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Approach to Construct Polysubstituted 1,2-Dihydronaphtho[2,1-*b*]furans and Their Aerobic Oxidative Aromatization

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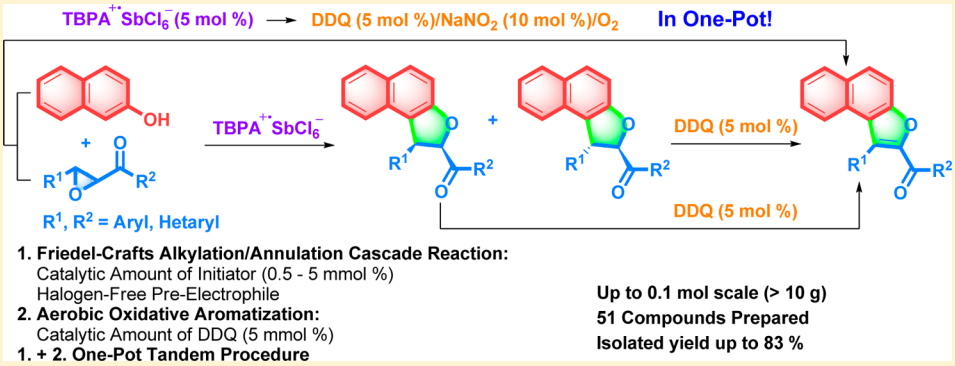
Supporting Information



ABSTRACT: Triarylaminium salt was disclosed as an efficient initiator for the novel Friedel–Crafts alkylation/annulation cascade reaction between chalcone epoxides and 2-naphthols to construct polysubstituted 1,2-dihydronaphtho[2,1-*b*]furans. The $DDQ/NaNO_2/O_2$ catalytic system was first applied to the aerobic oxidative aromatization of heterocycles, and a simple and efficient one-pot tandem FC alkylation/annulation/aerobic oxidative aromatization procedure was also developed for the synthesis of complex naphtho[2,1-*b*]furans.

Friedel–Crafts (FC) alkylation is one of the oldest but also most powerful methods for carbon–carbon bond construction and has been widely used to generate important classes of building blocks.[1−5,6a] With the recent increased environmental and economic awareness, the development of greener and/or sustainable methods for this fundamental transformation has emerged in recent years. First of all, the development of FC reactions using catalytic amounts of catalyst is highly desirable.[2] At the same time, the developments of protocols that replace toxic alkyl halides with more benign and environmentally acceptable alkylating reagents were recently focused on π-activated alcohols as pre-electrophiles.[1c] For example, benzyl alcohols have become valuable pre-electrophiles in FC alkylation through the formation of stabilized benzylic cation intermediates, due to their availability, lower toxicity, and highly atom-economical character[3−5] (Scheme 1).

Our group has had a long-standing interest in the stable triarylaminium salt initiated radical cation mediated transformation and its synthetic potential.[6] Recently, we demonstrated that tris(4-bromophenyl)-aminium hexachloro-antimonate ($TBPA^{+\cdot}SbCl_6^-$) is a highly efficient (1–5 mol %) initiator for the FC reaction between chalcone epoxides and heteroarenes to construct complex β-heteroaryl α-ketols.[6a] The development of the FC reaction of electron-rich arenes seems generally behind that of relatively reactive electron-rich heteroarenes.[2b] Hence, it is necessary to try to expand our method to electron-rich arenes. In this paper, we disclosed that naphthols were also good donors in triarylaminium salt initiated FC alkylation. Also, very interestingly, 2-naphthols gave 1,2-dihydronaphtho[2,1-*b*]furans as products through a FC alkylation/annulation cascade reaction with good yield (Scheme 1). The 1,2-dihydrofuran compounds could then be easily and efficiently aromatized to the corresponding naphtho[2,1-*b*]furans by employing a catalytic amount of DDQ and molecular oxygen as terminal oxidant. It is worth mentioning that the direct transformation of chalcone epoxides with 2-naphthols into naphtho[2,1-*b*]furans could also be carried out in one pot with a simple and efficient tandem procedure (Scheme 1).

Naphthofuran derivatives have been isolated from various natural sources, and are well-known for various types of biological activity.[7a−e,8] However, the reports on the synthesis of naphthofurans, especially 1,2-dihydronaphthofurans, are relatively limited.[7f−l] A few analogues of our one-pot prepared polysubstituted naphtho[2,1-*b*]furans have been synthesized in 3–4 steps to evaluate their bioactive potential.[8] Therefore, the development of a versatile method to synthesize polysubstituted 1,2-dihydronaphtho[2,1-*b*]furans and naphtho[2,1-*b*]furans is

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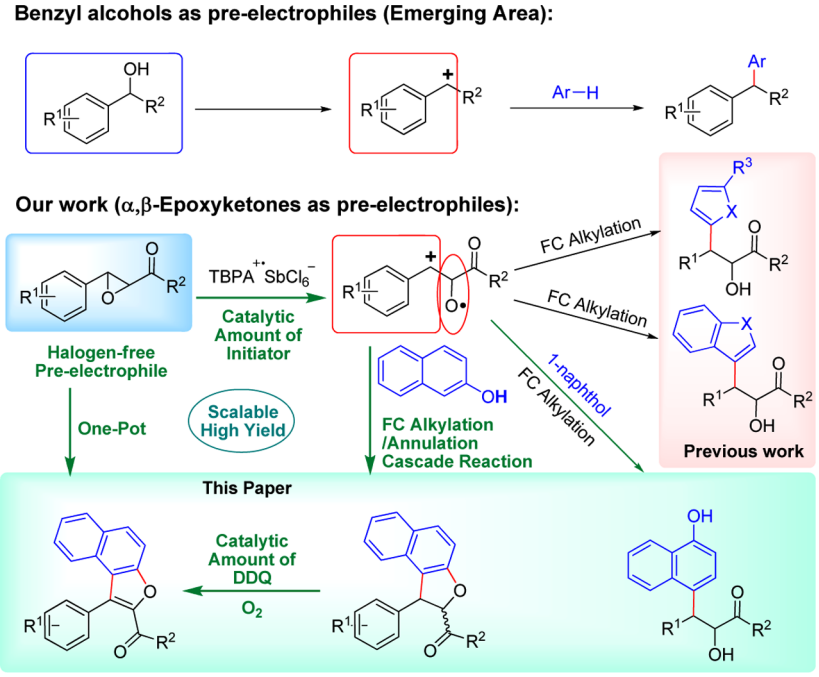
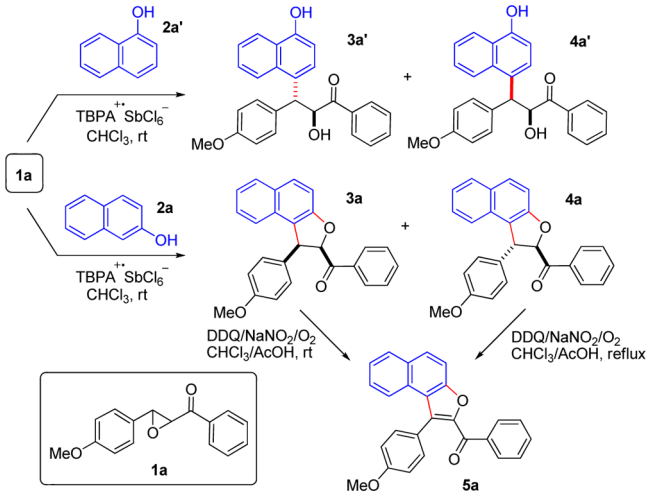
Scheme 1. To Make FC Alkylation Greener and/or Sustainable



