−**2f** in good yields. In the case of meta-monosubstituted phenyl esters **1g**−**1i** that have two potential reaction sites for the formation of a 6-membered ring, the C−C bond cyclization is favored at the para position of the substituent R. This selectivity is because of steric hindrance, which mainly affords **2g**−**2i** with a small amount of regioisomers **2′g** and **2′h** for the reactions of **1g** and **1h**, respectively. In the series of ortho-monosubstituted phenyl esters **1j**−**1m**, the generated products are dependent on the ortho-substituent R. Cyclized products were obtained from both **1j** (R = Me) and **1k** (R = CO_2Me). Although **1l** (R = OMe) and **1m** (R = Cl) were consumed in the reaction conditions, no cyclized products were obtained. *meta*-Dimethoxyphenyl ester **1n** cyclized to **2n** with a high yield. Binaphthyl lactone **2o** was obtained from 3-(1-naphthyl)-oxycarbonyldiazonaphthoquinone **1o** with a 47% yield.

The introduction of a methyl, phenyl, or methoxy substituent at the 4-position to 3-aryloxycarbonyl-2-diazonaphthoquinone

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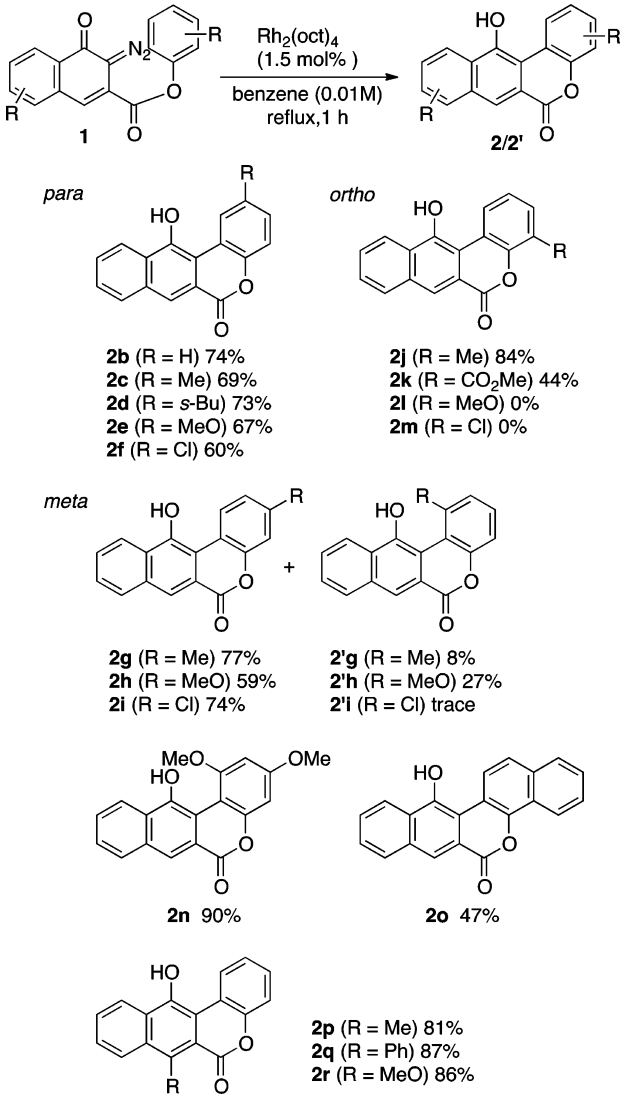
Table 3. Rh-Catalyzed Cyclization of Various 3-Aryloxycarbonyldiazonaphthoquinones 1[a]



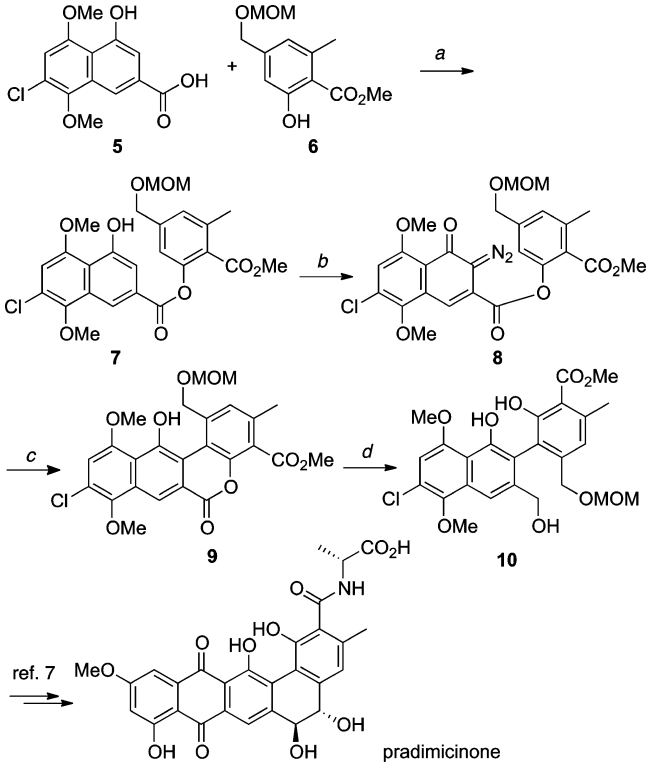
[a]Reaction conditions: **1** (0.3 mmol), $Rh_2(oct)_4$ (1.5 mol %) in benzene (30 mL) at reflux for 1 h.

1 efficiently yielded the cyclized products, and **2p**−**2r** were obtained in high yields from their corresponding 4-substituted diazonaphthoquinones **1p**−**1r**.

To demonstrate the efficiency of our newly developed methodology for lactone formation, we addressed the synthesis of a natural product. We previously achieved the synthesis of pradimicinone via biaryl lactone **9** and diol **10**.[7] We then attempted the synthesis of these intermediates with our newly developed reaction sequence, which involves the diazo-transfer reaction and Rh-catalyzed lactone formation (Scheme 2).

Polysubstituted ester **7** was synthesized through a condensation reaction of carboxylic acid **5** with phenol **6**. The diazo-transfer reaction of ADMC to polysubstituted 1-naphthol **7** afforded diazonaphthoquinone **8**. As shown in Table 1, the diazo-transfer reaction to **1** proceeded smoothly in the absence of 15-crown-5, but the addition of 15-crown-5 at a low temperature was essential for the diazo-transfer reaction of **7**.[13] The Rh-catalyzed cyclization of **8** and its subsequent reduction from lactone **9** successfully afforded triol **10**. Because diazo-transfer product **8** and lactone **9** were rather unstable, their

Scheme 2. Formal Synthesis of Pradimicinone[a]



[a]Reaction conditions: (*a*) 1-Ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDCl), *N*,*N*-dimethyl-4-aminopyridine, CH_2Cl_2, rt, 2 h (51%). (*b*) DMC (4.5 equiv), NaN_3 (4.4 equiv), 15-crown-5 (30 mol %), CH_3CN, −20 °C, 1 h: then **7**, Et_3N (2 equiv), THF, −30 °C, 6 h. (*c*) $Rh_2(oct)_4$ (1.5 mol %), benzene, reflux, 2.5 h. (*d*) $NaBH_4$ (4.0 equiv), THF, MeOH, −45 °C, 4 h (3 steps 55%).

following transformations were conducted without further purification of these compounds. In summary, triol **10** was obtained with a 55% yield in 3 steps from 1-naphthol **7**.

The plausible reaction mechanism for the Rh-catalyzed cyclization of 3-aryl-2-diazonaphthoquinones **1** is shown in Scheme 3. In the first step, the Rh(II) catalyst reacts with **1** to form rhodium−carbene complex **I**, which can then form lactone **2** via intermediate **II**. Intermediate **II** may be formed via Büchner reaction intermediates **III** and/or **IV** or a direct intramolecular C−H insertion reaction of **I**.[14,15] No formation of cyclized product **2** from ortho-substituted **1l** (R = OMe) and **1m** (R = Cl) could be attributed to the formation of rhodium ylide **I′** and the successive decomposition.[16]

We developed an efficient method for the synthesis of *β*-phenylnaphthalene lactones from 3-aryloxycarbonyl-1-naphthols through a 2-step synthetic sequence that involves a (i) diazo-transfer reaction with ADMC and (ii) Rh-catalyzed cyclization of diazonaphthoquinones. This methodology can be applied to the formal total synthesis of pradimicinone, which demonstrates the wide applicability of our methodology for polysubstituted substrates.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under a nitrogen or argon atmosphere. NMR spectra were recorded in $CDCl_3$ [TMS (for ^1H, δ = 0) or $CDCl_3$ (for ^{13}C, δ = 77.0) was used as an internal standard] or DMSO-d_6 [TMS (for ^1H, δ = 0), DMSO (for ^1H, δ = 2.5), or DMSO (for ^{13}C, δ = 40.0) was used as an internal standard]. High-resolution mass spectra (HRMS) were obtained by an electron

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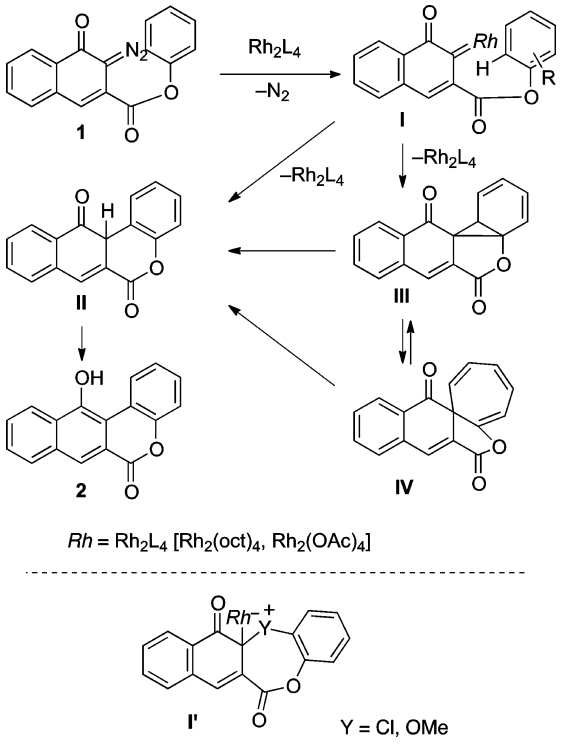
Scheme 3. Possible Reaction Mechanism



ionization (EI) method of ionization with a double focusing sector detector. Column chromatography was performed on silica gel.