highly desired. In this paper, 51 highly substituted 1,2-dihydronaphtho[2,1-*b*]furan or naphtho[2,1-*b*]furan derivatives were provided by our procedure in one step. Studies on the bioactivity of these new naphthofuran derivatives are currently underway.

Naphthols were chosen as model compounds, because they have been demonstrated to be good donors in some FC alkylation examples.[2a−c,9] We first investigated the reaction of chalcone epoxide **1a** with 1-naphthol under the previously optimized reaction conditions (5 mol % $TBPA^{+\bullet}SbCl_6^-$ in Ch_2Cl_2 at room temperature).[6a] A similar FC reaction occurred, and *β*-functionalized *α*-ketol diastereomers **3a**′ and **4a**′ were given in high yield (90%, Scheme 2). However, when 2-naphthol was employed as a nucleophile, to our surprise, a FC alkylation/annulation cascade reaction occurred and 1,2-dihydronaphtho-[2,1-*b*]furans **3a** and **4a** were achieved in good yield (71%,

Scheme 2. $TBPA^{+\bullet}SbCl_6^-$ Induced Reaction between 1a and 1-Naphthol or 2-Naphthol



Scheme 2). Compound **3a** was easily and efficiently aromatized to the corresponding naphtho[2,1-*b*]furans **5a** by oxidation with DDQ at room temperature in an hour. The aromatization of **4a** was also efficient but with a little higher temperature and a little longer time. However, the use of a stoichiometric amount of DDQ would detract from our effort to make a greener FC reaction. Recently, the use of a catalytic amount of DDQ with $NaNO_2$ as co-catalyst under acidic conditions has been reported for the aerobic oxidation of alcohol.[10] We envisioned that this system might also be utilized to promote aerobic oxidative aromatization in our study. To our delight, after simple screening, DDQ (5 mol %)/$NaNO_2$ (10 mol %)/AcOH/O_2 was identified as the optimal reaction condition, which functioned as well as a stoichiometric amount of DDQ. This should be the first application of the DDQ/$NaNO_2$/O_2 catalytic system to the aerobic oxidative aromatization of heterocycles. The structures of **3a**, **4a**, and **5a** were fully characterized, and stereochemistry of **3j**, **4j**, and **5j** was determined by X-ray crystallographic analysis.[11]

Encouraged by the above-mentioned initial results, we started to optimize the transformation. A range of solvents were screened first. Optimization revealed that the reaction was quite sensitive to the solvents. The highest yield and diastereoselectivity was observed when $CHCl_3$ was used as solvent (91%, 3:1). We next explored the synthesis of naphtho[2,1-*b*]furans in one pot. At first, the model reaction of **1a** (1 mmol) with 2-naphthol (1.2 mmol) was carried out under the above optimized condition (5 mol % $TBPA^{+\bullet}SbCl_6^-$ in 5 mL $CHCl_3$ at room temperature) for 0.5 h, after washing with 5% NaOH (2.5 mL) to remove excess 2-naphthol, then AcOH (1 mL), DDQ (5 mol %), and $NaNO_2$ (10 mol %) were added, and the reaction was performed at reflux for 6 h under O_2 atmosphere. To our delight, the desired product **5a** was obtained with a complete conversion and an excellent isolated yield (81%, Table 1, entry 1). This tandem reaction in one pot could simplify the synthetic procedure and enhance the efficiency of preparing the naphtho[2,1-*b*]furans,

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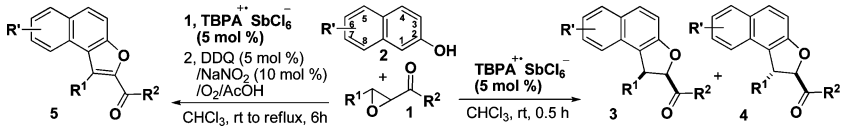
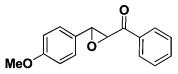
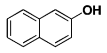
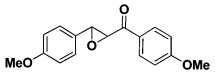
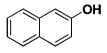
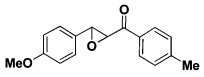
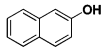
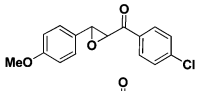
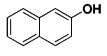
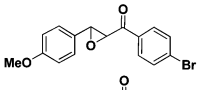
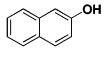
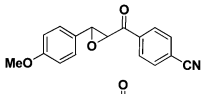
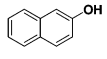
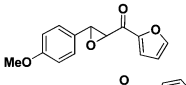
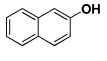
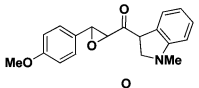
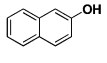
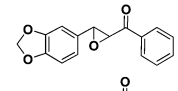
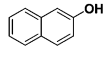
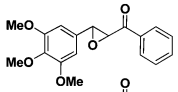
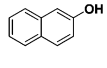
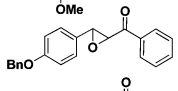
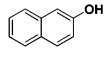
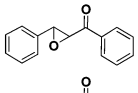
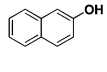
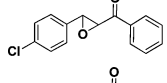
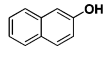
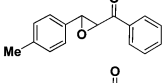
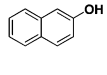
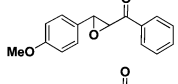
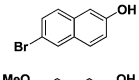
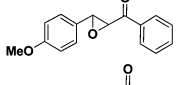
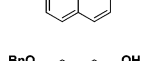
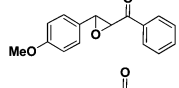
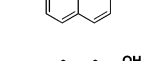
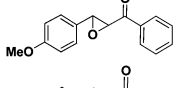
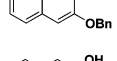
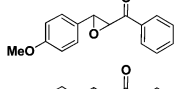
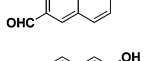
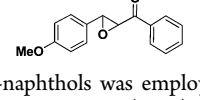
Table 1. $TBPA^{+\cdot}SbCl_6^-$ Induced Reaction of Chalcone Epoxides 1 with Naphthols 2



Entry	1	R^1	R^2	2[a]	Products Yields (%) Isolated Yield (NMR yield, 3 : 4)	5	
1[b]	(1a)		(2a)		(3a&4a)	78 (91, 3.0 : 1)	(5a)	81 (90)
2	(1b)		(2a)		(3b&4b)	73 (80, 2.9 : 1)	(5b)	75 (81)
3	(1c)		(2a)		(3c&4c)	71 (87, 3.3 : 1)	(5c)	77 (91)
4	(1d)		(2a)		(3d&4d)	76 (92, 2.2 : 1)	(5d)	78 (88)
5	(1e)		(2a)		(3e&4e)	75 (89, 2.3 : 1)	(5e)	83 (86)
6	(1f)		(2a)		(3f&4f)	83 (90, 1.5 : 1)	(5f)	80 (85)
7	(1g)		(2a)		(3g&4g)	74 (88, 2.7 : 1)	(5g)	80 (89)
8	(1h)		(2a)		(3h&4h)	70 (82, 2.8 : 1)	(5h)	72 (83)
9	(1i)		(2a)		(3i&4i)	80 (87, 2.4 : 1)	(5i)	78 (86)
10	(1j)		(2a)		(3j&4j)	77 (93, 3.6 : 1)	(5j)	80 (83)
11[b]	(1k)		(2a)		(3k&4k)	81 (91, 3.2 : 1)	(5k)	81 (85)
12	(1l)		(2a)		(3l&4l)	- (32, 3.0 : 1)	(5l)	-
13	(1m)		(2a)		(3m&4m)	- (26, 4.2 : 1)	(5m)	-
14	(1n)		(2a)		(3n&4n)	- (22, 3.4 : 1)	(5n)	-
15	(1a)		(2b)		(3o&4o)	76 (86, 2.3 : 1)	(5o)	61 (84)
16	(1a)		(2c)		(3p&4p)	61 (75, 2.4 : 1)	(5p)	53 (59)
17	(1a)		(2d)		(3q&4q)	67 (73, 2.0 : 1)	(5q)	60 (68)
18	(1a)		(2e)		(3r&4r)	52 (70, 2.3 : 1)	(5r)	58 (69)
19	(1a)		(2f)		(3s&4s)	68 (77, 1.9 : 1)	(5s)	66 (75)
20	(1a)		(2g)		(3t&4t)	64 (74, 2.0 : 1)	(5t)	61 (70)

[a]In each case, 1.2 equiv of 2-naphthols was employed. [b]The reactions in entries 1 and 10 were scaled up to 0.1 mol (>10 g); no yield loss was observed with even lower initiator loading (0.5%).

avoiding the separation and purification of intermediates, and saving time and the use of solvents.

The generality and scope of this $TBPA^{+\cdot}SbCl_6^-$ initiated FC alkylation/annulation cascade reaction were similar to our

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previously reported $TBPA^{+\cdot}SbCl_6^-$ initiated FC reaction of chalcone epoxides with heteroarenes.[6a] Chalcone epoxides with electron-rich aryl groups (such as 4-methoxyphenyl, piperonyl, 3,4,5-trimethoxyphenyl, and 4-(benzyloxy)phenyl groups) as R^1 substituents gave the corresponding products in good to excellent yields (entries 1−11, Table 1). It should be noted that, with all changes in the R^2 substituents, electron-rich aryls (4-Me-C_6H_4, 4-MeO-C_6H_4), electron-deficient aryls (4-Cl-C_6H_4, 4-Br-C_6H_4, 4-CN-C_6H_4), and heteroaryls such as 2-furanyl and 1-methyl-1*H*-indol-3-yl groups were all tolerant of the reaction conditions. Without a strong electron donating group on R1 substituents, the yields decreased significantly (entries 12−14, Table 1).

The derivatives of 2-naphthol with electron donating groups (such as 7-MeO-2-naphthol, 7-BnO-2-naphthol, 3-BnO-2-naphthol) and with electron withdrawing groups (such as 6-Br-2-naphthol, 6-CHO-2-naphthol, 6-CN-2-naphthol) were all transformed into the corresponding naphthofurans smoothly (entries 15−20, Table 1).

To evaluate the practicability of our method,[12] the reaction between chalcone epoxides (**1a**) and 2-naphthol (**2a**) has been performed on a 0.1 mol scale [25.4 g **1a** + 17.3 g **2a** (1.2 equiv)] in a single batch, and to our delight, no yield loss was observed with even lower initiator loading (0.5 mol % $TBPA^{+\cdot}SbCl_6^-$ in 250 mL $CHCl_3$ at room temperature, finished in 18 min, 80% isolated yield based on **1a**) (Table 1, footnote b). That is to say, here we present a practical and scalable synthetic entry to the polysubstituted 1,2-dihydronaphtho[2,1-*b*]furan derivatives.

In summary, we have demonstrated a concise and scalable method to construct polysubstituted 1,2-dihydronaphtho[2,1-*b*]furans. Chalcone epoxides acted as valuable halogen-free pre-electrophiles. Triarylaminium salt was disclosed as a highly efficient initiator for this FC alkylation/annulation cascade reaction. $DDQ/NaNO_2/AcOH/O_2$ was proven to be efficient in the aerobic oxidative aromatization of 1,2-dihydronaphtho[2,1-*b*]furans, and the direct transformation of chalcone epoxides with 2-naphthols into complex naphtho[2,1-*b*]furans was also developed in one pot with a simple and efficient tandem procedure.

EXPERIMENTAL SECTION

General Information. The starting materials and reagents, purchased from commercial suppliers, were used without further purification. Literature procedures were used for the preparation of chalcone epoxides. Solvents were purified by standard methods. Flash chromatography was carried out using silica gel 200−300. ^{1}HNMR (400 MHz) and ^{13}CNMR (100 MHz) spectra were measured with TMS as internal standard when $CDCl_3$ was used as solvent. High-resolution electrospray ionization (HRESI) mass spectra were recorded by a QTOF-2 Micromass spectrometer.