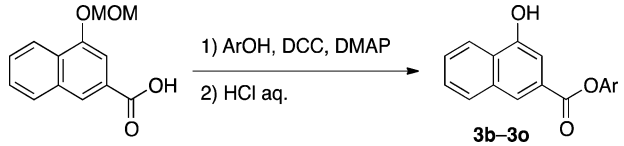
Materials. Benzene was distilled from P_2O_5 and stored over 4A molecular sieves. $Rh_2(OAc)_4$ and $Rh_2(oct)_4$ were purchased from suppliers and were used as received. Sodium azide was purchased from a supplier and was used as received. Triethylamine was distilled from KOH and stored over KOH.

*4-(tert-Butyl)phenyl 4-Hydroxy-2-naphthalenecarboxylate (**3a**).* To a solution of potassium carbonate (30.9 g, 224 mmol) and methyl 4-hydroxy-2-naphthalenecarboxylate (14.7 g, 146 mmol) in acetone (110 mL), chloromehtyl methyl ether (11.8 g, 146 mmol) was added at 0 °C, and the mixture was stirred for 2 h at room temperature. The mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 9/1) to give methyl 4-methoxymethyl-2-naphthalencarboxylate (20.3 g) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30–8.28 (m, 1H), 8.28 (d, 1H, J = 1.0 Hz), 7.92 (d, 1H, J = 7.7, 1.5 Hz), 7.64 (d, 1H, J = 8.3, 6.9, 1.4 Hz), 7.55 (ddd, 1H, J = 8.2, 6.8, 1.3 Hz), 5.45 (s, 2H), 3.97 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 152.8, 133.5, 129.1, 128.1, 127.7, 127.6, 127.0, 124.6, 122.0, 106.6, 94.7, 56.4, 52.2 ppm.

To a solution of methyl 4-methoxymethyl-2-naphthalencarboxylate (20.3 g, 82.3 mmol) in methanol (50 mL), potassium hydroxide (10.8 g, 166 mmol) was added at room temperature, and the mixture was stirred for 0.5 h at 80 °C. After cooling to 0 °C, the mixture was acidified with 2 N HCl. The precipitates were collected by filtration to afford crude compounds. The crude materials were purified by recrystallization (hexane/ethyl) to give 4-methoxymethyl-2-naphthalenecarboxylic acid (14.8 g, 78% yield) as a white solid. IR (KBr) 3457, 2950, 1684, 1580, 1463, 1426, 1371, 1303, 1155, 1057 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.32 (dd, 1H, J = 8.1, 0.7 Hz), 7.96 (dd, 1H, J = 7.4, 1.2 Hz), 7.70 (d, 1H, J = 1.3 Hz), 7.63 (ddd, 1H, J = 8.2, 6.8, 1.4 Hz), 7.58 (ddd, 1H, J = 8.1, 6.9, 1.3 Hz), 5.48 (s, 2H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 153.0, 133.4, 129.3, 128.6, 128.1, 127.2, 126.7, 125.7, 122.1, 106.7, 94.8, 56.5 ppm. To a solution of 4-*tert*-butylphenol (1.33 g, 8.84 mmol), 4-methoxymethyl-2-naphthalenecarboxylic acid (1.86 g, 8.00 mmol), and *N,N*-dimethyl-4-aminopyridine (DMAP) (44 mg, 0.36 mmol) in dichloromethane (15 mL), *N,N′*-dicyclohexylcarbodiimide (1.91g, 9.27 mmol) was added at 0 °C, and the mixture was stirred for 1.5 h at room temperature. The mixture was filtered, and the solvent was removed *in vacuo*. The crude materials were purified by recrystallization (hexane/ethyl acetate) to give 4-methoxymethyl-2-naphthalenecarboxylic-4-(*tert*-butyl)phenyl ester (2.16 g, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.33 (dd, 1H, J = 8.3, 0.7 Hz), 7.97 (dd, 1H, J = 7.4, 1.1 Hz), 7.75 (d, 1H, J = 1.4 Hz), 7.64 (ddd, 1H, J = 8.4, 6.9, 1.5 Hz), 7.59 (ddd, 1H, J = 8.1, 6.9, 1.3 Hz), 7.47–7.44 (m, 2H), 7.19–7.17 (m, 2H), 5.48 (s, 2H), 3.57 (s, 3H), 1.35 (s, 9H). To a solution of 4-methoxymethyl-2-naphthalenecarboxylic-4-(*tert*-butyl)phenyl ester (2.16 g, 5.92 mmol) in THF (10 mL), 6 M HCl (5 mL) was added at 50 °C, and the mixture was stirred for 16 h. The mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 13/1) to give naphthol **3a** (1.72 g, 90% yield) as a white solid. IR (KBr) 3393, 2961, 1715, 1698, 1578, 1509, 1401, 1310, 1231, 1092 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.26 (d, 1H, J = 8.3 Hz), 7.96 (d, 1H, J = 7.6 Hz), 7.64 (ddd, 1H, J = 8.3, 6.9, 1.4 Hz), 7.59 (ddd, 1H, J = 8.1, 6.9, 1.2 Hz), 7.54 (d, 1H, J = 1.4 Hz), 7.45 (dt, 2H, J = 8.8, 3.0 Hz), 7.17 (dt, 2H, J = 8.7, 3 Hz), 5.64 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 151.8, 148.8, 148.6, 133.8, 129.3, 127.9, 127.4, 127.0, 126.9, 126.4, 124.6, 122.0, 121.0, 107.7, 34.5, 31.4 ppm. Anal. Found: C, 78.73; H, 6.29%. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29%; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{20}O_3$ 320.1412; found, 320.1408; mp 173–174 °C (dec).

Compounds **3b–3o** were prepared in a manner similar to the preparation of **3a** (Table 4).

Table 4. Preparation of 3b–3o



run	Ar	first step (%)	second step (%)
1	Ph	quant	**3b** 78
2	4-MeC_6H_4	92	**3c** 81
3	4-$MeOC_6H_4$	64	**3d** 57
4	4-ClC_6H_4	91	**3e** 73
5	4-*s*-BuC_6H_4	90	**3f** 72
6	3-MeC_6H_4	quant	**3g** 74
7	3-$MeOC_6H_4$	quant	**3h** 72
8	3-ClC_6H_4	quant	**3i** 72
9	2-MeC_6H_4	quant	**3j** 84
10	2-$MeOC_6H_4$	94	**3k** 86
11	2-ClC_6H_4	quant	**3l** 73
12	2-$CO_2MeC_6H_4$	92	**3m** 68
13	3,5-$(MeO)_2C_6H_3$	90	**3n** 52
14	1-naphthyl	92	**3o** 77

*4-Phenyl 4-Hydroxy-2-naphthalenecarboxylate (**3b**).* White solid (861 mg); IR (KBr) 3369, 1702, 1578, 1401, 1311, 1226, 1189 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.26 (dd, 1H, J = 8.1, 0.3 Hz), 7.96 (d, 1H, J = 7.4, 1.2 Hz), 7.64 (ddd, 1H, J = 8.3, 6.9, 1.4 Hz), 7.59 (ddd, 1H, J = 8.1, 6.9, 1.2 Hz), 7.57 (dd, 1H. J = 1.4 Hz), 7.47–7.43 (m, 2H), 7.31–7.25 (m, 3H), 5.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 152.1, 150.9, 133.7, 129.5, 129.2, 127.9, 127.3, 127.2, 126.7, 126.0, 124.5, 122.1, 121.7, 107.6 ppm. Anal. Found: C, 76.98; H, 4.62%. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58%; mp 169–170 °C (dec).

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*4-Methylphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3c**).* Pale yellow solid (882 mg); IR (KBr) 3441, 1721, 1508, 1402, 1308, 1276, 1221, 1199, 1064 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.25 (d, 1H, J = 8.4 Hz), 7.96 (d, 1H, J = 7.4, 1.2 Hz), 7.64−7.56 (m, 3H), 7.24 (d, 2H, J = 8. Two Hz), 7.13 (dt, 2H, 6.4, J = 2.0 Hz), 5.88 (s, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 152.0, 148.6, 135.6, 133.7, 130.0, 129.2, 127.9, 127.3, 127.1, 126.8, 124.4, 122.1, 121.3, 107.7, 20.9 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{14}O_3$ 278.0943; found, 278.0941; mp 155−156 °C (dec).

*4-Methoxyphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3d**).* White solid (389 mg); IR (KBr) 3375, 1708, 1597, 1579, 1507, 1402, 1311, 1277, 1230, 1197 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.26 (d, 1H, J = 8.4 Hz), 7.96 (d, 1H, J = 7.9 Hz), 7.63 (ddd, 1H, J = 8.3, 6.9, 1.4 Hz), 7.57 (ddd, 1H, J = 8.1, 6.9, 1.2 Hz), 7.55 (d, 1H, J = 1.3 Hz), 7.17 (dt, 2H, J = 9.0, 2.3 Hz), 6.96 (dt, 2H, J = 9.1, 2.3 Hz), 5.81 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 157.3, 151.8, 144.5, 133.8, 129.2, 127.9, 127.4, 127.0, 126.8, 124.6, 122.4, 121.9, 114.6, 107.6, 55.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{14}O_4$ 294.0892; found, 294.0890; mp 184−185 °C (dec).

*4-Chlorophenyl 4-Hydroxy-2-naphthalenecarboxylate (**3e**).* White solid (981 mg); IR (KBr) 3449, 1719, 1489, 1405, 1309, 1282, 1223 cm^{-1}; ^1H NMR (500 MHz, DMSO) δ 10.6 (s, 1H), 8.30 (s, 1H), 8.21 (dd, 1H, J = 7.7, 1.0 Hz), 8.11 (dd, 1H, J = 7.5, 1.6 Hz), 7.65 (ddd, 1H, J = 8.3, 6.8, 1.4 Hz), 7.63 (ddd, 1H, J = 8.3, 6.9, 1.4 Hz), 7.56 (d, 2H, J = 8.8 Hz), 7.48 (d, 1H, J = 1.5 Hz), 7.39 (d, 2H, J = 8.8 Hz); ^{13}C NMR (125 MHz, DMSO) δ 165.2, 154.2, 150.0, 133.9, 130.6, 130.0, 129.7, 128.2, 127.8, 127.6, 126.7, 124.4, 122.8, 122.5, 107.0 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_{11}{}^{35}ClO_3$ 298.0397; found, 298.0399; mp 184−185 °C (dec).