Typical Procedure for $TBPA^{+\cdot}SbCl_6^-$ Induced Reaction of Chalcone Epoxides and 2-Naphthols. Chalcone epoxides (**1**, 1 mmol) and 2-naphthols (**2**, 1.2 mmol) were dissolved in CH_3Cl (10 mL) at ambient temperature; $TBPA^{+\cdot}SbCl_6^-$ (0.05 mmol) was then added in portion under stirring. The reaction completed within half an hour as monitored by TLC. The diastereomer products were isolated by column chromatographic separation with the rapidly eluting the trans isomer **4** and the slowly eluting the cis isomer **3**.

Typical Procedure for the Synthesis of Naphtho[2,1-*b*]furans in One Pot. Chalcone epoxides (**1**, 1 mmol) and 2-naphthols (**2**, 1.2 mmol) were dissolved in CH_3Cl (10 mL) at ambient temperature, $TBPA^{+\cdot}SbCl_6^-$ (0.05 mmol) was then added in one portion under stirring. After 0.5 h, the reaction mixture was washed with 5% NaOH (2.5 mL) to remove excess 2-naphthol, then AcOH (1 mL), DDQ (5 mol %) and $NaNO_2$ (10 mol %) were added, and the reaction mixture was heated under reflux for 6 h under O_2 atmosphere. Then, the solvent was evaporated and the residue was purified by column chromatography over silica gel to afford the naphtho[2,1-*b*]furans **5**.

(1-(4-Methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(phenyl)methanone (cis isomer 3a). White filamentous crystals, mp 165−167 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 9.1 Hz, 2H), 7.68 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.48−7.32 (m, 3H), 7.34−7.18 (m, 3H), 6.66 (d, J = 8.8 Hz, 2H), 6.53−6.43 (m, 3H), 5.30 (d, J = 9.6 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.9, 158.4, 156.7, 136.0, 133.2, 130.3, 130.0, 129.9, 129.6, 129.6, 129.5, 128.7, 128.4, 127.8, 126.9, 123.2, 122.5, 121.1, 113.4, 112.4, 89.0, 54.9, 51.4. LRMS (EI) m/z 380 (M^+, 17.6). HRMS (ESI) exact mass calcd for $C_{26}H_{24}NO_3$ $[M+NH_4]^+$ 398.1751, found 398.1758.

(1-(4-Methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(phenyl)methanone (trans isomer 4a). Colorless block crystals, mp 132−133 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03 (d, J = 7.0 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.51 (dd, J = 8.4, 7.1 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 7.32−7.25 (m, 2H), 7.22 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 5.95 (d, J = 5.4 Hz, 1H), 5.30 (d, J = 5.4 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.8, 158.8, 157.0, 134.4, 134.2, 133.8, 130.4, 130.3, 130.1, 129.3, 129.0, 128.8, 128.8, 128.7, 126.8, 123.2, 122.8, 120.0, 114.4, 112.1, 91.7, 55.2, 50.1. LRMS (EI) m/z 380 (M^+, 13.6). HRMS (ESI) exact mass calcd for $C_{26}H_{24}NO_3$ $[M+NH_4]^+$ 398.1751, found 398.1745.

(1-(4-Methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)(phenyl)-methanone (5a). Yellow block crystals, mp 145−147 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98−7.89 (m, 4H), 7.80 (d, J = 8.3 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.56−7.33 (m, 7H), 6.99 (d, J = 8.6 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.8, 159.6, 152.9, 147.8, 137.5, 132.3, 131.3, 131.1, 131.0, 130.2, 129.7, 129.2, 128.8, 128.0, 126.9, 125.1, 124.6, 123.2, 122.1, 114.0, 112.7, 55.3. LRMS (EI) m/z 378 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{26}H_{22}NO_3$ $[M+NH_4]^+$ 396.1594, found 396.1586.

(4-Methoxyphenyl)(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methanone (cis isomer 3b). Colorless needle crystals, mp 185−187 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 8.8 Hz, 1H), 7.33−7.13 (m, 3H), 6.87 (d, J = 8.9 Hz, 2H), 6.69 (d, J = 8.7 Hz, 2H), 6.49 (d, J = 8.7 Hz, 2H), 6.43 (d, J = 9.6 Hz, 1H), 5.28 (d, J = 9.6 Hz, 1H), 3.87 (s, 3H), 3.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.1, 163.6, 158.4, 156.8, 130.2, 130.0 (2C), 129.7, 129.6, 129.0, 128.8, 126.9, 123.2, 122.6, 121.2, 113.7, 113.4, 112.5, 88.9, 55.5, 55.0, 51.6. LRMS (EI) m/z 410 (M^+, 12.5). HRMS (ESI) exact mass calcd for $C_{27}H_{26}NO_4$ $[M+NH_4]^+$ 428.1856, found 428.1859.

(4-Methoxyphenyl)(1-(4-methoxyphenyl)naphtho[2,1-*b*]-furan-2-yl)methanone (5b). Yellow block crystals, mp 165−167 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 8.6 Hz, 2H), 7.92 (dd, J = 12.2, 8.6 Hz, 2H), 7.80 (d, J = 8.5 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.45 (m, 3H), 7.36 (t, J = 7.7 Hz, 1H), 7.02 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 183.2, 163.1, 159.5, 152.6, 148.1, 132.2, 131.1, 131.0, 130.6, 130.2, 129.8, 129.1, 128.8, 126.8, 125.1, 124.9, 123.3, 122.1, 114.0, 113.4, 112.7, 55.4, 55.2. LRMS (EI) m/z 408 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{27}H_{24}NO_4$ $[M+NH_4]^+$ 426.1700, found 426.1691.

(1-(4-Methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(*p*-tolyl)methanone (cis isomer 3c). White filamentous crystals, mp 176−178 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.32−7.23 (m, 2H), 7.19 (d, J = 7.9 Hz, 2H), 6.68 (d, J = 8.7 Hz, 2H), 6.55−6.38 (m, 3H), 5.28 (d, J = 9.5 Hz, 1H), 3.61 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.3, 158.5, 156.8, 144.2, 133.5, 130.3, 130.0 (2C), 129.7, 129.6, 129.2, 128.8, 128.0, 126.9, 123.2, 122.6, 121.2, 113.4, 112.5, 89.0, 55.0, 51.5, 21.7. LRMS (EI) m/z 394 (M^+, 9.9). HRMS (ESI) exact mass calcd for $C_{27}H_{26}NO_3$ $[M+NH_4]^+$ 412.1907, found 412.1918.

(1-(4-Methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(*p*-tolyl)methanone (trans isomer 4c). Colorless block crystals, mp 123−124 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.40−7.21 (m, 6H), 7.17 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 5.89 (d, J = 5.3 Hz, 1H), 5.21 (d, J = 5.4

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Hz, 1H), 3.77 (s, 3H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.3, 158.8, 157.0, 144.8, 134.5, 131.6, 130.4, 130.3, 130.0, 129.4 (2C), 129.0, 128.7, 126.7, 123.1, 122.7, 120.0, 114.4, 112.1, 91.6, 55.2, 50.2, 21.7. LRMS (EI) m/z 394 (M^+, 3.0). HRMS (ESI) exact mass calcd for $C_{27}H_{26}NO_3$ $[M+NH_4]^+$ 412.1907, found 412.1899.

(1-(4-Methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)(*p*-tolyl)-methanone (5c). Yellow block crystals, mp 176−178 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02−7.87 (m, 4H), 7.82 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.56−7.43 (m, 3H), 7.38 (t, J = 7.0, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 3.91 (s, 3H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.4, 159.6, 152.7, 148.0, 143.1, 134.9, 131.1, 131.0, 130.9, 130.0, 129.9, 129.2, 128.8 (2C), 126.9, 125.1, 124.8, 123.3, 122.1, 114.0, 112.7, 55.3, 21.6. LRMS (EI) m/z 392 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{27}H_{24}NO_3$ $[M+NH_4]^+$ 410.1751, found 410.1755.

(4-Chlorophenyl)(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methanone (cis isomer 3d). White filamentous crystals, mp 175−178 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.6 Hz, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.36 (t, J = 8.1 Hz, 3H), 7.27 (s, 3H), 6.68 (d, J = 8.2 Hz, 2H), 6.50 (d, J = 8.1 Hz, 2H), 6.39 (d, J = 9.6 Hz, 1H), 5.28 (d, J = 9.6 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.0, 158.6, 156.6, 139.6, 134.4, 130.4, 130.1, 130.0, 129.7, 129.4, 129.3, 128.8, 127.0, 123.3, 122.5, 120.9, 113.5, 112.4, 89.0, 55.0, 51.5. LRMS (EI) m/z 414 (M^+, 55.0). HRMS (ESI) exact mass calcd for $C_{26}H_{23}ClNO_3$ $[M+NH_4]^+$ 432.1361, found 432.1364.

(4-Chlorophenyl)(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methanone (trans isomer 4d). Colorless block crystals, mp 163−165 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.6 Hz, 2H), 7.74−7.82 (m, 2H), 7.48 (d, J = 8.6 Hz, 2H), 7.38−7.24 (m, 4H), 7.20 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 5.84 (d, J = 5.5 Hz, 1H), 5.29 (d, J = 5.5 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.8, 158.9, 156.8, 140.3, 134.2, 132.6, 130.8, 130.5, 130.3, 130.1, 129.1, 129.0, 128.8, 126.8, 123.3, 122.8, 119.9, 114.5, 112.0, 91.7, 55.2, 49.9. LRMS (EI) m/z 414 (M^+, 52.0). HRMS (ESI) exact mass calcd for $C_{26}H_{23}ClNO_3$ $[M+NH_4]^+$ 432.1361, found 432.1359.

(4-Chlorophenyl)(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)methanone (5d). Yellow block crystals, mp 156−157 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H), 7.80 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.48 (t, J = 7.5 Hz, 1H), 7.38 (dd, J = 16.9, 6.6 Hz, 5H), 7.00 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 183.3, 159.7, 153.0, 147.5, 138.6, 135.8, 131.8, 131.1, 131.0, 130.6, 129.2, 128.8, 128.3, 127.1, 125.3, 124.4, 123.2, 122.0, 114.1, 112.6, 55.5. LRMS (EI) m/z 412 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{26}H_{21}ClNO_3$ $[M+NH_4]^+$ 430.1204, found 430.1210.

4-(1-(4-Methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-carbonyl)benzonitrile (cis isomer 3f). White needle crystals, mp 187−189 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, J = 7.5 Hz, 2H), 7.67 (m, 4H), 7.37 (d, J = 8.8 Hz, 1H), 7.21−7.30 (m, 3H), 6.66 (d, J = 6.8 Hz, 2H), 6.49 (d, J = 6.9 Hz, 2H), 6.39 (d, J = 9.8 Hz, 1H), 5.31 (d, J = 9.8 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.7, 158.7, 156.5, 139.1, 132.2, 130.6, 130.1, 129.8, 129.7, 129.2, 128.8, 128.3, 127.1, 123.5, 122.5, 120.6, 117.8, 116.2, 113.6, 112.2, 89.3, 55.0, 51.4. LRMS (EI) m/z 405 (M^+, 35.5). HRMS (ESI) exact mass calcd for $C_{27}H_{23}N_2O_3$ $[M+NH_4]^+$ 423.1703, found 423.1697.

4-(1-(4-Methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-carbonyl)benzonitrile (trans isomer 4f). Pale yellow flake crystals, mp 189−191 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J = 8.3 Hz, 2H), 7.76−7.82 (m, 4H), 7.38−7.22 (m, 4H), 7.17 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.81 (d, J = 5.6 Hz, 1H), 5.32 (d, J = 5.7 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.0, 159.0, 156.5, 137.5, 133.9, 132.4, 130.6, 130.2 (2C), 129.8, 129.0, 128.8, 127.0, 123.4, 122.8, 119.7, 117.8, 116.9, 114.5, 111.9, 91.9, 55.3, 49.6. LRMS (EI) m/z 405 (M^+, 20.8). HRMS (ESI) exact mass calcd for $C_{27}H_{23}N_2O_3$ $[M+NH_4]^+$ 423.1703, found 423.1704.

4-(1-(4-Methoxyphenyl)naphtho[2,1-*b*]furan-2-carbonyl)-benzonitrile (5f). Yellow needle crystals, mp 186−188 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98−7.93 (m, 4H), 7.79 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 9.0 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 (m, 3H), 6.98 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 183.0, 159.9, 153.5, 147.0, 141.2, 132.8, 131.7, 131.3, 131.1, 129.9, 129.3, 128.8, 127.3, 125.5, 124.0, 123.2, 122.0, 118.1, 115.1, 114.1, 112.6, 55.3. LRMS (EI) m/z 403 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{27}H_{21}N_2O_3$ $[M+NH_4]^+$ 421.1547, found 421.1552.