*4-(sec-Butyl)phenyl 4-Hydroxy-2-naphthalenecarboxylate (**3f**).* White solid (778 mg); IR (KBr) 3397, 2963, 1704, 1578, 1508, 1401, 1271, 1228, 1186 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.26 (d, 1H, J = 7.7 Hz), 7.96 (d, 1H, J = 7.6 Hz), 7.63 (ddd, 1H, J = 8.3, 6.9, 1.4 Hz), 7.59 (ddd, 1H, J = 8.1, 6.9, 1.3 Hz), 7.56 (d, 1H, J = 1.4 Hz), 7.25 (d, 2H, J = 7.9 Hz), 7.17 (d, 2H, J = 8.6 Hz), 5.76 (s, 1H), 2.68−2.61 (m, 1H), 1.65−1.58 (m, 2H), 1.26 (d, 3H, J = 6.9 Hz), 0.86 (t, 3H, J = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 152.1, 148.8, 145.4, 133.7, 129.2, 128.0, 127.8, 127.3, 127.1, 126.8, 124.4, 122.1, 121.3, 107.7, 41.1, 31.2, 21.8, 12.2 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{20}O_3$ 320.1412; found, 320.1408; mp 137−138 °C (dec).

*3-Methylphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3g**).* White solid (1.12 g); IR (KBr) 3448, 1722, 1582, 1402, 1307, 1277, 1215, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.26 (d, 1H, J = 8.4 Hz), 7.96 (dd, 1H, J = 7.5, 1.2 Hz), 7.64 (ddd, 1H, J = 8.4, 6.9, 1.6 Hz), 7.59 (ddd, 1H, J = 8.1, 6.9, 1.3 Hz), 7.55 (d, 1H, J = 1.4 Hz), 7.33 (t, 1H, J = 7.7 Hz), 7.10 (d, 1H, J = 8.2 Hz), 7.06−7.04 (m, 2H), 5.78 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 152.1, 150.8, 139.7, 133.7, 129.26, 129.22, 127.8, 127.3, 127.2, 126.8, 126.7, 124.4, 122.2, 122.1, 118.6, 107.6, 21.3 ppm. Anal. Found: C, 77.53; H, 5.12%. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07%; mp 158−159 °C (dec).

*3-Methoxyphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3h**).* White solid (1.09 g); IR (KBr) 3421, 1706, 1583, 1492, 1408, 1308, 1274, 1225, 1138 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.26 (d, 1H, J = 8.5 Hz), 7.96 (d, 1H, J = 8.6 Hz), 7.64 (ddd, 1H, J = 8.3, 6.9, 1.6 Hz), 7.59 (ddd, 1H, J = 8.1, 6.9, 1.4 Hz), 7.55 (d, 1H, J = 1.4 Hz), 7.34 (t, 1H, J = 8.2 Hz), 6.87−6.81 (m, 3H), 5.77 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.2, 160.7, 154.2, 152.2, 133.9, 130.5, 129.7, 128.1, 127.8, 127.5, 127.0, 122.6, 122.5, 114.5, 112.3, 108.4, 107.0, 55.9 ppm. Anal. Found: C, 73.16; H, 4.78%. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79%; mp 145−146 °C (dec).

*3-Chlorophenyl 4-Hydroxy-2-naphthalenecarboxylate (**3i**).* White solid (966 mg); IR (KBr) 3434, 3062, 1703, 1585, 1471, 1404, 1308, 1269, 1066 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.27 (d, 1H, J = 7.6 Hz), 7.96 (d, 1H, J = 7.6 Hz), 7.65 (ddd, 1H, J = 8.2, 6.7, 1.2 Hz), 7.60 (ddd, 1H, J = 8.2, 7.0, 1.2 Hz), 7.51 (d, 1H, J = 1.2 Hz), 7.38 (t, 1H, J = 8.2 Hz), 7.31−7.27 (m, 2H), 7.18−7.16 (m, 1H), 5.76 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 151.9, 151.5, 134.8, 133.8, 130.3, 129.3, 128.2, 127.5, 127.2, 126.3, 126.2, 124.8, 122.4, 122.0, 120.2, 107.5 ppm. Anal. Found: C, 68.40; H, 3.75%. Calcd for $C_{17}H_{11}{}^{35}ClO_3$: C, 68.35; H, 3.71%; mp 178−179 °C (dec).

*2-Methylphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3j**).* Pale yellow solid (887 mg); IR (KBr) 3452, 1715, 1597, 1583, 1403, 1310, 1278, 1228 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.26 (d, 1H, J = 8.4 Hz), 7.97 (d, 1H, J = 7.5, 1.1 Hz), 7.64 (ddd, 1H, J = 8.4, 7.0, 1.6 Hz), 7.61−7.58 (m, 2H), 7.31−7.23 (m, 2H), 7.21−7.16 (m, 2H), 5.84 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 152.2, 149.5, 133.7, 131.2, 130.3, 129.2, 127.9, 127.3, 127.2, 127.0, 126.5, 126.2, 124.4, 122.1, 121.9, 107.7, 16.2 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{14}O_3$ 278.0943; found, 278.0950; mp 152−153 °C (dec).

*2-Methylphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3k**).* Pale yellow solid (919 mg); IR (KBr) 3417, 1719, 1598, 1581, 1505, 1403, 1307, 1282, 1220 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.25 (d, 1H, J = 8.2 Hz), 7.95 (d, 1H, J = 7.7 Hz), 7.64−7.55 (m, 3H), 7.29−7.24 (m, 1H), 7.20 (dd, 1H, J = 3.9, 1.4 Hz), 7.05−6.99 (m, 2H), 5.84 (s, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 152.1, 151.3, 139.9, 133.7, 129.2, 127.8, 127.2, 127.1, 127.0, 126.5, 124.5, 122.9, 122.0, 120.9, 112.5, 107.9, 55.9 ppm. Anal. Found: C, 73.26; H, 4.82%. Calcd for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79%; mp 159−160 °C (dec).

*2-Chlorophenyl 4-Hydroxy-2-naphthalenecarboxylate (**3l**).* White solid (913 mg); IR (KBr) 3445, 1721, 1597, 1581, 1477, 1403, 1309, 1280, 1220, 1067 cm^{-1}; ^1H NMR (500 MHz, DMSO) δ 10.7 (s, 1H), 8.34 (s, 1H), 8.22 (d, 1H, J = 7.9 Hz), 8.13 (d, 1H, J = 7.3 Hz), 7.68−7.62 (m, 3H), 7.53−7.46 (m, 3H), 7.39 (ddd, 1H, J = 7.8, 7.4, 1.7 Hz); ^{13}C NMR (125 MHz,DMSO) δ 164.5, 154.3, 147.3, 133.9, 130.6, 129.8, 129.1, 128.4, 128.3, 127.9, 127.7, 126.4, 126.2, 124.9, 122.9, 122.6, 106.9 ppm. Anal. Found: C, 68.21; H, 3.67%. Calcd for $C_{17}H_{11}{}^{35}ClO_3$: C, 68.35; H, 3.71%; mp 197−198 °C (dec).

*2-Methoxycarbonylphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3m**).* Beige solid (863 mg); IR (KBr) 3405, 3056, 1707, 1604, 1579, 1484, 1404, 1305, 1278, 1226, 1087 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.41(s, 1H), 8.23(d, 1H, J = 8.3 Hz), 8.09(dd, 1H, J = 7.8, 1.7 Hz), 7.95(d, 1H, J = 7.5 Hz), 7.65−7.55(m, 4H), 7.38(ddd, 1H, J = 8.7, 7.7, 1.1 Hz), 7.28 (dd, 1H, J = 8.1, 1.0 Hz), 5.95 (s, 1H), 3.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 165.2, 151.9, 150.8, 133.9, 133.8, 131.9, 129.2, 127.8, 127.2, 127.1, 126.6, 126.1, 124.7, 123.9, 123.4, 122.0, 107.6, 52.3 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{19}H_{14}O_5$ 322.0841; found, 322.0833; mp 169−170 °C (dec).

*3,5-Dimethoxyphenyl 4-Hydroxy-2-naphthalenecarboxylate (**3n**).* White solid (603 mg); IR (KBr) 3425, 1707, 1622, 1590, 1476, 1406, 1305, 1271, 1218, 1191, 1153, 1058 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.26 (d, 1H, J = 8.5 Hz), 7.96 (d, 1H, J = 8.0 Hz), 7.64 (ddd, 1H, J = 8.3, 6.9, 1.5 Hz), 7.59 (ddd, 1H, J = 8.1, 6.9, 1.3 Hz), 7.55 (d, 1H, J = 1.4 Hz), 6.43 (d, 2H, J = 2.2 Hz), 6.40 (t, 1H, J = 2.2 Hz), 5.90 (s, 1H), 3.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.2, 152.4, 152.1, 133.7, 129.2, 127.9, 127.3, 127.1, 126.6, 124.4, 122.2, 107.6, 100.3, 98.5, 55.5 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{19}H_{16}O_5$ 324.0998; found, 324.0993; mp 140−141 °C (dec).