Furan-2-yl(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methanone (cis isomer 3g). Purple needle crystals, mp 175−177 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 1.6 Hz, 1H), 7.38 (d, J = 8.9 Hz, 1H), 7.32 − 7.21 (m, 3H), 7.11 (dd, J = 3.6, 0.7 Hz, 1H), 6.78 (d, J = 8.7 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 6.48 (dd, J = 3.6, 1.7 Hz, 1H), 6.23 (d, J = 9.7 Hz, 1H), 5.43 (d, J = 9.7 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.0, 158.6, 156.7, 151.3, 146.0, 130.3, 130.1, 130.0, 129.7, 129.3, 128.8, 126.9, 123.3, 122.7, 121.1, 118.1, 113.6, 112.6, 112.4, 89.0, 55.0, 51.2. LRMS (EI) m/z 370 (M^+, 34.8). HRMS (ESI) exact mass calcd for $C_{24}H_{22}NO_4$ $[M+NH_4]^+$ 388.1543, found 388.1546.

Furan-2-yl(1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methanone (trans isomer 4g). White powder solid, mp 102−104 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 1.0 Hz, 1H), 7.35 (d, J = 3.6 Hz, 1H), 7.33−7.21 (m, 4H), 7.17 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.56 (dd, J = 2.8, 1.4 Hz, 1H), 5.61 (d, J = 5.4 Hz, 1H), 5.25 (d, J = 5.4 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.5, 158.8, 157.0, 150.3, 147.5, 134.3, 130.5, 130.3, 130.1, 128.9, 128.8, 126.8, 123.3, 122.9, 120.4, 119.8, 114.3, 112.5, 111.9, 91.9, 55.2, 50.7. LRMS (EI) m/z 370 (M^+, 22.3). HRMS (ESI) exact mass calcd for $C_{24}H_{22}NO_4$ $[M+NH_4]^+$ 388.1543, found 388.1547.

Furan-2-yl(1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)-methanone (5g). Yellow needle crystals, mp 240−241 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, J = 8.5 Hz, 2H), 7.71−7.60 (m, 4H), 7.44−7.54 (m, 3H), 7.37 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 8.4 Hz, 2H), 6.61 (dd, J = 3.2, 1.4 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.2, 159.6, 152.7, 151.4, 147.1, 146.7, 131.4, 131.0, 130.9, 130.3, 129.2, 128.8, 127.0, 125.2, 124.4, 123.3, 122.3, 120.6, 114.0, 112.5, 112.2, 55.3. LRMS (EI) m/z 368 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{24}H_{20}NO_4$ $[M+NH_4]^+$ 386.1387, found 386.1386.

(1-(Benzo[*d*][1,3]dioxol-5-yl)-1,2-dihydronaphtho[2,1-*b*]-furan-2-yl)(phenyl)methanone (cis isomer 3i). Colorless block crystals, mp 193−195 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.54 (td, J = 7.4, 1.4 Hz, 1H), 7.39 (dd, J = 16.3, 9.0 Hz, 3H), 7.34−7.19 (m, 3H), 6.46 (dd, J = 9.6, 2.4 Hz, 1H), 6.37 (d, J = 7.9 Hz, 1H), 6.24 (d, J = 8.0 Hz, 1H), 6.20 (t, J = 1.2 Hz, 1H), 5.75 (d, J = 23.9 Hz, 2H), 5.25 (dd, J = 9.6, 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.7, 156.8, 147.4, 146.6, 136.1, 133.3, 131.3, 130.5, 130.1, 130.0, 128.8, 128.5, 127.9, 127.0, 123.3, 122.5, 122.1, 120.8, 112.5, 109.0, 107.6, 100.8, 89.0, 51.9. LRMS (EI) m/z 394 (M^+, 92.0). HRMS (ESI) exact mass calcd for $C_{26}H_{22}NO_4$ $[M+NH_4]^+$ 412.1543, found 412.1540.

(1-(Benzo[*d*][1,3]dioxol-5-yl)-1,2-dihydronaphtho[2,1-*b*]-furan-2-yl)(phenyl)methanone (trans isomer 4i). Colorless needle crystals, mp 186−188 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (d, J = 7.1 Hz, 2H), 7.79 (t, J = 8.8 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.22−7.36 (m, 4H), 6.76 (s, 2H), 6.69 (s, 1H), 5.94 (d, J = 1.3 Hz, 1H), 5.89 (d, J = 5.2 Hz, 2H), 5.21 (d, J = 5.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.7, 157.0, 148.3, 146.9, 136.2, 134.2, 133.8, 130.5, 130.3, 130.1,129.3, 128.8, 128.7, 126.8, 123.2, 122.7, 121.2, 119.8, 112.1, 108.5, 108.1, 101.1, 91.5, 50.5. LRMS (EI) m/z 394 (M^+, 91.8). HRMS (ESI) exact mass calcd for $C_{26}H_{22}NO_4$ $[M+NH_4]^+$ 412.1543, found 412.1545.

(1-(Benzo[*d*][1,3]dioxol-5-yl)naphtho[2,1-*b*]furan-2-yl)-(phenyl)methanone (5i). Yellow block crystals, mp 144−146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03−7.89 (m, 4H), 7.84 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.60−7.32 (m, 5H), 7.12−6.80 (m, 3H), 6.04 (d, J = 34.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.7, 152.9, 147.8, 147.7, 137.5, 132.3, 131.1, 131.0, 130.3, 129.6, 129.2, 128.7, 128.0, 127.0, 126.0, 125.2, 123.4, 123.3, 122.0, 112.7, 110.3, 108.6,101.2. LRMS (EI) m/z 392 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{26}H_{20}NO_4$ $[M+NH_4]^+$ 410.1387, found 410.1381.