*Naphthalenyl 4-Hydroxy-2-naphthalenecarboxylate (**3o**).* White solid (375 mg); IR (KBr) 3429, 1719, 1404, 1388, 1280, 1218, 1078 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.27 (dd, 1H, J = 8.4, 1.0 Hz), 8.00 (dd, 1H, J = 7.3, 1.3 Hz), 7.96 (dd, 1H, J = 7.9, 1.3 Hz), 7.91 (dd, 1H, J = 7.5, 2.1 Hz), 7.80 (d, 1H, J = 8.3 Hz), 7.66−7.58 (m, 3H), 7.55−7.46 (m, 3H), 7.41 (dd, 1H, J = 7.5, 0.9 Hz), 5.87 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5, 154.3, 146.9, 134.7, 134.0, 129.8, 128.6, 128.3, 127.8, 127.7, 127.4, 127.2, 126.9, 126.7, 126.5, 126.3, 122.9, 122.6, 121.3, 119.2, 107.0 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{14}O_3$ 314.0943; found, 314.0936; mp 195−196 °C (dec);

*Phenyl 4-Hydroxy-1-methyl-2-naphthalenecarboxylate (**3p**).* To a suspention of sodium hydride (60%, dispersion in mineral oil, washed with hexane (4.28 g, 107 mmol)) in toluene (40 mL) was added to dimethyl succinate (18.7 g, 128 mmol) and methanol (39.5 mg, 1.23 mmol) at 0 °C and was sttired for 15 min. A solution of acetophenone (5.15g, 42.8 mmol) in toluene (10 mL) was added at 0

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°C. The reaction mixture was warmed to room temperature, and the stirring was continued overnight. The mixture was poured over ice and stirred for 1 h at room temperature. The organic layer was extracted three times with 1 M K_2CO_3 (aq), and the aqueous layer was washed three times with ethyl acetate. The aqueous layer was acidified with conc. HCl, and the organic layer was extracted three times with ethyl acetate. The combined extracts were washed with water and brine and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. Sodium acetate (7.03 g, 85.7 mmol) and acetic anhydride (100 mL) were added to this crude material at room temperature. The reaction mixture was heated at reflux for 1.5 h. After cooling to room temperature, the reaction was stopped by adding water, and then, the solvent was removed *in vacuo*. The mixture was extracted three times with ethyl acetate. The combined extracts were washed with water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 9/1) to give methyl 4-acetyloxy-1-methyl-2-naphthalenecarboxylate (4.67 g, 42% yield) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24−8.21 (m, 1H), 7.90−7.86 (m, 1H), 7.65 (s, 1H), 7.63−7.59 (m, 2H), 3.94 (s, 3H), 2.94 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 168.1, 144.5, 135.9, 134.0, 128.2, 127.9, 127.1, 127.0, 125.8, 121.5, 118.2, 52.2, 20.9, 15.6 ppm. To a solution of methyl 4-acetyloy-1-methyl-2-naphthalenecarboxylate (513 mg, 1.98 mmol) in methanol (3 mL), potassium hydroxide (454 mg, 8.09 mmol) was added at room temperature, and the mixture was stirred for 2 h at 80 °C. After cooling to room temperature, the mixture was diluted with water and then washed with Et_2O. After the aqueous layer was acidified with 2 M HCl (aq), the organic material was extracted three times with ethyl acetate. The combined extracts were washed with water and brine and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. *N,N*-Dimethyl-4-aminopyridine (24.0 mg, 0.196 mmol), acetic anhydride (604 mg, 5.92 mmol), and pyridine (3 mL) were added to this crude material at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The reaction was quenched with water, and the aqueous layer was acidified with 2 M HCl (aq). The organic materials were extracted three times with ethyl acetate. The combined extracts were washed with water and brine and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: chloroform/methanol = 99/1) to give 4-acetyloxy-1-methyl-2-naphthalenecarboxylic acid (405 mg, 84% yield). ^{1}H NMR (500 MHz, acetone-d_6) δ 11.5 (s, 1H), 8.35−8.31 (m, 1H), 8.03−7.99 (m, 1H), 7.71−7.66 (m, 3H), 2.96 (s, 3H), 2.47 (s, 3H). To a solution of phenol (163 mg, 1.73 mmol), 4-acetyloxy-1-methyl-2-naphthalenecarboxylic acid (404 g, 1.65 mmol) and *N,N*-dimethyl-4-aminopyridine (DMAP) (16.7 mg, 0.136 mmol) in dichloromethane (8 mL), *N,N′*-dicyclohexylcarbodiimide (391 mg, 1.89 mmol) was added at 0 °C, and the mixture was stirred for 1.5 h at room temperature. The mixture was filtered, and the solvent was removed *in vacuo*. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 7/1) to give phenyl 4-acetyloxy-1-methyl-2-naphthalenecarboxylate (452 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17−8.16 (m, 1H), 7.90−7.86 (m, 2H), 7.60−7.54 (m, 2H), 7.42−7.37 (m, 2H), 7.26−7.22 (m, 3H), 2.96 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 165.8, 150.8, 144.7, 137.4, 134.0, 129.4, 128.5, 128.3, 127.2, 126.0, 121.7, 121.5, 120.3, 118.4, 115.1, 20.9, 15.7 ppm. To a solution of phenyl 4-acetyloxy-1-methyl-2-naphthalenecarboxylate (445 mg, 1.39 mmol) in acetone (10 mL), 3 M HCl (5 mL) was added at 70 °C, and the mixture was stirred for 4 h. The mixture was extracted three times with ethyl acetate. The combined extracts were washed with sat. $NaHCO_3$ (aq) and brine and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 13/1) to give naphthol **3p** (346 mg, 89% yield) as a pale yellow solid. IR (KBr) 3394, 1706, 1597, 1491, 1382, 1355, 1287, 1212, 1165, 1143, 1085, 1068; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28−8.25 (m, 1H), 8.21−8.17 (m, 1H), 7.64−7.60 (m, 2H), 7.46−7.42 (m, 3H), 7.41 (s, 1H), 7.30−7.27 (m, 1H), 7.24 (dd, 1H, J = 7.5, 2.0 Hz), 5.50 (s, 1H), 2.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 150.9, 149.5, 134.2, 131.2, 129.5, 127.17, 127.15, 126.4, 126.1, 125.9, 125.5, 122.2, 121.7, 108.3, 15.4 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{14}O_3$ 278.0943; found, 278.0934; mp 146−147 °C (dec).

*Phenyl 4-Hydroxy-1-phenyl-2-naphthalenecarboxylate (**3q**).* Compound **3q** was synthesized in 32% yield (1.23 g) as a white solid from benzophenone instead of acetophenone similar to the preparation of **3p**. IR (KBr) 3421, 3074, 2962, 2923, 1731, 1698, 1595, 1491, 1380, 1303, 1240, 1189, 1074; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.7 (s, 1H), 8.29 (d, 1H, J = 8.2 Hz), 7.62 (ddd, 1H, J = 8.2, 6.7, 1.2 Hz), 7.54−7.44 (m, 5H), 7.37−7.33 (m, 5H), 7.21 (t, 1H, J = 7.4 Hz), 6.77 (dd, 2H, J = 8.5, 0.9 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ 167.1, 153.4, 150.7, 139.1, 133.5, 131.8, 130.6, 129.8, 128.6, 128.3, 127.8, 127.7, 127.3, 127.1, 126.5, 126.3, 122.6, 121.8, 107.3 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{23}H_{16}O_3$ 340.1099; found, 340.1100; mp 188−189 °C (dec).

*Phenyl 4-Hydroxy-1-methoxy-2-naphthalenecarboxylate (**3r**).* To a solution of phenyl 1,4-dihydroxy-2-naphthoate (840 mg, 3.00 mmol) in dichloromethane (15 mL), pyridinium *p*-toluenesulfonate (PPTS) (73.6 mg, 0.293 mmol) and 3,4-dihydro-2*H*-pyrane (DHP) (716 mg, 8.51 mmol) were added, and the mixture was stirred for 1 day at room temperature. The mixture was washed with sat. $NaHCO_3$ (aq) and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 98/2) to give phenyl 4-tetrahydro-2*H*-pyranyloxy-1-methoxy-2-naphthalenecarboxylate (727 mg, 67%). To a solution of phenyl 4-tetrahydro-2*H*-pyranyloxy-1-hydroxy-2-naphthalenecarboxylate (727 mg, 2.00 mmol) and potassium carbonate (829 mg, 6.00 mmol) in dimethoxyethane (DME) (5 mL), dimethyl sulfate (266 mg, 2.11 mmol) was added at room teperature, and the mixture was stirred for 5 h at reflux. After cooling to room temperature, the reaction was stopped by adding Et_3N. The mixture was filtered through a Celite pad (washed with ethyl acetate). The solvent was removed *in vacuo* to afford crude compounds. Acetic acid (4 mL), THF (2 mL), and water (1 mL) were added to this crude material at room temperature. The mixture was stirred for 7 h at 45 °C. The mixture was extracted three times with ethyl acetate. The combined extracts were washed with brine and then dried over anhydrous sodium sulfate. The mixture was washed with sat. $NaHCO_3$ (aq) and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo*. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 9/1) to give naphthol **3r** (376 mg, 64% yield) as a yellow solid; IR (KBr) 3394, 1733, 1627, 1597, 1477, 1375, 1303, 1266, 1193, 1141, 1066; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, 1H, J = 6.8, 1.6 Hz), 8.22 (dd, 1H, J = 6.9, 1.6 Hz), 7.66−7.59 (m, 2H), 7.46−7.42 (m, 2H), 7.39 (s, 1H), 7.30−7.23 (m, 3H), 5.66 (s, 1H), 4.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 153.1, 150.8, 147.6, 129.54, 129.50, 128.1, 127.2, 125.9, 123.7, 122.3, 121.7, 117.9, 108.9, 108.0, 63.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{14}O_4$ 294.0892; found, 294.0896; mp 146 °C (dec).

*Typical Procedure for the Preparation of Diazonaphthoquinone **1**. Synthesis of **1b**.* To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (477 mg, 2.82 mmol) in acetonitrile (3 mL), sodium azide (228.6 mg, 3.52 mmol) was added at −20 °C, and the mixture was stirred for 1 h. Naphthol **3b** (477.3 mg, 1.81 mmol) and triethylamine (0.5 mL, 3.58 mmol) in THF (18 mL) were added to the mixture, which was stirred for 30 min. The reaction was quenched with water, and organic materials were extracted three times with ethyl acetate. The combined extracts were washed with water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 4/1) to give diazonaphthoquinone **1b** (508 mg, 97%).

*4-(tert-Butyl)phenyl 3-diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1a**).* Orange solid; 92% yield (1.71 g); IR (KBr) 3070, 2963, 2105, 1716, 1615, 1577, 1510, 1431, 1308, 1220 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.9 Hz), 7.70−7.75 (m, 3H),

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7.65 (ddd, 1H, J = 8.3, 6.7, 1.8 Hz), 7.47 (d, 2H, J = 8.9 Hz), 7.15 (d, 2H, J = 8.6 Hz), 1.35 (s, 9H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 179.1, 162.4, 149.5, 147.9, 134.6, 133.0, 131.1, 130.0, 129.9, 126.6, 125.8, 124.0, 120.7, 118.6, 34.6, 31.4 ppm. Anal. Found: C, 72.49; H, 5.24; N, 8.13%. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09%; mp 162−163 °C (dec).

*Phenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1b**).* Orange solid; 97% yield (508 mg); IR (KBr) 2104, 1715, 1619, 1430, 1306, 1214, 1190, 1001 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.9, 0.5 Hz), 7.76 (s, 1H), 7.79−7.70 (m, 2H), 7.65 (ddd, 1H, J = 8.3, 6.6, 1.8), 7.49−7.45 (m, 2H), 7.35−7.31 (m, 1H), 7.25−7.23 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 162.1, 150.2, 134.5, 132.9, 131.1, 130.0, 129.7, 126.5, 125.7, 124.1, 121.4, 121.4, 118.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_{10}N_2O_3$ 290.0691; found, 290.0684; mp 137−138 °C (dec).

*4-Methylphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1c**).* Yellow solid; 97% (592 mg); IR (KBr) 2107, 1720, 1616, 1577, 1507, 1432, 1308, 1220 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, 1H, J = 8.0, 0.6 Hz), 7.73−7.70 (m, 3H), 7.64 (ddd, 1H, J = 8.1, 6.7, 1.7 Hz), 7.25 (d, 2H, J = 8.2 Hz), 7.11 (d, 2H, J = 8.5 Hz), 2.39 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 162.3, 148.0, 136.2, 134.5, 132.9, 131.0, 130.1, 130.0, 129.9, 125.7, 123.9, 121.0, 118.4, 20.8 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_3$ 304.0848; found, 304.0859; mp 119−120 °C (dec).

*4-Methoxyphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1d**).* Orange solid; quant (339 mg); IR (KBr) 2103, 1712, 1621, 1509, 1428, 1305, 1238 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.4, 0.5 Hz)7.76−7.69 (m, 3H), 7.65 (ddd, 1H, J = 8.3, 6.5, 1.8 Hz), 7.15 (dt, 2H, J = 9.1, 3.7 Hz), 6.97 (dt, 2H, J = 9.1, 3.6 Hz), 3.83 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 162.5, 157.7, 143.6, 134.5, 132.9, 131.0, 130.0, 129.9, 125.7, 123.9, 122.1, 118.4, 114.7, 55.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_4$ 320.0797; found, 320.0790; mp 138−139 °C (dec).

*4-Chlorophenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1e**).* Yellow solid; quant (690 mg); IR (KBr) 2110, 1719, 1632, 1490, 1431, 1305, 1236 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.3, 0.6 Hz), 7.76−7.69 (m, 3H), 7.66 (ddd, 1H, J = 8.0, 6.8, 1.6 Hz), 7.43 (dt, 2H, J = 8.8, 2.1 Hz), 7.19 (dt, 2H, J = 8.9, 2.2 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 178.9, 161.9, 148.6, 134.9, 133.0, 132.0, 131.1, 130.1, 130.0, 129.7, 125.8, 124.3, 122.8, 118.0 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_9{}^{35}ClN_2O_3$ 324.0296; found, 324.0303; mp 150−151 °C (dec).

*4-(sec-Butyl)phenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1f**).* Orange solid; 86% yield (466 mg); IR (KBr) 3067, 2960, 2105, 1716, 1616, 1577, 1508, 1431, 1304, 1218 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.4, 0.5 Hz), 7.70−7.76 (m, 3H), 7.64 (ddd, 1H, J = 8.3, 7.7, 1.8 Hz), 7.26 (d, 2H, J = 8.5 Hz), 7.15 (d, 2H, J = 8.5 Hz), 2.65 (q, 1H, J = 7.0 Hz), 1.61 (q, 2H, J = 7.3 Hz), 1.26 (d, 3H, J = 6.9 Hz), 0.85 (t, 3H, J = 7.3 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.1, 162.3, 148.1, 146.0, 134.5, 132.9, 131.0, 130.0, 129.9, 128.2, 125.7, 124.0, 120.9, 118.5, 41.2, 31.2, 21.8, 12.2 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{18}N_2O_3$ 346.1312; found, 346.1317; mp 147−148 °C (dec).

*3-Methylphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1g**).* Orange solid; 79% yield (447 mg); IR (KBr) 3064, 2098, 1715, 1617, 1583, 1448, 1430, 1307, 1213 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.9, 0.6 Hz), 7.69−7.76 (m, 3H), 7.64 (ddd, 1H, J = 8.2, 6.7, 1.7 Hz), 7.34 (t, 1H, J = 7.7 Hz), 7.13 (d, 1H, J = 7.6 Hz), 7.05−7.02 (m, 2H), 2,41 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 162.2, 150.2, 140.0, 134.5, 132.9, 131.0, 130.0, 129.9, 129.4, 127.3, 125.7, 124.0, 121.9, 118.5, 118.3, 21.3 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_3$ 304.0848; found, 304.0849; mp 139−140 °C (dec).

*3-Methoxyphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1h**).* Yellow solid, 94% yield (604 mg); IR (KBr) 2114, 1717, 1618, 1489, 1427, 1301, 1212 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 8.0, 0.6 Hz), 7.76−7.69 (m, 3H), 7.65 (ddd, 1H, J = 8.3, 6.7, 1.8 Hz), 7.36 (t, 1H, J = 8.2 Hz), 6.78−6.88 (m, 3H), 3.84 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 162.0, 160.7, 151.2, 134.4, 132.9, 131.0, 130.1, 130.03, 130.00, 125.7, 124.1, 118.3, 113.5, 112.3, 107.5, 55.5 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_4$ 320.0797; found, 320.0804; mp 144−145 °C (dec).

*3-Chlorophenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1i**).* Yellow solid; 84% yield (537 mg); IR (KBr) 2105, 1714, 1624, 1588, 1476, 1428, 1310, 1232 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.9, 0.6 Hz), 7.69−7.77 (m, 3H), 7.66 (ddd, 1H, J = 8.3, 6.8, 1.6 Hz), 7.40 (t, 1H, J = 8.0 Hz), 7.29−7.33 (m, 2H), 7.16 (dq, 1H, J = 8.1, 1.0 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 161.7, 150.6, 135.0, 134.4, 133.0, 131.2, 130.4, 130.2, 130.1, 126.8, 125.8, 124.4, 122.1, 119.8, 117.9 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_9{}^{35}ClN_2O_3$ 324.0302; found, 324.0307; mp 152−153 °C (dec).

*2-Methylphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1j**).* Orange solid; 97% yield (592 mg); IR (KBr) 3060, 2111, 1720, 1619, 1577, 1488, 1427, 1321, 1301 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, 1H, J = 8.0 Hz), 7.77 (s, 1H) 7.76−7.72 (m, 2H), 7.65 (ddd, 1H, J = 8.3, 6.5, 2.0 Hz), 7.32−7.21 (m, 3H), 7.15 (dd, 1H, J = 7.9, 1.3 Hz), 2.27 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 179.0, 161.9, 148.9, 134.5, 132.9, 131.4, 131.1, 130.08, 130.06, 130.0, 127.2, 126.7, 125.8, 124.0, 121.7, 118.3, 16.2 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_3$ 304.0848; found, 304.0838; mp 169−170 °C (dec).

*2-Methoxyphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1k**).* Orange solid; 97% yield (623 mg); IR (KBr) 3069, 2944, 2102, 1716, 1586, 1577, 1488, 1427, 1321, 1301 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.9, 0.5 Hz), 7.76 (s, 1 H), 7.75−7.69 (m, 2H), 7.64 (ddd, 1H, J = 8.3, 6.5, 2.0 Hz), 7.29 (ddd, 1H, J = 8.3, 7.6, 1.7 Hz), 7.18 (dd, 1H, J = 7.9, 1.6 Hz), 7.00−7.06 (m, 2H), 3.85 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 179.1, 161.7, 151.0, 139.2, 134.6, 132.9, 131.1, 130.0, 129.9, 127.5, 125.7, 124.2, 122.7, 120.9, 118.3, 112.5, 55.9 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_4$ 320.0797; found, 320.0803; mp 153−154 °C (dec).

*2-Chlorophenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1l**).* Orange solid; 79% yield (515 mg); IR (KBr) 3071, 2113, 1728, 1621, 1574, 1475, 1430, 1307 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.8, 0.4 Hz), 7.81 (s, 1H), 7.75−7.69 (m, 2H), 7.66 (ddd, 1H, J = 8.1, 6.3, 2.2 Hz), 7.53 (dd, 1H, J = 7.5, 1.5 Hz), 7.37 (ddd, 1H, J = 8.3, 7.3, 1.6 Hz), 7.31−7.26 (m, 2H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 161.3, 146.5, 134.5, 133.0, 131.198, 130.197, 130.5, 130.19, 130.17, 128.0, 127.7, 126.8, 125.8, 124.7, 123.6, 117.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_9{}^{35}ClN_2O_3$ 324.0302; found, 324.0317; mp 184−185 °C (dec).

*2-Methoxycarbonylphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1m**).* Orange solid; 83% yield (288 mg); IR (KBr) 2102, 1718, 1625, 1429, 1305, 1268, 1219, 1084 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (dd, 1H, J = 7.8, 0.5 Hz), 8.12 (dd, 1H, J = 7.9, 1.6 Hz), 7.77 (s, 1H), 7.76−7.62 (m, 4H), 7.42 (ddd, 1H, J = 7.7, 6.6, 1.1 Hz), 7.27 (dd, 1H, J = 7.9, 1.1 Hz), 3.83 (s, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.1, 164.5, 162.2, 150.1, 134.6, 134.1, 132.8, 132.0, 131.1, 130.1, 129.8, 126.6, 125.7, 124.3, 123.7, 122.9. 118.3, 52.3 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{19}H_{12}N_2O_5$ 348.0746; found, 348.0741; mp 174−175 °C (dec).

*3,5-Dimethoxyphenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1n**).* Yellow solid; 97% yield (341 mg); IR (KBr) 2102, 1715, 1630, 1481, 1427, 1305, 1231, 1127, 1054 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, 1H, J = 7.8, 0.4 Hz), 7.72 (s, 1H), 7.76−7.71 (m, 2H), 7.65 (ddd, 1H, J = 8.2, 6.7, 1.7), 6.43−6.39 (m, 3H), 3.81 (s, 6H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 179.1, 162.0, 161.3, 151.7, 134.5, 133.0, 131.1, 130.06, 130.05, 125.8, 124.1, 118.3, 100.0, 98.8, 55.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{19}H_{14}N_2O_5$ 350.0903; found, 350.0906; mp 154−155 °C (dec).

*Naphthalenyl 3-Diazo-3,4-dihydro-4-oxo-2-naphthalenecarboxylate (**1o**).* Orange solid; 47% yield (280 mg); IR (KBr) 2102, 1718, 1637, 1428, 1302, 1230 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, 1H, J = 7.8, 0.6 Hz), 7.95 (s, 1H), 7.93 (ddd, 2H, J = 7.5, 2.6, 2.6 Hz), 7.84 (d, 1H, J = 8.3 Hz), 7.77 (d, 2H, J = 3.7 Hz), 7.70−7.66 (m, 1H), 7.57−7.52 (m, 3H), 7.39 (dd, 1H, J = 7.5, 0.9 Hz); ^{13}CNMR (100 MHz, $CDCl_3$) δ 179.0, 162.3, 146.1, 134.7, 134.5, 133.3, 131.2, 130.14, 130.13, 128.2, 126.8, 126.7, 126.5, 125.8, 125.3, 124.2, 120.7,

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118.2, 118.1, 76.8 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{12}N_2O_3$ 340.0848; found, 340.0852; mp 183−184 °C (dec).

*Phenyl 3-Diazo-3,4-dihydro-1methyl-4-oxo-2-naphthalenecarboxylate (**1p**).* Orange solid; 93% yield (184 mg); IR (KBr) 2113, 1715, 1633, 1599, 1494, 1393, 1313, 1236, 1197, 1064 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (dd, 1H, J = 7.9, 1.2 Hz), 7.96 (d, 1H, J = 8.1 Hz), 7.78 (ddd, 1H, J = 8.4, 7.3, 1.5 Hz), 7.64 (ddd, 1H, J = 8.0, 8.0, 0.9 Hz), 7.50−7.46 (m, 2H), 7.35−7.32 (ddd, 1H, J = 8.5, 8.4, 0.9 Hz), 7.24−7.22 (m, 2H), 2.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9, 163.1, 150.0, 136.4, 133.0, 130.3, 129.8, 129.7, 129.2, 126.6, 126.2, 125.9, 121.3, 116.3, 16.4 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_3$ 304.0853; found, 304.0848; mp 135−136 °C (dec).

*Phenyl 3-Diazo-3,4-dihydro-4-oxo-1-phenyl-2-naphthalenecarboxylate (**1q**).* Orange solid; 85% yield (279 mg). IR (KBr) 3052, 2108, 1704, 1621, 1593, 1490, 1392, 1304, 1229, 1193 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (dd, 1H, J = 6.7, 2.6 Hz), 7.61−7.56 (m, 2H), 7.51−7.44 (m, 3H), 7.37 (dd, 2H, J = 8.0, 1.4 Hz), 7.28−7.25 (m, 3H), 7.17 (t, 1H, J = 7.4 Hz), 6.66 (d, 2H, J = 7.7 Hz); ^{13}CNMR (125 MHz, $CDCl_3$) δ 178.5, 163.1, 149.7, 137.6, 136.4, 133.8, 132.7, 130.4, 129.9, 129.3, 129.2, 129.0, 128.4, 128.0, 126.2, 125.6, 120.7, 117.6, 77.4 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{23}H_{14}N_2O_3$ 366.1004; found, 366.1006; mp 163−164 °C (dec).

*Phenyl 3-Diazo-3,4-dihydro-1-methoxy-4-oxo-2-naphthalenecarboxylate (**1r**).* Orange solid; 94% yield (301 mg); IR (KBr) 2942, 2100, 1710, 1628, 1573, 1484, 1400, 1300, 1226, 1186, 1014 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, 1H, J = 8.0, 0.9 Hz), 8.04 (dd, 1H, J = 8.1, 0.6 Hz), 7.80 (ddd, 1H, J = 8.2, 7.3, 1.3 Hz), 7.69 (ddd, 1H, J = 8.2, 7.3, 1.2 Hz), 7.50−7.45 (m, 2H), 7.32 (ddd, 1H, J = 4.6, 4.6, 1.0 Hz), 7.27−7.25 (m, 2H), 4.06 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 177.8, 161.6, 150.6, 150.2, 133.1, 132.7, 131.9, 130.3, 129.7, 126.5, 126.2, 124.6, 121.3, 108.0, 75.4, 63.7 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}N_2O_4$ 320.0797; found, 320.0809; mp 131−132 °C (dec).

*Typical Procedure for the Rh-Catalyzed Cyclization of Various 3-Aryloxycarbonyldiazonaphthoquones **1**. Reaction of Diazonaphthoquione **1b**.* To a solution of diazonaphthoquione **1b** (88.3 mg, 0.304 mmol) in benzene (30 mL), $Rh_2(oct)_4$ (3.5 mg, 1.5 mol %) was added at room temperature. The mixture was stirred for 1 h at 90 °C as the bath temperature. After cooling the mixture, the precipitates were collected by filtration to afford **2b** (15.8 mg, 20% yield). The filtrate were concentrated *in vacuo* to afford the crude compound, which was purified by flash column chromatography (silica gel, hexane/ethyl acetate = 6:1) to give **2b** (42.9 mg, 54% yield).

*12-Hydroxy-2-(tert-butyl)-6H-naphtho[2,3-c]chromen-6-one (**2a**).* Yellow solid; 92% yield (58.7 mg); IR (KBr) 3323, 2948, 1698, 1624, 1490, 1399, 1343, 1253, 1199 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, 1H, J = 2.1 Hz), 8.74 (s, 1H), 8.07 (t, 2H, J = 9.2 Hz), 7.75 (t, 1H, J = 7.3 Hz), 7.63 (t, 1H, J = 7.0 Hz), 7.49 (dd 1H, J = 8.6, 2.1 Hz), 7.31 (d, 1H, J = 8.8 Hz), 6.29 (s, 1H), 4.06 (s, 9H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 161.9, 148.3, 148.1, 147.4, 132.5, 130.4, 129.2, 127.3, 127.2, 126.5, 125.7, 124.9, 120.5, 119.2, 117.6, 116.9, 115.3, 34.8, 31.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{18}O_3$ 318.1256; found, 318.1252; mp 261−263 °C (dec).

*12-Hydroxy-6H-naphtho[2,3-c]chromen-6-one (**2b**).* Yellow solid; 74% yield (58.7 mg); IR (KBr) 3444, 1702, 1627, 1408, 1349, 1216, 753 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.9 (brs, 1H), 9.32 (dd, 1H, J = 8.2, 1.6 Hz) 8.61 (s, 1H) 8.51 (d, 1H, J = 8.7 Hz) 8.20 (d, 1H, J = 8.1 Hz) 7.77 (ddd, 1H, J = 8.4, 6.8, 1.2 Hz), 7.68 (ddd, 1H, J = 7.8, 6.9, 0.8 Hz), 7.50 (ddd, 1H, J = 8.4, 7.7, 1.6 Hz), 7.44−7.38 (m, 2H); ^{13}CNMR (100 MHz, DMSO-d_6) δ 161.2, 151.5, 149.9, 132.9, 130.1, 129.3, 128.9, 128.8, 128.7, 127.9, 124.9, 124.1, 123.0, 120.3, 119.1, 117.3, 114.9 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_{10}O_3$ 262.0630; found, 262.0621; mp 254−256 °C (dec).

*12-Hydroxy-2-methyl-6H-naphtho[2,3-c]chromen-6-one (**2c**).* Yellow solid; 69% yield (57.1 mg); IR (KBr) 3231, 1697, 1624, 1583, 1402, 1349, 1263, 1219 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.8 (brs, 1H), 9.15 (s, 1H), 8.60 (s, 1H), 8.49 (d, 1H, J = 8.6 Hz), 8.21(d, 1H, J = 8.2 Hz), 7.76 (ddd, 1H, J = 8.3, 6.7, 1.2 Hz), 7.68 (t, 1H, J = 7.7), 7.32−7.27 (m, 2H), 2.44 (s, 3H); ^{13}CNMR (125 MHz, DMSO-d_6) δ 160.8, 151.0, 147.5, 133.2, 132.4, 129.6, 129.4, 128.4, 128.3, 128.2, 127.4, 123.6, 122.4, 119.9, 118.2, 116.5, 114.5, 21.0 ppm. Anal. Found: C, 78.03; H, 4.41%. Calcd for $C_{18}H_{12}O_3$: C, 78.25; H, 4.38%; mp 261−269 °C (dec).

*12-Hydroxy-2-(sec-butyl)-6H-naphtho[2,3-c]chromen-6-one (**2d**).* Yellow solid; 73% yield (70.8 mg); IR (KBr) 3287, 2957, 2919, 2870, 1705, 1624, 1580, 1409, 1276, 1212 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.9 (brs, 1H), 9.21 (d, 1H, J = 1.7 Hz), 8.61 (s, 1H), 8.50 (d, 1H, J = 8.5 Hz), 8.21(d, 1H, J = 8.1 Hz), 7.76 (ddd, 1H, J = 8.4, 6.8, 1.2 Hz), 7.67 (ddd, 1H, J = 7.9, 0.8 Hz), 7.35−7.31 (m, 2H), 2.68−2.69 (m, 1H), 1.65 (q, 2H, J = 6.9 Hz), 1.29 (d, 3H, J = 6.9 Hz), 0.84 (t, 3H, J = 7.4 Hz); ^{13}CNMR (125 MHz, DMSO-d_6) δ 161.3, 151.5, 148.2, 143.4, 132.9, 130.1, 128.9, 128.8, 127.94, 127.92, 127.0, 124.1, 122.9, 120.4, 118.8, 117.1, 115.1, 41.4, 31.2, 22.5, 12.6 ppm. Anal. Found: C, 79.20; H, 5.77%. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70%; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{18}O_3$ 318.1256; found, 318.1260; mp 231−232 °C (dec).

*12-Hydroxy-2-methoxy-6H-naphtho[2,3-c]chromen-6-one (**2e**).* Pale beige solid; 67% yield (59.0 mg); IR (KBr) 3317, 1697, 1623, 1579, 1405, 1344, 1263, 1219 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.0 (brs, 1H), 8.89 (d, 1H, J = 3.0 Hz), 8.60 (s, 1H), 8.50 (d, 1H, J = 8.4 Hz), 8.21 (d, 1H, J = 8.1 Hz), 7.76 (ddd, 1H, J = 8.1, 6.8, 1.1 Hz), 7.68 (ddd, 1H, J = 7.9, 7.2, 0.7 Hz), 7.34 (d, 1H, J = 8.9 Hz), 7.09 (dd, 1H, J = 8.9, 3.0 Hz), 3.86 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.8, 155.4, 151.2, 143.7, 132.5, 129.6, 128.5, 128.3, 127.5, 123.7, 122.5, 119.8, 119.0, 117.5, 114.8, 114.4, 112.5, 55.4 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_4$ 292.0736; found, 292.0741; mp 263−269 °C (dec).