Phenyl(1-(3,4,5-trimethoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methanone (cis isomer 3j). Colorless block crystals, mp 207−209 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, J = 8.7 Hz,

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2H), 7.64 (d, J = 8.1 Hz, 2H), 7.52 (t, J = 7.5 Hz, 1H), 7.38 (m, 3H), 7.27−7.33 (m, 3H), 6.50 (d, J = 10.0 Hz, 1H), 5.92 (s, 2H), 5.23 (d, J = 10.0 Hz, 1H), 3.66 (s, 3H), 3.46 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.9, 156.9, 152.6, 136.9, 136.5, 133.2, 133.1, 130.5, 130.0 (2C), 128.8, 128.4, 127.7, 127.0, 123.3, 122.6, 120.2, 112.5, 106.0, 89.0, 60.6, 55.8, 55.7, 52.5. LRMS (EI) m/z 440 (M^+, 31.6). HRMS (ESI) exact mass calcd for $C_{28}H_{28}NO_5$ $[M+NH_4]^+$ 458.1962, found 458.1960. Crystal data for p21c: $C_{28}H_{24}O_5$, M = 440.47, monoclinic, a = 15.598(8) Å, b = 5.885(7) Å, c = 24.320(3) Å, α = 90.00°, β = 99.165(10)°, γ = 90.00°, V = 2204(4) Å^3, T = 296(2) K, space group $P2(1)/c$, Z = 4, 15036 reflections measured, 4079 independent reflections (R_{int} = 0.0539). The final R_1 values were 0.0502 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1078 ($I > 2\sigma(I)$). The final R_1 values were 0.0874 (all data). The final $wR(F^2)$ values were 0.1297 (all data).

Phenyl(1-(3,4,5-trimethoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)methanone (trans isomer 4j). Colorless block crystals, mp 188−190 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J =8.3 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.63 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.20−7.36 (m, 4H), 6.45 (s, 2H), 5.94 (d, J = 5.6 Hz, 2H), 5.23 (d, J = 5.3 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.7, 157.0, 153.6, 137.9, 137.1, 134.2, 133.9, 130.6, 130.4, 130.0, 129.4, 128.7, 128.6, 126.8, 123.3, 122.8, 119.3, 112.1, 104.8, 91.4, 60.8, 56.1, 51.0. LRMS (EI) m/z 440 (M^+, 18.4). HRMS (ESI) exact mass calcd for $C_{28}H_{28}NO_5$ $[M+NH_4]^+$ 458.1962, found 458.1960. Crystal data for p-1: $C_{28}H_{24}O_5$, M = 440.47, triclinic, a = 8.064(2) Å, b = 9.030(2) Å, c = 16.884(5) Å, α = 97.742(3)°, β = 98.905(3)°, γ = 111.668(2)°, V = 1104.0(5) Å^3, T = 296(2) K, space group $P\bar{1}$, Z = 2, 6748 reflections measured, 4002 independent reflections (R_{int} = 0.0178). The final R_1 values were 0.0429 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1031 ($I > 2\sigma(I)$). The final R_1 values were 0.0590 (all data). The final $wR(F^2)$ values were 0.1154 (all data).

Phenyl(1-(3,4,5-trimethoxyphenyl)naphtho[2,1-*b*]furan-2-yl)methanone (5j). Yellow block crystals, mp 154−156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (m, 2H), 7.85 (t, J = 7.4 Hz, 3H), 7.76 (d, J = 9.1 Hz, 1H), 7.57−7.30 (m, 5H), 6.68 (s, 2H), 3.92 (s, 3H), 3.78 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.1, 153.3, 153.1, 147.6, 137.6, 132.3, 131.3, 131.0, 130.5, 129.4, 129.3, 128.6, 127.9, 127.1, 125.3, 123.4, 121.7, 112.7, 107.1, 60.9, 56.1. LRMS (EI) m/z 438 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{28}H_{26}NO_5$ $[M+NH_4]^+$ 456.1805, found 456.1800. Crystal data for p21n: $C_{56}H_{44}O_{10}$, M = 876.91, monoclinic, a = 9.627(6) Å, b = 22.777(15) Å, c = 20.968(14) Å, α = 90.00°, β = 90.706(7)°, γ = 90.00°, V = 4597(5) Å^3, T = 296(2) K, space group $P2(1)/n$, Z = 4, 21885 reflections measured, 8308 independent reflections (R_{int} = 0.0430). The final R_1 values were 0.0588 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1052 ($I > 2\sigma(I)$). The final R_1 values were 0.1454 (all data). The final $wR(F^2)$ values were 0.1468 (all data).

(1-(4-(Benzyloxy)phenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(phenyl)methanone (cis isomer 3k). White filamentous crystals, mp 96−99 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 7.1 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.22−7.41 (m, 11H), 6.66 (d, J = 8.7 Hz, 2H), 6.55 (d, J = 8.7 Hz, 2H), 6.48 (d, J = 9.6 Hz, 1H), 5.29 (d, J = 9.6 Hz, 1H), 4.85 (dd, J = 18.8, 11.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.9, 157.7, 156.7, 136.8, 136.1, 133.2, 130.3, 130.0, 129.9, 129.8, 129.7, 128.8, 128.5, 128.4, 127.9, 127.8, 127.4, 126.9, 123.2, 122.6, 121.0, 114.4, 112.5, 89.0, 69.7, 51.4. LRMS (EI) m/z 456 (M^+, 8.5). HRMS (ESI) exact mass calcd for $C_{32}H_{28}NO_3$ $[M+NH_4]^+$ 474.2064, found 474.2060.

(1-(4-(Benzyloxy)phenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(phenyl)methanone (trans isomer 4k). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (d, J = 7.4 Hz, 2H), 7.77 (dd, J = 8.9, 5.1 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.58−7.25 (m, 11H), 7.17 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H),5.89 (d, J = 5.4 Hz, 1H), 5.24 (d, J = 5.4 Hz, 1H), 5.01 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.6, 158.1, 157.0, 136.8, 134.7, 134.2, 133.8, 132.0, 130.4, 130.1, 129.3, 129.0, 128.8, 128.7, 128.6, 128.0, 127.5, 126.8, 123.2, 122.8, 120.0, 115.3, 115.1, 112.1, 91.7, 70.0, 50.1. LRMS (EI) m/z 456 (M^+, 7.0). HRMS (ESI) exact mass calcd for $C_{32}H_{28}NO_3$ $[M+NH_4]^+$ 474.2064, found 474.2067.

(1-(4-(Benzyloxy)phenyl)naphtho[2,1-*b*]furan-2-yl)(phenyl)-methanone (5k). Yellow block crystals, mp 145−147 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02−7.90 (m, 4H), 7.80 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.58−7.34 (m, 12H), 7.05 (d, J = 8.4 Hz, 2H), 5.13 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.9, 158.8, 153.0, 147.8, 137.5, 136.8, 132.3, 131.3, 131.2, 131.0, 130.3, 129.7, 129.2, 128.8, 128.6, 128.1, 128.0, 127.6, 127.0, 125.2, 124.9, 123.3, 122.1, 114.9, 112.7, 70.0. LRMS (EI) m/z 454 (M^+, 37.0). HRMS (ESI) exact mass calcd for $C_{32}H_{26}NO_3$ $[M+NH_4]^+$ 472.1907, found 472.1901.