*2-Chloro-12-hydroxy-6H-naphtho[2,3-c]chromen-6-one (**2f**).* Gray solid; 60% yield (53.4 mg); IR (KBr) 3200, 1696, 1622, 1576, 1399, 1342, 1261, 1220, 1100 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.2 (brs, 1H), 9.32 (d, 1H, J = 2.8 Hz), 8.59 (s, 1H), 8.49 (d, 1H, J = 8.5 Hz), 8.22(d, 1H, J = 8.2 Hz), 7.78 (ddd, 1H, J = 8.2, 6.7, 1.2 Hz), 7.70 (t, 1H, J = 7.1 Hz), 7.53 (dd, 1H, J = 8.6, 2.8 Hz), 7.42 (dd, 1H, J = 8.6 Hz); ^{13}CNMR (125 MHz, DMSO-d_6) δ 160.2, 151.4, 148.2, 132.7, 129.6, 128.6, 128.3, 128.11, 128.09, 127.8, 127.2, 123.6, 122.5, 120.1, 119.5, 118.6, 113.1 ppm. Anal. Found: C, 68.82; H, 3.06%. Calcd for $C_{17}H_9ClO_3$: C, 68.53; H, 3.13%; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_9{}^{35}ClO_3$ 296.0240; found, 296.0242; mp 278−285 °C (dec).

*12-Hydroxy-3-methyl-6H-naphtho[2,3-c]chromen-6-one (**2g**).* Yellow solid; 77% yield (67.7 mg); IR (KBr) 3405, 1708, 1623, 1400, 1266 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.8 (brs, 1H), 9.16 (d, 1H, J = 8.1 Hz), 8.59 (s, 1H), 8.48 (d, 1H, J = 8.7 Hz), 8.19 (d, 1H, J = 8.1 Hz), 7.75 (ddd, 1H, J = 8.4, 6.8, 1.2 Hz), 7.66 (ddd, 1H, J = 7.8, 0.8 Hz), 7.24 (d, 1H, J = 1.2 Hz), 7.21 (s, 1H), 3.34 (s, 3H); ^{13}CNMR (125 MHz, DMSO-d_6) δ 160.8, 150.5, 149.4, 139.0, 132.2, 129.6, 128.37, 128.35, 128.0, 127.2, 125.3, 123.6, 122.4, 119.7, 116.9, 115.8, 114.8, 20.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_3$ 276.0786; found, 276.0787; mp 257−258 °C (dec).

*12-Hydroxy-1-methyl-6H-naphtho[2,3-c]chromen-6-one (**2′g**).* Yellow solid; 8% yield (6.5 mg); IR (KBr) 3223, 1699, 1624, 1560, 1410, 1240, 1217, 1114 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) 8.56 (s, 1H), 8.40 (d, 1H, J = 8.5, 0.7 Hz), 8.04 (d, 1H, J = 8.1 Hz), 7.72 (ddd, 1H, J = 8.3, 6.8, 1.2 Hz), 7.66 (ddd, 1H, J = 8.1, 6.9, 1.2 Hz), 7.39 (ddd, 1H, J = 7.8 Hz), 7.26 (d, 1H, J = 7.1 Hz), 7.23 (d, 1H, J = 8.0 Hz), 5.59 (s, 1H), 2.55 (s, 3H); ^{13}CNMR (125 MHz, $CDCl_3$) δ 161.7, 150.8, 147.4, 135.0, 133.0, 129.3, 128.9, 128.7, 128.1, 127.8, 127.7, 124.4, 122.4, 121.7, 116.9, 114.7, 112.7, 22.2 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_3$ 276.0786; found, 276.0784; mp 215−217 °C (dec).

*12-Hydroxy-3-methoxy-6H-naphtho[2,3-c]chromen-6-one (**2h**).* Yellow solid; 59% yield (51.5 mg); IR (KBr) 3385, 1699, 1616, 1508, 1287, 1254, 1137, 1031 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.7 (s, 1H), 9.22 (d, 1H, J = 9.0 Hz), 8.58 (s, 1H), 8.46 (d, 1H, J = 8.5 Hz), 8.18 (d, 1H, J = 8.1 Hz), 7.74 (ddd, 1H, J = 8.4, 6.8, 1.2 Hz), 7.64 (ddd, 1H, J = 7.7, 0.7 Hz), 7.02 (dd, 1H, J = 9.0, 2.7 Hz), 6.99 (d, 1H, J = 2.6 Hz), 3.87 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.9, 159.5, 150.8, 149.7, 131.9, 129.6, 129.3, 128.44, 128.40, 126.9, 123.6, 122.2, 119.1, 115.1, 111.35, 111.29, 101.6, 55.5 ppm; HRMS

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(EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_4$ 292.0736; found, 292.0736; mp 279−280 °C (dec).

*12-Hydroxy-1-methoxy-6H-naphtho[2,3-c]chromen-6-one (**2′h**).* Pale yellow solid; 27% yield (23.8 mg); IR (KBr) 3158, 2949, 1717, 1562, 1468, 1392, 1301, 1244, 1197, 1080 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.0 (s, 1H), 8.64 (s, 1H), 8.56 (d, 1H, J = 8.3 Hz), 7.99 (d, 1H, J = 7.7 Hz), 7.70−7.62 (m, 2H), 7.45 (t, 1H, J = 8.2 Hz), 7.17 (dd, 1H, J = 8.1, 0.7 Hz), 7.03 (d, 1H, J = 8.2 Hz), 4.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 153.6, 151.2, 150.5, 133.1, 129.4, 129.2, 128.7, 128.4, 128.0, 124.5, 124.2, 120.6, 113.0, 110.8, 109.9, 109.7, 58.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_4$ 292.0736; found, 292.0735; mp 164−165 °C (dec).

*3-Chloro-12-hydroxy-6H-naphtho[2,3-c]chromen-6-one (**2i**).* Yellow solid; 74% yield (66.4 mg); IR (KBr) 3380, 1703, 1625, 1487, 1395, 1261, 1212 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) 11.0 (brs, 1H), 9.26 (d, 1H, J = 8.8 Hz), 8.56 (s, 1H) 8.49 (d, 1H, J = 8.6 Hz), 8.18 (d, 1H, J = 8.1 Hz), 7.75 (ddd, 1H, J = 8.4, 6.9, 1.2 Hz), 7.66 (t, 1H, J = 7.4 Hz), 7.48 (d, 1H, J = 2.3 Hz), 7.44 (dd, 1H, J = 8.8, 2.3 Hz); ^{13}CNMR (100 MHz, DMSO-d_6) δ 160.7, 151.6, 150.5, 133.0, 132.8, 130.1, 130.0, 129.0, 128.7, 128.1, 124.9, 124.2, 123.0, 119.9, 118.1, 117.2, 114.1 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{17}H_9{}^{35}ClO_3$ 296.0242; found, 296.0238; mp 282−284 °C (dec).

*12-Hydroxy-4-methyl-6H-naphtho[2,3-c]chromen-6-one (**2j**).* Yellow solid; 84% yield (69.7 mg); IR (KBr) 3336, 1698, 1624, 1407, 1346 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.8 (brs, 1H), 9.19 (dd, 1H, J = 8.1, 0.8 Hz), 8.61 (s, 1H), 8.50 (d, 1H, J = 8.5 Hz), 8.20 (d, 1H, J = 8.1 Hz), 7.75 (ddd, 1H, J = 8.3, 6.8, 1.1 Hz), 7.67 (ddd, 1H, J = 7.8, 7.8, 0.8 Hz), 7.37 (dd, 1H, J = 7.2, 0.4 Hz), 7.29 (t, 1H, J = 7.6 Hz), 2.43 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.2, 151.8, 148.1, 132.9, 130.6, 130.0, 129.0, 128.9, 127.9, 126.4, 125.7, 124.2, 123.8, 123.1, 120.3, 118.6, 115.3, 16.4 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_3$ 276.0786; found, 276.0788; mp 280−285 °C (dec).

*12-Hydroxy-4-methoxycarbonyl-6H-naphtho[2,3-c]chromen-6-one (**2k**).* Yellow solid; 44% yield (40.0 mg). IR (KBr) 3421, 1732, 1704, 1624, 1508, 1439, 1399, 1248 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.0 (brs, 1H), 9.52 (d, 1H, J = 7.7 Hz), 8.61 (s, 1H), 8.51 (d, 1H, J = 8.5 Hz), 8.22 (d, 1H, J = 8.1 Hz), 7.80−7.76 (m, 2H), 7.70 (t, 1H, J = 7.2 Hz), 7.48 (t, 1H, J = 7.9 Hz), 3.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 160.4, 151.9, 147.8, 133.2, 132.0, 130.1, 129.8, 129.0, 128.9, 128.2, 124.3, 124.0, 123.1, 120.9, 120.0, 119.9, 114.3, 52.9 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{19}H_{12}O_5$ 320.0685; found, 320.0682; mp 283−284 °C (dec).

*12-Hydroxy-1,3-dimethoxy-6H-naphtho[2,3-c]chromen-6-one (**2n**).* Yellow solid; 90% yield (87.2 mg); IR (KBr) 3106, 1717, 1622, 1450, 1393, 1301, 1247 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.87 (brs, 1H), 8.50 (s, 1H), 8.41 (d, 1H, J = 8.4 Hz), 8.14 (d, 1H, J = 8.2 Hz), 7.73−7.64 (m, 2H), 6.77 (d, 1H, J = 2.5 Hz), 6.76 (d, 1H, J = 2.5 Hz), 4.12 (s, 3H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 161.3, 161.0, 155.6, 151.8, 149.1, 132.1, 129.3, 129.0, 128.9, 128.0, 123.7, 123.5, 120.4, 111.3, 101.6, 97.4, 96.3, 58.2, 56.4 ppm. Anal. Found: C, 70.53; H, 4.37%. Calcd for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38%; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{19}H_{14}O_5$ 322.0841; found, 322.0832; mp 230−231 °C (dec).

*14-Hydroxy-8H-dinaphtho[2,3-c][1,2-e]pyran-8-one (**2o**).* Gray solid; 47% yield (41.0 mg); IR (KBr) 3449, 1701, 1624, 1498, 1330, 773 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.9 (brs, 1H), 9.42 (d, 1H, J = 7.3 Hz), 8.67 (s, 1H), 8.51 (d, 1H, J = 6.8 Hz), 8.40 (d, 1H, J = 6.5 Hz), 8.22 (d, 1H, J = 6.5 Hz), 7.99 (d, 1H, J = 6.1 Hz), 7.89 (d, 1H, J = 7.3 Hz), 7.77 (t, 1H, J = 5.9 Hz), 7.69−7.62 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.1, 151.6, 144.9, 133.2, 133.0, 130.1, 129.1, 128.9, 127.9, 127.8, 127.7, 127.3, 125.4, 124.2, 123.9, 123.4, 123.0, 121.7, 120.3, 115.6, 114.6 ppm. Anal. Found: C, 70.53; H, 4.37%. Calcd for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38%; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{21}H_{12}O_3$ 312.0786; found, 312.0793; mp >300 °C (dec).

*12-Hydroxy-7-methyl-6H-naphtho[2,3-c]chromen-6-one (**2p**).* Yellow solid; 81% yield (67.7 mg); IR (KBr) 3369, 1702, 1616, 1407, 1380, 1277, 1242, 1222, 1108 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.5 (brs, 1H), 9.29 (dd, 1H, J = 8.2, 1.4 Hz), 8.49 (dd, 1H, J = 8.5, 0.7 Hz), 8.43 (d, 1H, J = 8.4 Hz), 7.79 (ddd, 1H, J = 8.4, 6.7, 1.2 Hz), 7.73 (ddd, 1H, J = 8.1, 6.7, 1.2 Hz), 7.46 (ddd, 1H, J = 8.7, 8.0, 1.5 Hz), 7.35 (ddd, 1H, J = 8.4, 7.2, 1.4 Hz), 7.33 (dd, 1H, J = 8.1, 1.3 Hz), 3.12 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.8, 149.8, 149.2, 134.8, 133.2, 129.3, 129.1, 129.0, 128.7, 128.0, 126.5, 124.5, 123.4, 119.2, 118.4, 116.6, 116.0, 17.3 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_3$ 276.0796; found, 276.0786; mp 234−235 °C (dec).

*12-Hydroxy-7-phenyl-6H-naphtho[2,3-c]chromen-6-one (**2q**).* Yellow solid; 87% yield (88.2 mg); IR (KBr) 3366, 1708, 1610, 1410, 1388, 1162 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.9 (s, 1H), 9.36 (dd, 1H, J = 8.2, 1.4 Hz), 8.55 (d, 1H, J = 8.5 Hz), 7.75 (ddd, 1H, J = 8.3, 6.8, 1.0 Hz), 7.54 (ddd, 1H, J = 7.9, 6.8, 1.0 Hz), 7.49−7.37 (m, 5H), 7.33−7.31 (m, 2H), 7.22 (dd, 2H, J = 8.2, 1.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.4, 150.9, 149.9, 140.7, 137.9, 133.4, 129.5, 129.4, 129.0, 128.8, 128.71, 128.68, 128.3, 128.1, 124.5, 123.0, 119.1, 117.9, 116.8, 115.6 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{23}H_{14}O_3$ 338.0943; found, 338.0945; mp 281−284 °C (dec).

*12-Hydroxy-7-methoxy-6H-naphtho[2,3-c]chromen-6-one (**2r**).* Yellow solid; 86% yield (76.0 mg). IR (KBr) 3421, 1716, 1618, 1412, 1376, 1281, 1241, 1160, 1089 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.5 (s, 1H), 9.30 (dd, 1H, J = 8.2, 1.4 Hz), 8.47 (d, 1H, J = 8.5 Hz), 8.33 (d, 1H, J = 8.3 Hz), 7.82 (ddd, 1H, J = 8.3, 6.8, 1.1 Hz), 7.34 (ddd, 1H, J = 7.8, 7.8, 0.7 Hz), 7.47 (ddd, 1H, J = 8.6, 8.2, 1.5 Hz), 7.36 (ddd, 1H, J = 8.4, 7.2, 1.3 Hz), 7.33 (dd, 1H, J = 8.0, 1.2 Hz), 3.97 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 157.5, 154.6, 150.0, 147.0, 130.4, 129.6, 129.4, 128.9, 128.5, 128.0, 124.5, 124.2, 123.4, 119.0, 116.8, 115.6, 111.3, 63.2 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{18}H_{12}O_4$ 292.0736; found, 292.0744; mp 231−232 °C (dec).

*4-(tert-Butyl)phenyl 4-Hydroxy-3-phenyl-2-naphthalenecarboxylate (**4**).* Beige solid; 46% yield (27.3 mg); IR (KBr) 3499, 2962, 1723, 1541, 1508, 1467, 1383, 1295, 1208, 1173, 1063 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, 1H, J = 9.8, 1.4 Hz), 8.26 (s, 1H), 7.96 (dd, 1H, J = 8.9, 1.9 Hz), 7.66−7.53 (m, 4H), 7.49−7.43 (m, 3H), 7.30 (d, 2H, J = 8.7 Hz), 6.74 (d, 2H, J = 8.7 Hz), 5.68 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 149.0, 148.4, 148.2, 135.2, 132.7, 130.1, 129.4, 128.6, 128.4, 128.3, 127.8, 127.4, 126.1, 125.7, 123.7, 122.6, 120.6, 120.1, 34.4, 31.3 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{27}H_{24}O_3$ 396.1725; found, 396.1738.

*2-Methoxycarbonyl-4-(methoxymethoxy)methyl-3-methylphenyl 7-Chloro-4-hydroxy-5,8-dimethoxy-2-naphthoate (**7**).* To a solution of phenol **6**[7a] (1.76 g, 7.35 mmol), carboxylic acid **5**[7a] (1.00 g, 3.54 mmol) in dichloromethane (35 mL), 1-ethyl-3-(3-(dimethylamino)-propyl)carbodiimide (EDCI) (0.742 g, 3.87 mmol), and *N*,*N*-dimethyl-4-aminopyridine (DMAP) (0.423 g, 3.46 mmol) were added at room temperature, and the mixture was stirred for 1.5 h. The reaction was quenched with water, and organic materials were extracted three times with ethyl acetate. The combined extracts were washed with water and brine and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 6/1) to give ester **7** (0.909 g, 51% yield) as a white solid. IR (KBr) 3477, 3073, 2960, 1685, 1508, 1451, 1410, 1348, 1315, 1207, 1005 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.41 (d, 1H, J = 1.6 Hz), 7.56 (d, 1H, J = 1.6 Hz), 7.19 (s, 1H), 7.16 (s, 1H), 6.86 (s, 1H), 4.72 (s, 2H), 4.62 (s, 2H), 4.07 (s, 3H), 3.99 (s, 3H), 3.74 (s, 3H), 3.41 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.7, 164.5, 155.3, 152.3, 148.9, 147.3, 141.4, 138.7, 130.7, 129.2, 127.0, 125.1, 123.5, 119.3, 116.9, 116.3, 110.9, 108.0, 95.8, 68.0, 61.5, 56.7, 55.4, 52.1, 20.1 ppm; HRMS (EI$^+$) m/z [M]$^+$ Calcd for $C_{25}H_{25}{}^{35}ClO_9$ 504.1187; found, 504.1180; mp 107−108 °C (dec).

*Methyl 3-(6-Chloro-1-hydroxy-3-hydroxymethyl-5,8-dimethoxyaphthalen-2-yl)-2-hydroxy-4-(methoxymethoxy)methyl-6-methylbenzoate (**10**).*[7a] To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (152.0 mg, 0.899 mmol) in acetonitrile (1 mL), sodium azide (228.6 mg, 3.52 mmol) and 15-crown-5 (12.2 mg, 0.0554 mmol) were added at −30 °C, and the mixture was stirred for 1 h. Ester **7** (101.0

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mg, 0.200 mmol) and triethylamine (36.3 mg, 0.0358 mmol) in THF (2 mL) were added to the mixture, which was stirred for 6 h. The reaction was quenched with buffer (pH 7), and organic materials were extracted four times with ethyl acetate. The combined extracts were washed with water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. $Rh_2(oct)_4$ (3.5 mg, 1.5 mol %) was added to a solution of the crude material in benzene (20 mL) at room temperature. The mixture was stirred for 2.5 h at 90 °C as the bath temperature. After cooling the mixture, the solvent was concentrated *in vacuo*. The residue was diluted with THF/MeOH (20:1) (6.3 mL). To the mixture, $NaBH_4$ (30.6 mg, 0.0809 mmol) was added at −45 °C. After stirring the mixture for 4 h, the reaction was stopped by adding two drops of AcOH at that temperature. After warming the mixture to room temperature, water was added, and the mixture was extracted three times with ethyl acetate. The combined extracts were washed with water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* to afford crude compounds. The crude materials were purified by flash column chromatography (silica gel: hexane/ethyl acetate = 7/3) to give triol **10** (56.0 mg, 55% yield) as a yellow solid. IR (KBr) 3384, 2936, 1734, 1655, 1597, 1451, 1362, 1258, 1202, 1106, 1041, 1014, 973, 945 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 11.76 (s, 1H), 9.45 (s, 1H), 7.80 (s, 1H), 7.03 (s, 1H), 6.73 (s, 1H), 4.53 (d, 1H, J = 6.6 Hz), 4.46 (d, 2H, J = 5.7 Hz), 4.42 (d, 1H, J = 6.6 Hz), 4.33 (d, 1H, J = 12.3 Hz), 4.27 (d, 1H, J = 12.3 Hz), 3.99 (s, 3H), 3.98 (s, 3H), 3.97 (s, 3H), 3.13 (s, 3H), 2.74 (t, 1H, J = 6.0 Hz), 2.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 159.9, 152.5, 151.2, 146.5, 143.6, 141.3, 141.2, 131.0, 123.1, 122.7, 121.2, 117.1, 113.9, 113.0, 111.9, 105.8, 96.1, 67.3, 64.0, 61.2, 56.5, 55.2, 52.3, 24.2 ppm.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra of 1, 2, 2′, 3, 4, 7, and 10. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01251.

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Notes

The authors declare no competing financial interest.

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