7-Bromo-1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]-furan-2-yl)(phenyl)methanone (cis isomer 3o). White needle crystals, mp 179−180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (s, 1H), 7.68 (m, 3H), 7.53 (t, J = 7.5 Hz, 1H), 7.45−7.22 (m, 4H), 7.15 (dd, J = 8.8, 4.9 Hz, 1H), 6.63 (d, J = 8.7 Hz, 2H), 6.47 (m, 3H), 5.28 (d, J = 9.7 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.6, 158.6, 157.1, 135.9, 133.4, 131.2, 130.7, 130.2, 129.6, 129.5, 129.2, 128.5, 128.4, 127.8, 124.2, 121.4, 116.9, 113.6, 113.5, 88.9, 55.0. LRMS (EI) m/z 458 (M^+, 46.7). HRMS (ESI) exact mass calcd for $C_{26}H_{23}BrNO_3$ $[M+NH_4]^+$ 476.0856, found 476.0853.

7-Bromo-1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]-furan-2-yl)(phenyl)methanone (trans isomer 4o). Colorless block crystals, mp 218−220 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06−7.82 (m, 3H), 7.79−7.57 (m, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.15 (m, 3H), 6.85 (d, J = 8.7 Hz, 2H), 5.91 (d, J = 5.5 Hz, 1H), 5.23 (d, J = 5.5 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.5, 159.0, 157.3, 134.1, 134.0, 133.9, 131.2, 130.7, 130.1, 129.6, 129.3, 129.0, 128.8, 124.5, 120.4, 116.8, 114.5, 113.2, 91.7, 55.3. LRMS (EI) m/z 458 (M^+, 42.3). HRMS (ESI) exact mass calcd for $C_{26}H_{23}BrNO_3$ $[M+NH_4]^+$ 476.0856, found 476.0849.

(7-Bromo-1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)-(phenyl)methanone (5o). Yellow block crystals, mp 156−157 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (s, 1H), 7.95−7.84 (m, 2H), 7.84−7.56 (m, 3H), 7.55−7.23 (m, 6H), 7.07−6.87 (m, 2H), 4.01−3.70 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.7, 159.7, 152.7, 148.0, 137.3, 132.4, 132.3, 131.1, 131.0, 130.8, 130.1, 129.6, 129.0, 128.0, 127.3, 124.8, 124.1, 122.1, 118.9, 114.1, 113.8, 55.3. LRMS (EI) m/z 456 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{26}H_{21}BrNO_3$ $[M+NH_4]^+$ 474.0699, found 474.0702.

(8-Methoxy-1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(phenyl)methanone (cis isomer 3p). White needle crystals, mp 153−155 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85−7.62 (m, 4H), 7.53 (t, J = 7.4 Hz, 1H), 7.38 (t, J = 7.9 Hz, 2H), 7.23 (d, J =8.7 Hz, 1H), 6.90 (dd, J = 9.0, 2.5 Hz, 1H), 6.69 (d, J = 8.7 Hz, 2H), 6.52 (d, J = 2.5 Hz, 1H), 6.48 (dd, J =9.7, 2.9 Hz, 3H), 5.23 (d, J = 9.7 Hz, 1H), 3.62 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.0, 158.5, 158.3, 157.3, 136.1, 133.2, 131.2, 130.3, 130.0, 129.7, 129.5, 128.5, 127.8, 125.4, 120.3, 115.6, 113.4, 109.8, 101.2, 88.9, 55.0, 54.9, 51.5. LRMS (EI) m/z 410 (M^+, 42.5). HRMS (ESI) exact mass calcd for $C_{27}H_{26}NO_4$ $[M+NH_4]^+$ 428.1856, found 428.1857.

(8-Methoxy-1-(4-methoxyphenyl)-1,2-dihydronaphtho[2,1-*b*]furan-2-yl)(phenyl)methanone (trans isomer 4p). Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 7.4 Hz, 2H), 7.68 (t, J = 8.8 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.8 Hz, 1H), 6.83−6.91 (m, 3H), 6.54 (d, J = 2.4 Hz, 1H), 5.91 (d, J = 5.6 Hz, 1H), 5.18 (d, J = 5.6 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.8, 158.8, 158.2, 157.5, 134.2, 133.8, 131.6, 130.3, 130.1, 129.3, 129.1, 128.7, 125.4, 119.3, 115.6, 114.4, 109.4, 101.4, 91.7, 55.3, 54.9, 50.2. LRMS (EI) m/z 410 (M^+, 34.5). HRMS (ESI) exact mass calcd for $C_{27}H_{26}NO_4$ $[M+NH_4]^+$ 428.1856, found 428.1851.

(8-Methoxy-1-(4-methoxyphenyl)naphtho[2,1-*b*]furan-2-yl)-(phenyl)methanone (5p). Yellow block crystals, mp 174−176 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 8.3 Hz, 2H), 7.84 (dd, J = 10.9, 9.1 Hz, 2H), 7.58 (d, J = 9.0 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.45 (d, J = 8.8 Hz, 2H), 7.40 (t, J =7.4 Hz, 2H), 7.14 (d, J = 2.5 Hz, 1H), 7.09 (dd, J = 8.9, 2.6 Hz, 1H), 7.00 (d, J =8.8 Hz, 2H), 3.86 (s, 3H), 3.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 184.7, 159.6, 158.4, 153.5, 147.5, 137.6, 132.3, 131.4, 131.3, 130.5, 130.2, 130.0, 129.7, 128.0, 125.8, 124.8, 121.5, 116.9, 113.9, 110.1, 103.0,55.4, 54.9. LRMS (EI) m/z 408 (M^+, 100). HRMS (ESI) exact mass calcd for $C_{27}H_{24}NO_4$ $[M+NH_4]^+$ 426.1700, found 426.1709.

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■ ASSOCIATED CONTENT

Supporting Information

Characterization of products **3**, **4**, and **5**, and X-ray crystallography data for **3j**, **4j**, and **5j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) The X-ray crystal data (excluding structure factors) of compounds **3h**, **4h**, and **5h** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 849649, 849650, and 849651. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: t44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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